DOCTORAL THESIS

THEORETICAL AND EXPERIMENTAL CONTRIBUTIONS REGARDING THE OPTIMIZATION OF COMPOSITE MATERIALS WITH RUBBER MATRIX USED IN MACHINE BUILDING
-ABSTRACT-

Doctoral Student:
Eng. Cristinel Sabin DIMULESCU

Doctoral coordinator:
Prof. univ. dr. eng. habil. Dan DOBROTĂ

SIBIU2023

TABLE OF CONTENTS

1. CURRENT STATE OF RESEARCH ON THE USE OF INDUSTRIAL WASTE IN THE MANUFACTURE OF COMPOSITE MATERIALS

The first chapter serves as the introductory part of the thesis and contains information and definitions related to composite materials (types of matrices and reinforcements), followed by a presentation of research from the specialized literature on composite materials with rubber matrices and FA and/or PVC inserts. The chapter concludes with a list of the proposed and completed objectives for the current doctoral thesis.

A composite material is a material made up of two or more different components, each with distinct individual properties, which are combined to create a material with improved or specific properties. These components typically include a matrix and fillers, reinforcement materials, or simply referred to as reinforcements.

The widespread use of composite materials in engineering has occurred due to several important properties they possess, including:
- high mechanical strength
- high wear resistance
- high temperature resistance
- ability to be manufactured into various complex shapes
- high resistance to aggressive environments, and so on.

All these properties are achieved by strategically combining multiple materials in the matrix and reinforcement [43].

In general, a composite material is composed of:
- matrix: the main component of the composite material, serving as the medium that binds and supports the other components; typically, the matrix is a weaker material (with inferior mechanical properties compared to the reinforcement) or softer, such as polymers (plastics), metals, or ceramics;
- reinforcements - these components are added to the matrix to enhance or modify its properties; reinforcements provide the composite material with high mechanical strength, thermal conductivity, etc.

The definitions and characteristics of the matrix presented here are based on recommendations and classifications from [29, 64, 68, 69, 70, 313]. The matrix's role is to encapsulate the reinforcement (without destroying it through dissolution, melting, chemical reaction, or mechanical action) and provide the composite with resistance to high temperatures and corrosion. The matrix typically represents the deformable part of the material, with lower mechanical strength compared to the reinforcement. It ensures the composite's cohesion, structural stability, transfer of external loads to the reinforcement, and protection of the reinforcement elements against mechanical damage and erosion. Matrices used for composite material manufacturing include organic matrices, thermosetting matrices, thermoplastic matrices, ceramic matrices, and metallic matrices.

Rubber is an elastic polymer, either natural or synthetic, used in various applications due to its elastic and resilient properties. It can be categorized as:
- natural rubber: obtained from the milky latex of rubber trees, especially Hevea brasiliensis; this latex is collected and processed to produce natural rubber, known for

its excellent elasticity, used in tire production, waterproof clothing, and various consumer products;

- synthetic rubber: produced in laboratories and has a chemical composition similar to natural rubber but can be modified to obtain specific properties; various types of synthetic rubber include styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR), ethylene-propylene-diene rubber (EPDM), and many others; synthetic rubbers are used in a wide range of products, from tires to sealing gaskets, and more.

The main properties of rubber include elasticity, resistance to extreme temperatures, moisture resistance, abrasion resistance, chemical resistance, etc. The resistance to moisture, extreme temperatures, and abrasion makes rubber suitable for tire manufacturing.

One recent research challenge is the recycling of rubber waste from used tires. On average, a tire, if used under normal conditions, has a lifespan of approximately 4-5 years. After this period, it becomes non-biodegradable waste. Due to its short lifespan and non-biodegradability, large stocks of used tires accumulate annually, which tend to increase with population growth and the number of cars in use. These stockpiles lead to various problems, such as the risk of fires that are difficult to extinguish (an example of a tire depot fire is given in [282]) and pollutant emissions that affect the environment [288].

The initial research into using rubber for composite materials involved combining epoxy resin with a small amount of low molecular weight liquid rubber before the actual polymerization process. This addition resulted in a solid system with a microstructure consisting of two phases and increased toughness compared to pure epoxy resin. The combination of these elements led to a decrease in the longitudinal modulus (from 3.51 to 2.65 GPa), an increase in elongation at break (from 2.47 to 5.64%), a decrease in tensile strength (from 70.4 MPa to 56.3 MPa), and a change in the glass transition temperature (by approximately 5°C) [292]. It was demonstrated that the toughening effect of rubber on brittle composite materials depends on factors such as particle cavitation, shear yielding of the matrix, and the particles' deformability [330]. These factors, when combined, create a bridge (membrane) that suppresses intergranular fracture [222]. It has also been found that the introduction of rubber into epoxy resin increases viscosity, making it difficult to impregnate with reinforcement [292, 298, 295]. Often, a non-homogeneous distribution of rubber in epoxy resins has been observed, leading to a partial transfer of the hybrid resin's properties to the final composite [296].

Polyvinyl chloride (PVC) is a type of thermoplastic polymer. PVC is produced by polymerizing monomeric vinyl chloride and is an extremely versatile plastic material widely used in various fields. It begins as a white powder and has been commercially available since the 1920s as a component for producing polymeric materials [256, 285].

The main advantages of PVC compared to other polymers include low cost, resistance to moisture (making it suitable for outdoor or submerged applications), durability, chemical resistance, and ease of processing. However, its disadvantages include non-biodegradability, becoming rigid at low temperatures, melting at high temperatures, environmental impact due to chlorine content, and the presence of toxic additives [221, 286].

Fly ash (FA) is the residue resulting from the combustion of coal in thermal power plants. It is also produced in industries manufacturing cement and using natural biomass for burning purposes, leading to a significant quantity of FA production [55].

From a geometric perspective, FA particles are typically spherical, with diameters ranging from 10 to 100 μm ([25]).

In FA composition, oxides of various metals such as Si, Al, Fe, Ca, Na, or K are commonly found. Trace amounts of Cr, Ni, V, or Pb may also be present [329]. These heavy metals are stable under normal environmental conditions, but there is a risk of their leaching in acidic conditions, so FA should not be treated with acidic chemical solutions [216]. In terms of component elements, FA is found to be composed of quartz and a silicon-based mineral referred to in the literature as mullite or porcelainite [38].

The color of FA is determined by the amount of unburned carbon and iron present in it. If there is a significant amount of unburned carbon, the color can range from orange to dark red or brown. If there is a significant amount of iron, the color can range from white to yellow [25].

It is well-known that improper disposal of FA residue can pollute soil and water. Therefore, research has aimed at finding ways to recycle FA and explore potential engineering applications [26, 94]. Approximately 20% of FA production is used as an aggregate in concrete ([61, 211, 314]).

Following the analysis of research conducted worldwide and presented briefly in the previous subsections, it has been observed that there are numerous engineering applications for rubber, PVC, or FA (fly ash) waste materials. Although these applications are numerous, it should be noted that they cannot cover the very large annual quantities of waste generated from these materials. This is also due to the fact that the best technologies for producing products from such materials with the best performance in operation have not yet been identified. Therefore, within the scope of this doctoral thesis, the main objectives are:

O1 - Optimization of specific technology parameters for the production of high-performance composite materials that include waste rubber, PVC, and FA.

O2 - Production of composite materials with high-performance properties that incorporate all three types of waste materials: rubber (recovered rubber + rubber powder), PVC, and FA, as current studies have not addressed technologies for obtaining composite materials that simultaneously contain all three types (most studies present samples that contain recycled rubber + FA or recycled rubber + PVC).

O3 - Optimization of the composition of rubber composite materials (recovered rubber + rubber powder), PVC, and FA depending on the field of use of that composite material.

O4 - Production of rubber, PVC, and FA composite materials that can be used in the manufacture of products that operate in very harsh working environments (dust, freeze-thaw cycles, high temperatures, vibrations, etc.).

O5 - Identification of potential areas of use for samples containing waste rubber, FA, and PVC based on the results obtained from experimental research.

From the study conducted in this chapter, the following conclusions can be drawn:

- the quantities of rubber, PVC, and FA waste are increasing from year to year, and current applications (for waste use) do not cover these quantities, so it is necessary to continuously find uses for them to reduce environmental pollution;

- rubber is an extremely versatile material used in a wide range of applications, from the automotive industry and construction to electronics and sports equipment;

- PVC is a widely used plastic material due to its versatility in various applications, with the caveat that continuous efforts should be made to find applications where it can be recycled; otherwise, PVC waste negatively affects the environment and human health, and alternative PVC-based materials that are more environmentally friendly should be sought and researched;

- coal is a non-renewable resource that depletes as it is extracted, and its combustion leads to emissions of CO_2 and other atmospheric pollutants; The waste left after burning carbon is called fly ash and is usually used in the field of civil

construction; it should be noted that FA contains heavy metals and toxic substances, so environmental and safety regulations must be adhered to for its reuse;

- recycled materials can be integrated into building and renovation, contributing to resource conservation and waste reduction.

- by using recycled materials in construction helps reduce costs and promotes sustainable construction practices.

2. MATERIALS, TECHNOLOGIES, AND METHODS USED FOR THE ANALYSIS OF COMPOSITE MATERIALS WITH RUBBER MATRIX AND FLY ASH AND PVC ADDITIVES

Until composite material is obtained, it is necessary to initially recover rubber from used products (tires, conveyor belts, technical articles, etc.) as well as to technologically prepare FA (fly ash). Thus, for the recovery of rubber from waste, these must be initially processed and brought into a form that can be used in combination with various additives. Depending on the desired final product, used rubber products can be reduced in size from large pieces, strips, chips, granules to fine powder [116, 274].

Next, various studies from the specialized literature will be presented where composite materials with a rubber matrix and additives of FA or PVC are analyzed. The composition of these materials will be specified, and in the following subsections, a review of the technology and research methods used in the studies will be provided.

High efficiency in recovering rubber waste from rubber articles can be achieved by using them in the production of thermoplastic elastomer composite materials [53, 318]. These composites can be used as replacements for thermoplastic materials. Such substitutions can lead to cost savings due to the reduced use of thermoplastic materials, and at the same time, they allow for the utilization of industrial rubber waste. Furthermore, the production of such materials does not generate waste due to the recycling of scraps and rejects. Thermoplastic-based composite materials with rubber powder are obtained by mixing a dispersed elastic filler and a thermoplastic in a molten state at a temperature above the melting point of the thermoplastic matrix, using an extruder-granulator, Brabender plastograph [119], or electrically heated rolls. These materials are processed and shaped using a technique similar to that used in processing plastic and rubber mixtures (compression molding, injection molding, extrusion, etc.) [339, 340].

Polyvinyl chloride (PVC) is a versatile polymer used in flexible, semi-rigid, and rigid forms. In the global production of plastic materials, it ranks second after polyolefins [120]. The rapid expansion and consumption of PVC are due to its lower costs, greater availability, good mechanical properties, and diverse range of properties [319]. One of the most important requirements for PVC in industrial applications is permanent plasticization. One of the most important and commercially relevant mixtures with high-performance properties is that of NBR (nitrile butadiene rubber) and PVC. NBR acts as a permanent plasticizer for PVC, and at the same time, PVC improves the ozone resistance, thermal aging, and chemical resistance of NBR. The presence of PVC enhances the aging resistance of NBR because both PVC and NBR are polar, and mixing NBR with PVC increases their compatibility [229].

Recent research includes investigations into the use of functionalized acrylonitrile-butadiene rubber (NBR-g-MAH) as an impact modifier and compatibilizing agent in the recycled mixture of PVC and polymethyl methacrylate (PMMA). It was found that the performance of NBR as an impact modifier was improved by adding

maleic anhydride. Furthermore, varying the concentration of NBR-g-MAH/NBR mixture has different effects on the mechanical, thermal, and morphological properties of the recycled mixture. The recycled mixture containing 9% by weight of NBR-g-MAH/NBR had the best impact strength and elongation at break. Differential thermal analysis (DTA) and microscopic analysis indicated partial miscibility and good compatibility of the polymer constituents in the mixture [24, 255].

Composite materials with a rubber matrix and additives of PVC can be used for the manufacture of flexible pipes, gaskets, insulation materials, etc. Their manufacturing process is characterized by the following steps:

- preparation of base materials (as presented in the previous paragraphs).

- mixing of materials: PVC and rubber are mixed together, usually in a specialized mixer or a twin-screw extruder; depending on the application of the final product and the desired mechanical properties, additional additives such as plasticizers (to make the material more flexible), stabilizers (to prevent thermal degradation), lubricants, and colorants may be introduced during the mixing process.

- extrusion or shaping: the mixed composite material is subjected to extrusion or another forming technique to produce profiles, pipes, sheets, or other shapes; if the extrusion method is used, the material is pushed through a die by a punch.

- cooling and cutting: the materials are cooled and then cut to remove excess material and achieve the desired final dimensions.

- finishing and testing: additional surface treatments can be applied, and the samples undergo tests for strength, flexibility, and so on.

Composite materials with a rubber matrix and FA additives can be used as components for construction materials (mortar, cement, concrete, etc. - refer to Chapter 1) or as insulating materials. Their manufacturing process involves the following steps:

- collection of FA: it is collected from the combustion of coal in power plants; it may contain fine particles and harmful chemicals, so it must be managed carefully.

- preparation of FA: it is processed to remove impurities and obtain suitable granulation for mixing with rubber.

- mixing with rubber: this can be done through extrusion, using twin-screw extruders [144].

- insertion of additives and modifiers: additives are added to improve the properties of the composite; these can include plasticizers, reinforcing agents, lubricants, and other chemical additives, depending on the specific application requirements.

- actual formation of the composite material: it can be extruded into profiles, pressed to obtain sheets or other forms.

- vulcanization: this provides durability and strength to the final material.

- finishing and testing: excess material is removed, and the samples are subjected to tests for strength, flexibility, vibration resistance, acoustic properties, thermal insulation, etc.

To obtain composite materials with a rubber matrix and additives of both FA and PVC, the two technologies mentioned above can be combined. Since the presented technologies are general in nature, the following sections will detail the manufacturing processes of composite materials with a rubber matrix and additives of FA or PVC from specialized research works.

The final step after the production of a composite material is its actual testing. Tests are conducted to ensure that the material meets specific characteristics in accordance with its intended purpose. These characteristics can be highlighted through experimental tests or analyses.

In [310], several experimental tests were conducted to determine mechanical properties of composite materials with a rubber matrix and PVC inserts. The first test was tensile testing using a Schopper machine with a pulling speed of 460 mm/min. The modulus of elasticity, tensile strength, and elongation at break were determined according to ISO 37/2012 [304].

In addition to tensile testing, [310] also conducted Shore hardness testing, scale A, according to ISO 7619/2011 [302]. A penetrator came into contact with the studied material through a sufficiently large force. The holding time was 3 seconds for vulcanized rubber and 15 seconds for thermoplastic rubber. Another test for composite materials of rubber and PVC described in [310] was accelerated aging resistance testing, conducted according to specifications from [303].

The determination of abrasion resistance was performed according to ISO 4649/2008 [300], the cylindrical method, using a pressing force of 10 N. Abrasion resistance was expressed as the relative volume loss compared to calibrated abrasive paper. A wear tester with abrasive fabric and electrocorundum-based abrasive with a grain size of 212-80 µm (PE 80) was used, and its abrasiveness had to be 180-220 mg for the control rubber. Samples were obtained from laminated mixtures and then pressed with a rotary die. The samples had a cylindrical shape with a diameter of 16 mm and a minimum height of 6 mm.

In the research, composite materials with a rubber matrix were fabricated, incorporating industrial rubber waste recovered from car tires, FA, and PVC. Rubber recipes included recycled rubber and rubber powder obtained by fine grinding of rubber waste. Five types of composite materials were produced, starting with a rubber mixture (S01) containing recovered rubber + rubber powder obtained by recycling and grinding tire waste. Using this type of rubber mixture as the matrix, new composite materials were created by adding PVC (S02), FA (S03), PVC and FA in moderate quantities (S04), and PVC and FA in very large quantities (S05).

The FA used in the experimental research was obtained from the combustion of lignite in power plants at the Oltenia Energy Complex, Romania. Since the combustion of lignite can result in FA with various properties, 10 samples were collected (using a 100 ml glass container; samples were selected from 10 different locations) and analyzed in terms of particle size, chemical composition, and SEM images. Additionally, the FA used for analysis underwent an initial grinding and sieving process to improve granulation. Sieved FA was initially analyzed for polydispersity by optical microscopy (Olympus BX 51M Optical Microscope [169]), and the obtained values were processed using analysis of variance (ANOVA [170]). Thus, the estimation of the average particle size of FA (numerical size Dn, gravimetric size Dw), and the polydispersity index (Dw/Dn) was performed by measuring 100 particles.

After measuring the particle sizes and calculating the numerical average size Dn and gravimetric average size Dw, the polydispersity index value was determined: 0.911.

Granules of recycled PVC were obtained from S.C. CRILELMAR S.R.L Targu-Jiu, Romania, through recycling on an EREMA-type granulator. The granules obtained from recycled PVC were further transformed into fine material particles through grinding and sieving.

To manufacture the specimens used in this thesis, styrene-butadiene rubber (SBR) was used, which contained material resulting from the grinding of waste from car tires (recovered rubber + rubber powder) in a proportion of 50 phr. The rubber mixture was chosen considering the aim of using as much FA and PVC as possible. The produced specimens were in the form of plates with a thickness of 18 mm. It should be noted that a significant portion of the rubber in the composition was obtained from recycling tire waste. In addition, a vulcanization solution of the GDT+ type with 5%

Desmodur R crosslinking agent, produced by Covestro AG, and trichloroethylene for pickling operations were used.

Obtaining composite materials with a rubber matrix involves several technological operations, but the initial operation consists of homogenizing the materials used. This homogenization operation was applied to all the specimens obtained, even in the case of specimens without FA and/or PVC additives, to ensure that all components in the materials are as evenly distributed as possible. The materials used were first mixed with the coupling agent KWQ-EL, produced by S.C. ARTEGO S.A, Târgu-Jiu, Romania, using a double-helix mixer model LS-S130 ([179]) for 2.5 minutes. Five mix batches were prepared for the five types of specimens. The batches were homogenized separately on a mill equipped with two rolls. The working temperature of the rolls was set at 80°C. The friction ratio between the peripheral speeds of the two rolls, known as the friction, was set at 1:1.10. The processing time for each batch was set at 10 minutes. To avoid excessive rolling, which reduces the thermal stability of the material, processing was done in small batches relative to the mill's capacity. This had to be taken into account, especially when using waste. The load can only be increased when using waste that has been homogenized and requires only reheating. After homogenizing the batches, the next processing step is calendering. Through calendering, sheets of different thicknesses can be obtained. In our case, with small batches for experiments, we chose to process the mixture sheets at the specified thickness on the mill by adjusting the distance between the rolls.

The final step of the specimen production process was vulcanization. The adjustment of vulcanization parameters was made to ensure a correlation between pressure and vulcanization temperature as follows:
- temperature 25°C - 45°C - pressure 70 bar;
- temperature 45°C - 75°C - pressure 85 bar;
- temperature 75°C-105°C - pressure 110 bar;
- temperature 105°C-120°C - pressure 125 bar;
- temperature 120°C-145°C - pressure 160 bar.

The properties of the materials manufactured in this chapter are almost exclusively temperature-dependent, with their behavior being determined by the strength of the forces between atoms, the number of chemical bonds per unit volume, and the resistance of the bonds to degradation under the action of external agents. The vulcanization time, pressure, and temperature are chosen based on the material's properties and thickness. In the manufacturing technology, the choice of material and the optimal parameters represent the most important aspect. Process optimization after analysis and research in this field can lead to a significant improvement in the lifespan of composite materials. One possible solution to improve the vulcanization conditions of composite materials with a rubber matrix that include FA and PVC would be the use of ultrasound, which would allow for better uniformity of vulcanization parameters (temperature, pressure) throughout the material mass. In these conditions, the research conducted makes an important scientific contribution to the field in that the tests performed are on real products that can be used in practice, demonstrating the technical advantage of the presence of FA and PVC particles in such products.

3. DETERMINATION OF PHYSICAL-MECHANICAL PROPERTIES FOR COMPOSITE MATERIALS WITH RUBBER MATRIX AND FLY ASH AND PVC ADDITIVES

In this chapter, hardness Shore A tests and tensile tests were performed on the specimens manufactured in Chapter 2 (5 types of specimens with different proportions of additives with rubber waste, FA, and PVC). The tensile test results were validated by using the finite element method.

The hardness of plastic materials, elastomers, and rubbers is measured using a Shore durometer (hardness tester) [290]. The Shore hardness test is standardized, with the most common standards being SR ISO 48-4 [306] (European) and ASTM D2240-15 [15] (American).

The experimental results regarding Shore A hardness for all five analyzed specimens are presented in Table 3.1. For the sake of simplicity in presenting the experimental results, the following notation was used: phr1 - FA concentration, phr2 - PVC concentration.

Table 3.1. Experimental results of Shore A hardness for the analyzed specimens

S01		S02		S03		S04		S05	
phr1	phr2	phr1	phr2	phr1	phr2	phr1	phr2	phr1	phr2
0	0	30	0	0	30	30	30	50	50
Shore A= 79		Shore A= 74,5		Shore A= 71		Shore A= 71,5		Shore A= 64	

The results in Table 3.1 represent the arithmetic mean of 10 measurements taken along the longitudinal axis of symmetry, at the midpoint of the specimen width.

Tensile testing is a type of destructive mechanical testing used to determine material properties concerning its resistance to this type of stress, its behavior under tension, and the appearance of the fracture surface (which provides information about whether a material is ductile or brittle). This test involves applying a gradually increasing force to a specimen, the value of which increases until it breaks or reaches a predetermined value, in order to determine various mechanical properties. This type of testing is used for a wide range of materials, such as steel, aluminum, plastic, rubber, fiberglass, concrete, and more.

Tensile testing was conducted on the same 5 types of specimens. An example of a specimen used for tensile testing is shown in Figure 3.1.

Figure 3.1. A specimen used for the tensile test

The dimensions of the specimens were: 250 mm in length, 25 mm in width, and 6 mm in thickness. Tensile testing was conducted using a universal testing machine Instron 1000 HDX equipped with BlueHill 3 software for real-time data acquisition and machine control. The Bluehill 3 program allows for the following actions: automatic calibration of sensors, generation of predefined and user-edited reports, system monitoring, real-time result visualization, determination of conventional and true stress-strain curves, and plasticity characteristics [187]. The experimental results obtained from the tensile tests are presented in Table 3.2. Specific stress-strain curves for a representative specimen from sets S01-S05 are shown in Figures 3.2-3.4.

Table 3.2. Experimental results of mechanical properties for the analyzed specimens obtained from tensile testing

S01		S02		S03		S04		S05	
phr1	phr2	phr1	phr2	phr1	phr2	phr1	phr2	phr1	phr2
0	0	30	0	0	30	30	30	50	50
σ_r=22 [MPa]		σ_r=11.2 [MPa]		σ_r=8.4 [MPa]		σ_r=9.7 [MPa]		σ_r=2.5 [MPa]	
A=350 [%]		A=428 [%]		A=445 [%]		A=435 [%]		A=495 [%]	
E= 52.4 [MPa]		E= 26.3 [MPa]		E=20.1 [MPa]		E=21.6 [MPa]		E=19.8 [MPa]	

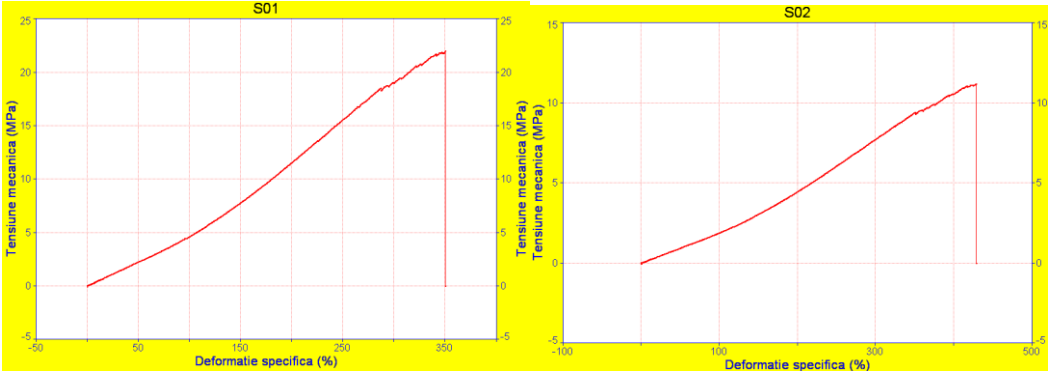The results in Table 3.2 represent the arithmetic mean of 15 tested specimens per material set.

Figure 3.2. Stress-strain curve for the S01 and S02 specimens
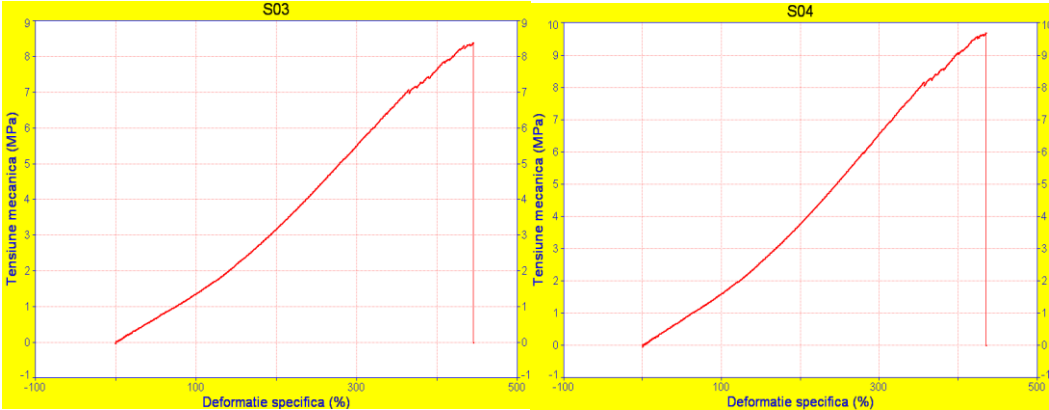

Figure 3.3. Stress-strain curve for the S03 and S04 specimens
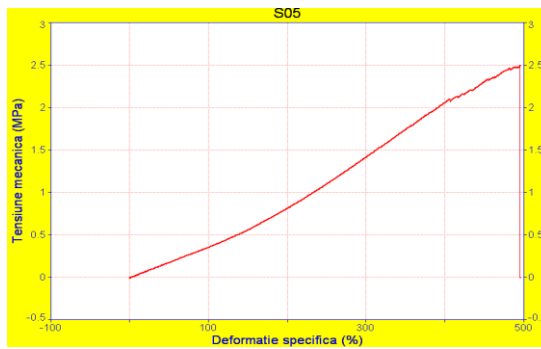
Figure 3.4. Stress-strain curve for the S05 specimen

From the analysis of the figures and tables with results, several observations can be made regarding the behavior of both specimen S01 (without residues) and the other composites containing different proportions of FA and/or PVC (from 10 to 50 phr). It was observed that the introduction of FA into the rubber matrix leads to an increase in elasticity (indicated by the elongation at break values of the specimens) with a decrease in tensile strength. One explanation for this phenomenon is that the granular-level FA particles inserted into the matrix can act as extension elements for the rubber granules due to the impurities they contain, allowing the entire structure to elongate more. By using flexible PVC waste, the introduction of these particles into the rubber matrix resulted in increased elasticity (as flexible PVC is characterized by high elongation at break) with decreased tensile strength (as flexible PVC is characterized by low tensile strength compared to S01 rubber). Samples that have both FA and PVC show higher elongation and lower strength compared to S01, which does not have such inserts. This result was obtained because both FA and PVC lead to increased elasticity and decreased strength when introduced separately into the rubber matrix. Due to the fact that FA residues contain harder chemical elements compared to PVC, when they are introduced alongside PVC into the rubber matrix, they increase tensile strength (they have higher rigidity) but reduce elongation at break (reducing the elasticity of the material) compared to specimens that have only PVC in the composition.

Next, finite element analysis will be used to validate the experimental results. The finite element analysis will be performed using Abaqus software because it allows for both the creation of a 3D model of the part and subsequent finite element analysis (there is no need for importing the geometry of the analyzed part in file formats such as .igs or .step). The stress distribution results for specimen S01 are shown in Figure 3.5.
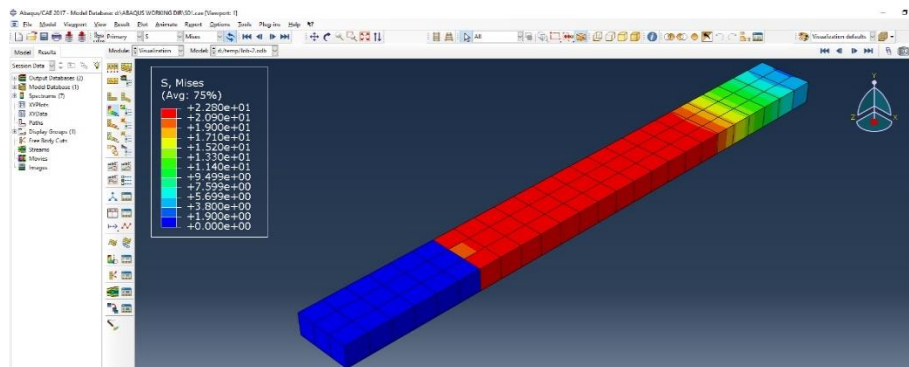

Figure 3.5. Distribuția tensiunilor mecanice pentru epruveta S01

From the analysis of the figures obtained from finite element analysis, values close to the tensile stress values obtained from the tensile test are observed. For specimen S01, an error of 3.63% was obtained, no errors were obtained for specimen S02, an error of 1% was obtained for specimen S03, an error of 6.1% was obtained for specimen S04, and an error of 8.4% was obtained for specimen S05. Slightly higher errors are observed for specimens S04 and S05. This can be explained by the fact that the number of PVC and FA particles increases inside the rubber matrix (30 phr PVC and 30 phr FA for S04, and 50 phr PVC and 50 phr FA for S05), and the material considered is an approximation of the real one (based only on the tensile stress-strain curve).

In this chapter, several physico-mechanical properties were determined for composite materials with a rubber matrix and FA and PVC inserts at different concentrations (ranging from 0 to 50 phr).

From the analysis of the results obtained (for hardness and tensile properties), the following conclusions can be drawn:

- the additions of FA and PVC lead to a decrease in the hardness of the specimens, which is consistent with findings in the literature;

- specimens containing both FA and PVC have higher hardness compared to specimens with only PVC additives; one possible explanation for this phenomenon is that FA particles contain hard metals that contribute to the increase in Shore hardness compared to flexible PVC particles, which do not contain such materials;

- tensile strength of the specimens decreases with an increase in the concentration of PVC and FA, with the lowest value obtained for specimens with 50 phr PVC and 50 phr FA;

- elastic modulus increases with increasing tensile strength and decreases with increasing elongation at break; this phenomenon can be explained by the fact that as elongation at break increases, the material becomes more elastic, loses rigidity, and consequently, the longitudinal elastic modulus decreases.

- an increase in elongation at break was observed with an increase in the concentration of FA; one possible explanation for this phenomenon is that impurities in FA behave during tension as chain extensions of chemical bonds, contributing to an increase in elongation at break.

4. RESEARCH ON THE STRUCTURE OF COMPOSITE MATERIALS WITH RUBBER MATRIX AND FLY ASH AND PVC ADDITIVES

Scanning electron microscopy (SEM) is an advanced imaging technique that uses an electron microscope to study the fine details of structures and materials at an extremely small scale, with magnification powers ranging from hundreds to tens of thousands. The term "baleiaj" refers to detailed surface characteristics such as irregularities, cracks, roughness, and other imperfections that cannot be easily visualized with optical microscopes (whose typical magnification ranges from 50x to a maximum of 1000x).

SEM analysis was used to study the internal structure of composite materials. The analysis was performed using a scanning electron microscope (SEM) model (Phenom PURE, Thermo Fisher Scientific, Netherlands). An example SEM image for specimen S01 is provided in Figure 4.1.

In Figure 4.1, you can see an SEM image of specimen S01, made from rubber mixtures that also contain recycled rubber (recycled from tires). The SEM analysis reveals that the material has excellent compactness, but there are also some whitish areas where traces of talcum powder are present. When FA was added, the material corresponding to specimen S02 with a composition of 30 phr was obtained. SEM analysis showed strong interaction between the rubber and FA, which is due to the high SiO_2 content in FA, and silicon particles form strong filler-filler interactions with adjacent silica particles. Additionally, the presence of certain amounts of sulfur in the FA structure can add additional cross-linking to the polymer. The use of KWQ-EL also improves the compatibility between FA and the rubber matrix. The material compactness obtained for specimen S02 was very good, with very small pores comparable in size to those obtained for specimen S01. SEM analysis of specimen S02 containing FA demonstrated that rubber products with very good structural homogeneity can be obtained.

With the addition of PVC to the rubber composition, specimen S03 was obtained, and SEM analysis revealed that adding PVC increases the material's porosity. This phenomenon was also observed in the SEM analyses of specimens S04 and S05. It's worth noting that the highest porosity was obtained for specimen S05, which contains a large amount of both FA and PVC. One possible solution to eliminate the pores that occur when PVC is added is to use ultrasonics in the vulcanization process, as their presence ensures uniform temperature and pressure inside the material during the vulcanization process.
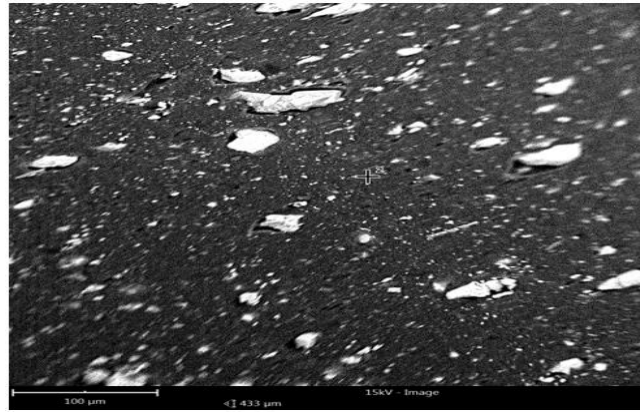
Figure 4.1. SEM analysis of S01 sample

The research conducted primarily aimed to investigate the influence of the composite material's structure on the topography of the surface layer. Thus, the topography of specimen S01, which consists only of rubber, was analyzed, as well as that of composite materials formed from mixtures of rubber and FA, rubber and PVC, and mixtures of rubber, FA, and PVC (Figure 4.2 will be given next for exemplification). Under these conditions, the impact of using FA and PVC on the surface roughness of composite materials could be established. A high surface roughness can influence how certain substances adhere to the surfaces of the composite materials produced.
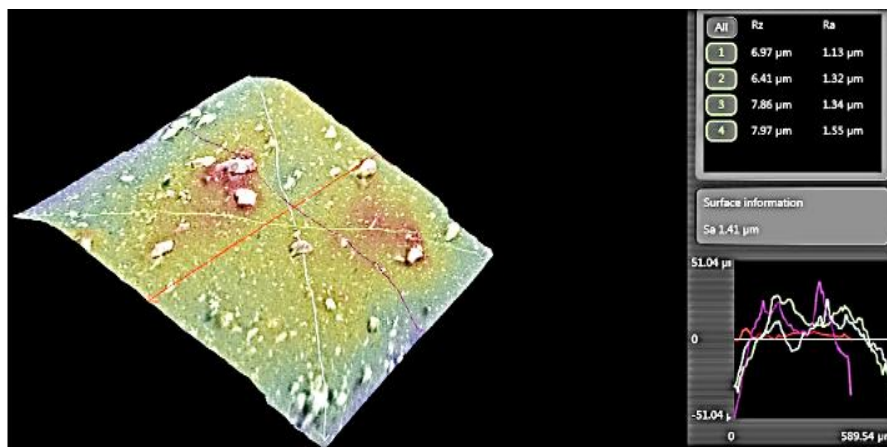

Figure 4.2. The 3D reconstruction and roughness measurement for S01 sample

Some research studies [315, 326] also specify that a high surface roughness can significantly influence the aging processes of composite materials with rubber matrices because high surface roughness can accelerate aging by forming a network of microcracks in the surface layer.

The analysis of material structure through scanning was performed using X-rays, and the equipment used was the CT ZEISS METRO-TOM 1500. This type of equipment, due to its characteristics, provides the possibility to obtain the best results in the analysis of composite material structures. With the help of this system, a computerized tomography of each individual sample can be performed. The VGSTUDIO MAX software was used to analyze the images provided by the CT ZEISS METRO-TOM 1500. This image analysis software is structured into 6 modules and

allows inspection of a wide range of materials. To illustrate, the topography obtained through scanning for sample S01 is presented in Figure 4.3.
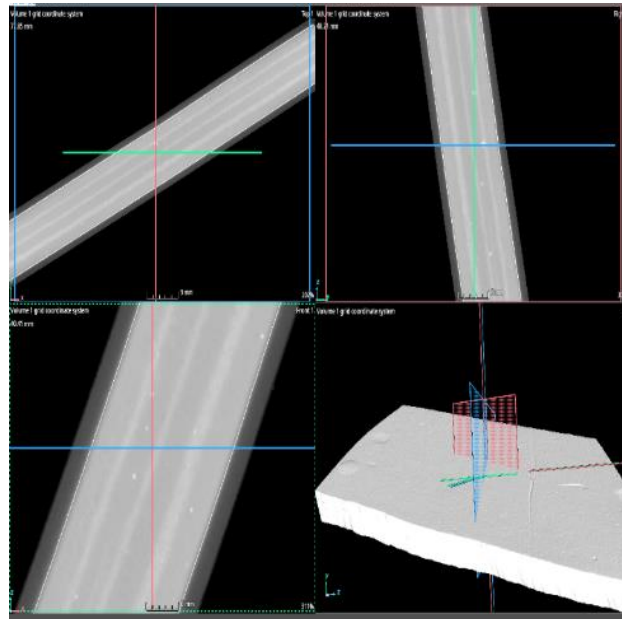

Figure 4.3. The topography of sample S01 through scanning

From the analysis of Figure 4.3, in the case of sample S01, a good compactness of the material is observed (no pores or other defects are visible in its structure), with some white areas likely due to the presence of talcum powder in the rubber composition. For sample S02, very small pores are observed in the material compared to S01, and it exhibits good compactness. One possible explanation for the good compactness of the material in sample S02 could be the presence of SiO_2 particles in the FA composition, which helps form strong filler-filler interactions with adjacent silica particles. Analyzing sample S03, it is evident that porosity has increased compared to S01 and S02, indicating a decrease in material compactness. The increased quantity of fly ash and PVC particles in the material composition leads to reduced homogeneity, as seen in samples S04 and S05. This phenomenon is attributed to the fact that adding these components can create variations in material properties, such as chemical composition or particle size. Additionally, this can lead to increased porosity, as fly ash and PVC particles may occupy spaces within the material's structure, leaving voids or gaps, which affect its density and homogeneity.

To test how dust adheres to the surfaces of the five experimental material types (S01-S05), a dust test chamber, ST 1000 U, produced by Weisstechnick company Germany, was used.

To determine how dust adheres to the surfaces of the specimens, the following operating parameters were established:

- the dust used in the tests was of type "A2 fine" ARIZ-TD/A2.
- testing was carried out with 6-second pulses (fan on) followed by a 15-minute pause.
- a total of 20 cycles (19 repetitions) were applied (20 cycles x 15 min. = 5 hours).
- after exposure to dust, the specimens were placed vertically, allowing the deposited dust on the upper side to fall off.

To analyze the influence of the microgeometry of the surface layer of the specimens on dust adhesion, a study of the surface topography was conducted. After dust deposition, the specimens were placed vertically, allowing the dust deposited on

the upper side to fall off. Subsequently, the surfaces of the specimens were analyzed, and conclusions were drawn regarding the amount of dust remaining on them. For illustrative purposes, the surface of sample S01 obtained after dust deposition is presented in Figure 4.4.

Figure 4.4. The surface layer of sample S01 after it was placed vertically

The analysis of dust deposits on samples S01-S05 allows us to draw conclusions regarding their topography after the deposition of "A2 fine" ARIZ-TD/A2 dust. On the samples that do not contain residues of FA and/or PVC, a significant amount of dust residue can be observed. This finding indicates the need to identify solutions to reduce dust deposition in rubber matrix materials. Analyzing the topography of sample S02, we can observe a high-quality surface without significant dust residue. This can be explained by the kinetics of vulcanization and processability of rubber compounds, which benefit positively from the presence of FA particles, thus reducing dust deposition (FA particles contribute to the creation of a stable and homogeneous network). For sample S03, a significant dust deposition is evident compared to samples S01 and S02. This phenomenon can be attributed to the PVC inserts in the samples, which lead to increased porosity. Additionally, surfaces composed of PVC can often be rougher or coarser than those of rubber. This rough texture can act as a suitable substrate for dust particle deposition, facilitating its accumulation. An improvement in dust deposition can be observed for sample S04 compared to S03, which can be explained by the presence of FA particles, positively influencing the reduction of dust quantity. This improvement continues for sample S05, but the topography of the analyzed surfaces is inferior to that of samples S01 and S02 due to the negative influence of PVC, which contributes to maintaining a significant dust deposition.

From the analysis of the research conducted, the following conclusions can be drawn:

- no cracks or other obvious irregularities were observed in the samples due to the introduction of FA or PVC particles;

- SEM images indicate an increase in white spots with an increasing amount of FA, and these spots were observed inside the rubber matrix;

- the poor dispersion of FA in the rubber matrix can be attributed to the low viscosity of rubber; to improve FA dispersion in the rubber matrix, ultrasonic activation systems are recommended;

- the formation of agglomerates may be caused by the fact that FA consists of very fine particles, and excessive addition of FA may be responsible for agglomerate formation;

- the formation of agglomerates can lead to a decrease in material hardness, which was also observed in Chapter 3, where a decrease in Shore A hardness was noted as the phr concentration of FA increased;

- FA contributes to an increase in the amount of metal oxides (such as Al_2O_3, CaO, and MgO); these metal oxides act as activators, accelerating the vulcanization process; this can be a practical benefit for rubber manufacturers as it reduces production time.

- the addition of PVC particles to the polymeric structure of the samples causes significant changes in the morphology of the composite material and the mobility of macromolecules in the boundary layers between rubber and PVC; for sample S03, where PVC particles were added, an increase in porosity in the material structure is observed; in the case of sample S04, which contains both FA and PVC, an improvement in porosity is observed; for sample S05, which contains large quantities of both FA and PVC, the bonds between the filler elements and the rubber matrix appear to break; these findings may be due to the lack of bonding between the rubber matrix and the filler elements; to improve these bonds, various agents capable of improving filler dispersion can be added, leading to more uniform integration into the rubber matrix; in this context, carbon black (CB) can play a crucial role as the primary filler (a similar conclusion was also formulated in [264]).

5. THERMOGRAVIMETRIC ANALYSIS OF COMPOSITE MATERIALS WITH RUBBER MATRIX AND FLY ASH AND PVC ADDITIVES

The thermogravimetric analysis (TGA) involved the following steps:
- a crucible was loaded for each analysis with a fraction of the sample, with a mass below the maximum value indicated by the manufacturer (1 gram);
- a heating rate of 100°C/min was selected;
- the files for each analyzed sample were named sequentially.

The program used was characterized by the Ramp method with a heating rate of 100°C/min up to 500°C in a nitrogen atmosphere (purity 6.0), followed by cooling in air for 20 minutes.

The maximum heating temperature of 500°C was chosen because beyond this temperature, the weight loss of the rubber composites stabilizes.

As a result of the TGA analysis, two curves were plotted, representing the mass loss of the sample (%) as a function of temperature (°C), and then the derivative of mass (%) per °C as a function of temperature.

For illustrative purposes, the TGA-DTGA results using high-resolution TGA for sample S01 are presented in Figure 5.1.
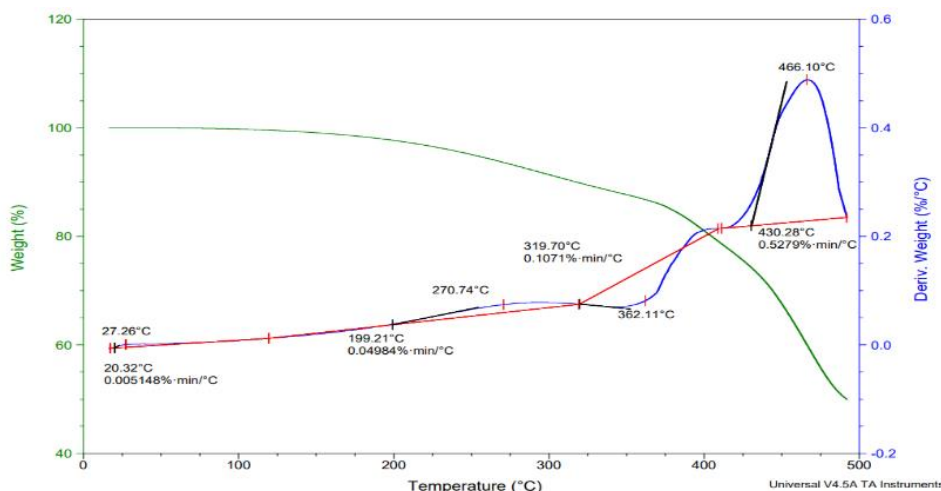

Figure 5.1. The TGA analysis for S01 sample

From the analysis of the experimental results, it is evident that the lowest mass loss was obtained for sample S01, which does not have residues (either FA or PVC) added to it. When FA is added to the rubber, there is an increase in both mass loss and the rate of mass loss. Furthermore, the maximum rate of mass loss was recorded at a temperature of 281.03°C, which is higher than that of sample S01, but also at a temperature of 461.74°C, which is slightly lower than that of sample S01. This suggests that the FA residue retains properties somewhat similar to the base rubber material.

The research conducted with the objective of obtaining composite materials with high performance from rubber waste, FA, and PVC has demonstrated the following:

- it is possible to obtain composite materials from waste that exhibit high performance in use, provided their composition is optimized.

- TGA/DTGA analysis has shown that the addition of FA and PVC leads to changes in the mass loss values and the temperature range over which this loss occurs.

- the mass losses are not very significant, indicating that these types of composite materials can be used in various different industrial applications.

6. ARTIFICIAL AGING ANALYSIS OF COMPOSITE MATERIALS WITH RUBBER MATRIX CONTAINING FLY ASH AND PVC ADDITIVES

One of the crucial properties of all materials, especially rubber matrix composites, relates to their behavior during aging processes. This property was analyzed because composite materials with a rubber matrix are used to manufacture parts that undergo various temperature variations during use. To observe how these composite materials behave under thermal shocks, they were subjected to an artificial aging process. Thus, the elastic properties of the samples were determined both after the manufacturing process and after exposure to thermal shocks. The testing procedure in this doctoral thesis was conducted according to the SR ISO 188:2023 standard [307].

The testing of the behavior of composite materials from the five types of specimens was carried out using a thermal chamber, the Temp Shock Votsch VT3 7012 S2 test chamber, produced by Test Equipment Co., Ltd, Jin Hui Industrial Park, China [203]. This type of thermal chamber allows for very rapid temperature changes in the range of -80°C to 220°C. Since in practical conditions, products made from these types of composite materials are used in environments with temperatures ranging from -45°C to +85°C, the testing conditions were similar. Consequently, the samples were tested for 3000 cycles with temperature variations in the range of -45°C to +85°C. The stabilization time varied, with 60 minutes set for the first 1000 cycles and 25 minutes for the subsequent 2000 cycles. Stabilization was carried out in conditions of ventilated air.

The elastic properties of the composite materials were determined using a Zwick/Roell Z05 TN testing machine with testXpertII software version 3.6, produced by BRECON Vibra-tionstechnik GmbH, Stolberger, Köln, Germany.

The tests were performed in accordance with SR ISO 188:2013. Deformation results obtained for sample S01 are illustrated in Figure 6.1.
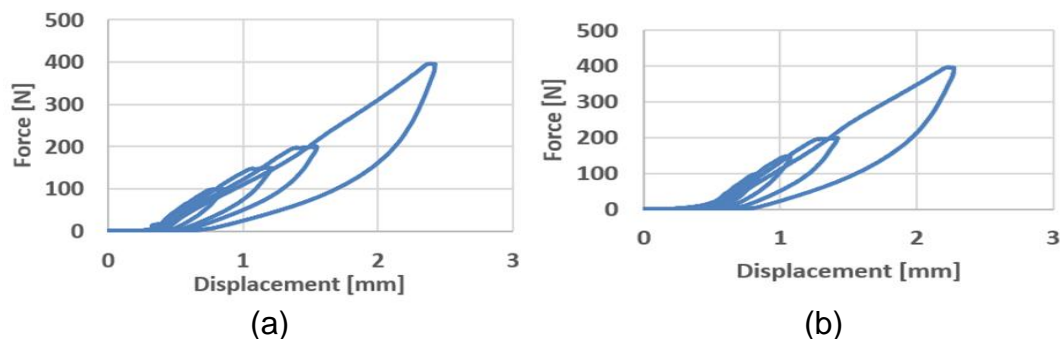

(a)   (b)

Figure 6.4. The S01 sample deformation results; a) initial state; b) after aging.

In this process, the modification of material elasticity was determined by measuring the displacement for specific applied forces. Testing was performed on both the material from new samples and the material subjected to accelerated aging. The testing was carried out at a penetration speed of 30 mm/min, considering multiple stages involving different force values: stage 1 - F = 10 N; stage 2 - F = 50 N; stage 3 - F = 75 N; stage 4 - F = 100 N; stage 5 - F = 150 N; stage 6 - F = 200 N; stage 7 - F = 400 N.

From the analysis of the results, it can be observed that an artificial aging process leads to a reduction in the elasticity of the materials, but this loss was not very significant for all the analyzed samples S01-S05. In practice, it is desirable for a material to have minimal loss of elasticity after the aging process. Regarding the material from sample S01, its initial elasticity was not very high due to the presence of recycled rubber and rubber in powder form in the composition. It is worth noting that this composite material showed a relatively small loss of elasticity, less than 4%. The addition of FA to the composition of the materials (sample S02) resulted in an increase in initial elasticity of approximately 14.2%, with a very small loss of elasticity (less than 8%). This result confirms that the addition of FA allows both an increase in the initial elasticity of the material and good stability of elasticity after the aging process.

Thus, a significant increase in the quantity of PVC and FA (samples S04 and S05) allows for an increase in the elasticity of composite materials (compared to sample S01, which is made only of rubber matrix) with a moderate loss of elasticity after the aging process. In these conditions, the research conducted makes an important scientific contribution to the field, demonstrating the durability of rubber matrix composite materials with the addition of FA and PVC.

7. MODAL IDENTIFICATION FOR COMPOSITE MATERIALS WITH RUBBER MATRIX AND FLY ASH AND PVC INSERTS

According to [271], rubber materials are frequently used for vibration attenuation in various structures due to their specific mechanical properties. The behavior of rubber can be classified into two main categories: hyperelastic and viscoelastic. Hyperelastic materials, also known as "rubber-like materials," exhibit a nonlinear relationship between stress and strain. This means that the deformation (elongation) of the material is not directly proportional to the applied mechanical stress. Instead, the relationship follows a hyperelastic or nonlinear curve. Rubber materials often exhibit this hyperelastic behavior, which is described by mathematical models such as the Mooney-Rivlin model, the Ogden model, or the Neo-Hookean model. Hyperelastic materials are commonly used in applications where large deformations are expected, and they can efficiently absorb and dissipate mechanical energy. Viscoelastic materials combine characteristics of elasticity and viscosity. They exhibit time-dependent properties, meaning their mechanical response depends on the loading rate and duration.

For modal identification, the experimental setup shown in Figure 7.1 was used. The components of the setup are as follows: 1 - the specimen under analysis; 2 - accelerometer; 3 - excitation point; 4 - rubber pads to prevent the transmission of vibrations to the clamping jaw 5; Ltot - total length of the specimen in the cantilever (65 mm); width of the specimens 6 mm and thickness 6 mm; these specimens were obtained by cutting from initial specimens with a length of 200 mm, width of 50 mm, and thickness of 6 mm; the mass was obtained by weighing these initial specimens.
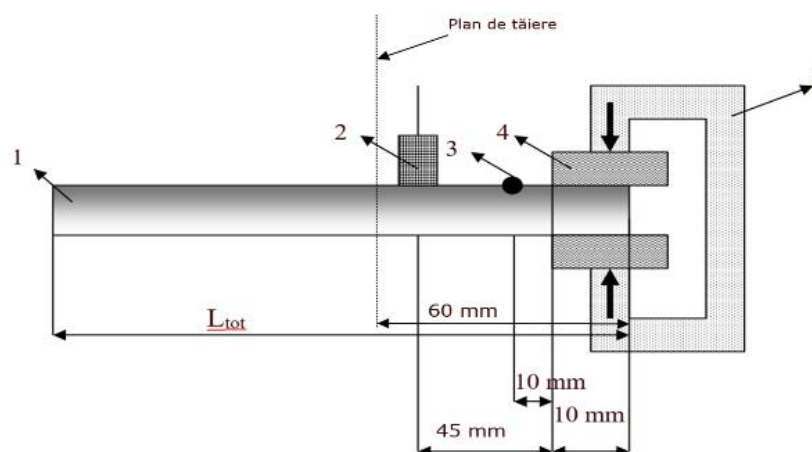

Figure 7.1. Experimental setup for natural vibration modes identification

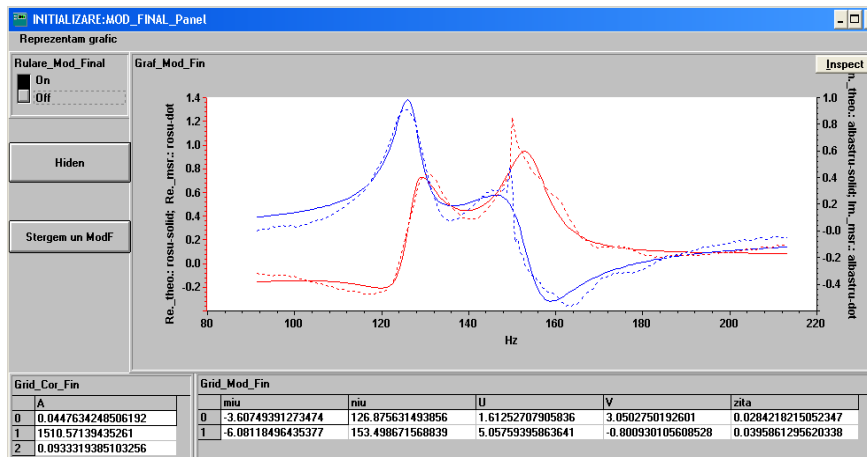An example of the natural vibration modes obtained for S01 is provided in Figure 7.2.

Figure 7.2. Natural vibration modes determination for S01 sample

The notations used are as follows: μ (miu) represents the vibration damping factor per unit mass; ν (nu) denotes the natural frequency or eigenfrequency; U and V represent the real and imaginary parts; ζ (zita) signifies the critical damping; 0, 1, 2, etc. refer to the natural vibration modes identified.

From the analysis of the vibration results, the following trends can be observed:

-1-3 natural vibration modes were determined, depending on the analyzed sample.

- for sample S01, natural frequencies in the range of 126 to 153 Hz were identified, and the corresponding damping factor (known in the literature as the damping factor per unit mass) for the first natural mode was 3.607 (Ns/m/kg);

- sample S02 showed a single natural vibration mode at a frequency of 119 Hz with a damping factor of 17.666 (Ns/m/kg);

- sample S03 had natural frequencies in the range of 116 to 122 Hz, and the damping factor for the first natural mode was 7.117 (Ns/m/kg);

- samples S04 and S05 had similar natural frequencies, and the damping factors for the first natural vibration mode were approximately equal.

Regarding dynamic mechanical properties, the following can be observed:

- the addition of PVC and FA particles to rubber-based composite materials leads to a decrease in stiffness and an increase in elasticity; this can be explained by the fact that FA particles act as extensions of chemical bonds during tension, contributing to increased elongation at yield; additionally, the use of flexible PVC contributes to increased material elasticity, as evident from the higher damping factor compared to sample S01;

- samples S04 and S05 exhibit low vibration damping properties and low energy loss factors; consequently, these materials can be used in applications where oscillations need to continue without significant attenuation.

8. OWN CONTRIBUTIONS. FUTURE RESEARCH PERSPECTIVES

The present doctoral thesis is heavily focused on experimental analyses and results (except for Chapter 1, all other chapters contain experimental determinations). From the analysis of the experimental research conducted in this doctoral thesis, the following contributions can be extracted:

- the presence of FA and PVC particles in the structure of composite materials with rubber matrix leads to a decrease in hardness compared to samples containing only rubber; superior hardness is observed for samples containing FA inserts compared to those with PVC inserts only;

- the presence of FA and PVC particles in the structure of composite materials with a rubber matrix leads to a decrease in tensile strength but an increase in elasticity (as seen from the analysis of characteristic curves regarding elongation at break);

- SEM-based topography analysis revealed that the addition of PVC or FA particles to the rubber matrix does not introduce fissures or other structural damage; agglomerates are observed due to the introduction of these particles, contributing to a decrease in Shore hardness and an increase in surface roughness;

- scanning topography analysis showed that S01-type samples had a homogeneous structure without porosities. Similar conclusions were drawn for S02 samples, which contained FA particles (at a concentration of 30 phr); for S03 samples, the structure was observed to be less homogeneous compared to S01 and S02 samples, indicating that the addition of PVC (at a concentration of 30 phr) had a negative impact on homogeneity and porosity; for S04 and S05 samples, structural homogeneity decreased as the concentration of PVC and FA increased, suggesting that high-quality rubber products with FA inserts can be obtained.

- from the analysis of thermogravimetric curves and graphs (mass loss as a function of temperature and mass loss derivative as a function of temperature), it was observed that waste composite materials with high performance can be obtained, provided that their composition is optimized;

- TGA/DTGA analysis demonstrated that the addition of FA and PVC leads to a modification of mass loss values and the temperature range in which this loss occurs (which varies significantly for all five samples);

- mass losses are not significant, indicating that the composite materials analyzed in this thesis can be used in various industrial applications, even in high-temperature working environments;

- the thermal stability of S04 (30 phr PVC and 30 phr FA) and S05 (50 phr PVC and 50 phr FA) composites decreases compared to sample S01, which does not contain FA or PVC in its composition.

The research presented in this thesis provides significant contributions to understanding the behavior and utilization of composite materials with rubber matrices, especially when containing FA and PVC additives. Notable contributions include:

-   effects of adding FA and PVC particles on the mechanical, thermal, and topographical properties of rubber matrix composite materials were comprehensively evaluated;

-evaluation of thermal behavior revealed that these materials can be used in high-temperature applications;

-the influence of accelerated aging on the mechanical properties of composite materials was assessed, demonstrating that the addition of FA and PVC particles can significantly influence elasticity and material strength based on composition.

Future research can explore various directions, including:

-conducting fatigue and fracture mechanics tests to evaluate durability and performance under practical conditions;

-performing additional chemical analyses, such as FT-IR or Raman, to investigate chemical changes in materials following the addition of FA and PVC;

-utilizing composite materials in practical applications, such as furniture, construction, or the automotive industry, to evaluate real-world performance;

-continuing research to develop more high-performance and durable composite materials that meet the requirements of different industries.

These directions have the potential to make valuable contributions to the development of new composite materials and optimize their practical applications.

SELECTIVE REFERENCES

5. Alam, M.N., Kumar, V., Potiyaraj, P., Lee, D.J., Choi, J., Mutual dispersion of graphite–silica binary fillers and its effects on curing, mechanical, and aging properties of natural rubber composites, Polym. Bull., Vol. 79, pp. 2707–2724, 2022. https://link.springer.com/article/10.1007/s00289-021-03608-x

15. ASTM D2240-15, Standard Test Method for Rubber Property—Durometer Hardness, 2021. https://www.astm.org/d2240-15r21.html

24. Benkreira, H,. Khan, A., Horoshenkov, K.V., Sustainable acoustic and thermal insulation materials from elastomeric waste residues, Chem. Eng. Sci., Vol. 66, No. 18, pp. 4157-4171, 2011. https://doi.org/10.1016/j.ces.2011.05.047

25. Bhatt, A., Priyadarshini, S., Mohanakrishnan, A.A., Abri, A., Sattler, M., Techapaphawit, Physical, chemical, and geotechnical properties of coal fly ash: a global review, Case Stud. Constr. Mater., Vol. 11, pp. 1-14, 2019. https://doi.org/10.1016/j.cscm.2019.e00263

26. Blissett, R.S., Rowson, N.A., A review of the multi-component utilisation of coal fly ash, Fuel, Vol. 97, pp. 1–23, 2012. https://doi.org/10.1016/j.fuel.2012.03.024

29. Carcea, I., Materiale compozite. Fenomene la interfață, Editura Politehnun, Iași, 2008. https://sim.tuiasi.ro/wp-content/uploads/2015/Carcea4-Materiale%20Compozite.%20Fenomene%20la%20interfata.pdf

30. Cañavate, J., Carrillo, F., Casas, P., The use of waxes and wetting additives to improve compatibility between HDPE and ground tyre rubber, J. Compos. Mater., Vol. 44, No. 10, pp. 1233-1245, 2010. https://doi.org/10.1177/0021998309351602

38. Dana, K., Das, S., Das, S.K., Effect of substitution of fly ash for quartz in triaxial kaolin– quartz–feldspar system, J. Eur. Ceram. Soc., Vol. 24, pp. 3169–3175, 2004. https://doi.org/10.1016/j. jeurceramsoc.2003.10.008

42. Dobrotă, D., Experimental research regarding processing rubber waste with metalic insertion, Materiale plastice, Vol. 43, No. 1, pp. 65 – 67, 2006. https://revmaterialeplastice.ro/Articles.asp?ID=968

43. Dobrotă, D., Considerations on constituent equations used in the study of mincing rubber waste reinforced with metallic insertion, Materiale Plastice, Vol. 43, No. 3, pp. 225-229, 2006. https://revmaterialeplastice.ro/Articles.asp?ID=1023

53. Goncharuk, G.P., Knunyants, M.I., Serenko, O.A., Kryuchkov, A.N., Mechanical properties of modified thermoplastic elastomers based on low-density polyethylene and rubber powder, Polymer Recycling, vol. 5, no. 3, pp. 161–164, 2000. https://www.researchgate.net/publication/291461125_Mechanical_properties_of_modified_thermoplastic_elastomers_based_on_low-density_polyethylene_and_rubber_powder

54. Gonzaga, G.H., da Silva Morais, C.R., Cunha, C.T.C, Incorporation of SBR Rubber Waste into PVC/CARBONATE Systems, Research Square, pp. 1-17, 2022. https://doi.org/10.21203/rs.3.rs-1663007/v1

55. Goswami, K.P., Pakshirajan, K., Pugazhenthi, G., Process intensification through waste fly ash conversion and application as ceramic membranes: A review, Science of the Total Environment, Vol. 108, pp. 1-20, 2022. http://dx.doi.org/10.1016/j.scitotenv.2021.151968

61. He, P., Zhang, X., Chen, H., Zhang, Y., Waste-to-resource strategies for the use of circulating fluidized bed fly ash in construction materials: A mini review, Powder

Technology, Vol. 393, pp. 773-785, 2021.
https://doi.org/10.1016/j.powtec.2021.08.035

64. http://mihaelabucur.blogspot.com/2009/05/materiale-compozite-i.html

68. https://ro.wikipedia.org/wiki/Material_compozit

70. https://www.materiale-compozite.ro/

94. https://www.sciencedirect.com/topics/engineering/natural-pozzolans

119. https://www.brabender.com/en/product/extruder-and-extrusiograph-30-25-and-30-32/

120. https://ro.scribd.com/document/457505715/Poliolefine

144. https://ro.fangli.us/conical-type-twin-screw-plastic-extruder.html

169. https://microscopecentral.com/products/olympus-bx51m-metallurgical-microscope

170. https://www.tibco.com/reference-center/what-is-analysis-of-variance-anova

179. https://www.magnetcenter.ro/malaxor-cu-paleta-de-amestecare-130-lt-0-75kw-ls-s130-mono

187. https://www.instron.com/-/media/literature-library/products/2020/08/high-force-universal-testing-machines.pdf

203. https://www.aeroexpo.online/prod/voetsch-industrietechnik/product-182765-24115.html

211. Ilic, M., Cheeseman, C., Sollars, C., Knight, J., Mineralogy and microstructure of sintered lignite coal fly ash, Fuel, Vol. 82, pp. 331–336, 2003. https://www.researchgate.net/publication/223641095_Mineralogy_and_microstructure_of_sintered_lignite_coal_fly_ash

217. Janowski, B., Jankowska, B., Radwańska, J., Rogoża, J., Weda, P., Kozak, R., Novel functionalized solution styrene-butadiene rubbers (SSBR) for tire treads, Elastomery, Vol. 23, pp. 252–262, 2019. https://elastomery.pl/wp-content/uploads/streszczenia-pdf/E2019_4_Janowski.pdf

221. Keane, M.A., Catalytic conversion of waste plastics: focus on waste PVC, J. Chem. Technol. Biotechnol., Vol. 82, 787–795, 2007. https://onlinelibrary.wiley.com/doi/epdf/10.1002/jctb.1757

222. Kinloch, A.J., Young, R.J., Fracture behavior of polymers, London: Applied Science Publishers, 1983. https://link.springer.com/book/10.1007/978-94-017-1594-2

228. Kuźnia, M., Magiera, A., Zygmunt-Kowalska, B., Kaczorek-Chrobak, K., Pielichowska, K., Szatkowski, P., Benko, A., Ziabka, M., Jerzak, W., Fly Ash as an Eco-Friendly Filler for Rigid Polyurethane Foams Modification, Materials, Vol. 14, pp. 1-14, 2021. https://www.mdpi.com/1996-1944/14/21/6604

229. Lapa, V. L. D. C., Visconte, L. L. Y., Affonso, J. E. D. S., Nunes, R. C. R., Aluminum hydroxide and carbon black filled NBR/ PVC composites—vulcanization and processability studies, Polymer Testing, vol. 21, no. 4, pp. 443–447, 2002. https://doi.org/10.1016/S0142-9418(01)00108-8

239. Lu, L., Li, W., Cheng, Y., Liu, M., Chemical recycling technologies for PVC waste and PVC-containing plastic waste: A review, Waste Management, Vol. 166, pp. 245-258, 2023. https://doi.org/10.1016/j.wasman.2023.05.012

255. Mujal-Rosas, R., Marin-Genesca, M., Orrit-Prat, J., Dielectric, mechanical and thermal characterization of HDPE composites with ground tire rubber, J. Thermoplast Compos. Mater., Vol. 25, No. 5, pp. 537-559, 2011. https://doi.org/10.1177/0892705711411344

256. Mulder, K., Knot, M., PVC plastic: a history of systems development and entrenchment, Technol. Soc., Vol. 23, 265–286, 2001. https://doi.org/10.1016/S0160-791X(01)00013-6

264. Orczykowski, W., Bieliński, D.M., Anyszka, R., Pędzich, Z., Fly Ash from Lignite Combustion as a Filler for Rubber Mixes. Part I: Physical Valorization of Fly Ash, Materials, Vol. 15, pp. 1-24, 2022. https://www.mdpi.com/1996-1944/15/14/4869

271. Prasada, V.B.S.R., Dr.G.V, Rao, Idrees, M., Identification of Damping Characteristics of EPDM-RUBBER with applications to sandwiched beams and considerations to Engine Mounts for Performance Evaluation, Materials Today: Proceedings, Vol. 24, pp. 628–640, 2020.
https://doi.org/10.1016/j.matpr.2020.04.317

280. Rotaru, A., Rusu, I.D., Microscopia electronică, Universitatea Ștefan cel Mare din Suceava, https://www.academia.edu/39213678/Microscopia-electronica

282. Schwink, T., Tire Fire Alert: Week Six [Online], 2013.
http://www.solidverbal.com/wp-content/uploads/2013/10/TireFire1-e1380850871485.jpg

285. Semon, W.L., Stahl, G.A., History of vinyl chloride polymers, J. Macromol. Sci. Chem., Vol. A 15, pp. 1263–1278, 2006.
https://doi.org/10.1080/00222338108066464

286. Sharma, K., Vyas, A., Singh, S.K., Conversion of waste PVC into liquid fuel, Int. J. Technol. Enhancement Emerging Eng. Res., Vol. 3, pp. 49–52, 2015.
https://www.researchgate.net/publication/280314018_Conversion_Of_Waste_PVC_Into_Liquid_Fuel

288. Singh, A., Spak, S.N., Stone, E.A., Downard, J., Bullard, R.L., Pooley, M., Stanier, C.O., Uncontrolled combustion of shredded tires in a landfill – part 2: population exposure, public health response, and an air quality index for urban fires, Atmos. Environ., Vol. 104, pp. 273–283,
2015.https://doi.org/10.1016/j.atmosenv.2015.01.002

290. Sheng, X.W.,, Zheng, W.Q., Zhu, Z.H., Luo, T.J., Zheng, Y.H., Properties of rubber under-ballast mat used as ballastless track isolation layer in high-speed railway, Construction and Building Materials, Vol. 240, pp. 1-10, 2020.
https://doi.org/10.1016/j.conbuildmat.2019.117822

292. Sobrinho, L.L., Calado, V.M.A., Bastian, F.L., Effects of Rubber Addition to an epoxy resin and its fiber glass composites, Polym. Compos., Vol. 33, No. 2, pp.295–305, 2012. https://doi.org/10.1002/pc.21265

295. Sprenger, S., Kothmann, M.H., Altstaedt, V., Carbon fiber-reinforced composites using an epoxy resin matrix modified with reactive liquid rubber and silica nanoparticles, Compos. Sci. Technol., Vol. 105, pp. 86-95, 2014.
https://doi.org/10.1016/j.compscitech.2014.10.003

296. Sprenger, S., Fiber reinforced composites based on epoxy resins modified with elastomers and surface modified silica nanoparticles, J. Mat. Sci., Vol. 49, pp. 2391–2402, 2014. https://link.springer.com/article/10.1007/s10853-013-7963-8

298. Srinivasarao, D., Amareswari Reddy, M., Krishna Veni, M.N.V., Sandeep Kumar, M., Effect of nano rubber additions on wear and mechanical properties of epoxy glass fibre composites, J. Mater. Sci. Eng., Vol. 3, No. 2, pp. 1-8, 2014.
https://www.hilarispublisher.com/open-access/effect-of-nano-rubber-additions-on-wear-and-mechanical-properties-of-epoxy-glass-fibre-composites-2169-0022.1000143.pdf

300. SR ISO 4649, Cauciuc, vulcanizat sau termoplastic. Determinarea rezistenţei la abraziune cu ajutorul unui dispozitiv cu tambur cilindric rotative, 2008.
https://magazin.asro.ro/ro/standard/166234

302. SR ISO 7619-1, Cauciuc vulcanizat sau termoplastic. Determinarea durităţii de indentare. Partea 1: Metoda durometrului (duritate Shore), 2011.
https://magazin.asro.ro/ro/standard/186928

303. SR ISO 188, Cauciuc, vulcanizat sau termoplastic. Încercări de rezistență la îmbătrânire accelerată și la căldură, 2011. https://magazin.asro.ro/ro/standard/280921

304. SR ISO 37, Cauciuc vulcanizat sau termoplastic. Determinarea caracteristicilor de efort-deformaţie la tracţiune, 2012. https://magazin.asro.ro/ro/standard/196150

306. SR ISO 48-4, Cauciuc vulcanizat sau termoplastic. Determinarea durității. Partea 4: Duritatea la indentare prin metoda durometrului (duritate Shore), 2022. https://magazin.asro.ro/ro/standard/27833

307. SR ISO 188, Cauciuc, vulcanizat sau termoplastic. Încercări de rezistență la îmbătrânire accelerată și la căldură, 2023. https://magazin.asro.ro/ro/standard/280921

310. Stelescu, M.D., Polymer Composites Based on Plasticized PVC and Vulcanized Nitrile Rubber Waste Powder for Irrigation Pipes, ISRN Materials Science, Vol. 2013, pp. 1-5, 2013. https://downloads.hindawi.com/archive/2013/726121.pdf

311. Suciu, V., Suciu, V.M., Studiul Materialelor, Editura Fair Partners, București, 2007. https://marcel.suciu.eu/Cartea_Std_Mater.pdf

313. Tărâță, D.F., Mirițoiu, C.M., Tehnici avansate de investigare a materialelor, Editura SITECH, Craiova, 2022.

314. Temimi, M., Camps, J.P., Laquerbe, M., Valorization of fly ash in the cold stabilization of clay materials, Resour. Conserv. Recycl., Vol. 15, pp. 219–234, 1995. https://doi.org/10.1016/0921-3449(95)00038-0

315. Thakur, VK, Grewell, D., Thunga, M., Kessler, M., Novel Composites from Eco - Friendly Soy Flour/SBS Triblock Copolymer, Macromol., Mater. Eng., Vol. 299, pp. 953– 958, 2014. https://onlinelibrary.wiley.com/doi/abs/10.1002/mame.201300368

318. Tipanna, M., Kale, D.D., Composites of waste, ground rubber particles and poly(vinyl chloride), Rubber Chemistry and Technology, Vol. 70, No. 5, pp. 815–819, 1997. https://meridian.allenpress.com/rct/article-abstract/70/5/815/92543/Composites-of-Waste-Ground-Rubber-Particles-and?redirectedFrom=PDF

319. Titow, W.V., PVC Technology, Elsevier Applied Science Publishers, 4th edition, 1984. https://onlinelibrary.wiley.com/doi/10.1002/pi.4980170319

326. Wu, H., Thakur, V.K., Kessler, M.R., Novel low-cost hybrid composites from asphaltene/SBS tri-block copolymer with improved thermal and mechanical properties, J. Mater. Sci., Vol. 51, pp. 2394–2403, 2016. https://link.springer.com/article/10.1007/s10853-015-9548-1

329. Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S., Xi, Y.Q., A comprehensive review on the applications of coal fly ash, Earth-Sci. Rev., Vol. 141, pp. 105–121, 2015. https://doi.org/10.1016/j.earscirev.2014.11.016

330. Yee, A.F., Pearson, R.A., J. Mat. Sci., Vol. 21, pp. 2462-2471, 1986. https://link.springer.com/article/10.1007/BF01114293

339. Zuga, D., Cincu, C., Use of cured butadiene styrene rubber powder in preparing polymer composites, Leather and Footwear Journal, Vol. 3, pp. 22–26, 2005. https://www.revistapielarieincaltaminte.ro/vol5_3.html

340. Zuga, D., Cincu, C., Polymer composites by reclaiming rubber wastes resulting from finishing the rubberized rolls used in printing industry, UPB Scientific Bulletin Series B, Vol. 68, No. 1, pp. 25–30, 2006. https://www.scientificbulletin.upb.ro/rev_docs_arhiva/full30056.pdf