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STUDY ON THE COMPOSITION OF VULCANIZED RUBBER MIXTURES FROM WASTE TIRE

MARIA DANIELA STELESCU[1], MIHAI GEORGESCU[1*], MARIA SÖNMEZ[1],
LÓRÁNT KISS[2], DOINA CONSTANTINESCU[3]

[1]*The National Research and Development Institute for Textiles and Leather - Division: Leather and Footwear Research Institute (INCDTP-ICPI), 93 Ion Minulescu St., Bucharest, Romania; maria.stelescu@icpi.ro*

[2]*Budapest University of Technology and Economics, Faculty of Mechanical Engineering, Department of Polymer Engineering. Műegyetem rkp. 3., Budapest, Hungary*

[3]*SC MONOFIL SRL, Uzinei, 1, Savinesti, Piatra Neamt, Romania; monofil.srl@gmail.com*

As a result of the development of the automobile industry, the number of used tires has significantly increased. Since they are non-biodegradable and represent a danger to the environment, methods have been developed to capitalize on them, namely: by reusing, by recycling or recovering energy. The following materials are generally found in the tire composition: 14-30% natural rubber, 11-30% synthetic rubber, 20-30% carbon black, 12-27% steel, 0-10% textiles, 7-14% other components. From the mixture of vulcanized rubber existing in used tires, following a grinding and sieving process, rubber granules and rubber powder can be obtained. They can be used to make polymer composites for different fields. The properties of these types of materials are greatly influenced by the composition of the rubber powder, especially the filler content and the type of natural or synthetic rubber that the initial products had. The purpose of this study is to analyze the composition of the vulcanized rubber mixture from four types of used tires. The samples were analyzed by: determining the ash content and acetone extract, Burchfield test and FTIR spectroscopy. The identification of the type of rubber by the Burchfield test and FTIR spectroscopy showed that the samples contain natural rubber, or a mixture of natural rubber with butadiene-styrene rubber. The ash test and the acetone extract, together with their FTIR analysis, indicated that the crosslinking of the rubber mixtures was obtained with sulfur in the presence of vulcanization accelerators and zinc oxide. The amounts of resins, antioxidants, mineral oils, waxes or fatty acids is below 10%. The development of methods for determining the composition of rubber powder can contribute to obtaining new types of polymer composites with improved properties.

Keywords: waste tire rubber, ash, acetone extract, FTIR.

INTRODUCTION

The dynamic increase in the production of rubber products, especially those used in the automotive industry, is responsible for the large amount of vulcanized rubber waste, especially in the form of used tires. More than 17 million tons are produced globally each year. China, the European Union (EU), the US, Japan and India generate the largest amounts of used tire waste – almost 88% of the total number of used tires worldwide (Sienkiewicz *et al.*, 2012; www.jatma.or.jp). For example, in the EU, the number of used tires increased from 2.1 million tons in 1994 to 3.4 million tons in 2010, and 3.55 million tons in 2020, respectively (Table 1) (Sienkiewicz *et al.*, 2012; Sienkiewicz *et al.*, 2017; www.etrma.org).

The diversification of chemical compositions and three-dimensional structures existing in vulcanized rubber from tires (see Table 2) is the main reason why they are highly resistant to biodegradation, photochemical decomposition, chemical reagents and high temperatures. Given the increased number of used tires, they represent a serious threat both to the natural environment and to human health due to fire risks and their use as a suitable habitat for rodents, snakes and mosquitoes (Sienkiewicz *et al.*, 2012; www.jatma.or.jp; Jahirul *et al.*, 2021).

The progress made in recent years in the management of polymer waste has led to the perception of used tires as a potential source of energy or new raw materials. The development

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of studies on their more efficient recovery and recycling and the restrictive legal regulations of the European Union regarding the management of used tires, have led to solutions that favor the transformation of this substantial flow of rubber waste into new polymeric materials or alternative fossil fuels (Sienkiewicz *et al.*, 2012).

Table 1. Recovery of used tires in 2010 and 2020 (www.etrma.org, Sienkiewicz *et al.*, 2012)

Recovery Method	2010		2020	
	Romania	UE	Romania	UE
Amount of used tires collected (kT)	33	3420	54	3555
Amount of scrap tires recovered (kT)	33	2600	54	3265
• Recycled materials (kT)	1	1200	0	1920
• Civil engineering and public works (kT)	0	240	0	112
• Energy recovery (kT)	32	1160	54	1249
The quantity of unrecycled tires (kT)	0	170	0	290
Percentage of recycled tires (%)	100	95	100	92

Table 2. Component materials of tires (%) (Sienkiewicz *et al.*, 2012; Ramarad *et al.*, 2015)

Ingredient	Amount (%)	Function
Natural rubber	14-30	Structural element
Synthetic rubber	11-30	Properties improvement
Carbon black	20-30	Rubber reinforcement
Steel	12-27	Casing reinforcement
Textile	0-10	Structural element
Additives (antioxidants, curing system, etc.)	7-14	Rubber performance improvement

The legal ban on landfilling tires has been driven by increased levels of recovery and recycling. In this sense, the policies of most countries regarding the disposal of used tires are based on their selective collection and management through the following methods (www.jatma.or.jp; www.etrma.org; www.rma.org; www.wbcsd.org): reprocessing for reuse (extending the life of tires), energy recovery, pyrolysis, product recycling, material recycling (grinding and devulcanization), etc.

Currently, end-of-life tires have become the source of materials for obtaining “environmentally friendly” polymer composites with useful properties. Thus, rubber granules and powder can be obtained from used tires following a grinding and sieving process; they can be reused to obtain different types of composites with elastomeric or thermoplastic polymer matrix. The method of manufacturing polymer composites using rubber powder from recycled tires is very simple and can be done using already known technologies, machines and equipment used in the polymer industry. The implementation of these composites in industrial production does not require large investments. These composites are used to manufacture items such as: floor materials, windshield wipers, washers, strips, molds, cable housings, shoe soles, etc. (Sienkiewicz *et al.*, 2017). The properties of these types of materials are influenced by the method of obtaining the rubber powder (cryogenic or ambient temperature grinding), the size of the rubber granules, the crosslinking method of the rubber mixture, the filler content and the type of natural or synthetic rubber that the initial products had. At the same time, their properties depend on the type of polymer matrix used and, therefore, on the nature of the interactions between the matrix, the type and size of the rubber granules and the amount of rubber powder in the composite (Ramarad *et al.*, 2015; Formela, 2022; Kiss *et al.*, 2022).

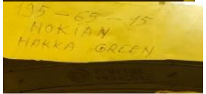
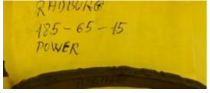
The purpose of this paper is to determine the composition of vulcanized rubber mixtures derived from four types of used tires and to compare the results obtained with the existing data in the scientific literature.

EXPERIMENTAL

Materials

During the experiments, four types of vulcanized rubber mixtures were analyzed, which were obtained from four types of used tires, according to Table 3.

Table 3. Types of used tires for which the composition of the rubber mixture is determined

Sample code	Type of used tire	Producer	Characteristics	Photo
1	Nankang Cross Season 185 -60 - 15	Nankang Rubber Tire Corporation Ltd., Taiwan	All season tires The speed index: H Load index 88	
2	Laufenn 225 – 65 – 16 C	Hankook Tire Co. Ltd., Hanover, Germany	Winter tires Speed index: R Load index: 112/110	
3	Nokian Hakka Green 195 – 65 - 15	Nokian, Finland	Summer tires Speed index: H Load index: 95	
4	Radbeug 185 – 65 – 15 Power	Radburg Center SRL, Romania	Summer tires Speed index: T Load index: 88	

Laboratory Analyses

The vulcanized rubber samples obtained from used tire waste were tested to determine the composition by: Burchfield test, determining the ash, determining the acetone extract and FTIR spectroscopy.

Burchfield test – the identification of the type of rubber present in the post-consumer tire rubber waste by a Burchfield test was carried out using Burchfield reagent 1, which consists of: 1 g of para-dimethylaminobezaldehyde, 0.01 g of hydroquinone and 100 ml of absolute methyl alcohol, to which are added 5 ml of concentrated hydrochloric acid. The color change that occurs during the test indicates the presence of a specific elastomer. The method was the following: about 1 gram of the ground rubber sample was placed in a glass test tube with fusible glass, and in another test tube, 2 ml of reactive solution type 1 was poured. The tube filled with rubber sample was heated with a flame, until the vapors that released reached the second tube with type 1 reactive solution. The color of the solution after cooling and mixing was noted. Then the solution was diluted with 5 ml of methanol and the specimen was introduced in a boiling water bath (at 100° C) for 3 minutes. The color obtained was noted, because the color change provides information about the type of elastomer (Braun, 1986; Verleye *et al.*, 2001; Burchfield, 1946).

The determination of the ash content (mineral substance content) – in accordance with ISO 247, Rubber, Determination of ash — Part 1: Combustion method. For the determination, an amount of 5-6 g of waste rubber sample was cut into parallelepipedal pieces with sides of about 2 mm and then placed in a porcelain crucible previously brought to constant weight. The crucible with material was burned with the help of a gas bulb, in the niche, until the organic material was exhausted, after which it was placed in a calcination furnace at high temperature (800°C) until reaching constant mass. Ash content was calculated using relation (1) (Test Methods of Rubber Materials and Products, Matador Rubber S.R.O., 2007):

$$ash\ content(\%) = \frac{m_i}{m_f} x100 \qquad (1)$$

in which: m_i is the mass of the material weighed initially and m_f is the mass of the residue after calcination, in g.

The determination of the acetone extract – according to ISO 1407, Rubber, Determination of solvent extract, Method B. The method is based on the property that resins have to dissolve in certain organic solvents. An amount of 5-6 g of sample cut into small pieces (about 2 mm) was weighed and a medium porosity filter paper cartridge was formed. The sample cartridge was inserted into the Soxhlet apparatus (mounted on a water bath) and attached to the extraction flask previously brought to constant weight (by heating to 105°C). The required amount of acetone was added and extracted until the liquid was observed in the level tube (18 hours). After extraction, the cartridge was removed, the acetone was removed by distillation, and the flask was dried and brought to a constant mass (in an oven at 105°C for 3 hours). The acetone extract content was calculated from the relation (2):

$$acetonic\ extract(\%) = \frac{m_1 - m_2}{m} x100 \tag{2}$$

in which: m_1 is the mass of the flask with residue, m_2 is the mass of the empty flask, and m is the mass of the rubber waste test sample, in g.

Fourier Transform Infrared Spectroscopy (FTIR) spectra of samples was obtained using Nicolet iS50 FT-IR spectrophotometer in the wave number ranging from 400 cm^{-1} to 4000 cm^{-1}. To analyze the type of rubber in the samples, the samples were tested as such (coded 1T-4T) as well as by analyzing the uncured elastomer that dissolved after immersing the samples in toluene for 72 hours. Before testing, the toluene was evaporated by keeping the samples at room temperature for 3 days, then placing them in an oven at 80°C for 8 hours. These samples were coded 1N-4N.

RESULTS AND DISCUSSION

Results of the Analyses Carried out in Order to Identify the Types of Elastomers

According to the scientific literature, car tires generally contain natural rubber, or a mixture of natural rubber with other types of elastomers (Ramarad *et al*., 2015; Formela, 2022). The identification of the types of elastomers present in the analyzed tire waste was achieved both by a Burchfield color test and by FTIR spectroscopy.

The results obtained from the Burchfield test (Fig. 1) indicate that all types of analyzed waste contain natural rubber, because the color initially obtained was brown (Fig. 1b). After adding 5 ml of methanol and keeping the samples in a boiling water bath for 3 minutes (Fig. 1c), samples 1-2 had a dark blue violet color, the other samples had a dark green color. According to scientific literature (Verleye *et al*., 2001; Burchfield, 1946) samples 3 and 4 contain a mixture of natural rubber (NR) and styrene-butadiene rubber (SBR), and samples 1 and 2 contain natural rubber.

In order to verify the results obtained with the elastomer identification by the Burchfield test, FTIR analyses of the samples were performed (Fig. 2), as well as the analysis of the unvulcanized elastomers, which were extracted in toluene (Fig. 3). Analyzing the obtained FTIR spectra, in all the samples the existence of the bands corresponding to natural rubber is observed, namely: the specific bands from 810-814 cm^{-1} corresponding to the C-H deformation vibration from the chemical group cis -C=C-, those from 1370-1376 cm^{-1} and 1427-1498 cm^{-1} corresponding to the deformation of the C-H bond from $-CH_3$ and $-CH_2$, or those from 1600-1665 cm^{-1} due to the stretching of the C-C bond from -C=C-, as well as the bands from 2910-2921 cm^{-1} and 2847-2852 cm^{-1} specific C-H symmetrical or asymmetrical from $-CH_2-$ or $-CH_3$. For samples 3 and 4 the band at 1012 cm^{-1} specific to C-H (trans) from the -(CH=CH)- groups of the butadiene chains of SBR can be observed in Fig 2., and in Fig. 3 the band at 699-700 cm^{-1} can be seen, specific to C-H deformation in monosubstituted benzene, specific to polystyrene chains in SBR. Other absorption bands that can be observed are those from 450-550 cm^{-1} and the bands from 600-700 cm^{-1} specific to C-S from sulfur vulcanization. The bands from 952 cm^{-1} appear due to the deformation of the C-H bond from trans -C=C-, while the bands from 720-722 cm^{-1} and 740-746 cm^{-1} may be due to the C-H bond from $-CH_2$. For samples 3-4 bands of low intensity can be observed in the range 2000 -1660 cm^{-1} specific to the C-H deformation corresponding to SBR polystyrene chains (Roy & De, 1992; Manaila *et al*., 2022).

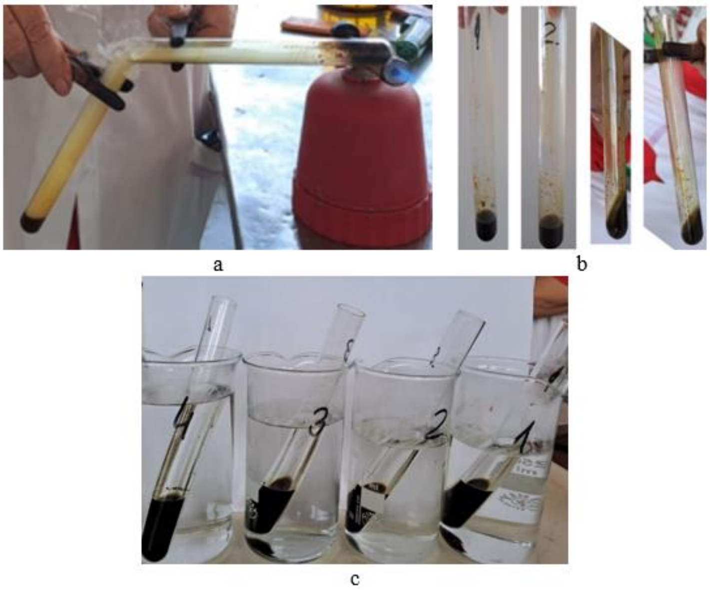


Figure 1. Images during the identification of the type of rubber from waste tires by the Burchfield test: (a) the two test tubes, with the rubber sample and the respective reagent type 1, (b) the colors obtained initially, (c) the colors obtained after the addition of methanol and immersion in a hot water bath

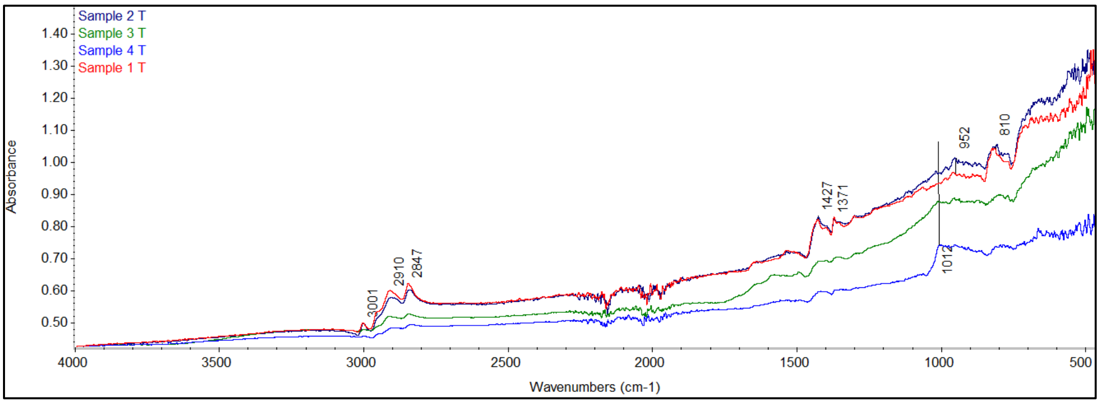


Figure 2. FTIR spectra of vulcanized rubber samples from used tires (coded 1T-4T)

Ash Analysis

The amount of ash obtained from tire waste provides information regarding the amounts of inorganic compounds in the powder such as metal oxides, inorganic dyes or inorganic fillers. According to the results presented in Table 4, it can be observed that for all four samples small amounts of ash were obtained, of 2.26-3.74% (Fig. 4a). FTIR spectroscopy was performed to identify the ingredients present in the ash (Fig. 5).

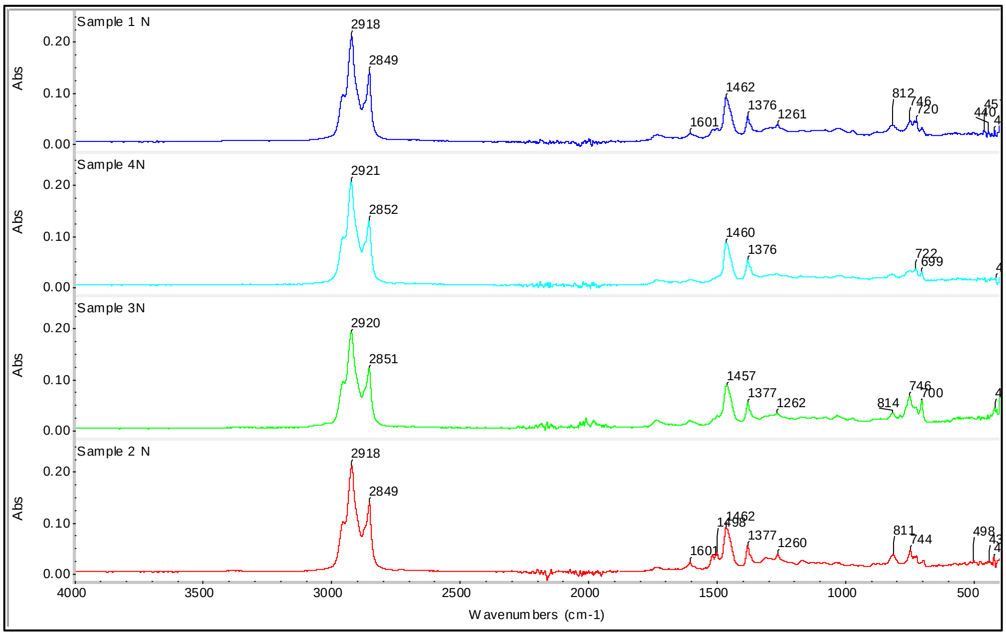


Figure 3. FTIR spectroscopy of the unvulcanized elastomer extracted in toluene (immersion 72 hours) – coded 1N-4N


(a) ash (b) acetonic extract

Figure 4. Images of the ash samples (a) and the respective acetone extract (b) after analyses

Table 4. Results of ash and the acetone extract determination from the analyzed samples

Sample code	Type of used tire	Ash, %	Acetone extract, %
1	Nankang Cross Season 185 -60 -15	3.74	5.73
2	Laufenn 225 – 65 – 6 C	2.88	8.27
3	Nokian Nakka Green 195 – 65 -15	2.26	5.02
4	Radbeug 185 – 65 – 15 Power	3.64	9.88

The FTIR spectrum of the ash obtained from the analyzed samples (Fig. 5) can indicate the presence of precipitated silica through the band at 1101 cm^{-1} specific to Si-O, the bands from 869-978 cm^{-1} specific to Si-OH, or the bands from 475 -673 cm^{-1} due to Si-O-Si bonds, but it can also indicate the existence of ZnO and sulfur bridges (bands from 550-450 cm^{-1}) (Eissa *et al.*, 2022; Katumba *et al.*, 2008).

Acetone Extract

The amounts of resins, free sulfur, antioxidants, mineral oils, waxes, organic accelerators, fatty acids can be identified through the acetone extract. The amount of acetone extract in the samples was 5.02-9.88% (Table 4). From the FTIR spectra of the acetone extracts shown in

Fig. 6, it can be concluded that the samples may contain several types of ingredients (such as organic acids, aldehydes, ketones, esters, mineral oils and waxes, etc.), and the composition of the acetone extracts obtained is similar for the analyzed samples (Coates, 2000).

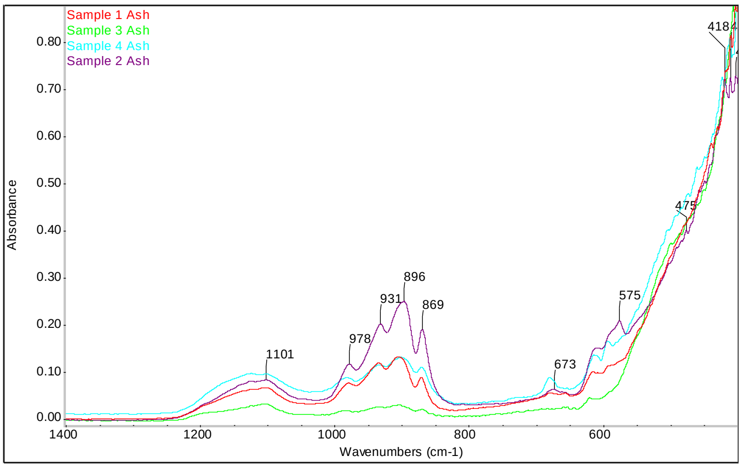


Figure 5. FTIR spectroscopy of ash, coded 1-4 Ash

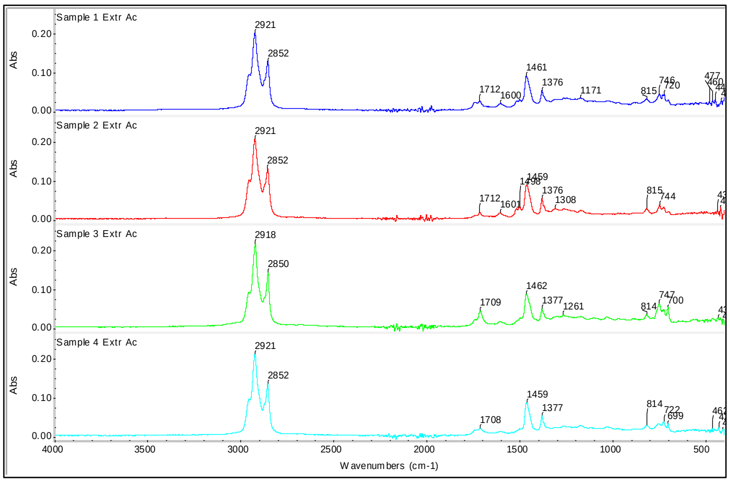


Figure 6. FTIR analyses of acetone extracts for the analyzed samples, coded 1-4 Extr Ac

CONCLUSIONS

Four vulcanized rubber samples from four different types of used tires were analyzed. From the Burchfield test and FTIR Spectroscopy, it was concluded that samples 1 and 2 contain natural rubber, and samples 3 and 4 contain a mixture of natural rubber and butadiene-styrene rubber. The amount of ash obtained after the analyses is in the range of 2.26-3.74% and according to the FTIR spectra, it can be composed of zinc oxide, sulfur and precipitated silica. These compounds can come from vulcanization with sulfur and accelerators in the presence of activators. According to the results obtained with the acetone extract, it was observed to be 5.02-9.88%, being composed of resins, antioxidants, waxes, organic accelerators or fatty acids. The experimental data obtained are in accordance with those existing in the specialized literature (Ramarad *et al.*, 2015; Formela, 2022).

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