Using of wood ash as the alternative filler for preparation of rubber mixtures

A Feriancová, M Pajtášová, K Moricová and B Pecušová

Department of Material Technologies and Environment, Faculty of Industrial Technologies, I. Krasku 1809/34, 020 01 Púchov, Slovakia

Email: andrea.feriancova@fpt.tnuni.sk

Abstract. Processing and material recovery of waste is an important aspect of environmental policy. Ash is waste in terms of legislation, but it is also a material that can be reused. Various works propose that biofuel ash could be used as inorganic fertilizer. The object of this work is based on using of wood ash (WA) from biomass and its modified form as the alternative filler in rubber mixtures. The WA samples with particle size of 25 and 40 µm were modified by silanization and properties of ash samples were characterized by elemental analysis (EDX), Scanning Electron Microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR). Model rubber blends were prepared by using modified wood ash as a partial replacement of conventional filler. Furthermore, the influence of the addition of ash on the cure characteristics (minimum torque – $M_L$, maximum torque – $M_H$, optimal cure time – $t_{90}$, scorch time $t_s$), mechanical properties (tensile strength at break – $T_S$, elongation at break – $E_b$, hardness) and physical properties (cross-link density) in sulfur-cured SBR composites were investigated. Dispersion of the WA filler and its incorporation into vulcanizates were based on observation of the fracture surfaces of vulcanizates by SEM. The results confirmed that the wood ash did not significantly affects the mechanical properties of the vulcanizates and can be used as a partial replacement of carbon black in SBR vulcanizates.

1. Introduction

Wood ash is a residue powder that is left after combustion of wood in heating plants and power plants. In addition to treating the ash as waste, the price of the rubber compound and thus the products can be reduced. The type of wood, combustion temperature and time are important parameters for chemical composition of ash and its quantity [1]. Some studies have shown that the major elements of wood ash are calcium, potassium, silicon, magnesium, aluminium, phosphorous, iron, sodium and zinc [2, 3]. The wood ash has been used for the agricultural application because it is good source of potash, lime and other important plant nutrients. The available chemical information on wood ash has revealed that the present minerals are the oxides of different elements (hydroxides, carbonates). During the combustion of wood, organic compounds are mineralized and cations are transformed to their oxides [4, 5]. One of the important compound in wood ash is CaO and varies from 4 % to 70 %. Therefore, it is also potentially useful in the cement industry. The ash containing less CaO and significant quantity of SiO$_2$ may be used for replacement of cement [6]. According to the Somershwar [7], wood ash may also contain some organic compounds in significant concentrations, notably polyaromatic hydrocarbons, chlorobenzenes, chlorophenols, etc. More than 80 % of wood ash is composed of particles <1.0 mm, the remainder being non-incinerated wood. Compared to the granulometric classes, wood ash can
contain all particle sizes ranging from coarse sand to clay [5]. A new possibility of WA reusing can be partial replacement of ash as a filler in rubber mixtures instead of carbon black.

In various studies, the properties of rubber compounds and vulcanizates from different types of rubber (natural rubber and synthetic rubber) were compared using fly ash (treated or untreated) as a filler and its modified forms were characterized by elemental analysis (EDX), Scanning Electron Microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR). This paper presents a comparative study of basic rubber mixtures and vulcanizates properties (required for static or dynamic rubber products) of styrene–butadiene rubber (SBR-1500, 1723) compounds filled with a non-modified or modified wood ash. Model rubber blends were prepared using WA and its modified form as a partial replacement for commonly used filler and they were analyzed subsequently. Furthermore, the influence of the addition of ash on the cure characteristics (minimum torque \(M_t\), maximum torque \(M_H\), cure time \(t_90\), scorch time \(t_s\), coefficient of vulcanization rate \(R_v\)), mechanical properties (tensile strength at break \(TS_b\), elongation at break \(E_b\) and hardness) and physical properties (cross-link density) in sulfur-cured SBR composites were investigated. Dispersion of the filler and its incorporation into vulcanizates were investigated by electron microscopy, observing the vulcanized fracture surfaces.

2. Experiment

2.1. Materials used
Wood ash (WA) was obtained from heating plant TERMONOVA, Nová Dubnica Slovak republic. APTES – (3-aminopropyl)trioethoxysilane \((\text{H}_3\text{N(CH}_3)_2\text{SiOC}_2\text{H}_3)\) was purchased from Sigma Aldrich, Ltd. Styrene–butadiene rubber (SBR-1500, 1723) was obtained from CMR Púchov Ltd., Slovak Republic. Carbon black (N121) was obtained from CS CABOT Valašské Meziříčí (CZ), Zinc oxide (ZnO), sulphur and stearic acid (SA) were purchased from local supplier (Centralchem, Ltd.). Sulfenamid CBS (N-cyclohexyl-2benzothiazole sulfenamide) was purchased from Istrochem Inc., Slovak Republic. Dusantox 6PPD N-(1,3-Dimethylbutyl)-N’-phenyl-p-phenylenediamine, DTPD (3100) – N,N’-Diphenyl-p-phenylenediamine were obtained from DUSLO Inc. Slovak Republic. Processing oil RAE was obtained from local chemical suppliers.

2.2. Modification of wood ash
The wood ash sample was sieved using 25 µm and 40 µm test sieves to obtain the samples with designation of WA25 and WA40. Silyating agent (APTES) was hydrolyzed in mixture of ethanol and distilled water (in a ratio of 9:1) for 15 minutes with occasional stirring. Two solutions of hydrolyzed APTES were prepared in this way. WA25 was added to the first hydrolyzed APTES solution and WA40 was added to the second one. These ash solutions were heated to 50 °C with continuous stirring for 4 hours. Excess silyating agent was removed by washing three times with ethanol. Prepared samples were dried in an oven for 18 hours at 60 °C and they were designated as WA25s and WA40s.

2.3. Characterization of wood ash sample
The EDX analysis was carried out by the energy dispersive fluorescence X-ray spectrometer (Shimadzu EDX-7000). Scanning electron microscopy images were taken using VEGA 3; TESCAN with BSE...
detector and field of view 40 mm with Wide Field Optics. FT-IR Nicolet iS50 Thermo Scientific spectrometer was used for attenuated total reflection infrared spectroscopy (FTIR/ATR) experiments. The results were obtained from the spectra where the number of scans was 32 and it was in the range from 4000 to 400 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\). The experiments were carried out at the workplace of the CEDITEK (Centre for diagnostics and quality of materials), Faculty of Industrial Technologies in Puchov.

2.4. Preparation of wood ash/SBR rubber composites
Styrene–butadiene rubbers (SBR-1500 in combination with SBR-1723) were used as a matrix. Composites were prepared with different amounts of non-modified (WA25, WA40) and modified (WA25s and WA40s) wood ash at 2.5, 5, 10 and 20 phr as replacement for standard filler – carbon black (N121). The model WA/SBR composites were prepared by two-step mixing in Plasti-Corder Brabender® EC plus (chamber volume of 80 cm\(^3\)), with constant speed of 50 rpm, at temperature of 140°C in step I (mixing time – 10 min) and at 90°C temperature in step II (mixing time – 5 min), as per ASTM D15-627. The basic formulation used in the study is given in table 1. The mixed model rubber compounds were homogenized in the first and second steps in laboratory double-rolled device (LaboWalz W80T; Vogt, 300 X 200) with a friction ratio of 1:1.2. The experiments were carried out at the workplace of the CEDITEK.

Table 1. Prescription for SBR composite filled with wood ash.

| Ingredients | Standard (ST) phr* | WA 25, 40 phr* | WA 25s, 40s phr* |
|-------------|-------------------|----------------|-------------------|
| SBR 1500    | 100.79            | 100.79         | 100.79            |
| SBR 1723    | 26.70             | 26.70          | 26.70             |
| ZnO         | 1.9               | 1.9            | 1.9               |
| Stearic acid| 0.9               | 0.9            | 0.9               |
| N121        | 87                | 86.5;82;77;67  | 86.5;82;77;67     |
| WA (25, 40) | -                 | 0.5;5;10;20    | -                 |
| WA (25s, 40s)| -               | -              | 0.5,5,10,20       |
| 6PPD        | 2                 | 2              | 2                 |
| DTPD        | 2.1               | 2.1            | 2.1               |
| RAE         | 19.7              | 19.7           | 19.7              |
| Sulphur     | 2.1               | 2.1            | 2.1               |
| CBS         | 1.9               | 1.9            | 1.9               |

* phr – parts per hundred rubber

2.5. Characterization of rubber composites
Cure characteristics (\(M_s\), \(M_l\), \(t_{90}\), \(t_c\), and \(R_v\)) of modified and non-modified wood ash/SBR compounds were studied using PRPA 2000 rheometer; Alpha Technologies at temperature of 150°C for 60 min. The compounds were vulcanized to their required cure time in a hydraulic press (LabEcon 600; Fontijne) at cure temperature of 150 °C and at pressure of 20 MPa. The results of the cure time are discussed later. The mechanical properties of SBR/WA composites with various proportions of WA fillers were studied and compared with those containing conventional carbon black (CB) filler. The mechanical properties (tensile strength at break – \(TS_b\), elongation at break – \(E_b\)) were determined using universal testing machine (Autograph AG-X plus 5kN; Shimadzu) at a speed of 500 mm min\(^{-1}\) as per ASTM standard D 412 87. Hardness of the samples was measured as per ASTM D 2240 86, using an indentation hardness tester (Shore A Durometer). The experiments were carried out at the workplace of the CEDITEK.

The determination of the crosslink density of the vulcanized rubber compounds was carried out with a swelling method in xylene. The experimental procedure commenced when the vulcanized rubber
samples were cut into small pieces and then weighed before they were immersed in xylene. The samples were kept in a dark place. After every 30 minutes, we removed the excess liquid on the surface of the samples by blotting them with filter paper. The weight of the swollen samples was measured. The swelling kinetics of the samples was for 48 hours. The crosslink density (ν) was calculated from equilibrium swelling data using the Flory-Rehner equation (1), as follows [11, 12]:

$$-[\ln(1 - V_r) + V_r + \chi^2 V_r^2] = 2V_s \nu \left( V_r^{1/3} - \frac{V_r}{2} \right)$$

(1)

where $V_r$ is the molar volume of solvent (xylene = 106.17 cm$^3$ mol$^{-1}$) and $\chi$ is the interaction parameter for a specific polymer-solvent pair. It should be noted that the value of $\chi$ for SBR-xylene system (0.385) was used in this calculation. $V_r$ is the volume fraction of polymer in the swollen film and it can be calculated according to the method of Ellis and Welding (2) [13]:

$$V_r = \frac{(D - FT) \rho_r^{-1}}{(D - FT) \rho_r^{-1} + A_s \rho_s^{-1}}$$

(2)

where $D$ is the deswollen weight of latex film, $F$ is the weight fraction of insoluble components (i.e., other than the rubber) in the latex film, $T$ is the initial weight of the latex film before swelling, $A_s$ is the weight of solvent in the swollen film. $\rho_r$ and $\rho_s$ are the densities of rubber and solvent (xylene = 0.86 g cm$^{-3}$), respectively.

3. Results and discussion

3.1. Characterization of wood ash samples

EDX composition analysis shows a predominance of calcium oxide and silica (table 2). Other major components are alumina, potassium oxide, sulphur trioxide, iron oxide and others. The chemical composition of wood ash depends on the composition of wood chips, whether it is soft or hard wood. Silica is an important component in rubber as filler, and alumina is commonly used as a flame retardant in rubber composites [14].

Table 2. Chemical composition of wood ash samples.

| Oxides            | WA25 (%) | WA25s (%) | WA40 (%) | WA40s (%) |
|-------------------|----------|-----------|----------|-----------|
| Calcium oxide     | 21.28    | 21.20     | 21.10    | 17.12     |
| Silica            | 12.13    | 13.79     | 14.50    | 16.38     |
| Alumina           | 3.19     | 3.53      | 3.66     | 3.38      |
| Potassium oxide   | 2.72     | 2.81      | 3.03     | 2.89      |
| Magnesium oxide   | 1.70     | 1.75      | 1.99     | 1.68      |
| Sulphur trioxide  | 1.64     | 1.79      | 1.64     | 1.54      |
| Iron oxide        | 1.29     | 1.42      | 1.44     | 1.47      |
| Phosphorus pentoxide | 0.42   | 0.56      | 0.60     | 0.56      |
| Manganese oxide   | 0.42     | 0.44      | 0.41     | 0.38      |

EDX analysis showed that the amount of silica decreased in the sample with lower particle size (WA25). However, the modified WA40s fraction showed an increase in silica. Conversely, the CaO content decreased by increasing the fraction.
FTIR spectra of WA25, WA40, WA25s and WA40s are shown in figure 1, respectively. After mutual comparison, the spectra of untreated and treated ash do not differ significantly. Approximately, from the wavelength of 1800 to 600 cm\(^{-1}\), we could observe an increasing absorbance intensity in both samples with particle size of 25 µm. The central peaks at 1407, 873 and 712 cm\(^{-1}\) were attributed to the out-of-plane bending vibration, asymmetric stretching vibration, and the in-plane bending mode for powdered CaCO\(_3\), respectively and this condition confirms that raw wood ash sample contained some Ca, K and Mg carbonates. A small peak at ~ 1092–1089 cm\(^{-1}\) were attributed to asymmetric stretching vibration of Si-O-Si. A small peak at ~ 1124 cm\(^{-1}\) can be attributed to the asymmetric stretching mode of pyrophosphate (P-O). The FTIR spectra also showed considerable weak peaks at ~ 3641–3640 cm\(^{-1}\) in all samples and it can correspond to the functional -OH group. This may be due to the presence of water in the samples of wood ash [15, 16]. The significant changes were not observed for the silanized samples in comparison with untreated wood ash samples.

![FTIR spectra of wood ash samples](image)

**Figure 1.** FTIR spectra of wood ash samples: WA25, WA40, WA25s and WA40s.

SEM images of sample WA25 at different magnifications are shown in figure 2. These SEM results indicate a mixture of particles with rough surfaces, high porosity and large surface areas in wood ash. The most of the particles represents spherical shape. Wood ash grains/particles are characterized by a complex morphology [17]. The dominant number of irregular particles is noticeable. The size of individual grains ranges from less than 10 µm to more than 25 µm (figure 2a). The finest grains occur in the form of aggregates, which are building larger particles. Grains have both angular and rounded edges [15]. The interiors of larger particles are filled with smaller ash particles (figure 2b). In ash, there are also spherical pyrospheres (finer particles are on their surface) and unburnt fragments of sharp-edged wood chips (figure 2a).

SEM images of WA25 and WA25s samples (figure 3) illustrate the porous and spongy nature of ash particles. Figures 3b and 3c show the presence of small mineral aggregates and agglomerated particles of different size, which are accumulated on the ash surface as a result of silanization [3].

![SEM images of sample WA25](image)
Figure 2. a), b) The SEM images of WA25 sample at various magnifications.

Figure 3. Wood ash particle: a) WA25, b) and c) modified WA25s.
3.2. Characterization of wood ash/SBR rubber composites

3.2.1 Cure characteristics

Figure 4 shows the effect of WA25, WA40, WA25s and WA40s doses (2.5, 5, 10 and 20 phr) on cure time (t₉₀) of the WA/SBR composites, in comparison with standard mixture (ST). Optimum cure time (t₀₀), which is the time to develop 90% of full torque or time for torque to increase to t₀₀ = 0.9 min \((M_H - M_L) + M_L\) [18, 19]. \(M_H\) is the highest torque attained during specified period of time and \(M_L\) is the minimum torque obtained during cure tests carried out in oscillating disc rheometer. The \(t₀₀\) reflects the formation of maximum crosslink density responsible for the highest possible physical and mechanical properties.

The scorch time of composites decreased not only with the dosing of filler, but also with the chemical modification of wood ash particles. Parameters \(t₁₂\) and \(t₀₀\) (figure 4) in the WA40/SBR composites increased significantly in comparison with ST and other types of composites. The increase in the cure time in mixtures WA/40 (at 2.5, 5 and 20 phr) was probably influenced by the larger particle size (40 µm) of the non-modified wood ash in rubber composites. In figure 4b we can observe, that when the content of modified wood ash (WA25s and WA40s) was changed, the \(t₀₀\) was not change noticeably – it had only fluctuating trend. It can be due to the good filler-rubber interaction in WA25, 25s and 40s composites. This can be caused by excessive metal oxides (\(\text{Al}_2\text{O}_3\), \(\text{CaO}\), \(\text{MgO}\)) present in the WA particles [9, 20], as listed in table 2. These oxides probably acted as activators and accelerated the cure process. SBR has a benzene group in the molecule, which could also cause a stearic effect in the crosslinking reaction [21]. The interesting fact is that the rubber mixtures with WA (modified and non-modified) needed the same cure time to vulcanize as standard. This result could be a practical benefit of wood ash for rubber manufacturers.

Figure 5 shows the minimum torque of the rubber compounds filled with WA fillers. Minimum torque, which is related to the composites viscosity, decreased with increasing of WA filler dosing for all WA/SBR composites. Compared with standard sample, comparable values of \(M_L\) for the silanized WA25s sample were recorded. A similar trend was observed for maximum torque in all samples, compared with the standard. The difference in the mixture torque behavior between ST and WA/SBR composites could be associated with the carbon black formation network in the standard, while WA fillers are dispersed in the rubber matrix. It can be also probably due to the incompatibility of the SBR matrix with the ash filler. As a consequence, there was the decrease in the values of \(M_H\). This decrease indicates the lower stiffness as well as the viscosity of the mixture at the end of vulcanization [22].
Figure 5. Minimum torque of WA/SBR composites.

3.2.2 Physical and mechanical characteristics

Figure 6 shows the crosslink density of the SBR vulcanizates filled with WA25, WA40, WA25s and WA 40s. For WA/SBR vulcanizates, the crosslink density was not dependent on modification of WA and on the filler amount. There was significant difference in the crosslink densities between the ST and SBR vulcanizates filled with modified wood ash. Below the concentrations of 10 phr, the crosslink density of the WAs/SBR vulcanizates increased. The WA25s and WA40s – SBR interactions via the silane coupling agent are high and effective at phr of 2.5 and 5. The higher surface areas of the WA25s and WA40s samples were caused by silanization and it probably enhanced the crosslink interactions. The surface modification in wood ash particles reduces the polarity of the filler particles [14, 23] and it is responsible for the better processability of modified wood ash/SBR composite.

Figure 6. Effect of WA content on the crosslink density ($\nu$) of WA/SBR vulcanizates.

Figure 7 shows the elongation at break of vulcanizates at various contents of WA fillers. $E_b$ increased throughout the entire range of WA dosing. The results confirmed that the elasticity of the SBR vulcanizates increased with the addition of wood ash that provides direct evidence of the enhanced polymer - filler interactions. The ash content in the SBR vulcanizates did not affect significantly the tensile strength of the samples. Further addition of WA fillers results in a slight decrease in tensile
strength due to the agglomeration of filler particles. Furthermore, a reduction in $T_S_b$ was observed mainly at WA dose of 20 phr [21, 26].

![Figure 7. Mechanical properties of WA/SBR vulcanizates: elongation at break.](image)

The use of WA as a filler ensured rubber products with better elasticity than it was for ST vulcanizate. Initially the raw wood ash has a spherical shape, with smooth surface and with low surface activity. The large interfacial area of WA seems to play an important role in the improvement of mechanical properties, since higher $T_S_b$ of the composites was obtained even at low dosing (2.5 phr), thus resulting in composites with high strength to weight ratio.

Figure 8 shows the hardness of the composites by varying the filler dosing. There was slight change in Shore A hardness values during increasing the filler dosage, excluding the composites which showed a decrease in hardness when dosing was beyond 10 phr. Hardness of vulcanizates is usually increased by the addition of reinforcing fillers. When the dosing of filler in the polymer increases, elongation at break decreases and the reduction in elongation at break is considered as the criterion for the reinforcing fillers [26]. On the basis of the above mentioned fact, we can state that wood ash acts as low-reinforcing filler for SBR composites.

![Figure 8. Hardness Shore A of WA/SBR vulcanizates.](image)
Figures 9a–9d display the SEM micrographs of the tensile-fractured surfaces of Standard and SBR composites with 20 phr dosing of WA25, WA25s, and WA40s. It can be observed that the wood ash particles at dosing of 20 phr are found to be uniformly dispersed in the polymer with a smooth surface. The WA/SBR phase interaction was more porous than that in the ST mixture (figure 9a and 9b), as indicated by some voids present between the WA particles and the rubber phase. It was seen that the wood ash come together (aggregate) to form interfaces. These interfaces appear to be regions where the tearing of the wood-ash added compounds begins. The formation of interfaces increases the plastic deformation. It is also confirmed by the mechanical test results that the interaction between the added WA and the rubber decreases as the fillers, used in the rubber matrix, form interfaces. The surface of the WA is not affected by the rubber (figure 9b) and the fractured surface shows delaminating tendency at the filler-rubber interface [9, 28]. This effect would make the rubber phase less continuous and would decrease the tensile strength of vulcanizates. Compared with ST, another reason for the lower tensile strength of WA/SBR is the greater amount of the non-rubber phase.

Modifying wood ash with silane leads to the formation of smooth particles on the surface of ash particles. The smooth and spherical structure of wood ash particles after the silanization (figures 9c and 9d) can be helpful in increasing the effective surface area for interacting with the polymer chains. However, as the particle size of ash increased to 40 µm, the tensile-fractured surface of the composite became mottled, indicating the agglomeration of greater fly ash particles (figure 9d).

Figure 9. The SEM images of vulcanizates: a) ST, b) WA25/20/SBR, c) WA25s/20/SBR and d) WA40s/20/SBR, magnified at 250×.
4. Conclusion
The potential of wood ash as a filler in SBR composites was analyzed in comparison with commercial used carbon black. Four groups of SBR-based composites were prepared using wood ash (20 µm and 40 µm) with dosing of 2.5, 5, 10 and 20 phr. The scorch time of composites decreases not only with the dosing of filler, but also with the chemical modification of wood ash particles. When the content of modified wood ash was changed, the cure time was not changed significantly, there is just fluctuating trend. One of the interesting facts is that, the rubber mixtures with WA needed the same cure time to vulcanize in comparison with standard mixture. This result would be a practical benefit of wood ash for rubber manufactures. Minimum and maximum torque, which are related to the composites viscosity, decrease with WA filler dosing for all composites. It indicates the lower stiffness as well as the viscosity of the mixture at the end of vulcanization. Below the concentrations of WA 10 phr, the increasing of crosslink was caused by silanization and it probably enhanced crosslink interactions. Addition of WA fillers results in a slight decrease in tensile strength due to the agglomeration of filler particles. There was also slight change in Shore A hardness values during increasing the filler dosage, excluding the composites which showed a decrease in hardness when dosing was beyond 10 phr. The elongation at break increased throughout the entire range of WA dosing. The use of WA as a filler led to rubber products with better elasticity than it was for ST vulcanize. On the basis of the above mentioned facts, we can state that wood ash acts as low-reinforcing filler for SBR composites. Based on the results, wood ash can be used as a partial replacement for the conventional reinforcing filler – carbon black, for example in mixtures that do not require high hardness.

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