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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

RECYCLING SOLID WASTES AS POLYMER COMPOSITES

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ABSTRACT. Recycling and / or reuse of by-products (waste) is a goal to be achieved under the current economic and ecological crisis. The reuse of waste leads to saving energy and raw materials reduces environmental pollution and risk factors for public health and so on. The solid organic or inorganic wastes have been immobilized in polymer resins used as a binder matrix. All obtained composites present very good physical-mechanical properties: high hardness, good strengths at abrasion and the compressive strengths are all above 90 MPa. They also have good thermal stability at high temperature variation and high stability in different aggressive media. Some of such polymeric composites have good sound absorption capacity depending on the proportion and nature of the waste used.

Keywords: *Solid wastes recycling, polymer composites, noise attenuation, organic wastes; inorganic wastes*

INTRODUCTION

Composites are materials made by the association of at least two components whose properties complement each other, thus results a material with properties superior to either component alone.

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A special class is represented by the polymer composites [1]. Of all composites, the metal ones occupy 10 ÷ 15%, the ceramic composites 15 ÷ 20% and the polymer composites represent 70 ÷ 75%.

The polymer composites have expanded because they have a number of technological advantages compared to ceramics and metals: doe not require high temperature, long period of times and complicated processes for obtaining and finishing. They can be easily processed at low temperatures, with no danger of destruction of reinforcement materials.

Solid wastes recovery in various types of composite materials has many environmental impacts and represents an economic advantage. Every type of solid waste results from processes which requires significant quantities of resources, primarily fossil fuels, both as a raw material and as a source of energy for the manufacturing process. Therefore, their recovery in such special composite with high durability involves significant economic and ecological effects.

Recycling and/or reuse of by-products (waste) is a goal to be achieved under the current economic and ecological crisis. Ecosystem problems are acute problems in the current context of sustainable development. The reuse of waste leads to important savings of raw materials and energy. Also reduces pollution of the environment factors and decrease risk factors for public health.

To date, the purpose of the composite materials technology is to recover wastes and other recycled substances and to obtain new and performing materials with long life cycle [1-3].

The fields of application of polymer composites can be enlarged depending upon the properties of composite materials [1,2,4-6]. For example, dense materials can be obtained very resistant with high durability in an epoxy polymer matrix or unsaturated polyester type resin, but also, some porous composites polyester or formaldehyde resins can be obtained with good sound absorption capacity.

The waste composition is influenced by many factors [7] as: the level of economic development, the cultural norms, the geographical location, energy sources, climate and others.

Global composition of wastes in 2009 [7] is illustrated in Figure 1:

Table 1. Types of waste and their sources [7]

Type	Sources
Organic	Food scraps, yard waste, wood, process residue
Paper	Paper scraps, cardboard, newspapers, magazines, bags, boxes, wrapping paper, telephone books, shredded paper, paper beverage cups.
Plastic	Bottles, packaging, containers, bags, lids, cups

Type	Sources
Glass	Bottles, broken glassware, light bulbs, coloured glass
Metal	Cans, foil, tins, non-hazardous cans, appliances, railings, bicycles
Other	Textiles, leather, rubber, multilaminates, appliances, ash, other inert materials

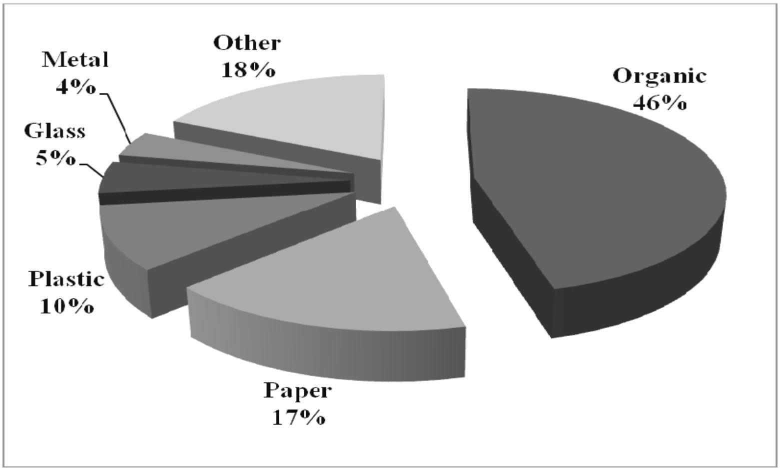

Figure 1. Global waste composition.

Table 2 shows the countries that produce the most trash in the world [8].

Table 2. The countries that produce the most trash in the world [8].

No.	Country	Quantity of trash/year, [million tons]
1	China	300
2	United States	236
3	Russia	200
4	Japan	52.36
5	Germany	48.84
6	United Kingdom	34.85
7	Mexico	32.17
8	France	32.17
9	Italy	29.74
10	Spain	26.34
11	Turkey	25.99

According to European Trade Association for Plastic Manufacturers, 265 millions tones of plastic are produced globally each year. The impacts of plastic waste on our health and the environment are only just becoming apparent. Most of our knowledge is around plastic waste in the marine environment and once the plastic waste enters the oceans it is influenced by global currents that distribute it around the world [9]. Some researches indicate that plastic waste in landfill and in badly managed recycling systems also could have an impact, mainly from the chemicals contained in plastic. Other important wastes are wood chips and rubber powder. The wood chips waste is generated by constructions, commercial and industrial works, including furniture manufacture, and municipal wood waste. The used tires are in large quantities and are extremely cheap for the production of rubber powder [10,11]. Therefore, the immobilization of these wastes using fastest and cheapest methods is a current challenge.

EXPERIMENTAL SECTION

To obtain polymer composite materials the solid wastes of organic or inorganic nature were mixed with a polymer matrix, as a binder system, that. Four classes of resins with different behaviour at hardening were used: epoxy and unsaturated polyester resins which are hardened at room temperature and polyester or formaldehyde resins which are hardened following some thermal treatment. In what follows the resins are depicted as:

- Epoxy (E), in which the corresponding hardening component was teta-triethylentetramine;
- Unsaturated polyester resin: isophthalic (IPh), orthophthalic (OPh) and orthophthalic with additive (OPha) with peroxide methyl cetone as the hardening component;
- Polyester (Pe) resins;
- Formaldehyde (F) resins: phenol-formaldehyde (PhF), urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins.

The resins characteristics are presented in detail in the PhD thesis [1,6]. Because the resins are hydrophobic it is absolutely necessary to make a dry preparation of solid wastes composite. The presence of water determines a decrease of the mechanical properties.

Both unsaturated polyester and epoxy resins were hardened in presence of hardening component (teta-triethylentetramine for epoxy and peroxide methylcetone for polyester) at room temperature, while the formaldehyde and saturated polyester resins were hardened at thermal curing at 80-120°C.

As reinforcement materials were used inorganic and organic solid wastes.

Organic wastes: polyethylene terephthalate (PET) flakes and granules, polypropylene (PP) / polystyrene (PS) granules, rubber powder and wood chips.

Inorganic wastes: silica sand, cullet and glass fibber, furnace slag from thermal power stations, steel slag, fly ash and burned husks ash.

The granulometry of the reinforcing agent was chosen depending on the properties that one wants to achieve for the composite material. Generally, the maximum dimension of solid waste used as reinforcement materials of polymer matrix was 3 mm. Only the size of wood chips was up to 5 mm. Granulometric spectrum of each type of waste used was carefully controlled.

Thus, all inorganic wastes were characterized by the same size distribution. For example, the sand, slag and cullet granulometry was quite similar: the fraction 0 ÷ 0.3 mm represents 48-50%, that of 0.3 ÷ 1 mm is 40 ÷ 42% and the higher fraction 1.00 ÷ 3.00 mm is only 9 ÷ 10% mass. Other solid wastes, such as fly ash and husk ash, are characterized by very fine particles: the particles under 100 μm was 85% by mass.

Organic wastes as (PET) flakes and granules, (PP)/(PS) granules, rubber powder and wood chips were very different in size. As example, rubber powder was very fine, more than 96% of mass was under 1 mm, while the wood chips have dimensions between 0.1 ÷ 5 mm.

For all type of resins and reinforcement agent the flow chart of polymer composites preparation, in laboratory, is very similar - Figure 2. The reinforcement agent, the resin and the hardening component (as applicable) are dosed with an accuracy of ± 0.01 ÷ 0.03 g for a batch of 100 g. The mass ratio between solid waste and resin was (73 ÷ 85) / (15 ÷ 27) that to obtain a good viscosity, and therefore a good workability for the composite samples. The homogenization was performed very intensive in a shock resistant container. The mixture was then cast in properly cleaned and lubricated forms.

As mentioned, the hardening of composite material takes place as follows: 5 hours at room temperature in the presence of hardening component or by heating at 120°C for 4 hours followed by cooling at room temperature.

The resulted composites have been tested for mechanical properties (compressive and flexural strength), density, water adsorption–open porosity, resistance to freezing, chemical stability in water at 100°C and in aggressive media solutions. For composite samples with controlled porosity the capacity of sound absorption has been determined. The composites structure has been examined by SEM and by selection the elemental chemical analysis at the interface was evidenced.

RESULTS AND DISCUSSION

The physical and mechanical properties of synthesized composites depend both on the nature and the characteristics of reinforcement agent, and on the nature of polymer matrix. From this point of view the epoxy composites with inorganic wastes reinforcement have the best behaviour – see Figure 3 and 4.

After 4 curing days a remarkable compressive strengths have the epoxy composites with sand, steel slag, cullet and flay ash (R_c = 114 ÷ 129 MPa). Such values are superior even to those of special high-strength concretes.

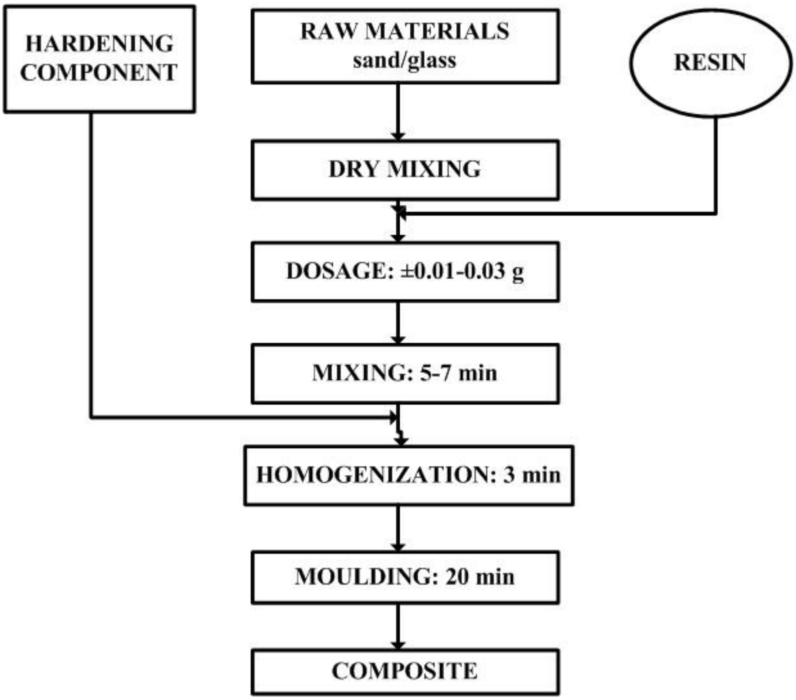

Figure 2. Flow diagram of laboratory polymer composites preparation

The composites with husks ash, PET granules or flakes, PP/PS granules and wood chips have less compressive strength (R_c = 77 ÷ 89 MPa) and those with rubber powder have rather small resistances to compression (R_c = 43 MPa).

A direct dependence between the density and the compressive strength was evidenced. The density of the polymer composites for the same resin is directly affected by the nature of reinforcement materials, respectively their density.

In terms of flexural strength, things are a little different. Thus, one finds the best flexural behaviour of reinforced polymer composite with wood chips (R_i = 41 MPa). This decreases in the series:

Wood chips (41) > rubber powder (38) > PET granules (32) > PP/PS granules (31) > PET flakes (30)

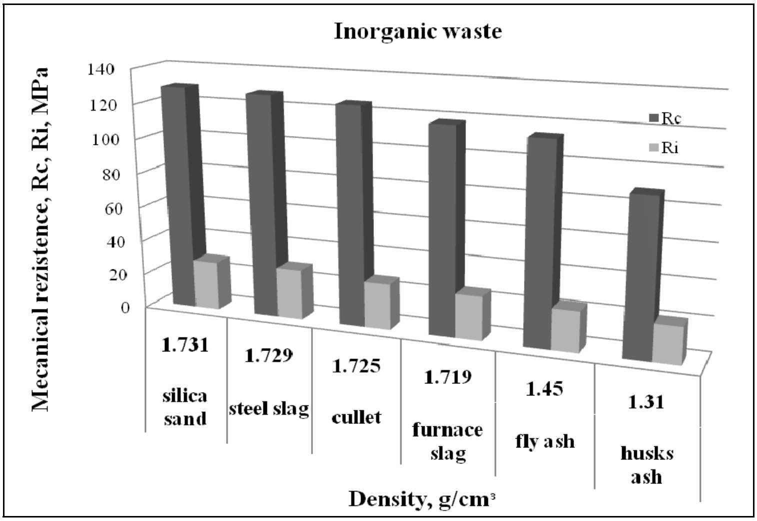

Figure 3. Compressive and flexural strength (MPa) vs. density (g/cm^3) for some inorganic wastes.

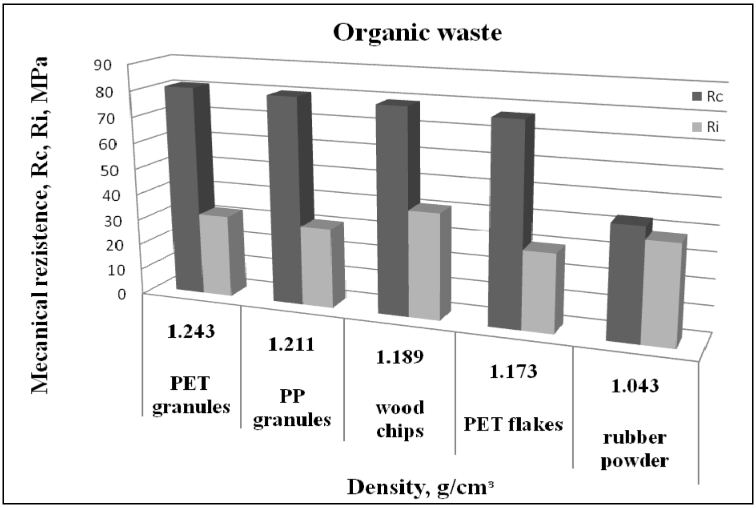

Figure 4. Compressive and flexural strength (MPa) vs. density (g/cm^3) for some organic wastes.

The flexural strength for polymer reinforced with inorganic wastes decreases reaching 21 MPa when husks ash was used as reinforcement agent.

All this can be explained by structural changes of the polymer composite in presence of different reinforcement materials. When dense wastes as reinforcing agent in the polymer structure are used successive layers of resin occur on the surface of reinforcing grains, resulting a compact material, with good mechanical properties - Figures 5, 6. Between epoxy matrix and inorganic wastes there is a very good compatibility. Also, a good compatibility exists between epoxy resin and PET granules (Figure 7) or PET flakes (Figure 8).

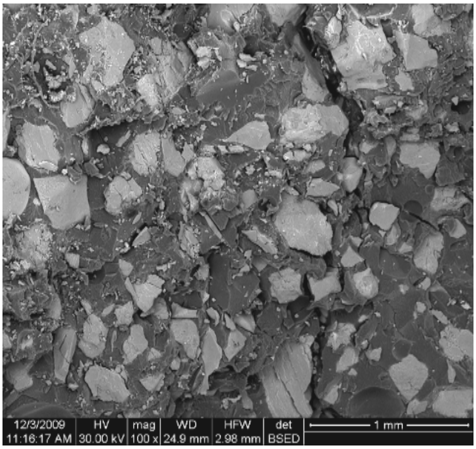

Figure 5. Composite with silica sand

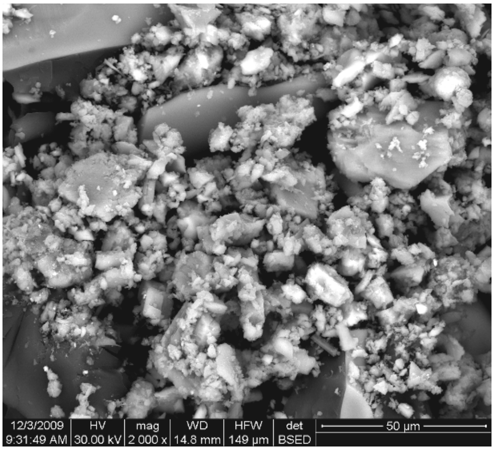

Figure 6. Composite with cullet

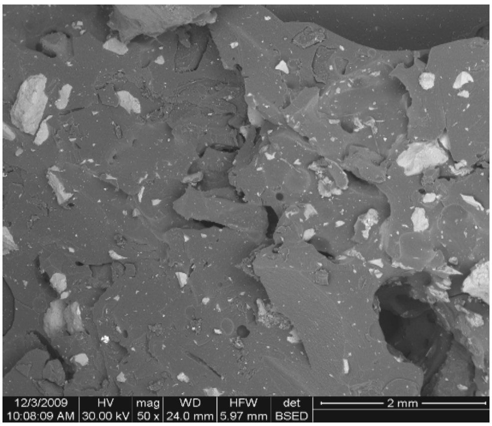

Figure 7. Composite with PET granules

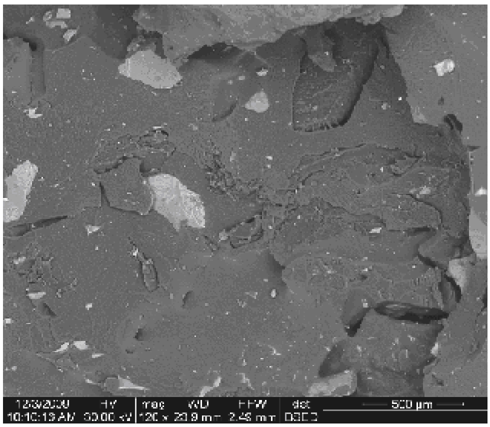

Figure 8. Composite with PET flakes

If the rubber powder was used as reinforcement agent in the epoxy composite often occur some areas not covered completely with resin and there are numerous pores in the structure, which explains the poor behaviour in compression of the samples - Figure 9 and 10. However, due to the elastic nature of the rubber powder, the flexural strength is good in comparison with other reinforcing agents.

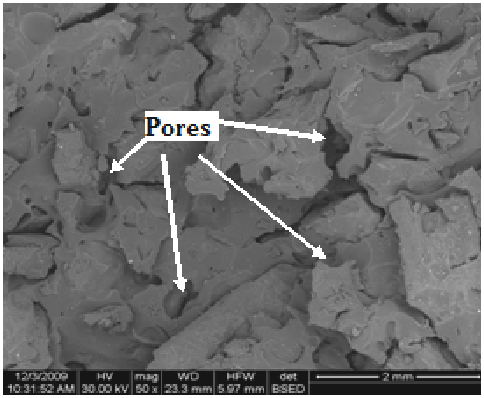

Figure 9. Composite with rubber powder

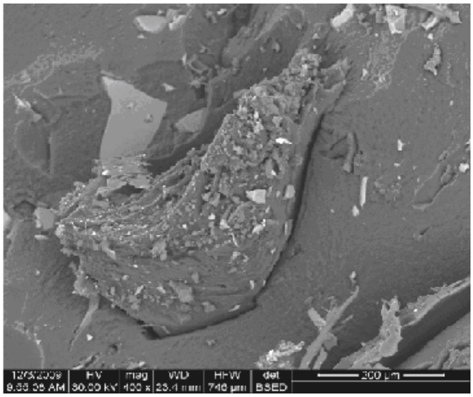

Figure 10. Composite with cullet and rubber powder

Thus, depending on the property that one wishes to improve, for example, the compression or the flexural strengths suitable mixtures of the reinforcing agents could be used. When the same reinforcement agent was used it was important to choose the matching resin. As expected, the resin type, together with the aggregate type are those which determine the polymer composite properties.

In all cases, for every type of solid waste used as reinforced material, the epoxy resin composites showed higher mechanical properties in comparison with other resins. Thus, from the three unsaturated polyester resins categories, only isophthalic, resin shows a good behaviour of composite samples from mechanical point of view - Figure 11.

The other two, orthophthalic (OPh) and orthophthalic with additive (OPha) resins generated porous polymer composites with a structure more heterogeneous in comparison with epoxy or isophthalic mass matrix (see Figure 11 and Figure 12-15.

In this case, the use of rubber powder as reinforcement leads to a heterogeneous structures (Figure 12 compared to composites made from the same resin (isophthalic) but with glass aggregate (Figure 13), sand (Figure 14) or PET (Figure 15). As can be seen from Figure 11, the polyester and the formaldehyde resins (PhF, UF and MF) also form weaker matrix of polymer composites.

It should be noted that, although the rubber powder has an advanced fine (more than 96% of the mass was under 1 mm), its embedding in resin has been developed with difficulty regardless of the type of resin used. It is necessary to use a filler to improve the adhesion.

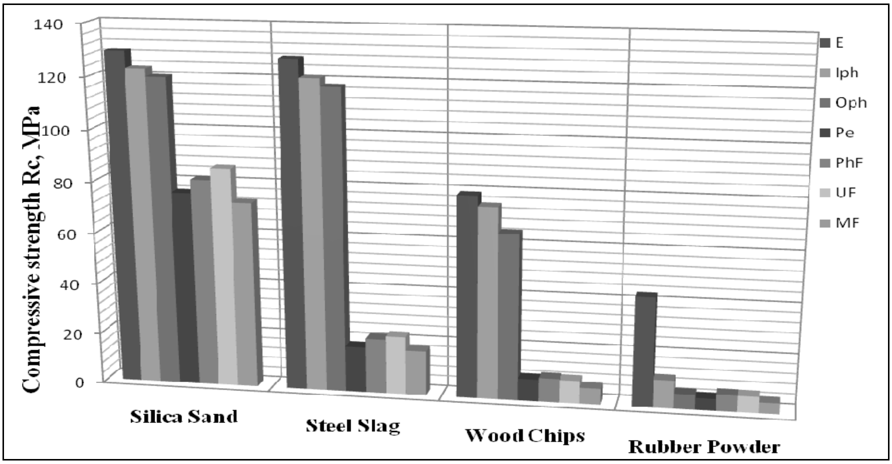

Figure 11. Compressive strength for different resins

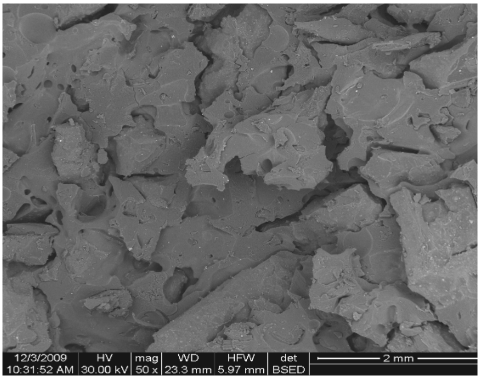

Figure 12. Rubber powder polyester composite (IPh)

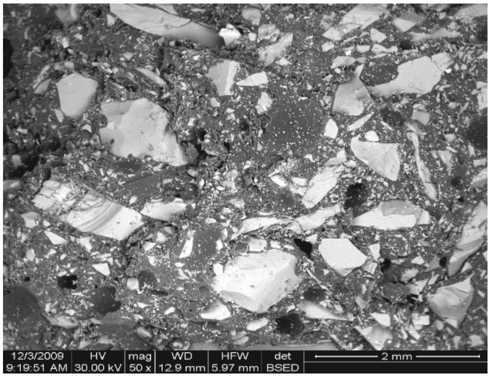

Figure 13. Glass polyester composite (IPh)

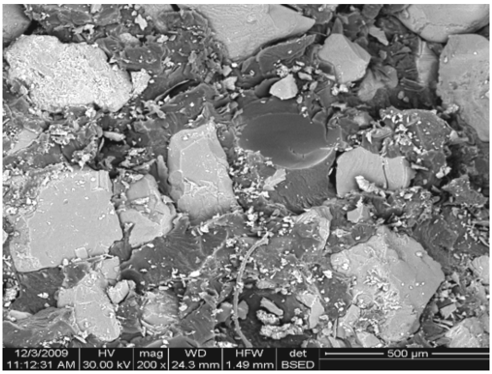

Figure 14. Sand polyester composite (IPh)

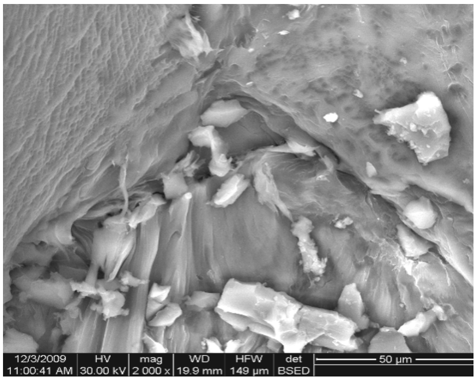

Figure 15. PET flakes polyester composite (IPh)

The compact structure of epoxy and the isophthalic composites which have practically zero porosity give their high stability [12]. There were no observed losses of mass or decreases in mechanical properties at freeze-thaw, or when they were kept in the hot water at 100°C or other aggressive media at ambient temperature [12]. These composites can be used in construction for pedestrian walkways, floors in areas subject to corrosion or other aggressive environmental actions, rehabilitation of buildings in earthquake zones, seal tanks, reservoirs, swimming pools etc. They also have good thermal stability and high stability in different aggressive media.

As has been mentioned above, the composites which have as organic matrix polyester and formaldehyde resins (PhF, UF and MF) led to more diverse structural composite materials with high porosity, often more than 10-12% and inhomogeneities in the structure.

Thus, polymer composites reinforced with wood chips (Figure 16) or steel slag (Figure 17), with high porosity, above 25 – 46 % have a high capacity for noise absorption [6]. Although, they do not have very high mechanical strength (35÷48 MPa), however, one can obtain composite panels used as noise protection materials. SEM analyses show very clear an inhomogeneous structure with large pores with various dimensions. In the same time, the elemental analysis of the interface between reinforced aggregate and resin evidences a good interaction between the composite phases.

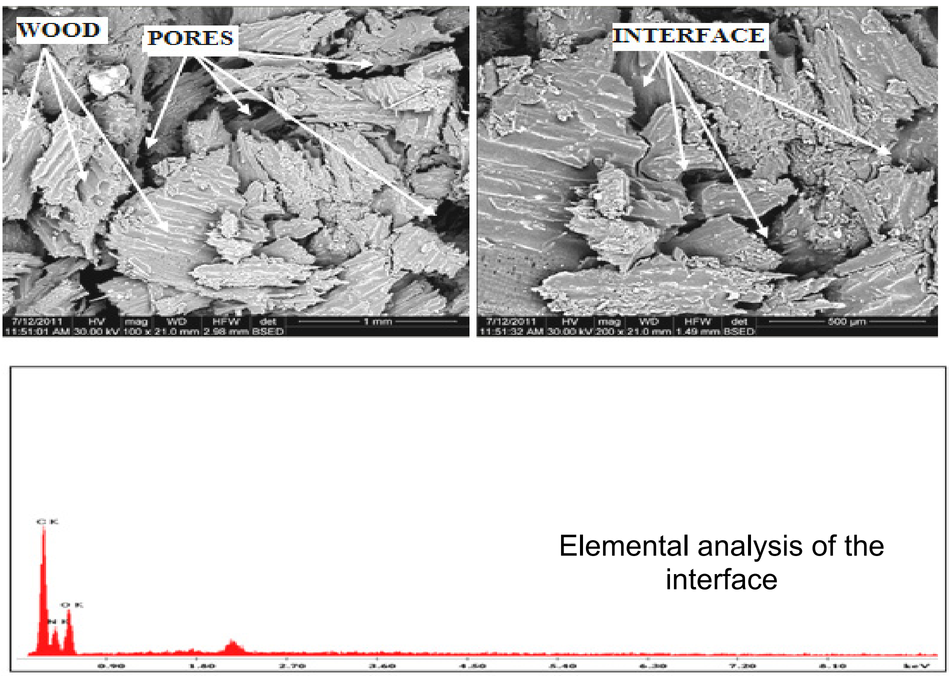

Figure 16. Wood chips formaldehyde composite (PhF), ≥ 25 - 46 %

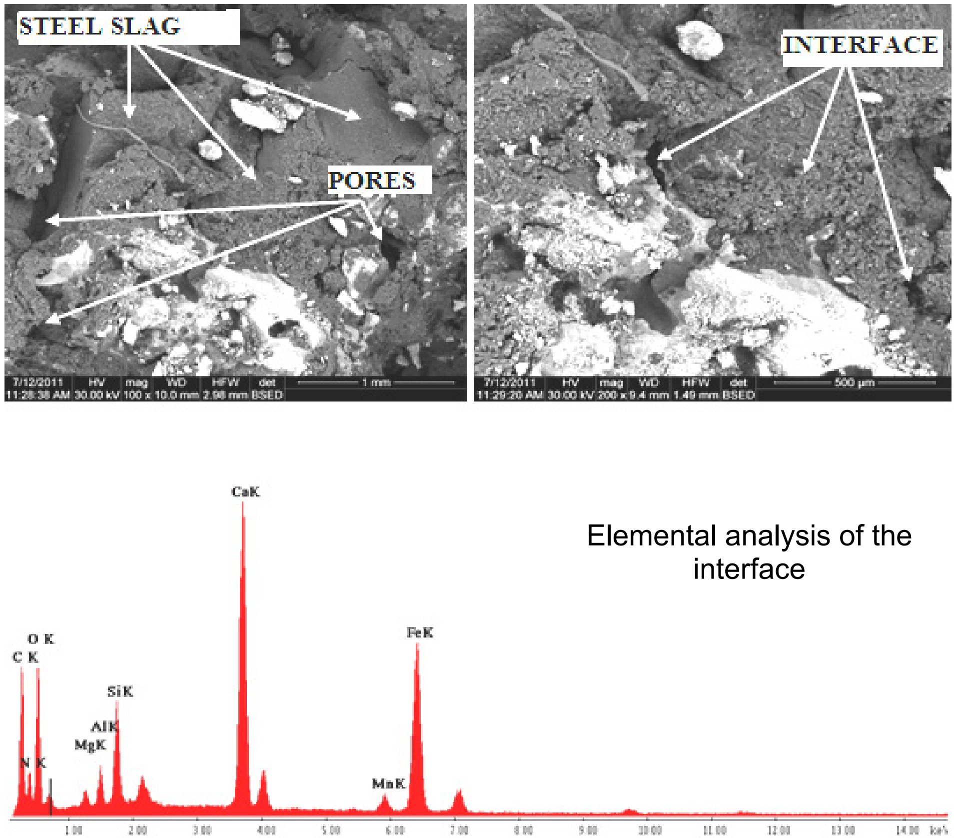

Figure 17. Steel slag formaldehyde composite (PhF), porosity ≥ 42 %

Both materials were characterized by a good sound absorption coefficient (class A and class B) [5,6] and can be used to manufacture absorbent panels to be used in industry, transport, road rails or air.

CONCLUSIONS

From the above results the main conclusions are:

One can obtain polymer composites with various solid wastes as reinforcing agent and different type of resins as organic matrix;

Some composites evidenced excellent physical and mechanical properties especially when epoxy or isophthalic resins were used;

Porous polymer composites based on phenol-formaldehyde resin and wood waste or steel slag were obtained with good sound absorption capacity.

REFERENCES

1. I. Ropota, "Polymeric Composites with Special Purpose", PhD Thesis, University Politehnica of Bucharest, **2010**.
2. I. Ropota, E. Zamfirache, M. Muntean**,** *Environmental Engineering and Management Journal*, **2009**, *8(4),* 931.
3. K.A. Hossain, F.I. Khan., K. Hawboldt, *Journal of Hazardous Materials*, **2008**, *150*, 4.
4. I. Ropotă, O. Dumitrescu, M. Muntean, *International Review of Chemical Engineering (I.RE.CH.E.)*, **2010**, *2(3),* 430.
5. M. Bratu, I. Ropota, O. Vasile, O. Dumitrescu, M. Muntean, *Romanian Journal of Materials*, **2011**, *41(2),* 147.
6. M. Bratu, "Ecological composite materials for noise reduction", PhD Thesis, University Politehnica of Bucharest, **2012**.
7. Information on http://siteresources.worldbank.org/INTURBANDEVELOPMENT/ Resources /336387-1334852610766/Chap5.pdf (last citation February **2013**)
8. Information on http://greenanswers.com/q/63410/recycling-waste/garbage/what-countries-produce-most-trash (last citation March **2013**).
9. Information on http://www.plasticoceans.net/the-facts/a-global-issue/
10. Information on http://www.guardian.co.uk/environment/2011/dec/29/plastic-packaging-waste-solution (last citation March **2013**).
11. Information on http://www.wealthywaste.com/rubber-powder-from-waste-tyres-an-approach-to-tyre-recycling (last citation February **2013**).
12. ***, SR EN 12720/2004, "Resistance to different aggressive media", **2004**.