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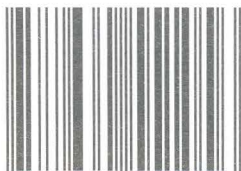
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NR/CSM/WOOD FLOUR POLYMER COMPOSITES IN RAILWAY INDUSTRY

Gordana MARKOVIĆ¹
Vojislav JOVANOVIĆ²
Milena MARINOVIC-CINCOVIĆ³
Suzana SAMARŽIJA JOVANOVIĆ⁴

Abstract – Wood flour composites can be optimized to obtain new materials for a part of the railroad infrastructure. Curing, mechanical and morphological characteristics of carbon black- and silica-filled natural rubber (NR)/chlorosulphonated (CSM)/wood flour rubber blends were studied. Results indicate that the minimum torque and maximum torque increase with increasing filler loading in the compounds, whereas scorch time shows a decreasing trend. The cure time of carbon black-filled NR/CSM/wood flour rubber blends decreases with increasing filler loading whereas silica-filled NR/CSM/ wood flour rubber blends show an opposite trend. Incorporation of filler loading has improved the tensile strength and hardness. However, elongation at break exhibit a different trend. For tensile strength and hardness optimum values were obtained at 30 phr for carbon black and 40 phr for silica, respectively. Overall results show that carbon black (N330) is more suitable to be used as a filler in natural /chlorosulphonated rubber/ wood flour compared to silica (Vulcasil S). Possible application of wood flour rubber blend composites in the manufacture of rubber metal parts for railway vehicles can be expected.

Keywords – NR/CSM rubber blends, carbon black, silica, wood flour, mechanical properties, railway infrastructure.

1. INTRODUCTION

Composite materials are a combination of two or more materials that have different properties, such that the combinations render a product which has intermediary characteristics of the components. Rubber is one of commercially used polymeric matrix mainly due to the good energy absorbing properties. It can undergo much more elastic deformations under stress than other materials and still return to its original shape without permanent deformation after the stress is released [1]. This unique property gives rubber an extensive variety of applications

The properties of polymer blend composites can be controlled by regulating blend morphology, blend compositions and processing condition. Wood flour (WF, wood finely ground to a powdery consistency) has been used as a filler in synthetic plastics, primarily thermosetting polymers (e.g., phenolics) for decades.

Natural rubber (NR) and chlorosulphonated polyethylene rubber (CSM) have been blended for a

long time [2].

The carbon black (CB) and silica (SiO₂) are two basic groups of reinforcing fillers that are able to form their own network in a polymer matrix that is consistent with the specific surface, structure and especially surface reactivity (filler-filler and polymer-filler interaction).

By creating a multi-phase system, characteristics of individual phases can be partly preserved or significantly changed due to the influence of intermolecular interactions. The wood itself is a complex, three-dimensional, polymer composite made up primarily of cellulose (45–50% by weight), hemicellulose (20–25%), and lignin (20–30%).

Therefore, the modern research and industrial practice of rubber industry leaders are directed towards the use of existing starting polymers and the new materials as a filler such as wood flour for a part of the railway infrastructure.

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2. EXPERIMENTAL

Materials: Polyisoprene rubber, NR SMR-20 was supplied by Malaysia; Chlorosulphonated polyethylene rubber (CSM), Hypalon 40S, produced by Goodrich Chemical ($q \frac{1}{4} 1.18 \text{ g/cm}^3$, $M_w \frac{1}{4} 5.52 \times 10^5$, $M_w/M_n \frac{1}{4} 1.97$), contains 35 wt% by weight of chlorine and 1–1.5% by weight of sulphur as sulphonyl chloride (SO_2Cl) units; Fillers: wood flour (WF), a 250–300 μm ponderosa pine was supplied by Kosla Metal Powder (India), $q \frac{1}{4} 2.7 \text{ g/cm}^3$ and carbon black (N-330), primary particle 60 nm, $q \frac{1}{4} 1.32 \text{ g/cm}^3$; silica (Vulcasil S), primary particle 15 nm. Very fast accelerator— tetramethylthiuram disulfide (TMTD) and low fast accelerator— N-cyclohexyl-2-benzothiazol sulphenamide (CBS). The content of fillers: wood filler was 10phr; carbon black type N-330 (primary particle size 28–36 nm) - Volgograd (Russia) and silica filler (Vulcasil S) were 10, 20, 30, 40, 50 phr.

The curing system was: N-cyclohexyl-2-benzothiazolsulfonamide - CBS (1,4 phr); diphenyl guanidine, DPG, (1 phr); N-(cyclohexylthio)phthalimide, CTP 100 (0.2 phr) and sulfur (2 phr). In all rubber, blend compounds the network precursor ratio was NR/CSM/WF 80/20/10 (w/w/w). The content of zinc oxide was 3 phr. The stearic acid content was 2 phr. Plasticator as naphthenic oil content was 10 phr.

All samples are mixed in a laboratory two roll mill Rheometer curves were carried out using an Alpha technologist Rheometer MDR 2000 according to at 160°C and are there used to determine the start of crosslinking t_{s2} , optimum of crosslinking t_{c90} , as well as the maximum and minimum torques (M_{max} and M_{min}). The crosslinking was carried out in an electrically heated hydraulic press (E-604 Metrohm Herisau) under a pressure of 20 MPa and 160°C . The scorch time (t_{s2}), optimum cure time (t_{c90}) and maximum (M_{max}) and minimum torque (M_{min}) were determined from rheometer data.

Tensile tests were performed on dumbbell samples that were cut from elastomeric sheets (2 mm thick). The tensile strength (TS) and the elongation at break (E_b), were determined at room temperature using a Zwick 1425 universal tensile testing machine. The tests were performed according to ASTM D41298a. The given results are the mean value of three specimens. The error in these measurements was $\pm 0.5\%$. Samples with flat surface were cut for hardness test. The measurement was done using Durometer Model 306L Type A.

3. RESULTS AND DISCUSSION

3.1 Cure characteristics

Silica achieves a more pronounced filler-filler

interaction, that is, a larger network of fillers in the polymer matrix, while the carbon black produce a stronger polymer-filler interaction

The cure characteristics as a function of the CB and silica loading (10, 20, 30, 40, and 50 phr) of the NR/CSM/WF (80/20/10) rubber blends are show in Figure 1.

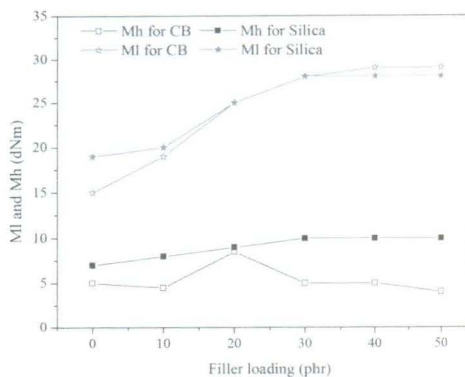


Fig.1. The effect of CB and silica loading on M_h and M_i in NR/CSM/WF rubber blend.

The variation of torque during crosslinking of rubber compounds at 160°C given in Fig. 1 shows that the maximum torque increases gradually as loading of carbon black and silica in NR/CSM/WF (80/20/10) rubber blend increases. The increase in maximum torque is attributed to the better polymer-filler interaction that becomes more pronounced in 30 phr filler loading. It is reported that maximum torque depends on the crosslink density and chain entanglements. The minimum torque, a measure of the stock viscosity, shows a slight increase with increasing filler loading. This indicates that the processability of the compounds becomes a little more difficult.

The increase could be due to the agglomeration of carbon black or silica particles in the NR/CSM/WF rubber matrix. The other possibility is that filler is already crosslinked, and do not easily flow in the matrix, so an increase in filler loading will reduce the flow and consequently increase the torque.

WF is non-reinforcing filler and has a particle size bigger than carbon black and silica. The other possibility is that WF in NR/CSM present are already crosslinked, and do not easily flow in the matrix, so an increase in carbon black or silica loading will reduce the flow and consequently increase the torque.

WF presence in NR/CSM rubber blend also influenced to the optimum curing time (t_{c90}) values, as shown in Fig. 2. The cure time values are reduced with carbon black increase but increase with silica increase, substantially. Similar trends were also observed by many authors [3] using different types

and sizes of WF particles. The composite based on NR/CSM/WF rubber blends are decreased with CB content increase, i.e. crosslinking process became faster. Lower values of the scorch time indicate that a "period dissolving" of the compound reduces, i.e. crosslinking process starts sooner.

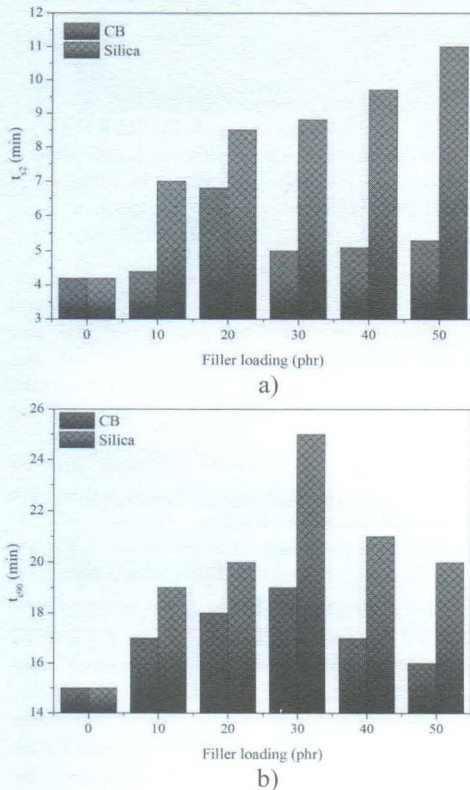


Fig.2. The effect of CB (a) and silica (b) loading on t_{s2} and t_{c09} in NR/CSM/WF rubber blend

3.2. Mechanical Properties

WF is low-cost natural material and the most widely used. A disadvantage of using WF as extender and reinforcement for rubber is that the resulting composites usually have reduced mechanical properties. This is a result of poor adhesion between the hydrophilic filler material and the hydrophobic polymer matrix.

The relationships between carbon black and silica with NR/CSM/WF rubber blend and values of the mechanical properties of NR/CSM rubber blend are shown in Figs. 3–6.

Figure 3 shows the effect of CB and silica loading on the tensile strength of NR/CSM/WF rubber blend. Tensile strength required to break the composite, depends on the rubber macromolecule structure, i.e. on the rubber blend, and to the greatest extent on the

filler activity, filler dispersion degree in the elastomeric matrix, and filler-elastomer interaction degree. The maximum value for NR/CSM/WF rubber blend composites reinforced with carbon black is obtained at 30 phr, and with silica filler at 40 phr. Higher values have carbon black reinforced rubber blend composites, according to agglomerates are dispersed to aggregates, where a big contribution to the breaking strength is given by formation of permeating crosslinks polymer-polymer, polymer-filler, and filler-filler. Enhanced tensile strength and reduced elongation are considered as the criteria for better interfacial adhesion. These two properties are also related to the nature and number of crosslinks.

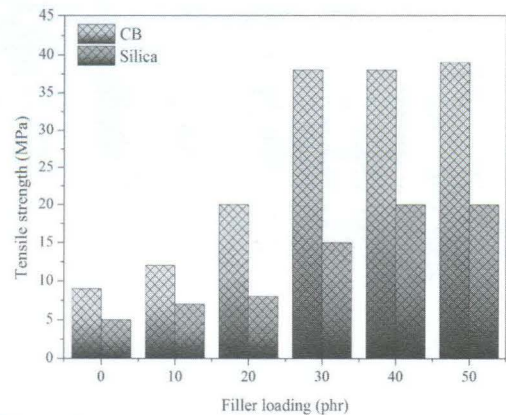


Fig.3. The effect of CB and silica loading on the tensile strength of NR/CSM/WF rubber blend

It is obvious from Fig. 4 that the hardness of NR/CSM/WF rubber blend reinforcing by carbon black shows higher values than those reinforced by silica. The extent of the hardness of the vulcanizate generally depends upon its degree of crosslinking. When the crosslink density increases hardness also increases.

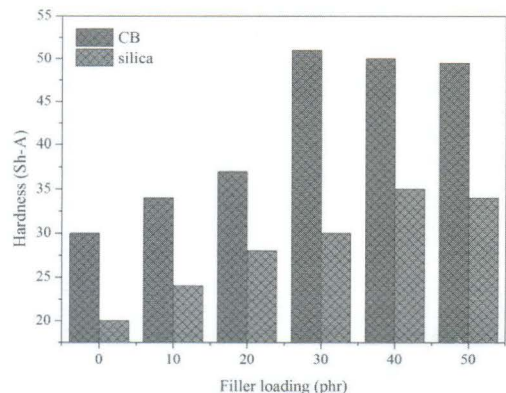


Fig.4. The effect of CB and silica loading on the hardness of NR/CSM/WF rubber blend

Increasing the filler loading in NR/CSM/WF rubber blend reduces the elongation at break of (Fig. 5). By the carbon black ratio increase to 30 phr, and silica ratio increase to 40phr, the filler-polymer interaction increases, elastomeric components ratio in the total quantity of the crosslinked material is reduced, and the rubber chains elasticity is reduced around 60%.

The optimal charging for rubber composites is assumed that all agglomerates fillers are dispersed to the aggregate.

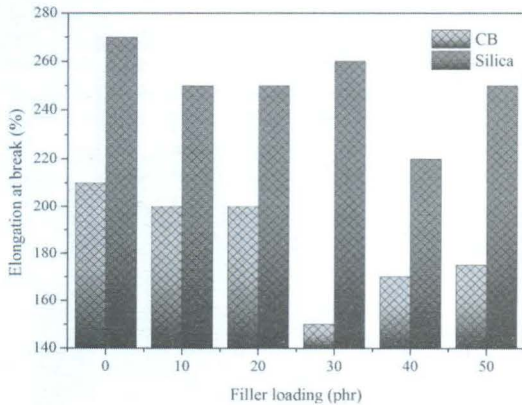


Fig.5. The effect of CB and silica loading on elongation at break of NR/CSM/WF rubber blend

Consequently, the crosslinking density increases when the filler loading is higher what results in a substantial increase in the modulus.

3.3 Morphological study

Figure 6 shows the scanning electron micrograph (SEM) of the tensile fracture surface of NR/CSM/WF (80/20/10) rubber blends with 30 phr of carbon black filler at 2000 magnifications, respectively. Less tearing lines can be observed on fracture surfaces in Figure 6, which indicated that the blend cannot withstand high stress and breaks easily and good adhesion between carbon black and NR/CSM/WF matrix can be observed.

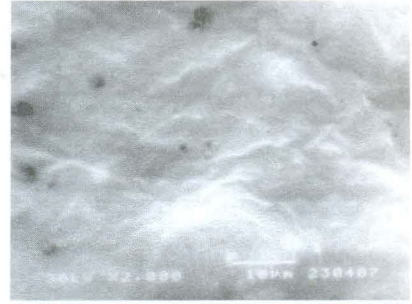


Fig.6. The SEM micrograph of NR/CSM/WF/CB (80/20/10/30) rubber blend at 2000 magnification

4. CONCLUSION

Some conclusions can be drawn as follows:

1. By monitoring crosslinking regime in systems obtained from NR/CSM/WF rubber blend composites, it was found that when CB and silica content increase, the values of the minimum (M_{min}) and maximum (M_{max}) torque, scorch time (t_{s2}) and optimum cure time (t_{90}) are an increase.
2. The hardness and tensile strength are an increase, but elongation at break values are decreasing with filler loading.
3. Morphological study noticed good adhesion between carbon black and NR/CSM/WF matrix.

Possible application of wood flour rubber blend composites in the manufacture of rubber metal parts for railway vehicles can be expected.

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