STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF WORN AUTOMOBILE TIRES FOR USE AS MODIFIED BITUMEN COMPONENTS

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https://doi.org/10.5281/zenodo.18998067

Abstract. *This study presents a comprehensive physicochemical investigation of carbon-containing material obtained from thermo-oxidative pyrolysis of worn automobile tires at an industrial unit with a capacity of one ton per day. Thermal degradation behavior was analyzed using a Labsys Evo (Setaram) derivatograph, revealing a two-stage decomposition process occurring within 50–500 °C and 500–800 °C. The total mass loss reached 48.8% at 900 °C, indicating substantial conversion of the organic rubber matrix and formation of a stable carbonaceous residue. Morphological analysis performed using a scanning electron microscope (EVO MA 10) under vacuum conditions demonstrated a heterogeneous, porous structure with dispersed metallic inclusions. Energy-dispersive X-ray spectroscopy (EDS) confirmed that the material predominantly consists of amorphous carbon (approximately 72–73 wt.%) along with oxygen, zinc, iron, and minor mineral components originating from tire additives. Particle size reduction improved bulk density and surface activity, while magnetic separation effectively removed metallic impurities. The obtained carbon-containing material can be recommended as a functional filler for polymer-modified bitumens used in road construction, contributing to enhanced mechanical performance, improved thermal stability, and sustainable recycling of waste tires.*

Keywords: *Thermo-oxidative pyrolysis; waste tire recycling; carbon-containing material; thermogravimetric analysis (TGA); SEM–EDS analysis; particle size distribution; polymer-modified bitumen; asphalt pavements; sustainable road materials; carbon black filler.*

Introduction

The rapid growth of automobile transport has led to a continuous increase in the accumulation of worn automobile tires, creating serious environmental and technological challenges worldwide. Waste tires are characterized by high durability, chemical resistance, and slow natural degradation, which makes conventional disposal methods environmentally unsafe and economically inefficient [1,2]. Among various recycling technologies, pyrolysis has emerged as one of the most promising approaches due to its ability to convert waste rubber into valuable products, including pyrolysis oil, gas fractions, and carbon-containing solid residue [3–5]. Thermal degradation of tire rubber is a complex multistage process involving devulcanization, polymer chain scission, and carbonization of organic components.

Thermogravimetric studies have demonstrated that rubber materials typically undergo two or three main degradation stages depending on heating conditions and atmosphere [6–8]. The first stage is associated with the decomposition of natural and synthetic rubber components, while the second stage corresponds to further carbonization and decomposition of carbonaceous structures [7,9]. Quantitative thermal analysis provides essential data for optimizing pyrolysis parameters and predicting product yields [6]. The solid carbonaceous residue obtained after pyrolysis consists mainly of amorphous carbon, residual inorganic fillers, and metallic inclusions originating from tire reinforcement elements [10-12]. Its structure and surface morphology strongly influence potential application fields.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) are widely applied to characterize the microstructure and elemental composition of pyrolysis-derived carbon materials [13-15]. Previous studies have reported that carbon content in tire pyrolysis char may exceed 70 wt.%, with zinc oxide, silica, and iron compounds as the main inorganic components [10,16]. Due to its high carbon content and developed porous structure, pyrolysis-derived carbon material has attracted attention as a reinforcing filler in polymer systems [17–19]. Carbon black is traditionally used in polyethylene, polypropylene, polyvinyl chloride, and elastomeric materials to enhance mechanical strength, thermal stability, and resistance to photo-oxidative aging [20-22]. The possibility of replacing commercial carbon black with pyrolytic carbon offers significant economic and environmental advantages [16].

In recent years, growing interest has also been directed toward the application of recycled rubber products and carbonaceous materials in road construction. Polymer-modified bitumens (PMB) are widely used to improve rutting resistance, fatigue life, and low-temperature performance of asphalt pavements [24,25]. Incorporation of crumb rubber and carbon-based fillers into bitumen has demonstrated improvements in elasticity, thermal stability, and aging resistance [24]. However, detailed studies of pyrolysis-derived carbon materials as fillers for modified bitumens remain limited. Therefore, comprehensive investigation of the thermal behavior, morphology, elemental composition, and physicochemical characteristics of pyrolysis-derived carbon-containing material is necessary to justify its application in polymer-modified bitumens for road construction.

The present study aims to evaluate these properties and determine the feasibility of utilizing this secondary carbon product as a functional filler in modified bituminous systems. Recent studies have demonstrated the effectiveness of incorporating secondary industrial by-products into polymer–bitumen compositions to enhance thermal stability, frost resistance, and mechanical performance. Yoqubov et al. (2023) developed a polymer–bitumen insulating composition based on petroleum bitumen and secondary products of the chemical industry, including pyrolysis resin, carbon-containing materials derived from worn-out tires, and crushed tire powder. Their investigation showed that crumb rubber undergoes swelling and partial devulcanization at 180 °C within 6–8 hours, forming an active structural network within the bituminous matrix. The addition of gas pyrolysis resin (3–5 wt%) significantly increased the softening temperature of the composition by up to 120 °C, improving thermal stability.

Furthermore, carbon-containing material obtained via tire pyrolysis was shown to enhance adhesion strength and heat resistance due to its high amorphous carbon content (approximately 88%) and active surface structure confirmed by IR and X-ray diffraction analyses. The incorporation of secondary alkanolamines as vulcanization accelerators (5 wt%) contributed to improved structural formation and resistance to extreme climatic conditions [26]. These findings

confirm that the integration of recycled industrial materials not only improves the physicochemical and mechanical characteristics of polymer–bitumen systems but also increases sustainability and resource efficiency, which is particularly important for regions with sharply continental climates.

Materials and Methods. Thermal analysis of worn automobile tires was carried out using a modern derivatographic technique, which enables the simultaneous determination of mass variation (TG), mass loss rate (DTG), and thermal effects (DSC) over a broad temperature range. The experiments were performed on a Labsys Evo (Setaram) thermal analyzer. The resulting derivatogram is presented in Figure 1. The morphology and elemental composition of the carbon-containing material obtained after thermo-oxidative pyrolysis were investigated using a scanning electron microscope (SEM) of the EVO MA 10 brand under vacuum conditions. Elemental analysis was performed using an integrated energy-dispersive X-ray spectroscopy (EDS) detector.

Results and Discussion. The thermogravimetric (TG) curve (Figure 1) demonstrates a two-step degradation mechanism, characterized by two distinct sigmoidal regions corresponding to successive stages of thermal decomposition. The first degradation stage occurs within the temperature range of 50–500 °C, while the second stage is observed between 500 and 800 °C. In the first temperature interval (50–500 °C), the sample exhibits a mass loss of 17.9 mg, corresponding to 40.6% of the initial mass. This stage is associated with intensive thermal decomposition of the rubber matrix, during which the maximum degradation rate reaches 2.508 mg/min.

The rapid mass reduction in this region is attributed to polymer chain scission, release of volatile components, and partial devulcanization processes. The second degradation stage, occurring between 500 and 800 °C, proceeds at a comparatively lower rate of 1.837 mg/min. In this temperature range, the overall mass loss increases from 40.6% to 46.6%. This stage is primarily related to further carbonization of the residual organic structure and gradual breakdown of carbonaceous components. At 900 °C, the total mass loss reaches 48.8%, while the remaining solid residue corresponds mainly to metallic cord reinforcements and inorganic fillers originally present in the tire structure. The obtained results confirm the multistage thermal degradation behavior of worn rubber materials and provide quantitative parameters necessary for optimizing pyrolysis and recycling processes.

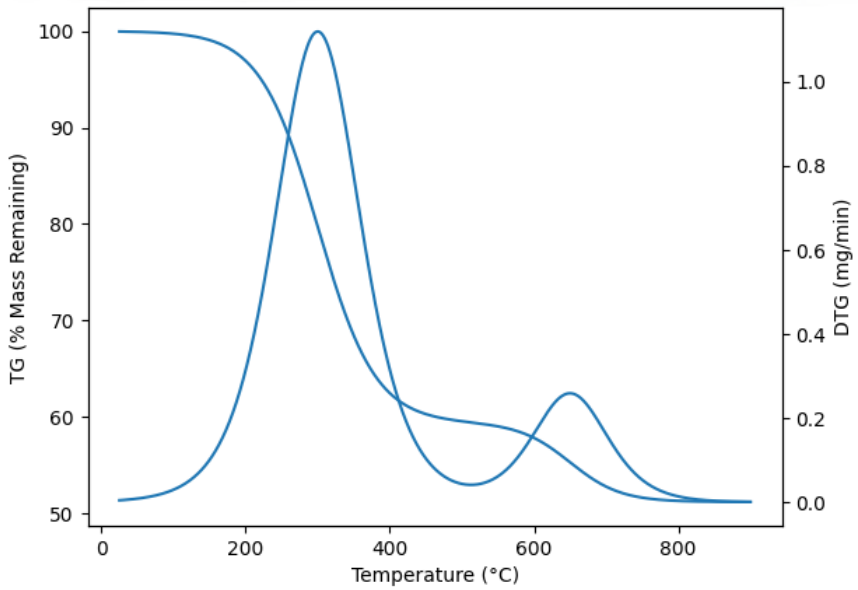


Figure 1. Derivatogram of Worn Automobile Tires (Labsys Evo Setaram)

At the Central Mining Department of the Navoi Mining and Metallurgical Combine, a pyrolysis unit with a capacity of one ton per day is currently in operation. Therefore, in order to identify and expand the potential application areas of the carbon-containing material obtained, a detailed study of its physicochemical characteristics is required. During the thermo-oxidative pyrolysis process, a carbon-containing material is formed. It is a relatively brittle, lump-like substance of black color with a grayish tint and an unpleasant odor (Fig. 2a). In some fragments, metallic inclusions are observed (Fig. 2b).

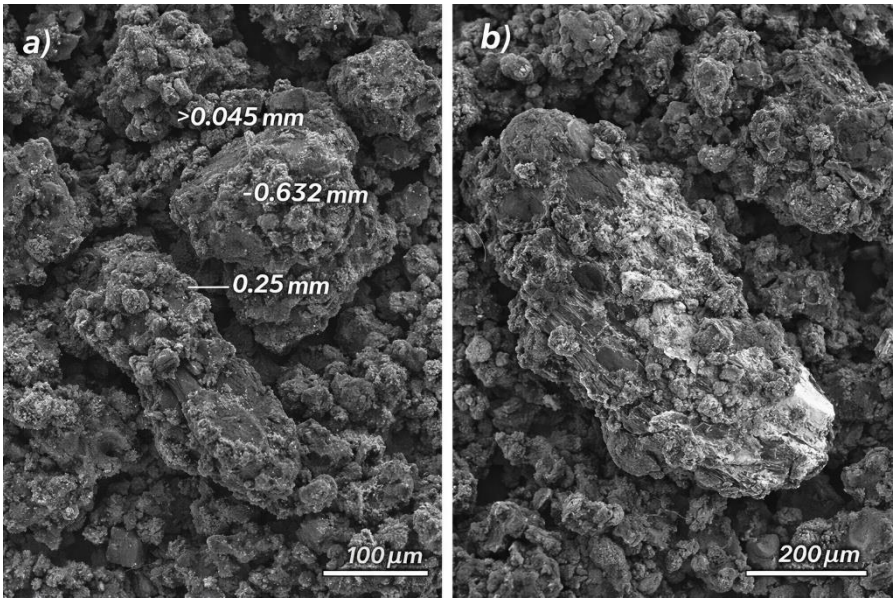


Figure 2. Microscopic general view of the carbon-containing material after pyrolysis.

Prior to use, the technical carbon was ground using a laboratory jaw crusher (model BB 600). Analysis of the results (Fig. 2) shows that the particles of the carbon-containing material vary in size. Among the particles, those larger than 0.045 mm and smaller than 0.25 mm ($0.045 < d < 0.25$ mm), with an average size of approximately 0.062 mm, account for 62.0% of the total particle content. Particles in the size range from 0.062 mm to 0.5 mm (approximately 0.25 mm fraction) represent 23.0 wt%. Additionally, particles with a size of 0.5 mm constitute about 10.0 wt%. The use of carbon-containing material containing finely dispersed metallic inclusions as a filler in rubber products negatively affects the quality of rubber goods. To remove these metallic inclusions, magnetic separation is applied.

After grinding, the carbon-containing material becomes a dispersed powder of dark black color. The ground carbon-containing material can be recommended as a filler for polymers and polymer-based materials. Carbon black is mainly used as a structural filler for polyethylene, polypropylene, polyvinyl chloride, and other polyolefins. The incorporation of carbon black enhances the durability of polymer materials and improves their resistance to photo-oxidative aging. The physicochemical characteristics of the carbon-containing material before grinding (CM-1) and after grinding (CM-2) are presented in Table 1.

Table 1. Physicochemical characteristics of the carbon-containing material before grinding (CM-1) and after grinding (CM-2).

Properties	**Rn, g/sm^3**	**pH**	**A^d, %**	**W^a, %**
CM-1	0,324 ± 0,02	6,4	21,66 ± 0,44	0,23 ± 0,05
CM-2	0,407 ± 0,02	6,4-5,5	23,71 ± 0,44	0,40 ± 0,05

The analysis of the results indicates that reducing the particle size of the carbon-containing material leads to an increase in bulk density, acidity, and moisture content, while having practically no effect on ash content. SEM micrographs (Fig. 2a, b) reveal that the carbon-containing material has a heterogeneous structure characterized by irregularly shaped particles with a rough and porous surface morphology. The particles exhibit varying sizes, confirming the polydispersity of the material after grinding. In several regions, bright contrast areas are observed, corresponding to metallic inclusions embedded within the carbon matrix. These inclusions are attributed to residual metallic cord components originating from worn automobile tires.

The EDS spectrum confirms that carbon is the dominant element in the material, accounting for approximately 72–73 wt.%, which is consistent with the formation of a carbon-rich pyrolysis product. Oxygen is present at about 14 wt.%, indicating partial surface oxidation during thermo-oxidative processing. Zinc (approximately 9 wt.%) is detected as one of the major inorganic components, which is typically associated with zinc oxide used in tire formulations as a vulcanization activator (Figure 3).

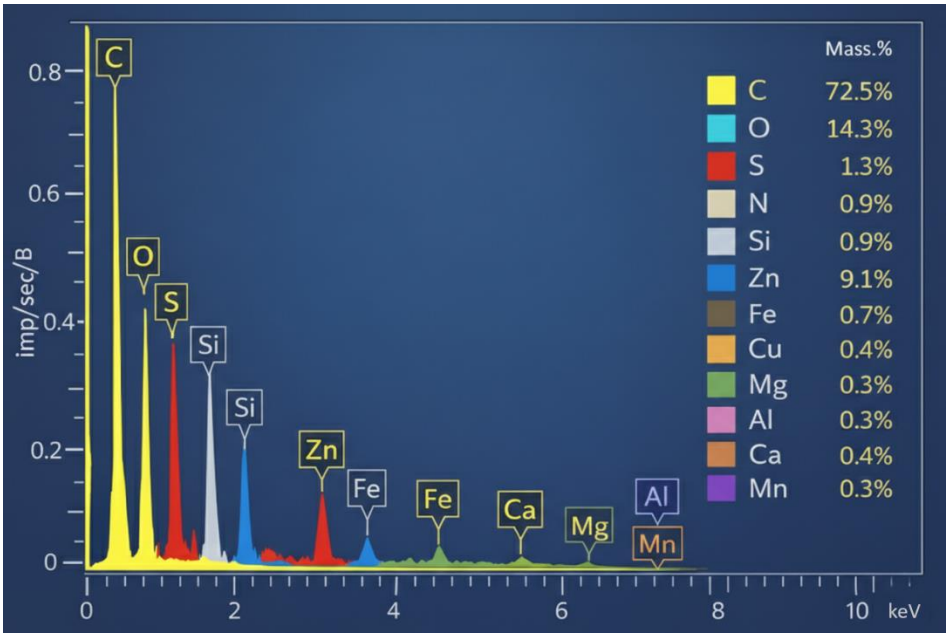


Figure 3. EDS spectrum of the carbon-containing material after pyrolysis.

Minor amounts of sulfur (1–2 wt.%) confirm the presence of vulcanization residues. Silicon, calcium, magnesium, and aluminum are detected in small concentrations, indicating the presence of mineral fillers such as silica and other inorganic additives used in tire manufacturing. Iron and copper peaks correspond to metallic cord residues and reinforcing wire fragments. Trace amounts of manganese are also detected (Table 2). The results demonstrate that the pyrolysis-derived carbon-containing material consists predominantly of amorphous carbon with dispersed inorganic and metallic phases. The presence of residual metallic inclusions justifies the application of magnetic separation prior to its use as a filler material.

Overall, the combined SEM and EDS analysis confirms that the obtained product possesses structural and compositional characteristics suitable for use as a reinforcing filler in polymeric and composite materials, provided that metallic impurities are effectively removed.

Table 2. Elemental composition of automobile tire sample determined by EDS analysis:

Element	**C**	**O**	**S**	**N**	**Si**	**Zn**	**Fe**	**Cu**	**Mg**	**Al**	**Ca**	**Mn**
Mass, %	72.5	14.3	1.3	1.9	0.9	9.1	6.1	0.7	0.4	0.3	0.3	0.3

σ	1.0	0.7	0.1	0.2	0.2	0.6	0.6	0.1	0.1	0.1	0.1	0.1

Conclusions

A comprehensive thermal, morphological, and elemental analysis confirmed that worn tires undergo a two-stage degradation process through thermal-oxidative pyrolysis, resulting in the formation of a carbon-rich solid residue. Thermogravimetric data indicate a 48.8% mass retention at 900°C, indicating the development of organic rubber matrices and the formation of thermally stable carbon structures. Scanning electron microscopy (SEM) analysis revealed a heterogeneous porous morphology with dispersed metallic inclusions, while material dispersive analysis (EDS) results established that the primary composition is amorphous (72–73 wt%), including minor amounts of inorganic components such as Zn, Fe, Si, and Ca, derived from tire components and reinforcing elements.

Reducing particle size increases bulk irradiance and surface activity without compromising the environmental impact of ash content, thereby maximizing the material's dispersibility and interaction potential. After magnetic separation to remove residual metals and inclusions, the resulting carbon-containing material can be effectively used as a functional filler for polymer-modified bitumen for road construction applications. Its rich carbon composition, developed surface structure, and adhesion to hydrocarbon chains provide mechanical strength, resistance to rutting and thermal cracking, and increased stability of asphalt concrete pavements. Thus, a method is proposed for using supports to improve the performance of modified bitumen and for sustainable recycling of waste tires for zero-waste technologies.

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