Multifunctional Rubber Seed Biomass Usage in Polymer Technology and Engineering: A Short Review

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Hevea brasiliensis is the most relevant source of natural rubber-based products in the world, and it is mostly found in Southeast Asia. This species is highly functional because its seeds can be utilized as a starting material for many essential applications related to polymer engineering and technology. The main practical compositions are its shell and kernel. The importance of each composition is varied based on the content of each structure. The kernel is predominantly composed of oil, where the oil can be utilized for the production of biofuel and to impart flexibility in many polymer-based composites. Furthermore, the carbon and lignocellulosic contents are heavily represented in the shell of the rubber seed, making the shell useful as a natural resource for carbon-derived applications.

Keywords: Rubber seed; Shell; Kernel; Polymer; Lignocelluloses; Technology

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INTRODUCTION

Hevea brasiliensis or natural rubber tree is a tropical plant originating from the Amazon, Brazil (Corpuz 2013) and extensively cultivated in Southeast Asia including Malaysia, Indonesia, Philippines, and Thailand (Guardiola-Claramonte *et al.* 2010). *Hevea brasiliensis* grows in a humid and temperate climate, maturing in a span of five years and is able to produce its rubber for up to 20 years. This particular species can grow up to 130 feet tall with a typical economical lifespan of 25 to 40 years per tree; it is normally replanted every 25 to 30 years to ensure the productivity and usability of the latex produced (Teoh *et al*. 2011; Brahma *et al*. 2017). However, this planned procedure is subject to environmental changes such as soil fertility, global warming, and total rainfall (Herrmann *et al*. 2016). Natural rubber (NR) can be extracted from more than 3,000 species of plants including *Ficus elastica* (Moraceae), *Parthenium argentaturn* and *Taraxacum koksaghyr* (Compositae). Limited sources of NR are found in many other species such as *Euphorbia intisy* (Euphorbiaceae), *Cryptostegia grandiflora*, and *Cryptostegia madagascariensis* (Asclepiadaceae), *Funtumia elastica*, and *Landolphia*. However, *Hevea brasiliensis* is the most important commercial source of NR (Siler *et al.* 1997; Collins-Silva *et al.* 2012).

Natural rubber contains natural polymers that are versatile due to their inherent properties such as high flexibility and strength, excellent resistivity to many chemicals, and good electrical insulation (Vijayaram 2009). Thus, NR is extensively used in the manufacturing of more than 40,000 products of medical, automotive, aerospace, logistic, and textile industries (Mooibroek and Cornish 2000). NR is often referred to as the dry state of a latex, which is a milky colloidal dispersion containing natural rubber particles extracted from the latex vessels or the cells of rubber-producing plants (Yip and Cacioli 2002; Venkatachalam *et al.* 2013). Latex in *Hevea brasiliensis* trunk is transported *via* a network of connected vessels, and it is harvested easily by a special incision on its trunk (Arias and van Dijk 2019). Malaysia has approximately 1,021,540 hectares of rubber plantations that are capable of producing more than 120,000 tons of rubber seeds annually (Gimbun *et al.* 2013). Table 1 compares the different values of rubber seed yield in some Asian countries. Rubber seed is an abundant natural by-product in rubber plantations, where the main product is raw rubber. Malaysia is one of the largest rubber producers in the world, and rubber seed is considered agricultural waste (Hameed and Daud 2008). One dehiscent rubber fruit comprises four seeds, which fall to the ground when the fruit harvests and splits (Nwokolo 1996). Each tree yields approximately 800 seeds twice per annum, and one plantation produces 500 to 2000 kg of seed per hectare every year (Onoji *et al*. 2016; Cheah *et al*. 2017; Yubao *et al*. 2017).

Table 1. Estimated Yield of Rubber Seed in some parts of Asia

Country or Region	Estimated Average Rubber Seed Yield	Reference
Malaysia	500 kg/ha yr	Cheah *et al.* 2017
Indonesia	5 million tons/ yr	Ulfah *et al.* 2018
China	2000 kg/ha yr	Yubao *et al*. 2017

Rubber seed is an ovoid-shaped and light-weighted substance that weighs approximately three to six grams, depending on age of the seed and moisture content (Shafiq and Ismail 2021). A fresh rubber seed is constituted of 35% shell, 40% kernel, and 25% moisture (Onoji *et al.* 2016). Both shell and kernel consist of organic substituents, where the rubber seed shell (RSS) is mainly composed of ash (0.82%), lignin (2.98%), hemicellulose (24.56%), and cellulose (71.64%) (Ekebafe *et al.* 2010). The rubber seed kernel (RSK) is made up of moisture, protein, fat, ash, and carbohydrate (Chanjula *et al.* 2010). Hassan *et al.* (2014) reported the trace amount of cellulose content that is made up of 3.6% extractives, 26.9% hemicellulose, and 69.5% cellulose.

Main Usage

Both rubber seed shell (RSS) and rubber seed kernel (RSK) have their own dominant area of uses due to various natural compositions. However, rubber seed as a whole contains sufficient nutrients as food for human and animals. With a protein content of 17.41 to 27 g per 100 g of seed, consumption of 300 g of rubber seeds daily would provide sufficient protein intake for an adult (56 g for males and 46 g for females) (Eka *et al.* 2010). Furthermore, a high amount of minerals and fat justifies the potential use of rubber seed as food. However, the discovery of toxic cyanogenetic glucoside in rubber seed may disqualify its used as a food source. Fortuna and co-workers (2015) mentioned that fresh rubber seeds can contain up to 186 ppm of cyanogenic glycoside, which is known as Linamarin. Linamarin can be hydrolyzed to produce glucose, acetone cyanohydrin, and hydrogen cyanide (Fortuna *et al*. 2015; Bolarinwa *et al*. 2016). Nevertheless, from the FTIR analysis, no cyanide (CN) functional group peak appeared in rubber seed oil (Salimon *et al.* 2012). Despite the toxic content, boiled and drained rubber seed are consumed by indigenous peoples in the Amazon Valley of South America without any health effects (Eka *et al.* 2010). The hydrogen cyanide content can be lowered by storing the rubber seed at room temperature for two months (Narahari and Kothandaraman 1983). Selle *et al.* (1983) reported that the cyanide content in the rubber seed can be effectively reduced by soaking the seeds in water for 20 hours, followed by one hour of cooking.

Hassan *et al.* (2014) revealed that most elemental contents in RSK are higher than in RSS as tabulated in Table 2.

Table 2. Elemental Content of Rubber Seed (Hassan *et al.* 2014)

	C	H	N	S	O
RSS	48.8	5.9	1.5	0.1	43.7
RSK	64.5	8.2	3.6	0.3	23.4

Rubber Seed Kernel (RSK): Engineering Applications

Biofuel

Rubber seed kernel is well known for its oil content, with of an oil yield of 33.1 wt% (Hassan *et al.* 2014). The rubber seed kernel can be utilized for its oil content, leading to its usage in rubber-producing countries. The production of biofuel is getting attention for the recent decades due to its sustainable reputation; conversion from fossil fuels to the use of biofuels reduces greenhouse gas emissions (Raman and Mohr 2014). Biodiesel is one of the well-studied biofuels as an alternative for traditional diesel due to its efficient performance that is on par with diesel fuel. Importantly, biodiesel offers a less serious threat to the environment, due to its renewability, biodegradability, and non-toxicity (Mohsin *et al.* 2014; Yesilyurt *et al.* 2020).

Fig. 1. Transesterification of rubber seed oil (RSO) to biodiesel fuel (BDF) (Le *et al.* 2018)

Rubber seed-derived biodiesel was found to be efficient for use as a partial substitute for diesel engines (Ulfah *et al.* 2017). Several methods have been explored to produce biodiesel from rubber seed. Typical biodiesel production employs an esterification or/and transesterification process, where esterification is a process of reaction between alcohol and carboxylic acid such as free fatty acid using an acid catalyst, while transesterification involves a reaction between triglyceride and alcohol, yielding fatty acid methyl ester and alcohol (Kirumakki *et al.* 2006). Figure 1 shows the transesterified biodiesel fuel (BDF) from rubber seeds (Le *et al*. 2018). Wibowo (2013) produced an environmentally friendly high yield biodiesel with controllable density and viscosity by an *in-situ* transesterification that entails the extraction of oil from rubber seed kernel and a reaction with methanol using a sulfuric acid catalyst. Le *et al.* (2018) used a similar method in which the rubber seed oil was (RSO) was esterified and transesterified using fatty acid methyl esters (FAME) as a co-solvent. They revealed that the quality of the derived biodiesel fuel (BDF) with high FAME content met the criteria of the EN14214 (2008) and JIS K2390 (2016) standards (Le *et al.* 2018). These standards outline specific physical and chemical properties and the content of biodiesel fuel required to ensure a good quality of bio-derived fuel for safety, energy efficiency, and transportation (Masjuki *et al.* 2013).

One of the main principal challenges to produce biodiesel from rubber seed kernel is the oil content. Various extraction methods have been used in an attempt to maximize the oil content of RSK, including mechanical press with an absence and presence of solvent and cold percolation. A laboratory-scaled mechanical press only yields about 5.35% of oil (Morshed *et al.* 2011). The cited authors also discovered that the maximum rubber seed oil yield can be extracted when hexane is used as a percolation solvent at a volume of 3 times the rubber seed. They also reported that a periodic solvent and mechanical press method can increase the yield to up to 49% at just 0.8 solvent to seed ratio.

Roschat *et al.* (2017) used a simple solvent extraction method to optimise the oil yield and revealed that only 0.5 v/wt. of hexane produced more oil content compared to other more polar counterparts. This is predominantly due to the non-polarity of triglyceride. It can be only extracted by a non-polar solvent, also yielding less polar free fatty acid (FFA) content. High FFA content is not favourable for transesterification reaction due to the inhibition of biodiesel conversion; therefore, the FFA content in the feedstock should be reduced prior to esterification and transesterification (Seithtanabutara *et al.* 2020). FFA content reported in Roschat *et al*. (2017) (5.2 wt%) is the least by far compared to Morshed *et al*. (2011) (17 wt%) and Ramadhas *et al*. 2005 (45 wt%). This may be caused by the type of solvent used during the oil extraction process. The FFA content in Roschat *et al*. (2017) was further reduced by using heterogenous catalysts (CaO-based coral fragment, disodium metasilicate granule, and CaO-based eggshell). These catalysts recorded high biodiesel yield and high FAME content of 97 to 98%, and a more thermally stable biodiesel compared to the petroleum-based diesel as presented in Fig. 2 (Roschat *et al.* 2017). Petroleum-based oil contains evaporative solvents; meanwhile the high thermal stability of biodiesel is due to the ester compound, giving the biodiesel a high boiling point (Roschat *et al*. 2017).

In a separate work, the high yield of rubber seed oil- derived methyl esters at 96.7% can be achieved by using biowaste (kola nut pod husk) as a heterogenous catalyst (Oladipo and Betiku 2020). The activation of catalytic sites of the calcinated kola nut husk pod responds to a high biofuel yield. Calcination and carbonization processes increase the metallic and catalytic content of biomass, which revealed a high content of alkaline metals such as potassium and calcium (Betiku *et al.* 2019). Similar findings were reported by Dhawane *et al*. (2017), who used carbonized flamboyant pods as a heterogenous catalyst precursor in producing high yield biodiesel from rubber seed oil.

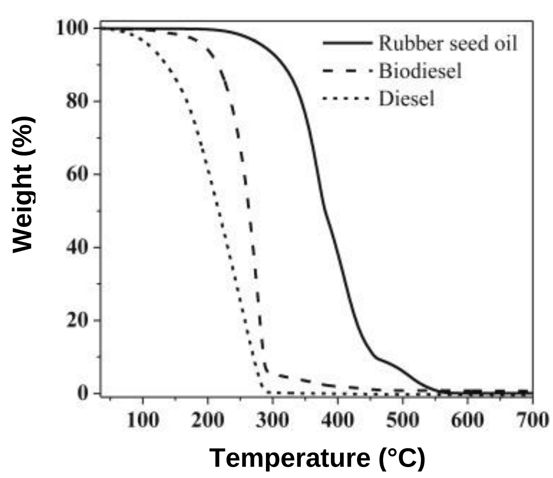

Fig. 2. Thermogram of raw rubber seed oil, diesel, and synthesized biodiesel (Roschat *et al.* 2017, with permission from Elsevier

Plasticizer

The oil content of RSK makes it suitable to be modified as a plasticizer for polymer composites. A plasticizer is a multifunctional additive in polymer (plastic and rubber) products that enhances their flexibility and is used as an aid during processing (Nasruddin and Tri Susanto 2018). Mineral and petroleum-derived oils are the most common precursors or end materials for plasticizers in the rubber industry (Nasruddin and Tri Susanto 2018). The usage of plant-based oil evolved in the early 2000s, steadily replacing synthetic oil predominantly due to its abundance, renewability, and low cost. The oil content in the rubber seed constitutes 52% fatty acids; monounsaturated (oleic 18:1), and polyunsaturated acids such as linoleic 18:2 or linoleic 18:3 carboxylic acids (Joseph *et al.* 2004; Salimon *et al.* 2012). Table 3 tabulates the composition of fatty acid in rubber seed oil (RSO) reported by Joseph *et al.* (2003), Yousif *et al.* (2013), and Jisieike and Betiku (2020). The incorporation of RSO as a plasticizer in acrylonitrile-butadiene rubber (NBR) revealed mechanical properties enhancement which included elongation at break, tear strength, abrasion resistance, and compression set. The elongation at break of the RSO-plasticized NBR rubber was also increased (at 431% compared with only 323% for unplasticized composites) after the sample underwent thermal ageing at 70 °C (Joseph *et al.* 2003). The same group of researchers performed an epoxidation of RSO and discovered that epoxidized RSO-plasticized NBR rubber gained increases in tensile and tear strengths, abrasion resistance, compression set and elongation at break when unaged and aged at 70 °C (Joseph *et al.* 2003).

Table 3. Fatty Acid Content in Rubber Seed Oil

Fatty Acid	Composition (%)		
	Joseph *et al.* (2003)	**Yousif *et al.* (2013)**	**Jisieike *et al.* (2020)**
Palmitic acid	11	9.10 ± 0.06	9.32
Stearic Acid	12	12.63 ± 0.01	11.42
Oleic Acid	17	25.31 ± 0.13	24.95
Linoleic Acid	35	36.31 ± 0.09	33.55
Linolenic Acid	24	15.78 ± 0.18	20.17

RSO and epoxidized-RSO have been used as secondary plasticizers (used with dioctyl phthalate (DOP)) and heat stabilizers in PVC compounds (Joseph *et al.* 2013). DOP is a common plasticizer for PVC, converting rigid plastics into flexible plastic films, profiles, or sheets (Pita *et al.* 2002; Al-Mosawi *et al.* 2018). The incorporation of epoxidized-RSO into a DOP-plasticized PVC compound resulted in an increase in the stabilizing torque during processing. Nevertheless, with epoxidation, RSO does not function well as a secondary plasticizer (Joseph *et al.* 2013). The presence of epoxidized-RSO also increased the thermal degradation time during processing and recorded a high glass transition temperature (T_g) of the compounded PVC.

Rubber Seed Shell (RSS): Engineering Applications

Composite materials

Polymer composites using natural-based fillers have inherent properties that are on par with man-made fillers. Transformation towards a sustainable lifestyle enables wide opportunities for natural-filled composites in producing eco-friendly plastic, replacing synthetic fibers composites such as carbon and glass fibers (Shafiq and Ismail 2021). Natural fillers exist in fibrous form and are abundantly available. Typical examples include sisal, jute, kenaf, bamboo, banana, hemp, straw, rice husk, and empty fruit bunch (Taj *et al*. 2007). The practicability of these naturally sourced fillers in polymer composites is predominantly due to their lignocelluloses content, which can be treated and modified to provide a reinforcing effect on the composites or making the composites susceptible to environmental conditions (Jagadeesh *et al*. 2020). Table 4 compares the lignocellulosic content of RSS, and Table 5 tabulates various kinds of polymer matrices used along with RSS as a reinforcing filler. Rubber seed shell (RSS) was incorporated in polyolefins to produce natural-filled polymer composites (Shafiq and Ismail 2021). The aspect ratio of the filler is one of the major contributing factors on the properties development of natural-filled polymer composites. There is no specific aspect ratio of RSS reported yet, but many works done indicated that the ground RSS were sieved down to 150 mesh or about 100 microns (Ekebafe *et al*. 2010; Xu *et al*. 2016; Ekebafe *et al*. 2017).

Table 4. Composition of RSS (Ekebafe *et al*. 2010)

Composition	Amount (%)
Ash	0.82
Lignin	2.98
Hemicellulose	24.56
Cellulose	71.64

Table 5. Rubber Seed Shell as a Filler in Polymer Composites

Polymer matrix	Characteristic of RSS used	Properties	Suggested Applications	References
Polypropylene and High-Density Polyethylene	Ground powder of average size of 100 µm	Tensile, flexural, impact thermal and water absorption	Environmentally friendly daily used products	Ismail and Shafiq 2014
High-Density Polyethylene	Treated in a superheating vapour environment with a range of size from 60- 120 mesh size	Flexural, tensile, thermal and water absorption	Biocomposites for non-structural decorative products	Xu *et al.* 2016
Natural rubber	Carbonised at up to 800 °C with an average size of 150 µm	Tensile, flex fatigue, abrasion, hardness, compression	Structural applications	Ekebafe *et al.* 2010
Starch foam	Milled at up to 600 rpm for up to 60 mins with a size range from 50-200 µm	Flexural and thermal	Bio based packaging	Chaireh *et al.* 2019

When the mechanical, thermal, and water absorption properties of RSS-filled polyolefin composites were investigated, these properties were found to be within a similar range to other types of natural-filled composites (Ismail and Shafiq 2014). Xu *et al*. (2016) performed a thermal modification on RSS in high-density polyethylene (HDPE) composites by superheated vapour treatment. At an optimum superheated vapour temperature of 200 °C, the flexural and tensile strengths of the composites were significantly increased, and strong interfacial bonding between HDPE and RSS was revealed from the scanning electron microscope (SEM) micrographs. The same sample also portrayed an excellent water resistivity and thermal stability owing to the enhanced interfacial bonding (Xu *et al.* 2016). Ekebafe *et al*. (2010) discovered the enhancement of physicomechanical properties of natural rubber vulcanisates using optimized rubber seed shell as a filler. The rubber seed shell was optimized at high temperatures, and the rubber vulcanisates exhibited superior mechanical properties when optimized at 600 °C. The hardness, abrasion resistance, and modulus at 100% were recorded nearly equal to N330 carbon black vulcanisates at most filler loadings (Ekebafe *et al.* 2010). Chaireh *et al.* (2019) used milled rubber seed shell as a filler in starch foam and reported that the optimum concentration of 5.0 wt.% of milled RSS (at 600 rpm) produced a starch foam with superior flexural properties. Starch foam with milled RSS (at 600 rpm) had a low density and narrow foam cell distribution owing to optimized interactions between RSS and starch arising from the large surface interfacial area of milled RSS (Chaireh *et al.* 2019).

Carbon derivation

Activated carbon filtration is an effective, low cost, and widely used technology to adsorb organic and inorganic contaminants in wastewater water from taps and wells (Sigworth and Smith 1972; Mohan *et al.* 2006). The adsorption properties of activated carbon are determined by the surface characteristics and pore sizes of the filters, capable of removing over 99% of the total suspended solids in water (Shen *et al.* 2011; San-Pedro *et al.* 2020). Activated carbon efficiently removes chemical residues such as phenol, lead, copper, and reactive dyes from water (Hameed and Rahman 2008; Imamoglu and Tekir 2008: Santhy and Selvapathy 2006). Activated carbon is produced from carbonaceous substances *via* chemical and physical means. The raw materials used to produce activated carbon include coal, coconut shells, wood, and lignocellulosic materials (Chingombe *et al*. 2005; Sodeinde 2012; Nor *et al*. 2013). Rubber seed shell is a useful feedstock for activated content production due to its high carbon content.

Numerous works have been demonstrated to develop and optimize the applicability of activated carbon derived from rubber seed shell in the recent decade. Okieimen *et al*. (2005) optimized the function of activated carbon from rubber seed shell as a sequestrant for heavy metals and organic compounds in water. The affinity of the metal ions onto the biomass-derived activated carbon determines the efficiency of natural resources to remove heavy metals in water (Godwin *et al*. 2019). This depends on the availability of the sorption sites and interaction between carbon and the metal ions. The pH of the slurry is vital to favor metal adsorption on the carbon surfaces (Yang *et al*. 2019). This is predominantly contributed by the carbon surface acidity (Sato *et al.* 2007). Carbon derived from physical activation tended to raise the pH to more than 6.5, making precipitation of metals exist as hydroxides (Okieimen *et al.* 2005). Meanwhile, acid-activated carbon would normally reduce the pH, making the carbon surface acidic (Girgis *et al.* 1994), and not favorable to attract the positively-charged metal ions. Carbon derived from RSS possess a pH of around 7.38 with an efficiency of zinc(II) adsorption of 44% and maximum binding capacity of 0.43 mmol/g (Okieimen *et al.* 2005).

Chemical activation of RSS-derived carbon using potassium hydroxide was shown to impart characteristics of good liquid and gas absorption in a fluid. The characteristics include optimised surface area and pore volume of 1290 m^2/g and 0.81 cm^3, respectively (Azry and Ahmad 2012). Yan *et al.* (2019) investigated the characteristics of physically activated carbons derived from rubber seed shell using carbon dioxide for the removal of phenol-laden contaminants in water. The physical activation was performed at 900 °C for

30 and 90 min, with the materials named AC1 and AC2, respectively. FTIR analysis revealed that the derived activated carbon and raw RSS had similar FTIR spectrum trends. AC2 absorbed more phenols than AC1 with maximum adsorption capacities recorded at 262 mg/g and 108 mg/g for AC2 and AC1, respectively (Yan *et al.* 2019).

Azani *et al*. (2019) used activated carbon derived from RSS *via* chemical process using potassium hydroxide for the removal of methylene blue dye in aqueous-based solutions. Chemically treated activated carbon derived from RSS had an average pore diameter of 3.35 nm and was able to remove 99% of methylene blue dye in acidic and basic media at a dosage of 100 mg/L (Azani *et al*. 2019). It was similarly reported that a large surface area of carbonized RSS resulted at a carbonization temperature of 500 °C, and the product was able to absorb crystal violet dye in water with a maximum adsorption capacity of 97.93% at 75 min. The reported adsorption data were in an agreement to four adsorption isotherms (Freundlich, Langmuir, Temkin, and Frumkin) (Anegbe *et al.* 2020). In separate work, RSS was impregnated with malic acid to produce activated carbon to capture carbon dioxide (Borhan *et al.* 2020). The ultimate analysis revealed that the carbon content in activated RSS was higher compared to raw RSS, recorded at 73.8% as opposed to only 59.4% in raw RSS. The carbon dioxide uptake for activated RSS was 2.26 mmol/g, which was among the highest and at par compared to other derived counterparts reported in their work (Borhan *et al*. 2020).

Carbon-derived rubber seed shell *via* pyrolysis was used along with reduced graphene oxide and poly(vinyl alcohol) to investigate their potential as electrode materials (Md Disa *et al.* 2020). As depicted in Fig. 3, the surface of the carbon derived from RSS is composed of tunnel-shaped pores, which enable greater active sites for accumulation of ions and the formation of electrochemical double layer for high-density energy storage. The addition of reduced graphene oxide in the system improved the performance of the supercapacitor owing to the formation of multilayers and sheet-like morphology (Md Disa *et al.* 2020).

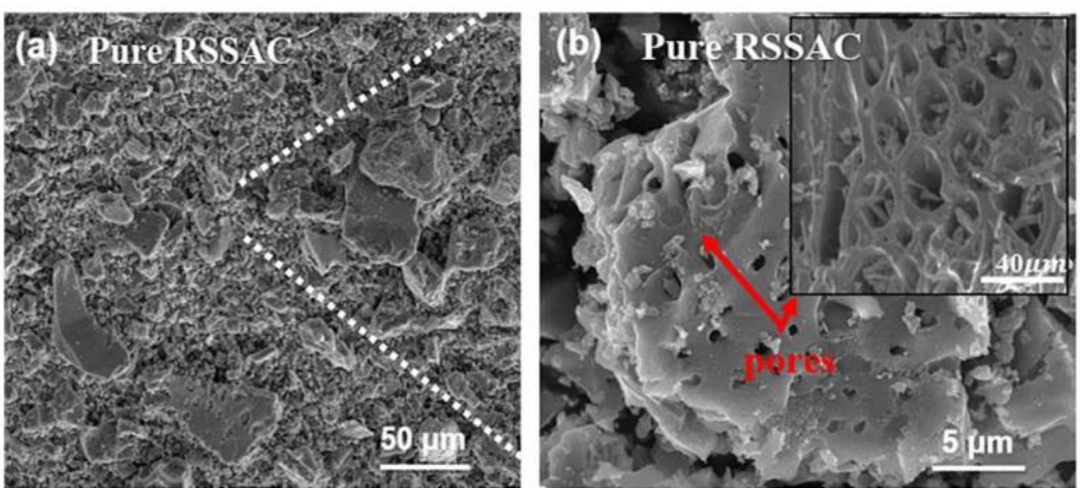

Fig. 3. Tunnel-shaped pores of carbon derived RSS (Md Disa *et al.* 2020)

CONCLUSIONS AND FUTURE PROSPECTS

Rubber seed is an abundant renewable resource that has many uses for critical and complex polymer engineering and technology applications. Both rubber seed kernel and shell were revealed as functional supplies for various unique uses due to specific contents of each element constitute to certain applications. Rubber seed is a newly appreciated non-toxic natural resource, and it has extensive potential in many sophisticated applications for a greener and more sustainable future.

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