

GORDANA MARKOVIĆ¹
MILENA
MARINOVIĆ-CINCOVIĆ²
BLAGA RADOVANOVIĆ³
JAROSLAVA
BUDINSKI-SIMENDIĆ⁴

¹Tigar, Pirot
²Institute of Nuclear Science
"Vinča", Belgrade
³Faculty of Science, Niš
⁴Faculty of Technology,
Novi Sad, Serbia

SCIENTIFIC PAPER

678-116:53

RHEOLOGICAL AND MECHANICAL PROPERTIES OF WOOD FLOUR FILLED POLYISOPRENE /CHLOROSULPHONATED POLYETHYLENE RUBBER BLENDS

The effect of wood flour (WF) on curing behaviour and swelling properties of polyisoprene rubber/chlorosulphonated polyethylene (NR/CSM) rubber blends was investigated. The mechanical properties, as well as the equilibrium swelling characteristics of the elastomeric composites filled with WF (particle size from 300 to 400 μm) were measured as a function of filler loading (the range of 0 to 50 phr) and compared with the values for the elastomers based on commercial grade carbon black filler (nano-sized particles, 26–30 nm). In some formulations phenol-formaldehyde (PF) resins are used to achieve better adhesion between rubber macromolecules and filler particles. For WF filled elastomers the maximum tensile strength of 11 MPa at 20 phr was recorded. Hardness of samples filled with WF increased with filler loading. Abrasion resistance decreases marginally with increasing filler loading. The equilibrium sorption in toluene of NR/CSM vulcanizates filled decreased with increasing filler loading for both type of filler.

Key words: Polyisoprene rubber/chlorosulphonated polyethylene (NR/CSM) rubber blends, wood flour, carbon black.

The search for methods of improving the properties and processing of rubbers dates back to over a century ago. One way of achieving the extension of rubber service life is the incorporation of additives into the polymer matrix. The additives are materials which, when incorporated into a polymer base, help to ensure an easy processing, reduce the cost of a product and enhance service properties [1–2]. Different types of additives used in processing of rubber into products include a vulcanizing agents accelerator, an activator, anti – degradants, fillers, a softener, thickeners, a gel sensitizer, a colorant etc. [3,4]. Fillers are one of the major additives used in a natural rubber compound and have had the effect and influence on rubber materials. Fillers modify physical and, to some extent, chemical properties of vulcanizates [5]. The mechanism of reinforcement of elastomers by fillers has been reviewed by several workers [6]. They considered that the effect of filler is to increase the number of chains, which share the load of a broken polymer chain. It is well known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. This includes a particle size, a particle shape, particle dispersion, a surface area, a surface reactivity, the structure of the filler and the bonding quality between the filler and the rubber matrix. In the rubber industry, fillers that are commonly used are carbon black, china clay and calcium carbonate. Carbon black is derived from petrochemical sources but the unstable price of crude oil has led to the search for fillers that are derived from other sources [7]. Agricultural

products: cellulose, sugar cane chaff, rice husk, plantain peel and others are low cost materials and readily available for use in large quantity everywhere, over 300 million tones of the same being produced annually.

In the present applicative investigations, the effect of carbon black and wood flour (WF) on the cure characteristics, mechanical and swelling properties of polyisoprene rubber/chlorosulphonated polyethylene rubber blends (NR/CSM) were examined.

EXPERIMENTAL

Materials

NR (SMR L) was purchased from Sungei Krudda Estate (Malaysia) and CSM (Hypalon 40S; $\rho = 1.18 \text{ g/cm}^3$, $M_w 5.52 \cdot 10^5$, $M_w/M_n 1.97$) was produced by Goodrich Chemical Co. The WF, a 40-mesh ponderosa pine (particle size from 300 to 400 μm), was supplied by American Wood Fibers (Scho.eld, Wisconsin). In some formulations, phenol-formaldehyde (PF) resins were used to achieve better adhesion between rubber macromolecules and WF particles. Commercial grade carbon black type N330 with nano-sized particles (26–30 nm) was used as filler (Table 1). The rubber compounding chemicals such as zinc oxide, stearic acid, processing oil, N-330 carbon black (Table 1),

Table 1. Technical Specifications of nano-sized carbon black, type N-330

Property	
Specific gravity (g/cm^3)	1.81
DBP absorption (ml/100g)	102
Particle size (nm)	26–30
Surface area (m^2/g)	70–90

Author address: Tigar Factory, Nikole Pasica str. 213, 18300 Pirot
E-mail: gmarkov@tigar.com
Paper received: May 24, 2007
Paper accepted: October 25, 2007

sulphur, mercaptobenzothiozole sulphanamide (CZ) and tetramethylthiuramdisulphide (TMTD) from Vulnay were of commercial grades.

Compounding

The recipes used in the formulation of NR/CSM compound are given in Tables 2 and 3. Mixing was carried out using a laboratory two-roll mill according to the ASTM-D3184-80.

Table 2. Formulation of carbon black filled NR/CSM rubber blends

Ingredient (phr) ^a	A1	A2	A3	A4	A5	A6
NR	80	80				80
CSM	20	20				20
Zinc oxide	4.0	4.0				4.0
Stearic acid	2	2				2
Carbon black, type N-330 (26-30 nm)	0	10	20	30	40	50
Naphtenic oil	10	10				10
Magnesium oxide	0.8	0.8				0.8
TMTD	0.8	0.8				0.8
CZ	0.8	0.8				0.8
Sulphur	1.8	1.8				1.8

^a Parts per hundred

Table 3. Formulation of WF filled NR/CSM rubber blends

Ingredient (phr) ^a	B1	B2	B3	B4	B5	B6
NR	80	80				80
CSM	20	20				20
Zinc oxide	4.0	4.0				4.0
Stearic acid	2	2				2
WF (particle size from 300 to 400)	0	10	20	30	40	50
Naphtenic oil	10	10				10
PF resin	15	15				15
Magnesium oxide	0.8	0.8				0.8
TMTD	0.8	0.8				0.8
CZ	0.8	0.8				0.8
Sulphur	1.8	1.8				1.8

^a Parts per hundred

Cure characteristics

The cure characteristics of the compound mixes were measured at 175°C using an Oscillating Disc Rheometer (ALPHA ODR 2000) in accordance with the ISO 3417 method. The cure time (t_{c90}) and torque (minimum, M_{min} , and maximum, M_{max}) were determined from the rheograph. The ODR torque and cure rate

index (CRI), which is a measure of the rate of the crosslinking reaction [8], were calculated using equations 1 and 2, respectively:

$$\text{ODRtorque} = \frac{90(M_{max} - M_{min})}{100} + M_{min} \quad (1)$$

$$\text{CRI} = \frac{100}{T_{c90} - T_{s2}} \quad (2)$$

where M_{min} and M_{max} are the minimum and maximum torque; T_{c90} is the cure time; and T_{s2} is the scorch time.

Mechanical properties

Tensile strength. The test specimens were molded in an electrically heated press in conditions predetermined from the rheograph. Tensile properties of the vulcanizates were measured with a Monsanto Tensile Tester (Mode 1/m) at cross – head speed of 500 mm/min using dumb bell test specimens (type H) according to the ASTM-D412-87 (method A). The tensile strength and elongation at break were recorded.

Compression set. Wallace compression set machine (Mode/Ref No (2, H2 50) was used to determine the compression set (CS in %) of the vulcanizates:

$$\text{CS} = \frac{t_0 - t_r}{t_0} 100 \quad (3)$$

where t_0 and t_r are the height of a sample before and after the compression.

Hardness test. The hardness test of a rubber is the relative resistance of the surface to indentation by an indenter of a specified dimension, under a specified load. Hardness of the vulcanizates was determined by the standard dead load method (BS903 part A 26).

Abrasion resistance. Wallace Akron tester was used in accordance with the ASTM D 5963-04 method

$$\text{Abrasive resistance index} = \frac{S}{T} 1000 \quad (4)$$

where S and T are the mass weight of a sample after and before abrading.

Swelling properties. The resistance of the vulcanizates to toluene was determined by using the method described by the ASTM-D3010. Three different shapes of the cured samples were cut from the 1 mm thickness mould and weighed and immersed in air tight containers of diesel, kerosene and toluene solvents at ambient temperature for 24 h. The samples were then removed from the bottles, wiped dry with the filter paper and weighed immediately. The change in the weight of the sample was expressed as percentage swelling:

$$\% \text{ Swelling} = \frac{W_2 - W_1}{W_1} 100 \quad (5)$$

where W_1 and W_2 are the initial and the final weight of the swollen sample, respectively.

RESULTS AND DISCUSSION

Commercial grade carbon black contains some quantities of chemically combined hydrogen (0.2–1%), oxygen (0.1–4%) and even sulfur (up to 1%) depending on the quality of the process and feed-stock. A large variety of oxygen containing functional groups exists on carbon black surface, for instance carboxyl and hydroxyl groups, phenol, lactones, quinines, ketones, aldehydes, hydroperoxydes. Hydroxyl groups are present on the wood particles surface, also. Figure 1 represents the surface chemistry of carbon black and wood particle. Relevant dimensions of carbon black – rubber interactions [18] and the proposed covalent bonding between wood and rubber are presented in Figure 2.

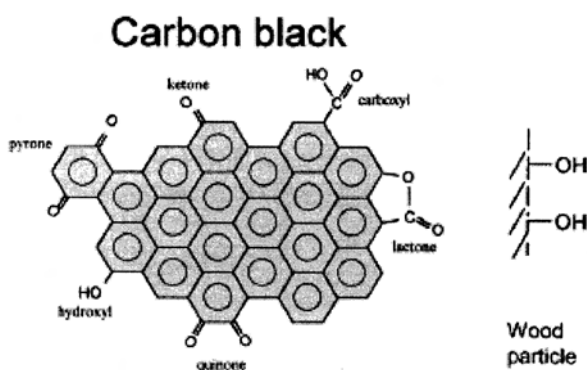


Figure 1. Surface chemistry of carbon black [18] and wood particle

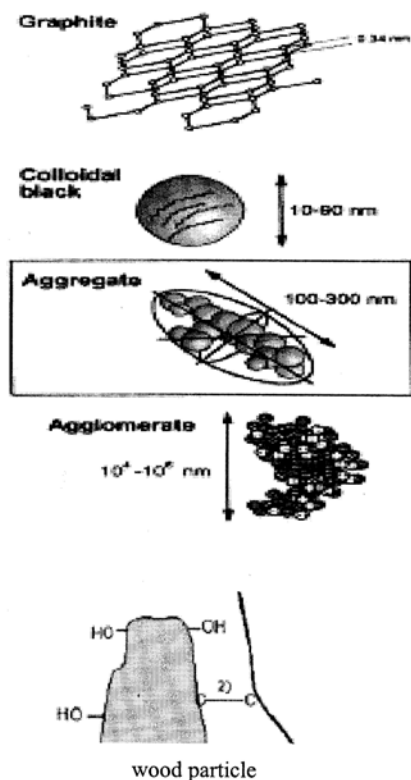


Figure 2. Relevant dimensions in rubber-filler interactions [18] and proposed covalent bonding between wood and rubber

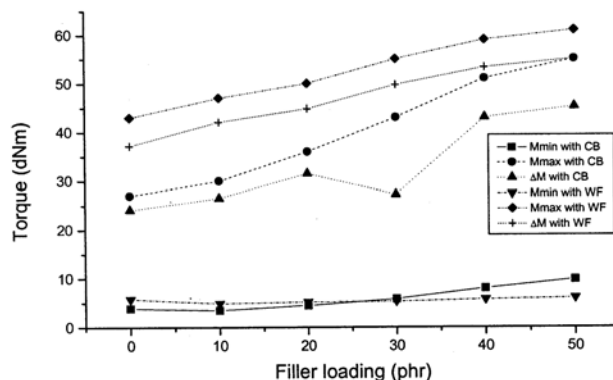


Figure 3. M_{min} , M_{max} and ΔM versus filler loading curve of NR/CSM rubber blends

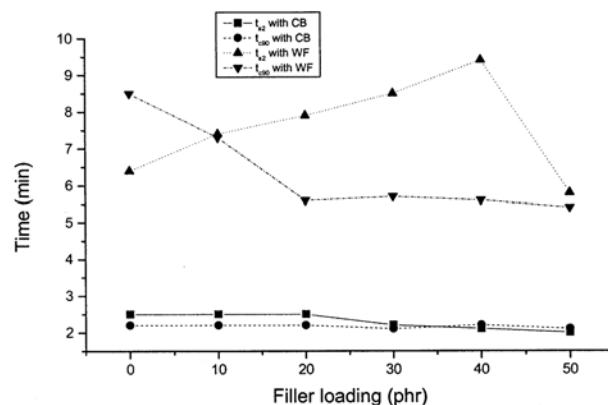


Figure 4. Scorch time (t_{s2}) and cure time (t_{c90}) versus filler loading for NR/CSM rubber blends

Figure 3 and 4 show the maximum (M_{max}), minimum (M_{min}) and the difference of maximum and minimum torque (ΔM) and the cure time (t_{c90}) and the scorch time (t_{s2}) of the WF and carbon black filled NR/CSM vulcanizates.

The difference in cure characteristics may be attributed to the fact that each type of filler possesses different properties such as a surface area, surface reactivity and particle size (Table 1) [9]. It was obvious (Figure 3) that the obtained torque values were dependent on the filler loading for WF and carbon black filled vulcanizates. The higher maximum torque value was observed for WF filled vulcanizates up to 50 phr filler loading. The maximum torque value of carbon black was observed to be higher at 50 phr filler loading with the increased filler content. The highest torque values of 61 and 55 dNm were recorded at 50 phr filler loading for WF and carbon black, respectively. The higher minimum torque of 4.9 dNm at 10 phr filler loading recorded in the case of the WF – filled vulcanizates may be attributed to the nature of the WF fillers (Figure 1), such as a surface area, surface reactivity and a particle size [10]. In general, a faster cure rate was obtained with fillers having a low surface area, high moisture content and smaller particle size [11]. It was reported that the cure rate was directly related to the humidity and water content of the rubber

compound. However, the most probable factors to account for the observed cure enhancement of carbon black fillers over WF ones were the surface area, the surface reactivity and the particle size. It was believed that with the smaller particle size, hence the larger surface area, there was the greater interaction between the filler and rubber matrix.

Figures 5 to 10 summarize the mechanical properties of WF and carbon black (N330) filled NR/CSM rubber vulcanizates. It could be seen that the

tensile strength of WF-filled vulcanizates was inferior to that of commercial fillers because WF has a larger particle size. It has been reported by several workers [5,12] that a significant reinforcement is only attainable when the particle size of the filler is from 0.02 to 0.05 mm. Nasir and Choo [10-13] found that decreasing the particle size of carbon black filler generally enhanced mechanical properties such as tensile strength. A similar observation has been encountered by Parkinson [14-17] in the case of carbon black.

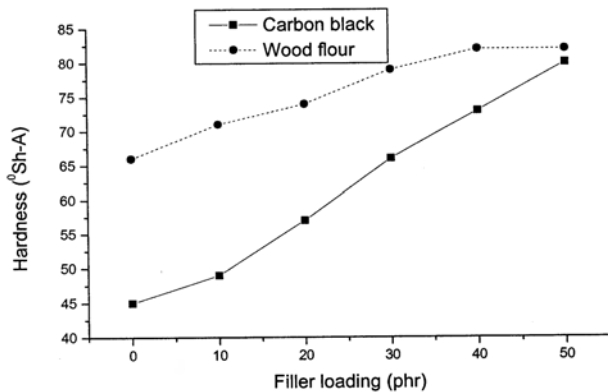


Figure 5. The effect of filler loading on hardness of NR/CSM rubber blends

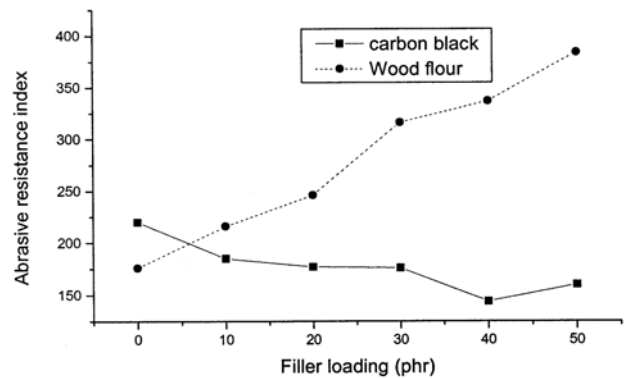


Figure 8. The effect of filler loading on abrasion loss index of WF and carbon black-filled NR/CSM rubber blends

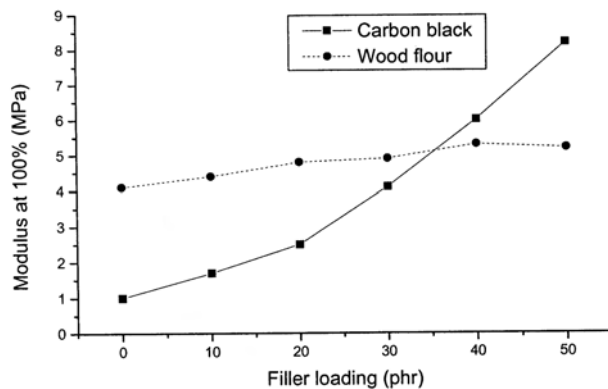


Figure 6. The effect of filler loading on modulus at 100% of elongation for WF and carbon black-filled NR/CSM rubber blends

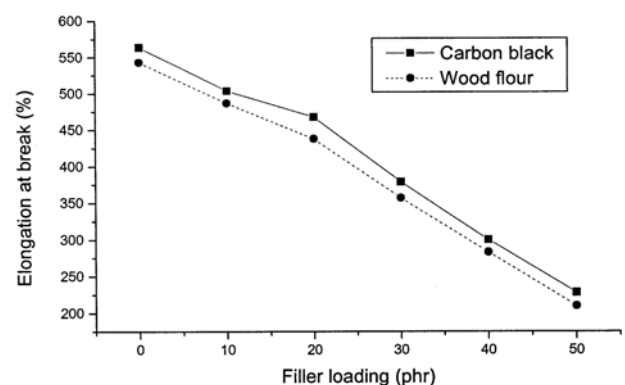


Figure 9. The effect of filler loading on elongation at break of WF and carbon black-filled NR/CSM rubber blends

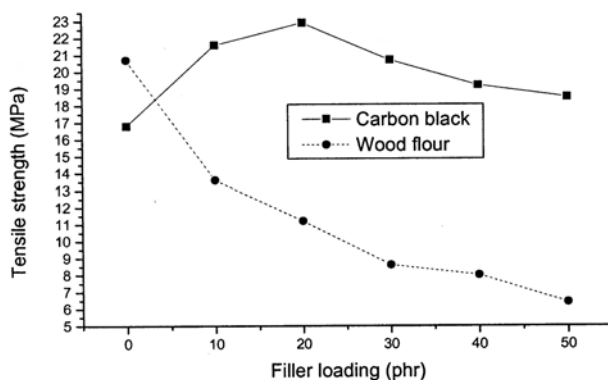


Figure 7. The effect of filler loading on tensile strength of WF and carbon black-filled NR/CSM rubber blends

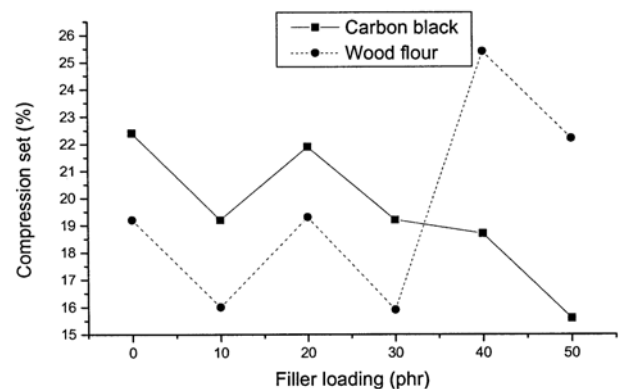


Figure 10. The effect of filler loading on compression set of WF and carbon black-filled NR/CSM rubber blends

The WF filled vulcanizates displayed lower tensile strength values as compared to the commercial one (carbon black N330) (Figure 7). This may be attributed to the nature of surface properties, the particle size and the surface area of wood particles. Tensile strength is affected by the particle size and the surface area of the filler. The tensile strength increases with the decrease of the particle size of the filler [8]. In addition, it is also controlled by the nature of both the rubber and the filler [9]. As for the modulus at 100% properties (Figure 6) the trend observed was expected. WF – filled vulcanizates has higher modulus than carbon black (N330) – filled vulcanizates up to 30 phr. This again may be explained in terms of the difference in the filler properties. Parkinson and Wagner [11,14] reported that the modulus of filled vulcanizates could be enhanced by improving the surface area and surface reactivity of the fillers, filler dispersion and the filler–rubber interaction. The inferior modulus of WF-filled vulcanizates might be explained by two main factors. Firstly, it is a well known fact that these fillers have a larger particle size and hence a smaller surface area than carbon black (N330) fillers. Secondly, WF fillers show a greater tendency towards the filler agglomeration. The results interpreted by Figure 9, give a graph of elongation at break as a function of filler loading for both the WF and carbon black. The values of elongation at break (E_b) decreases with the increase in filler loading for both the WF and carbon black vulcanizates.

Decreases in elongation at break have been explained in terms of adherence of the filler to the polymer phase, leading to the stiffening of the polymer chain and hence the resistance to stretch when a strain is applied [1,2]. Figure 10 shows that unfilled, and the systems with 40 and 50 phr WF filler, have the largest compression. The compression decreases with the increase in filler loading. The observation may not be unconnected with the amount of filler incorporated into the matrix, the degree of dispersion of the filler and its particles size. Carbon black has a higher compression set. The hardness of WF and carbon black vulcanizates (Figure 5) increased with the increase of the filler content. It is expected because as more filler particles get into the rubber, the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates. The hardness of WF vulcanizates with PF resin is superior to those of carbon black vulcanizates. The abrasion resistance (Figure 8) showed an irregular pattern of the increase with increasing the filler loading for the WF filler used. This indicates that the filler loading is not a function of the measured parameter. The observation may therefore be attributed to the degree of dispersion of the fillers.

Equilibrium swelling

Figure 11 and 12 show the influence of filler loading on the equilibrium swelling of WF and carbon

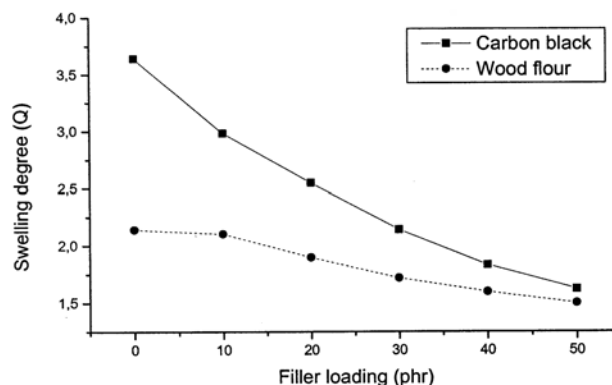


Figure 11. The effect of filler loading on swelling degree of WF and carbon black-filled NR/CSM rubber blends

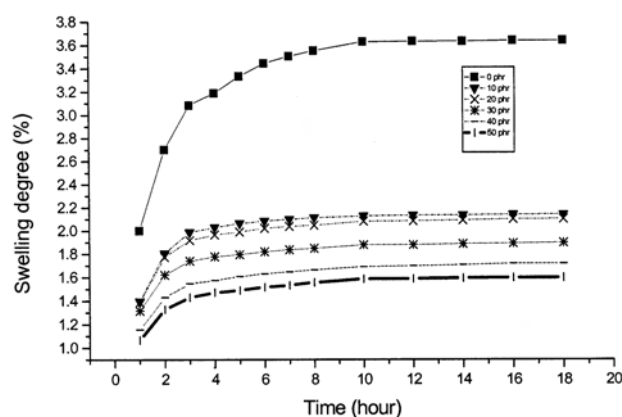


Figure 12. The swelling ratio versus time for WF and carbon black-filled NR/CSM rubber blends

black filled NR/CSM rubber vulcanizates. Several factors can influence the equilibrium swelling in a solvent of unfilled and filled vulcanizates; these factors are the level of cross-linking, filler dispersion, the nature of the solvent and fillers. Gent and Lui [13] explained why higher sorption values were obtained for unfilled vulcanizates.

Toluene with the lower molecular weight may be expected to diffuse faster and be accommodated in the rubber matrix with less hindrance. The decrease in sorption with increasing the filler loading may be that each filler particle behaves as an obstacle to the diffusing molecule. As filler loading in the rubber matrix increases, the rubber–carbon black and rubber–wood particles interaction increases, and more and more obstacles are created to the diffusing molecule and thus the amount of penetrated solvent is reduced.

CONCLUSION

The effect of different fillers (WF and carbon black) on the NR/CSM rubber blend properties was investigated. The results of mechanical properties show that WF is potential filler for elastomeric composites based on NR/CSM rubber blends. PF resins are thermosetting polymers which are used to achieve.

However, the carbon black (N330) exhibited relatively better reinforcing properties than WF. This study indicates that the potential of WF as alternative filler, especially in combination with PF resin, can be further exploited by controlling the particle size and the particle distribution, improving filler dispersion and also its surface functionality.

REFERENCES

- [1] C. Hephbum, C.M. Blow, *Rubber Technology and Manufacture* 3rd Edition Butterworth Publishing, 1971, p. 188.
- [2] D. Rivin, *Rubb Chem. Tech.* **36** (1963) 729.
- [3] F.E. Okieimen, A.K. Akinlabi, A.I. Aigbodion, I.O. Bakare, N.A. Oladoja, *Nig. J. Polym. Sci. Technol.* **3** (2003) 233.
- [4] F.E. Okielmen, J.E. Imanah, *Nig. J. Polym. Technol.* **3** (2003) 201.
- [5] H.F. Mark, *Encyclopedia of Polymer Sciences and Technology*, Interscience New York. 12 1964, p. 42.
- [6] J.J. Brennan, T.E. Jermyn, *J. Appl. Sci.* **9** (1965) 27.
- [7] K.B. Ski, *Engineering Material. Properties and selection*, Reston Publishing Company (1970) p. 40.
- [8] L. Hoday, *Composite Material*. Elsevier. New York (1966) p. 313.
- [9] M. Morton, *Rubber Technology* 3rd Edition Vani Nostrand, New York (1987). p. 74.
- [10] M. Nasir, C.H. Choo, *Enr. Polym. J.* **25** (1989) 355.
- [11] M.P. Wagner, **50** (1976) 342.
- [12] M.Q. Patterman, *Rubber world* **194** (1986) 38.
- [13] N. Gent, G.L. Lui, *J. Polym. Sci. Polym. Phys.* **29** (1991) 1313
- [14] D. Parkinson, *Reinforcement of Rubbers*, Lakeman and Co. London (1957) p. 12.
- [15] P.J. Donnelly, *Rubb. Technol. Int.* **52** (1999) 56.
- [16] W.E. Drivers, *Plastic Chemistry and Technology*, Van Nostreand Company, London (1979) p. 243.
- [17] Z.A.M. Ishak, A.A. Baker, *Enr. Polym. J.* **31** (1995) 259.
- [18] J.L. Leblanc, *Progr. Polym. Sci.* **27** (2002) 627