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REVIEW OF NATURAL FIBER REINFORCED ELASTOMER COMPOSITES

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ABSTRACT

This paper is a review on mechanical characteristics of natural fibers reinforced elastomers (both thermoplastics and thermosets). Increasing environmental concerns and reduction of petroleum resources attracts researchers attention to new green eco-friendly materials. To solve these environmental related issues, cellulosic fibers are used as reinforcement in composite materials. These days natural fibers are at the center of attention as a replacement for synthetic fibers like glass, carbon, and aramid fibers due to their low cost, satisfactory mechanical properties, high specific strength, renewable resources usage and biodegradability. The hydrophilic property of natural fibers decreases their compatibility with the elastomeric matrix during composite fabrication leading to the poor fiber-matrix adhesion. This causes low mechanical properties which is one of the disadvantages of green composites. Many researches have been done modifying fiber surface to enhance interfacial adhesion between filler particles and elastomeric matrix, as well as their dispersion in the matrix, which can significantly affect mechanical properties of the composites. Different chemical and physical treatments are applied to improve fiber/matrix interlocking.

1 Introduction

Among different polymer, elastomers are common amorphous polymers containing polymeric chains, which are joined in a network structure possess high degree of flexibility and deformability. Elastomers have good damping properties making them appropriate in energy dissipation. These appropriate char-

acteristics make elastomers desired for applications in different field like automobile tires and conveyor belts, adhesives, aircraft industry, etc [1]. Elastomers have to be crosslinked to get rubber elasticity, and there are some elastomers demonstrating hyperplastic characteristics and behaving like thermoplastics [2]. As the pure elastomers (rubbers and thermoplastics elastomers) demonstrate little tracking and erosion resistance, some properties of elastomers should be improved to extend service life and improve service effect. Adding filler into elastomers can enhance particular properties and also reduce costs [3]. Different studies have been done by using different fillers like SiO_2 , TiO_2 , carbon black, polyester fiber, and ultra-fine calcium carbonate to induce mechanical, electrical and thermal conductivities of elastomers [4]. However, few studies have been done on the use of organic fillers to reinforce elastomers.

Over the past few years there is an increasing demand for products made from renewable and sustainable non-petroleum-based resources. A wide range of natural fibers are utilized instead of synthetic and glass fiber in biocomposites. Although mechanical properties of these green composites are not the same as glass fiber reinforced composites, their modest mechanical properties and biodegradability make them appropriate for applications in housing sectors, secondary and tertiary structures, automotive sector (e.g. door panels, instrument panels, arm-rests), textile (geotextiles and nonwoven textiles), packing materials, entertainment accessories (archery bows, golf clubs and boat hulls), etc [5]. Natural grown fibers like hemp, flax or jute are more of interest, particularly as a replacement of glass fibers. These natural fibers are low cost, have better stiffness per unite weight, and have a lower impact on the environment. How-

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TABLE 1. Mechanical properties of typical elastomers used in natural fiber composites fabrication [9]

Elastomers	Durometer (ShoreA)	Tensile (MPa)	Elongation at break%
Ethylene propylene diene	40-90	13.78	400
Styrene butadiene rubber	40-90	17.23	500
Natural rubber	30-90	24.13	600
Butyl	40-80	17.23	800
Nitrile	40-90	20.68	400
Hydrogenated Nitrile	45-90	24.13	400
Polychloroprene	40-90	17.23	500
Fluoroelastomers	55-90	17.23	200
Silicone	40-80	10.34	1100
Urethane	60-95	48.26	800
Epychlorohydrin	40-80	13.78	500

ever, the applications of natural fibers have been mainly limited to upholstery applications [6]. This is because the hydrophilic property of natural fibers decreases their compatibility with the non-polar elastomeric matrix leading to the poor fiber-matrix adhesion. This causes low mechanical properties which is one of the disadvantages of natural fibers. Therefore, many researches have been done modifying filler surface to enhance interfacial adhesion between filler particles and polymer macromolecules as well as their dispersion in the polymer matrix [5, 7]. Different chemical and physical fibers surface treatment have been used to improve fiber/matrix interfacial adhesion [8]. This study reviews the effect of different physical and chemical treatments on fiber dispersion in matrix and fiber/matrix interface. Moreover, the impression of natural fiber loading on mechanical and dynamic mechanical properties of biocomposites based on natural fibers/elastomer is reported.

2 Composites of Elastomer and Natural Fibers

2.1 Material properties of elastomers

Elastomers have been developed to provide a wide range of applications. These elastomers differ in their properties like their elasticity, temperature range, strength, and compatibility. Two principle types of elastomers are thermoset and thermoplastic elastomers. Generally, thermoset elastomers have the capability to provide both flexibility and durability, which makes them an appropriate material for a wide variety of industrial applications. Table 1 lists the most popular elastomers with their material properties, where durometer measures the hardness of a

TABLE 2. Material properties of natural fibers used in reinforcement.

Natural Fibers	Tensile (MPa)	E (GPa)	Elongation at break (%)	Ref
Jute	200-600	15-45	1.3	[10]
Bamboo	200-500	15-30	1.4	[11]
Flax	800-1500	60-80	1.2-1.6	[11]
Hemp	550-900	70	1.6	[11]
Sisal	600-800	38	2-3	[11]
Kenaf	930	53	1.6	[12]
Pineapple	200-1000	60-80	2.4	[12]
Ramie	500	44	2	[13]
Coir	220	6	15-25	[13]

material (the higher the harder [14]) and elongation at break is the maximum amount of length the material can be stretched before it breaks with the tensile force. Most materials are in the range of 100-600% while some can go more than 1000% [15]. To highlight a few [16, 17], ethylene propylene is a thermoset elastomer with excellent ozone/weathering resistance, excellent hot water and steam resistance, good resistance to inorganic and polar organic chemicals, but has low resistance to hydrocarbons. Styrene butadiene is usually utilized in car and light vehicle tyres, shoes soles and roll covering, but it has a low strength without reinforcement. Natural rubber has high resilience and tensile strength, good abrasion resistance, and low cost, but has poor oil resistance and weathering resistance. Butyl has low permeability to gases which make them an appropriate material to be used for inner tubes. Moreover, this material has high damping at ambient temperature, Silicone is also a thermoset elastomer with moderate physical properties, good electrical resistance, and high temperature capabilities. Some of them are affected by moisture. Due to its high elongation capability, it is widely utilized in different fields like pharmaceutical, medical, wire and cable, automotive and aerospace.

2.2 Material properties of natural fibers

Elastomers have excellent resilience property, but it is relatively weak in strength. Therefore, it is commonly reinforced by glass fibers to produce composite material, and nowadays there is a growing interest to use natural fibers. The composite characteristics are affected directly by the fibers properties. Natural fibers are divided into 6 categories as follow:

1. bast fibers (jute, flax, hemp, ramie and kenaf);
2. leaf fibers (abaca, sisal and pineapple);
3. seed fibers (coir, cotton and kapok);

4. core fibers (kenaf, hemp and jute);
5. grass and reed fibers (wheat, corn and rice); and
6. other types (wood and roots).

Table 2 provides the information of the most common natural fibers. The fibers have a tensile strength at a level of hundred or thousand MPa, which is 10 – 100 times higher than the elastomers. However, they have very low elongation before breaking, which is just around 2 – 3% extension of original length for most fibers. Natural fibers may not be as strong as glass fibers (e.g., 2400 MPa in tensile strength [18]), but their stiffness are comparable to glass fibers. In addition, natural fibers are green and much lighter than glass fibers. However, natural fibers properties are highly variable due to the conditions of growth, and thus the values of material properties may vary much even for the same fiber.

2.3 Composites and fabrication challenges

Table 1 and 2 show that natural fibers have higher tensile strength and stiffness compared with typical elastomers that used as the matrices. Therefore, natural fibers are used as reinforcement for elastomers [19]. If the interface compatibly between fibers and matrices are desirable, the load will be transferred from matrices to fiber which results in a stronger material [20, 21]. One of the most important issue in elastomer-based composites fabrication is that fibers should be well dispersed in matrix. To make an appropriate interaction between elastomer matrix and fiber, physical and chemical linkage are required. Different parameters can affect fiber matrix interaction like fiber size, morphology and surface activity [2]. The inherent hydrophilic nature of natural fibers and non-polar characteristics of elastomeric matrix can also affect fiber/matrix interaction, and led to non-uniformed dispersion of fibers in matrix. Another factor that can affect interfacial compatibility is that natural fibers absorb moisture leading to poor interaction between fibers and matrix that caused by swelling and voids. The fiber/matrix interaction depends on the lignin, hemicellulose, waxes and other non-cellulose fiber sections. These non-cellulose sections avoid fiber/matrix adhesion and absorb moisture leading to fiber agglomeration trough the matrix [22–24]. To address these challenges, different surface treatments have been attempted to make the physical and chemical linkage between fibers and elastomeric matrix, which are presented in next section.

3 Natural Fiber Treatment and Characterization

Different chemical treatments are applied to enhance interface interaction between the reinforcement and matrix. Many efforts have been done to modify natural fiber surface such that the interfacial adhesion between fibers and matrices are improved. There are review papers on different physical and chemical treatment for natural fibers including corona treatment, plasma treat-

ment, heat treatment, coupling agents (silane treatment), and mercerization [25]. Here, the common methods which mostly used in the fabrication of natural-fibers-reinforced elastomers are mentioned.

3.1 Alkaline treatment

One of the common approaches which is applied in modifying the natural fiber surface to lower surface tension and to improve interfacial adhesion between natural fibers and polymer is alkali treatment. This method increases fibers surface roughness and thus improve the mechanical interlocking between fibers and polymer macromolecules [5, 26, 27]. Different studies have been done on effect of alkaline treatment on fibers matrix interaction. Gu [28] studied the effect of NaOH treatment on coir fiber surfaces. The study revealed that NaOH treatment can remove all the impurities and make the surface rougher which increases mechanical bonding between fiber and matrix.

3.2 Silane treatment

Silane coupling agents are widely used due to their wide availability. Moreover, silane has alkoxy silane groups at one end that hydrolyze in water, and produce silanol which can react with OH reach surface. Silane as a coupling agent improve the degree of cross-linking in the interface region, and increase fiber surface area for the optimization of fiber resin reinforcement [29–31]. Debasish et al. [19] studied the effect of alkaline treatment of grass fiber on mechanical properties of the composites based on natural rubber. The results revealed that incorporation of treated grass fibers in natural rubber increased the tensile strength and elongation at break of the composites. Jacob et al. [26] did study on mechanical properties of the sisal/oil palm reinforced natural rubber composites. It was shown that composites containing treated fibers have higher tensile strength compared with the untreated one.

3.3 FTIR and SEM characterization

Fourier Transform Infrared Spectroscopy (FTIR) is an effective analytical method to identify chemical functional groups interacting within natural fibers. FTIR is used to give information about covalent bonding between fibers and matrix after fibers silanization [32]. The chemical structure of the untreated and treated fibers are studied using this test. Surface microscopic examinations are carried out using a Scanning Electron Microscope (SEM). SEM provide an useful mean for industry to study failure issues, and identify the interaction between filler and substrate [33]. SEM characterization is used to study the changes in fiber morphology, so that fine details can be measured and assessed via image analysis [34]. Researchers have been utilizing FTIR and SEM to investigate the effect of silane and alkaline treatments and to make the comparison between treated

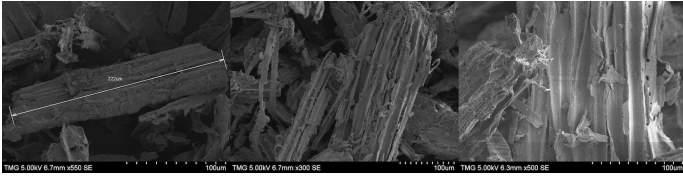


FIGURE 1. (a) Surface of the hemp fiber. (b) Surface of the hemp fiber after alkaline treatment. (c) Surface of the hemp fiber after silane treatment.

and untreated fibers. Sepe et al. [35] studied influence of chemical treatment on mechanical properties of reinforced composites. The FTIR results revealed that before treatments, the spectrum shows the peaks that are related to the main components of fibers (cellulose, hemicellulose, and lignin). The chemical composition of the fibers is modified after the chemical treatments. The identified peaks are decreased after treatment. This phenomenon is due to the removal of a part of the hemicellulose from the fibers surface. Moreover, it is reported that FTIR can demonstrate the reaction between silane coupling agent and fiber surface. As a result of silane treatment, new absorption peaks are appeared which are specific to the silane coupling agent. As it was mentioned, the prehydrolyzed silane is reacted with the hydroxyl groups on the fiber surface during silane treatment. Therefore, after silane treatment, the FTIR results show the specific peak assigned to the vibrations of Si-O-cellulose [36]. The morphological properties of natural fibers after and before treatment are studied using SEM. The image analysis of natural fiber after alkali treatment demonstrates that after alkali treatment all the waxy residual are removed which is led to higher surface hardness. The higher surface hardness, the more interfacial compatibility between fibers and matrix. SEM images demonstrate the effect of alkaline and silane treatment on morphological properties and the interaction between fibers and matrices [37]. The SEM images are shown in Fig.1 to demonstrate the effect of treatments on fiber surface. The use of alkaline and silane treatments can make the surface rougher to improve mechanical interlocking between fiber and matrix.

4 Fabrication Techniques

Table 3 shows different processing techniques which have been used to fabricate elastomeric composites reinforced by natural fibers. This table clarified that the common method to fabricate composites based on thermoset elastomers is using of two-roll laboratory mill. In the calendaring process, rubber is masticated in a huge vat and combined with other additives. The resulting material is compressed and flattened by passing through the series of rollers. The fibers are fed in the rubbery sheet once the slab becomes thinner. The most important drawbacks of this method are size and cost of mixing and calendaring equipment

which prevent firms and university from using such process [48]. By utilizing mixing devices like internal mixer, extruder, and two-roll mill, thermoplastic elastomers can be combined in the molten state. The disadvantage with this technique is the poor dispersion due to the high viscosity of material that is increased by incorporation of filler. One of the recommended solution for this problem is the utilization of higher shear mixing to overcome the viscosity of the material, however this method can damage the filler structure which can affect composite properties [49]. Besides the processing techniques, different conditions can also affect the resultant material properties, some of which are discussed like fiber loading and fibers surface treatment.

4.1 Effect of fiber loading

Intuitively, one can load more fibers into the matrix to keep increasing the strength of composite. However, its proven that strength of the composites could decrease by increasing the fiber loading [50]. Ismail et al. [39] investigated the effect of fiber loading and bonding agent on mechanical properties of the composites based on bamboo fibers and natural rubber. The results shown that by increasing fiber loading in natural rubber composites with different sizes of bamboo fiber, the strength decreased while the hardness and tensile modulus increased. El-Shekeil et al. [51] studied the effect of fiber loading on mechanical properties of cocoa pod husk fibers reinforced thermoplastic polyurethane composites. The results revealed that increasing fiber loading increases tensile strength, modulus, and flexural strength, but decreases tensile strain, and impact strength. A similar trend was observed in other researches [52, 53]. El-Shekeil et al. [54] investigated the effect of fiber content on mechanical properties of composites based on kenaf fiber reinforced thermoplastic polyurethane. Different fiber loadings (20%, 30%, 40% and 50% weight) were prepared. A 30% fiber loading demonstrated the best tensile strength. Moreover, the results revealed modulus increase by increasing fiber content, while strain deteriorated with increasing fiber loading. Karthikeyan [47] did study on influence of fiber content on the mechanical properties of silicone. It was demonstrated that the incorporation of fibers increases tensile strength of composites for 10%, 15%, and 20% fiber loading. For the composites which were incorporated 20% fibers, there was an increase in tensile strength by 25%.

4.2 Effect of chemical treatment and bonding agent

As it was mentioned to achieve good fiber reinforcement, good interfacial compatibility is required which depends on the surface topology of the fibers. Different studies have been done to investigate the effect of chemical treatment on mechanical properties. Mathew et al. [55] fabricated short-isora-fiber-reinforced natural rubber composites. It was observed that fiber treatment significantly improved mechanical properties (e.g., tensile modulus, tensile strength, tear strength) of the designed

TABLE 3. Different processing techniques to fabricate natural fibers reinforced elastomers

Fibers	Type of fiber	Type of matrix	Processing techniques	Ref
Coir fiber			The composite materials were prepared on a two-roll laboratory mill. The samples were milled for sufficient time to disperse the fibers in the matrix.	[38]
Bamboo fiber				[39]
Sisal/oil palm hybrid fiber	Short fiber	Natural rubber		[26]
Pineapple leaf fiber				[40]
Grass fibers				[19]
Pineapple Leaf fiber	Short fiber	Natural rubber by blending with acrylonitrile butadiene rubber	The mixing of the composite components was carried out using a laboratory two-roll mill.	[41]
Sisal fibers	Short fibers	Rubber seed oil-based polyurethane	The fibers were embedded in mould and the polyurethane resin was poured onto the mould and squeeze, and the mould was put in a vacuum chamber for 8 h at 30 C., then the composite was compression moulded at 80 C for 24 h under 3 Mpa pressure.	[42]
Bagasse cellulose whiskers	Nanofiber	Natural rubber	Solvent cast method. The NR matrix was blended with whiskers aqueous suspension using magnetic stirrer to obtain final dry films around 1 mm thick.	[43]
Flax fibers	Short fiber	Ethylene propylene diene rubber	The EPDM rubber was melted using laboratory electrically heated roller mill equipped with a cooling system. After getting uniform mixture fibres were added.	[44]
Kenaf bast fiber	Short fiber	Thermoplastic natural rubber, (TPNR) and polypropylene/ ethylenepropylene dienemonomer (PP/EPDM)	Double melt blending was used to fabricate the composites. After mixing fibers and matrix, samples were prepared using compression molding	[45]
Coconut coir	Short fiber	Natural rubber	Mixing of natural rubber and fibres was done using a co-rotating twin screw extruder. The material was rolled mill after extruding. Composites samples were prepared by hot press	[46]
Sisal Fiber	Short fiber	Silicone	The fibers were mixed with laboratory mixer (rotor speed :50rpm). After dispersing fiber in matrix uniformly, the samples were prepared using compression molding	[47]

composites. Fiber treatment improves mechanical properties due to induced covalent bonds that avoid debonding at fiber matrix interface [56]. It has been proven that fiber surface modification can affect mechanical properties and material characteristics. Ismail et al. [56] showed that use of bonding agent prolonged cur-

ing time of natural rubber, and increasing oil palm fiber loading increase mechanical properties.

4.3 3D printing of natural fiber composites

Recently, there is an increasing demand for designing printable polymer composites with high functionalities. One of the famous methods to fabricate the component with complex geometries and desirable mechanical properties is the use of three-dimensional (3D) printing. Different from traditional manufacturing methods, this additive paradigm offers various benefits like cost effective, increased productivity, high accuracy, enhanced collaboration and customized geometry [57, 58]. Extrusion process technique has been applied for printing liquid silicone rubber (Fig. 2). This technique provides myriad advantages in case of controlling porosity of the products. One of the procedure which has been applied to print UV curable polymers like polyurethane and acrylic-based polymers is stereolithography (SLA) [58].

One of the critical point in composites 3D printing is choosing suitable matrix material. The elastomers which can be used as matrix are silicone rubber, polyurethane, natural rubber, vinyl rubber, and heat curable silicone rubber which is known as the typical printable elastomer [59, 60]. Few studies have been done on 3D printing of magnetorheological elastomers, and composites based on carbon fiber and elastomers. Giffney et al. [61] did study on fabrication of composites based on multi-walled carbon nanotube/silicone rubber. The results demonstrated that the designed composite can be applied in wearable electronics and soft robots. It was proven that use of advanced manufacturing for fabricating composites incorporated fibers can affect mechanical properties of composites. Pitt et al. [62] compared the characteristics of two composites based on wood flour-glass fiber incorporated urea formaldehyde fabricated by different processing techniques. It was shown that 3D printing has a significant effect on fibers orientation leading to higher mechanical properties compare to those fabricated by moulding. The printed samples have less void content compared with moulded one resulting in densification of the paste as it was extruded through the nozzle.

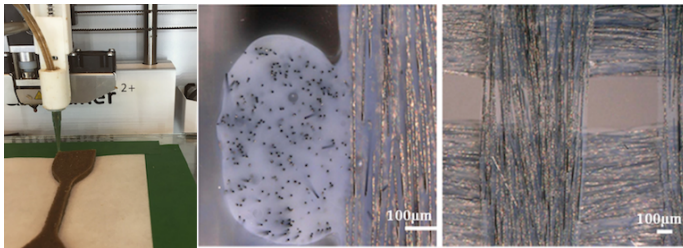


FIGURE 2. Controlling fibers alignment in the polymer matrix using the printer nozzle [63].



FIGURE 3. Components of a BMW sedan fabricated with lignocellulosic fiber reinforced polymer composites [69]

5 Applications

5.1 Automotive and aerospace industries

Polymers have great applications in sound and vibration damping for noise control in automobiles and airplanes (Fig. 3). One of the critical points is the ability of the polymer to convert sound and mechanical vibration energy to heat at the glass transition point [64]. Many studies have been done on damping properties of magnetorheological elastomers [38, 65], but few study have been done on damping characteristics of natural fibers reinforced elastomers [66]. Geethamma et al. [67] studied dynamic mechanical behavior of short coir fiber reinforced natural rubber composites. Dynamic behavior of fiber reinforced composite gives information about damping [68]. Effect of fiber loading and interfacial bonding on damping properties were studied. It was demonstrated that increasing fiber loading increases heat dissipation in the designed composites. These composites show good damping characteristics at high temperature. Incorporation of filler changes matrix properties making it appropriate to be applied in different applications. The incorporation of fibers affects polymer chains mobility leading to shifted Tg with higher temperature and changed dynamic properties [69].

5.2 Biomedical engineering

Recently, elastomeric blends and composites have been utilized in a wide range of biomedical applications including vascular grafts, cardiac assist pumps, blood bags, and implants. These elastomeric composites provide advantages like biocompatibility and biodegradability, and acceptable mechanical properties [70]. Chandramohan et al. [71] developed biocomposites based on natural fibers and epoxy resins, and investigated their desirability as a replacement of orthopaedic alloys. It was revealed that the bio-

composites based on sisal and roselle fibers are appropriate for being applied for both internal and external fixation on human body. As cartilage tissue gets hurt during daily life especially in the elderly, many reviews have been done on the development and testing of composites scaffolds for the tissue engineering of articular cartilage. Many efforts have been done on providing biocomposites based on synthetic fibers, but few studies have been done in case of using natural fibers as a reinforcement for scaffolds. Pei et al. [72] work on hydrogel scaffolds based on silk fibers. This study demonstrated that the reinforced biocomposites have achieved optimal load bearing which is similar to cartilage tissue. The goal of this study was designing biocompatible and biodegradable scaffold that can be utilized to simulate natural tissues.

5.3 Elastomeric resin material for 3D printing

Great electrical and thermal properties of elastomers make them an appropriate material to be used in different fields like soft robotic, smart biomedical and flexible electronics. The challenge with 3D printing elastomers is that this kind of materials need to be heated rapidly in order to be cured or especial chemistry has to be used to cure elastomers. Recently, there is a great interest in 3D printing of silicon rubber and PDMS. 3D printing with elastomers has been attracted researchers attention due to its different advantages for biomodeling including the ability to create complex interior structures, different degrees of hardness which make it appropriate to be utilized in different applications. The capability of silicone to be cut and stitched, making it desirable to be used for pre-surgical planning and testing [73, 74]. Current market of medical applications like prostheses or epithese can be notably multiplied by 3D printing with silicone. 3D printing silicone has a significant impact on providing models with educational functions like the models utilizing at medical schools in biology. The new idea is manufacturing a simple extrudable material that can be placed in a 3D print to directly prototype porous and flexible structures. Therefore, the matrices which are based on elastomers incorporated natural fibers is placed in 3D printer to print different models for different applications.

5.4 Other applications

Thermoplastics elastomers can be applied in different area according to the characteristics that they achieve using natural fibers. These applications include food packaging, footwear, wires and cables, building, and constructions [75]. Sapuan et al. [76] investigated the application of kenaf fiber reinforced polymer composites for portable laptop table. Angellier-Couss et al. [77] studied the utilization of lignocellulosic fibres-based biocomposites materials in food packaging.

6 Conclusion

This paper has shown that different natural fibers can be used in elastomeric composites as reinforcement. The idea is designing sustainable product using renewable recourses. Nowadays, natural fibers like kenaf, flax, jute, hemp, and sisal offering alternative materials to synthetic fiber like glass fiber. These ecofriendly bio-composites which are based on renewable feedstock would play a critical role in material world. Although natural fibers provide many advantages such as low cost, light weight, and biodegradability over glass fiber; they have some disadvantages like, lower impact strength, poor thermal stability, and higher moisture absorption [78]. High moisture absorbing is the major disadvantages with natural fibers which leads to less durability, crack generation, and swelling. Other disadvantages include supply and demand cycles based on product availability and harvest yields, and quality variations based on growing sites and seasonal factors [79]. As it was mentioned in Section 3, different fiber modifications techniques have been done to reduce the water absorption of natural fibers. Recently, some researchers have studied plasma modification of natural fibers to enhance the interface between natural fiber and various matrices [80, 81].

Different processing conditions can affect characteristics of the composite material and make it suitable for some specific applications. However, conventional method to fabricate natural fiber reinforced polymer composites limits their application due to the low mechanical properties. One of the fabrication method providing enhanced mechanical properties is 3D printing of composites material which is under extensive exploration [82]. Currently, there are limited printable polymers including thermoplastic polymers with suitable viscosity, and some photocurable polymers. However, there is critical need for printing soft materials in different field like soft robotics, biomedical engineering (implants, prosthetics, and anatomical models). To improve composites printing technology, it's required to discover desired mixing composition. Moreover, sustainable materials are promising to be developed to decrease material cost and environmental impact [83]. All thermoplastics elastomers can be printed using selective laser sintering (SLS). However, there are limited types of thermoset elastomers which are printable.

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REFERENCES

- [1] Bokobza, L., 2017. "Mechanical and electrical properties of elastomer nanocomposites based on different carbon nanomaterials". *C*, 3(2).

- [2] Pazat, A., Barrs, C., Bruno, F., Janin, C., and Beyou, E., 2018. "Preparation and properties of elastomer composites containing graphene-based fillers: A review". *Polymer Reviews*, **0**(0), pp. 1–41.
- [3] Momen, G., and Farzaneh, M., 2011. "Survey of micro/nano filler use to improve silicone rubber for outdoor insulators". *Rev. Adv. Mater. Sci.*, **27**(1), pp. 1–13.
- [4] Peng, Z., Feng, C., Luo, Y., Li, Y., and Kong, L. X., 2010. "Self-assembled natural rubber/multi-walled carbon nanotube composites using latex compounding techniques". *Carbon*, **48**(15), pp. 4497 – 4503.
- [5] Asha, A. B., Benozir, A., Sharif, A., and Hoque, M. E., 2017. "Interface interaction of jute fiber reinforced pla biocomposites for potential applications". In *Green Biocomposites*. Springer, pp. 285–307.
- [6] Bledzki, A. K., Sperber, V. E., and Faruk, O., 2002. *Natural and wood fibre reinforcement in polymers*, Vol. 13. iSmithers Rapra Publishing.
- [7] Brahmakumar, M., Pavithran, C., and Pillai, R., 2005. "Coconut fibre reinforced polyethylene composites: effect of natural waxy surface layer of the fibre on fibre/matrix interfacial bonding and strength of composites". *Composites Science and Technology*, **65**(3), pp. 563 – 569. JNC13-AMAC-Strasbourg.
- [8] Karthikeyan, and Rajasekaran, 2017. "Analysis of natural fiber orientation in polymer composites produced by injection molding process". PhD thesis, University of Toronto (Canada).
- [9] Hanhi, K., Poikelisp, M., and Tiril, H., 2007. *ELASTOMERIC MATERIALS*.
- [10] Okubo, K., Fujii, T., and Yamamoto, Y., 2004. "Development of bamboo-based polymer composites and their mechanical properties". *Composites Part A: Applied Science and Manufacturing*, **35**(3), pp. 377 – 383.
- [11] Zhang, Y., Li, Y., Ma, H., and Yu, T., 2013. "Tensile and interfacial properties of unidirectional flax/glass fiber reinforced hybrid composites". *Composites Science and Technology*, **88**, pp. 172 – 177.
- [12] Saba, N., Paridah, M. T., and Jawaid, M., 2015. "Mechanical properties of kenaf fibre reinforced polymer composite: A review". *Construction and Building Materials*, **76**, pp. 87 – 96.
- [13] yan Cheung, H., po Ho, M., tak Lau, K., Cardona, F., and Hui, D., 2009. "Natural fibre-reinforced composites for bioengineering and environmental engineering applications". *Composites Part B: Engineering*, **40**(7), pp. 655 – 663.
- [14] Ponte, E., 2017. Shore hardness and soft tpes. <https://www.teknorapex.com/thermoplastic-elastomers-and-measuring-shore-hardness-chart>.
- [15] Hickman, J., 2001. Rubbers and elastomers - an introduction. <https://www.azom.com/article.aspx?ArticleID=317>.
- [16] Barhorst, B., President, V., and Corporation, F., 2016. 12 commonly used elastomers for molded rubber applications: Part 1 general purpose elastomers. <http://www.flexan.com/blog/12-commonly-used-elastomers-for-molded-rubber-applications-part-1-general-purpose-elastomers>.
- [17] Walker, J., 2016. Elastomers elastomer engineering guide. <https://www.jameswalker.biz/de/pdfdocs/148-elastomer-engineering-guide>.
- [18] Wambua, P., Ivens, J., and Verpoest, I., 2003. "Natural fibres: can they replace glass in fibre reinforced plastics?". *Composites Science and Technology*, **63**(9), pp. 1259 – 1264. Eco-Composites.
- [19] De, D., De, D., and Adhikari, B., 2006. "Curing characteristics and mechanical properties of alkali-treated grass-fiber-filled natural rubber composites and effects of bonding agent". *Journal of applied polymer science*, **101**(5), pp. 3151–3160.
- [20] Malkapuram, R., Kumar, V., and Negi, Y. S., 2009. "Recent development in natural fiber reinforced polypropylene composites". *Journal of Reinforced Plastics and Composites*, **28**(10), pp. 1169–1189.
- [21] Holbery, J., and Houston, D., 2006. "Natural-fiber-reinforced polymer composites in automotive applications". *JOM*, **58**(11), pp. 80–86.
- [22] Cisneros-Lopez, E. O., Gonzalez-Lopez, M., Perez-Fonseca, A. A., Gonzalez-Nunez, R., Rodrigue, D., and RobledoOrtiz, J. O., 2017. "Effect of fiber content and surface treatment on the mechanical properties of natural fiber composites produced by rotomolding". *Composite Interfaces*, **24**(1), pp. 35–53.
- [23] Islam, M. S., Pickering, K. L., and Foreman, N. J., 2010. "Influence of alkali treatment on the interfacial and physico-mechanical properties of industrial hemp fibre reinforced polylactic acid composites". *Composites Part A: Applied Science and Manufacturing*, **41**(5), pp. 596 – 603.
- [24] Shuhimi, F. F., Abdollah, M. F. B., Kalam, M. A., Masjuki, H. H., Ashafie, M., Kamal, S. E. M., and Amiruddin, H., 2017. "Effect of operating parameters and chemical treatment on the tribological performance of natural fiber composites: A review". *Particulate Science and Technology*, **35**(5), pp. 512–524.
- [25] Kalia, S., Kaith, B. S., and Kaur, I., 2009. "Pretreatments of natural fibers and their application as reinforcing material in polymer composites a review". *Polymer Engineering & Science*, **49**(7), pp. 1253–1272.
- [26] Jacob, M., Thomas, S., and Varughese, K., 2004. "Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites". *Composites Science and Technology*, **64**(7), pp. 955–965.
- [27] Karaduman, Y., Onal, L., and Rawal, A., 2015. "Effect of stacking sequence on mechanical properties of hybrid

- flax/jute fibers reinforced thermoplastic composites”. *Polymer Composites*, **36**(12), pp. 2167–2173.
- [28] Gu, H., 2009. “Tensile behaviours of the coir fibre and related composites after naoh treatment”. *Materials & Design*, **30**(9), pp. 3931–3934.
- [29] Huda, M. S., Drzal, L. T., Mohanty, A. K., and Misra, M., 2008. “Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (pla) and kenaf fibers”. *Composites Science and Technology*, **68**(2), pp. 424 – 432.
- [30] Abdelmouleh, M., Boufi, S., Belgacem, M. N., and Dufresne, A., 2007. “Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading”. *Composites Science and Technology*, **67**(7), pp. 1627 – 1639.
- [31] Bisanda, E. T. N., and Ansell, M. P., 1991. “The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites”. *Composites Science and Technology*, **41**(2), pp. 165 – 178.
- [32] Manimaran, P., Senthamaraiannan, P., Sanjay, M., Marichelvam, M., and Jawaid, M., 2018. “Study on characterization of furcraea foetida new natural fiber as composite reinforcement for lightweight applications”. *Carbohydrate Polymers*, **181**, pp. 650 – 658.
- [33] Kavita, S., and Kala, T. F., 2016. “Bamboo fibre analysis by scanning electron microscope study”. *International Journal of Civil Engineering and Technology*, **7**, pp. 234–241.
- [34] Oushabi, A., Sair, S., Hassani, F. O., Abboud, Y., Tanane, O., and Bouari, A. E., 2017. “The effect of alkali treatment on mechanical and morphological and thermal properties of date palm fibers”. *Journal of Chemical Engineering*, **23**, pp. 116–123.
- [35] Sepe, R., Bollino, F., Boccarusso, L., and Caputo, F., 2018. “Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites”. *Composites Part B: Engineering*, **133**, pp. 210 – 217.
- [36] Zhou, F., Cheng, G., and Jiang, B., 2014. “Effect of silane treatment on microstructure of sisal fibers”. *Applied Surface Science*, **292**, pp. 806 – 812.
- [37] Sinha, A. K., Narang, H., and Bhattacharya, S., 2017. “Effect of alkali treatment on surface morphology of abaca fibre”. *Materials Today: Proceedings*, **4**(8), pp. 8993 – 8996.
- [38] Cvek, M., Mrlik, M., Ilkov, M., Mosnek, J., Mnster, L., and Pavlinek, V., 2017. “Synthesis of silicone elastomers containing silyl-based polymer-grafted carbonyl iron particles: An efficient way to improve magnetorheological, damping, and sensing performances”. *Macromolecules*, **50**(5), pp. 2189–2200.
- [39] Ismail, H., Shuhelmy, S., and Edyham, M., 2002. “The effects of a silane coupling agent on curing characteristics and mechanical properties of bamboo fibre filled natural rubber composites”. *European Polymer Journal*, **38**(1), pp. 39–47.
- [40] Pittayavinai, P., Thanawan, S., and Amornsakchai, T., 2016. “Manipulation of mechanical properties of short pineapple leaf fiber reinforced natural rubber composites through variations in cross-link density and carbon black loading”. *Polymer Testing*, **54**, pp. 84 – 89.
- [41] Hariwongsanupab, N., Thanawan, S., Amornsakchai, T., Vallat, M.-F., and Mougín, K., 2017. “Improving the mechanical properties of short pineapple leaf fiber reinforced natural rubber by blending with acrylonitrile butadiene rubber”. *Polymer Testing*, **57**, pp. 94 – 100.
- [42] Bakare, I. O., Okieimen, F. E., Pavithran, C., Khalil, H. P. S. A., and Brahmakumar, M., 2010. “Mechanical and thermal properties of sisal fiber-reinforced rubber seed oil-based polyurethane composites”. *Materials & Design*, **31**(9), pp. 4274 – 4280.
- [43] Bras, J., Hassan, M. L., Bruzesse, C., Hassan, E. A., El-Wakil, N. A., and Dufresne, A., 2010. “Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites”. *Industrial Crops and Products*, **32**(3), pp. 627 – 633.
- [44] Stelescu, M. D., Airinei, A., Manaila, E., Craciun, G., Fifere, N., and Varganici, C., 2017. “Property correlations for composites based on ethylene propylene diene rubber reinforced with flax fibers”. *Polymer Testing*, **59**, pp. 75 – 83.
- [45] Anuar, H., and Zuraida, A., 2011. “Improvement in mechanical properties of reinforced thermoplastic elastomer composite with kenaf bast fibre”. *Composites Part B: Engineering*, **42**(3), pp. 462 – 465.
- [46] Ujjianto, O., Noviyanti, R., Wijaya, R., and Ramadhoni, B., 2017. “Effect of maleated natural rubber on tensile strength and compatibility of natural rubber/coconut coir composite”. In IOP Conference Series: Materials Science and Engineering, Vol. 223, IOP Publishing, p. 012014.
- [47] Karthikeyan, R., 2017. “Analysis of natural fiber orientation in polymer composites produced by injection molding process”. PhD thesis, University of Toronto (Canada).
- [48] Peel, L., Jensen, D. W., and Suzumori, K., 1998. “Batch fabrication of fiber-reinforced elastomer prepreg”. *Journal of advanced materials*, **30**(3), pp. 3–10.
- [49] Liliane, B., 2017. “Mechanical and electrical properties of elastomer nanocomposites based on different carbon nanomaterials”. *Journal of carbon research*, **3**, p. 10.
- [50] Kumar, R. P., Amma, M., and Thomas, S., 1995. “Short sisal fiber reinforced styrene-butadiene rubber composites”. *Journal of Applied Polymer Science*, **58**(3), pp. 597–612.
- [51] El-Shekeil, Y. A., Sapuan, S. . M., and Algrafi, M. . W., 2014. “Effect of fiber loading on mechanical and morphological properties of cocoa pod husk fibers reinforced ther-

- moplastic polyurethane composites”. *Materials and Design*, **64**, pp. 330–333.
- [52] JOFFE, R., and ANDERSONS, J., 2008. “13 - mechanical performance of thermoplastic matrix natural-fibre composites”. In *Properties and Performance of Natural-Fibre Composites*, K. L. Pickering, ed., Woodhead Publishing Series in Composites Science and Engineering. Woodhead Publishing, pp. 402 – 459.
- [53] Vilay, V., Mariatti, M., Taib, R. M., and Todo, M., 2008. “Effect of fiber surface treatment and fiber loading on the properties of bagasse fiberreinforced unsaturated polyester composites”. *Composites Science and Technology*, **68**(3), pp. 631 – 638.
- [54] El-Shekeil, Y., Sapuan, S., Abdan, K., and Zainudin, E., 2012. “Influence of fiber content on the mechanical and thermal properties of kenaf fiber reinforced thermoplastic polyurethane composites”. *Materials and Design*, **40**, pp. 299–303.
- [55] Mathew, L., and Joseph, R., 2007. “Mechanical properties of short-isora-fiber-reinforced natural rubber composites: Effects of fiber length, orientation, and loading; alkali treatment; and bonding agent”. *Journal of applied polymer science*, **103**(3), pp. 1640–1650.
- [56] Ismail, H., Rosnah, N., and Rozman, H. D., 1997. “Curing characteristics and mechanical properties of short oil palm fibre reinforced rubber composites”. *Polymer*, **38**(16), pp. 4059 – 4064.
- [57] Creegan, A., and Anderson, I., 2014. “3d printing for dielectric elastomers”. In *Electroactive Polymer Actuators and Devices (EAPAD) 2014*, Vol. 9056, International Society for Optics and Photonics, p. 905629.
- [58] Luki, M., Clarke, J., Tuck, C., Whittow, W., and Wells, G., 2016. “Printability of elastomer latex for additive manufacturing or 3d printing”. *Journal of Applied Polymer Science*, **133**(4).
- [59] Bastola, A. K., Hoang, V. T., and Li, L., 2017. “A novel hybrid magnetorheological elastomer developed by 3d printing”. *Materials & Design*, **114**, pp. 391 – 397.
- [60] Li, W., and Nakano, M., 2013. “Fabrication and characterization of pdms based magnetorheological elastomers”. *Smart Materials and Structures*, **22**(5), p. 055035.
- [61] Giffney, T., Bejanin, E., Kurian, A. S., Travas-Sejdic, J., and Aw, K., 2017. “Highly stretchable printed strain sensors using multi-walled carbon nanotube/silicone rubber composites”. *Sensors and Actuators A: Physical*, **259**, pp. 44 – 49.
- [62] Pitt, K., Lopez-Botello, O., Lafferty, A. D., Todd, I., and Mumtaz, K., 2017. “Investigation into the material properties of wooden composite structures with in-situ fibre reinforcement using additive manufacturing”. *Composites Science and Technology*, **138**, pp. 32 – 39.
- [63] Lewicki, J. P., Rodriguez, J., Zhu, C., Worsley, M., Wu, A. S., Kanarska, Y., and Horn, J., 2017. “3d-printing of meso-structurally ordered carbon fiber/polymer composites with unprecedented orthotropic physical properties”. *Scientific reports*, **7**, p. 43401.
- [64] Jain, U., 2017. “On curing silicone elastomers with a plasticising solvent”. *arXiv preprint arXiv:1712.06125*.
- [65] Stepanov, G., Borin, D. Y., Bakhtiarov, A. V., and Storozhenko, P. A., 2017. “Magnetic properties of hybrid elastomers with magnetically hard fillers: rotation of particles”. *Smart Materials and Structures*, **26**(3), p. 035060.
- [66] Jayamani, E., Bakri, M., and Khusairy, B., 2018. “Lignocellulosic fibres reinforced polymer composites for acoustical applications”. In *Lignocellulosic Composite Materials*. Springer, pp. 415–444.
- [67] Geethamma, V. G., Kalaprasad, G., Groeninckx, G., and Thomas, S., 2005. “Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites”. *Composites Part A: Applied Science and Manufacturing*, **36**(11), pp. 1499 – 1506.
- [68] Chandra, R., Singh, S. P., and Gupta, K., 1999. “Damping studies in fiber-reinforced composites a review”. *Composite Structures*, **46**(1), pp. 41 – 51.
- [69] Pollitt, E., 2011. Automotive composites, February. <http://www.globalhemp.com/2011/02/automotive-composites.html>.
- [70] Kanyanta, V., Ivankovic, A., and Murphy, N., 2013. “Bio-medical applications of elastomeric blends, composites”. In *Advances in Elastomers II*. Springer, pp. 227–252.
- [71] Chandramohan, D., and Marimuthu, K., 2011. “Applications of natural fiber composites for replacement of orthopaedic alloys”. In *Nanoscience, Engineering and Technology (ICONSET), 2011 International Conference on*, IEEE, pp. 137–145.
- [72] Pei, B., Wang, W., Fan, Y., Wang, X., Watari, F., and Li, X., 2017. “Fiber-reinforced scaffolds in soft tissue engineering”. *Regenerative biomaterials*, **4**(4), pp. 257–268.
- [73] Watkin, H., 2017. Researchers develop stretchable elastomers for 3d printing. <https://all3dp.com/researchers-develop-stretchable-elastomer-for-3d-printing/>.
- [74] Willam, M., 2017. How 3d printing with silicones might change medical science. <https://medium.com/healthcare-3d-printing-stories/how-3d-printing-with-silicones-might-change-medical-science-d54a398bce74>.
- [75] Nikpour, N., 2016. “Production and characterization of natural fiber-polymer composites using ground tire rubber as impact modifier”. PhD thesis, Universite Laval.
- [76] Sapuan, S., Purushothman, K., Sanyang, M., and Mansor, M., 2018. “Design and fabrication of kenaf fibre reinforced polymer composites for portable laptop table”. In *Lignocellulosic Composite Materials*. Springer, pp. 323–356.
- [77] Angellier-Couss, H., Guillard, V., Gastaldi, E., Peyron, S., and Gontard, N., 2018. “Lignocellulosic fibres-based bio-

- composites materials for food packaging”. In *Lignocellulosic Composite Materials*. Springer, pp. 389–413.
- [78] Thiruchitrabalam, M., Athijayamani, A., Sathiyamurthy, and Thaheer, A., 2010. “A review on the natural fiber-reinforced polymer composites for the development of roselle fiber-reinforced polyester composite”. *Journal of Natural Fibers*, *7*(4), pp. 307–323.
- [79] Karens, 2017. Advantages and disadvantages of natural fibers. <https://oureverydaylife.com/advantages-disadvantages-of-natural-fibers-12366265.htm>.
- [80] Joseph, S., Sreekala, M. S., Oommen, Z., Koshy, P., and Thomas, S., 2002. “A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibres and glass fibres”. *Composites Science and Technology*, *62*(14), pp. 1857–1868.
- [81] Li, X., Tabil, L. G., and Panigrahi, S., 2007. “Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review”. *Journal of Polymers and the Environment*, *15*(1), pp. 25–33.
- [82] Matsuzaki, R., Ueda, M., Namiki, M., Jeong, T. K., Asahara, H., Horiguchi, K., Nakamura, T., Todoroki, A., and Hirano, Y., 2016. “Three-dimensional printing of continuous-fiber composites by in-nozzle impregnation”. *Scientific reports*, *6*, p. 23058.
- [83] Rossiter, J., Walters, P., and Stoimenov, B., 2009. “Printing 3d dielectric elastomer actuators for soft robotics”. In *Electroactive Polymer Actuators and Devices (EAPAD) 2009*, Vol. 7287, International Society for Optics and Photonics, p. 72870H.