Research Article

Determination of the distribution of different filling materials in SBR matrix compounds by image processing

Saban Bulbul [a],* (iD) and Hasan Serdar [a] (iD)

aNecmettin Erbakan University, Faculty of Seydişehir Ahmet Cengiz Engineering Faculty, Konya, 42370, Turkey

ARTICLE INFO	ABSTRACT
	In this study, the distribution of walnut shell ash and cone ash, which were used in different proportions as the filling materials of SBR rubber compounds, in the matrix were investigated by the developed image processing program. Styrene-Butadiene Rubber (SBR 1502) was employed as the main matrix material. Adhering to the same compound in the experiments, in addition to the carbon black in the compound, 5 different and 10% by mass of Walnut Shell Ash (WSA) was added to the dough, and the Cone Ash (CA) by 5% and 10% by mass, creating a total of 5 different compounds. SEM images of the rupture surfaces were taken and transferred to the developed image processing program, in which the areas covered by walnut shell ash and cone ash in the images were determined. The number of designated surface areas and the area it covers on the image were removed.

1. Introduction

Rubber materials are used in many industrial areas such as automobile wheels, windshield wipers, toys, water pipes and seals and especially shoe soles. That's why; Many scientific articles and studies on rubbers, fillers, and mechanical properties have been made [1-5].

With the increase in the use of synthetic rubbers, it also brought forward some features sought in elastomer materials. These are lightness, flexibility, dimensional stability, tensile strength, dielectric properties and wear resistance. Also, aging properties are desired. It is a known fact that synthetic rubbers have an aging feature in a long time compared to natural rubber. It is necessary to investigate the use of SBR rubber on the shoe outsole. To have the properties expected from the product to be obtained from SBR and other rubber compounds, a large number of fillers and additives are added to the compound pulps [6]. Moreover, carbon black and silicate groups are the leading materials added to the rubber paste. However, due to the unstable oil prices, it has been given importance to use organic and inorganic materials as fillers [7,8]. It is remarkable that different fillers such a

glass sphere, rice husk, wollastonite, mica powder, gum, carbon black, phosphate, nano clay, silica, calcite, blast furnace flue powder, regenerated rubber, wood ash, and nano calcium carbonate, etc. are added to the rubber compounds [9–15]. Environmental awareness is one of the primary reasons that scientists use different materials that cannot be recycled as fillers. Also, there are many studies to improve the mechanical and physical properties of the compounds and to decrease the cost.

In our previous study [16], a certain proportion of carburized hazelnut shells were added to a Nitrile-Butadiene Rubber (NBR) matrix rubber paste, and as a result, made a study to determine the effect of crosslink density on the mechanical properties. Although it causes an increase in the stiffness of the compounds with increasing crosslink density, it is advantageous in rupture strength and rupture elongation. It was also sorted out that increased nutshell ash increased density [16]. In another study, the recovery of the mechanochemical properties of Ethylene Propylene Diene (EPDM) rubber, which is a waste, was carried out as a recovery material under a specific working condition using Disulfide Oil (DSO), which is an oily waste produced in gas refineries.

20-80% of waste rubber was incorporated into the raw rubber. Crosslink densities sol-gel and Mooney Viscosity methods were used in the produced compounds. In the compounds up to 60% by mass, no adverse effects were observed on combustion and optimum hardening time [17].

It is known that the distribution of filling materials added to the rubber matrix significantly affects the mechanical and physical properties. It is not possible to determine the fill distributions by looking only at the SEM images. For this reason, it has become important to analyze SEM images using image processing methods. Image analysis is an approach used to obtain meaningful information from images by putting algorithms on image data or performing a series of calculations in images [18]. Image processing work generally consists of data collection, data processing and interpretation of data [19]. In recent years, the use of image analysis has become one of the very powerful analytical techniques in evaluating material images, as in every field. This is done by using pictures taken through a camera and by applying a standard procedure to evaluate the data obtained from pictures [20].

This study aims to identify the volumes occupied by the fillings in the matrix material due to the recovery on the rupture surfaces with the help of image processing on SEM images and to design a standard operating procedure that will provide comparable results in future studies. In the study carried out, SEM images were analyzed with the help of the developed image processing software. The Otsu method was used to divide images in this study into correct sections [21].

2. Material and Method

SBR, filling and additive materials used in the study were supplied by all LBS Composition and Laboratory Technologies LTD of Turkey. The properties and trade names of rubber and fillers used in the study are given in Table 1. Pine cones were collected from pine trees in the central district of Manisa in Turkey. The walnut shells were collected from the walnut tree in Inegol of Bursa in Turkey. 5 different compounds were obtained by adding walnut shells and cones of 5% and 10% to the compounds used in experimental studies. These are expressed as O (Original), WSA5, WSA10, CA5, CA10. Filling and additive ratios added to the compounds shown in Table 2 are given by mass ratios.

The dough compounds preferred in the experiment were homogenously mixed for 5 minutes at 80 ºC and 60 rpm in a laboratory-type Banbury. The mixed dough was conditioned for 24 hours under room conditions. Then, in addition to carbon black, in the SBR rubber two-cylinder open mixer (Guncanlar brand), 0 %, 5 %, 10 % walnut shell ash and cone ash were added to the compounds and mixing was continued for another 5 minutes. Finally, sulfur, process facilitators, anti-aging, vulcanizers were added and mixing was continued for another 2 minutes. In total, mixing was carried out for 12 minutes at 60 ºC and 40 rpm and the process was completed. After the mixing process, the vulcanization process was completed by holding the dough mixture under the pressure of 160 ºC and 16 MPa for 6 minutes in 180x120x3 mm hot press molds.

Table 1 Technical properties of filling materials used in the study

Filling	Trade Names	Density (g/cm^3)	Grain size (µm)
Styrene-Butadiene Rubber	SBR 1502	0.4	-
Carbon Black	HAF N330	1.8	0.028
Silica	Egesil BS 20 A	2	20
Walnut Shell Ash	-	2.2	20
Cone Ash	-	2.1	10

Table 2. Mass ratios of fillers and additives used in the compound

Filling and Additives	O	WSA5	WSA10	CA5	CA10
SBR 1502	100	100	100	100	100
Carbon Black	70	70	70	70	70
Walnut Shell Ash	0	5	10	0	0
Cone Ash	0	0	0	5	10
Zinc Active	4	4	4	4	4
Sulfur	1.5	1.5	1.5	1.5	1.5
DPG	1	1	1	1	1
DM	1	1	1	1	1
CZ	1	1	1	1	1
Stearic acid	2	2	2	2	2
PEG 4000	2	2	2	2	2
MBT	5.5	5.5	5.5	5.5	5.5

All experiments and conditioning processes were carried out by the ISO norms set for rubber-based shoe sole materials. Samples were made after 24 hours at 23 ° C (± 2 ° C Temperature tolerance) and 50% relative humidity before testing.

The tensile test was carried out on the Tinius brand H25KS model pulling device at 10 mm/s pulling speed according to ISO 37 standard. After the rupture test, the morphology of the rupture surfaces of the samples was examined by using Zeiss Ultra/Plus scanning electron microscope (SEM). The rupture surfaces of the samples are coated with 5 nm thick pure gold to increase its conductivity [22]. During the examination of the microstructure images, the operating voltage of the microscope was chosen as 20 kV.

To detect the volumes occupied by the fillings in the matrix material due to the recoveries they create on the rupture surfaces, it is necessary to check the regions where the rebounds and to perform image analysis accordingly. In computerized image and image processing, point-based, statistical, spatial filtering, Fourier transform and morphological processes can be used to highlight or characterize the images [23]. In this study, the Otsu method was used for the segmentation of SEM images in image processing. The grassy algorithm divides pixels into two classes, as foreground and background, and calculates them based on a single density threshold. Thus, the variance between classes is maximized.

Otsu Algorithm:
1. Calculation of all point densities
2. Calculation of the probability of the initial weights $w_i(0)$ and their mean $\mu_i(0)$
3. Weights of all possible threshold values (t = 1,…) are updated for maximum intensity w_i and averages μ_i
4. Class variance $\sigma_b^2(t)$ is calculated
5. Desired threshold reaches maximum

Each of the recovery created by the fillers in the matrix material on the rupture surfaces was found separately on the SEM image and the volume it occupied on the image was given in percentage. In this study, SEM images were analyzed with the help of developed image processing software.

3. Evaluating Experimental Studies

SEM images of the compounds formed by adding 0, 5% and 10% cone ash and walnut shell ash to the original mixture are given in Figures 1-5.
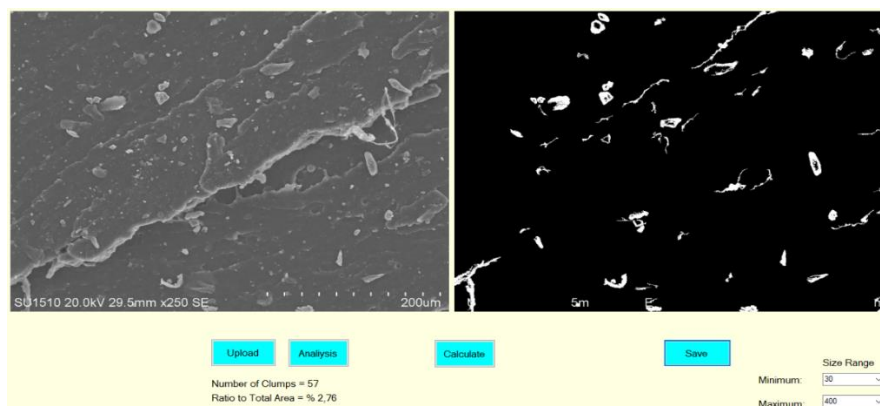

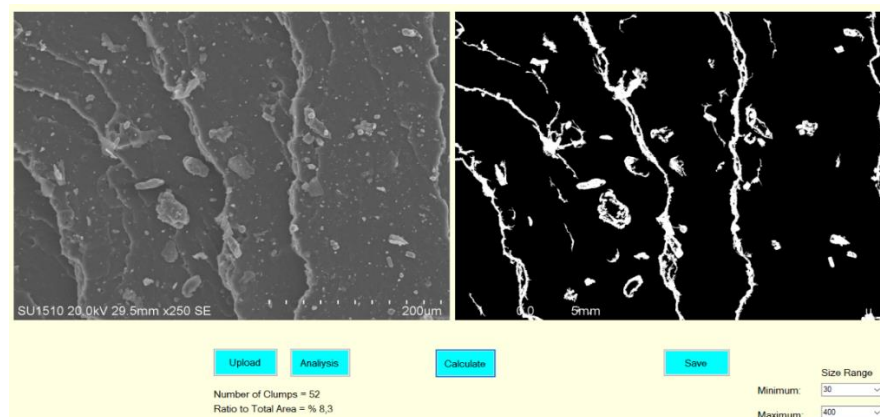Figure 1. SEM and analysis results of the rupture surface of the O compound.

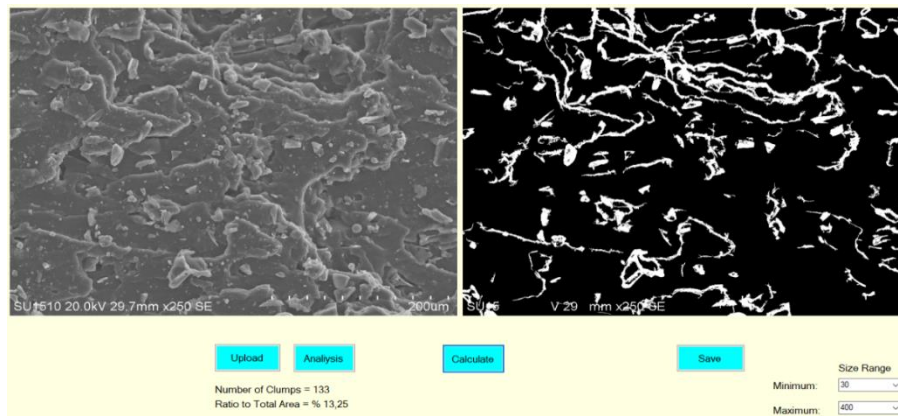Figure 2. SEM and analysis results of the rupture surface of CA5 compound

Figure 3. SEM and analysis results of the rupture surface of CA10 compound
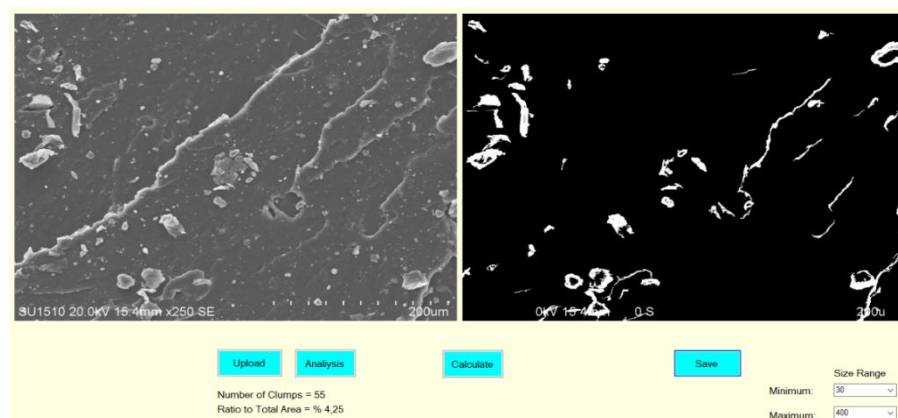

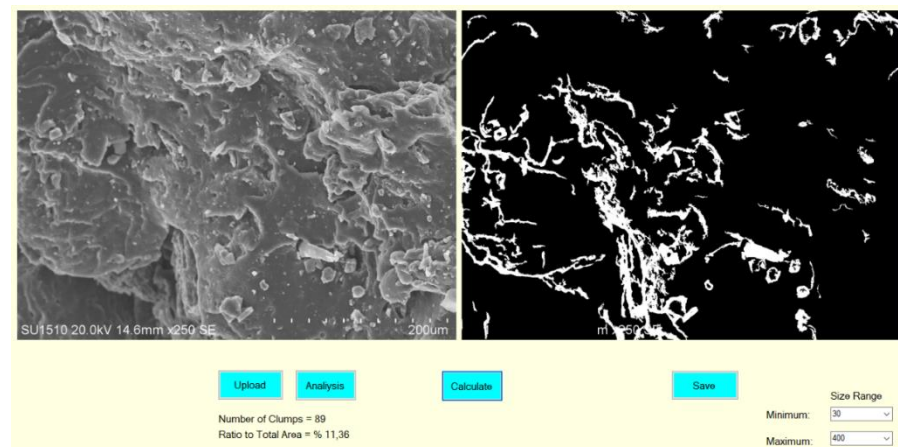Figure 4. SEM and analysis image of the rupture surface of WSA5 compound

Figure 5. SEM and analysis results of the rupture surface of WSA10 compound

When the rupture surfaces were analyzed as shown in Figures 1-5 with the help of the developed image processing software, it was observed that the fillings were detached from the material during drawing and as a result, deep gaps were formed on the sample surfaces. It is understood from the SEM images and image processing software results that the filling density increases as the ratio of cones ash and walnut shell ash added to the compounds increases. When Figures 1-5 are examined, it is seen that as the rate of addition of walnut shell ash and cone ash in the compounds increases, the fillings are distributed heterogeneously in the main matrix and grouped by agglomerating among themselves. It seems that the hollow structure has increased with the increase in the amount of CA and WSA. It was observed that the grain sizes of the fillers added to the compounds are not homogeneous and their geometric shapes are different from each other. In Figure 6, the results of the clumping number and density analysis are presented graphically with the help of the image processing software of the SEM images of the compounds.
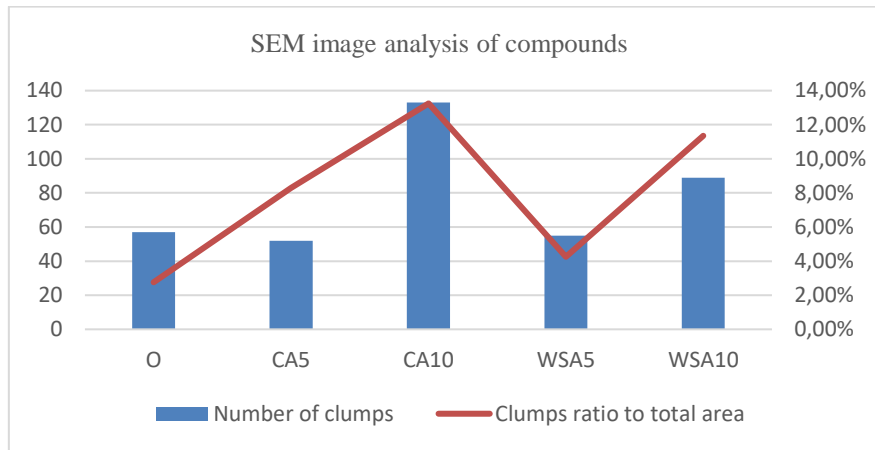
Figure 6. Clumping analysis results with the help of image processing software developed SEM images of the compounds

It has been understood from the results of image processing software developed that the increase in filling rates in the compounds increases the number and density of recovery in the compounds. The highest clumping density occurred in the compound CA10. The lump rate in CA10 compound increased by 583.7% compared to that of compound O. The lowest aggregation amount was observed in 5% walnut shell ash added compound, namely WSA5 compound (153.98%). It is understood from the graph that there is an increase in other compounds compared to the O compound. It can be understood from the results that the clumping density of SEM images also increases. Although the number of agglomeration seems to be high in unfilled material, the fact that the percentage rate in the material is low indicating that the area covered by the agglomeration is low. In similar studies, it was found that with the increasing amount of fillers, especially recycling materials used in the compounds may cause lumps in the rubber matrix [16, 24].

4. Conclusions

With the developed image processing software, in this study, the aggregation density of SEM images was determined by visually trying to predict the agglomeration density of SEM images before detecting clumps on SEM images. Thanks to this method, more accurate information has been revealed based on numerical data. It was observed that lumps increased with an increasing amount of filling added to the compounds. It was determined that the number of clumping fell. The utility of the method presented in this study has been proved in similar studies.

Declaration

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

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