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RECYCLING OF THERMOSETS BY DIRECT MOULDING OF FINE POWDER

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ABSTRACT

A recycling technology is proposed for recycling of thermosets. An experimental approach is reported to design a "direct powder moulding" (i.e. compression moulding of thermoset fine powders in absence of virgin material or any linking agent). Experimental tests were performed by moulding fine and medium size powders from shredding of rubbers and polyurethane. Small samples were produced to show the process feasibility. The process is fast and easy and it is not required any treatment of the shredded material or binder addition. Even if the moulding pressure was limited in the proposed experimentation, the final performance of the samples seems to be sufficient for a lot of structural and functional applications.

KEYWORDS: recycling, thermosets, rubbers.

1. INTRODUCTION

The modern industrial development must take under consideration the enormous waste of materials and energy in these last years. Even if people have been made aware of the environmental risk connected with the industrial production, there are only few initiatives which allow to reduce the related energy consumption or to extract raw materials from waste. Nowadays the social and political attention on these themes is very strong but the Government agencies do not operate efficiently and the scientific research is absolutely insufficient. A typical example is given by the management of spent tyres. The disposal of spent tyres is already an increasing problem for the European Union where estimates are that around 250 million car and truck tyres are scrapped each year, representing about 2.6 million tons of tyres. Moreover spent tyres represent the main part of the total amount of the spent rubber material which is produced every year in the world. In fact, of the annual total global production of rubber material, which amounts to 16-17 million tons, approximately 65% is used for the production of tyres. In the most industrialized countries the tyres are usually dumped in landfills or left in the open air, generating significant environmental disturbances as non-biodegradable residues and dangerous situations as the risk of fire. In order to face this problem, new regulations have been imposed which force the tyre manufacturers to manage the tyre disposal but these regulations do not solve the problem. Actually the tyre manufacturers are looking for the easiest solution with no regard for the human safety or the environmental conservation. At present, the only proposed solution is the energy reclaim by combustion of the rubber as there are some factories (e.g. cement kilns) which need high energies for their processes. The use of shredded tyres for energy reclaim in cement kilns allows to solve the regulatory problem of the tyre manufacturers as the cement kilns are able to burn almost all the rubber coming from the spent tyres but this solution is absolutely not sustainable or environmentally conscious. In fact, the rubber from spent tyres cannot be used to produce other tyres but it is not true that it cannot be used in any other manufacturing process. Even if it is politically right, it seems to be ethically wrong to burn the rubber only to remove the tyres from the landfills. Instead, the scientific research should propose new recycling technologies which would be able to add further manufacturing steps between the initial tyre manufacturing and the final energy reclaiming. It is always possible to reclaim energy from the rubber by combustion and it would be environmentally correct to use this solution when other technological solutions are not practicable. The case of the spent tyres is well known but not unique. Dealing with glass fibre reinforced plastics (GFRP), there is no effective recycling technology and the problem of their disposal is increasing more and more. Actually, it is not clear how spent GFRPs were disposed until now. The case of GFRPs is evident due to the diffusion of this kind of materials in many factories such as shipbuilding yards or vehicle manufacturers. However, many other cases are present where the low production runs do not allow any effective recycling policy: the carbon fibre reinforced plastics used for light-weight structures or the glass filled phenolic resins used for electric insulators. All the discussed materials (the rubber of tyres, the glass and carbon fibre reinforced plastics of boats, the reinforced phenolic resins of electric insulators) as well as other materials (the rigid or flexible polyurethanes used in construction, the cross-linked polyethylene of thermo-shrinkable cables) pose a serious recycling problem as they share the same technological characteristic. In fact all these materials are thermosets or behave like them. Thermosets polymerise during the production process: as a result, a molecular network is generated which prevents the material flow under heating. For this reason, thermosets cannot be recycled by using the same technologies of thermoplastics (i.e. re-melting and re-plastification) and are generally considered rubbish at the end of their use. It is evident that thermoplastics should be preferred but thermosets are used when their unique properties may not be guaranteed by any thermoplastic material. Thermosets are used in the field of transports or electric insulation where the human safety is more important than the environmental impact. Therefore, the problem of their recycling will always exist and should be faced by the scientific community. Until now, the solutions for thermoset recycling seem to be ineffective due to their high costs or emissions: only the energy reclaim is considered a valid strategy even if it is a very old idea. Factories are interested in developing industrial processes which provide high economical profits. The material recycling is felt by the factories as a cost and not as a business activity. If present, the recycling systems of thermosets are too expensive, large or complex. In many cases, these systems are ineffective and a very expensive research activities would be necessary to design an effective recycling technology. As a result, all the factories which produce thermosetting parts agree to their combustion for energy reclaim. This is a dramatic situation and the research is the only possible solution but this research has to be financed by the Governments. Environmentally consciousness of the people is increasing, and the European policy is pressing to define a sustainable development of the industrial activities, but the absence of new technological solutions does not allow any change. Unfortunately, in the past, research activities on these themes were not financially supported by the Governments as the energy reclaim was considered a valid solution. In this study, the researchers state that thermosets are high performance materials which can not become rubbish at the end of their life. Many other properties of these materials may be used apart from their ability in being burning: structural and functional properties useful in a lot of applications. The current study is a technological innovation that may be able to fill the lack of knowledge about thermoset recycling. The idea at the basis of this new recycling technology is very simple: pulverizing materials to give new reactivity to the resulting powder. In fact the broken links on the external surface of the particles may act as polymerising sites in further processing steps. If a residual reactivity of the bulk material is also present, it is useful to increase this powder reactivity. Rubbers, fibre reinforced plastics, polyurethanes may be pulverized to produce a powder which may be moulded by compression moulding without any addition of linking agents or virgin materials. As a result, a finished product would be obtained with good mechanical and functional properties. This product would be also recyclable by means of the same technology and the energy reclaim is configured as the last step when further recycling steps are not technically feasible.

2. THE STATE OF THE ART

In the scientific literature there are many articles which deal with the recycling of thermosets, even if the rubber of tyres is mainly mentioned. The case of the tyres is particularly interesting due to the interest of the scientific community. However the result of this interest does not seem so impressive. Even if many solutions are proposed, only the energy reclaiming is considered a valid strategy for tyres. Dealing with the problem of the tyre recycling, many interesting studies have been performed in the last 10 years. There are several solutions to recycle waste tyre rubbers; Fattuhi and Clark (1996) proposed the fabrication of cement-based, mortar, and concrete using various proportions of rubber made by shredding scrap tyres [1]. They found that rubber type had only marginal effect but, in any case, density and compressive strength were reduced by addition of rubber. In the same year Cecich et al. (1996) investigated engineering properties of shredded tyres, they used the waste materials as lightweight backfill for retaining structures [2]. In comparison with the conventional retaining structures filled with the sands, using shredded tyres can cause a substantial cost reduction and an increase in the factor of safety. Ferrer (1997) deeply discussed the economics of tyre remanufacturing [3]. There are two competing technologies in tyre retreading: the mould cure process and the pre-cure process. In both cases retreaded tyres deliver the same mileage as comparable new tyres, although they are sold with discounts between 30 and 50%. In his study, the author concluded that retreading is the sole alternative for maximizing tyre utilization. However, there are several stages in the retreading process where some material is lost, and tyre retreading is not always technically feasible. In these cases, heat generation is the only recovery alternative. Jang et al. (1998)

analyzed the tyre recycling practices in the United States, Japan and Korea [4]. They observed that the U.S. was moving towards disposing discarded tyres by using them as asphalt mixtures for highways while Japan used discarded tyres mostly for their fuel value, for example, in cement kilns. Afterwards, Adhikari, De and Maiti (2000) suggested that, among various methods of disposal of scrap/waste rubber products, recycling or reclaiming of rubber is the most positive approach, because it not only saves our limited resource fossil feedstock but also maintains our environmental quality [5]. Fang, Zhan and Wang (2001) discussed different kinds of recycling approaches to waste rubber, such as reclaiming energy as fuel, reuse of the products of thermal decomposition, cleaning of leaking oil, reuse after simple modification, regenerative rubber and powdered rubber (PR) [6]. They concluded that activated PR and fine rubber powder (RP) have a wider application field than common PR. More recently, Sunthonpagasit and Duffey (2004) observed that general demand of crumb rubber was increasing, and submarkets for crumb products were growing in size and variety [7]. However, the optimistic expectations of potential investors and government agencies contrasted sharply with the experiences of many producers. Lebreton and Tuma (2006) proposed a quantitative approach to assess the profitability of car and truck tyre remanufacturing [8]. They observed that retreading still remained only one alternative among others with a fraction varying from 1% up to 80% market share depending on the tyre type. Furthermore, they concluded that retreaded car and truck tyres turned out to be a competitive alternative, although these faced higher recovery costs. Unfortunately, tyre retreading had already reached its limits with respect to the fraction of the demand willing to buy ''green tyres'' eventually. The role of economic and policy instruments, such as the combined product tax-recycling subsidy scheme or a tradable permit, for scrap tyre recycling is of crucial importance in a market-oriented environmental management system. Very recently, Chang (2008) has discussed the economic and policy instrument analyses in support of the scrap tyre recycling program in Taiwan [9]. As a conclusion, different subsidy settings for collection, processing, and end use of scrap tyres should be configured to ameliorate the overall managerial effectiveness. In an European case study, Ferrão, Ribeiro and Silva (2008) has discussed the interaction between the different governmental, private and academic institutions for the creation of the integrated management system for end-of-life tyres [10].

Dealing with new recycling technologies, Holst, Stenberg, and Christiansson (1998) discussed that micro-organisms able to break sulphur-sulphur and sulphur-carbon bonds can be used to devulcanize waste rubber in order to increase binding upon vulcanization with virgin rubber [11]. Ishiaku, Chong and, Ismail (1999) determined the optimum of De-Link R (a devulcanizing agent) suitable for recycling the rubber powder [12]. Smith et al. (2001) investigated the cryogenic mechanical alloying as a viable strategy by which to produce highly dispersed blends composed of thermoplastics and tyre [13]. Hernandez-Olivares et al. (2002) investigated mechanical behaviour under static and dynamic load of concrete filled with small volumetric fractions of crushed tyre rubber and polypropylene short fibres [14]. In the same year Fukumori et al. (2002) create a new technology to recycling tyres [15]. They used a modular screw to crush into small pieces and devulcanized the waste rubbers in order to obtain a continuous recycling technology applicable to the new tyre rubber compounds. Sulkowski et al. (2003) obtained a rubber waste-polyurethane composite and investigated the influence of the polyurethane resin on hardness, elasticity, glass transition temperature and thermal stability of composites [16]. In the same year Franzis (2003) reinforced bituminous binders used in the construction of flexible pavements with crumb rubber produced from waste tyres [17]. It was shown that the binder has the potential to be used as an all-weather wearing course in flexible roads. A very interesting contribution was given by Bilgili et al. (2003) who proposed the compression moulding of pulverized rubber waste in the absence of virgin rubber [18]. In this study, the granulates of the waste were pulverized into small particles by using a single screw extruder in the solid shear extrusion process. The produced powder was moulded in absence of virgin rubber and used to produce rubber slabs which showed low-medium tensile strength. In fact, after the pulverization, the single rubber particle acquires new reactivity because of the broken links on the external particle surface that act as reactive sites.

The use of shredded tyres in civil engineering applications is discussed in most scientific papers. Li et al. (2004) used waste tyres in the form of fibres and developed waste tyre fibre modified concrete [19]. Their test results showed that, while the strength and stiffness of the concrete modified with waste tyre fibres were still lower than those without waste tyres, they were higher than those with waste tyre chips. Shalaby and Khan (2005) deepened the construction of road embankments by using large size tyre shreds [20]. Bignozzi and Sandrolini (2006) prepared self compacting concrete using different amounts of untreated tyre waste; they investigated mechanical and microstructural behaviour and compared fresh and hardened properties of such materials with those of the typical reference formulation of self-compacting concrete [21]. Turatsinze and Garros (2008) investigated properties of the self compacting concrete incorporating rubber aggregates, obtained by grinding end-of-life tyres; results showed that the new material goes against some governing principles of mechanical behaviour of ordinary cement-based concrete [22]. Unusual properties were interpreted as results of the ability of rubber aggregates to reduce the stress singularity at the first crack into the rubber-matrix interface.

In order to mention other technological alternatives for tyre recycling, Scaffaro et al. (2005) studied the formulation, characterization and optimization of the processing condition of blends of recycled polyethylene and ground tyre rubber [23]. Colom et al. (2006) also reused tyre powders as reinforcement in HDPE matrix improving stiffness and tensile strength and providing a more brittle behaviour [24]. These results were obtained performing several pre-treatments over the rubber tyres to improve the compatibility between both components. Grigoryeva et al. (2006) deepened the thermal analysis of thermoplastic elastomers based on recycled polyethylene and ground tyre rubber [25]. Another method to reuse waste tyres is a thermochemical recycling by pyrolisis. In fact Murillo et al. (2006) proposed this method to obtain some products: oils, gases and solid residue; they studied the effects of the main process variables on yields of derived products [26]. Aylon et al. (2007) performed pyrolisis of rubber from old tyres, three different phases were obtained: solid, liquid and gas and they studied the emission from combustion of the gas obtained in the recycling process [27]. Instead, Lin, Huang and Shern (2008) studied the possibility of applying waste tyre powder as a sorbent for the recovery of spilled oil [28].

The case of the rubber is interesting as shredded tyres are used only for asphalt filling or energy reclaiming, despite of the numerous solutions proposed. There are only few alternatives to these solutions such as the use of rubber particles in HDPE compounds. In other cases, such as the glass fibre reinforced thermosets, there is no one solution and it is not clear how these materials are managed at the end of their life. It is evident that the technological state of the art is not able to find a solution to the problem of the thermoset recycling. In this research program, an idea similar to the study of Bilgili et al. [18] is used. These researchers first demonstrated that the thermosets may be re-activated after comminution. They proposed a comminution process called “solid state shear extrusion” SSSE which consisted of an extruder in which rubber pellets were inserted. They observed that the final powder could be moulded by compression moulding without any addition of linking agent or virgin rubber, and discussed that the powder reactivity depended on the broken links of the particle surface. However they did not discuss that other comminution processes, different from SSSE, could produce the same effect.

3. EXPERIMENTAL

In this study, the authors studied the feasibility of the direct moulding process of comminuted powders to recycle thermosets. Spent tyres, polyurethane rigid foams and EPDM were used in the experimentation. All these material were collected from industrial waste and mechanically grinded. The rubber powder was supplied by Sycorex Ricerche Italia S.p.A. (Caserta, Italy) which produces sound absorbing sheets and tiles by adding a resin binder to the rubber particles.

Polyurethane and EPDM powders were moulded in a cylindrical steel mould with a cavity of 50 mm diameter. Rubber powders were moulded in the shape of quadrangular plates with a thickness above 30 mm, and the edge length of 150 mm. In this case, an aluminium mould was used. For compression moulding, the moulds were placed between the plates of a hot parallel plate press which provided the necessary heat and pressure. This press was a hydro-pneumatic press by ATS FAAR with a maximum load of 264 kN and the plate size of 300x300 mm^2. EPDM and rubber powders were moulded at the temperature of 250 °C for a time of 30 min. The temperature was limited to 180 °C for the polyurethane powder.

Figure 1 shows a piece of the rigid polyurethane foam before recycling. After mechanical grinding, the powder has the appearance of Fig. 2. The powder was inserted into the steel mould as Fig. 3 shows. After moulding, the material turned yellow probably due to the occurrence of an incipient surface degradation (Fig. 4). The initial density of the polyurethane foam was 0.04 g/cm^3. After moulding the density become 0.76 g/cm^3, i.e. 19 times the initial value.

The recycled polyurethane is rigid and brittle and a good consolidation was found through the sample section (Fig. 5). Figure 6 shows the appearance of the EPDM thick disk. The final thickness was about 17 mm, and the density about 1 g/cm^3.

Fig. 1. Rigid polyurethane foam to be recycled

Fig. 2. Polyurethane comminuted powder

Fig. 3. Polyurethane powder into the steel mould

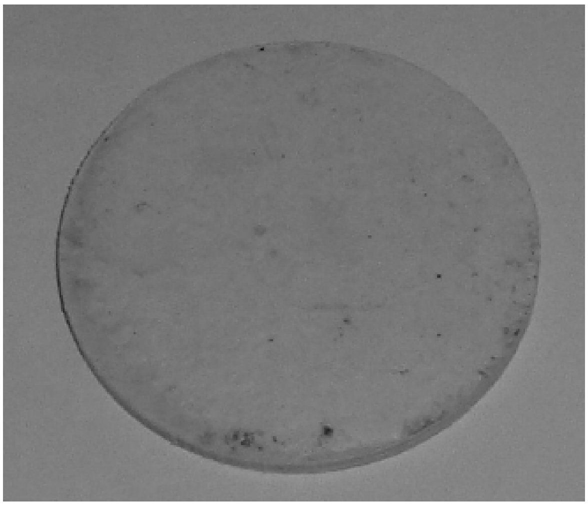

Fig. 4. Moulded polyurethane disk

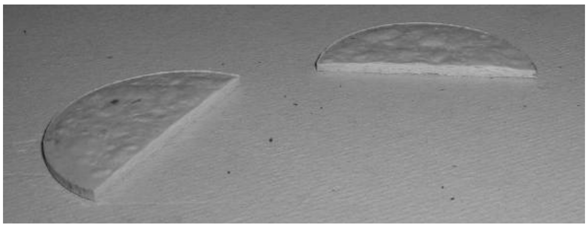

Fig. 5. Cut polyurethane disk

Fig. 6. Moulded EPDM disk

Figure 7 shows a large rubber pad with a complex structure. Thick pads are shown in fig. 8. The density of the rubber pads was about 1.12 g/cm^3, and a very good surface quality was obtained.

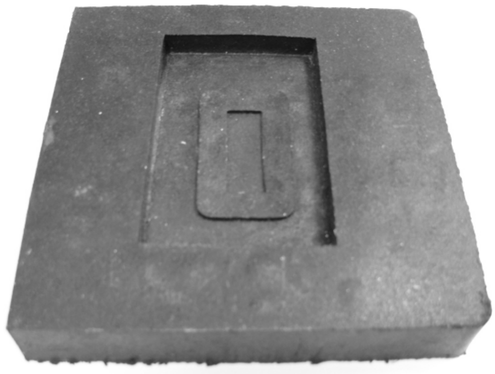

Fig. 7. Large moulded rubber pad

Fig. 8. Large and thick moulded rubber pads

All the moulded parts showed good consolidation and mechanical consistency. It was not possible to provide mechanical data because of the complexity for the extraction of samples. In the further experimentation, specimens for mechanical testing will be directly moulded.

The proposed experimentation shows the feasibility of the direct moulding of pulverised recycled thermosets. For this reason, an effort was made to identify the operative conditions to reach this goal. A further experimentation is necessary to evaluate the performances of the recycled parts. However, it is important to note that a step was taken forward in comparison with the study of Bilgili et al. [18]. In fact, Bilgili et al. proposed a new two-stage recycling process: first, the pulverization of the rubber granulates into small particles using a single screw extruder in the Solid State Shear Extrusion (SSSE) process; then, the compression moulding of the produced powder in absence of virgin rubber. In the present work, the authors showed that the SSSE process is not the only way to provide new reactivity to the recycled rubber particles and, above all, that not only rubbers can be recycled but also rigid thermosets.

3. CONCLUSION

In this study, for the first time, a recycling strategy was described for all the thermosets, rigid and soft. It is proposed to pulverise the materials and to directly mould the resulting powders without using any linking agent or virgin material. This process is very innovative in comparison with the technological state of the art in the field of recycling, and is a necessary step to allow the sustainable development of the related manufacturing processes. In fact, the production of high performance materials is developing very fast, and many new products are every day available on the market. As a result, recycling procedures are generally not suitable for this kind of materials. Among these materials, rubbers, foams, and elastomers are also present. This study shows the feasibility of the direct moulding process to recycle thermosets. Particularly rigid polyurethane foams were also efficiently recycled, and that is an absolute innovation for the present state of the art.

Generally thermosets are considered exhausted materials when the part, which is made of it, is no more working. Instead, also a thermoset should be considered a resource which can be used for a production process. For example, large rubber pads (shown in Figs. 7 and 8) could be used as bumpers, support for road signs, and floors.

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REFERENCES

[1] Fattuhi, N.I., Clark, L.A., *Cement-based materials containing shredded scrap truck tyre rubber*, Construction and building materials, 10, 1996, pag. 229-236;

[2] Cecich, V., Gonzales, L., Hoisaeter, A., Williams, J., Reddy, K., *Use of shredded tires as lightweight backfill material for retaining structures*, Waste management and resarch, 14, 1996, pag. 433-451;

[3] Ferrer, G., *The economics of tire remanufacturing,* Resources, conservation and recycling, 1997, 19, pag. 221-225;

[4] Jang, J., Yoo, T., Oh, J. and Iwasaki, I., *Discarded tire recycling practices in the United States, Japan and Korea*, Resources, conservation and recycling, 22, 1998, pag. 1-14;

[5] Adhikari, B., De, D., Maiti, S., *Reclamation and recycling of waste rubber*, Progress in polymer science, 25, 2000, pag. 909-948;

[6] Fang, Y., Zhan, M., Wang, Y., *The status of recycling of waste rubber*, Material & Design, 22, 2001, pag. 123-127;

[7] Sunthonpagasit, N., Duffey, M., *Scrap tires to crumb rubber: feasibility analysis for processing facilities*, Resources conservation & recycling, 40, 2004, pag. 281-299;

[8] Lebreton, B., Tuma, A., *A quantitative approach to assessing the profitability of car and truck tire remanufacturing*, International Journal of production economics, 104, 2006, pag. 639-652;

[9] Chang, N., *Economic and policy instrument analyses in support of the scrap tire recycling program in Taiwan*, Journal of environmental management, 86, 2008, pag. 435-450;

[10] Ferrão, P., Ribeiro, P., Silva, P., *A management system for end-of-life tyres: A Portuguese case study*, Waste management, 28, 2008, pag. 604-614;

[11] Holst, O., Stenberg, B., Christiansson, M., *Biotechnological possibilities for waste tyre-rubber treatment*, Biodegradation, 9, 1998, pag. 301-310;

[12] Ishiaku, U.K., Chong, C.S., Ismail, H., *Polyethylene/ground tyre rubber blends: influence of particle morphology and oxidation on mechanical properties*, Polymer testing, 18, 1999, pag. 621-633;

[13] Smith, A.P., Ade, H., Koch, C.C., Spontak, R.J., *Cryogenic mechanical alloying as an alternative strategy for the recycling of tires*, Polymer, 42, 2001, pag. 4453-4457;

[14] Hernandez-Olivarez, F., Barluenga, G., Bollati, M., Witoszek, B., *Static and dynamic behaviour of recycled tyre rubber-filled concrete*, Cement and concrete research, 32, 2002, pag. 1587-1596;

[15] Fukumori, K., Matsushida, M., Okamoto, H., Sato, N., Suzuki, Y., Takeuchi, K., *Recycling technology of tire rubber*, JSAE, 23, 2002, pag. 259-264;

[16] Sulkowski, W.W., Danch A., Moczynski M., Radon A., Sulkowska A., Borek J., *Thermogravimetric study of rubber waste- polyurethane composites*, Journal of thermal analysis and calorimetry, 78, 2004, pag. 905-921;

[17] Frantzis, P., *Development of crumb rubber reinforced bituminous binder under laboratory conditions*, Journal of material and science, 38, 2003, pag. 1397-1401;

[18] Bilgili, E., Dybek, A., Arastoopour, H., Bernstein, B., *A New Recycling Technology: Compression Molding of Pulverized Rubber Waste in the Absence of Virgin Rubber*, Journal of Elastomers and Plastics, 35, 2003, pag. 235-256;

[19] Li, G., Garrick, G., Eggers, J., Abadie, C., Stubblefield, M., Pang, S., *Waste tire fiber modified concrete*, Composites Part B: Engineering, 35, 2004, pag. 305-312;

[20] Shalaby, A., Khan, R., *Design of unsurfaced roads constructed with large-size shredded rubber tires: a case study*, Resource conservation & recycling, 44, 2005, pag. 318-332;

[21] Bignozzi, M.C., Sandrolini, F., *Tyre rubber waste recycling in self-compacting concrete*, Cement and concrete research, 36, 2006, pag. 735-739;

[22] Turatsinze, A., Garros, M., *On the modulus of elasticity and strain capacity of self-compacting concrete incorporating rubber aggregates*, Resources, conservation and recycling, 52, 2008, pag. 1209-1215;

[23] Scaffaro, R., Tzankova Dintcheva, N., Nocilla, M.A., La Mantia, F.P., *Formulation, characterization and optimization of the processing condition of blends of recycled polyethylene and ground tyre rubber: Mechanical and rheological analysis*, Polymer degradation and stability, 90, 2005, pag. 281-287;

[24] Colom, X., Canavate, J., Carillo, F., Velasco, J. I., Pages, P., Mujal, R., Nogues, F., *Structural and mechanical studies on modiWed reused tyres composites*, European polymer J, 42, 2006, pag. 2369-2378;

[25] Grigoryeva, O., Fainleib, A., Tolstov, A., Pissi, P., Spanoudaki, A., Vatalis, A., Delides, C., *Thermal analysis of thermoplastic elastomers based on recycled polyethylenes and ground tyre rubber*, Journal of thermal analysis and calorimetry, 86, 2006, pag. 229-233;

[26] Murillo, R., Aylon, E., Navarro, M.V., Callen, M.S., Aranda, A., Mastral, A.M., *The application of thermal processes to valorise waste tyre*, Fuel processing technology, 87, 2006, pag. 143-147;

[27] Aylon, E., Murillo, R., Fernandez-Colino, A., Aranda, A., Garcia, M.F., Callen, M.S., Mastral, A.M., *Emissions from the combustion of gas-phase products at tyre pyrolysis*, J of analytical and applied pyrolysis, 79, 2007, pag. 210-214;

[28] Lin, C., Huang, C. Shern, C., *Recycling waste tire powder for the recovery of oil spills*, Resources, conservation and recycling, 52, 2008, pag. 1162-1166.