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**Maleated high oleic sunflower oil-treated cellulose fiber-based styrene
butadiene rubber composites**

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Abstract

Surface treatment of cellulose fibers was carried out with maleated high oleic sunflower oil (MSOHO). The MSOHO-treated cellulose fibers and unmodified cellulose fibers were dispersed in styrene butadiene rubber (SBR) using a two roll mill. Vapour grown carbon nanofibers (VGCNF) were also incorporated at only 1 phr in unmodified cellulose fibers/SBR composites. The curing characteristics, mechanical properties and water absorption of the resulting composites were determined. MSOHO-treated fibers completed curing at much slower rate and also decreased the cure density of composites, compared to unmodified fibers. In contrast, the combination of VGCNF and unmodified cellulose fibers accelerated the SBR curing process, but reduced the cure density. MSOHO treatment improved the dispersion of the fibers in the SBR which resulted in improved mechanical properties of composites. The composite incorporating 1 phr VGCNF and 15 phr unmodified cellulose fibers showed the greatest increase in tensile strength as compared with neat SBR.

Keywords: carbon nanofibres; cellulose fibres; mechanical properties; cure characteristics

Introduction

Fillers are incorporated into rubber compounds to improve physical and mechanical properties. Good dispersion of filler in the rubber matrix is crucial for improving the physical properties of resulting composites [1-3]. Materials such as nano silica, calcium carbonate, talc, aluminum oxide, zinc oxide, titanium dioxide and zirconium oxide are used as fillers or co-fillers in rubber compounding [4, 5] and carbon black and silica are also currently used as reinforcing fillers in rubber compounding [3, 6]. Natural fibers, such as cellulose fibers, are also of interest as fillers in rubber compounds [7].

Cellulose fibers are renewable natural polymeric fibers which have very low cost [8].

Commercial cellulose fibers are mainly derived from cotton and wood and make up to 40–45% of wood [9]. Short cellulose fibers have been studied as reinforcing fillers in rubber composites.

Cellulose fiber-reinforced rubber composites are mainly used for making ropes, hoses, belts, mats and insulations, and also have potential to be used in tyres [10]. However, the characteristics of cellulose fiber-reinforced/rubber composites are undermined due to poor mechanical properties attributed to weak interfacial bonding between cellulose fibers and rubber [11]. Due to their hydrophilic nature, cellulose fibers have poor compatibility with hydrophobic polymers. Thus surface treatment of cellulose fibers is necessary to develop improved bonding interactions with the matrix [9], e.g. styrene butadiene rubber.

Styrene butadiene rubber (SBR) is a copolymer which has good mechanical properties, abrasion resistance, weather and ozone resistance [6]. It is extensively used for fabrication of tyres, tubes, conveyor belts, ropes and vessel linings. Various types of fibers have been incorporated in SBR to produce composites. However, there are few reports on cellulose fiber reinforced/SBR composites. Kumar et al. [12] studied the effect of surface treatment of cellulose fibers on the

melt behaviour of cellulose fibers/SBR composites. They found that benzylation of alkali treated cellulose fibers, which resulted in esterification of hydroxyl groups on the fibers, increased the melt viscosity of cellulose/SBR melt. Ismail et al. [13] developed a natural rubber composite by incorporating silane-coated bamboo fibers. The authors reported that the silane coupling agent improved the adhesion between the filler and rubber resulting in enhanced mechanical properties of the resulting composites. Bai et al. [14] partially replaced the silica nanoparticles which are commonly employed in rubber products with cellulose fibers. They found that such partial substitution of cellulose fibers in the rubber compound facilitated processing. Recently, Cao et al. [15] published their findings on the effect of reinforcement by cellulose nanocrystals (CNs) in nitrile butadiene rubber (NBR). The cellulose nanocrystals increased the tensile strength of the resulting composites from 7.7 to 15.8 MPa as the CN content increased from 0 to 20 parts per hundred rubber (phr), attributed to the formation of a strong filler-filler network in the NBR matrix. Furthermore, they reported that CNs enhanced the thermal stability of NBR composites.

Several surface treatments of natural fibers have been carried out and their effect on the properties of resulting composites were reported. Geethamma et al. [16] reported treatment of coir (lignocellulosic fiber) with sodium hydroxide which enhanced the bonding of coir fibers with a natural rubber matrix. Alkali treatment increases the surface roughness of cellulose fibers by removing hemicellulose, wax and lignin that are present on the surface of the fibers resulting in better mechanical interlocking of the matrix with the fibers and an increase in the number of reactive sites on the surface of fibers [17]. Kumar et al. [18] reported that the treatment of short sisal fibers with dry bonding agents consisting of resorcinol and hexamethylene tetramine resulted in shorter curing time and enhanced mechanical properties of sisal fiber/SBR

composites. Coupling agents contains functional groups which can improve interfacial adhesion between fiber and matrix and some researchers have studied various coupling agents such as dimethyl urea, alkyl functional silanes and polyphenylisocyanate to improve the properties of cellulose fiber-based composites [19]. Treatment of cellulose fibers with polymethylene polyphenyl isocyanate increased strength and stiffness of cellulose/polypropylene composites due to formation of chemical bonds between the isocyanate and the hydroxyl group on the fiber surface [19]. Valadez et al. [17] reported that henequén fiber when functionalised with silane after treatment with alkali gave much a stronger interface with a thermoplastic matrix. Maleated high oleic sunflower oil (MSOHO) is used as a sizing agent in paper making [20]. However, MSOHO can also provide hydrophobicity to cellulose fibers by attaching its non-polar hydrocarbon chain (Fig. 1) on the surface of the fibers through its anhydride groups which can rapidly react with the hydroxyl groups of the glucose component in cellulose to form a covalent ester bond at the interface [21]. The resulting hydrophobic surface of the cellulose fibers can make them more compatible with hydrophobic polymers. The presence of the double bond in the MSOHO chains (Fig. 1) also offers the potential to link with SBR molecules via sulphur crosslinks.

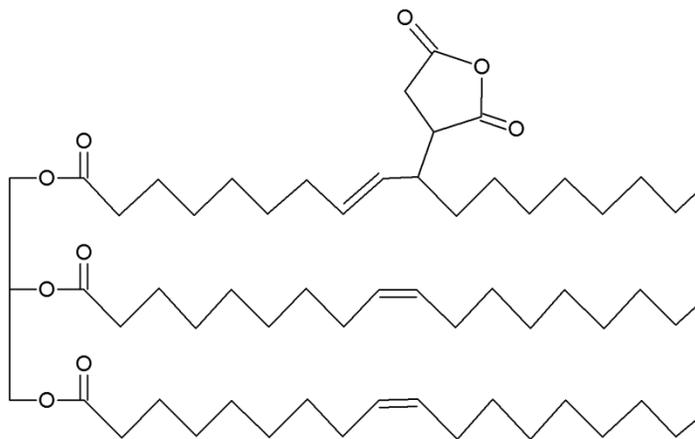


Fig. 1 Molecular structure of MSOHO [21, 23].

In the present research, the surface of cellulose fibers was modified by treating them with MSOHO which served as a coupling agent between cellulose fiber and SBR. The MSOHO-treated cellulose fibers were compounded in an SBR matrix using a two roll mill. This work reports the effects of using MSOHO-treated cellulose fibers on the curing behaviour and mechanical properties of resulting SBR composites. Furthermore, the effect of addition of a small amount of vapour grown carbon nanofibers (VGCNFs) on the properties of cellulose fiber/SBR composites is also reported.

Experimental

Materials

Bleached eucalyptus Kraft pulp was supplied by Valdivia pulp mill, Chile (brand name Arauco, EKP). The chemical composition (supplier's figures by weight) of the pulp is cellulose 91.6%, hemicellulose 7.99%, lignin 0.16%, extractives 0.07, ash 0.18%. The bulk density of fibers obtained from the pulp (as per supplier's data sheet) was $1.7 \text{ cm}^3/\text{g}$ and average fiber length was 0.7 mm. VGCNFs (ex Applied Sciences, USA) have diameters in the range of 70-200 nm and lengths 50-100 μm [22] and used as-received. Styrene-butadiene rubber (grade SBR-1712) was obtained from Kumho Petrochemicals Ltd, Korea. The following industrial grade chemicals were used: N-cyclohexyl-2-benzothiazolesulfonamide (CBS, accelerator), zinc oxide and stearic acid (activators) and sulphur (vulcaniser). Maleic anhydride, high oleic sunflower oil, aluminium chloride and xylene were used for synthesis of MSOHO.

Methods

MSOHO Synthesis

Maleated high-oleic sunflower oil (MSOHO) was synthesised according to the procedure reported in [23] by reacting high-oleic sunflower oil with maleic anhydride at molar ratio of 1:2 at temperature of 215 °C for 7 h in the presence of 0.5% aluminium chloride.

Fiber preparation

Bleached Eucalyptus Kraft pulp was extensively washed with water and then cellulose fibers were separated with a deflaker and dried in an oven at about 105 °C for 6 h.

Surface modification of cellulose fiber by MSOHO

Cellulose fibers were treated with MSOHO at a concentration of 2.5 wt % with respect to the weight of fibers. For this esterification reaction, pre-dried fibers were placed in a round-bottom flask equipped with a water condenser. Xylene/MSOHO at a ratio of 80/20 (vol/vol) was added into the flask such that the fiber to solution ratio was 1:20 by weight. The solution was refluxed at a temperature of 110 °C for 30 min. After cooling, the fibers were washed with acetone to remove unreacted MSOHO. Finally, the treated fibers were washed thoroughly with water to remove residual chemicals and dried in an oven at 80 °C for 8 h.

Preparation of cellulose fiber/SBR composites

Cellulose fiber/SBR composites were produced with unmodified cellulose fibers and MSOHO-treated fibers incorporated in SBR at various concentrations from 5-15 phr and, in some of the unmodified cases, 1 phr VGCNF was also included. SBR and activators were added into a two roll mill (150 mm roll width and 300 mm roll length) having a nip gap of 1.25 mm and were compounded for 15 min. Then the fibers were added into the two roll mill and mixed for 30 min to obtain a uniform dispersion. After this, the curing agents (CBS and sulphur) were added and mixed for 15 min to obtain the final batch. Samples were then made into sheets by compression moulding at ca. 160 °C which was chosen based upon their curing curves. Table 1 shows the

composition of fiber/SBR batches produced with unmodified cellulose, MSOHO-modified cellulose and VGCNF/unmodified cellulose fibers. The addition of other compounding ingredients was carried out according to ASTM D 3182–89.

Table 1. Composition of cellulose fiber/SBR composites

Batch No.	Cellulose fiber/SBR composites	SBR (phr)	ZnO (phr)	Stearic acid (phr)	CBS (phr)	Sulphur (phr)	VGCNF (phr)	Cellulose fiber (phr)
1	Neat SBR	136	4.5	2.2	1.1	1.7	0	0
2	Untreated fiber (5 phr)	136	4.5	2.2	1.1	1.7	0	5
3	Untreated fiber (10 phr)	136	4.5	2.2	1.1	1.7	0	10
4	Untreated fiber (15 phr)	136	4.5	2.2	1.1	1.7	0	15
5	MSOHO treated fiber (5 phr)	136	4.5	2.2	1.1	1.7	0	5
6	MSOHO treated fiber (10 phr)	136	4.5	2.2	1.1	1.7	0	10
7	MSOHO treated fiber (15 phr)	136	4.5	2.2	1.1	1.7	0	15
8	1 phr VGCNF & untreated fiber (5 phr)	136	4.5	2.2	1.1	1.7	1	5
9	1 phr VGCNF & Untreated fiber (10 phr)	136	4.5	2.2	1.1	1.7	1	10
10	VGCNF (1 phr) & untreated fiber (15 phr)	136	4.5	2.2	1.1	1.7	1	15

Characterization

Mooney viscosity of pre-vulcanised SBR composites was measured using a Mooney Viscometer (UM-2050, U-CAN Dynatex Inc, Taiwan) according to ASTM D1646. Mooney viscosities were measured with a large rotor at an oscillating rate of 2 rpm. Mooney viscosity at 100 °C was recorded after one minute of pre-heating and the total time of testing was 4 min.

Vulcanizing characteristics of rubber composites were determined using a Rheometer (UR-2010, U-CAN Dynatex Inc, Taiwan) in accordance with ASTM D2084. The vulcanizing temperature for SBR fiber composites was 160 °C. The oscillating frequency was 1.7±0.1 Hz with an amplitude of ±3.0°. The volume of each specimen was between 3 and 6 cm³. The total testing

time was 50 min. Scorch time (t_{s2}), cure time (t_{c90}), maximum torque value (M_H), minimum torque value (M_L), cure rate index ($1/(t_{c90}-t_{s2})$) and cure density (difference of M_H-M_L) of compounds [24] were measured.

The tensile properties of composites were determined using a Tensile Strength Tester (UT-2080, U-CAN Dynatex Inc, Taiwan). Dumb-bell shaped samples with dimensions $25 \times 5 \times 2 \text{ mm}^3$ were tested at a crosshead speed of 100 mm/min. The data was averaged by testing at least three samples of each composite. Hardness testing was performed according to ASTM D 2240-1997 using a Shore-A type Durometer.

Water absorption of SBR composites was determined according to ASTM D-570. Pre-dried specimens ($75 \times 25 \times 3 \text{ mm}^3$) were immersed in distilled water at room temperature for 30 days. The percentage weight gain of the samples after 30 days was measured and reported as % water absorption.

Results and discussion

Curing characteristics of cellulose fiber/SBR composites

The Mooney viscosities of SBR compounds as a function of various types of fiber loadings are shown in Fig. 2. It can be seen from Fig. 2 that the Mooney viscosity of SBR increases with increasing fiber loading. Both unmodified and MSOHO-treated cellulose fibers increased SBR viscosity at all fiber loadings, except for the 5 phr unmodified fiber/SBR compound whose viscosity was lower than that of SBR. However, MSOHO-treated fiber-based compounds have much higher viscosities than corresponding compounds produced with unmodified cellulose fibers. This may be due to good dispersion and better interaction of MSOHO-treated fibers with the SBR matrix. The increase in Mooney viscosities of MSOHO-treated cellulose fiber/SBR composites is in agreement with Kumar et al.'s [12] work, which reported that benzoylation of

cellulose fibers increases melt viscosities of their SBR compounds due to fiber/SBR interactions. The addition of only 1 phr VGCNFs to unmodified cellulose fiber/SBR compounds noticeably increased the Mooney viscosity in all cases. This may be because VGCNFs have high aspect ratio [2] and, if properly dispersed, they can introduce significant hindrance to the mobility of polymer molecules. VGCNFs might also have created more filler-filler interaction which resulted in increase in viscosity of the composites.

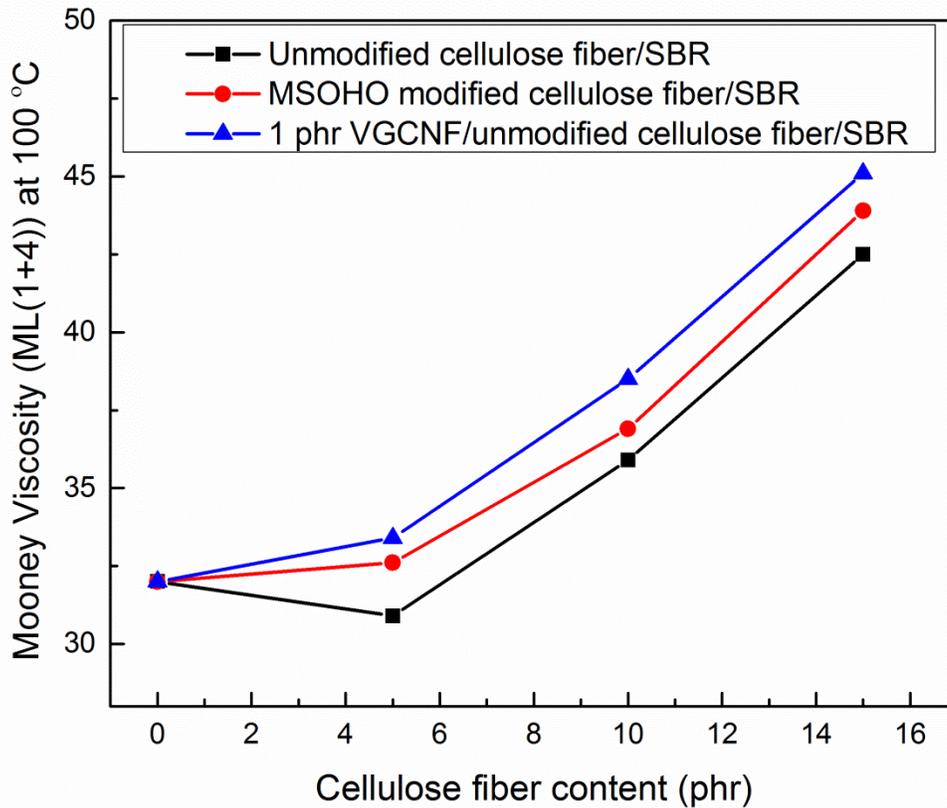


Fig. 2 Mooney viscosity of SBR as a function of cellulose fiber content measured at 100 °C.

The minimum (M_L) and maximum (M_H) torque of SBR composites as a function of fiber loading are presented in Fig. 3. For all the composites, the torque first decreased up to 5 phr and then

increased with increasing fiber loading in SBR. This suggests increased dispersion of fibers at low loading which tends to avoid structural hindrances developing within the composite. The composites consisting of 1 phr VGCNF/ unmodified cellulose fibers displayed the smallest increase in both M_L and M_H compared to other composites. They also all have lower torques than neat SBR. Thus torque data suggest that incorporation of 1 phr VGCNF in unmodified cellulose composites at higher loadings of unmodified cellulose fibers increases dispersion quality of the fibers, but it is relatively inferior than the composite produced at 5 phr unmodified cellulose/1 phr VGCNF as can be seen from increasing values of torques (Fig.3) [33]. The lowest value of M_L and M_H of unmodified cellulose fiber/SBR composites containing VGCNFs suggests that less energy is required for processing in roll mill and the lowest cross linking of SBR in the presence of VGCNF.

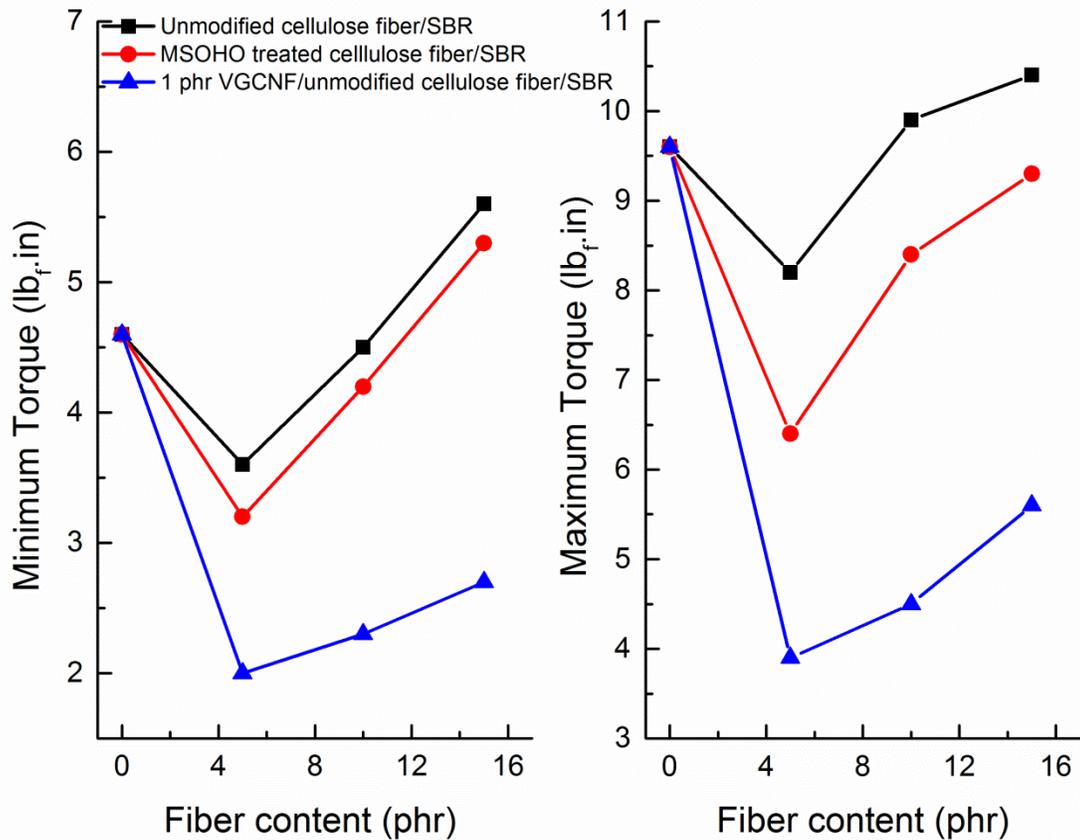


Fig. 3. Minimum (M_L) and maximum (M_H) torque of composites as a function of fiber content.

The cure densities of all types of SBR compounds as a function of fiber loading are presented in Fig. 4. In the case of unmodified cellulose fiber/SBR composites, the cure density remained almost the same as that of neat SBR. However, their cure density decreased significantly upon incorporation of VGCNFs. The VGCNF fibers might have deactivated some fraction of the curing agents by adsorbing the agents onto their surface due to their high surface area, resulting in low cross-linking density in the resulting composites [15]. The MSOHO-modified cellulose fibers also reduced the cure density of the composites although they still have higher cure densities than those of the corresponding VGCNF-based unmodified cellulose fiber/SBR

composites. The MSOHO-coated fibers may have hindered the curing process either by adsorbing the activators or by hindering the movement of SBR molecules [15].

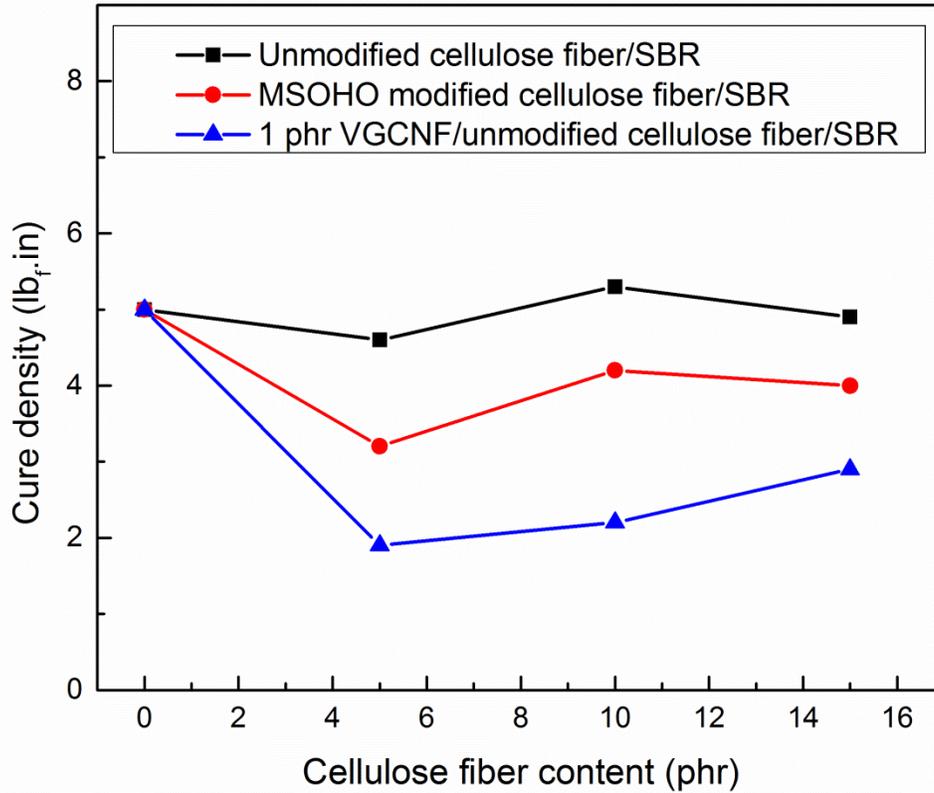


Fig. 4. Cure density of composites as a function of cellulose fiber content obtained from the difference of minimum and maximum torque.

The scorch and cure times of cellulose fiber/SBR composites are presented in Fig. 5. The ts_2 indicates the time when curing starts (scorch time) and ts_{90} (cure time) indicates the time when curing completes. The scorch times are higher than SBR for all the compounds formed. The highest scorch times and cure times were obtained when MSOHO-treated cellulose fibers were loaded in SBR (Fig. 5). This suggests that MSOHO molecules on fibers hindered the curing

process as mentioned above. On the other hand, the unmodified cellulose fibers and 1 phr VGCNF/unmodified cellulose fibers have similar, smaller effects on the t_{s2} and t_{s90} of SBR (Fig. 5). Both unmodified cellulose fiber- and VGCNF-based SBR composites delayed the curing of SBR at a fiber loading of 5 phr by hindering the free mobility of SBR molecules, possibly due to their low loading leading to better dispersion in the SBR matrix. As the fiber loading increased, their cure time decreased slightly and this might be due to their relatively less dispersion at higher loadings of fibers [25], as suggested above, allowing the curing agents to easily reach and hence cross-link the SBR molecules. On the other hand, the increase in scorch and cure times of MSOHO-modified cellulose fiber/SBR composites suggests that MSOHO molecules attached to the fibers have interacted with or absorbed the curing agents resulting in delayed curing of SBR as mentioned above.

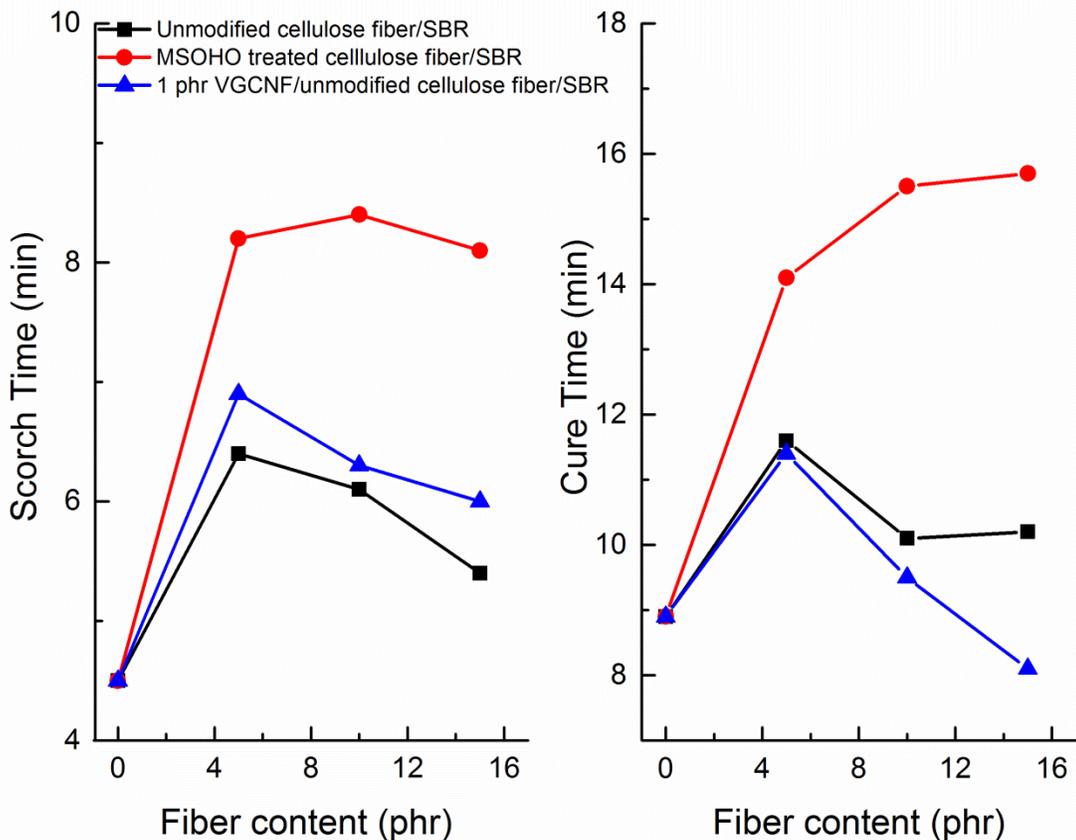


Fig. 5. Scorch time and cure time of SBR composites as a function of cellulose fiber content.

The cure rate index (CRI) of cellulose fibers/SBR compounds is presented in Fig. 6. A higher CRI relates to faster curing. The CRI of unmodified cellulose fibers/SBR compounds is almost same as that of SBR, which indicates that the unmodified fibers do not interfere with the curing agents or the curing process. However, incorporation of 1 phr VGCNF in these compounds increased the CRI of SBR significantly. Despite reducing the cure density of composites (Fig. 4), possibly by deactivating some portion of the curing reagents, VGCNF supported rapid curing reaction at all loadings of fibers. On the other hand, the MSOHO-based composites have an overall lower CRI than SBR. This result suggests that MSOHO-modified cellulose fibers may

hinder the curing process either by adsorbing the activators or by hindering the movement of SBR molecules and that this might be encouraged by their high degree of dispersion in the SBR matrix.

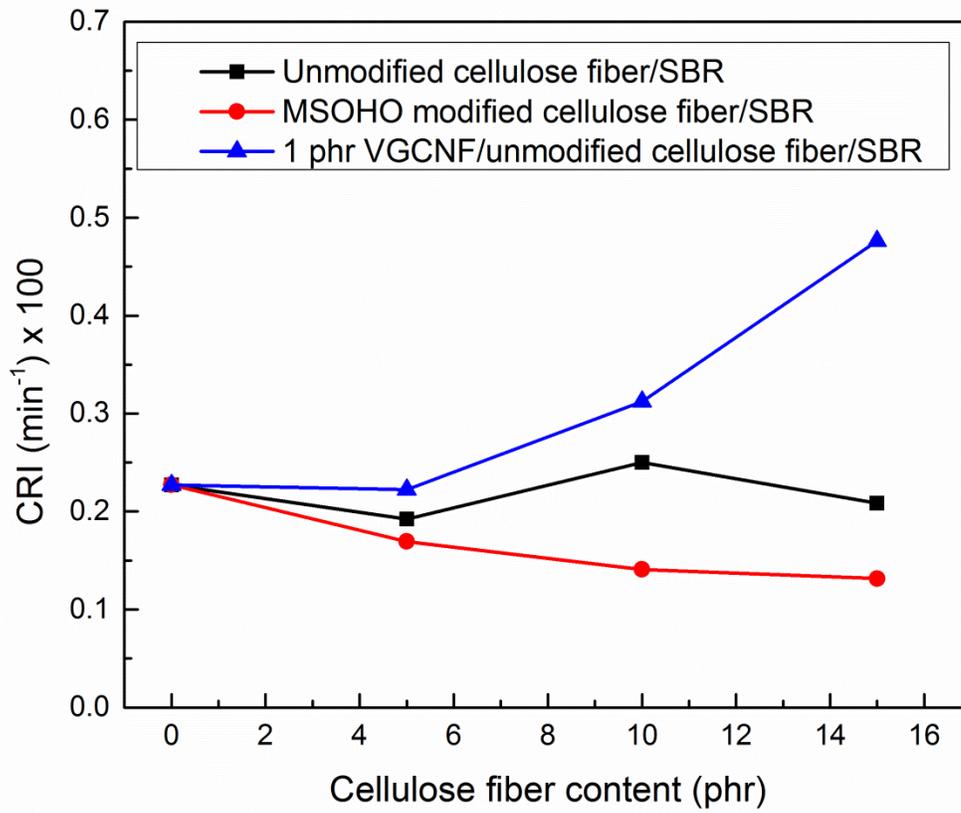


Fig. 6. Cure rate index (CRI) of SBR composites as a function of cellulose fiber content; CRI calculated by taking the inverse of the difference between cure time and scorch time.

Mechanical Properties

The tensile strengths, tensile moduli, % elongations to failure and Shore hardnesses of cellulose fiber/SBR composites are presented in Fig. 7. It can be seen from Fig. 7 that the tensile strength of SBR composites generally increases with increase of fiber loading. The MSOHO-treated

cellulose fiber/SBR composites have higher tensile strengths than the corresponding unmodified cellulose fiber/SBR composites. This result clearly suggests that MSOHO treatment of cellulose fibers increased the dispersion and interfacial interaction between the filler and matrix, resulting in increased tensile strength of these composites. Interestingly, the % elongation of MSOHO fiber-based composites also increased with fiber loading whereas it decreased for unmodified fiber-based composites. Generally, when tensile strength of composites increases their elongation usually decreases [26] but increasing elongation with increasing strength has also been observed in other composites [27, 28]. The increased elongation can be explained by two mechanisms. Firstly, MSOHO treatment improved the dispersion of cellulose fibers in the SBR matrix. Secondly, MSOHO treatment made the fibers more hydrophobic which improved their compatibility with the SBR matrix. It might be possible that MSOHO-treated fibers have developed some cross links with SBR molecules via anhydride bonds as suggested in the introduction section. The attachment of well-dispersed MSOHO-treated fibers to SBR might therefore have increased the molecular mobility of SBR by acting as a plasticiser between SBR molecules, thereby resulting in the remarkable increase in elongation of the resulting composites. In contrast to the tensile strengths of SBR composites based on MSOHO-treated fibers and unmodified fibers, the moduli of these composites decreased with increasing fiber loading (Fig. 7). The cellulose fibers may have reduced the stiffness of SBR slightly by acting as a spacer between the SBR molecules and thereby reducing the Van der Waal's forces between the SBR molecules. The combination of increased strength and high elongation for the MSOHO-treated cellulose fiber/SBR composites results in a very tough rubbery material. Previously, Gauthier et al. [29] had reported that addition of VGCNF up to 7 wt.% loading decreased the tensile strength of SBR, which was attributed to poor dispersion of VGCNF in

SBR. Interestingly, in this work the addition of VGCNF at only 1 phr in the unmodified cellulose fiber composites has remarkably increased the tensile strength of the composites as shown in Fig. 7. The tensile strength of the composite consisting of 1 phr VGCNF and 15 phr unmodified cellulose fibers (total fiber loading, 16 phr) is 86 % greater than that of neat SBR. Cao et al. [15] also reported 105 % increase in tensile strength upon addition of cellulose nanocrystals at 20 wt.% loading in NBR. In the present work, it can be seen that incorporation of only small amounts of VGCNF along with natural fibers can produce significant improvements on the mechanical properties of unmodified cellulose fiber/SBR composites. The enhancement in mechanical properties obtained by combination of VGCNF and unmodified cellulose fibers is even greater than that obtained by MSOHO modification of cellulose fibers. Other researchers have reported that combination of nanofillers along with micron sized fillers produce synergistic enhancements to the properties of composites [30, 31]. VGCNF are much stronger fibers than cellulose fibers and also have very high aspect ratio compared to cellulose fiber [2]. Due to their high aspect ratio VGCNF might have developed good inter-filler contacts, resulting in increase in the tensile strength of the composites. Unlike tensile strength, the tensile modulus of the VGCNF-based composites at 5 phr fiber loading reaches 3 MPa and then decreases, like that of other composites (Fig. 7). The increasing amount of cellulose fibres thus acted as a spacer between the SBR molecules and reduced the stiffness of SBR. Overall, the incorporation of the MSOHO treated cellulose fiber and VGCNF/unmodified cellulose fiber composites reduces the stiffness of SBR for the composites studied which is in accordance with decrease in cure density of composites (Fig. 4)[32].

The Shore hardnesses of the cellulose fiber/SBR composites as a function of filler loading are also presented in Fig. 7. The hardness of these composites increases almost linearly as a function

of fiber loading. The maximum hardness was obtained for 1 phr VGCNF/unmodified cellulose/SBR composites and the lowest for MSOHO-treated cellulose fibers/SBR composites. The lower hardness of MSOHO-treated cellulose fibers/SBR composites could be attributed to better interaction of the fibers with SBR matrix as suggested in introduction section.

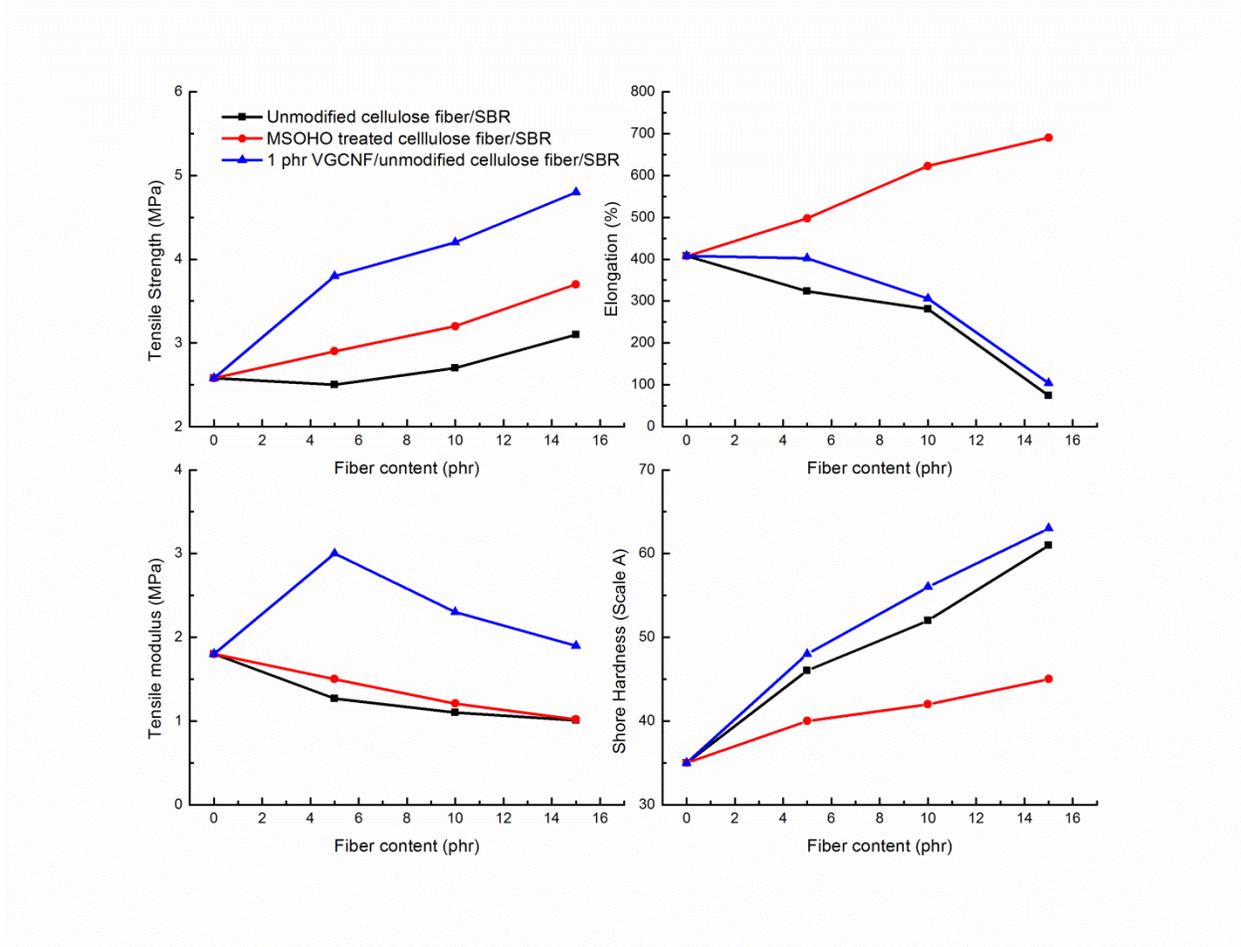


Fig. 7. Mechanical properties and Shore hardness of SBR composites as a function of fiber content (the average values obtained by testing at least three samples of each composite).

Water absorption

The percentage water absorption of cellulose fiber/SBR composites as a function of fiber loading is shown in Fig. 8. The neat SBR absorbed 2 % water after 30 days of immersion in water. The inclusion of cellulose fibers, which are hydrophilic in nature, increases the water uptake of all the SBR composites. The MSOHO treatment of cellulose fibers decreased the water absorption of composites as it made the cellulose fibers more hydrophobic. The lowest water absorption occurs when the fibers and matrix form a covalent bond with each other [33]. Thus the relatively lower water absorption of the MSOHO-treated fibers is also attributed to their increased interaction with the SBR matrix. Interestingly, VGCNF-based unmodified cellulose fiber/SBR composites showed the lowest water absorption. VGCNFs have aromatic hydrocarbons adhered to their surface [34] which render them hydrophobic, both encouraging their dispersion in SBR matrix and lowering the water absorption of the resulting composites.

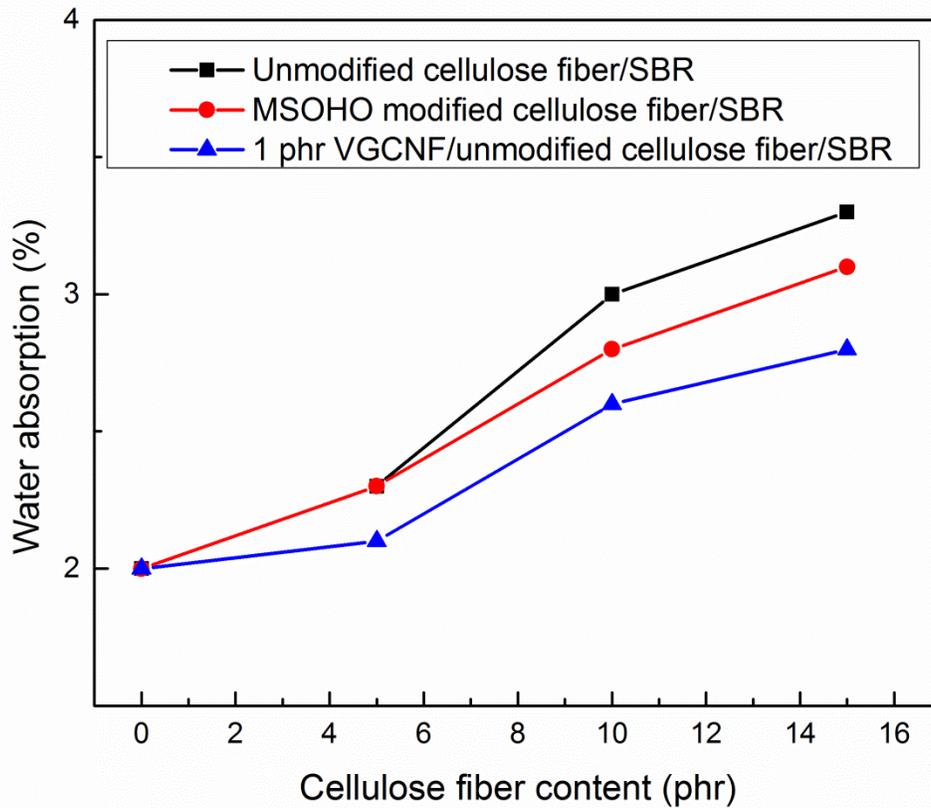


Fig. 8. Percentage water absorption of SBR composites as a function of fiber content.

Conclusions

MSOHO-treated cellulose fibers become hydrophobic in nature and their compatibility with SBR matrix increases, which resulted in better dispersion of these fibers in SBR. Both MSOHO-treated and unmodified cellulose fibers increased the Mooney viscosity of SBR. MSOHO treated fibers increased both scorch and cure time of SBR composite compared to unmodified cellulose fiber composites. The curing of SBR completed at a much slower rate in the presence of MSOHO-treated fibers and the cure rate index of MSOHO-treated fibers/SBR composites decreased with increasing fiber loading. It is suggested that the curing process is slowed by these

treated fibers adsorbing the curing activators and/or by hindering the movement of SBR molecules and that this might be encouraged by these fibers' high degree of dispersion in the SBR matrix. Incorporation of MSOHO-treated fibers also decreased the cure density of composites, compared to unmodified fibers, for similar reasons. In contrast, incorporation of unmodified cellulose fibers had little effect on SBR curing rate and cure density.

The tensile strength of SBR composites generally increases with increase of fiber loading and incorporation of MSOHO-treated fibers further enhanced tensile strength of their composites at all loadings. This was attributed to enhanced dispersion and interfacial interaction of cellulose fibers in SBR matrix due to the hydrophobic MSOHO treatment. The attachment of well-dispersed MSOHO-treated fibers to SBR may increase the molecular mobility of SBR by acting as a plasticiser between SBR molecules, thereby also resulting in a remarkable increase in elongation of the resulting composites. The combination of increased strength and high elongation for the MSOHO-treated cellulose fiber/SBR composites results in a very tough rubbery material. Inclusion of cellulose fibers, which are hydrophilic in nature, increases the water uptake capability of all the SBR composites, although less so in the case of the more hydrophobic MSOHO-treated fibers.

Incorporation of VGCNF at 1 phr into unmodified cellulose fiber/SBR composites produced remarkable impact on curing and mechanical properties of resulting composites. Incorporation of VGCNF increased the curing rate of SBR but also significantly reduced the cure density in its composites, even more than use of MSOHO-treated fibers, possibly due to VGCNF's interaction with curing agents. VGCNF incorporation in unmodified cellulose fiber/SBR composites enhanced the tensile strength of resulting composites. The tensile strength of the composite consisting of 1 phr VGCNF and 15 phr unmodified cellulose fibers is 86 % greater than that of

neat SBR (and also greater than that of the corresponding MSOHO-treated fiber composite). Due to their high aspect ratio, VGCNF may develop good inter-filler contacts, resulting in this increase in the tensile strength of the composites. Therefore, whereas incorporation of cellulose fibers in the other composites may reduce the stiffness of SBR slightly by acting as a spacer between the SBR molecules and thereby reducing the Van der Waal's forces between these molecules, this is not the case in the VGCNF composites. In contrast, the hardness of all three types of composites increases with fiber loading (although less markedly in the case of MSOHO-treated cellulose fiber/SBR composites due to enhanced dispersion of the fibers in SBR). The results suggest that using combination of nanofiller with natural fibers could be a good way of improving the mechanical properties of natural fiber based composites. Addition of small amount of VGCNF in cellulose fiber/SBR composites can also improve the electrostatic dissipation and heat dissipation ability of resulting composites. VGCNF-based unmodified cellulose fiber/SBR composites showed the lowest increase in water absorption compared to neat SBR owing to their very hydrophobic nature which both encourages their dispersion in SBR matrix and lowers the water absorption of the resulting composites.

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