Chapter 8

Recycled Rubber: Composite Matrix

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1. Introduction

Rubber is produced from natural or synthetic sources. Natural rubber is obtained from the milky white fluid called latex, found in many vegetal, while synthetic rubbers are produced from unsaturated hydrocarbons. Natural rubber has been used for commercial vehicles such as lorries, buses and trailers; synthetic rubbers, with specific properties is used for targeted applications, in small lorries, private cars, motorbikes and bicycles. The synthetic rubbers, commonly used for tire manufacturing are styrene-butadiene and/or butadiene rubber. Butyl rubber, since it is gas-impermeable, is commonly used for inner tubes.

There is a large wastage of rubber tires in many countries and the aim of this brief review is to give some ideas on what can be done with this valuable resource. Whether rubber tires are reused, reprocessed or hand crafted into new products, the end result is that there is less waste and less environmental degradation. There are many ways in which tires and inner tubes can be reused or reclaimed. The waste management hierarchy dictates that re-use, recycling and energy recovery, in that order, are superior to disposal and waste management options. Traditional rubber recycling processing paths are outlined in Table 1.

Efforts to develop recycled rubber – plastic blends have followed earlier blending research on pure polymers that produced both thermoplastic elastomers and rubber-toughened plastics. The large interfacial area and particle/filler interaction is modifying the glass transition temperature and mechanical properties.

The end-of-life tires can be recycled and used as a second raw material. The waste tires can be recovered through blending recycled rubber with other materials (organic and inorganic compounds) as an efficient alternative in waste rubber recycling, to obtain composite materials. The rubber can act as matrix in composites and the filler may consist of other (recycled) organics, such as plastic materials, or fillers (inorganics, wood, etc.).
Table 1. Traditional rubber recycling processing paths [1]

<table>
<thead>
<tr>
<th>Process</th>
<th>Kind of recovery</th>
<th>Recovery process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product reuse</td>
<td>repair</td>
<td>retreading, re-grooving use as weight, use of form, of properties, of volume</td>
</tr>
<tr>
<td></td>
<td>physical reuse</td>
<td>physical tearing apart, cutting processing to crumb reclamation</td>
</tr>
<tr>
<td>Material reuse</td>
<td>chemical</td>
<td>chemical reclamation</td>
</tr>
<tr>
<td></td>
<td>thermal</td>
<td>thermal pyrolysis, combustion</td>
</tr>
<tr>
<td>Energy reuse</td>
<td></td>
<td>incineration</td>
</tr>
</tbody>
</table>

One challenge is to obtain rubber-based composites embedding other plastic wastes with very low biodegradability as there is PET, which cannot be reused as such due to the change in its crosslinking factor during primary manufacturing. Rubber and PET are usually reported to develop poor interfaces and phase separation can appear, thus the amount of plastic material that can be included in rubber is limited at 10……25 %. This can give rise to poor mechanical properties and undesirable performance for targeted end uses. Increasing this percent represents a subject that is detailed in this chapter.

Despite these problems, a wide range of new materials, with improved properties have been obtained by the addition of a third component, for increasing compatibility. It is well known that blends of immiscible polymer pairs are characterized by large interfacial tension which makes dispersion during blending difficult, and contributes to unstable morphology and poor adhesion. The main difficulty is the generation of sufficient adhesion between the two phases.

Good interfacial adhesion and reduced interfacial tension between the components can be obtained for compatibilized PET and rubber materials. The compatibility can be done by the addition of other polymers, such as high density polyethylene (HDPE), low density polyethylene (LDPE) and/or inorganic compounds (TiO₂). Inorganic oxides (CaO, ZnO and fly ash) were also tested for enhancing the mechanical properties.

The chapter presents novel results obtained in increasing the recycled PET content, up to 35% in a recycled rubber matrix, using as additive recycled polyethylene and, as fillers, oxides that also improve the overall mechanical properties. The use of another inorganic waste, fly ash is a viable option, completing the sustainability of the novel composites.

Using different recipes, the composites can be tailored for various indoor and outdoor applications. The chapter presents optimized composites (in terms of mechanical properties) for applications as building materials as paving slabs, as thermal and electrical insulators, etc.

1.1. Traditional Methods Rubber Recycling Processing

Rubber wastes represent an important category of recyclable materials as well as a secondary source of recyclable raw stock and of alternative fuel.
Rubbers are macromolecular products with great nerviness. Under the action of external stress, rubber goes through elastic deformation, its elongation reaching up to 200 %; when the stress is removed rubber returns to its original configuration. Due to this basic characteristic, rubbers are called elastomers.

Scrapped tires represent a type of resource which can and should be widely used. Nowadays the world is focused on deposits of scrapped tires that must be recycled and reused as industrial material, energy source or reactivated after tire soling.

A tire is composed of a number of materials: the rubber content is in between 46-48 %, carbon black 25-28 %, steel 10-12 %, oil, vulcanizing agents 10-12 % and textiles 3-6 %. The rubber extracted from scrapped tires can encompass synthetic rubber under the form of styrene-butadiene-rubber, butadiene rubber and in small amounts of natural rubber.

The regular structured rubber, in the form of 1,4 cis-polyisoprene, shows a pronounced crystallinity, while other types of rubbers, due to their irregular structure, do not crystallize. When there are unsaturated polymer structures alongside the polymer chain, a few different types of isomers are possible.

Butadiene rubber presents a few different forms of isomers due to the existence of the unsaturated structure of the polymer’s chain. The best isomer for commercial purposes is 1,4-poli(1,3-butadiene), where all the 4 atoms of C from the repetitive structure are positioned along the macromolecular chain. The structure of the butadiene used in the styrene-butadiene-rubber is mainly the 1,4-trans isomer, which contains 1,4-cis isomer and 1,2-poli(1,3-butadiene), [2].

Styrene-butadiene-rubber is a thermoplastic elastomer, with amorphous areas built up by styrene, and reticulated butadiene, [3,4]. This is very much dependant on the composition: if the rubber presents a higher percentage of butadiene, then the elastic proprieties prevail.

The study of elasticity, of the plastic and vitreous state requires a thorough knowledge of the composition, the structure and the morphological change at the level of molecular conformation and heat endurance of the polymers. Heat endurance represents the maximal temperature that a material can endure over a long period of time without modifying the other characteristics. Moreover, one has also to consider the minimum temperature of use, since both elastic polymers and plasticized polymers modify their mechanical properties considerably at low temperatures. Heat endurance is also connected with the strength of macromolecular products which could be under load action or free of load action [5,6].

The natural rubber is amorphous at temperatures higher than 10 °C; it crystallizes at lower temperatures and the maximum crystallization rate is at -25 °C. When strained (at room temperature) with over 70 % crystallization also occurs and one way of reducing this effect is vulcanizing, so natural vulcanized rubber crystallizes at room temperature at over 200 % strain. In the low oxygen content atmosphere, the natural rubber can tolerate heating at 200 °C, but at temperatures higher than 220 °C the thermal decomposition initiates, resulting liquid products; heated for a few hours at 250…300 °C, these are transformed in a resinous product, insoluble in benzene. When vacuum heated at 250…300 °C, over 60 % of the natural rubber is decomposed, resulting volatile products and what is left of it remains in the resinous residue. In the absence of oxygen, the UV radiation induces the natural rubber structuring, with emission of volatile products. In the presence of oxygen, there is a decomposition followed by structuring. The natural rubber macromolecules are sensitive to ozone cracking, [7].

Different types of natural rubber and some synthetic rubbers (especially the ones synthesized through heat polymerization) are characterized by high values of the molecular
weight. This aspect confers a great elasticity and high viscosity which ensures high physical–mechanical properties for the vulcanized product. For a proper treatment of these tires their flexibility can be reduced and their plasticity can be increased [8].

The increase in the elastomers’ elasticity is correlated with a reduction in the strength properties of the vulcanized product and an increase in the remaining deformations of the elastomers. A higher plasticity ensures a good adhesion of the elastomers to other materials increases their molding potential and allows manufacturing of concentrated solutions with smaller viscosity. Natural rubbers vulcanizates differentiate themselves through a high elasticity, at room temperature as well as at relatively high temperatures (100 °C), good abrasion resistance, a good response to low temperatures and superior dynamic properties.

**Rubber recycling**

When a rubber has been de-vulcanized, it is of interest to re-vulcanize it as a new product and to see whether the mechanical properties are comparable to the virgin rubber. Recycling of rubber is considered as a way to save the material cost by reshaping the used rubber into a new product or otherwise reusing it to replace some fraction of the virgin material. The effect of incorporating reclaimed tire rubber into virgin natural rubber (NR) on the mechanical properties has been already reported [9, 10].

Recycling and recycling of rubber can contribute to saving the oil resources and solve the problem of rubber wastes disposal. There are several forms of recycling rubber, namely: regeneration, retreading, material and energy recovery.

**Rubber reclaiming** is one of the most common recycling processes. It stands for the conversion of a reticulated polymer, insoluble and hard, infusable thermoplastic bidimensional, viscous/thick, light, treatable and vulcanizable, which presents a great part of the virgin rubber properties. Since 1910 many trials of reprocessing rubber wastes have been done [11]. Rubber reclaiming can be classified in three categories:

- Physical reclaiming process
- Chemical reclaiming process (Warner)
- Biotechnical reclaiming process

The choice of the reclaiming process is depends on the nature and type of rubber from the wastes (tires, inner tubes, footwear, technical articles, natural or synthetic rubbers) as well as on the proprieties that the regenerate/reclaimed rubber must have (plasticity, physical-mechanical indices, reprocessing properties, etc.)

In the regeneration process there are both chemical degradation of macromolecular chain under the influence of thermal and oxidative and mechanical processes of plasticization on the vulcanized wastes. In the regeneration process of rubber waste can be present a number of plasticizers such as cracked oil, petroleum plasticizers, depending on the type of recycled rubber. The goal is to transform vulcanized rubber with elastic properties into a material with plastic properties that can be reused in different proportions in the rubber blends [12].

Natural regeneration process consists of crosslinked rubber waste decomposition by external energy. Macromolecular blends will split into smaller pieces so easier mixing with virgin rubber becomes possible. The rubber obtained in this way can be used as matrix and reinforcing fibers in composites.
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Rubber reclaiming through chemical processes

For rubber chemical reclaiming, use chemical reclaiming agents, that are used exclusively (disulphide, mercaptan) during the mechanical processing at very high temperatures. There is a large number of chemical reclaiming agents for natural and synthetic rubber using diphenyl disulfide, dybenzil disulfide, butyl mercaptan and phenyl mercaptan and other tiols, xylene. Reclaimed rubber has reduced mechanical proprieties; when chemically treated, the C-S, S-S bonds are broken but not the C-C bonds. A few inorganic compounds were also used as reclaiming agents (carbon, soda smelt, FeCl₂, Cu₂Cl₂) and also chemical decomposition was used. The use of these resulted in C-C bonds splitting [13, 14].

Rubber reclaiming through biotechnological processes

Rubber reclaiming through biotechnological processes can develop, using a chemolithotrope bacterium in water slurry to attack elastomers only at surface in such a way that the mixing with the untapped rubber during vulcanization is facilitated, [15, 16].

In all the reclaiming processes mentioned above the reclaiming degree is specified. The physical as well as the chemical processes supposes splitting of the polymer chains due to the mechanical action at high or low temperatures, due to the chemical action at high temperatures, thermal splitting or through ultrasonic energy at high temperatures. The splitting of the vulcanized rubber chain during reclaiming is supposed to increase the plasticity and the content of colloidal system, [17].

Types of reclaimed rubber and their properties

Following natural and synthetic rubber, reclaimed rubber is a third raw material for rubber processing industry. The different types of reclaimed rubber can be classified according to the waste type, the reclaiming process and according to the technical qualities that the regenerate has to fulfill [11].

Reclaimed rubber obtained from auto tires, having the best possible properties is used on industrial scale at manufacturing tires and inner tubes.

The other types of reclaimed rubber came from wastes of technical items, footwear, etc. They have inferior properties, since they depend on the type of rubber, on the quality of the other ingredients that were used, on the reclaiming process, refinement and homogenization, etc. The latter are used to manufacture rubber products which are exposed to lighter static and dynamic loading.

Uses of reclaimed rubber

Reclaimed rubber is used, in different proportions, in natural and synthetic rubber mixtures, to manufacture various rubber products [18]. When reclaimed rubber is used the following must be considered:

- the approximate rubber content
- the reclaiming process, which can influence the vulcanization optimum
- the quantity and type of softening agents that it contains
- the quantity and types of filling ingredients
- proportion of sulphur and accelerators
- plasticity and physical-mechanical properties
- degree of purity and homogeneity/uniformity
- technical conditions of quality and operation that are required for the rubber product.

Reclaimed rubber introduced in the compound substitutes part of the natural or synthetic rubber, as well as a part of the infilling materials. The quantities of sulphur and accelerators that must be added to the rubber compound with reclaimed rubber are established considering the total amount of hydrocarbons, the reclaims content of sulphur and of accelerators. Generally, the compounds with a reclaim contain of 15-30 % must contain less sulphur and accelerators than the compound without reclaim.

The fillers and the types of synthetic rubber must allow the embedment of a large quantity of reclaim to obtain a homogeneous mixture with physical-mechanical characteristics of superior elasticity. Generally, in rubber compounds when the quantity of the reclaim added, the stretch resistance, the endurance, the adherence of the rubber covers to fabrics, the abrasion resistance decreases, whilst the breaking elongation and the residual elongation augment [19]. Natural rubber based products with a certain amount of reclaim give better results in processing than the same products based on synthetic rubbers.

**Tire retreading**

Retreading is the most direct form of tire recycling. Used rubber is replaced with a new layer of rubber introduced in the old carcass for vulcanization.

This technology supposes a number of important steps such as:

- *Examination of used tires* for to track down any structure flaws that can be tracked down visually.
- *Tire detreading* - removal of the tire tread;
- *Repairing the flaws* - any flaws that have appeared after detreading are repaired (cuts, wholes made by sharp objects)
- *Applying the tire tread* - on the skinned carcass a contact rubber strip is applied, that is going to connect the carcass and the new tire tread;
- *Devulcanizing* – the devulcanizing rubber can be re-vulcanized by conventional curing process with sulfur-accelerator vulcanizing system.
- *Final inspection*

Retreading process also has some advantages such as saving a considerable amount of raw materials and energy, saving oil and the retreaded tire can be said to have the same life (in kilometers) with a new tire, but costs less. By retreading the problem of waste from the tires is not entirely solved but the tires make recovery clearly an improvement in this sector [19].

**Reclaiming material and energy**

By making an attempt to save more and more energy and raw materials, are researched and deployed new options of retreaded tire usage. Resource reclaiming thermal treatment appear to be the most advanced and recommendable methods, able to eliminate some of the biggest problems in this field. At the base of thermal treatment the following processes can be identified: *cryogenic grinding, gasification, pyrolysis* [20].
Cryogenic grinding usually begins with chips of a fine crumb, which is cooled with liquid nitrogen as the medium using a chiller, or pre-cooler where it is sprayed with liquid nitrogen at 320 °F or 195 °C. This embrittles the rubber and makes it easier to grind to fine crumb (40 to 100 meshes). The frozen rubber is put through a high velocity impact type mill.

Tire pyrolysis (thermal decomposition in an oxygen-free environment) is currently receiving renewed attention. Recycling of tires by pyrolysis offers an environmentally attractive method. The products of the tire pyrolysis process are: solid char (30-40 wt %), liquid residue (40-60 wt %), and gases (5-20 wt %) [19]. The solid residue contains carbon black and the mineral matter initially present in the tire. This solid char may be used as reinforcement in the rubber industry, as activated carbon very efficient in gases’ separation or as smokeless fuel. The liquid product consists of a very complex mixture of organic components. Thus, the derived oils may be used directly as fuels, petroleum refinery feedstock or a source of chemicals. The gaseous fraction is composed of non-condensable organics as, H₂, H₂S, CO, CO₂, CH₄, C₂H₄, C₃H₆ etc. The gas fraction can be used as fuel in the pyrolysis process.

The above mentioned treatments present the following advantages:

- Waste volume (scrapped tires) can be reduced with over 90%.
- The processes referred to are energy producers with material reclaiming properties.

It must be mentioned that there are also a number of issues, such as:

- **ashes**: through the presence of cadmium salts;
- **toxic gases**: when tires are incinerated they generate toxic gases (SO₂, H₂S, HCl, HCN);
- **carbon black**: “imperfect” incineration of wastes is going to produce carbon black. Generally, this type of materials has heating values higher than the municipal wastes, needing a larger firing floor and a higher burning point.
- **adequate incinerators** – to solve the above mentioned problems.

1.2. Advanced recycling rubber

Advanced rubber reclaiming can be done together with other materials as composites.

In developing the field of composites, a meaningful contribution was brought by rapid progress in polymers chemistry and physical - chemistry which allowed the development and diversification of a new class of materials called polymeric composites.

When polymers are mixed with inorganic materials, a series of problems appear, such as:

- material compatibility,
- obtaining a uniform dispersion of components,
- processes and equipment that can be efficiently used to obtain materials.
When two or more polymers need to be processed together, there are two ways of obtaining them. One is to obtain a master-batch which is afterwards fed to the forming device matrix and the other one refers to separate feeding of the mixtures components at the same forming device. A number of theoretical and technological aspects remain still unsolved. Some of the most important ones are [12, 22]:

- The principles of reinforcing polymers with dispersed fillers and the low or high deformations control are still not elucidated;
- Calculations of mechanical properties of composites with polymeric matrix, according to experiments; there are considerable theoretical difficulties when infill materials are used;
- Breakage mechanisms, must be taken into consideration when calculating the final endurance characteristics of the polymeric composites;
- Impact strength of polymeric matrices replete with rigid particles or fibers;
- Interfacial layers in polymeric matrix composites have attracted researchers’ attention due to the fact that these layers have a considerable influence upon mechanical properties, and data regarding their organization are scarce. Theoretical analyses usually comply with good or weak adherence patterns;
- In the case of reinforced thermoplastic materials important matters are linked to preserving the initial report of the infilling material, providing a good orientation and improving adhesion between reinforcement material and matrix.

Many trials have been made to find economic applications for GTR fractions. They have been incorporated in rubbers, thermoplastic and thermoset polymers, asphalts, bitumen, concrete etc. However, untreated crumb only can be added in a small amount before the properties of the blend start to degrade. Once the ground rubber is already vulcanized, it is difficult to blend it with other existing polymers because there is little interfacial bonding between the rubber powder and the matrix.

Albeit efforts are in progress to use 100 % GTR to make new rubber products (e.g. [23]), majority of the works tackles the GTR use as filler. Recognizing the problem with interfacial bonding/adhesion numerous approaches were introduced for the surface modification of GTR. The “common denominator” of these approaches is to enhance the polarity of the GTR surface. This should yield a change in the surface energies favoring the wetting by the matrix.

Therefore, a variety of technologies have been developed for powder surface modification and devulcanization to enhance the rebounding of crumb and improve its mechanical performance in compounds.

**Composite materials procurement technologies**

Diverse manufacturing technologies of these materials involve machines and processes for: procurement of polymeric matrix, preparing the reinforcing components, fibers impregnation or treatment, cutting the fibers, making the reinforcement (network, netting, web, etc.), making the adequate composition through injection, extrusion, compression – molding, other proceedings. Basically, for every type of composite polymeric material a distinct technology, with specific operations and devices is necessary. Composite materials
procurement technologies are a lot more different than the ones applied in the case of classic materials (metals, glass, ceramic, etc.). The choice of the optimum technological alternative is made according to the shape and size of the pieces, the size of the fabricated products, and the nature of polymeric matrix, molding process, quality and molding costs [12].

Recycling of scrapped tires will give three product categories and these products harness various destinations, such as:

- *Granulates and powders rubber* (0 - 4 mm) – Granulates and powders have been used to produce noise absorbing sheets, floor tiles, paving blocks and the like (*floor systems for railway level crossings, flooring for stables, pavement for sports, protective rubber carpets for construction and work environments in factories, insulating material for tunnels and other structures, products for noise insulation, rubber car mats, rubber soles for footwear, asphalt mixes, etc., mattress environmental protection recycled rubber construction.*). These applications are often termed “Downcycling” as the recycled product has a different application than the initial (i.e. tyre) one [24].
- *steel wire* – steel will be remolded
- *synthetic yarns* - synthetic yarns can be used as solid fuel and any insulating material.

### 1.3. Rubber – PET composites

#### 1.3.1. Obtaining Rubber – PET composites

There is no doubt that the main reasons for blending are – with equal importance, the environment and the economy targeting the development of new high-performance materials in terms of recycling processes. While recycling rubber have plenty of options, recycling PET and developing new products, raises serious problems due to the structural changes in the material during primary manufacturing, leading to 3D structures. Therefore, developing blends with high PET content dispersed in a matrix of moldable polymer is one topic that still requires research. Tire rubber mixing is preferred due to lower cost and higher existent quantities. However, PET–rubber blends are immiscible and incompatible and have poor physical-chemical properties. This problem results from the low intermolecular forces between the components of the immiscible blends. As a result, most of the studies have been focused on techniques able to improve the compatibility and physical-chemical properties of these composites.

A wide range of compatibilizers has been investigated to obtain compatible and high physical-chemical property blends. For developing marketable products, it is important to find low-cost, efficient compatibility agents. On the other hand, for developing sustainable recycling process these agents should be non-toxic. Therefore, we propose the use of another waste, as second raw material, for increasing the compatibility of PET-rubber, up to a high PET content.

To obtain composites recycled materials were used, namely:

- poly-ethylene terephthalate (PET) - derived from soft drink bottles;
- rubber - from tires and bicycle tubes
- High density polyethylene (HDPE) - from yogurt containers, etc.;
- low density polyethylene (LDPE) – from packaging;
Mechanical properties and composite environmental behavior can be tailored by dispersing different oxide powders. Efficient dispersing occurs when the powders are in the range of nano- or mezzo- scale, resulting hybrid inorganic-organic composites. Therefore, blends were developed using:

- TiO$_2$ powder (Degussa P25), with an average size of 21 nm primary and specific surface 50 m$^2$ / g TiO$_2$ nanoparticles consisting of 80% anatase and 20% rutile.
- CaO powder (Reagent Bucharest, Romania, purity > 90%)
- ZnO powder (Scharlau, purity > 99%)
- fly ash powder with the following composition: SiO$_2$ (53.32%), Al$_2$O$_3$ (22.05%), Fe$_2$O$_3$ (8.97%), CaO (5.24%), MgO (2.44%), K$_2$O (2.66%), Na$_2$O (0.63%), TiO$_2$ (1.07%), MnO (0.08%), the rest being unburned carbon, (CPH Brasov, Romania)

**Composite structure:**

*a) Matrix - rubber tires*

To discuss the reuse of waste tires the knowledge of materials and substances used to produce tires is essential. Synthetic or natural rubber is mixed with ingredients resulting in a mixture which, after vulcanization represents the tire rubber. A mixture may contain:

- natural / synthetic elastomer
- curing agent (sulfur)
- primary accelerators
- secondary accelerators
- inorganic activator (zinc oxide)
- ingredients (carbon black)
- plasticizers (oil)
- protective agents (anti-oxidants, stabilizers).
- antioxidants and anti-ozonants

Thus tires represent a complex combination of composite rubber/hydrocarbons and minerals along with insertion materials (like metal or polymeric cord). The main ingredient is indeed rubber - which may be natural or synthetic or even rubber recycled rubber. Car tires (small) and van tires are generally made of synthetic rubber (polystyrene and polybutadiene) and car-truck tires are made of natural rubber [25].

There is 30% rubber within the tire mass, the other materials being steel, nylon, polyester, viscose, carbon black, glass fiber, aramid and brass. The tires are made for specific use and are in a large variety of sizes and shapes, [26].

The data presented were obtained using waste tires containing in addition to natural rubber synthetic rubber as well, such as butadiene and the butadiene-styrene, and various additives. The main physical and mechanical characteristics of natural rubber are given in Table 2, [27].
Table 2. Physical and mechanical properties of natural rubber

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline structure</td>
<td>amorphous-semi-crystalline, 50-70%</td>
</tr>
<tr>
<td>Glassy transition temperature (° C)</td>
<td>-67-/-7</td>
</tr>
<tr>
<td>Melting point (° C)</td>
<td>190</td>
</tr>
<tr>
<td>Pour point (g/10min)</td>
<td>190°C/2,16kg: 0.7</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.93</td>
</tr>
<tr>
<td>Tensile strength (N/mm²)</td>
<td>22+/-7</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>650</td>
</tr>
</tbody>
</table>

b) Fillers - polyethylene terephalate (PET)

Polyethylene terephalate (PET) is thermoplastic polyester obtained from the poly-condensation of dimetil terephthalate with ethylene glycol. The material can be amorphous or with different crystallinity. Depending on the degree of crystallinity, some mechanical properties vary as well. It is in the form of granules, compounds with or without filling powders. Physical-mechanical properties of PET are shown in Table 3.

c) Additives - High density polyethylene (HDPE)

High density polyethylene is industrially produced by low-pressure ethylene polymerization (100-100 daN / cm²) with catalysts. HDPE is presented in granular form colorless, opaque, intensely colored or transparent. It is a highly crystalline polymer (60-90 %). HDPE parts can be used at maximum continuous working temperatures of 100-120 °C and minimum continuous working temperatures - 70 ° C. The physico-mechanical properties of HDPE are shown in Table 3.

Table 3. Physical and mechanical properties of PET and HDPE material

<table>
<thead>
<tr>
<th>Properties</th>
<th>PET [16]</th>
<th>HDPE[26]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline structure</td>
<td>amorphous-semi-crystalline, 30-40%</td>
<td>semi-crystalline, 60-70%</td>
</tr>
<tr>
<td>Glassy transition temperature (° C)</td>
<td>-95+/-5</td>
<td>-120+/-5</td>
</tr>
<tr>
<td>Melting point (° C)</td>
<td>255+/-15</td>
<td>130+/-5</td>
</tr>
<tr>
<td>Pour point (g/10min)</td>
<td>260°C/2,16kg: 19+/-16</td>
<td>190°C/2,16kg</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.37</td>
<td>0.96</td>
</tr>
<tr>
<td>Tensile strength (N/mm²)</td>
<td>47+/-7</td>
<td>29+/-11</td>
</tr>
<tr>
<td>Elastic modulus (N/mm²)</td>
<td>3100+/-200</td>
<td>1000+/-400</td>
</tr>
<tr>
<td>Impact strength (0 ° C) (kJ/m²)</td>
<td>4+/-2</td>
<td>7.5+/-2.5</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>300</td>
<td>130</td>
</tr>
</tbody>
</table>

Method of producing the composites

The samples were obtained by compression molding, Figure 1. Modeling compression is a specific method for thermoreactive and thermoplastic materials. The method consists in applying pressure on the powder pressing right dose, enclosed in a mold, Figure 2, the matrix is subjected to heat treatment in an oven thermostat, type ECv 200-300 at predetermined
temperature and time. Mold temperature and pressure are high, leading to possible physical-chemical reactions. After the molding time expires, molds are removed from the oven, placed in a water bath for rapid cooling and shape formation, then they are removed from the mold and characterized, [28].

To obtain PET-rubber composites that are based on recycled materials, the following steps are followed:

- Recycled rubber and plastics cleaning by washing, to remove impurities and labels;
- Grinding materials: grinding was performed using cutting tools (guillotines, shears) to obtain pellets about 1-2 mm size and using a centrifugal mill ZM 200 to obtain particulate size of 0.5-1mm.
- preparing mixtures dosed by various recipes and strengthening using additives;
- forming composite - produced by compression molding, resulting in samples of rectangular shape (10 * 10 * 120 mm$^3$), Figure 1.
- cooling - for completion the samples shape;
- removal of the mold from the samples.

The materials were initially used as pellets, and then as powders. Homogenization of dosed mixture was not ideally achieved, thus the obtained composites are statistical composites with anisotropic properties. Since the characteristic properties are partly different for every direction, they tend to a similar behavior of isotropic composite material, which resulted in the characterization methods.

1.3.2. Optimizing parameters of composition and technological parameters

Mechanical properties of materials are the consequence of two sets of parameters:

- **Composition parameters**: particle size, particle agglomeration and particle shape, type of recyclable rubber, type of filler material and additive, filler distribution in the matrix, the components mixing ratio;

- **Technological process parameters**: temperature and processing time, the mold clamping force, pressure.
To control the mechanical properties optimization studies were done for:

- the type and composition of the materials used for composites
- the compression molding duration
- the compression molding temperature
- the components distribution in the composite material
- the additive type and dosage

1.3.3. The mechanical properties of the rubber – PET composites

a) Optimizing the composition

Optimizing the composition of the composites based on recycled rubber was done testing several series of samples. They were marked as follows:

Series A - pieces 100% recycled rubber,
Series 1B - rubber : PET = 95: 5
Series 2B - rubber : PET = 90: 10
Series 1C - rubber : HDPE = 95: 5
Series 2C - rubber : HDPE = 90: 10

The samples were tested and analyzed (physical-chemical and mechanical properties), the results obtained for the samples made of rubber - PET and/or HDPE being compared with those containing only recyclable rubber. For each property evaluation, three samples were tested, and the mediated results are presented.

Calculation was done using average values the soft tensile test machine, Zwick for:

- longitudinal modulus of elasticity E (Young's modulus), Fmax - The maximum tensile strength, ε - Fmax - elongation to maximum force, ε - break - elongation to failure, W Fmax - the work / energy under the curve up to Fmax W tear - carried to power load, etc. Specific characteristics recorded during the mechanical test are shown in Table 4, [29].

Comparing the results it can be observed that the tensile strength demand is more pronounced for type C samples, the increase in the tensile strength is 20 % and elongation decreases by 9.09 % owing to a lower percentage of rubber in the composite. Comparing samples from the 2B series with the 2C series, it appears that PET introduction into the rubber matrix gives a higher resistance (σ = 2.25 MPa and ε = 9.3 % for samples obtained at 220 °C) than placing HDPE (σ = 1.9 MPa and ε = 4.7 % for the samples obtained at the same temperature). This could be explained based on the transition temperatures of PET and HDPE's. Analyzing the data of Table 4 shows that for the type C samples compressive forces were recorded by 50 % lower than in other series, achieving elastic structures.

Knowing the transition temperatures of the materials, it can be stated that in the temperature range 200-240 °C, rubber and HDPE are at a high-elastic state which allows an interface formation between these two components. In this temperature range, PET does not undergo phase transformation, this only occurs at a temperature close to 260 °C. This explanation justifies the behavior in compression tests, the samples obtained at 240 °C showing large compressive forces resistance.

Analyzing the values of elasticity modules, we conclude that between components weak interfaces were developed, following physical interactions or mechanical adhesion due to
compression. These values decrease with the molding temperature and are influenced by the manufacturing parameters, especially the pressure applied to the mould that can influence the sample density, resulting porous or dense structures.

Comparing the properties of the samples, it can be concluded that rubber material, PET and HDPE can be recycled together to form composite materials. Based on the studies conducted up to this point, the optimum composition (in mass %), would be Rubber: PET: HDPE = 85: 10: 5; this material can be used as construction materials for planning children's playgrounds or gardens.

Table 4. Results obtained from the mechanical tests

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Temperature [°C]</th>
<th>F_tr [N]</th>
<th>σ [N/mm²]</th>
<th>ε [mm]</th>
<th>E [N/mm²]</th>
<th>F_c [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – 1</td>
<td>220</td>
<td>175</td>
<td>1.75</td>
<td>9.30</td>
<td>0.188</td>
<td>500</td>
</tr>
<tr>
<td>A – 2</td>
<td>240</td>
<td>125</td>
<td>1.25</td>
<td>6.60</td>
<td>0.189</td>
<td>510</td>
</tr>
<tr>
<td>A – 3</td>
<td>260</td>
<td>185</td>
<td>1.85</td>
<td>10.5</td>
<td>0.176</td>
<td>1200</td>
</tr>
<tr>
<td>1B – 1</td>
<td>220</td>
<td>175</td>
<td>1.75</td>
<td>5.70</td>
<td>0.307</td>
<td>500</td>
</tr>
<tr>
<td>1B – 2</td>
<td>240</td>
<td>150</td>
<td>1.50</td>
<td>7.20</td>
<td>0.208</td>
<td>1100</td>
</tr>
<tr>
<td>1B – 3</td>
<td>260</td>
<td>75</td>
<td>0.75</td>
<td>6.30</td>
<td>0.119</td>
<td>1875</td>
</tr>
<tr>
<td>2B – 1</td>
<td>220</td>
<td>225</td>
<td>2.25</td>
<td>9.30</td>
<td>0.242</td>
<td>510</td>
</tr>
<tr>
<td>2B – 2</td>
<td>240</td>
<td>160</td>
<td>1.60</td>
<td>7.40</td>
<td>0.216</td>
<td>1090</td>
</tr>
<tr>
<td>2B – 3</td>
<td>260</td>
<td>80</td>
<td>0.80</td>
<td>6.50</td>
<td>0.123</td>
<td>2180</td>
</tr>
<tr>
<td>1C – 1</td>
<td>220</td>
<td>165</td>
<td>1.65</td>
<td>6.20</td>
<td>0.27</td>
<td>635</td>
</tr>
<tr>
<td>1C – 2</td>
<td>240</td>
<td>150</td>
<td>1.50</td>
<td>6.10</td>
<td>0.24</td>
<td>615</td>
</tr>
<tr>
<td>1C – 3</td>
<td>260</td>
<td>110</td>
<td>1.10</td>
<td>6.00</td>
<td>0.18</td>
<td>750</td>
</tr>
<tr>
<td>2C – 1</td>
<td>220</td>
<td>190</td>
<td>1.90</td>
<td>4.75</td>
<td>0.40</td>
<td>500</td>
</tr>
<tr>
<td>2C – 2</td>
<td>240</td>
<td>176</td>
<td>1.76</td>
<td>4.10</td>
<td>0.42</td>
<td>920</td>
</tr>
<tr>
<td>2C – 3</td>
<td>260</td>
<td>75</td>
<td>0.75</td>
<td>3.80</td>
<td>0.19</td>
<td>400</td>
</tr>
<tr>
<td>D – 1</td>
<td>220</td>
<td>140</td>
<td>1.40</td>
<td>5.75</td>
<td>0.24</td>
<td>540</td>
</tr>
<tr>
<td>D – 2</td>
<td>240</td>
<td>148</td>
<td>1.48</td>
<td>4.90</td>
<td>0.30</td>
<td>1100</td>
</tr>
<tr>
<td>D – 3</td>
<td>260</td>
<td>120</td>
<td>1.20</td>
<td>5.90</td>
<td>0.27</td>
<td>860</td>
</tr>
</tbody>
</table>

b) Optimizing the compression mold duration

Starting from these results, the mold duration was further optimized. Obtaining samples from recycled material requires a longer compounding duration, when the material passes from solid phase into the high-elastic state; being a mixture of three polymers, each of these with different transition temperatures (T_g, T_m), the temperature value and applied duration represents a key factor. It is important to notice that there were not degassing steps in this experiments, thus air (and oxygen) is still in a reasonable amount in the mould, and too long molding duration can induce partial oxidations (especially in rubber) with undesired consequences on the mechanical properties of the final products. Therefore, the study was conducted on samples obtained on a temperatures range from 180 °C to 260 °C, varying the processing the time, from 45 minutes (samples for series D) to 60 minutes (samples denoted as series E) with the same composition (rubber : PET: HDPE = 85: 10: 5).
Stress-strain curves shown in Figures 3 and 4 follow the same shape, while the traction application is short and an increase in tensile strength shows a moderate elasticity of the samples. In both cases, it can be seen that samples obtained at high temperatures, 240 °C - 260 °C, are more resistant to traction applications. This is highlighted by the higher traction forces (110-175 N for sample type D, 100-150 N for type E samples default values of stress, $\sigma$, following the completion of interfaces between components. Analyzing the values of tensile forces, physical interactions can be supposed between the components, forming weak interfaces.

![Figure 3](image1.png)

**Figure 3.** Stress-strain curve for samples obtained 45 minutes.

![Figure 4](image2.png)

**Figure 4.** Stress-strain curve for samples obtained 60 minutes.

By increasing temperature and time, the samples get more resistant to mechanical stress and higher levels of modules are registered. Extension of time for obtaining the samples, up
to 60 minutes, leads to the development of stronger interfaces between components, with rearrangement of the macromolecular chains.

c) The influence of the recycled rubber type

Using the optimized parameters two types of rubbers were comparatively used: rubber from tires and from bicycle tubes. Following the EDX analysis, sulphur content and zinc silicate was found higher in the rubber from the tires. The samples were mechanically tested and it was found that the samples with high content of sulfur and zinc obtained at temperatures above 220 °C, have increased stress (150 N) and compression resistance (2505 N). The study of the influence of the type of rubber on the mechanical properties of PET-rubber composites indicate that certain fillers present in recycled rubber (S, Si, Zn, black) must be controlled because it could be a way to achieve Mesh, a fact which is sometimes unwanted.

According to the mechanical properties obtained, composites based on rubber tires, can be used in practice as construction materials, such as paving slabs, while rubber composites with lower sulfur content, which may be more elastic, can be used as sound insulation material or impact damping materials, placed on the inside guardrail on the roads or parks and playgrounds.

d) The distribution of components in composite

To track the components distribution in the composite, two sets of samples were made – randomly mixed and layered - using previously optimized parameters, which are subjected to mechanical tests. The layered samples have the external layers containing rubber and HDPE, while the inner layer - contains rubber, PET and HDPE. These samples, have high tensile forces (values above 100 N) compared to the statistical mix, the maximum force registered was of 220 N, for the samples obtained at 220 °C. The results can be explained by the outer layers composition that faster reach a high-elastic state, physicochemical interactions with the formation of interfaces being possible.

In the case of layered samples, PET pellets are no longer dispersed throughout the sample’s mass, leading to improved resistance to mechanical stress. Still, for these samples a delaminating risk exists, these composites can therefore be recommended as materials for indoor applications as dry pavement.

e) Optimizing the molding temperature

The mechanical properties of the composites heavily depend on temperature and composition when obtaining rubber-rich composites (85 % by mass); the optimum processing temperature resulted to be 220°C. In more complex systems, temperature intervals were chosen, correlated with the thermal properties of the main recycled components in the composite, [19].

f) The effect of the additive at rubber - PET interface

Based on the interface properties, while maintaining the processing conditions, samples were made with the composition rubber: PET; additive = 85: 10: 5 as additive using HDPE (1E-1, 2, 3), LDPE (2E-1, 2, 3) and TiO2 (3E-1, 2, 3), Table 5, [31, 32].
We conclude that the three compositions are recommended in traction applications when using HDPE and remarkable properties has the sample obtained at 240 °C (σ = 1,22 MPa and ε = 1.5 mm). Comparing the samples obtained at 240 °C for the three compositions, we can say that it can be observed that those containing HDPE have a higher tensile strength than samples with 50% LDPE and 58 % higher than samples with TiO₂.

Table 5. Results obtained on the mechanical type E samples

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Temp. [°C]</th>
<th>Fₜₐᵣ [N]</th>
<th>σ [N/mm²]</th>
<th>ε [mm]</th>
<th>E [N/mm²]</th>
<th>Fₑ [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1E – 1</td>
<td>220</td>
<td>112</td>
<td>1,12</td>
<td>0,85</td>
<td>2,20</td>
<td>714</td>
</tr>
<tr>
<td>1E – 2</td>
<td>240</td>
<td>122</td>
<td>1,22</td>
<td>1,50</td>
<td>2,00</td>
<td>519</td>
</tr>
<tr>
<td>1E – 3</td>
<td>260</td>
<td>42</td>
<td>0,42</td>
<td>1,70</td>
<td>1,90</td>
<td>1148</td>
</tr>
<tr>
<td>2E – 1</td>
<td>220</td>
<td>150</td>
<td>1,50</td>
<td>1,00</td>
<td>3,15</td>
<td>3786</td>
</tr>
<tr>
<td>2E – 2</td>
<td>240</td>
<td>63</td>
<td>0,63</td>
<td>1,00</td>
<td>2,75</td>
<td>1807</td>
</tr>
<tr>
<td>2E – 3</td>
<td>260</td>
<td>65</td>
<td>0,65</td>
<td>0,80</td>
<td>2,30</td>
<td>2858</td>
</tr>
<tr>
<td>3E – 1</td>
<td>220</td>
<td>39</td>
<td>0,39</td>
<td>0,50</td>
<td>0,10</td>
<td>2132</td>
</tr>
<tr>
<td>3E – 2</td>
<td>240</td>
<td>58</td>
<td>0,58</td>
<td>1,00</td>
<td>0,39</td>
<td>1391</td>
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<tr>
<td>3E – 3</td>
<td>260</td>
<td>35</td>
<td>0,35</td>
<td>0,82</td>
<td>1,10</td>
<td>1506</td>
</tr>
</tbody>
</table>

HDPE has higher transition temperatures than LDPE, so that at this temperature HDPE enters in a high-elastic state forming a weak interface with rubber, attributed to physical interactions. LDPE having lower transition temperatures (as otherwise rubber), presents a more stable interface (tensile strength, 150 N) at 220°C than at 240 °C (63 N). At these temperatures TiO₂ does not undergo any structural change, even used in large quantity [32]; TiO₂ decreases the mechanical properties due to agglomerates of nanoparticles that basically lead to crushing the samples. Field studies [33, 34], show that improved properties using TiO₂ as fillers is achieved by low mass percentage such as 0.13 % [35].

Following the results, it was found that HDPE facilitates the development of interfaces stronger than other additives. Samples containing HDPE as additive can be used as construction materials.

g) Increasing the PET amount into the composite rubber - PET – HDPE

While waste rubber use is quite well established, the use of PET as second raw material is reported in composites in amount reported between 10 and 25%. Therefore, increasing the amount of PET in rubber based composites represents a challenge.

The percentage of PET in rubber - PET - HDPE composites was tested up to 45%. The following composite types were analyzed:

* series D - Rubber: PET: HDPE = 85: 10: 5
* series 1D - Rubber: PET: HDPE = 70: 25: 5
* series 2D - Rubber: PET: HDPE = 60: 35: 5
* series 3D - Rubber: PET: HDPE = 50: 45: 5
The results are similar to those presented so far, for the samples obtained at 240 °C showing high resistance to mechanical stress and small values of elongations, Table 6. Samples with 25 % PET have an elongation decreases by about 27 % comparing to pure rubber. At 240 °C rubber and HDPE are in the state of thermal processing while the PET does not chemically change so, between the rubber matrix and HDPE a weak interface develops. When increasing the PET percentage up to 45 %, crumby aspect results, with a significant decrease of the mechanical properties. Thus, the percentage of PET can be varied (10 – 35 %) depending on the material to be obtained and of course on its practical application.

Table 6. Results obtained on the mechanical type D samples

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Temp. [°C]</th>
<th>F_{tr} [N]</th>
<th>( \sigma ) [N/mm(^2)]</th>
<th>( \varepsilon ) [mm]</th>
<th>E [N/mm(^2)]</th>
<th>F_{c} [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D – 1</td>
<td>220</td>
<td>140</td>
<td>1.40</td>
<td>5.75</td>
<td>0.24</td>
<td>540</td>
</tr>
<tr>
<td>D – 2</td>
<td>240</td>
<td>148</td>
<td>1.48</td>
<td>4.90</td>
<td>0.30</td>
<td>1100</td>
</tr>
<tr>
<td>D – 3</td>
<td>260</td>
<td>120</td>
<td>1.20</td>
<td>5.90</td>
<td>0.27</td>
<td>860</td>
</tr>
<tr>
<td>1D – 1</td>
<td>220</td>
<td>165</td>
<td>1.65</td>
<td>2.50</td>
<td>0.66</td>
<td>720</td>
</tr>
<tr>
<td>1D – 2</td>
<td>240</td>
<td>120</td>
<td>1.20</td>
<td>1.75</td>
<td>0.68</td>
<td>520</td>
</tr>
<tr>
<td>1D – 3</td>
<td>260</td>
<td>105</td>
<td>1.05</td>
<td>1.50</td>
<td>0.70</td>
<td>1150</td>
</tr>
<tr>
<td>2D – 1</td>
<td>220</td>
<td>134</td>
<td>1.34</td>
<td>3.20</td>
<td>0.41</td>
<td>678</td>
</tr>
<tr>
<td>2D – 2</td>
<td>240</td>
<td>157</td>
<td>1.57</td>
<td>2.80</td>
<td>0.56</td>
<td>966</td>
</tr>
<tr>
<td>2D – 3</td>
<td>260</td>
<td>174</td>
<td>1.74</td>
<td>3.70</td>
<td>0.47</td>
<td>1308</td>
</tr>
<tr>
<td>3D – 1</td>
<td>220</td>
<td>75</td>
<td>0.75</td>
<td>0.75</td>
<td>1.00</td>
<td>540</td>
</tr>
<tr>
<td>3D – 2</td>
<td>240</td>
<td>100</td>
<td>1.00</td>
<td>0.90</td>
<td>1.11</td>
<td>500</td>
</tr>
<tr>
<td>3D – 3</td>
<td>260</td>
<td>40</td>
<td>0.40</td>
<td>0.70</td>
<td>0.57</td>
<td>1900</td>
</tr>
</tbody>
</table>

Following compression applications, significant values for the samples obtained at 260 °C were found for all cases discussed. Highest value of compressive strength (1900 N) was recorded for sample with 45 % PET, but it looks like a crumbly powder due to PET agglomeration which is currently the core issue and reduce the possibility of making rubber – PET interface.

It was found that using up to 35 % PET in the mixture, composites increased mechanical strength can be obtained. The percentage of PET is advisable to be chosen according to the applications. Composites with 35 % PET are recommended for construction materials (concrete paving) because they present good compression resistance, while those with lower content of PET can be used as insulating materials.

h) The TiO2 percentage in the inorganic – organic composite

As already shown, adding oxides targets the increase in the mechanical properties of the composite, therefore, the nanostructured TiO\(_2\) powder was added in composites with the general content: rubber: PET: HDPE: TiO\(_2\) = (60 - x): 35: 5: (x <2).

Low percentage of TiO\(_2\) (\(\leq 0.5\) %) improved the traction resistance (E = 9.5 MPa, respectively E = 10 MPa). Knowing the work of breaking and sectional area of the sample, tensile stiffness was calculated and resulted at 9.87 N/mm (0.5 % TiO\(_2\)) and, respectively 2.79M/mm for the samples with 0.25 % TiO\(_2\). These samples’ behaviors were attributed to
the inorganic filler content, [26]. Higher TiO\textsubscript{2} content results in agglomerated nanoparticles, that strongly decreases adhesion to the matrix, thus drastically reduces the mechanical strength.

At compression, very high maximal forces are obtained (the highest values found so far on the discussed types of samples) between 5000-7000 N, approximately 70 \% higher than for samples without TiO\textsubscript{2}. The samples with low TiO\textsubscript{2} percentage (0.25 - 0.5 \%) are representative, proving that, at a molding temperature of 240 °C, TiO\textsubscript{2} changes the degree of elasticity in rubber.

i) Development of novel composites: PET - rubber - metal oxides

Composites with inorganic structures embedded in the polymer matrix are a new class of materials with very interesting specific properties. It is demonstrated that inorganic materials in polymer composites result in performances unrecorded by pure polymer composites. However, inorganic material type, quantity, particle size and their molecular structure when dispersed in polymeric matrix are essential in achieving the expected performance. Thus, inorganic oxides (CaO, ZnO) of nanoscale dimensions were further used; as an oxide mixture, another waste, fly ash, was also tested, at the previously optimized moulding parameters. The sample composition was: rubber: polyethylene: HDPE: metal oxide = 59.75 : 35 : 5 : 0.25.

Differences occurring between the samples with different fillers can be attributed to their nature, primarily to their influence on the interface and on their thermo-oxidative stability.

Specific characteristics recorded during mechanical testing proved the superiority of composites containing CaO. Tensile tests, compression and impact resistance reveals that samples containing CaO develop organic-inorganic physical interactions, without forming any new chemical species.

The fly ash collected from the electro-filters of a CPH did not exhibit any significant influence on thermal behavior of the samples, without modifications to the transition temperatures, but the presence of a porous, heterogeneous structure can be noticed as an advantage in further developing good organic-inorganic interfaces.

Given the results obtained in preparing composites containing only recyclable materials, we recommend their use as paving material for indoor applications.

1.4. Aggressive environmental influence on composites. Applications of the rubber – PET composites

Composite material characteristics can be modified under the action of certain physical, chemical or mechanical factors, both at micro- and macroscopic level, which clearly reflected the state of tension and strain. Although aggressive state has a negative influence on the structure of composite materials (filler, matrix, filler-matrix interface), these materials represent an exciting field of research.

To use intaglio potential of the composite materials, their behavior to wetting action must also be known. Either outdoor or indoor applications are subjected to wetting and irreversible water adsorption/absorption can result in a strong decrease of the mechanical properties and in shortening the products’ lifetime.
The objective of this investigation is to determine the moisture content versus time, when the material is completely immersed in the solution. The aim was to assess changes in the fracture resistance of composite materials.

The previously optimized compositions were used and the samples were subjected to aggressive environments, by immersion in water, saline solution, surfactant solution (dawfax, ABEX); further tests were done at variable temperature changes, UV radiation and salt retention in the atmosphere.

The influence of aggressive factors on polymer composites with organic fillers (rubber : PET : HDPE = 85 : 10 : 5) has been studied [36, 37], but also those with inorganic fillers (rubber: PET; HDPE: oxide / ash = 59.75 : 35 : 5 : 0.25).

The results obtained when polymer composites with organic fillers are immersed in various solutions can be synthesized as follows:

- The amount of solution absorbed gives information on the sample porosity;
- Moisture absorbed by composite materials lead to significant decrease of the elasticity modulus for samples immersed for 500 hours, [38];
- At a longer soak, light scattering substances have a positive effect on the interface properties. During immersion in different solutions, the polymer system begins to reach a metastable state close to steady-state absorption system/desorption because small water molecules are absorbed faster;
- Low value modulus of the samples immersed in water and NaCl solution, may be associated with the destructive effect at the rubber-plastic interface and a low desorption which can be seen immediately after;
- The data prove that samples kept in various solutions have lower mechanical properties at room temperature.
- Increasing the molding temperature improves the elongations at break for the samples immersed in water-based systems.

The studies on the influence of environmental factors (temperature, UV radiation), [39, 40] and fast ageing (in fog of water, 3.5 % NaCl solution, and dawfax 0.01 % saline) on PET-rubber composites with inorganic fillers (TiO₂, ZnO, CaO, ash) found that:

- The fillers in the polymer nanocomposites structure increase the thermal stability of the material;
- Interactions between polymer and inorganic filler materials are strong and increase molecular cohesion, thus increasing the heat required for thermal degradation.

To follow the mechanical behavior of these samples and to select an application domain, samples were tested for physical-chemical and mechanical analysis.

- Samples containing CaO and fly ash have a high UV resistance thus, these composites can be used as paving in outdoor environments;
- Immersion leads to composites degradation, however, it was noted as bearing remarkable properties, the sample containing metal oxides with very good tolerance to water (CaO) and saline/surfactant environment (fly ash).
Based on these results, we may conclude that composites containing CaO can be used as paving slabs in wet environments, and those containing fly ash may be used in close proximity to the sea as paving slabs, mats to land or ship deck laundry where surfactants are present.

These studies show that, developing novel composites by using waste-polymers as second raw materials represents a broad study field and applications are numerous. Beside the economic aspect, this represents a truly sustainable approach for new materials with controlled properties.

REFERENCES

Cristina Cazan and Anca Duta