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Investigation on Properties and Pyrolysis Performance of Natural Rubber/Sugarcane Bagasse Biocomposites

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Sugarcane bagasse has been frequently used as a filler in natural rubber biocomposites to enhance mechanical properties. In addition, the presence of bagasse filler also enhances other properties of natural rubber biocomposites including thermal properties and chemical properties, which could influence the pyrolysis recycling process when recycled. Therefore, the effect of bagasse filler on the pyrolysis recycling process was investigated along with the mechanical and thermal properties. A pristine natural rubber (NR) and bagasse-natural rubber biocomposites (NR/BG) with various amounts of bagasse (5, 10 and 15 phr) were prepared. The pyrolysis processes were conducted at 400 ºC for all samples, and the obtained products were analyzed. It was found that most of the mechanical properties of the rubber samples including tensile strength, modulus and tear strength increased with increasing the amount of bagasse. In addition, thermal stability of NR/BG were better than that of NR. When pyrolyzing the rubber samples, it was observed that all the pyrolyzed liquids have the nearly heating values, between 43.1-44.2 MJ/kg suggesting no significant change in fuel property. However, the chemical composition of the obtained liquids considerably varied, especially limonene which was found higher in the liquids from NR/BG (61.9-73.4 wt.%) than that from NR (31.65 wt.%). The presence of BG inside NR/BG biocomposites changes chemical compositions of the biocomposites, especially Zn which possess the catalytic ability to convert the primarily-generated limonene into other products, and also provided low hydrogen-to-carbon source which reduced the conversion of limonene.

Keywords: Biocomposite, Limonene, Natural rubber, Pyrolysis.

INTRODUCTION

Sugarcane bagasse is a fibrous waste material generated in the production of sugar and ethanol. It has been frequently used as reinforcing agents in polymer matrixes due to its distinguished properties such as low density, light weight, biodegradability and so on [1]. Natural rubber is considered a natural polymer, which has been filled with sugarcane bagasse to obtain biocomposites and whose properties are enhanced by the bagasse as reported in many studies [2,3]. Natural rubber has several benefits over synthetic rubber including low cost, low density, acceptable specific strength properties, ease of separation, CO_2 removal, and particularly biodegradability [4]. Although natural rubber and its biocomposites are biodegradable, the rate of biodegradation can be slow, and take years to break down completely. Therefore, the used natural rubber products still cause adverse effects to the environment.

Pyrolysis is the process of thermal decomposition of materials (without access to oxygen) that can decompose natural rubber products completely and the consequence products such as pyrolytic oil and gas, liquid chemicals and char can be further used [5]. Therefore, it is an efficiently technique to manage wasted natural rubber products with less environmental impact. Various parameters influence pyrolysis performance and then the quality of the pyrolysis products including temperature, types of reactor and composition of feedstock [6,7]. For natural rubber products, particularly natural rubber composites, they usually compose of other materials than natural rubber such as vulcanizing agents and reinforcing fillers. The pyrolysis of natural rubber products with those materials could

be altered, partly depending on the properties of the material, especially fillers with its loading in the products being up to 20 wt.%.

The effects of natural reinforce fillers on mechanical and thermal properties of natural rubber biocomposites has been widely investigated [8,9]. However, the study on influence of those fillers in the pyrolysis recycling process were rarely observed. Januszewicz *et al*. [10] conducted the pyrolysis recycling process of selected used rubber products and explored the possibility of limonene production. It was found that some inorganic filler contained in the products results in lower mass loss during pyrolysis. However, the relation between the fillers inside the rubber matrix and the obtained liquid products was still not revealed. For limonene, it is a green solvent, which can be used instead of petroleum solvents for various applications such as extraction of natural products, food processing, fragrances and cleaning products, with estimated annual production of 50-75 million kg [11,12]. Under pyrolysis, natural rubber provides high amount of limonene due to polyisoprene degradation [13,14]. Several researchers have expressed concern over the production of limonene during the pyrolysis of natural rubber products [15-17].

Therefore, in this work, natural rubber/bagasse biocomposites were produced with various amounts of bagasse. The mechanical and thermal properties of the composites were determined with the standard methods. The obtained biocomposites were then brought to the pyrolysis at 400 ºC, the temperature at which most valuable chemicals in the liquid fraction are still not decomposed, especially limonene. The effects of bagasse fillers on the pyrolysis performance and the resulted products were then discussed.

EXPERIMENTAL

Sugarcane bagasse was collected from sugarcane juice factory in Ratchaburi province (Thailand), cut in piece, ground and screened with a 200-mesh sieve, dried and kept in a sealed container for further use. Natural rubber (STR 5L) was supplied by Union Rubber Products Corp. Ltd., Thailand. Zinc oxide (ZnO), stearic acid and *N*-*tert*-butyl-2-benzothiazolesulfenamide (TBBS) were obtained from Chemmin Co. Ltd., Thailand. *N*-(1,3-dimethyl)-N′-phenyl-*p*-phenylenediamine (6-PPD) and sulphur were purchased from Flexsys Co. Ltd., Thailand. Analytical grade chemicals *i.e*. citric acid, sodium hydroxide and ethanol were obtained from Merck. Methylene blue was supplied by the RFCL limited Co. Ltd.

Preparation of natural rubber samples: Natural rubber samples included a pristine natural rubber (NR) and natural rubber/bagasse biocomposites (NR/BG) were prepared with the formulation as shown in Table-1. All compositions were mixed using a magnetic stirrer at the set temperature of 70 ºC for 2 h. The mixture was then poured into a laboratory-sized two roll mill (model LRM150, Labtech, Thailand) at the set temperature of 60 ºC for 13 min. The obtained sample sheet was kept for further measurements.

Pyrolysis: The pyrolysis of NR and NR/BG were performed in a 0.5 L bath reactor, operating at 400 ºC around 2 h with heating rate of 10 ºC/min. A 25 g of samples was packed in the reactor flowed with N_2 (150 mL/min) for 30 min to remove oxygen prior pyrolysis. The vapour generated was cooled with the condensers, and the condensed liquid was kept and weighted to determine the product yield.

TABLE-1
COMPOUNDING FORMULATION
FOR NATURAL RUBBER SAMPLES

Composition	Part per hundred rubber (phr)	
	NR	Biocomposite (NR/BGXX)*
Natural rubber	100	100
Zinc oxide	4	4
Stearic acid	2	2
Bagasse	0	5, 10, 15
TBBS	2.25	2.25
Sulphur	0.75	0.75

*XX is according to the amount of bagasse (phr) *e.g.* NR/BG5 for biocomposite with 5 phr of bagasse.

Characterization: Mechanical properties of the samples were evaluated with a universal testing machine (UTM) (Comtech, QC-536M1-2L4), according to ASTM D412 (Die C) for their tensile properties and elongation at break, and ASTM D624 (Die B) for their tear strength. The prepared samples were cut to the required size and shape. Thermal stability of the samples was determined using a TGA technique with Perkin -Elmer PYRIS 1 TGA Thermogravimetric Analyzer. Samples of 10-20 mg were examined at a temperature ramping from 25 to 600 ºC at 10 °C/min under carrier gas, N_2 (UHP). The weight change of the samples was observed as a function of temperature. The morphologies of the samples were analyzed with a scanning electron microscope (SEM) using Tescan Mira3 scanning electron microscope. The sample was conductive to prevent charging by coating with gold particle by Cressington Sputter Coater 108 sputtering device. The SEM equipped energy dispersive X-ray spectroscopy (EDX) is also used to obtain chemical composition and reveal spatial distribution of elements.

Pyrolyzed liquid: The condensed liquid from the pyrolyzed sample was analyzed for its chemical composition using gas chromatography–mass spectrometry (GC-MS) (Thermo Scientific, TG-5MS), equipped with a capillary polar wax column, polyethylene glycol (PEG)-coated (length of 30 m, internal diameter of 0.25 mm and film thickness of 0.25 μm). The conditions used were as follows: injection volume of 0.2 μL, oven at 40 ºC (1 min) and continued with heating rate of 10 ºC min^{-1} to 300 ºC, split mode with a ratio of 100:1 and injection temperature of 290 ºC.

Pyrolyzed solid: The element composition of the obtained pyrolyzed solid was measured using X-ray fluorescence (XRF) with a PANalytical MiniPal 4 EDXRF spectrometer, equipped with a 30 kV rhodium anode tube with a helium purge facility. A high-resolution silicon drift detector was used to count X-rays intensity. Matrix corrections were made by using either a ratio to the Compton peak or theoretical alpha coefficients, using minipal 4 software.

RESULTS AND DISCUSSION

Characterization of natural rubber (NR) and natural rubber/bagasse biocomposites (NR/BG): Mechanical prop-

erties of natural rubber samples were evaluated with standard methods. The obtained results are shown in Table-2 and also shown in Fig. 1. It can be observed that most of the mechanical properties showed similar trends except elongation at break. They first decreased when a low content of BG (5 wt.%) introduced into NR, and almost constantly increased with higher contents of BG (10-15 wt.%). At the low amount of BG, decreases in mechanical properties of biocomposites are derived from disturbing of strain-induced crystallization (SIC) of NR matrix by BG. SIC is a phenomenon, which amorphous polymer chains transform into highly oriented and aligned crystalline domains due to an applied mechanical strain [18]. It endows the natural rubbers with excellent mechanical properties and good resistance to crack growth [19].

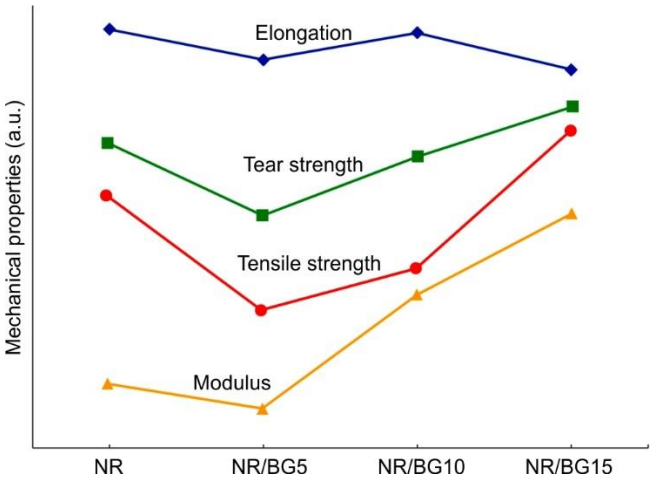


Fig. 1. Mechanical properties of the samples obtained from UTM (Elongation: elongation at break, and Modulus: modulus at 100% strain)

A small amount of BG can hinder the crystallization process and reduce the degree of strain-induced crystallization (SIC), thereby decreasing the mechanical properties of the composites. However, when the fiber volume (BG) reaches the critical volume, the NR matrix will be reinforced by BG. The critical volume varies depending on the nature of fibers, matrix and the degree of fiber–matrix interfacial adhesion [20]. In this study, the critical volume was revealed at around 5 wt.% of BG, above which the dispersion of BG and the interfacial interaction between BG and NR were improved. Thus, the applied stress could be transmitted and distributed from NR matrix into BG and then resulting to the higher strength of the biocomposites [21]. However, the excess loading of BG may cause adverse effect due to fiber-fiber interaction and agglomeration and then promoting weak points within the biocomposites. The SEM images of the samples in Fig. 2 also show non-directional fiber orientation and voids which may cause variation in mechanical properties as seen in the results.

For the elongation at break values, they decreased and fluctuated with BG loadings. It has been explained that adding more fibers in the composite should develop stress-concentrated areas, which are easy to be broken [22]. In addition, a rigid interface between the fibers and the matrix material reduces the deformability of the composites [23]. Nonetheless, in the present study the minor reduction of the elongation at break (about 5%) was observed even at the highest BG loading. Therefore, it can be concluded that all obtained biocomposites of NR/BG had overall better mechanical properties than the pristine NR, beneficial from the introduction of BG.

Thermal properties of the natural rubber samples and the pure bagasse (BG) were evaluated with thermogravimetric analysis (TGA) and the TGA curves are shown in Fig. 3. It can be seen that all NR/BG samples exhibited the similar TGA profiles, which are considerably differed from the one of BG. BG was decomposed faster, and had the residue at 600 ºC of 13.79 wt.%, which are inorganic components in the bagasse. NR had the residue of 3.26 wt.%, derived mainly from inorganic additives introducing during the processing, while NR/BGs had the residue between 3.44-5.61 wt.%. The change in residues are from the presence of the bagasse fillers in the samples.

The first derivative of the TGA curve known as differential thermogravimetry (DTG) are plotted and shown in Fig. 4. The DTG measuring the rate of weight change as a function of temperature can indicate to a specific thermal event such as decomposition occurring at onset temperature (T_{onset} noticed in the curve). Therefore, T_{onset} of all samples were determined from the DTG and displayed in Table-3, along with degradation temperatures at 5% and 10% weight loss, (T_{d5} and T_{d10}) as thermal stability indexes and activation energies of the decomposition reaction.

TABLE-3
THERMAL DEGRADATION TEMPERATURES: $T_{d5\%}$ AND $T_{d10\%}$ AND T_{ONSET} AND ACTIVATION ENERGY

Sample	T_{d5} (°C)	T_{d10} (°C)	T_{onset} (°C)	E_a* (kJ/mol)
NR	304	336	383	122.60
NR/BG5	313	342	383	141.04
NR/BG10	310	344	388	104.41
NR/BG15	296	333	384	106.18
BG	230	282	314, 374	–

*E_a (activation energy) are calculated using Arrhenius plot according to a first order reaction, around the onset temperature.

NR/BG5 and NR/BG10 showed the higher thermal stability observed from higher values of T_{d5} and T_{d10}, compared with NR. For NR/BG15, less thermal stability was observed probably due to non-uniform distribution of the bagasse part-

TABLE-2
MECHANICAL PROPERTY VALUES OF THE SAMPLES OBTAINED FROM UTM

Sample	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% strain (MPa)	Tear strength (N/mm)
NR	7.36 ± 0.63	552.51 ± 73.3	0.80 ± 0.08	70.66 ± 2.82
NR/BG5	4.42 ± 1.31	530.65 ± 53.1	0.64 ± 0.07	55.20 ± 8.87
NR/BG10	5.49 ± 0.90	550.14 ± 31.5	1.37 ± 0.02	67.77 ± 2.96
NR/BG15	9.02 ± 1.37	523.38 ± 48.4	1.89 ± 0.20	78.46 ± 2.94

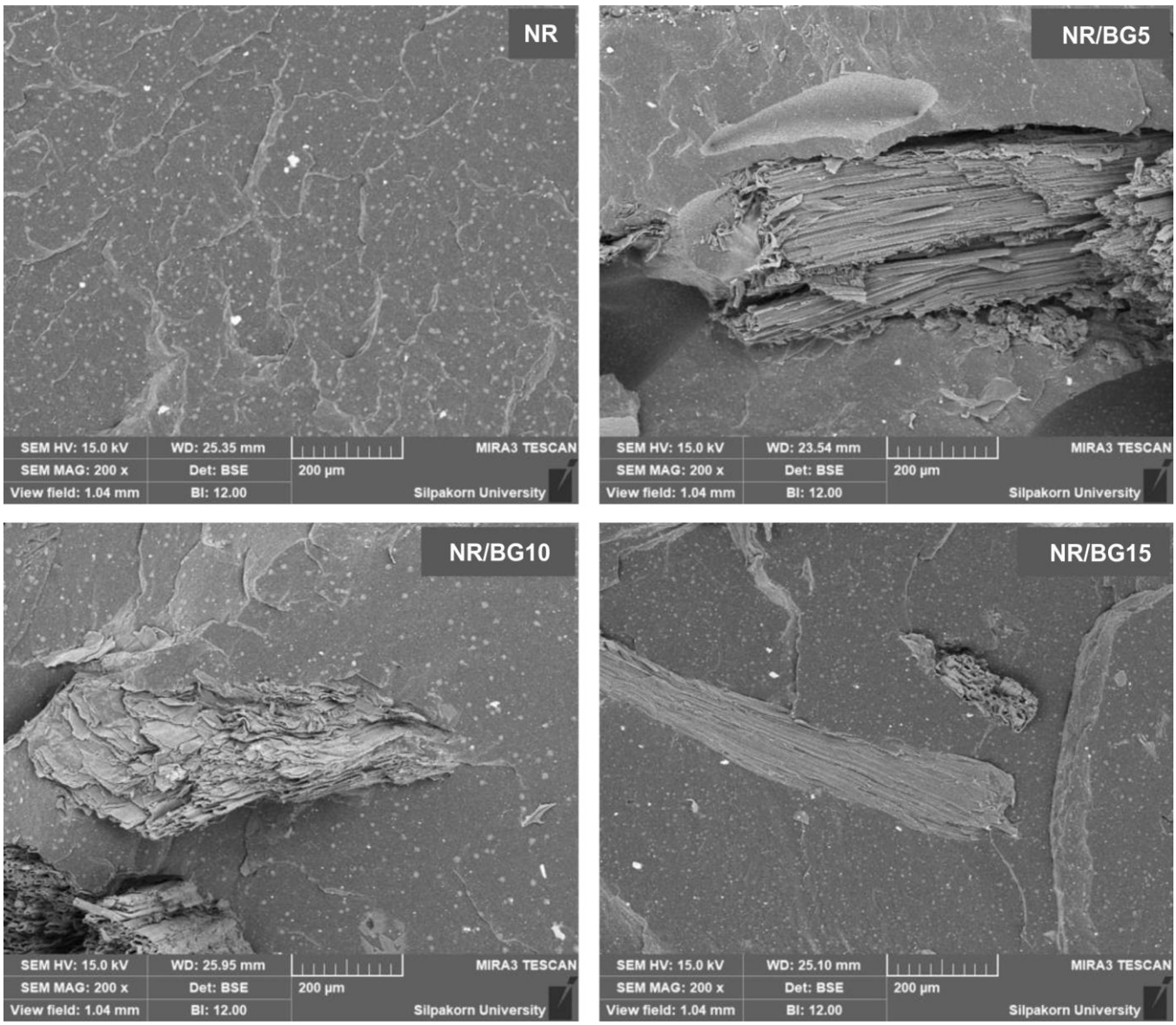


Fig. 2. SEM images of the fracture surfaces of the samples

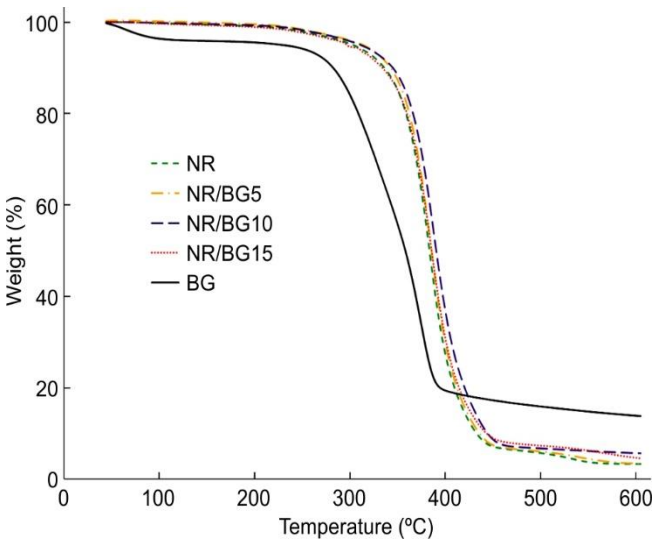


Fig. 3. TGA curve of the samples

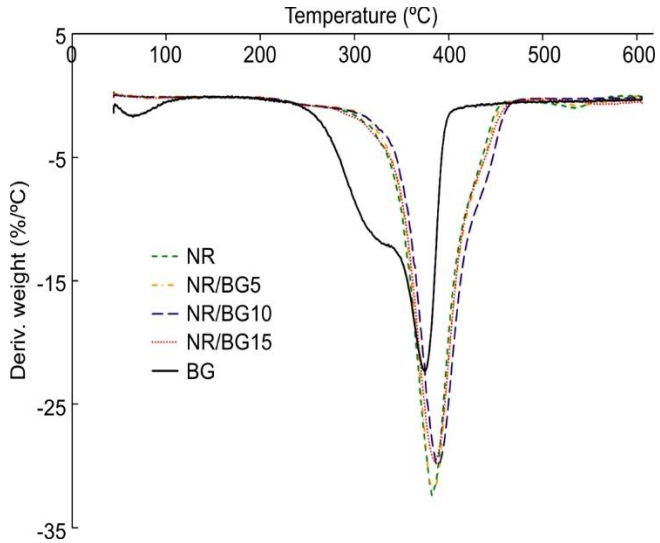


Fig. 4. DTA curve of the samples

icles in the microstructure of the composites caused from too much BG loading [4]. The negative effect to thermal stability of NR due to high loading of filler has been found with cellulose filler loading of 25, 50 and 75 wt.% [24], in the previous study about cellulose/NR composites. Nevertheless, there was suggestion that the effect of filler on the temperature interval of pyrolysis depends on the amount and type of filler, the compatibility between hydrophilic filler and the hydrophobic rubber matrix and the method of processing composites [25]. Considering on DTG peaks at T_{onset}, it was found that BG had two peaks at 314 ºC and 374 ºC attributed to the decomposetion of hemicelluloses and lignin for the first peak and of cellulose for the second peak [26]. For NR and NR/BG, they showed similar TGA profile with only one peak at around 380 ºC, where the breaking down of natural rubber composition occurs. However, the DTG peak positions were slightly different among all the natural rubber samples, arising from variations in the material's thermal behaviour, specifically its decomposition or degradation processes [27]. The differences in activation energy also supports the change in the decomposition processes of the samples. The activation energy for the samples are approximately calculated based on the first order reaction at the decomposition temperature (T_{onset}), assuming only the decomposed reaction of the natural rubber into vapour products occurring. Therefore, the presence of BG should be one of the factors influences the difference in decomposition processes, and also the activation energy.

When considering only NR/BG samples, it was found that NR/BG10 and NR/BG15 had considerably lower activation energies (104.41 and 106.18 kJ/mol), compared with NR/BG5 (141.04 kJ/mol). This is probably due to the better interfacial interaction (as indicated from their better mechanical properties) which facilitate the movement of molecules across the interface, reducing the energy barrier required for mass transport [28]. Thus, less energy required to reach the barrier of activation energy and could result in a quicker induction of the decomposition reaction [29]. In addition, the strong interfacial interactions can concentrate stresses and reactive species at the interface, leading to degradation initiation at the interfaces [30].

From the thermal analysis, it can be observed that thermal stability and thermal decomposition of the biocomposites samples were mostly enhanced by BG. Both parameters indicate changes of material under heating process with distinct aspects. Thermal stability is an ability to resist changes in physical characteristic at a molecular level, while thermal decomposetion is a process which a molecule breaks down into new materials [31,32]. For this study, the presence of BG in NR increased thermal stability by helping maintain the structure and properties of the samples at the higher evaluated temperatures, and accelerated thermal decomposition, resulted from the strong interfacial interactions between NR and BG.

One of the most important factors influencing the pyrolysis process is the elemental composition and distribution of feedstock materials. Therefore, the elemental composition of all samples was determined for the amounts and the distribution throughout the matrices using SEM/EDX mapping analysis. The selected elements chosen for the mapping were oxygen and zinc, which were expected to have crucial roles in the pyrolysis process. The result of EDX mapping of both elements is shown in Fig. 5. The oxygen contents in the samples increased with increasing BG. It was derived enormously from the bagasse as seen that it was dense at the bagasse located. For NR, the oxygen come from the activators introduced during

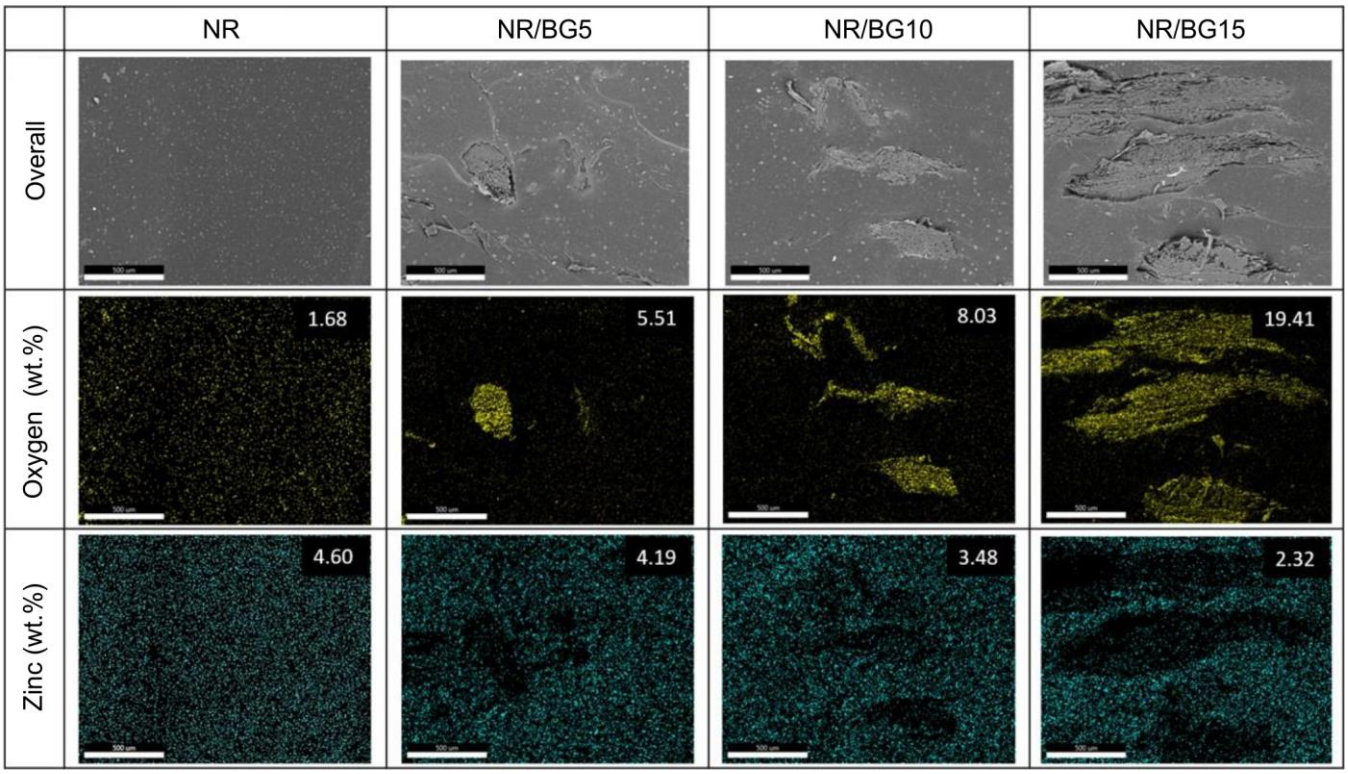


Fig. 5. SEM/EDX mappings of the samples

the rubber processing *i.e.* zinc oxide (ZnO) and stearic acid. Although they react each other to form zinc stearate, the oxygen would remain in the zinc stearate and also the unreacted substances due to the incomplete reaction.

For the amounts of zinc in the samples, it decreased with increasing the bagasse. In fact, it was filled as ZnO at the same amounts in phr unit for all samples. However, its contents decreased with increasing of BG due to the higher volume of BG leading to the lower ratio of Zn in the samples. Moreover, the presence of BG deteriorated the distribution of Zn all over the biocomposite matrices as observed in the mapping. The sources of Zn here were from zinc stearate and the remained ZnO.

Zinc has been known for its catalytic performance in the pyrolysis process. The Zn-containing catalysts like ZnO and Zn-modified zeolite can facilitate the deoxygenation, leading to the production of hydrocarbons and promote cracking reactions and selective production of aromatic hydrocarbons [33]. Supposing that most of the Zn in the samples are in the form of zinc stearate, it nevertheless can be decomposed under pyrolysis condition to form hydrocarbons and ZnO [34]. Thus, the variation of Zn contents and distribution among all samples could alter each pyrolysis process differently.

Characterization of pyrolysis product: The NR and all NR/BG were brought into the pyrolysis recycling process at 400 ºC under N_2 atmosphere. The condensed liquid fraction from the process were characterized for the chemical composition with GC-MS, and the amounts of selected compounds inside the samples are shown in Table-4. In addition, HHV of the obtained liquid (pyrolysis oil) were shown in Table-4, which were calculated from the chemical components contained in the liquid, according to the reported method [35].

It was found that high contents of limonene appeared in pyrolyzed liquid of all samples, ranging from 31.65-73.41 wt.%. A higher concentration of valuable chemicals including limonene as seen in this study makes the NR pyrolysis product more suitable for use as a feed stock in many applications, contrasting with those from the synthetic rubber which contain a broader range of compounds. In addition, the relatively low pyrolysis temperature (400 ºC) in this study could reduce limonene destruction and lead to higher limonene contents, compared to other studies [10,36].

The NR/BG provided the far higher limonene contents than NR. This suggests change in decomposition mechanism due to the presence of BG in the NR matrix. In general, limonene is primarily generated from isoprene (NR monomers) through radical reactions [36,37]. There have been three plausible pathways for the limonene generation from NR pyrolysis (**Scheme-I**) [10]. They all starts from β-bond scission of polyisoprene chains which generate various types of radicals including isoprene monomers and dimers, and short chain polyisoprene. Through pathway-1, two units of monomer radicals undergo dimerization *via* the Diels-Alder reaction to form limonene, while the dimer radicals can form limonene *via* isomerization and cyclization in pathway 2. For pathway 3, the hexahydric ring compounds of limonene are formed by cyclization of polymer radicals [37-39]. Nevertheless, due to its thermal instability, limonene can be further catalytically converted into other products such as aromatic hydrocarbons [40,41].

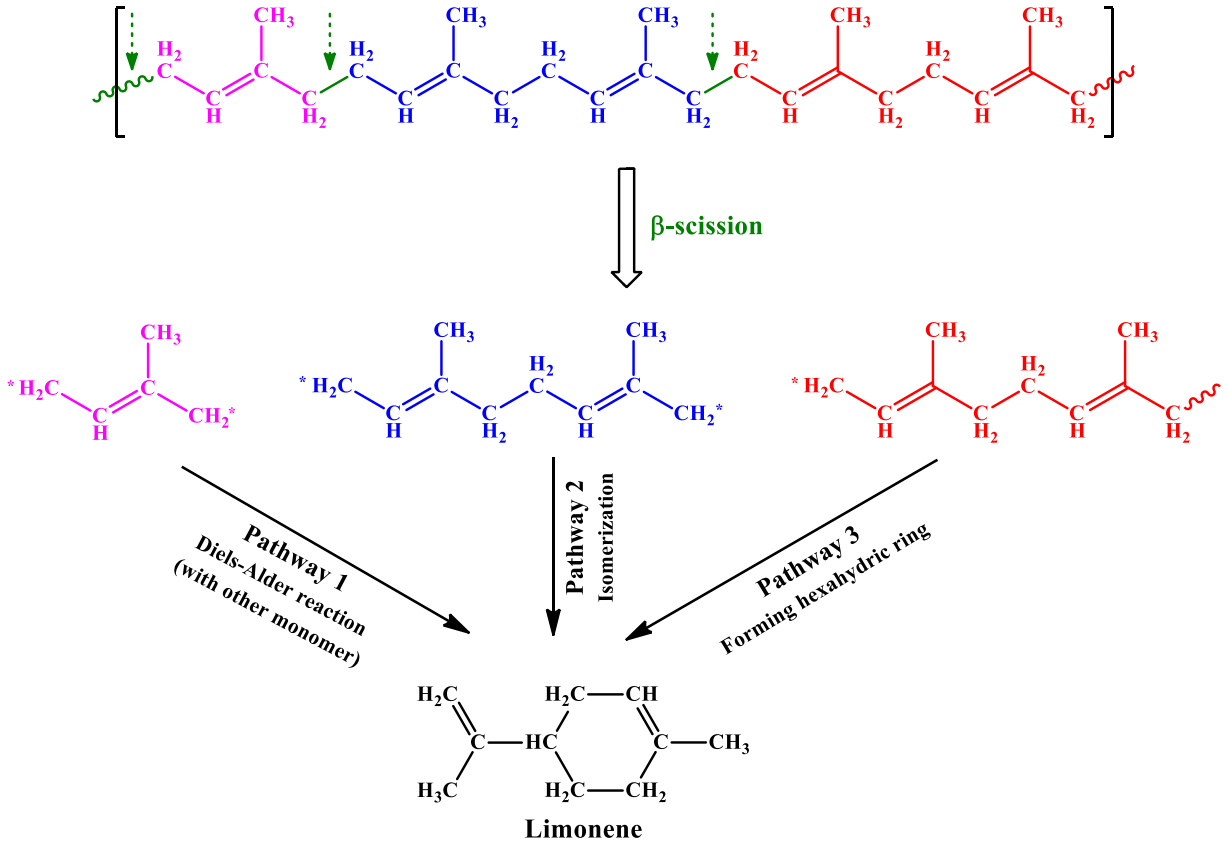
In this place, the existence of Zn as seen earlier, which was higher in NR than NR/BG could act as an active catalyst to promote the secondary reaction such as hydrogen transfer and aromatization, which turn instable limonene into other products [33]. It can be seen that the composition of NR-pyrolyzed liquid consisted of the high amounts of various hydrocarbon rings (no. 2-6) *i.e.* 1,3,5-cycloheptatriene, *o*-xylene, 3-methylenecyclohexene, (1-methylethylidene)cyclobutene and 1-methyl-1,4-cyclohexadiene,. For all NR/BG, it was observed that the contents of those chemicals decreased. This suggests the higher content of Zn favours the formation of those chemicals. The poor distribution of Zn developed by BG as observed in the mappings may also reduce the catalytic performance of Zn in NR/BG.

The presence of BG, a cellulosic material, in the NR/BG composites led to a modified internal structure, which in turn affected heat and mass transfer, as well as the decomposition

TABLE-4
COMPOUNDS IN THE LIQUIDS PRODUCED FROM THE PYROLYSIS OF NR AND NR/BG BIOCOMPOSITES AND HHV VALUES

Compound	NR (wt.%)	NR/BG5 (wt.%)	NR/BG10 (wt.%)	NR/BG15 (wt.%)
D-Limonene	31.65	73.41	61.91	67.33
1,3,5-Cycloheptatriene	14.50	1.46	6.31	5.53
o-Xylene	8.78	2.79	4.83	7.45
3-Methylenecyclohexene	3.54	0.31	0.97	–
Cyclobutane, (1-methylethylidene)-	3.10	0.34	1.22	1.51
1,4-Cyclohexadiene, 1-methyl-	2.74	0.40	0.62	1.46
Bicyclo[3.1.0]hexane, 1,5-dimethyl-	1.71	0.40	0.69	0.69
Cyclohexane, 1,3-dimethyl-	1.53	0.21	0.66	–
trans-3-Caren-2-ol	1.51	2.21	1.93	–
1,3-Cyclohexadiene, 1,3,5,5-tetramethyl-	1.30	0.82	0.97	1.51
3-Cyclohexene-1-carboxaldehyde, 4-methyl-	1.22	0.30	0.68	0.39
1,3,6-Heptatriene, 2,5,6-trimethyl-	1.44	–	–	1.40
Cyclohexane, 1,4-dimethyl-	1.10	–	0.44	–
Cyclohexene, 1-methyl-	1.08	–	–	–
1-Methylcyclohexa-2,4-diene	1.76	–	–	0.26
Total oxygen compounds (wt.%)	4.43	1.24	2.19	6.50
HHV (MJ/kg)	43.1	44.2	43.7	43.6

*Calculated from the chemical components.



Scheme-I: Mechanisms for the pyrolytic decomposition of natural rubber to limonene

kinetics within the composites. Thermal analysis also revealed changes in the decomposition behaviour of the biocomposites. The lower activation energy for the decomposition reactions (NR/BG10 and NR/BG15) could bring to the higher formation of limonene through the mechanism as shown in **Scheme-I**. Nevertheless, for NR/BG5 with the higher activation energy of decomposition reaction still provided the high limonene content and thus the other effects that cause the high amount of limonene should be more profound.

It has been known that NR or polyisoprene has high hydrogen-to-carbon effective ratio and the opposite is true for BG, a biomass with low hydrogen-to-carbon ratio, and also high oxygen content [42]. The presence of BG could create a low hydrogen-deficient hydrocarbon pool [43] and reduce the conversion of primarily-generated limonene into other products, particularly through hydrogen transfer reactions. This could make all NR/BG biocomposites retain the higher content of limonene. The oxygen compound contents of the pyrolyzed liquids from NR/BG5 and NR/BG10 (1.24 and 2.19 wt.%) were lower than NR (4.43 wt.%), even having the higher oxygen content in the feedstock derived from BG. This was due to the low conversion of limonene into other products including oxygen compounds. Nevertheless, when too higher content of oxygen in the feedstock *i.e.* NR/BG15, the pyrolyzed liquid reversely contained with a high content of oxygen compounds (6.50 wt.%). It is noteworthy that most oxygen in the samples could turn into pyrolyzed gases *i.e.* CO, CO_2 and H_2O, and thus the oxygen contents in the pyrolyzed liquids were not in proportional with the oxygen contents detected in the liquid samples.

Considering on the fuel property, it was observed that all pyrolyzed liquids have the nearly higher heating value (HHV), between 43.1-44.2 MJ/kg, closely matched to those reported in the literature [44]. The highest HHV belongs to the pyrolyzed liquid from NR/ BG5, caused from the lowest content of oxygen compounds and the highest content of limonene which has a high ratio of H/C. The chemical composition of the obtained pyrolysis solids (char) was determined using XRF analysis, as shown in Table-5. Zinc is the highest percentage element in all solids, excluding carbon (C) which is difficult

TABLE-5
ELEMENTAL COMPOSITION OF THE SOLIDS PRODUCED FROM THE PYROLYSIS OF NR AND liNR/BG BIOCOMPOSITES

Sample	Element composition (wt.%)							
	Mg	Si	P	S	K	Ca	Fe	Zn
NR	2.09	-	0.69	7.49	0.54	4.76	0.11	84.33
NR/BG5	2.23	0.45	0.76	6.39	0.89	5.45	0.13	83.72
NR/BG10	2.57	0.51	0.74	7.10	0.90	5.79	0.15	82.25
NR/BG15	2.73	1.00	0.90	6.82	1.21	6.92	0.13	80.29

to be detected by the XRF due to emitting low energy X-rays. The amount of Zn in the chars decreased with increasing BG in the samples, consistent with its existence prior the pyrolysis. Silica (Si) originated by BG was not observed in the char from NR, while the other elements which had already existed in NR slightly increased with the introduction of BG. The existence of sulfur (S) in the chars should be concerned and limited in use for some applications. It should be observed that the pyrolysis recycling of NR/BG biocomposites in this study resembled both the co-pyrolysis of polymers with biomass and the catalytic pyrolysis of polymers using solid catalysts. However, some characteristics of the composites such as interfacial interactions between NR and BG, and naturally presence of metal elements could make those pyrolysis systems quite different. The detailed investigation should be more conducted including thermodynamic and kinetic study with various types of fillers and polymer bases.

In summary, the positive effects of BG in the NR/BG biocomposites were showed on mechanical and thermal properties of the materials, and also during the pyrolysis recycling process, as seen in the obtained pyrolyzed products. Therefore, benefits of BG as a filler for biocomposites included utilizing agricultural residues, enhancing product properties and ability to produce high-value chemical feedstocks from the recycling processes.

Conclusion

A pristine natural rubber (NR) and its biocomposites (NR/BG) were prepared with various amounts of bagasse (5, 10 and 15 phr). It was found that the most mechanical properties of the samples increased with bagasse loading except elongation at break values. The thermal properties *i.e.* thermal stability of the biocomposites was also enhanced by the presence of BG. When conducting the pyrolysis recycling process of the samples, it was observed that the amounts of limonene in pyrolyzed liquids from NR/BG biocomposites (61.9-73.4 wt.%) were significantly higher than that of NR (31.65 wt.%). This was attributed to differences in the inorganic element content among the samples, particularly the presence of zinc, which has catalytic activity in converting primary limonene into other products. In addition, the presence of BG, a biomass with a low hydrogen-to-carbon ratio, may further suppress the conversion of limonene.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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