A Review of Hybrid polymer Bio-composites

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Abstract. There is a large scope for polymer composites in various fields of allocations like automotive, aerospace, civil construction materials, marine applications and many more. Developing a biodegradable industry based green materials, sustainable technology and optimal processes with low ecological impact is a general societal objective but this remains a considerable challenge to achieve. Various researchers worked for development of green or bio composites which may include use of bio waste materials like coconut shell, palm fruit, egg shell, sugarcane bagasse, banana fibers, bamboo fibers, etc. There has been less progress in the application of combination or hybridization of bio waste materials as reinforcement materials for producing polymeric composites of desired characteristics. In this paper, review of hybrid polymer Bio composites is carried out in order to identify future scope to develop novel hybrid Polymer Green composite (HPGC) for industrial applications.

1. Introduction
Developing a biodegradable industry based green materials, sustainable technology and optimal processes with low ecological impact is a general societal objective, but this remains a considerable challenge to achieve. There has been less progress in the use of bio waste materials as reinforcement materials for polymeric composite. In a composite, one phase is known as the matrix while the other phase is known as the reinforcement and it is distributed within the matrix. Reinforcement is in the form of fibrous or particulate depending upon its characteristics. One of the types of composites is the Polymer-matrix composite (PMCs) which consists of polymer resin as the matrix with fibers or particulate as the reinforcement medium. To overcome the limitations of polymers, like less stiffness and less strength, and to wide up their uses in various engineering fields, different combination of fillers are often added to merge the advantages of their constituent phases. Reinforcement of polymers with hybrid (different combination of fillers) plays a vital role in the improvement of the mechanical and other properties of materials for better performance.

1.1 Need of Green or Bio composites: Ecological importance have resulted interest in natural materials; reprocess characteristics and ecological safety are becoming necessity for the introduction of green or Bio materials and products. Polymer based products such as resins in thermoset plastics, are toxic and non-biodegradable. The resins and fibers used in the Bio/ green composites are biodegradable. Green composite are made from plant fibers with natural resins to produce natural
composite. The term green composites also referred as bio composites and eco composites. Historical reference shows that in ancient Egypt, people used straw as the filler with the mud based matrix for materials used for walls in building homes. As reinforcement, they made mud bricks with straw and used these bricks to build walls.

1.2 Classification of Green or Bio composites
- Green composites are classified on the basis of reinforcement and matrix polymer materials; they are divided into three main types as given below
  (a) Totally Green/Renewable composites: Matrix and reinforcement fillers are both made from renewable resources.
  (b) Partially or semi Green/Renewable composites: Matrix is obtained from renewable resources and reinforced with a synthetic material.
  (c) Partially or semi Green/Renewable composites: Synthetic matrix is reinforced with natural bio polymers. The classifications are based on the types of strengthening or reinforcements

1.3 Filler selection
- According to their origin or source, Fillers can be grouped as either natural or man-made or synthetic fibers. Natural fibers are extracted from different renewable resources, namely animals, vegetable plants and minerals. Synthetic /Man-made fillers have been incorporated into research with regard to their exceptional valuable properties. Glass fibers and carbon fibers are the commonly used synthetic fillers in the hybrid composites.

2. Hybridisation in Composites:
- Concept of ‘hybridization’ of composites is gaining more attention by the researchers
  1. Two or more fillers can be integrated into a common matrix to overcome the shortcomings of the other filler.
  2. However, this concept also applies to the combination of two or more polymers and reinforced with one filler
  3. Or more fillers and by adding the same filler type again, that has two or more sizes or dimensions

2.1 Parameters controlling characteristics of Hybrid composites
- There are three principal parameters, which have significant effect on the properties of the resulting hybrid composite product.
  1. Type of the materials used (matrix and filler), which depend mostly on the intended application. For example, it was found that bamboo/glass composites, displayed lower reinforcement than jute/glass hybrid under compressive load.
  2. Preparation method which depends on the filler and the matrix under research,
  3. Interaction between the fillers and the matrix. Natural fibers are treated by chemical agents in order to improve the interfacial adhesion between these components, to attain superior mechanical properties the interfacial adhesion should be strong chemical reaction or adsorption, which determines the extent of interfacial adhesion, can anchor matrix molecules to the fiber surface.

2.2 Factors that affect the development of polymer composites based on natural fibers
- 1. Stability of thermal energy 2. Level of humidity 3. Processability 4. Dispersion of fibers in polymer matrix 5. Adhesive fiber-matrix interaction 6. Natural fiber surface alteration 7. Fiber aspect ratio

2.3 Polymers from renewable resources can be classified into three major groups:
- 1. Natural polymers such as starch and cellulose;
- 2. Natural monomers Synthetic polymers such as poly lactic acid (PLA);
3. Polymers from microbial fermentation such as polyhydroxybutyrate (PHB).

2.3 Renewable resource Bio polymer matrix types Polymers can be classified into three main groups:
1. Natural polymers including cellulose and starch;
2. Natural monomers Synthetic polymers such as PLA;
3. Microbial fermentation polymers include polyhydroxybutyrate (PHB).

3. Poly (lactic acid) (PLA)
It is the first commercial bio polymer prepared from renewable resources. Wallace Carothers developed PLA in 1932. PLA is derived from 100% renewable agricultural sources such as corn starch, potatoes, sugarcanes or others biomasses. It is recyclable, biodegradable, thermoplastic, aliphatic linear polyester. PLA is one of the families of aliphatic polyesters usually made from α-hydroxy acids. PLA has properties which generally make possible to use it to replace petroleum-based plastics in many application areas. It is biocompatible with non-toxic degradation products (at low concentrations), making it a natural choice for many biomedical applications. However, the demerits like high cost, water sensitivity, fast physical aging, inherent brittleness, limited impact resistance and large stiffness and slow crystallization rate confine the industrial applicability of PLA. It is now normally finds applications in a wide range of areas like apparel, food packaging, nappies and wipes, and biodegradable composites.

usual methods such as injection moulding, blow moulding, extrusion and film forming can be used to process polylactic acid (PLA). PLA has a 55-65ºC Tg and a melting temperature of 150-175ºC. PLA's mechanical properties are compatible, or in most cases, even petrochemical polymers, such as polypropylene, are of better quality. PLA has therefore paid attention as a commodity polymer capable of replacing petrochemical polymers such as polypropylene and polyethylene, particularly for single-use packaging applications.

3.1 ROM for the prediction of the Mechanical properties of hybrid polymer composites
The prediction of the mechanical behavior of hybrid materials depend on material parameters, such as: the reinforcements (fibers or particles) mechanical properties, matrix mechanical properties, distribution and dispersion of reinforcements, volume fractions of the reinforcements and test conditions. Rule of mixture (ROM) is, often applied to predict the mechanical behaviors of hybrid materials. There are several models reported in the literature, based on ROM for the prediction of the mechanical properties of hybrid composite materials. As per literature review by [10] ROM shows that the modulus of a single type polymer reinforced with reinforcement (fibers or particles) can be calculated by using Equation (1). The volume fractions of the reinforcement (fibers in most cases) and polymer matrix are also determined, as shown in Equations (2) and (3):

\[ E_c = E_f V_f + E_m V_m \] (1)
\[ V_m + V_f = 1 \quad \text{or} \quad V_f = 1 - V_m \] (2)

Hence \[ E_c = E_f V_f + E_m (1 - V_f) \] (3)

Where \( E_c \) = Modulus of Composite, \( E_f \) = Modulus of fibre and \( E_m \) = Modulus of Matrix
\( V_f \) = Volume of Fibre
\( V_m \) = Volume of Matrix

4. Literature review
4.1 Bamboo-glass fiber reinforced epoxy based hybrid composites:
Polymer composites of Bamboo fiber reinforced have judicious mechanical properties but by mixing of synthetic fibers or by the alkali medium treatment of fiber, it is possible to enhance their properties. Hybrid composites [2] of nine different types of (bamboo and glass fiber) have been manufactured by hand layup method for finding physical and mechanical characteristics. Fiber loading of three types of bamboo with glass fibers was 5:15 wt. %, 10:10 wt. % and 15:5 wt. % by changing the length of fiber in each fiber loading from 0.5cm to 1.5cm respectively. Among all the composites, maximum tensile strength is 24.41MPa for fiber length of 0.5cm i.e.5wt.% bamboo fiber and 15wt.% glass fiber reinforcement respectively. Whereas, 1.5cm fiber length shows maximum modulus among all the manufactured composites. The hardness of the three different samples of hybrid composites for
0.5cm fiber length varies from 13.21 Hv to 15.95 Hv, for 1 cm fiber length 9.75 Hv to 18.51 Hv and for 1.5 cm 19.61 Hv to 21.25 Hv respectively.

4.2 Hybrid Glass/Carbon Fiber Reinforced Epoxy Composites:
Carbon fibers are also known as graphite fibers having a diameter of about 5-10 micro meters and composed of carbon atoms. It has properties such as high resistance to chemicals, stiffness, high tensile strength, temperature tolerance and hence suitable for marines, military, aerospace applications. Epoxy resin [3] is used in the preparation the hybrid composite. The composite [3] contains resin of 70 % of its volume and 30 % of glass fiber and carbon fibers are taken in combinations. The hybrid FRP manufactured by using vacuum bags assisted wet layup process and specimens were cut from sheet of thickness 14 mm having rectangular shape. The ACI440.3R and ASTMD 3039 specifications were referred for testing procedure and the test setup consist of universal testing machine having a capacity of 500 KN was used. The maximum stiffness was observed for specimen 01 and compared to specimen 01; Specimen 02 is having low strength and stiffness. Compressive loading shows that specimen 01 has the highest strength and stiffness but the less strength and stiffness was observed in specimen 02.

4.3 Coconut shell, Walnut shells and Rice husk hybrid composites:
The coconut shell powder, walnut shells powder and Rice husk powder are used as reinforcements with bio epoxy resin Grade 3554A and Hardener 3554B to form hybrid composite specimens. The compositions [4] of fibers were 1:1 in each specimen while the resin and hardener composition was 10:1 respectively. Moisture was removed by NaOH Chemical treatment and helps to increase strength of fibers. When water absorption test was conducted then less moisture (4 g) was absorbed by hybrid composite of walnut shell and coconut shell for various application environments. The hybrid of walnut shell and coconut shell composite has more tensile strength compared to other two hybrid composites. The walnut shell and coconut shell hybrid composite has flexural strength of 14.9 MPa in wet conditions and in dry condition it was 14.5 Mpa.

4.4 Coir and bagasse fiber hybrid composites
In the research work [5] an attempt has been made to produce epoxy based hybrid composites made of coir and bagasse fibres to analyze and study the effect of process parameters on thermal Analysis. Hand lay-up method was adopted for fabrication of composite panes to the size of 300mm x200mm x10mm with various weight percentage of natural fibers coconut coir (5 wt %) and bagasse (45 wt %). ASTM standard are used for testing mechanical properties such as tensile, impact strength and flexural strength.

4.5 Bamboo fiber with banana and linen fibre hybrid composites
The paper [6] is related with the comprehensive study of 2-4 mm long bamboo fiber, banana fiber and linen fiber with random orientations of epoxy resin. Different tests such as IZOD Impact Test and CHARPY Impact Test, FTIR (Fourier Transform Infra-Red) and to determine hardness Rockwell test were conducted on 10 specimens of bamboo epoxy resin composite (90/10), bamboo–banana (90/5/5) epoxy resin composite and bamboo linen (90/5/5) epoxy resin composite. It is tested and proved that bamboo–banana epoxy resin composite indicates better results in the impact test with reference to Izod test numerical values of 4 Joules and Charpy test gives value of 5 Joules while in the FTIR test, the compatibility of fibers with polymers in bamboo–banana epoxy resin composite is the highest, while bamboo–linen epoxy resin composite shows better results in the Rockwell toughness test with a value of 40 RHN.

4.6 Wood-Plastic hybrid composites (WPC)
Wood-plastic composites are a composite consists of wood fibers or particles and the matrix as polymer. Grounded sawdust or wood flour is used in WPCs. Other natural fibers can be used, like hemp or kenaf, jute may be also used. Injection moulding and extrusion are the manufacturing methods for WPC. The mechanical tests were performed with a Zwick Roell (2020) testing machine.
The mechanical properties were tested according to relevant standards: According to standard EN 310 flexural strength was tested, ISO 179 refereed for impact strength, hardness according to EN-1534, and ISO 527-2 was used for tensile strength. Standard EN 323 was referred for determination of density. EN 317 test has been used for water absorption and swelling of thickness. One composite WF-PP was manufactured without waste filler, Other composites were manufactured, Nevertheless, part of the wood fibers (WF) have been replaced by building waste. The building waste was mineral wool (MW), plasterboard waste (PB) and mixed construction and demolition waste (CDW). The composite WF-PP-MW-PB consists of 24% of WF, 20% of MW and 20% of PB. The composite WF-PP-CDW contains 44% of WF and 20% of CDW, besides plastics and additives. WF-PP composite has tensile strength of 23.35 Mpa, WF-PP-MW-PB has tensile strength 18.75 Mpa, WF-PP-CDW has tensile strength 17.79 Mpa. Flexural modulus for WF composite was 4.44 GPa, WF-PP-MW-PB composite was 3.84 Gpa, WF-PP-CDW composite was 4.04 Gpa.

| Type of Fibre | Reinforcement used | Method adopted | Testing parameters | Remark | Referenc e |
|---------------|---------------------|----------------|--------------------|--------|------------|
| Coir and Bagasse fiber | Epoxy resin | Hand lay | Tensile, flexural and impact strength | Semi Green composite | [1] |
| Bamboo, Banana and linen fibre | Polylactic Acid(PLA) | Injection moulding process | Tensile, flexural, Impact and Hardness, SEM analysis | Totally Green composite | [2] |
| Bamboo/ Glass fibre | Polyester resin | Hand lay-up | Flexural test, Impact test, Hardness | Semi Green composite | [3] |
| Bamboo/ Glass fibre | Epoxy resin | Hand lay-up | Tensile strength, flexural strength, Modulus | Semi Green composite | [4] |
| Glass and Carbon fibre | Epoxy resin | Wet layup moulding | Young’s modulus, Tensile strength, compressive strength, Poisson’s ratio | Semi Green composite | [5] |
| Coconut Coir-Bagasse Fibres | Epoxy resin | Hand lay-up | Tensile, flexural, Impact and Hardness | Semi Green composite | [6] |
| Wood-Plastic hybrid composites (WPC) | Phenolics and Epoxy | Injection moulding, compression moulding | Tensile, flexural, Impact and Hardness, SEM analysis | Semi Green composite | [7] |
| Marble waste powder, carbon black, Silica | Natural rubber | Not mentioned | Tensile strength, Tear strength, Modulus, Hardness, Swelling ratio | Totally Green composite | [8] |
5. Challenges and opportunities
1. Recyclability of the composites is one of the major issues for development of ecological materials. Recyclability of the composites will lead to the cost effective products as well as the corrective measure for the rise of waste materials. Green composites can replace all hazardous and waste-producing materials.
2. Life cycle analysis should be done for all newly composite materials and thus the biodegradability can be measured. This will help to select eco-friendly and acceptable materials.
3. Microfibrillar composites, their characteristics and applications created a lot of interest in research because of their innovative properties and applications.
4. Composite materials having long-term durability for continuous purposes are desirable and cost-effective.
5. Since the interface interactions exist between fiber and matrix has a significant role in property enhancement, new characterization techniques for interface will bring new opportunities.
6. Online monitoring of morphology of composites during processing is another area, which requires the attention of researchers.

6. Conclusion
Based on the above literature survey following points have emerged. Most of the researchers showed that the natural fibers vary vastly in their mechanical properties, morphology, surface composition and water uptake behavior depending on source geographical methods of extractions. The fiber as such available in nature will not have the required qualities to fulfill the demands of different industrial applications. There is a need to develop techniques and approaches to improve the properties of the natural fibers to homogenize the as-received fiber properties as required for high-end and high technology applications.

7. References
[1] Rizvi Syed Mazher Abbas, Dwivedi,Abhishek Syed Shane Raza ,AnshikaAwasthi, , Himanshu Gupta” An Investigation of Thermal Properties of Reinforced Coconut Coir-Bagasse Fibres Polymer Hybrid Composites” 2017 IJSRSET, Volume 3 ,Issue 1, Print ISSN: 2395-1990 , Online ISSN : 2394-4099
[2] Ramachandran M., Sahas Bansal, Pramod Raichurkar” Experimental study of bamboo using banana and linen fibre reinforced polymeric composites” Perspectives in Science (2016) 8, 313—316
[3] B Stanly, Jones Retnam,, M Sivapragash and P Pradeep”Effects of fibre orientation on mechanical properties of hybrid bamboo/glass fibre polymer composites” Bull. Mater. Sci., Vol. 37, No. 5, August 2014, pp. 1059–1064.
[4] Ojaswi Panda” Study on the Effect of Fiber Parameters on the Mechanical Behavior of Bamboo-Glass Fiber Reinforced Epoxy Based Hybrid Composites”B.Tech Thesis, National Institute of Technology,Rourkela-769008
[5] P. M. Bhagwat, M. Ramachandran, Pramod Raichurkar” Mechanical Properties of Hybrid Glass/Carbon Fiber Reinforced Epoxy Composites” Materials Today: Proceedings 4 (2017) 7375–7380
[6] D.Chandramohan ,A.JohnPresinKumar” Experimental data on the properties of natural fiber particle reinforced polymer composite material” Data in Brief 13 (2017)460–468
[7] Anna Keskisaari”The impact of recycled raw materials on the properties of wood-plastic composites” Phd thesis,Lappeenranta University of Technology,Lappeenranta, Finland,2017
[8] Khalil Ahmed”Hybrid composites prepared from Industrial waste: Mechanical and swelling behavior” Journal of Advanced Research, (2015) 6,pp 225–232
[9] Eustathios Petinakis, Long Yu, George Simon and Katherine Dean’Natural Fibre Bio-Composites Incorporating Poly(Lactic Acid) http://dx.doi.org/10.5772/52253
[10] M. J. Mochane” Recent progress on natural fiber hybrid composites foradvanced applications: A review eXPRESS Polymer Letters Vol.13, No.2 (2019) 159–198
[11] Nikola Španić“ Bio matrices and bio composites” Conference Paper· October 2012 ,ResearchGate
[12] M Noryani, S M Sapuan, M T Mastura, M Y M Zuhri1 and E S Zainudin” Material selection criteria for natural fibre composite in automotive component: A review The Wood and Bio fiber International Conference (WOBIC 2017)
[13] M. Ramachandran, B. K. Modi” A Review on various characterisation of PLA , International Journal on Textile Engineering and Processes “Vol. 4, Issue 1 January 2018 based biodegradable composites
[14] Amrinder Singh Pannu, Sehijpal Singh and Vikas Dhawan” Amrinder Singh Pannu1 , Sehijpal Singh and Vikas Dhawan” Asian Journal of Engineering and Applied Technology ISSN 2249-068X Vol. 7 No. 2, 2018, pp.7-15
[15] M. J. Mochane” Recent progress on natural fiber hybrid composites for advanced applications: A review”
[16] V.Durga Prasada Rao” Study of hardness and flexural strength of banyan and peepal fibre reinforced hybrid composites” MATEC Web of Conferences 172, 04009 (2018) https://doi.org/10.1051/matecconf/201817204009 ICDAMS 2018