MORPHOLOGY AND PROPERTIES
OF SUGARCANE BAGASSE
CELLULOSE- NATURAL RUBBER COMPOSITES

N.N. Sibiya, M.J. Mochane, T.E. Motaung , L.Z. Linganiso, S.P. Hlangothi
University of Zululand, Department of Chemistry
Kwadlangezwa, South Africa

S.P. Hlangothi
Nelson Mandela Metropolitan University, Centre for Rubber Science
and Technology, Department of Chemistry
Port Elizabeth, South Africa

ABSTRACT

This study investigated the mechanically treated sugarcane bagasse cellulose / natural rubber composites. The novelty of this work is based on sugarcane bagasse treated by supermass colloider and an acidification. Properties such as morphology, solvent uptake, diffusion coefficient, transport mechanism, and thermal stability of vulcanised natural rubber (RB) and its composites were investigated. The acid and mechanical treatment showed less aggregates in the composites than bagasse cellulose composite. The transportation mechanism of solvent diffusion suggested that irregular particles are responsible for solvent absorptions. The composites generally showed reduction in swelling rate which was attributed to tortuosity of the path and reduced transport area in the composites compared to neat natural rubber. There was a decrease in the thermal properties of natural rubber with the addition of the reinforcing fillers.

KEYWORDS: Natural rubber, bagasse, cellulose, supermass colloider, swelling.

INTRODUCTION

Natural rubber/fibers composites have attracted many researchers, especially as a synthetic fibres replacement in the rubber and plastics industry (Sipiáo et al. 2011, Manaila et al. 2015, Bras et al. 2010, Martins et al. 2002, Xu et al. 2012). The advantages of natural rubbers over synthetic are low cost, low density, acceptable specific strength properties, ease of separation, carbon dioxide removal, and biodegradability. Natural rubbers major weaknesses are such as low thermal resistance, hydroscopic in nature, particular polarization, less dimensional stability

and anisotropic fiber properties (Akhlaghi et al. 2015, Mathew and Joseph 2007, Lopattananon et al. 2011, Jacob et al. 2006). These disadvantages cause a weak fiber-resin interaction. However, in fibers-reinforced composites, the fibers as filler serve as reinforcements by giving strength and stiffness to the composite structure (Rajeev et al. 2001, Zhang et al. 2014). The filler is classified as reinforcement depending of their beneficial performance on the mechanical properties such as tear and tensile strength and abrasion resistance of the composite.

Amongst natural fibres, sugarcane bagasse (SB) received little attention as reinforcement of natural rubber, let alone cellulose extracted from it. Most work done around sugarcane bagasse is based on development of biofuel (Wong and Sanggari 2014, Cardona et al. 2010, Rabelo et al. 2011). However some researchers used it for reinforcement of polyolefins. For instance, Anggono et al. (2014) studied alkali treated sugarcane bagasse-polypropylene composites. Similar research was undertaken in literature (Motaung et al. 2015). The SB was compounded into low-density polyethylene and poly (ethylene oxide) using melt and solution mixing respectively. Agunsoye and Aigbodion (2013) produced bagasse filled recycled polyethylene bio-composites by compounding and compressive moulding method.

The results showed that treated sugarcane bagasse gave better properties for the resultant composites (Wong and Sanggari (2014), Rabelo et al. 2011, Motaung et al 2015). Uniform distribution of the bagasse particles in the microstructure of the polymer composites is the major factor responsible for the improvement of the mechanical and thermal properties. The bagasse particles added to polyolefins improved its rigidity and the hardness values of the composites. The tensile and bending strengths of the composite increased with increasing percentage of bagasse, while the impact energy and fracture toughness decreased. Improvement in thermal properties mostly favoured cellulose polymer composites. The developed composites have the best properties in the ranges of 30 wt % bagasse particle additions and for optimum service conditions, carbonized bagasse particles addition should not exceed 30 wt %. Seyyed et al. (2011) performed water absorption on bagasse fibre/polypropylene composites on the brown rotten bagasse. The results indicated that the highest water absorption (10.5 %) was observed in the brown-rotted composite samples for 8 weeks exposure time and after 24 hrs immersion in distilled water, and the lowest (3.8 %) was noted in the control composite samples after 2hrs immersion in distilled water.

The originality of this work is based on studying utilization of mechanically treated cellulose extracted from sugarcane bagasse for cellulose-natural rubber composites. Cellulose was systematically treated with supermass collider before mastication process for synthesis of the composites. The techniques such as X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA) are used for characterization.

MATERIAL AND METHODS

Materials

Natural rubber (SMR20) was supplied by Continental tyre (Port Elizabeth, South Africa). All vulcanization chemicals used in this study were obtained from S&N rubber (Port Elizabeth, South Africa) and were used as received: vulcanizing agent – Sulfur (rhombic), Activators – Zinc oxide (ZnO) and Stearic acid and Accelerators – 2- Mercaptobenzothiazole (MBT) and Diphenyl guanidine (DPG). Sugarcane bagasse was supplied Hullet Tongaat in KZN. NaOH pellets (99.9%), $NaClO_2$ (98%), KOH (85%) and H_2SO_4 (98%) were obtained from Minema, South Africa.

Extraction of cellulose

SB were treated at 80°C with 2% of each of NaOH, $NaClO_2$ and KOH for 4 hrs to produce sugar bagasse cellulose (CB). The cellulose fibres were subsequently washed repeated times with running tap water followed by deionised water to pH neutral and dried at 50°C for 48 hrs.

Chemical treatment

25g of CB fibres were placed in 250 ml beaker. 10% diluted sulphuric acid was added and stirred vigorously for 30 min before soaking for 8 hours. After completion the reaction was washed with distilled water to pH neutral to obtained acid treated cellulose (CA).

Mechanical defibrillation

SB, CB and CA samples were passed through 1 mm sieve and soaked in deionized water for 24 hours. It was then passed 500 times by gravity into the SMC consisting of two stone grinding disks rotating at 2500 rpm. The gap of the disks was set at approximately 100 µm. A zero gap was determined right at the contact position.

Preparation of the rubber composites

All composites were prepared using a Schwabenthan laboratory two-roll mill with speed 13.1 rpm and 11.6 rpm and a nip gap size of 4 mm at room temperature. The order in which the ingredients were added was kept constant in the following manner: elastomers, activators, sulfur, accelerators, inhibitor, and the fibres were added last. Amount of 5 to 90 % by weight of a fibre was added at a point of homogeneity of the rubber, which was approximately after 30 passes through the roll mills. The compound was folded over and rotated by 90° between each milling for 20 min.

Sorption experiments

Circular samples of 20 mm in diameter were used for swelling studies. Thickness, diameter and initial weight of the samples were taken prior to the swelling experiment. Specimens of known weight were immersed in xylene and toluene as the solvents in diffusion test bottles and kept at room temperature. Furthermore, the samples were constantly removed from the bottles at regular intervals. The wet surfaces of the samples were wiped quickly and weight after each interval. The experimental procedure was continued until equilibrium swelling was reached. All experiments were carried out in triplicate and the average value was used (Phomrak and Phisalaphong 2017, Du et al. 2017).

Characterization

The SEM and EDX measurements of the as-deposited thin films were performed on a Philips XL 30 FEG (at 10 kV) and DX4 detector (at 20 kV), respectively. The films were carbon-coated by using Edward's E306A coating system, prior to the analyses. FTIR spectroscopy analysis was carried out on a Bruker Tensor 27 FTIR spectrometer using a standard ATR cell; the catalysts were analysed as-synthesised with no prior preparation required. Force was adjusted to 90 gauge for sufficient contact between the surfaces. The catalysts were scanned over the mid-IR region (450 - 4000 cm^{-1}). The XRD characterization of all samples was performed on Powder X-Ray Diffraction spectroscopy (Bruker AXS Advance D8 diffractometer) with monochromatic Cu Kα (λ = 1.5406 Å) incident radiation at 40 kV and 40 mA at room temperature. The samples were scanned within the high angle 2θ range to get all characteristic diffractions of the materials at 0.5 scan speed and 0.01314 increments. Thermogravimetric analyses were performed using TGA

analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 mL·min^{-1}. Approximately 10-15 mg of a sample was heated from 25°C to 600°C at a heating rates rate of 10°C·min^{-1}. The sample weight loss and rate of weight loss were recorded continuously as functions of temperature. The analysis was only started when isothermal condition had been obtained.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

Fig. 1 represents the surface of of RB-SB composite. The dispersed phase of sugarcane bagasse shows large aggregate and some cracks indicated with an arrow, suggesting a poor interface adhesion (Fig. 1a). It should be pointed out that the cellulose (CB) extracted and acid treatd sugarcane composites (CA) shows less aggregates in the composites (Fig. 1a,b). Zhang et al. (2014) and Seyyed et al. (2011) related the similar observation to a better interfacial interaction. It means, in this study, the treament of sugar cane bagasse was accompanied by a better interfacial surface in the composites. The EDS analysis of the natural rubber and its reinforced are shown in Tab. 1. The carbon content increased in all composites and decreased for RB-CA composite. This may suggests that acid treatment rendered the cellulose better surface area to favour the observed interfacial interaction.
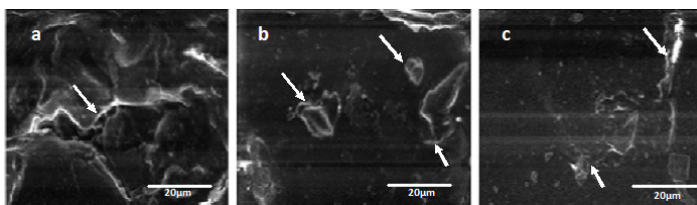

Fig. 1: SEM images of a) RB–SB b) RB–CB d)RB–CA compsoties.

Tab. 1: Chemical elements present on the surface of the composites evaluated by EDS spectroscopy.

Element	RB	RB-SB	RB-CB	RB-CA
C	67.8	80.7	96.1	76.1
O	30.5	19.3	11.6	21.1
Si	0.3	0.1	0.3	0.0

Fourier transform infrared (FTIR)

The FTIR spectra of RB, RB-SB, RB-CS and RB-CA composites are shown in Fig. 2. The spectra are nearly identical for RB and its reinforced composites except for minor differences, which come with the presence of the fibres in the matrix. The strong asymmetrical and symmetrical stretching of methylene group vibrations that are normally present in natural rubber are observed in the range of 3014 and 2913 cm^{-1}, respectively for RB and its composites. Phomrak et al. (2017) observed such stretching for RB around 2950 (asymmetrical) and 2853 (symmetrical). It is clear from the spectra of all samples that there is OH stretching vibrations at 3391 which is attributed to the hydroxyl group as results of possible moisture absorption (Du et al. 2017). The peaks related to sugarcane bagasse and its cellulose at 1267 and 1555 cm^{-1} became more resolved in the composites, while the interfacial interaction and interaction of -CH$_2$- and nonsymmetric bridge of C-O-C at 1160 cm^{-1} and 1267 cm^{-1} led to a reduced intensity respectively.
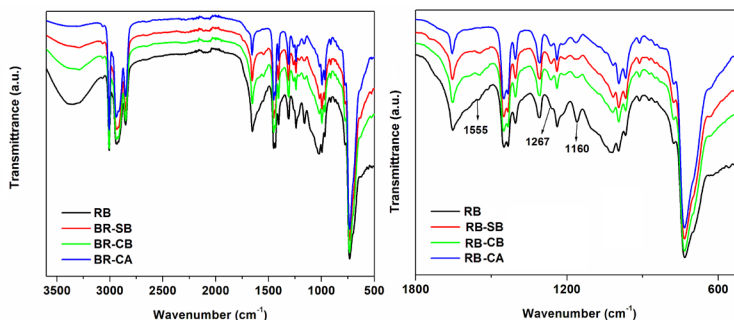
Fig. 2: The FTIR Spectra of RB (a), RB–SB (b) RB–CB (c) RB–CA (d) composites.

The intensity at 1267 and 1168 cm^{-1} for all composites is arguably similar, except for 1555 cm^{-1}, which is either little or absent for the CA composite. This, according to the SEM images, may in fact relates to a better interfacial interaction of CA than CB and SB composites. Motaung et al. (2015) observed similar results when investigating the effect of mechanical treatment on morphology and thermal and mechanical properties of sugarcane bagasse-low density polyethylene composites, however they related the observation to number of passes through SMC.

X-ray diffractometer (XRD)

Fig. 3 illustrates the XRD pattern peaks for natural rubber RB, RB-SB, RB-CB and RB-CA composites. The cellulose formed seemed to be cellulose I, since there is no doublet in the intensity of the main peak. The XRD pattern of natural rubber indicated a hallo peak at around 23°, from where all composites exhibited higher reflections than the rubber. The presence of SB in the RB matrix indicated a negligible improvement in crystallinity, as manifested by the intensity, while celluloses were effective with CA dominating all samples. There is now no doubt that the high surface area proven by SEM results is responsible for the promotion of crystallization between the filler and the elastomer which awarded the CA containing composite highest crystallinity. The same apply for CB. However, considering the possibility of sulphate functional groups and altered concentrations of OH groups during cellulose extraction (Phomrak et al. 2017, Du et al. 2017), it is also possible to claim higher crystallinity squarely on improved interfacial interaction.
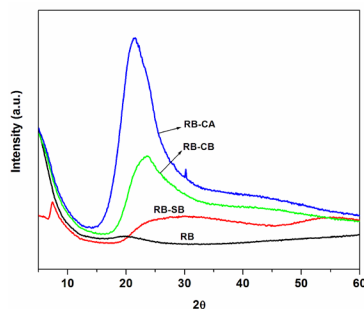

Fig. 3: XRD of RB (a), RB-SB (b) RB-CB (c) RB-CA (d) composites.

Thermogravimetric analysis

Figs. 4 and 5 shows the thermal degradation behavior of natural rubber (RB) reinforced with sugarcane bagasse (SB), cellulose (CB) and acid treated sugar sugarcane bagasse (CA). The summary of degradation temperatures at 20 and 80 % mass loss for all investigated samples is tabulated in Tab. 2.
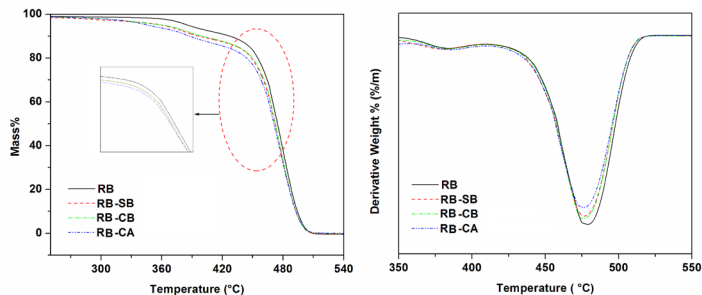

Fig. 4: TGA curves of RB (a), RB–SB (b) RB–CB (c) RB–CA (d) composites.

Tab. 2: Degradation temperatures at 20 and 80% mass loss for all investigated samples.

Sample ID	$T_{80\%}$	$T_{20\%}$
RB	456.5	490.2
RB-SB	448.6	488.2
RB-CB	488.6	486.2
RB-CA	444.6	484.1

There is a slight decrease in thermal stability, at almost the same temperatures, in the presence of SB and CB but CA presence seemed to have worsened the stability. The reduction is clearer at 20 % and become almost faded at 80 %. These were unexpected given the predicted interfacial interaction by SEM, FTIR and XRD, and the fact that the similar treatments of RB-cellulose in literature rendered improved thermal stability (Wong et al. 2014). Nonetheless, in this study one of the highly possible explanations is the preparation of cellulose by super mass-collider which seemed to have somehow altered the thermal degradation mechanism of composites.

Swelling analysis

Mol % uptake of the solvent

The solvent uptake **Mt (%)** was determined by using the following Eq. 1:

$$M_t = \frac{W_2 - W_1/M_S}{W_1} \times 100 \qquad (\%) \tag{1}$$

where: W_1 and W_2 - the weights of the samples before and after immersion in the solvent,

M_S - the molar mass of the solvent.

The diffusion experiments where carried using toluene and xylene as solvents. A plot of solvents uptake (M_t) of toluene and xylene against time as a function of filler is depicted in Figs. 5a-d. Because of the inclusion of sample thickness (h) the plots are referred to as sorption curves (Abraham et al. 2013). Figs. 5 a, c indicated two distinctive areas observed in the sorption curves of natural rubber and its composites. All the solvents seem to have followed the same

path within experimental uncertainties. The first zone (plotted in Figs. 5 b and d) is associated with the initial solvent absorption, and the solvent uptake rate is very high probably because of a huge concentration gradient at this zone. The second area indicates an increase in solvent uptake, however there is also an indication of equilibrium swelling which symbolize a reduction in concentration gradient. The diffusion in rubbers is known for indication of the capability of the polymer to produce pathway for the solvent in the form of irregular generated voids (Abraham et al. 2013). The voids apparently decrease with the addition of filler concurrent to solvent uptake. This explains the low absorption of composites in this study. The movement of solvent molecules is hindered by the presence of the filler particles which resulted in reduction of the solvent uptake (Figs. 5a-d) by the rubber polymer. Furthermore, it is clear that the SB composites showed higher solvent uptake than the other composites. This corresponds with the dispersed aggregates and some cracks indicated by arrows in SEM, which imply that an enhanced fibre/rubber composite prevents the transport of solvent to some degree.
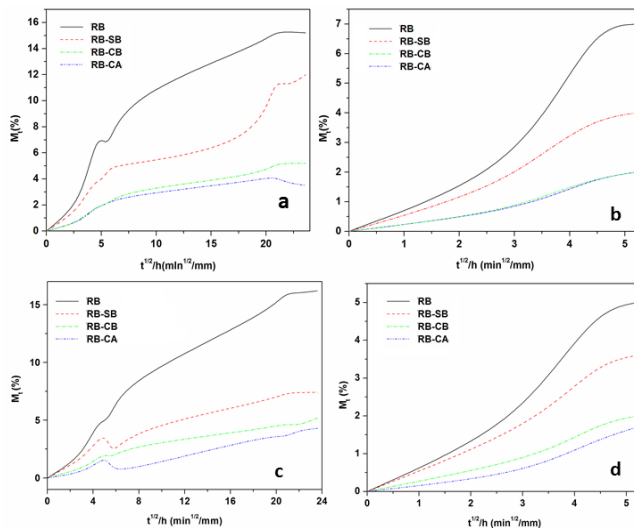

Fig. 5: Mt versus $t^{1/2}/h$ of composites in toluene (a) and c) in xylene (c) at 25 °C and their respective initial solvents uptakes (b and d).

Swelling coefficient

The swelling performance of the investigated samples were analysed from the swelling coefficient values as tabulated in Tab. 3. Swelling index indicates the ability of the sample to swell and it is computed by the following Eq. 2:

$$\text{Swelling coefficient } Q = \frac{m_s}{m_1} \; x \; \frac{1}{d} \tag{2}$$

where: m_s - the weight of the solvent sorbed at equilibrium swelling,
m_1 - the mass of the sample before swelling
d - the density of the solvent used.

The RB-CA and RB-CB composites showed lower values of swelling coefficient compared to RB and RB-SB composite. This emphasise the effect of aggregates as mentioned above.

Tab. 3: Swelling coefficient (Q) of the samples in toluene and xylene.

Sample ID	Toluene	Xylene
RB	78.1	70.7
RB-SB	46.0	34.2
RB-CB	19.7	19.5
RB-CA	7.8	12.3

Transport mechanism

Transport properties of RB and its composites where calculated using the following Eq. 3 and the graphs are shown in Fig. 6.

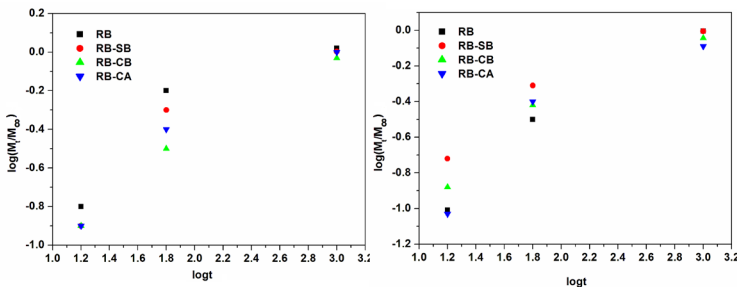$$\log\left(\frac{M_t}{M_\infty}\right) = \log k + n\log t \tag{3}$$

Fig. 6: Curves for log (Mt/M∞) vs logt of RB, RB-SB, RB–CB and RB-CA composites in toluene (a) and xylene (b).

The slope of the plot log (M_t/M_∞) related to log (t) gives the value of n (Tab. 4), which indicates the mechanism of transport.

Tab. 4: Values of n for RB and its composites for transport mechanism of toluene and xylene.

Sample ID	n (Toluene)	n (Xylene)
RB	0.41	0.46
RB-SB	0.28	0.30
RB-CB	0.42	0.39
RB-CA	0.31	0.47

The mechanism of solvent transportation which is symbolized by n values depends upon the structural significance of polymer together with its interaction with the solvent. As stated in the literature, depending on the n values different modes of transport can be differentiated. If n = 0.5, the diffusion mechanism is Fickian's, and that means the rate diffusion of molecules is less than the polymer segment mobility Johns and Rao (2009). It was further mentioned by the authors from same literature that if n=1, the diffusion will follow the non-Fickian, meaning that the stable molecules are faster than polymer segment. If the n lies between 0.5<n<1.0 the mechanism follows the anomalous, whereby the permanent molecules and polymer segment relaxation rates are similar. In this study the value of n lies below 0.5. If n<0.5 this is due to irregular-shaped particles, as a result it decreases comprehensively with increasing cross-linking. Thus, in this study, our mechanism was generally controlled by irregular shaped particles in both solvents.

CONCLUSIONS

The RB-SB, RB-CB and RB-CA composites were successfully prepared and investigated in this study. A better dispersion was observed for acid treated cellulose and non-acid treated cellulose compared with sugarcane bagasse. Furthermore, it was observed that the acid treated cellulose and non-acid treated cellulose composites in showed less solvent uptake comparison to RB and SB composites. Interestingly, the acid treated cellulose composite showed more decrease in solvents uptake (toluene and xylene) than non-acid treated cellulose composite. This indicated that the acid treatment improves the adhesion between fibre and rubber. The composites generally showed less thermal stability compared with the neat natural rubber with the acid treated composite showing more decrease in thermal stability. This may be due to the presence of the acid within the acid treated cellulose (CA) filler. The irregular shaped particles seemed be the main drive the transportation mechanism of solvent diffusion suggested that irregular particles are responsible for solvent absorptions. The composites generally showed reduction in swelling rate which was attributed to the tortuosity of the path and reduced transport area in the composites compared to neat natural rubber

ACKNOWLEDGEMENTS

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N.N. Sibiya, M.J. Mochane, T.E. Motaung*, L.Z. Linganiso, S.P. Hlangothi
University of Zululand
Department of Chemistry
Private Bag X1001
Kwadlangezwa 3886
South Africa
*Corresponding author: motaungt@unizulu.ac.za or motaungte@live.com

S. P. Hlangothi
Nelson Mandela Metropolitan University
Centre For Rubber Science and Technology
Department of Chemistry
P. O. Box 1600
Port Elizabeth 6000
South Africa