Study of new elastomeric composite systems containing wood ash based alternative filler

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Abstract. The presented paper deals with the preparation of the new types of elastomeric composite systems containing an alternative filler based on wood ash or fly ash. Wood ash (fly ash) is generated as the waste from the process of wood pellets burning in the pellet boilers. The results of the EDX analysis confirmed that CaO and SiO₂ are the most represented components of wood ash, which contains commonly used white fillers, such as kaolin or silica. Therefore, wood ash was used as an alternative ecological filler in a function of a partial replacement for the commonly used carbon black filler in the elastomer systems. Rheological properties and cure characteristics of prepared elastomer composite systems and tensile properties of resulting vulcanizates have been studied. The prepared elastomeric systems were also subjected to a Payne effect study. The obtained results showed the degree of filler - filler interactions as well as the degree of mutual interactions between alternative filler particles and elastomeric matrix.

Keywords: wood pellets, wood ash, alternative filler, elastomeric composite, filler - filler interactions

1. Introduction
Disposal of fly ash is a serious operational constraint and an environmental health hazard [1]. Fly ash is the by-product material that is generated during the burning of coal in power plants and the components of fly ash are oxides of silicon, aluminium, iron and some others. In relation to the total fly ash composition, SiO₂, Al₂O₃, and Fe₂O₃ compounds represent around 85% of this by-product [2]. It is therefore extremely cheap to acquire it [3]. Current trends are focused on using the by-products of thermal powerplants, including fly ash (FA) [4]. Application of fly ash in the polymer is also considered beneficial in relation to the environment because it is usually disposed in landfills and thus, the introduced application can lead to the great decrease of the negative environmental impacts [3]. There is a budding concern, regarding the safety aspects of fly ash, because it is recklessly disposed in the environment [1,5]. The technological advancements in different industries stand for constant searching for a higher strength, lightweight materials to replace the conventional materials used. Particulate reinforced composites achieve the gains in stiffness primarily, but they can also achieve increase in strength and toughness [6-8]. Natural rubber, when combined with fly ash, forms a composite with good mechanical strength and properties. This composite material has the properties of an insulator and at the same time, it has the dielectric property of the fly ash carbon. Thus, fly ash can be effectively used as a filler in the rubber composites to form flexible electromagnetic wave absorbers [1, 9]. In relation to one study, the aims were to determine the properties of natural rubber compounds by varying the Oil Palm Boiler Ash (OPBA) nanoparticles with weight variations (%). The results showed that the thermal properties of natural rubber compounds increased the melting point and cross-linking with an increase in OPBA composition. Morphology showed a homogeneous mixture [10]. Other studies investigate the effect of ash on the properties of epoxy composites [11] or concrete [12,13].
Rubber materials in practices are usually vulcanized and reinforced. Both the cured gums and reinforced nanocomposites exhibit Payne effect [14]. Payne effect is applied herein to study the influence of wood ash used as an alternative ecological filler in the function of the partial replacement for the commonly used carbon black filler in the elastomer systems. The Payne effect is a typical nonlinear softening response of rubber materials undergoing large-γ oscillation. During shear at large amplitudes, storage modulus (G’) decreases with increasing γ under loading and partially recovers with decreasing γ under unloading. On the other hand, loss modulus (G’’) takes a maximum (weak strain overshoot) or decreases synchronously with G’ [15]. Payne effect has been ascribed to several mechanisms [15,16], including the agglomeration/deagglomeration of filler aggregates, breakup/reformation of filler - filler network or polymer - filler network and others [15]. The Payne effect has been the subject of numerous studies on both experimental and theoretical aspects [17, 18] but to date remains not wholly understood. The existence of two different pictures to describe it is directly related to the nanoscopic size of the filler for which it is impossible to neglect either filler–filler interaction (with or without the involvement of the matrix) or filler–matrix interaction [19].

2. Experimental

2.1. Materials

The processing and material recovery of waste is an important aspect of environmental policy and therefore, we decided to deal with the use of waste – ash from the pellets, while the given ash was provided by ECPU, s.r.o. (Ltd.) company, after the combustion of pellets in pellet boilers. We used wood or fly ash as an alternative or ecological filler in the function of the partial replacement for the commonly used carbon black filler in the polymer system. Before the application into the polymer system, the obtained ash was prepared to have a particle size < 25 µm. This preparation process was based on drying, crushing and sieving procedures. The ash sample had 15% moisture and its oxide analysis, using EDX analysis, is given in Table 1. Relating to analysis, it can be seen that CaO and SiO₂ oxides are the most represented there and this content is predominantly typical for white fillers, such as wollastonite, kaolin or silica.

| Oxides | CaO | K₂O | SiO₂ | Al₂O₃ | MnO | Fe₂O₃ | SO₃ | P₂O₅ | TiO₂ |
|--------|-----|-----|------|-------|-----|-------|-----|------|------|
| Content (%) | 47.49 | 18.11 | 12.11 | 6.75 | 6.64 | 3.47 | 3.29 | 0.85 | 0.64 |

2.2. Preparation of rubber blends

The four blends were prepared by two-step mixing in laboratory mixer of Brabender type with chamber volume of 80 cm³ and 50 revolutions per minute. The proper order of the preparation steps, in relation to additives and cure system, was performed as it is predetermined. The specification of blends is given in Table 2. The difference between the individual prepared blends was connected with the different percentage of the alternative filler – wood ash, which was prepared with a particle size < 25 µm (Table 2).

| Component Sample | Rubber (phr) | Filler (100% = 40 phr) |
|------------------|--------------|-----------------------|
|                  | Carbon Black (%) | Wood Ash (%) |
| C-100%           | 100          | -                     |
| A-5%             | SBR 1723     | 95                    | 5       |
| A-15%            | SBR 1500     | 85                    | 15      |
| A-25%            | 75           | 25                    |

Table 1. EDX analysis of alternative filler – wood ash (fly ash)

Table 2. The formulation for C-100 %, A-5 %, A-15 %, A-25 % samples
2.3. Rheological properties and cure characteristics
The processing capacity of rubber blend can be predicted, using the curing characteristics. The rheological properties and curing characteristics were carried out by PRPA at temperature of 160 °C during 30 min. Based on the evaluated rheometric results of curing curves, the values of rheometric properties and curing characteristics were expressed in terms of curing rate index (CRI), pre-curing time (t₁₂), the curing period (t₉₀), minimum torque (M₀), maximum torque (M₉₀).

2.4. Tensile and mechanical properties
Prepared vulcanizate test samples in the shape of the double-sided blades were mechanically cut out from the vulcanized slabs. Tensile properties were measured using ISHIMADZU Autograph AG-X plus machine with a head speed of 50 mm.min⁻¹. Tensile strength and elongation of each sample at loading was obtained from the average of five tested samples. Hardness was measured by Shore A and IRHD hardness tester.

2.5. Payne effect
The elastic modulus (G’) for cured and uncured sample in the strain range between 0.28% and 100% and frequency of 1 Hz was studied by using RPA. Payne Effect (filler - filler interaction) was calculated by difference between the elastic modulus at 0.42% and the 100% strain (ΔG’=G’0.42%-G’100%) in cured and uncured samples [6,9,10].

3. Results and discussion
3.1. Rheological properties and cure characteristics
Based on the evaluated rheometric results of curing curves, the values of rheometric properties and curing characteristics are shown in Table 4. The values of minimum torque (M₀) and maximum torque (M₉₀) (Figure 1) for sample with the alternative wood ash filler are lower, compared with the reference sample (C-100 %). The decrease in values indicates the lower viscosity as well as the lower stiffness of the blends at the beginning and the end of the cure. In the case of the pre-curing time (t₁₂) or safety period of the curing process (Figure 2) of samples with alternative wood ash filler, there are the same values in comparison with the reference sample value. From Table 4, it can be seen that the values of the curing period (t₉₀) (Figure 2), samples with alternative wood ash filler exhibited lower value. It can be assumed that the content of the given alternative wood ash filler in the rubber blends has a positive effect on the optimum time and it is connected with positive effect on the economic aspect in production. Moreover, the curing rate index (CRI) (Figure 3) was increased for all samples with alternative wood ash filler. The sample, which is designated as A-5 %, has the most comparable rheometric properties as well as the curing characteristics properties, compared with the reference sample (C-100 %) and assuming that the difference between torques (ΔM=M₉₀-M₀) (Figure 1) is related to crosslink density. Samples with alternative wood ash filler caused decrease in the ΔM values but A-5 % sample reaches the nearest ΔM values, compared with reference sample (C-100 %). Based on the obtained results in relation to the cure rheometer parameters, we can state that A-5 % sample is the most favourable, predicting the best possibility of interaction/distribution of this alternative wood ash filler with the elastomer matrix.

Table 3. Rheological properties and curing characteristics of C-100 %, A-5 %, A-15 %, A-25 % samples

| Sample    | M₀ (dN.m) | M₉₀ (dN.m) | ΔM = (M₉₀ - M₀) (dN.m) | t₁₂ (min.) | t₉₀ (min.) | CRI (min⁻¹) |
|-----------|-----------|------------|------------------------|------------|------------|-------------|
| C-100 %   | 2.53      | 24.27      | 21.74                  | 2.00       | 5.10       | 32.26       |
| A-5 %     | 2.40      | 21.87      | 19.47                  | 1.57       | 3.91       | 42.74       |
| A-15 %    | 2.29      | 20.59      | 18.3                   | 1.50       | 3.81       | 43.29       |
| A-25 %    | 2.13      | 20.43      | 18.3                   | 1.50       | 3.94       | 40.98       |
3.2. Payne Effect
Vulcanization of high molecular weight rubbers always produces non-ideally crosslinked molecular network with the production of dangling and free chains. The chemical crosslinking sites and topologically trapped entanglements are elastically effective while the labile entanglements contribute additionally to the equilibrium moduli of the gum vulcanizates [15]. Considering the strain, the decrease...
in the elastic modulus (\(G'\)) due to the gradual degradation of the network, which was created from the filler particles, means that the filler - filler interaction and the filler - polymer interaction is deteriorated. The Figure 4 shows the graphical ratio of elastic modulus (\(G'\)) and strain (0.42 - 100%) for all uncured and cured samples.

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Figure 4. The ratio of storage modulus (\(G'\)) and deformation for samples: C-100%, A-5%, A-15%, A-25%: a) uncured, b) cured

Taking the strain into account, the decrease in the elastic modulus (\(G'\)) due to the gradual degradation of the network, which was created from the filler particles, means that the filler - filler interaction and the filler - polymer interaction is deteriorated. The Figure 1 shows the graphical ratio of elastic modulus (\(G'\)) and strain (0.42 - 100%) for all uncured and cured samples. The A-5% sample has higher \(G'\) values before cure in comparison with the reference sample (C-100 %) and therefore, we can state that there is better filler - filler interaction in polymer blend. The other samples with higher filler replacement have decreasing tendency of \(G'\) values. In comparison with reference sample (C-100 %), the \(G'\) values of cured samples with alternative wood ash filler exhibit rapid decrease. In the other side, the A-5% sample has nearest values of the elastic modulus (\(G'\)), compared with the reference sample (C-100 %) and based on this fact, we can state that A-5% sample stands for better filler - filler interactions.

Table 4. Payne effect evaluation of C-100 %, A-5 %, A-15 %, 25- % samples

| SAMPLE  | C-100% Uncured | Cured | A-5% Uncured | Cured | A-15% Uncured | Cured | A-25% Uncured | Cured | \(\Delta G'\) (kPa) |
|---------|----------------|-------|--------------|-------|---------------|-------|---------------|-------|----------------|
| \(G'\) 0.42% | 374.94          | 1231.03 | 374.02        | 1078.56 | 293.41        | 952.91 | 271.1         | 849.8 | 269.08          |
| \(G'\) 100% | 105.86          | 615.65  | 109.93        | 545.33  | 493.74        | 493.74 | 99.67         | 483.05 | 615.38          |

Payne effect evaluation of uncured and cured samples is given in Table 5. In comparison with the other samples, the reference uncured and cured sample (C-100 %) reaches the higher \(\Delta G'\) values, excluding the A-5 % sample, which reaches the nearest values of the \(\Delta G'\) to the reference sample, meaning a better filler - filler interaction. On the other side, the smaller the filler-filler interaction, the better the dispersion of the filler particles and therefore, we can assume that samples containing alternative wood ash filler have better dispersion, compared with the reference sample (C-100%).
3.3. Tensile and Mechanical properties

It is well known that the mechanical properties of crosslinked rubber systems are enhanced by the incorporation of particulate fillers, such as CB and silica. Furthermore, such reinforcements are related to the secondary structure of filler particles (agglomerate) and the rubber-filler interactions. It is accepted that the tensile stress at a relatively large strain (>100 %) is closely related to the rubber-filler interactions [20]. The tensile properties (tensile strength, elongation) are shown in Figure 5. The A-5 % sample reaches slightly higher values of tensile strength in comparison with the reference sample (C-100%). The other sample with alternative wood ash filler exhibit the decrease of tensile strength value. The all samples with alternative wood ash filler reach higher values of elongation at break in comparison with reference sample (C-100 %). The higher elongation at break is credited to the good distribution of reinforcement within the matrix. It is credited to the high dispersion of nanoparticles [11].

![Figure 5. Tensile properties of C-100 %, A-5 %, A-15 %, 25-% samples](image)

![Figure 6. Values of Hardnes Shore A and IRHD of C-100 %, A-5 %, A-15 %, 25-% samples](image)

In comparison with the reference sample (C-100 %), the lower values of Shore and IRHD hardness are exhibited in the case of all samples with alternative wood ash filler (Figure 6), excluding A-5% sample, which has the nearest values of hardness to reference sample (C-100 %). These results may be explained in terms of decrease in crosslinking density, caused by polymer-filler interactions [20].
4. Conclusion
The results of work provide new contributive information on utilization of wood ash waste from pellets which were provided by ECPU, s.r.o. (Ltd.) company, after the given pellets had been combusted in pellet boiler. The investigated wood ash waste was investigated from the aspect of its application as an alternative or ecological filler in the function of the partial replacement for the commonly used carbon black filler in the polymer system. Based on the obtained results relating to the cure rheometer parameters or cure characteristics, we can conclude that in relation to this alternative wood ash filler, the A-5 % sample shows the most favourable values, predicting the best possibility of interaction/distribution with the elastomer matrix. All samples with alternative wood ash filler showed the better dispersion and it means the better workability. From the result of tensile properties and mechanical properties, the A-5 % sample reaches comparable values to reference sample.

5. References
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Acknowledgement
This research work was supported by the project KEGA 003TnUAD-4/2019 and project “Advancement and support of R&D for “Centre for diagnostics and quality testing of materials ,in the domains of the RIS3 SK specialization, ITMS2014: 313011W442, supported by the Operational Program Integrated Infrastructure financed through European Regional Development Fund.