**Application of biowaste in rubber blend**

S Božeková¹, Z Mičícová¹, D Ondrušová¹, M Pajtášová¹, M Božek²

¹Alexander Dubček University od Trenčín, Faculty of Industrial Technologies in Púchov, Ivana Krasku 491/30, 020 01 Púchov, Slovak Republic

²ECPU, s. r. o., Streženická cesta 1025, 020 01 Púchov, Slovak Republic

Email: slavomira.bozekova@tnuni.sk

**Abstract.** Submitted paper deals with the incorporation of biological waste into the rubber blend and moreover, it is mainly connected with the determination of the influence of this biowaste on the basic properties of the blends and vulcanizate. Wood flour, which comes from the production of wood pellets, was used as the biowaste. Biowaste was used as a filler but also as a plasticizer. The effect of the mentioned biowaste (wood flour) in rubber blend was determined from the aspect of curing characteristics and physical-mechanical properties. In addition, Payne effect was also determined. Achieved results show the possibilities of partial use of biowaste in the rubber blend and provide other research possibilities.

**Keywords:** pellets, biowaste, wood flour, fillers, rubber blend

1. **Introduction**

Elastomeric blends have undergone a major development over the past decades in relation to the development of blends for special applications as well as the new trend of blends for green tires. In the most cases of elastomeric blends, the filling (with specific filler) of the blends plays a major role. The filler often improves the processability of the blend and modifies the resulting properties of the elastomeric vulcanizate (hardness, mechanical properties, rolling resistance, etc.), while the economic aspect (reducing the cost) has to be also taken into account during processing. Fillers are commonly added into the polymer to create new functional properties which are not typical for the polymer matrix. The incorporation of the filler into the elastomeric matrix and its effect on the elastomeric blend or on the elastomeric vulcanizate depends on several factors, such as: type of filler, particle size, surface area, particle shape and filling factor of the elastomeric blend. From the industrial processing aspect, the effect of the most commonly used filler – carbon black on the vulcanizate properties represents the most explored and reviewed research area. The carbon black proportionally increases the properties of the vulcanizate with a decreasing particle size. Enhancing effect magnitude also increases with the higher carbon black content [1].

Recently, the interest in composite materials with wood flour and natural fibers reinforcement increased considerably. Such materials offer various benefits: wood flour is obtained from natural resources easily, it is commonly available, light as well as cheap and it can be added to commodity matrices in large quantities, thus offering economically advantageous solutions. The main drawbacks of such composites are connected with their water sensitivity and relatively poor dimensional stability, poor adhesion to basically all matrix polymers [2].

Wood flour (WF) composites have been found for application in various thermosets and thermoplastics manufacturing industries due to their attractive light weight properties [3].

Preliminary experiments showed the excellent wood flour ability to be mixed with all widely used rubbers: natural rubber, isoprene rubber, styrene rubber, butadiene rubber, acrylonitrile–butadiene rubber, etc. [4]. Poplar wood flour linear low-density polyethylene (LLDPE) composites were prepared
with varying amount of the mentioned wood flour. Tensile strength and tensile modulus were found to be increased up to 30% of wood flour into the polymer matrix [5].

2. Experimental

2.1. Materials
The processing and the material recovery of waste is an important aspect of the environmental policy, thus we decided to deal with the use of biowaste – wood flour (WF) which was provided by ECPU, s.r.o. (Ltd.) company. We used biowaste as a partial replacement for the commonly used carbon black filler in the polymer system and as a total replacement for a plasticizer too. The WF sample was dried due to excess moisture which was about 27%, the structure of the wood flour fraction was between 125-25 μm (Figure 1). Using EDX analysis, the elements analysis of the WF sample is given in Table 1. In Table 1, we can see the percentage of the given elements, where the largest amount is represented by carbon, as wood flour contains cellulose, then there is silicon, aluminum, calcium and other elements are only the trace elements. Thermal analysis of the WF sample was performed in the temperature range from 30 °C to 600 °C with a heating rate of 10 °C/min by using TGA/DSC 2 (Metler Toledo). The TGA result indicated some changes in the thermal degradation as well as stability of this sample (WF).

![Figure 1. Weight percentage of wood flour fraction](image)

**Table 1.** EDX analysis of wood flour (WF) sample

| Element | C   | Si  | Al  | Ca  | S   | K   | P   | Fe  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Content (%) | 99.11 | 0.35 | 0.17 | 0.17 | 0.06 | 0.05 | 0.04 | 0.01 |

2.2. Processing and sample preparation
We prepared four tread mixtures for the research (Standard - S, SW 10, SW25, W). The aim of this research was to determine the effect of biowaste as a filler in the tread mixture. Biowaste was used as a filler but also as a plasticizer (Table 2).
Table 2. The formulation for S, SW10, SW25, W samples

| Component Sample | Rubber (phr) | Filler (phr) | Plasticizer (phr) |
|------------------|-------------|-------------|------------------|
|                  | Carbon Black | Wood flour | Oil RAE | Wood flour |
| S                | 87          | -           | 19.7    | -           |
| SW10             | SBR 1723    | 77          | 10      | 19.7        | -           |
| SW25             | SBR 1500    | 62          | 25      | 19.7        | -           |
| W                | 87          | -           | -       | 19.7        |

2.3. Vulcanization characteristics
The effect of the mentioned biowaste (wood flour) in rubber blend was determined from the aspect of vulcanization characteristics, expressed in terms of curing rate index (CRI), pre-curing time (t<sub>p</sub>), the curing period (t<sub>90</sub>), minimum torque (M<sub>L</sub>), maximum torque (M<sub>H</sub>) and they were determined with RPA oscillation rheometer at a cure temperature of 160 °C.

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

2.5. Payne effect
The polymer - filler and filler - filler interaction was estimated, based on the Payne Effect. By using RPA, it was also possible to study the elastic modulus (G') in cured and uncured sample in the strain range between 0.28% and 100% and frequency of 1 Hz. In the present study, the Payne Effect (filler - filler interaction) was calculated by difference between the elastic modulus at 0.28% and the 100% strain (∆G' = G'_0.28% - G'_100%) in cured and uncured samples [6-8].

3. Result and Discussion

3.1. Thermal stability of wood flour
The thermal degradation behavior of WF is shown in Table 3. Thermal degradation curves (Figure 2) reveal the thermal degradation of WF sample and in two phases: at 30-105 °C – a small mass loss is primarily due to evaporation of volatile substance and water, as described by Jeske in his study [9] but at 225-510 °C, there is a more dramatic mass loss. For temperature range of 200 °C-350 °C, several authors [9,10] attribute mass loss primarily to degradation of hemicellulose and cellulose, while for the temperature range of 250 °C -500 °C, it can be attributed to degradation of lignin.

Table 3. Thermal degradation of WF sample

| Sample WF | the 1<sup>st</sup> step | the 2<sup>nd</sup> step |
|-----------|-------------------------|-----------------------|
| Temperature range (°C) | 30-105 | 225-510 |
| ∆m (%) | 6.83 | 86.57 |
3.2. Vulcanization characteristics
The vulcanization characteristics parameters for samples are shown in Table 4. We can observe that the presence of the filler caused increase in the pre-curing time ($T_{s2}$) or safety period of the curing process. The curing period ($t_{90}$) of samples with WF caused increase, but W sample, in which WF was used as a plasticizer, reaches the nearest $t_{90}$ values, compared with the standard sample (S). The curing rate index (CRI) was the same for all samples, but SW25 sample achieved much lower values of CRI and it could be due to large quantities of wood flour in the blend.

Table 4. Vulcanization characteristics of S, SW10, SW25, W samples

| Samples | $M_L$ (dN.m) | $M_H$ (dN.m) | $\Delta M = (M_H - M_L)$ (dN.m) | $T_{c2}$ (min.) | $T_{90}$ (min.) | CRI (min.$^{-1}$) |
|---------|--------------|--------------|---------------------------------|----------------|----------------|-----------------|
| S       | 5.42         | 26.78        | 5.42                            | 1.85           | 5.65           | 26.32           |
| SW10    | 2.63         | 17.27        | 2.63                            | 2.88           | 6.68           | 26.32           |
| SW25    | 2.50         | 16.64        | 2.50                            | 2.38           | 7.42           | 19.84           |
| W       | 2.98         | 18.1         | 2.98                            | 2.69           | 6.49           | 26.32           |

It was assumed that the difference between torques ($\Delta M = M_H - M_L$) is related to crosslink density. The $\Delta M$ values of all samples are shown in Figure 3. The samples with wood flour caused decrease in the $\Delta M$ values, but W sample, in which WF was used as a plasticizer, reaches the nearest M values in comparison with the standard sample (S). Based on the obtained results relating to the cure rheometer parameters, we can state that W sample is the most favorable, predicting the best possibility of interaction/distribution of this biowaste (WF) with the elastomer matrix.
3.3. Physical-mechanical properties

The physical-mechanical properties, such as tensile strength, elongation and hardness are shown in the Figure 4-6. The tensile properties can be interpreted by a degree of reinforcement, provided by the filler to polymer [11]. Tensile strength of samples is shown in Figure 4. It can be seen that the SW10 sample shows higher value of tensile strength in comparison with the standard sample (S). The higher amount of WF as a filler (SW25) caused rapid decrease in the tensile strength value. The W sample seems to be favorable because its value approaches the tensile strength value of standard sample (S).

In the case of elongation (Figure 5), SW10 and W sample have lower value of elongation in comparison with the standard sample (S). The improved adhesion in the presence of bonding agent restricts the mobility of polymer segments and it finally results in a reduction in elongation.
The hardness measurement may be important for assessing the product performance and it can be used in identifications, classification, and quality control of products. Hardness test provides a rapid evaluation of variation in mechanical properties, affected by changes in chemical or processing conditions, adding of compounding ingredients, heat treatment, microstructure, and ageing [12, 13]. In comparison with the standard sample (S), the lower values of hardness can be observed in the case of all samples with WF (Figure 6). These results may be explained in terms of decrease in crosslinking density, caused by polymer - filler interactions.

3.4. Payne Effect

The occurrence of a three-dimensional network formed by the filler is important since it modifies the physical properties of the elastomeric compositions, significantly affecting the dynamic viscoelastic properties of the rubber articles or products. The filler - filler interaction is a ruling factor for hysteresis rise, and it is directly related to the breaking and reconstitution of these structures of secondary aggregates in filled rubber blends when submitted to strains [14 - 16]. The strain range of samples for the elastic modulus (G’) can be seen in Figure 7. After adding the WF to blend before cure (Figure 7 a)), the elastic modulus G’ rapidly lowers at low strain and slightly lowers at high strain. This decrease is caused by the worse formation of filler - filler interactions, which are formed in blend. After cure (Figure 7 b)), the elastic modulus (G’) has a decreasing tendency for all samples with WF. On the other side, it has to be pointed out that W sample, in which WF was used as a plasticizer, reaches the nearest
values of the elastic modulus (G’) in comparison with standard sample (S) and thus, we can state that the W sample has better filler - filler interactions.

![Figure 7](image_url)

**Figure 7.** The strain range for elastic modulus (G’) – samples: S, SW10, SW25, W

a) before cure, b) after cure

| SAMPLE | S       | SW10   | SW25   | W       |
|--------|---------|--------|--------|---------|
|        | Before cure | After cure | Before cure | After cure | Before cure | After cure | Before cure | After cure |
| G’ 0.28% | 2143.69 | 3354.97 | 605.76 | 1938.99 | 570.24 | 1632.09 | 651.45 | 2053.79 |
| G’ 100%  | 153.74  | 862.45 | 93.52  | 529.63  | 85.61  | 471.63  | 99.27  | 578.80  |
| ΔG’ (kPa) | 1989.95 | 2492.52 | 512.24 | 1409.36 | 484.63 | 1160.46 | 552.18 | 1474.99 |

Table 5 shows the data for Payne Effect for cured and uncured samples calculated from the difference between moduli at 0.28% and 100% strain (ΔG’=G’0.28%-G’100%). When Payne Effect is higher the value of ΔG’ is greater, meaning the better filler-filler interaction, and consequently, the higher amount of filler agglomerates in the elastomer matrix [15]. On the other side, the smaller the filler - filler interaction, the better the filler particles dispersion is occurred [9, 13]. The standard uncured and cured sample (S) reaches the highest one of the ΔG’ values in comparison with other samples but W sample, in which WF was used as a plasticizer, reaches the nearest values of the ΔG’, compared with the standard sample (S), meaning a better filler - filler interaction. In addition, it is important to point out that the lower ΔG’ values are better for processing properties.

4. Conclusion
Based on the obtained results relating to the cure rheometer parameters, we can conclude that W sample is the most favorable, predicting the best possibility of interaction/distribution of this biowaste (WF) with the elastomer matrix. From the physical-mechanical properties, it is possible to see that the SW10 sample exhibits the higher value of tensile strength in comparison with the standard sample (S). The standard sample (S) has the higher values of elastic modulus (G’) and ΔG’ (Payne Effect) but W sample, in which WF was used as a plasticizer, reaches the nearest values of the elastic modulus (G’) and ΔG’.
in comparison with the standard sample (S). Based on the mentioned fact hereinbefore, we can state that W sample has better filler - filler interactions. Achieved results show the possibilities of partial use of biowaste in the rubber blend and provide further research possibilities, especially the application of biowaste as a plasticizer or filler but amount has to be lower.

5. References

[1] Dányádi L, János Móczó J, Pukánszky B 2010 Effect of various surface modifications of wood flour on the properties of PP/wood composites Composites Part A: App Sci and Mang 41(2) 199–206. https://doi.org/10.1016/j.compositesa.10.008.
[2] Dominkovics Z, Dányádi L, Pukánszky B 2007 Surface modification of wood flour and its effect on the properties of PP/wood composites Composites Part A: App Sci and Mang 38(8) 1893–1901 https://doi.org/10.1016/j.compositesa.2007.04.001.
[3] Phiri M J, Phiri M M, Mpito K, Hlangothi S P 2020 Curing, thermal and mechanical properties of waste tyre derived reclaimed rubber–wood flour composites Mater Today Comm 25. https://doi.org/10.1016/j.mtcomm.2020.101204.
[4] Vlakdova T G, Dineff P D, Gospodinová D N, Avramová 2006 Wood Flour: New Filler for the Rubber Processing Industry. IV. Cure Characteristics and Mechanical Properties of Natural Rubber Compounds Filled by Non-Modified or Corona Treated Wood Flour J App Polym Sci 101(1) 651–658. https://doi.org/10.1002/app.23730.
[5] Kumar V, Gulati K, Lal S, Arora S 2020 Effect of gamma irradiation on tensile and thermal properties of poplar wood flour-linear low density polyethylene composites Radiat Phys and Chem 174. https://doi.org/10.1016/j.radphyschem.2020.108922.
[6] Sarkawi S S, Dierkes W K, Noordermeer J W M 2014 Elucidation of filler-to-filler and filler-to-rubber interactions in silica-reinforced natural rubber by TEM Network Visualization Eur Polym J 54 118-127. https://doi.org/10.1016/j.eurpolymj.2014.02.015.
[7] Ramier J, Gauthier C, Chazeau L, Stelandre L and Guy L 2007 Payne effect in silica-filler styrene-butadiene rubber: influence of surface treatment J. Polym Sci Part B: Poly Phys 45(3) 286-298. https://doi.org/10.1002/polb.21033.
[8] Wileczynski O, Pospíšil P 2000 RPA 2000 – univerzální nástroj pro gumárenský průmysl. In: Plasty a kaučuk 11-12.
[9] Jeske H, Schirp A, Frauke C 2012 Development of a thermogravimetric analysis (TGA) method for quantitative analysis of wool flour and polypropylene in wood plastic composites (WPC) Thermochim Acta 543 165-171. https://doi.org/10.1016/j.tca.2012.05.016.
[10] Chen Y, Mandala A Tshabalala, Gao J, Nicole M Stark, Fan Y and Rebecca E Ibach 2014 Thermal behavior of extracted and delignified pine wood flour Thermochim Acta 591. 40-44 https://doi.org/10.1016/j.tca.2014.06.012.
[11] Sapuan S M, Ismail H, Zainudin E S 2018 Natural Fiber Reinforced Vinyl Ester and Vinyl Polymer Composites: Development, Characterization and Applications (Woodhead publishing/Elsevier) p 392.
[12] Mostafa A, Abouel-Kasem A, Bayoumi M, El-Sebae M 2010 Rubber- Filler Interactions and Its Effect in Rheological and Mechanical Properties of Filled Compounds J Test Eval 38(3) 347-359. https://doi.org/10.1520/JTE101942.
[13] Gümel S M, Adam J L, Ladan M, Habibu S 2013 Effects of Treated Wood Flour on Physico-Mechanical Properties of Filled Natural Rubber Chemsearch J 4(1) 42-46.
[14] Shi X, Sun S, Zhao A, Zhang H, Zuo M, Song Y and Zheng Q 2021 Influence of carbon black on the Payne effect of filled natural rubber composites. Comp Scie and Tech 203. https://doi.org/10.1016/j.compscitech.2020.108586.
[15] Honorato L, Marcos L Dias, Azuma Ch, Regina C Reis Nunes 2016 Rheological properties and curing features of natural rubber compositions filled with fluororomica ME 100 Polímeros 26(3) 249-253. https://doi.org/10.1590/0104-1428.2352.
[16] Fröhlich J, Niedermeier W, Luginsland H D 2005 The effect of filler/fillerand filler-elastomer interaction on rubber reinforcement Comp Part A: App Sci and Manuf 36(4) 449-460. https://doi.org/10.1016/j.compositesa.2004.10.004.
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.