Surface Treated and Untreated Henequen Fiber Reinforced Polypropylene Composites

Pravin Gaikwad, Prakash Mahanwar, and Vaishali Bambole

Abstract**—** Short Henequen fiber (HF) reinforced Polypropylene (PP) composites were melt blended and then injection molded for characterization. These batches of fibers were made as 1%, 3%, 5%, 8%, 10% and 20% by weight to the polymer matrix. To facilitate the interfacial adhesion between matrix and hydrophilic fibers, these fibers were surface treated with coupling agent such as VinylTriMethylOxisilane (VTMO) after soaking these with Isopropyl Alcohol (IPA) and then dried in an air circulating oven at 65^0C for 3hrs.Composite prepared with 0.5% (w/w) VTMO to the total fibers showed better mechanical as well as electrical performance at 10wt% fiber concentration than untreated one. Morphological studies of tensile fractured surface of untreated and treated composite illustrated that better fiber matrix interfacial adhesion occurred in treated composites. The rheological data reveals flow behaviour characteristics of treated and untreated composites showed increased viscosity at low shear rates with increased in fiber content into the matrix.

Keywords**—** Coupling Agent, Henequen fibers (HF), Polymer Composites, Polypropylene (PP).

I. INTRODUCTION

GLOBAL warming of the world has been exploited to many researchers and scientists to opt for ecofriendly and cost effective natural fiber reinforced polymer composites. Synthetic fibers like carbon and glass though exhibits excellent mechanical, thermal properties and durability but difficulties in disposal processing which produce lot of black smoke and bad odours. Also reclamation process generates a large environmental load as synthetic fibers are not decomposed easily. In order to overcome this problem, necessity of natural fibers based composites is demanding to make the world 'green'. The composites referred to as biocomposites which are combine natural fibers such as kenaf, jute, hemp and sisal with biodegradable or non- biodegradable polymers. Natural fibers have many advantages over synthetic ones; easily available in abundance and cheap with higher specific properties, non abrasive to equipments, biodegradability, no harm to environment, low density, reduced dermal and respiratory irritation, renewable sources, etc [1-4]. Depending on their origin, natural fibers can be generally grouped into bast (jute, flax, ramie, hemp, banana, kenaf, mesta), leaf (pineapple, sisal, henequen, screw pine), and a seed or fruit fibers (Coir, cotton, oil palm). Henequen (Agave Fourcroydes) is long, hard & strong fibers obtained from the long leaves of agave plants which native to Yucatan, Mexico. These natural fibers have been used traditionally to make twines, ropes, carpets and cordages for a long period of time [5]. Composites made with natural fibers offers use in various applications such as aerospace, leisure, construction, sport, packaging, automotive industries and biodegradable application. However due to hydrophilic nature of natural fibers give rise to incompatibility between fiber / polymer composites. This leads to undesirable properties of the composites. Hence fiber surface is modified with coupling agent in order to have interfacial adhesion between fiber and matrix [6, 7]. Thermoplastic composite is manufactured using potentially high performance resin such as poly propylene (PP), Polyethylene (PE), Poly-vinyl chloride (PVC) etc. Polypropylene (PP) is a part of commodity polymer possesses outstanding properties like low density, good flex life, sterlizability, good surface hardness, scratch resistance and very good abrasion resistance [8-10]. PP is the lightest polymer as it has specific gravity ranging as 0.90 to 0.91. PP is excellent for electrical applications due to outstanding combination of thermal properties, low moisture pick up & good dielectric properties even at high frequency because of non polar in nature. Treated natural fibers reinforced PP composites exhibits in high values of mechanical, flexural properties & thermal stability [11-13]. Kudzu fiber-reinforced PP composites have been reported by Luo et al [14]. Development of HEMP fiber reinforced PP composites have been studied by Hargitai et al [15]. Haque et al. [16] used chemical treatment to palm & coir fibers reinforced PP composites to improve Physico-mechanical properties. Lee and Cho investigated the effect of fiber surface treatment on the interfacing and mechanical properties of Henequen/pp bio- composite by compression molding technique [17]. Chand and Dwivedi [18] reported effect of coupling agent on abrasive wear behaviour of chopped jute fiber reinforced PP composites and better wear resistance using coupling agent than that of without using coupling agent. Mechanical properties of pineapple leaf fiber reinforced PP composites have been reported by Arib et al. [19] Bledzki et al. reported abaca fiber reinforced PP composites compared with jute and flax fiber PP composites and achieved best tensile properties

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by jute fiber and impact properties by abaca fiber [20]. Pickering et al. [21] used fungal and alkali treatment for interfacial modification of hemp fiber reinforced PP composites. Mechanical behaviour and microstructural analysis of sugarcane bagasse fibers reinforced PP composites have been investigated by Luz et al. [22] Mi et al. reported bamboo fiber reinforced PP composites for crystallization and interfacial morphology [23]. Mahanwar et al. recently reported effect of coupling agent on the properties of short non-woven PET microfiber reinforced PP composites [24].

There is no literature available on PP reinforced Henequen fiber composites prepared by injection molding technique. Aim of this work is to optimize fiber loading in wt% for henequen fiber reinforced PP composites with and without coupling agent in terms of mechanical, electrical and rheological properties.

II. Experimental

A. Materials

The matrix polymer Polypropylene (PP) Repol, injection molding grade with MFI 11gm/10min was procured from Reliance Industries Ltd. The continuous Henequen fibers (HF) (Agave fourcroydes) extracted in laboratory was used. VinylTriMethylOxisilane (VTMO) was obtained from Degussa, Germany. Isopropyl Alcohol was supplied by S.D.fine chem. Ltd.

B. Surface Treatment of Henequen fibers

Henequen fibers were chopped 5-7mm in length manually. These fibers were first soaked in the isopropyl alcohol equal to that of total weight of the fibers and then silane was added at 0.5% by wt of fibers. In order to ensure uniform distribution of the coupling agent, the fibers were stirred manually for 5 min. These surface treated fibers then dried at 65^0C for 2-3 hrs in an air circulating oven.

C. Preparation of The Polymer Composites

The batch sizes of Henequen fibers constitute as 0, 1, 3, 5, 8, 10 and 20% by weight in the total polymer matrix. These batches of PP/Henequen fibers both treated and untreated were melt blended in a twin screw extruder (Model MP19 PC, M/SAPV BAKER,UK) having L/D ratio of 25:1. The speed of the screw was maintained 60 rpm for all the compositions. The extrudates were quenched in a water tank at 20-25 ^{0}C and then palletized. The temperature profile for the melt blending was kept as Zone1-160 ^{0}C, Zone 2-190^0C, Zone 3-210^0C, Zone 4-220^0C and Die-230^0C for the PP/ HF composites.

D. Injection Moulding

The granules of the extrudates were predried in an air circulated oven at 80^0C for 4 hours and then injection molded in a microprocessor based injection moulding machine (Boolani) fitted with a master mould containing the cavity for tensile, flexural and impact specimens. The temperature profile used for injection molding was as Zone1:170^0C, Zone2: 210^0C, Zone3:230^0C for PP/ Henequen fiber composites.

III. Characterization

A. Mechanical Properties

The tensile strength of polymer and polymer composites were evaluated as per ASTM D638 M-91, using Universal Testing Machine (UTM) LR50K [Lloyd Instrument Ltd., U. K.], the crosshead speed of 50mm/min was maintained for testing using a load cell of 50 KN. The flexural strength and flexural modulus was measured using universal testing machine [LR 50 K, LLOYD Instruments, and U.K.] according to ASTM D790 M-92 at Jaw speed of 2.8 mm/min with 3-point flexural strength and the span of 60 mm. The impact strength was determined as per ASTM D 256 using Avery Denison's pendulum Impact Strength Tester, [model 6709] with 2.7J striker. The results reported are the average values of at least 3 specimens for each test.

B. Electrical Properties

The Dielectric Strength was determined according to ASTM D 149 using Zaran Instruments (India) with a 2mm thick composite disc. The configurations of the instruments were as follows: voltage: 240 V, 50 Hz, 1 PH; output: 0-50 KV; capacity: 100mA; rating: 15 min.

C. Rheological properties

The melt Rheology of PP/ Henequen fiber composite (both treated and untreated) was studied using rotational rheometer (Physica MCR 101, Anton Paar, Germany). Oscillatory mode was used for rheological study using parallel plate assembly with a sensor having diameter of 35mm. The dynamic properties, that is storage modulus, G'(Pa),loss modulus G''(Pa) and phase angle, $\tan\delta = G''/G'$ as a function of frequency, ω (rad/s) were measured. The frequency of oscillation was varied from 0.01 to 200 rad/s. The rheological characteristics were measured at constant temperature of 230^0C. The samples were predried before analysis.

D. Morphological Properties

Scanning Electron Microscope (SEM) was used to study the morphology of the composites. SEM studies of tensile test fractured and liquid nitrogen fractured samples were carried out using JSM-6380LA analytical scanning microscope of Joel make, Japan. The accelerated voltage used was 20KV.The samples were sputter-coated with platinum to increase surface conductivity. The digitized images were recorded.

IV. Results and Discussion

A. Tensile Properties

Fig.1 depicts the variation in tensile strength of PP/HF composites at varying concentration. Tensile strength of composite was found to increase significantly with increase in the henequen fibers by wt% with and without coupling agent. The rate of increase of tensile strength is higher in case of 10 wt% loading of henequen fibers. This is due to the strong surface bonding of henequen fibers with polymer matrix. . It is also observed that at 20wt% loading of henequen fibers the tensile strength of the composite decreased. This can be attributed to the poor surface bonding of fibers.

Fig.2 shows the percentage elongation at break of untreated and treated PP/HF composites. It is seen that percentage elongation at break decreased on addition of henequen fibers with and without coupling agent into the polymer matrix. This is due to the interference of fibers in the mobility or deformability of the matrix. This creation of interference is due to the physical interaction and immobilization of the polymer matrix by the presence of mechanical restraints, which results in the reduction of elongation at break of the composite.

Fig.3 enumerates the variation of tensile modulus of PP/ HF composites with henequen fibers wt% loading. The tensile modulus of both untreated and treated HF reinforced PP composites shows a linearly increasing trend with the increasing concentration of fiber content upto 10 wt% and then lower at 20wt%. It is observed that the increment is more significant as in case of treated composites. It was described above that the treated HF would make more uniform dispersion and less agglomeration in the PP matrix. Accordingly, it is convinced that the uniform dispersion and the less agglomeration of the fibers should play a more effective role in the enhancement of tensile modulus.

B. Flexural Properties

Fig.4 represents the variation in flexural strength of untreated and treated PP/ HF composites. It is seen that the flexural strength of the composite increases with increasing wt% concentration of fibers for both of the treated and untreated PP/ HF composites. The flexural modulus of the composite also increases with increasing wt% concentration of fibers for both of the treated and untreated composites. The increase in the flexural strength of the composites may be owing to better interaction between treated fibers and the polymer matrix; silane increases the interfacial adhesion between the fibers and the matrix and also resists the stress propagation during the bending stress applied to the samples.

Fig.5 shows the variation of flexural modulus of untreated and treated PP/ HF composites. It is seen that flexural modulus increases with increasing wt% concentration of fibers for both of the treated and untreated PP/ HF composites. Due to the addition of coupling agent, flexural modulus of the composites drastically improved by 26% compared to untreated fibers at 10wt% fiber concentration into the polymer matrix. This change in phenomenon of variation in flexural modulus of untreated and treated HF composites may be owing to an increase in interfacial adhesion between the fibers and the matrix.

C. Impact Strength

Fig.6 shows the variation in impact strength of the PP/ HF composites with and without treatment of henequen fibers. It is seen that with the increase in wt% loading of the henequen fibers there is decrease in the impact strength of the composite. This is attributed to the reduction in the elasticity of the composite due to fiber addition and thereby reducing the deformability of the polymer matrix.

D. Dielectric Strength

Fig.7 represents the variation in the dielectric strength of the PP/ HF composites with wt % loading of henequen fibers. It is observed that the dielectric strength of the composite increase as there is an increase in wt % concentration of henequen fibers. The increase in dielectric strength is upto 10wt% loading of henequen fibers which may be owing to the proper encapsulation of fibers which provides same continuity for current to flow. The concentration wt% loading of natural fibers may have reached the threshold value at 10wt% and therefore the dielectric strength of the henequen fiber reinforced PP composites remain constant after 10wt% concentration of microfibers.

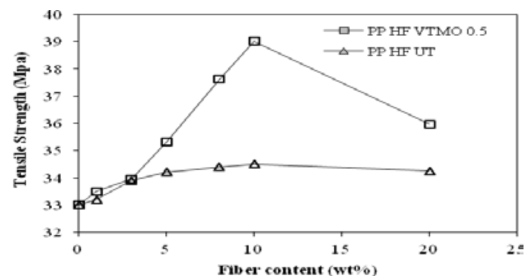


Fig. 1 Variation in tensile strength with Henequen fiber loading by wt%

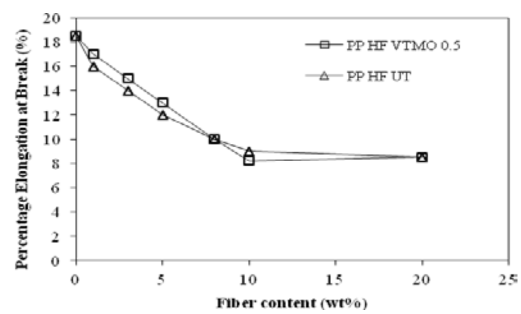


Fig. 2 Variation in percentage elongation at break with Henequen fiber loading by wt%

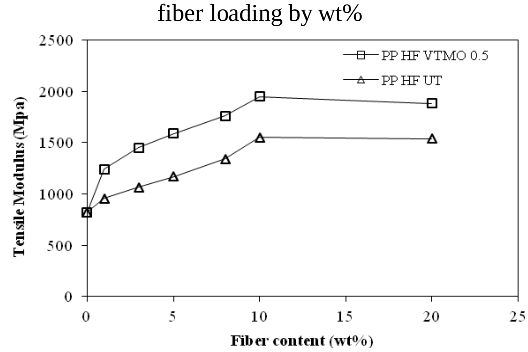


Fig. 3 Variation in tensile modulus with Henequen fiber loading by wt%

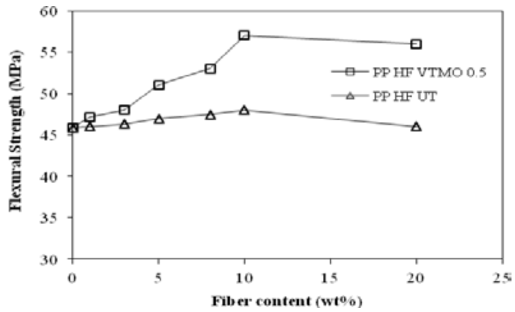


Fig. 4 Variation in flexural strength with Henequen fiber loading by wt%

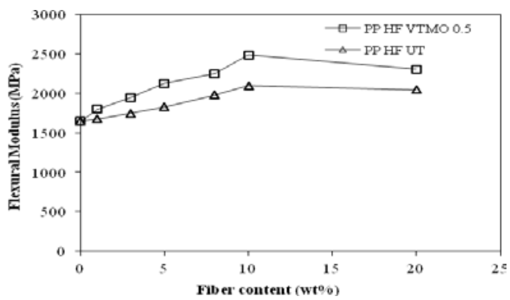


Fig. 5 Variation in flexural modulus with Henequen fiber loading by wt%

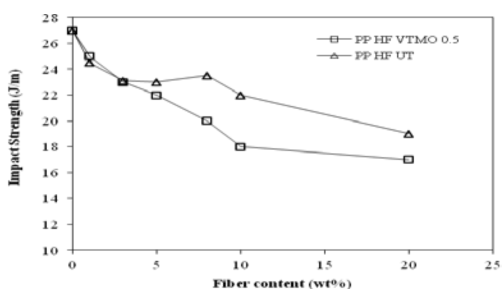


Fig. 6 Variation in impact strength with PET microfiber loading by wt%

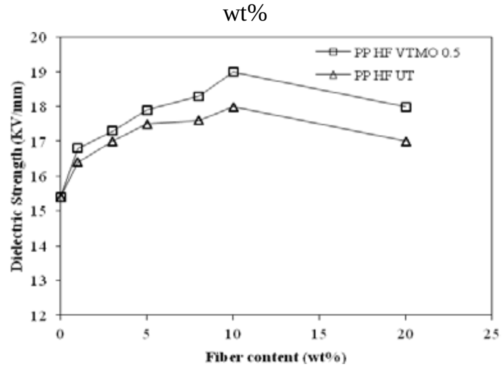


Fig. 7 Variation in dielectric strength with Henequen fiber loading by wt%

E. Rheological Properties

Steady shear viscosity (η). Fig.8 shows the viscosities behaviour of PP reinforced henequen fiber silane treated and untreated composite at 230^{0}C. The shear viscosities of untreated henequen fiber wt% loading are found to be at lower range than virgin PP at low shear rates. It can be seen that the surface treatment of fibers results in the change of rheological behaviour of composites, especially in low ω. The virgin PP and the values of η of composites are higher than those of PP untreated fibers and PP treated fibers composites, ranking as PP>10wt% untreated HF>10wt% treated HF. Also as compared to that of virgin PP, η of fiber reinforced polymer presents the characteristics of Newtonian fluids at lower shear rate γ and at higher shear rate γ shows shear thinning behaviour. The reason for this is the formation of active organic monolayer is induced by the silane coupling agent which on the other hand has the effect of lubricant on the flow. Chemical link which is formed between main chain in matrix and fibers strongly improved the movement of PP chain, leading to lower η for 10wt% untreated and VTMO treated HF.

Storage Modulus(G'). In general, the increase of dynamic viscoelastic functions in the low frequency (ω) is related to the extent of heterogeneity for the filled polymers. The higher the G', the more heterogeneous is the system which clearly suggest that better the value of G' approaches to that of virgin PP, the higher is the level of compatibility of the interface [25]. Fig.9 shows ω the dependence of the G' for virgin PP and PP/HF composites with VTMO treated fibers at 230^{0}C. The increase in the G' is mainly owing to stiffness imparted by the fibers to the matrix that allows efficient stress transfer. Further the addition of silane results in the additional decrease in the modulus of the matrix polymer thus indicating improved interfacial interaction between fibers and the PP.

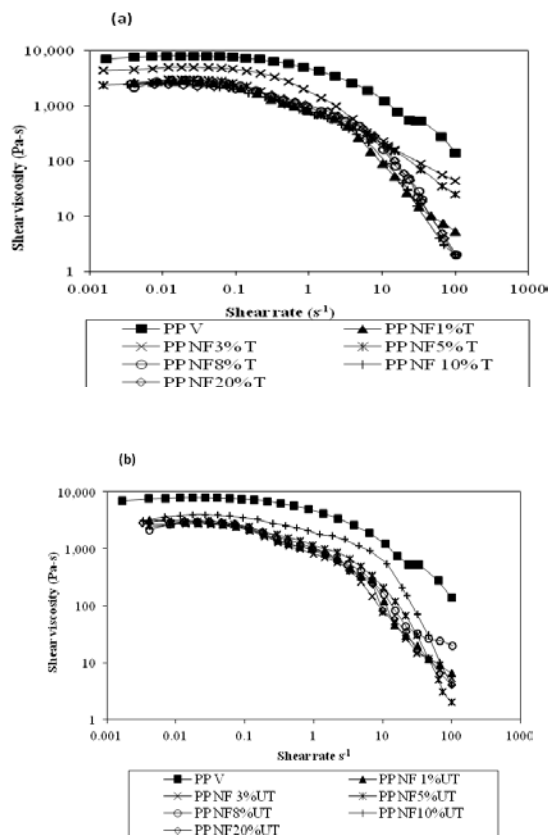


Fig. 8 Relationship between shear viscosity (η) and shear rate (γ) for matrix polymer and composites containing different wt% Henequen fiber loading (a) VTMO treated (b) Untreated

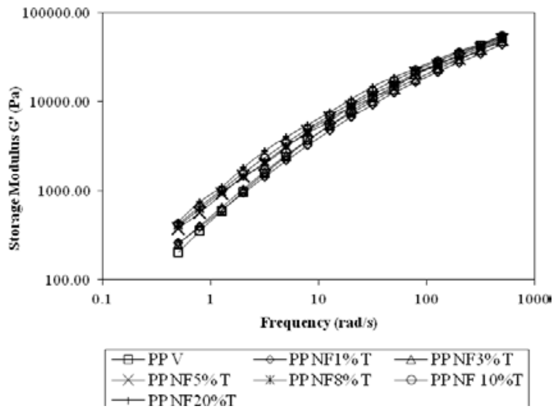
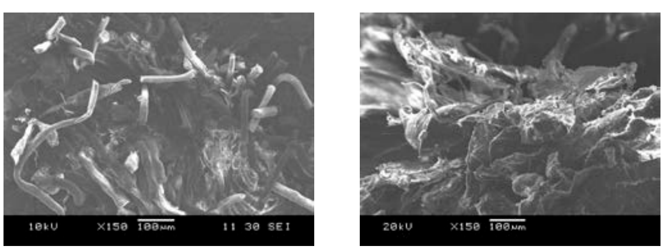


Fig. 9 Relationship between dynamic storage modulus G' and frequency (γ) for matrix polymer and composites containing different wt% VTMO treated Henequen fiber loading

F. Microstructure Characterizations

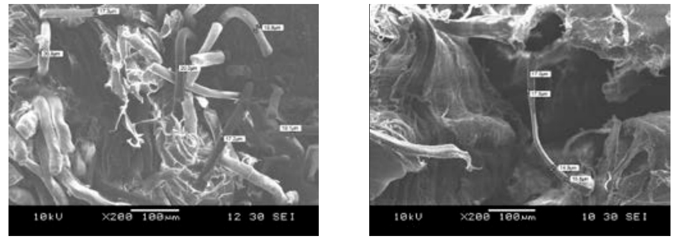
SEM is used to study the morphology of the composites. Fig.10 (A) shows the SEM micrographs of PP/HF composites at 10wt% composite with 0.5wt % concentration of coupling agent. With the addition of 10wt% fibers with silane treatment there seems to be better dispersion of henequen fibers into the PP matrix.Fig.10 (B) represents the SEM micrographs of PP/HF composites at 20wt% composite with 0.5wt % concentration of coupling agent. It can be seen from Fig.11there is a formation of agglomeration of fibers into the PP matrix which supports the decrement in the mechanical properties due to poor surface bonding.

Fig.11 (C) represents SEM micrographs of PP/HF composites at 10wt% untreated henequen fibers which also shows uniform distribution of fibers.Fig.11(D) represents SEM micrographs of PP/HF composites at 20% untreated henequen fibers which clearly shows agglomeration and uneven distribution of fibers.



A B

Fig. 10 (A) SEM micrographs of PP composite with 10wt% loading of Henequen (treated) microfiber loading
(B) SEM micrographs of PP composite with 20wt% loading of Henequen (treated) microfiber loading



C D

Fig. 11 (C) SEM micrographs of PP composite with 10wt% loading of Henequen (untreated) microfiber loading.
(D) SEM micrographs of PP composite with 20wt% loading of Henequen (untreated) microfiber loading.

V. CONCLUSION

The surface treated Henequen fibers filled PP composite shows better interaction found optimum at 10wt% fiber concentration. The following conclusions can be drawn for PP/HF composites (treated and untreated).

a) Treatment with silane mainly results in increase of tensile, flexural and dielectric strength of the composites.

b) The mechanical properties are enhanced when the content of silane treated fibers were at 10%.

c) An enhancement in tensile and flexural modulus of PP/HF composites were observed when fibers were surface treated with silane coupling agent.

d) The change shear viscosity (η) and storage modulus of the composite and PP matrix, especially those for systems treated with silane, which was attributed to the interfacial adhesion enhancement.

e) Morphological studies showed that 10% by weight addition of henequen treated fibers concentration into the polymer matrix have uniform dispersion.

f) The overall performance of composites treated with natural microfibers in PP matrix outrates that of untreated fibers in PP.

VI. REFERENCES

[1] M. Baiardo, E. Zini, and M. Scandola, "Flax fiber polyester composites," *Composites Part A: Applied Science and Manufacturing*, vol.35 (6), pp.703-710, 2004.

[2] A.K. Mohanty, M. Misra, and G. Hinrichsen, "Biofiber, biodegradable polymers and biocomposites: An overview," *Macromol. Mater. Eng.*, vol.276-277(1), pp.1-24, 2000.

[3] J.M. Park, S.T. Quang, B.S. Hwang, and K.L. Devries, "Interfacial evaluation of modified jute and hemp fibers/polypropylene (PP) maleic anhydride polypropylene copolymers (PP-MAPP) composites using micromechanical technique and nondestructive acoustic emission," *Composites Science and Technology*, vol.66 (15), pp.2686–2699, 2006.

[4] A.K. Rana, A.Mandal, and S. Bandopadhyay, "Short jute fiber reinforced polypropylene composites," *Composites Science and Technology*, vol. 63(6), pp.801–806, 2003.

[5] M.Anguilar-Vega, and C.A.Cruz-Ramos, "Properties of henequen cellulosic fibers," *Journal of Applied Polymer Science*, vol.56 (10), pp1245-1252, 1995.

[6] R. Malkapuram, V. Kumar, and Y.S. Negi, "Recent development in natural fibre reinforced polypropylene composites," *Journal of Reinforced Plastics and Composites*, vol.28, pp.1169-1189. 2008.

[7] P. Wambua, J. Ivens, and I. Verpoest, "Natural fibers: Can they replace glass in fibre reinforced plastics," *Composites Science and Technology*, vol. 63, pp.1259-1264. 2003.

[8] H.U. Zaman, M.A. Khan, R.A. Khan, M.A. Rahman, L.R. Das, and A Mamun, "Role of potassium permanganate and urea on the improvement of the mechanical properties of jute polypropylene composites," *Fibers and Polymers*, vol.11(3), pp.455-463,2010.

[9] M. M. I. Khalil, M.E.S. Naeem, and A.E.S. Gamil, "Irradiation effects on the thermal and structural characteristics of modified grafted polypropylene," *Journal of Applied Polymer Science*, vol. 102(1), pp.506-515, 2006.

[10] A.C. Karmarker, and G. Hinrichen, "Processing and characterization of jute fiber reinforced thermoplastics polymers," *Polymer-Plastics Technology and Engineering*, vol. 30(5-6), pp.609-618, 1991.

[11] K.L. Fung, R.K.Y. Li, and S.C. Tjong, "Interface modification on the properties of sisal fiber reinforced polypropylene composites," *Journal of Applied Polymer Science*, vol.85 (4), pp. 169-174, 2002.

[12] A. Karmarkar, S. Chauhan, J.Modak, and M.Chanda, "Mechanical properties of wood fiber reinforced polypropylene composites," *Journal of Applied Polymer Science*, vol. 38(2), pp.227-233, 2007.

[13] J.A. Khan, M.A. Khan, R. Islam, A.Gafur, "Mechanical, Thermal and Interfacial properties of jute fabric reinforced polypropylene composites: Effect of potassium dichromate," *Materials Sciences and Applications*, vol. 1, pp.350-357, 2010.

[14] X. Luo, R.S. Benson, K.M. Kit, and M. Dever, "Kudzu fiber reinforced polypropylene composites," *Journal of Applied Polymer Science*, vol. 85(9), pp.1961-1966, 2002.

[15] H.Hargitai, H. Racz, and R. Anandjiwala, "Development of hemp fiber reinforced polypropylene composites," *Journal of Thermoplastic Composite Materials*, vol. 21(2), pp.165-174, 2008.

[16] M.M. Haque, M. Hasan, and M.S. Islam, "Physico-mechanical properties of chemically treated palm and coir fiber composites," *Bioresource Technology*, vol.100 (20), pp.4903-4906, 2009.

[17] H.S. Lee, and D. Cho, "Effect of natural fiber surface treatments on the interfacial and mechanical properties of henequen PP biocomposites," *Macromolecular research*, vol. 16(5), pp.411-417, 2008.

[18] N. Chand, and U. Dwivedi, "Effect of coupling agent on abrasive wear behaviour of chopped jute fiber reinforced polypropylene composites," *Wear vol.261*, pp.1057-1063, 2006.

[19] R.M.N. Arib, S.M. Sapuan, M.M.H.M. Ahmad, M.T. Paridah, and H.M.D. Zaman, "Mechanical properties of pineapple leaf fiber reinforced polypropylene composites," *Materials and design*, vol. 27(6), pp.391-396, 2006.

[20] A.K. Bledzki, A.A. Mamun, and O. Faruk, "Abaca fiber reinforced polypropylene composites and comparison with jute and flax fiber polypropylene composites," *eXPRESS Polymer Letters* vol. 1(11), pp.755-762, 2007.

[21] K.L. Pickering, Y. Li, R.L. Farell, and M. Lay, Interfacial modification of hemp fiber reinforced composites using fungal and alkali treatment," *Journal of Biobased Materials and Bioenergy*, vol. 1, pp.109-117, 2007.

[22] S.M. Luz, A.R. Goncalves, and Jr. A.P. Del'Arco, "Mechanical behaviour and microstructural analysis of sugarcane bagasse fibers reinforced polypropylene composites," *Composites Part A: Applied Science and Manufacturing*, vol. 38(6), pp.1455-1461, 2007.

[23] Y. Mi, X. Chen, and Q. Guo, "Bamboo fiber reinforced polypropylene composites: Crystallization and interfacial morphology," *Journal of Applied Polymer Science*, vol. 64(7), pp.1267-1273, 1997.

[24] P.A.Mahanwar, and P.R.Gaikwad, "Effect of coupling agent on the properties of short non-woven PET microfiber reinforced PP composites," *International Conference on Advances in Materials, Mechanical and Industrial Engineering (AMMIE-2014) in Proceedings, ISBN 978-93-84468-03-3*,Sept.29-30,2014Phuket(Thailand).

[25] P.Malcolm, and Stevens, "*Polymer chemistry an Introduction,*" 2nd ed., Oxford University Press, New York 174, 1990.