

# Comparative Study of Dielectric Properties of Chicken Feather/Kenaf Fiber Reinforced Unsaturated Polyester Composites

Kwong Siong Kiew, Sinin Hamdan, and Md. Rezaur Rahman \*

The electrical properties of chicken feather fiber (CFF) and kenaf fiber (KF) unsaturated polyester (UP) composites have been studied with reference to fiber loading and frequency. Tests were carried out to compare the suitability of the two different composites as a dielectric material. The chicken feather fiber unsaturated polyester composite exhibited an overall lower dielectric constant, dissipation factor, and loss factor compared to the kenaf fiber unsaturated polyester composites. The values were high for the composites with fiber contents at 40%. The dielectric value increments were high at low frequencies, and they gradually reached significantly lower values at higher frequencies. Based on the results it was judged that chicken feather fiber composites would be suitable for application as high speed printed circuit board (PCB) material with good frequency stability at 1 MHz. Finally, an attempt was made to correlate the experimental values with theoretical calculations.

*Keywords:* Chicken feather fiber; Dielectric properties; Unsaturated polyester; Kenaf fiber; Biocomposite; Permittivity; Dielectric constant; Dissipation factor; Loss factor

*Contact information:* Faculty of Engineering, University Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia; \*Corresponding author: mdrezaurr@gmail.com

## INTRODUCTION

There has been an acceleration of research studies focusing on organic bio-composites obtained from agricultural reserves, prompted by concern about depletion of natural resources, or the unsustainability of inorganic fiber. Biocomposites are defined as composite materials containing at least one biological phase (Zhan *et al.* 2011). In the United States alone, approximately  $2 \times 10^9$  kg of chicken feathers are generated every year (Parkinson 1998). The disposal of the feathers is carried out, in most cases, by burial, whereas an improved, more effective, and expectantly beneficial utilization of chicken feather waste is desirable (Cheng *et al.* 2009).

Feathers are composed primarily of keratin protein, with the three basic parts of the feather identified as the quill, the barbs, and the barbules (Huda and Yang 2009). Keratin is relatively hydrophobic. It has a similar strength to that of nylon, but a diameter smaller than that of wool (Cheng *et al.* 2009).

It is anticipated that chicken feathers, as part of the organic fiber family, will not suffer from the wear of the polymer processing equipment and size reduction during processing, both of which may occur with the use of inorganic fibers or fillers (Barone and Schmidt 2005). Moreover, organic fibers such as chicken feathers may offer the possibility of covalently bonding the matrix polymer to the fiber either directly or through a similar type of chemical coupling, such that chemical processing can be carried

out more easily, as compared to inorganic fiber (*e.g.* glass fibers) (Barone and Schmidt 2005).

Kenaf and jute are warm-season annual row crops having a single, often straight, and unbranched stem. Kenaf and jute fibers have been used for rope, canvas, and sacking due to the easy availability, lightweight, low-cost, and other attractive features (Rashdi *et al.* 2009; Rahman *et al.* 2008, 2010).

Zhan *et al.* (2011) demonstrated the use of chicken feather fibers with epoxy resin to produce composite samples and proposed their potential application for printed circuit boards (PCBs). An investigation of using soybean resins and chicken feather fibers was conducted by Zhan and Wool (2010) to evaluate feasibility for possible applications in electronic devices such as printed circuit boards (PCBs). In recent studies, the need to produce materials with improved electrical properties versus the standard epoxy offerings is crucial to the development of the PCB industry. In particular, improvements in the dielectric constant (permittivity) and dissipation factor (loss tangent) are the properties of interest, as materials with the lower values of these properties are needed for circuits to operate at high frequencies (Kelley 2007). Consumer printed circuit boards (PCBs) intended for applications such as mobile phones or computers typically require low values of dielectric constant and loss (Kelley 2007). Various dielectric studies have been conducted by researchers utilizing different kinds of fibers and matrices (Sreekumar *et al.* 2012; Kulshrestha and Sastry 2006; Rahman *et al.* 2009; Bose *et al.* 2012; He *et al.* 2008; Sosa-Morales *et al.* 2010; Nuriel *et al.* 2000; Chand and Jain 2005; Zhou *et al.* 2012; Bhat *et al.* 2012; Barreto *et al.* 2010), but none have coupled the use of unsaturated polyester with chicken feather fibers or kenaf fibers yet.

The use of unsaturated polyester as the matrix for the composite has become increasingly popular with fiber reinforcements such as sisal fibers, flax fibers, hemp fibers, alfa fibers, and so on (Santhong *et al.* 2009; Haq *et al.* 2009a; Marais *et al.* 2005; Bessadok *et al.* 2009; Sawpan *et al.* 2012; Haq *et al.* 2009b). However, there have been few trials using a composite with chicken feather fibers or kenaf fibers.

In the present research, composites were fabricated using unsaturated polyester (UP) as a matrix material and chicken feather fibers (CFF) or kenaf fibers (KF) as the reinforcements. A dielectric study was undertaken for both composites to determine the suitability of each type of composite relative to its utilization as a dielectric material.

## EXPERIMENTAL

### Materials

The matrix material used in this study was based on the unsaturated polyester resin with the trade name "Reversol P9509" supplied by Revertex (Malaysia) Sdn. Bhd. Company. This type of unsaturated polyester resin has a rigid, low reactivity, and thixotropic general purpose othophthalic characteristics. For curing, the matrix needs to be mixed with a curing catalyst, namely methyl ethyl ketone peroxide (MEKP) at a concentration of 1% by weight ratio of the matrix. For reinforcements, kenaf fibers and chicken feather fibers were used to complete the composite materials.

### Fiber Preparation

The kenaf fibers obtained were drenched in hot water at 100°C. The kenaf fibers were left to soak, washed in a water-soluble ethanol, and sun-dried for 7 h. To make sure

that the fibers were completely dried, the fibers were left in an oven at 80°C for 24 h. The kenaf fibers were processed using a round vibratory sieves machine to remove the chunks of fiber. The kenaf fiber lengths after the separation were 3 to 6 mm.

The chicken feather fibers were obtained from a local poultry farm as raw chicken feather materials. The chicken feathers were left to soak, washed in a water-soluble ethanol, and sun-dried for 7 to 8 h. To make sure that the materials were completely dried, the chicken feathers were left in furnace at 80°C for 24 h. The raw chicken feathers obtained after the furnace were cut into sizes of 3 to 6 mm.

### Specimen Preparation Method

All of the fiber matrix materials were degassed in a vacuum for a minimum of 5 min to remove the air bubbles before curing. The unsaturated polyester composites were cured with MEKP at a 1% weight ratio of the unsaturated polyester matrix. The mold was compressed using a cold-press and left for 24 h. Each mold trial was comprised of three fiber composite samples. The dimensions presented for each fiber composite was disc-shaped with a diameter of 500 mm and a thickness of 5 mm. A schematic of the mold press is shown in Fig. 1.

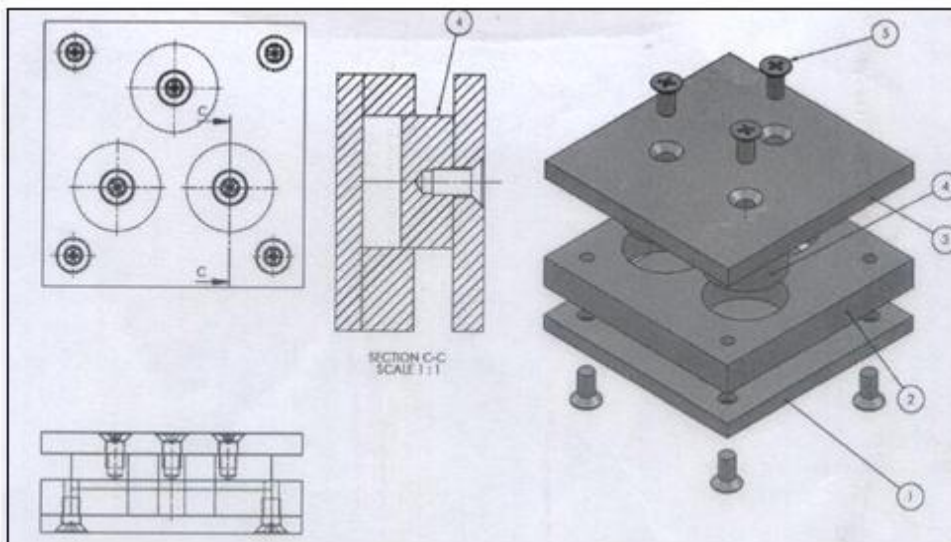


Fig. 1. Dielectric mold

### Composite Testing

The HP 16451B dielectric test fixture with an HP LCR impedance analyzer was utilized to obtain the dielectric properties of unsaturated polyester chicken feather fiber and kenaf fiber composites. The samples were analyzed using a contacting electrode method, which uses a rigid metal electrode. The samples fabricated have flat surfaces and low compressibility. Hence, by using this method, it can raise the accuracy of the measurement. The tests were done in the frequency range of 60 Hz, 1 KHz, 10 KHz, 100 KHz, and 1 MHz. The sample studies were disc-shaped with a diameter of 500 mm and a thickness of 5 mm. The average value was recorded by the HP impedance analyzer after the samples had been tested 15 times at a given frequency.

The dielectric constant ( $\epsilon_r$ ) of the testing materials can be calculated from the capacitance using the equation,

$$\epsilon_r = \frac{t \times C}{\pi r^2 \epsilon_0} \quad (1)$$

where  $t$  is the thickness,  $C$  is the capacitance,  $r$  is the radius of the test specimen, and  $\epsilon_0$  is the dielectric constant of the free space.

The loss tangent ( $\tan \delta$ ) can be obtained directly from the HP impedance analyzer. Table 1 shows the fiber ration and actual fiber content (%) in composites.

**Table 1.** Fiber Content (%) in Composites

CFF Sample Name	Actual fiber content (%)	KF Sample Name	Actual fiber content (%)
CFF10	12.82	KF10	12.8
CFF20	20.81	KF20	21.83
CFF30	31.67	KF30	33.25
CFF40	41	KF40	43.5

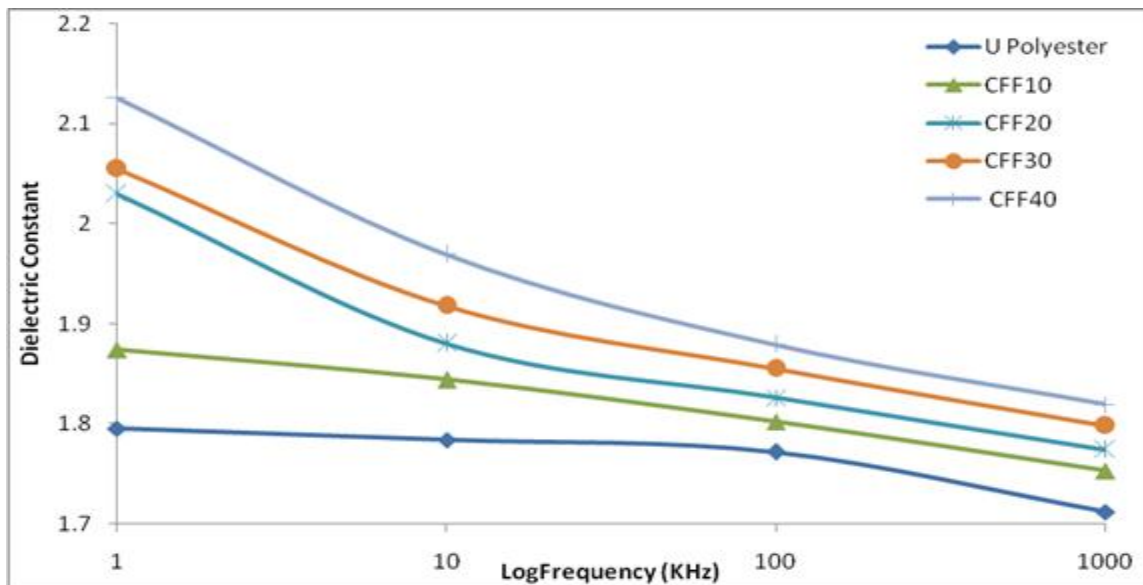
## RESULTS AND DISCUSSION

### Permittivity Measurement

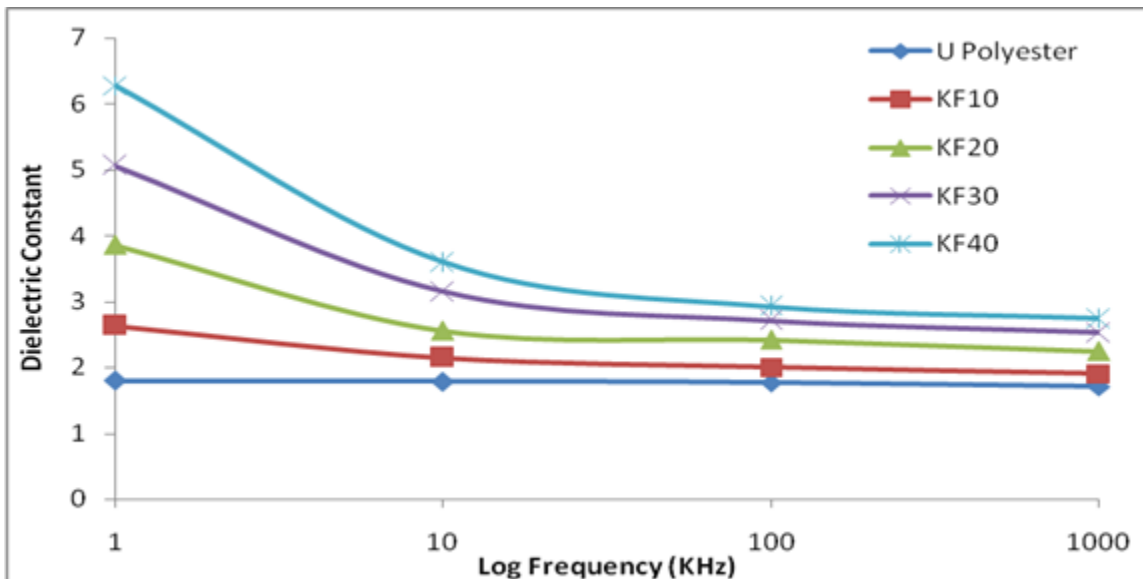
The dielectric constant of a material is defined as the ratio of the capacitance of a condenser containing the material to that of the same condenser under vacuum (Sreekumar *et al.* 2012). Figures 2 and 3 represent the dielectric constant of unsaturated polyester CFF composites and KF composites as a function of the fiber content and the frequency at room temperature, respectively. As observed from both Figs. 2 and 3, the dielectric constant of the unsaturated polyester CFF and the unsaturated polyester KF increased over the range of frequencies at the given orders of UP>CFF10>CFF20>CFF30>CFF40 and UP>KF15.8>KF21.83>KF37.25>KF43.5. The increase of the value is mainly contributed by the interfacial, orientation, atomic, and electron polarizations in the material (Kulshrestha and Sastry 2006). The polarization of the matrix and fillet contribute to interfacial polarization. An increase in the fiber loading of the CFF leads to increased orientation and interfacial polarization, which results from the polar groups' presence in the cellulose fibers (Sreekumar *et al.* 2012).

Other work has shown that unsaturated polyester has low dielectric constant values over the range of frequencies considered; this is because it only has induced atomic and electronic polarizations to account for (Kelley 2007). As shown from a single fiber loading trend, the dielectric constant is always highest at the lowest frequency due to the increase in orientation polarization at lower frequencies (Sosa-Morales *et al.* 2010). The process of complete orientation polarization is achievable only at lower frequencies, and this formulates the decrease in the dielectric constant as the frequency increases. The term is called “lag in orientation of polarization” (Sosa-Morales *et al.* 2010). Figure 4 compares the dielectric constants of the KF composites and the CFF composites at 20% fiber loading and 40% fiber loading, respectively. It can be seen that the KF composites exhibited high values at low frequencies and low values at high frequencies. In comparison with the KF composites, the CFF composites showed a better frequency stability at all ranges of frequencies. This is largely due to the physical attributes of the CFF, which is lightweight and in comparison to the kenaf fiber, the amount of fiber

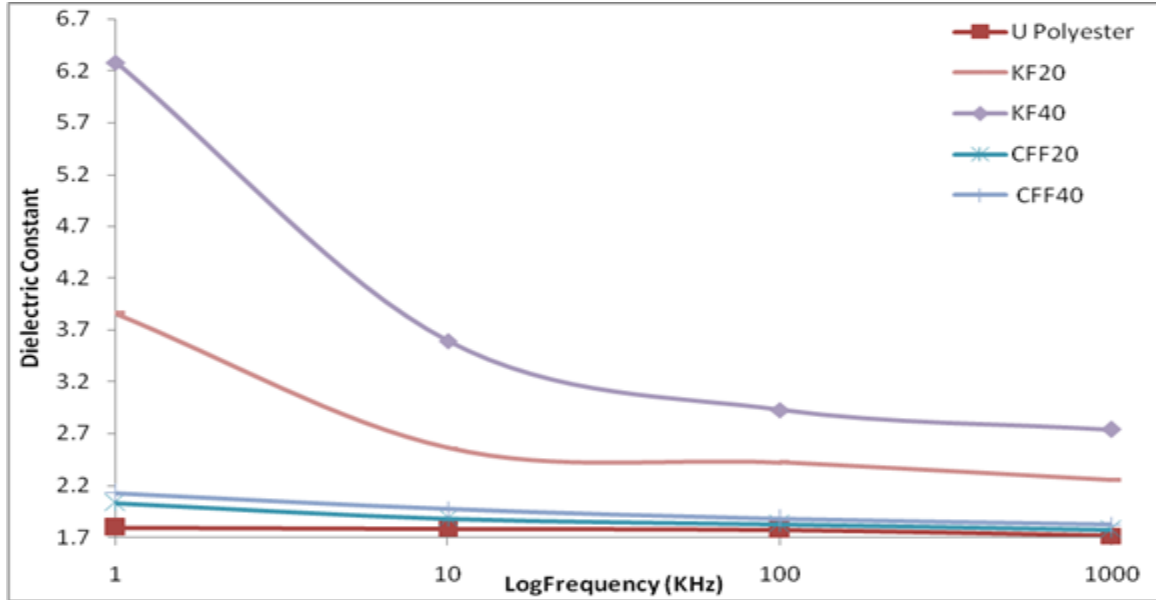
loading does not contribute to the same volume attributes. The CFF has a greater volume of fiber than the KF when comparing with the same mass amount of fiber loading. The greater volume of fiber contributes to more orientation and interfacial polarization in the CFF composites than the KF composites. Furthermore, the hollow structure of the chicken feathers incorporates air (dielectric constant = 1.0), which also contributes to the fact that the dielectric constant decreases with the increasing fiber contents (Zhan *et. al.* 2011).



**Fig. 2.** Dielectric constant of CFF/UP composites as a function of fiber content and frequency at room temperature

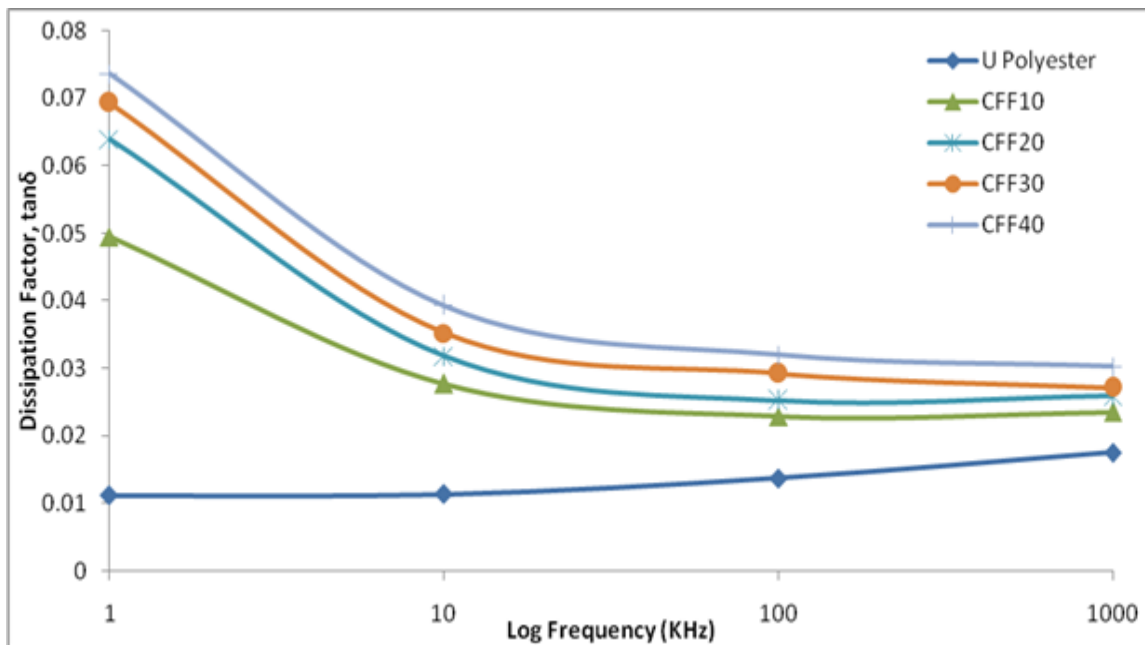


**Fig. 3.** Dielectric constant of unsaturated polyester KF composites as a function of fiber content and frequency at room temperature

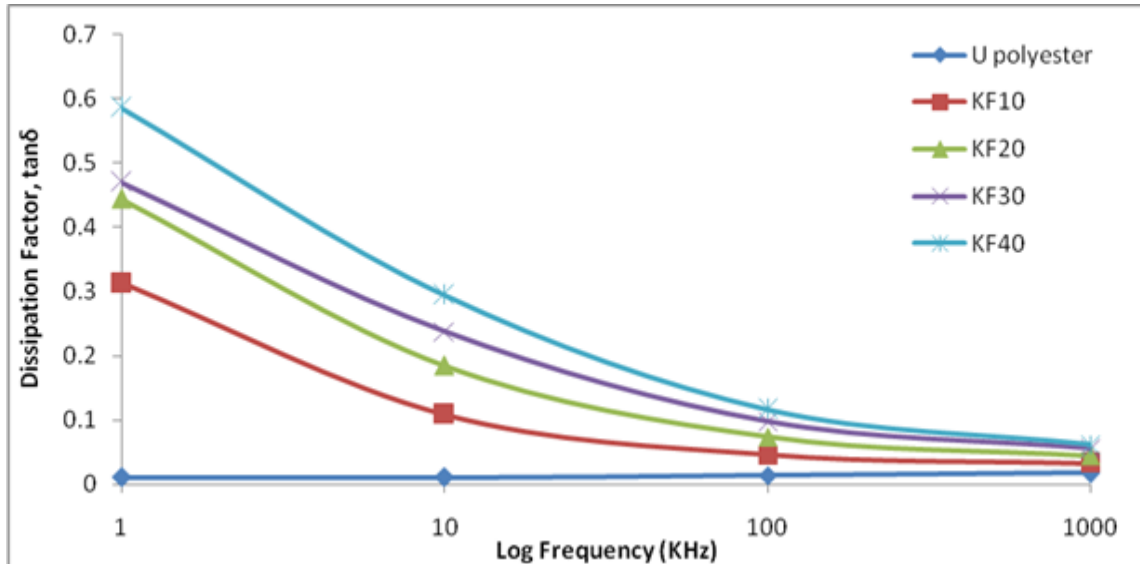


**Fig. 4.** Comparison of dielectric constant between KF composites and CFF composites as a function of fiber loading and frequency at room temperature

The dissipation factor ( $\tan \delta$ ) of an insulating material is the tangent of the dielectric loss angle, and it is strongly influenced by polar components, which make it a sensitive parameter. The dissipation factor can be obtained directly from the dielectric test fixture. The electrical energy is converted to heat energy in an insulating material, and it accelerates the deterioration. Figures 5 and 6 show variations of the dissipation factor of the CFF/UP and the KF/UP composites as a function of the log frequency at different fiber loading in room temperatures, respectively.

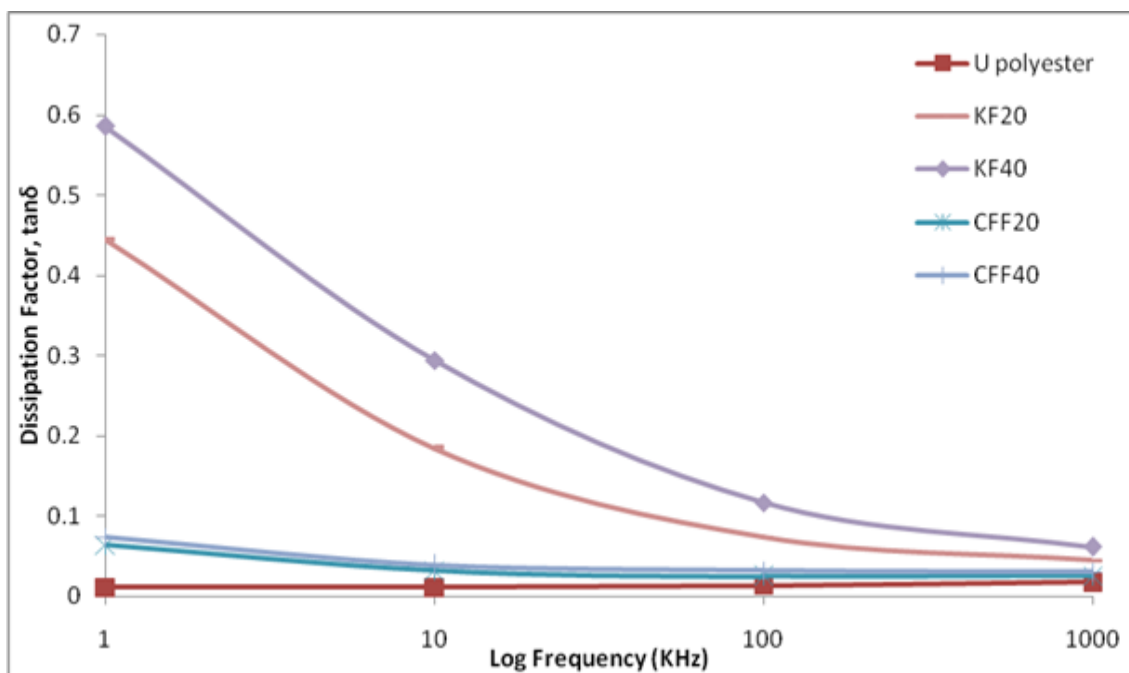


**Fig. 5.** Variations of the dissipation factor of the CFF/UP composites as a function of the log frequency at room temperature



**Fig. 6.** Variations of the dissipation factor of the KF/UP composites as a function of the log frequency at room temperature

It can be observed that the dissipation factor of the CFF/UP and the KF/UP composites decreased with an increasing frequency. This is due to the increase of the polar groups with the increases of the fiber content, factors tending to increase the orientation polarization. The orientation polarization is difficult at high frequencies which causes a significant decrease in the dissipation factor. Figure 7 shows the dissipation factor comparison between the CFF/UP and the KF/UP composites. The CFF/UP composites suggest better frequency stability characteristics compared to the KF/UP composites. The dissipation factor for the CFF/UP composites was lower than 0.1 for all of the fiber loading types.



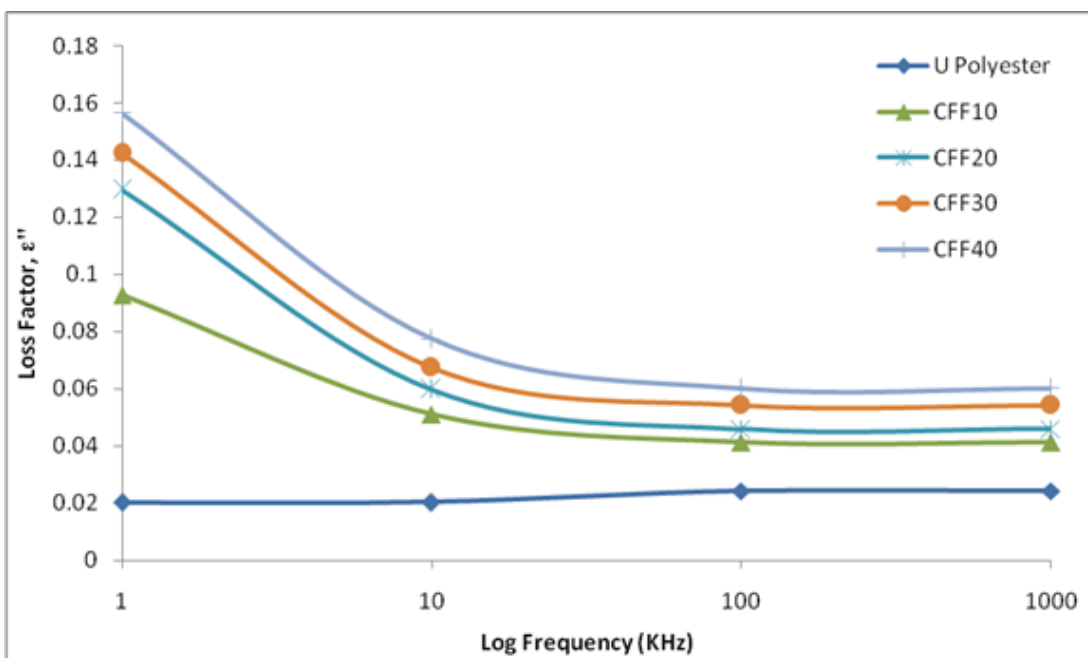
**Fig. 7.** Dissipation factor comparison of the KF/UP composites and the CFF/UP composites as a function of the log frequency at room temperature

The loss factor ( $\epsilon''$ ) is a term used to describe the average power factor over a given period of time. It is widely used in the energy industry to describe the losses in transmission and distribution (Bose *et al.* 2012). The loss factor can be calculated from the equation,

$$\epsilon'' = \tan \delta \times \epsilon' \quad (2)$$

where  $\epsilon'$  is the dielectric constant and  $\tan \delta$  is the dissipation factor.

The variations of the loss factor of the CFF/UP and the KF/UP as a function of the log frequency at room temperature are given in Figs. 8 and 9. It can be observed that in the low frequency region, the loss factor was high and it was the highest for the composite with the highest fiber loading (40%).

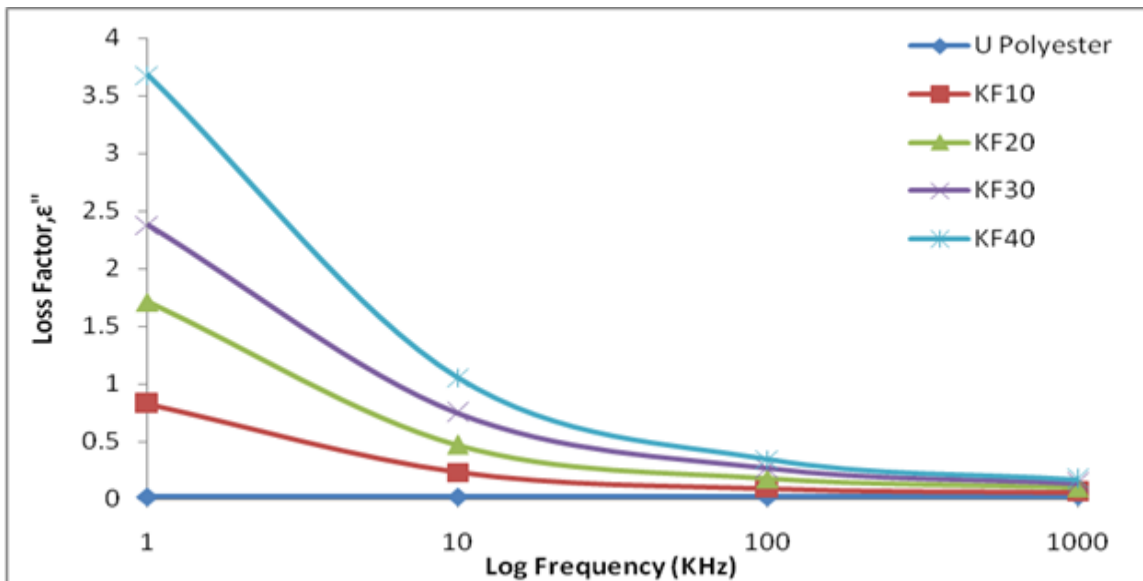


**Fig. 8.** Variations of the loss factor of the CFF/UP composites as a function of the log frequency at room temperature

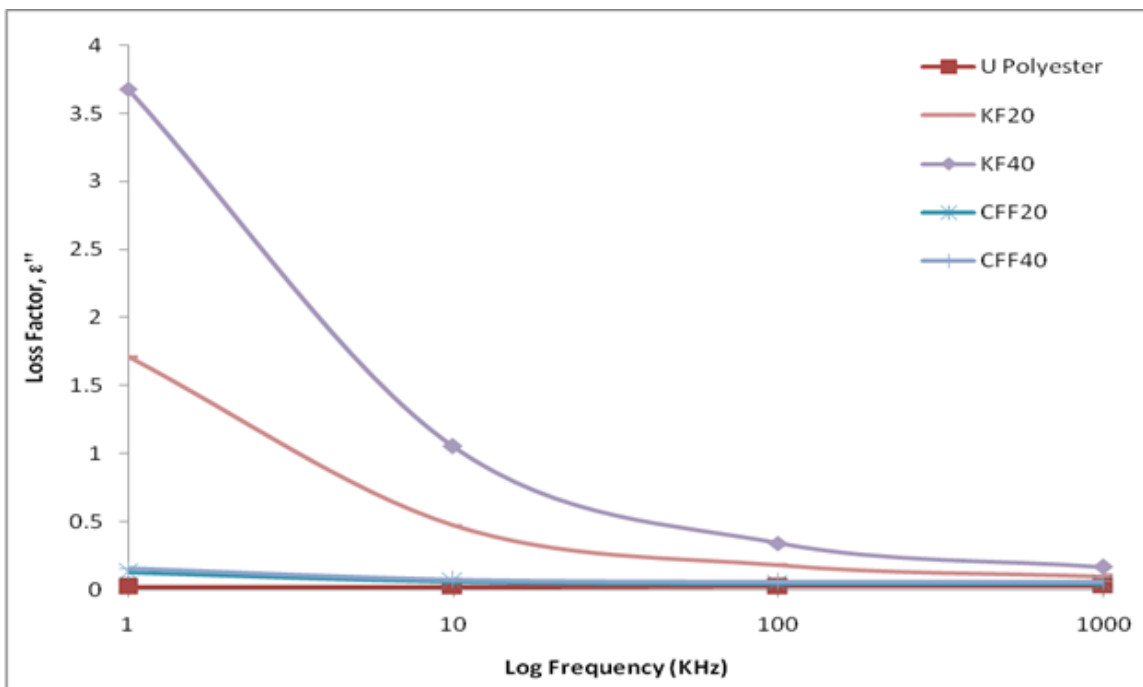
As the frequency increases, the loss factor decreases rapidly. This signifies that the loss factor depends on the fiber content, which is the polarization of fibers at low frequencies. As the fiber content increased, the heterogeneity, which consists of two phase matters (hydrophilic and hydrophobic) inside the composite, increased. This resulted in an increase of the composite polarization. Figure 10 compares the CFF/UP and the KF/UP with respect to the loss factor. It can be seen that the KF/UP composites were stable only at high frequencies, and that it had a high loss factor compared to the CFF/UP composites. The difference between 20% of the KF loading and 40% of the KF loading was huge, which suggests that there were high interfacial polarization increases with the increase of the fiber content. The CFF/UP suggests good frequency stability, which can be attributed to the presence of air content in the feathers' hollow shafts. Overall, all of the CFF/UP composites having a loss factor lower than 1.6 at a CFF 40% content can be utilized to make better PCB materials across a low and high range of frequencies.



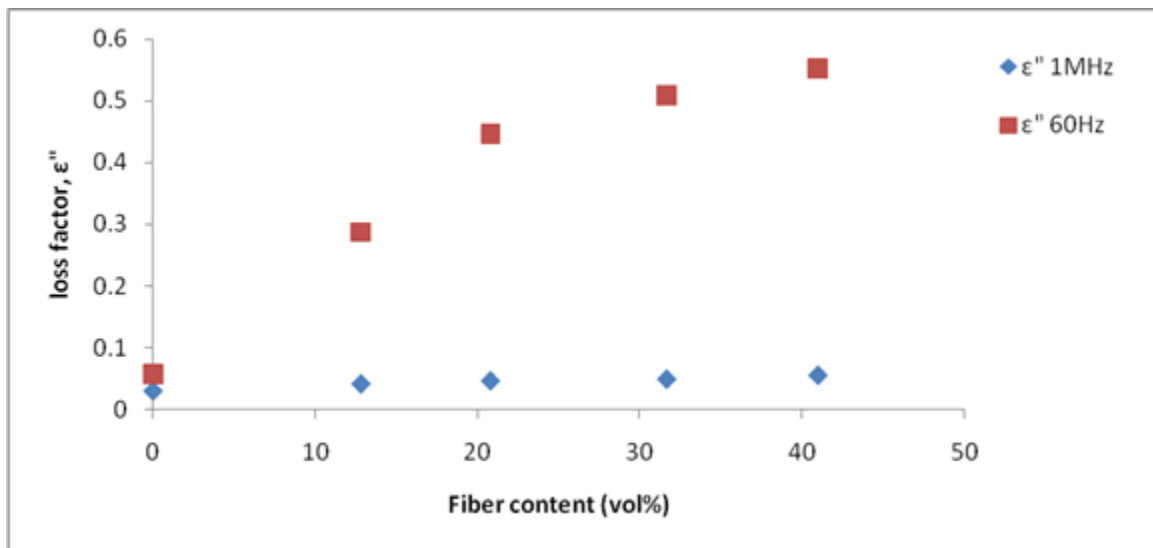
The composite consists of a two-phase system having two different dielectric materials, the fiber (CFF, KF) and the matrix (UP). The fibers are hydrophilic and polar, while the matrix is non-polar and hydrophobic. This interfacial bonding between the fiber and the matrix results in the dissipation of electrical energy at low frequencies; it also contributes to a high interfacial polarization (SreeKumar *et al.* 2012). The kenaf fiber has low frequency stability and high dielectric loss, whereas chicken feather fiber has high frequency stability and low dielectric loss. The latter can be utilized as a potential dielectric material where high frequency stability and low dielectric loss are desirable.



**Fig. 9.** Variations of the loss factor of the KF/UP composites as a function of the log frequency at room temperature



**Fig. 10.** Loss factor comparison of the KF/UP composites and the CFF/UP composites as a function of the log frequency at room temperature



**Fig. 11.** Loss factor of the CFF/UP composites at 60 Hz (low frequency) and 1 MHz (high frequency)

Figure 11 compares the loss factors for the CFF/UP composites at low frequency (60 Hz) and high frequency (1 MHz). It can be seen that the CFF/UP composites exhibited high frequency stability (1 MHz) across all of the increments of fiber contents. However, at the low frequency of 60 Hz, the loss factor gradually increased with increasing fiber loading. This phenomenon suggests the dependence of the loss factor towards the polarization of the fibers. At low frequencies, polarization of fibers can be achieved, yielding an increase of the dissipation factor. As the fiber loading increases, the polarization of the fiber also increases. Nevertheless, at high frequencies, the orientation polarization is difficult, yielding identical trends across the range of fiber contents.

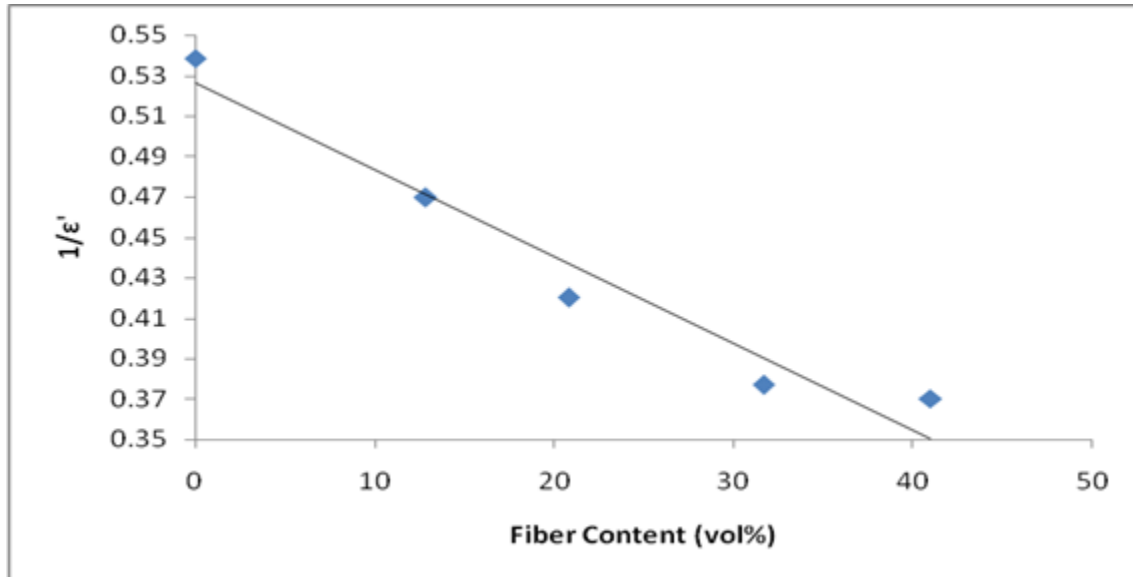
**Table 2.** Computation of Experimental Value of Dielectric Constant and Loss Tangent for CFF/UP at Frequency 1 MHz

CFF Wt%	$\tan \delta$	$\epsilon$
10	0.0229	1.89
20	0.0252	2.02
30	0.0292	2.066
40	0.032	2.129

Table 2 shows the experimental value of CFF/UP composite as dielectric constant and loss tangent at high frequency 1 MHz. At the high frequency of 1 MHz, chicken feather fiber composite reached a combination of dielectric constant and dissipation factors similar to those of commercial PCB materials (Kelley 2007).

### Theoretical Modeling

Figure 12 shows the reciprocal of the dielectric constant ( $1/\epsilon'$ ) of the CFF/UP composites as a function of the fiber content at 60 Hz. The intercepts that describe the line abide by the law of harmonic mixture, which shows a linear trend. This indicates the series mixture of the essential dielectrics present in the composites (Bose *et al.* 2012).



**Fig. 12.** Plot of the reciprocal of the dielectric constant as a function of the volume fraction of fiber at a frequency of 60Hz at room temperature

Extrapolation of the plot of the y-axis to the point where  $v_f$  (fiber volume) = 0 yields  $(1/\epsilon')$ , which describes the dielectric constant of the composite at frequency of 60 Hz. The value obtained by this graphical analysis (1.9) is slightly different from the experimental value (1.8). This slight difference was judged to be acceptable, since it is within the experimental error threshold.

## CONCLUSIONS

1. Increasing the fiber content of composites formed with either chicken feather fiber (CFF) or kenaf fiber (KF) in unsaturated polyester (UP) matrix gave rise to an increase in the dielectric constant, loss factor, and dissipation factor of the composites.
2. The increases in dielectric constant, loss factor, and dissipation factor were more apparent with a fiber content of 40%, such that the orientation and interfacial polarization were manifested to a larger extent which contributes significantly to the changes in the dielectric analysis.
3. A combination of dielectric constant and loss tangent values of 2.02 and 0.0252, respectively, was obtained with 20% of chicken feather fiber in a composite at a high frequency of 1 MHz. These results could be attributed to the good frequency stability that was achieved within this range.
4. Overall, the CFF/UP composites exhibited lower values of dielectric properties, suggesting better suitability of chicken feather fiber composite compared to the kenaf fiber as a dielectric material and a potential for PCB materials, with a good balance between properties, cost, and sustainability.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the Faculty of Engineering, UNIMAS for their financial support, Grant no. FPI(F02)/134/2013(03). The authors are also thankful to Dr. Su Hieng Tiong from Swinburne University of Technology Sarawak Campus for his help in borrowing the dielectric test fixture for the measurement of the dielectric properties for the composite materials.

## REFERENCES CITED

- Barone, J. R., and Schmidt, W. F. (2005). "Polyethylene reinforced with keratin fibers obtained from chicken feathers," *Composites Science and Technology* 65, 173-181.
- Barreto, A. C. H., Costa M. M., Sombra A. S. B., Rosa D. S., Nascimento R. F., Mazzetto S. E., and Fachine P. B. A. (2010). "Chemically modified banana fiber: Structure, dielectrical properties and biodegradability," *J. Polym. Environ.* 18, 523-531.
- Bessadok, A., Roudesli, S., Marais, S., Follain, N., and Lebrun, L. (2009). "Alfa fibres for unsaturated polyester composites reinforcement: Effects of chemical treatment on mechanical and permeation properties," *Composites: Part A* 40, 184-195.
- Bhat, A. H., Khalil, H. P. S. A., Bhat, I. U. H., and Banthia, A. K. (2012). "Dielectric and material properties of poly (vinyl alcohol): Based modified red mud polymer nanocomposites," *J. Polym. Environ.* 20, 395-403.
- Bose, S., Mishra, A. K., Kuila, T., and Kim, N. H. (2012). "Tunable electrical conductivity and dielectric properties of triglycine sulfate – polypyrrole composite," *Chemical Engineering Journal* 187, 334-340.
- Chand, N., and Jain, D. (2005). "Effect of sisal fibre orientation on electrical properties of sisal fibre reinforced epoxy composites," *Composites Part A* 36, 594-602.
- Cheng, S., Lau, K-T., Liu, T., Zhao, Y. Q., Lam, P.-M., and Yin, Y. S. (2009). "Mechanical and thermal properties of chicken feather fiber/PLA green composites," *Composites Part B* 40, 650-654.
- Haq, M., Burgueno, R., Mohanty, A. K., and Misra, M. (2009a). "Bio-based unsaturated polyester/layered silicate nanocomposites: Characterization and thermo-physical properties," *Composites: Part A* 40, 540-547.
- Haq, M., Burgueno, R., Mohanty, A. K., and Misra M. (2009b). "Processing techniques for bio-based unsaturated – polyester/clay nanocomposites: Tensile properties, efficiency, and limits," *Composites Part A* 40, 394-403.
- He, F., Fan, J., and Lau, S. T. (2008). "Thermal, mechanical, and dielectric properties of graphite reinforced poly (vinylidene fluoride) composites," *Polymer Testing* 27, 964-970.
- Huda, S., and Yang, Y. Q. (2009). "Feather fiber reinforced light-weight composites with good acoustic properties," *J. Polym. Environ.* 17, 131-142.
- Kelley, E. J. (2007). "Introduction to base materials," C. F. Coombs (ed.), *Printed Circuits Handbook*, McGraw-Hill, New York.
- Kulshrestha, S. A., and Sastry, S. K. (2006). "Low-frequency dielectric changes in cellular food material from ohmic heating: Effect of end point temperature," *Innovative Food Science and Emerging Technologies* 7, 257-262.
- Marais, S., Gouanve, F., Bonnesoeur, A., Grenet, J., Poncin-Epaillard, F., Morvan, C., and Metayer, M. (2005). "Unsaturated polyester composites reinforced with flax-

- fibers: Effect of cold plasma and autoclave treatments on mechanical and permeation properties,” *Composites: Part A* 36, 975-986.
- Nuriel, H., Kozlovich, N., Feldman, Y., and Marom, G. (2000). “The dielectric properties of nylon6, 6/aramid fibre microcomposites in the presence of transcrystallinity,” *Composites Part A* 31, 69-78.
- Parkinson, G. (1998). “Chementator. A higher use for lowly chicken feather?,” *Chem. Eng.* 105(3), 21.
- Rahman, M. R., Hasan M., Huque M. M., and Islam M. N. (2010). “Physico-mechanical properties of jute fiber reinforced polypropylene composites,” *Journal of Reinforced Plastics and Composites* 29, 445-455.
- Rahman, M. R., Huque M. M., Islam M. N., and Hasan M. (2009). “Mechanical properties of polypropylene composites reinforced with chemically treated abaca,” *Composites Part A* 40, 511-517.
- Rahman, M. R., Huque M. M., Islam M. N., and Hasan M. (2008). “Improvement of physic-mechanical properties of jute fiber reinforced polypropylene composites by post-treatment,” *Composites Part A* 39, 1739-1747.
- Rashdi, A. A. A., Sapuan, S. M., Ahmad, M. M. H. M., and Khalina, A. (2009). “Water absorption and tensile properties of soil buried kenaf fibre reinforced unsaturated polyester composites (KFRUPC),” *Journal of Good, Agriculture & Environment* 7 (3-4), 908-911.
- Santhong, S., Pongprayoon, T., and Yanumet, N. (2009). “Mechanical property improvement of unsaturated polyester composite reinforced with admicellar-treated sisal fibers,” *Composites: Part A* 40, 687-694.
- Sawpan, M. A., Pickering, K. L., and Fernyhough, A. (2012). “Flexural properties of hemp fiber reinforced polylactide and unsaturated polyester composites,” *Composites: Part A* 43, 519-526.
- Sosa-Morales, M. E., Valerio-Junco, L., and Lopez-Malo, A. (2010). “Garcia HS. Dielectric properties of foods: Reported data in the 21<sup>st</sup> century and their potential applications,” *LWT – Food Science and Technology* 43, 1169-1179.
- Sreekumar, P. A., Saiter, J. M., Joseph, K., Unnikrishnan, G., and Thomas, S. (2012). “Electrical properties of short sisal fiber reinforced polyester composites fabricated by resin transfer molding,” *Composites Part A* 43, 507-511.
- Zhan, M. J., and Wool, R. P. (2010). “Bio-based composite resins design for electronic materials,” *J. Appl. Polym. Sci.* 118(6), 3274-3283.
- Zhan, M. J., Wool, R. P., and Xiao, J. Q. (2011). “Electrical properties of chicken feather fiber reinforced epoxy composites,” *Composites: Part A* 42, 229-233.
- Zhou, W. Y., Zuo, J., and Ren, W. (2012). “Thermal conductivity and dielectric properties of AL/PVDF composites,” *Composites Part A* 43, 658-664.

Article submitted: December 14, 2012; Peer review completed: January 12, 2013;  
Revised version received and accepted: January 28, 2013; Published: February 5, 2013.