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Industrial Waste Reinforced PF Composites: Measurement and Evaluation of Effective Thermal Conductivity

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Abstract

Oil-palm fibers were obtained from the industrial waste of oil mills. The fibers were irradiated with γ- radiations, chemically treated with acrylonitrile and latex modified. Treated fibers were reinforced in phenol-formaldehyde (PF) resin matrix to prepare composites. Surface topology of the composites was investigated by scanning electron microscopy (SEM). The effect of treatment on thermal properties of composites has been investigated using a non-steady state method known as the Transient Plane Source (TPS) method. Effective thermal conductivity (ETC) and thermal diffusivity of the composites have been measured by TPS at room temperature and normal pressure. ETC of the composites has been evaluated by several theoretical models and compared with experimental results.

Keywords: Oil-palm fiber, Acrylonitrile grafting, Latex modified, γ-irradiation, Phenol-formaldehyde resin, Transient plane source (TPS) method, Chemical treatment, Effective thermal conductivity (ETC), Thermal diffusivity.

Introduction

Past two decades have been the era of natural fiber reinforced composites. Natural fibers have been receiving considerable attention as reinforcement in plastics due to ease of processability, low cost coupled with high strength, low density, thermal insulation properties, good mechanical properties[1-3] and environmental advantages such as renewability and bio-degrability[4]. Some of natural fiber reinforced thermoplastics and thermosets have found applications in automobile industry, building materials and packaging materials[5]. Phenolic resins are widely used as industrial materials due to high heat resistance, electrical insulation, dimensional stability and flame resistant properties. Toughness of phenolic resin can be modified by the incorporation of latex or latex coated fibers, nitrile phenolics are used in aerospace industry for structure bonding under severe environmental conditions. In recent years fire proof structures have been given a lot of importance from the view point of public security. Phenolic resin has a very high critical oxygen index hence is difficult to ignite and is among the lowest smoke producing resins. Fire resistant property of phenolics can further be improved by reinforcement of flame retardant materials such as styrene –acrylonitrile. Irradiation process can be used to introduce desired properties in the fiber by changing the radiation dose and exposure time.

Lingo-cellulosic natural fibers are hydrophilic[6]due to the presence of strongly polarized hydroxyl (-OH) group. Therefore, lignocellulosic fibers are incompatible with thermosetting matrix leading to poor wettability and adhesion between fibers and matrix[7]. Optimization of interfacial adhesion between lingo-cellulosic fiber and thermosetting resin has been an interesting subject of extensive research[8-9]. Interfacial bonding[10-12] can be enhanced by using radical induced adhesion, coupling agents, grafting process and by different chemical treatments[13-14] on the fiber surface.

Irradiation process, grafting and latex treatment on fiber surface modifies/changes inherent properties and the physical structure of the fiber due to the displacement of the atoms from their mean equilibrium position and modifies the lattice. These treatments enhance the stability of the natural fibers and treated fibers can withstand heat to a greater extent during thermal processing[15]. Thermal properties of natural fiber reinforced composites are of significance for their applications in electronic industry and in new materials' research. Keeping this in mind treated oil-palm fibers have been used as reinforcement in three dimensionally cross-linked resole type phenol formaldehyde thermosetting resin matrix. Oil-palm fiber is rich in cellulose content and contains 65% holocellulose (ASTM D 1104) and lignin 19% (ASTM D 1106. Density and diameter of oil-palm fiber varies from 0.7-1.55g/cm^3 and from 50-500 μm respectively. Scanning electron microscope (SEM) studies of oil-palm fiber surface reveals a wax like layer and the presence of micro-pores on the surface.

Materials and Methods

Materials: Oil-palm empty fruit bunches and Phenol-formaldehyde resole type resin were supplied by Oil Palm India Ltd., Kottayam, India and West Coast Polymers Pvt. Ltd, Kannur, Kerala, India respectively. All reagent grade chemicals are used for fiber surface modification.

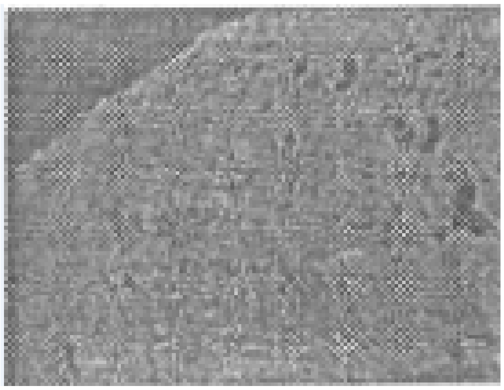

Figure-1
SEM (X400) of oil-palm fiber surface

Surface Modification of fibers: Gamma Irradiated: Fibers were exposed to Co^{60} gamma irradiation at a dose rate of 0.1 Mad per hour for about 30 minutes. γ-irradation produces R-OO peroxy radicals or R- OOH perhydroxy groups on the radiation sensitive surface of the lignocellulosic backbone.

Acrylonitrile grafting: Fibers were bleached with 2% alkali for 30 min and oxidized with 0.02 ml^{-1} $Kmno_4$ (liquor ratio, 1:150) for 10 min. Fibers were washed with water and were placed into 1% H_2SO_4 containing acrylonitrile in the ratio 30:1. Fibers were then placed in a thermostatic water bath at 50 ^{0}C for 2 h, washed and dried. Grafted fibers were isolated from any homo-polymer formed (PAN) by soxhlet extraction.

Latex modification: Fibers were soaked for 48 hours in 5% solution of NaOH and then washed with water containing few drops of acetic acid. Fibers were again washed with fresh water and dried. Washed fibers were dipped into a (10 % dry rubber) containing natural latex rubber solution.

Composite Fabrication: Fibers from oil-palm empty fruit bunches were obtained by retting process. The pithy material was removed and the fibers were washed and dried at 60^0C. The dried fibers were irradiated, grafted and chemically treated with acrylic acid. Fibers were chopped into 40 mm length segments and randomly oriented mats were prepared by the hand lay-up method followed by compression moulding at 100 ^{0}C for about 30 min. All the composites have 40% fiber loading by weight.

Measurements: Theory of transient plane source technique: In TPS method a bifilar spiral is sandwiched between the two thin layers of kapton, which also serves as a sensor of the temperature increase in the sample. The design number of the sensor is K-4521. Assuming the conductive pattern to be in the Y-Z plane of the co-ordinate system, the rise in the temperature at a point Y-Z at time t due to an output power per unit area Q is given by[16]

$$\Delta T(y,z,\tau)=\frac{1}{4\pi^{3/2}a\lambda}\int_0^{\tau}\frac{d\sigma}{\sigma^2}\int_A dy'dz'\times Q\left(y'z't-\frac{\sigma^2a^2}{\kappa}\right)\exp\left[\frac{-(y-y')^2-(z-z')^2}{4\sigma^2a^2}\right]$$

where: $\kappa(t\text{-}t') = \sigma^2 a^2$, $\theta = a^2/\kappa$, $\tau = (t/\theta)^{1/2}$, a is the radius of the hot disk, θ is known as the characteristic time, σ is a constant variable and λ is the ETC in the units of W/mK. The temperature increase ΔT (τ) gives rise to the change in the electrical resistance $\Delta R(t)$ because of the flow of the current through the sensor. ΔR (t) is given by

$$\Delta R(t)=\alpha R_0\Delta T(\tau)$$

where: R is the resistance of TPS element before the transient recording has been initiated, α is the temperature coefficient of resistance (TCR) and $\Delta T(\tau)$ is the mean value of the time dependent temperature increase of the TPS element. $\Delta T(\tau)$ is calculated by averaging the increase in the temperature of TPS element over the sample time because of the concentric ring source in the TPS element have different radii and are placed at different temperatures during the transient recording.

$$\Delta T(\tau)=\frac{P_0}{\pi^{3/2}a\lambda}D_s(\tau)$$

where

$$D_s(\tau)=[m(m+1)]^{-2}\int_0^{\tau}\frac{d\sigma}{\sigma^2}\times\left[\sum_{i=1}^{m}l\left\{\sum_{k=1}^{m}k\exp\frac{-(l^2+k^2)}{2\sigma^2m^2}L_0\left(\frac{lk}{2\sigma^2m^2}\right)\right\}\right]$$

Where: P_0 is the total output power and L_0 is the modified Bessel function. To record the potential difference variations which are of the order of few millivolts during the transient recording, a simple bridge arrangement as shown in Figure-2 has been used. The resistance increase will cause a potential difference variation $\Delta U(t)$ measured by the voltammeter in the bridge, the analysis of the bridge indicates that

$$\Delta E(t)=\frac{R_s}{R_s+R_0}I_0\Delta R(t)$$

$$\Delta E(t)=\frac{R_s}{(R_0+R_0)}\frac{I_0\alpha R_0P_0}{\pi^{3/2}a\lambda}D_s(\tau)$$

where:

$$\Delta E(t)=\Delta U(t)[1-C.\Delta U(t)]^{-1}$$

and:

$$C=\frac{1}{R_sI_0\left[1+\frac{\gamma R_P}{\gamma(R_s+R_0)+R_P}\right]}$$

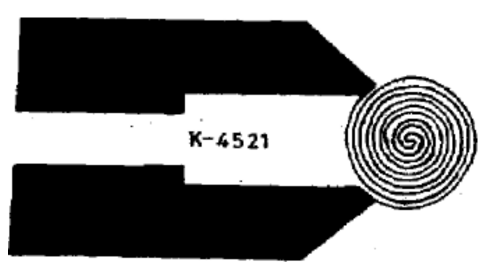

Figure-2
Schematic diagram of TPS sensor

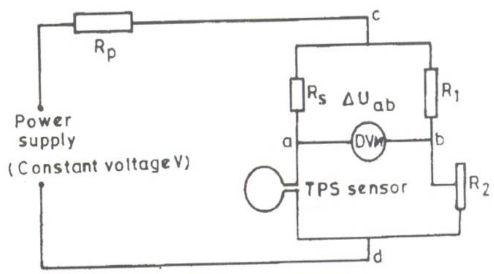

Figure-3
Circuit diagram for the TPS measurements

R_s is the standard resistance with a current rating that is much higher than I_0, which is the initial heating current through the arm of the bridge containing the TPS element. γ is having a value 100 in these measurements. Calculating $D_s(\tau)$ with the computer program and recording the change in the potential difference $\Delta U(\tau)$, thermal conductivity (λ) can be determined. Thermal conductivity and thermal diffusivity of the samples measured by TPS method are reproducible within 2-2.5 %. The sample size used for the TPS study is 1.3 x 1.3 x 0.3 cm^3. Experimental setup is shown in Figure-3.

Results and Discussion

The ETC and the thermal diffusivity measurements of oil palm fiber reinforced PF composites employing the TPS technique at room temperature and normal pressure have been listed in Table-1.

Y. Agari model[17-19] and Bruggman model[20] have been used to evaluate the thermal conductivity of untreated fibers[21]. Extrapolation of the volume percentage of the fiber to 100% loading gives the results in agreement as predicted by both the models. Thermal conductivity of the untreated fiber by above procedures came out to be 0.24 W/mK. Thermal conductivity of treated fiber has been evaluated using the Bruggman model. Thermal conductivity of the untreated as well as treated fibers obtained by the said model are coated in Table-1.

Table-1
ETC and thermal diffusivity measurements of oil palm fiber reinforced PF composites. λ_e , λ_f ,χ and ρC_p represent the ETC of the fiber, thermal diffusivity and specific heat respectively

Composite	λ_e (W/mK)	λ_f (w/mk)	χ (mm^2 /sec)	ρC_p (MJ/m^3K)
Untreated	0.293	0.240	0.158	1.854
Gamma irradiated	0.313	0.279	0.150	2.086
Acrylonitrile grafted	0.449	0.574	0.190	2.363
Latex modified	0.365	0.383	0.169	2.159

In literature several theoretical and empirical models have been proposed to predict the ETC of composites. Maxwell[22] model uses the mean field approach to evaluate the effective thermal conductivity. In this model the fact that the path of heat in one phase is perturbed by the presence of the other phase has been exploited. Babanov[23] model utilizes the cubes in simple cubic arrangement for the evaluation of ETC. Brailsford and Major[24] utilizes the mean field approach to evaluate ETC of the composites. This model is applicable where the second phase is represented by the random combination of the isolated particles. Verma et. al.[25] modifies the phase averaging approach of Hadley[26] to obtain the expression for the ETC. Hadely's model and Hamilton and Crosser's model[27] contain the shape parameter of the reinforced material. Q. Z. Que[28] model evaluates the ETC of the carbon nano-tubes reinforced composites. Though this model has been derived for nano-composites but does not contain any special feature/parameter such as particle size or shape which characterizes such composites. Ideally this model should be applicable to composites having two phases.

Table-2
Theoretically Evaluated values of ETC along with experimental results

Composite	Maxwell's Model	Babanov's Model	Hamilton and Crosser's Model C	Brailsford and Major's model	Verma et. al. Model	Q.Z. Que's Model	Experimental Results
Untreated		0.303	0.292	0.292	0.289	0.292	0.293
γ-irradiated	0.313	0.319	0.303	0.313	0.312	0.313	0.313
Acrylonitrile	0.448	0.424	0.449	0.449	0.439	0.450	0.449
Latex	0.365	0.356	0.365	0.365	0.362	0.365	0.365

Thermal conductivity data of treated fiber shows enhancement in the thermal conductivity of the fibers. It has been found in literature that if a matrix is reinforced with a fiber of higher conductivity than that of the matrix, the effective thermal conductivity of the composite thus formed is higher than that of the matrix and vice-versa[29]. On this basis the increase in the effective thermal conductivity of the treated composites seems to be justified.

Figure-4
SEM (X400) of γ- irradiated oil palm Fiber

Exposure of radiation affects the chemical properties and the physical structure of the fibers. These structural changes may give valuable information about the molecular structure and transport processes. Surface study of gamma irradiated fibers by SEM (Figure-4) shows that this process eliminates the inherent porous structure of the fibers and leads to micro-level disintegration. Radiation induced cracks are visible on the surface of the fiber. Occurrence of cracks affects the interfacial bonding and provide enhancement in ETC and thermal diffusivity of the composite. Gamma irradiation[30] method has been used on natural fibers to achieve better coupling between fibers and synthetic resin.

Oil-palm fiber has low lignin and high cellulose content. Presence of lignin content in the fiber retards the polymerization rate and acts as an inhibitor at higher lignin containing fibers. Due to high cellulose content grafting reaction is favoured. Scanning electron micrograph (Figure-5) of grafted oil-palm fiber shows the fibrillated porous structure. Initiation of longitudinal cracks visible on the grafted surface may be due to the presence of grafting material. Matrix resin fills the pores and gaps between the fibrils leading to enhanced coupling leading to increased ETC of the composite.

Latex treated fiber becomes smooth and fibrillation is minimized. Fiber becomes highly hydrophoblic and elastic due to the presence of rubber. Presence of rubber may reduce the interfacial adhesion[31] but due to the formation of conductive chains between latex and phenolic resin the overall thermal conductivity of the composite increases.

Figure-5
SEM (X400) of acrylonitrile grafted oil palm

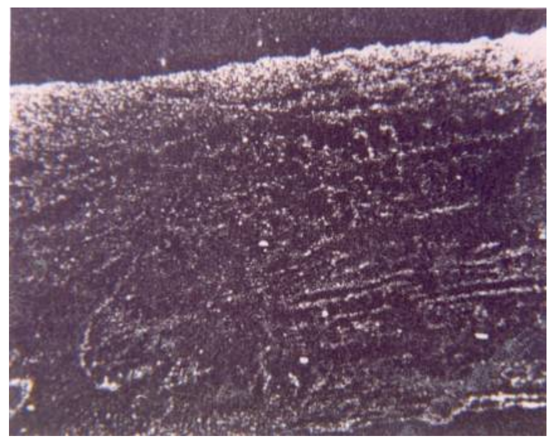

Figure-6
SEM (X400) of latex treated oil palm fiber

Conclusion

It can be concluded that treatments have enhanced the thermal conductivity and thermal diffusivity of the treated composites. Acrylonitrile grafted fiber reinforced composite has the highest thermal conductivity where gamma irradiated composite is least conductive from the set of the treated composites. Increase in the ETC values in these cases is attributed to the enhanced fiber matrix adhesion caused by treatments on the fiber surface.

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References

1. Ma X., Jiugao Y. and Kennedy J.F. (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate Polymers*, 62, 19–24.

2. Arbelaiz A. and Fernandez B. et. al. (2005). Mechanical properties of flax fibre/polypropylene composites. Influence of fibre/matrix modification and glass fibre hybridization. *Composites: Part A*, 36, 1637-1644.

3. Sreekala M.S. and George J. et. al. (2002). The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibres. *Comp. Sci. Tech.*, 62, 339-353.

4. Cantero G. and Arbelaiz A. et al. (2003). Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. *Comp. Sci. Tech.*, 63, 1247-1254.

5. Bledzki A.K. and Gassan J. (1999). Composites reinforced with cellulose based fibres. *Prog. Polym. Sci.*, 24, 221-274.

6. Westerlind B.S. and Berg J.C. (1988). Surface energy of untreated and surface-modified cellulose fibers. *J. Appl. Polym. Sci.*, 36523-34.

7. Vazguez A., Riccieri J. and Carvalho L. (1999). Interfacial properties and initial step of water sorption in unidirectional unsaturated polyester/vegetable fiber composites. *PolyImer Composites*, 20, 29-37.

8. Brahmakumar M., Pavithran C and Pillai R.M. (2005). *Coconut fibre* reinforced polyethylene*composites*: effect of natural waxy surface layer of the fibre on fibre/matrix interfacial bonding and strength of composites. *Comp. Sci. Tech.*, 65, 563-569.

9. Panthapulakkal S., Zereshkian A. and Sain M. (2006). Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites. *Bioresource Tech.*, 97, 265–272.

10. Maldas D., Kokta B.V., Raj R.G. and Daneault C. (1988). Improvement of the mechanical properties of sawdust wood. *Polymer*, 29, 1255-65.

11. Maldas D., Kokta B.V., Raj R.G.A and Daneault C. (1989). Surface modified cellulose nanofibrils. *Appl. Polym. Sci.*, 37, 751-75.

12. Joseph S. and Sreekala M.S.et al. (2002). A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibres and glass fibres. *Composites Sci. and Tech.*, 62, 1857-1868.

13. Gauthier R. and Joly C. et. al. (1998). Interfaces In Polyolefin Cellulosic Fiber Composites - Chemical Coupling, Morphology, Correlation With Adhesion And Aging In Moisture. *Polymer Composites*, 19(3), 287-300.

14. Sreekala M.S., Kumaran M.G. and Thomas S. (2002) .Water sorption in oil palm fiber reinforced phenol formaldehyde composites. *Composites Part A*, 33, 763-777.

15. Sreekala M.S., Kumaran M.G. and Thomas S. (1991). *Comp. Sci. and Tech.*, 41, 165.

16. Carslaw H.S. and. Jaeger J.C. (1959). Conduction of Heat in Solids. Oxford University Press: New York, 510.

17. Agari Y., Ueda A., Tanaka M. and Nagai S. (1993). Thermal conductivity of a polymer composite. *J. Appl. Polym. Sci.*, 49, 1625.

18. Agari Y. and Tanaka M. (1987). Thermal conductivity of a polymer composite filled with mixtures of particles. *J. Appl. Polym. Sci*, 34, 1429.

19. Agari Y. and Uno T. (1986). Estimation on thermal conductivities of filled polymers. *J. Appl. Plym. Sci.*, 32, 5705.

20. Bruggman D.A.G. (1935). Calculation of various physical constants of heterogeneous substances. I. dielectric constants and conductivities of the mixed body of isotropic substances. *Ann. Phys.*, 24, 636.

21. Agrawal R. and Saxena N.S. et. al. (2000). Effective thermal conductivity of three-phase styrene butadiene composites. *J. App.l Polym. Sci.*, 76, 1799-1803.

22. Maxwell J.C. (1892). A treatise on electricity and magnetism Vol. 1.Clarendon Press, Oxford, 194-216.

23. Babanov A.A. (1957). Methods for calculation of thermal conduction coefficients of capillary porous materials. *Sov. Phys. Technol. Phys.*, 2, 476-484.

24. Brailsford A.D. and K.G. Major. (1964). The thermal conductivity of aggregates of several phases, including porous materials. Br. *J. Appl. Phys*, 15, 313-319.

25. Verma L.S., Shortriya A.K., Singh R. and Choudhary D.R. (1991). Thermal conduction in two-phase materials with spherical and non-spherical inclusions. *J. Phys. D: Appl. Phys*, 24, 1729-1737.

26. Hadley G.R. (1986). Thermal conductivity of packed metal powders Int. *J. Heat mass Transfer*, 29, 909-920.

27. Hamilton R.L. and Crosser O.K. (1962). Thermal conductivity of heterogeneous two-component systems. *IEC Fundamentals*, 2, 187.

28. Que Q. Z. (2005). Model for thermal conductivity of carbon nanotube-based composites. *Physica B*, 368, 302-307.

29. Tye R.P. (1985). Factors influencing thermal conductivity measurements on composites (a review). *High Temp. High Press*, 17, 311.

30. Owolabi O., Czvikovszky T. and Kovacs I. (1985). Coconut-fiber-reinforced thermosetting plastics. *J. Appl. Polym. Sci*, 30, 1827.

31. Sreekala M.S. and Kumaran M.G. et. al. (2002). Oil palm fiber reinforced Phenolformaldehyde composites: Influence of fiber surface modification on mechanical performance. *Appl. Comp. Mater*, 7, 295.