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Abstract: The study on heat transport in composites is of fundamental importance in engineering design and for tailoring thermal and mechanical behaviour of materials. In this study, the thermal conductivity and thermal diffusivity of flax reinforced polypropylene (PP) composites were determined at room temperature. Chemical modification in the form of a biodegradable zein coating was applied to the flax nonwovens. The effect of fibre loading and chemical modification on the thermo-physical properties was investigated. Dielectric permittivity studies were also evaluated and the dielectric constant of fibre reinforced composites was found to be higher than that of PP. The heat flow and crystallinity effects of the composites were also determined by differential scanning calorimetric (DSC) studies. Zein modification of the flax fibres resulted in a decrease of thermal conductivity and diffusivity which was attributed to a decrease in velocity and mean free path of phonons due to increase in interfacial adhesion.

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Dear Editor

11/02/11

Enclosed please find a copy of the manuscript entitled, '**Effect of amphiphilic coupling agent on heat flow and dielectric properties of flax – polypropylene composites**' in favor of publication in Composites Part B. Kindly acknowledge the receipt of the same.

Thanking you

Sincerely yours

M. JOHN

1 1 **Effect of amphiphilic coupling agent on heat flow and dielectric**
2 2 **properties of flax – polypropylene composites**

3 3
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16 16
17 17 **Abstract**

18 18 The study on heat transport in composites is of fundamental importance in engineering
19 19 design and for tailoring thermal and mechanical behaviour of materials. In this study,
20 20 the thermal conductivity and thermal diffusivity of flax reinforced polypropylene (PP)
21 21 composites were determined at room temperature. Chemical modification in the form of
22 22 a biodegradable zein coating was applied to the flax nonwovens. The effect of fibre
23 23 loading and chemical modification on the thermo-physical properties was investigated.
24 24 Dielectric permittivity studies were also evaluated and the dielectric constant of fibre
25 25 reinforced composites was found to be higher than that of PP. The heat flow and
26 26 crystallinity effects of the composites were also determined by differential scanning
27 27 calorimetric (DSC) studies. Zein modification of the flax fibres resulted in a decrease of
28 28 thermal conductivity and diffusivity which was attributed to a decrease in velocity and
29 29 mean free path of phonons due to increase in interfacial adhesion.

30 30 Key words: A. Polymer matrix composites; A. Fibres; B. Electrical properties; B.
31 31 Thermal properties; E. Compression moulding

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1 34 **1. INTRODUCTION**

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6 36 The study of thermo-physical properties has been important for many applications such
7
8 37 as heat exchangers and heat dissipation materials especially in electronic products.
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10 38 Though natural fibre reinforced composites have advantageous properties, they also
11
12 39 have drawbacks in heat dissipation properties. Thermal conductivity, thermal diffusivity
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14 40 and specific heat are the three most important physical properties needed to study the
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16 41 heat transfer in materials. Thermal conductivity describes ability of the material to
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18 42 transport heat while thermal diffusivity is a measure of its ability to adjust temperature
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20 43 with the surroundings. Several methods for determination of thermal diffusivity and
21
22 44 thermal conductivity have been mentioned in the literature [Santos, 2007; Santos 2005].
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24 45 Steady state methods are those in which the desired property is measured in a steady
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26 46 state heat exchange, and calorimetric techniques employed in the determination of the
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28 47 thermal conductivity are examples of this category. Non-steady methods are those in
29
30 48 which the property is measured according to a transient regime of heat exchange e.g.
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32 49 laser flash technique.
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42 51 In this particular study, the thermophysical properties of composites prepared from
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44 52 needle punched flax nonwovens and polypropylene was investigated. Nonwovens are
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46 53 one of the products popularly used as reinforcements in composites for many
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48 54 applications since they possess a good combination of strength and flexibility compared
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50 55 to conventional materials [Bhat,1995]. The advantages of using polypropylene as matrix
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52 56 are good properties, lower cost and their relatively low processing temperature which is
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54 57 essential because of low thermal stability of natural fibres. As natural fibres are polar
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1 58 and require modification for bonding with non-polar PP, it would be desirable that the
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3 59 chemicals used for the modification preserve the biodegradable nature of natural fibres.
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5 60 Ideally, the chemicals used for modification should also be from renewable resources.
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8 61 In this study, we have used zein as a coating on natural fibres and have already reported
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10 62 on the enhanced mechanical properties due to increased interfacial adhesion [John &
11
12 63 Anandjiwala, 2009]. Zein is a natural protein derived from corn and is composed of a
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14 64 number of amino acids of which glutamic acid is the major proportion [Di Gioia et al.,
15
16 65 2000]. Zein is resistant to microbial attack and possesses the additional benefits of being
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18 66 renewable and biodegradable.
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25 68 Recently the effect of fibre loading and chemical treatments on thermophysical
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27 69 properties of banana fibre reinforced polypropylene commingled composites was
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29 70 reported by Paul et al. [2008]. It was observed that chemical modifications on natural
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31 71 fibres improved the thermo-physical properties however thermal conductivity and
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33 72 thermal diffusivity decreased with increasing fibre loading. Another interesting study
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35 73 reported on the thermal diffusivity and specific heat capacity of flax fibre reinforced
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37 74 HDPE composites at processing temperatures from 170°C to 200°C [Li et al. 2008]. It
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39 75 was found that thermo-physical properties decreased with fibre content but did not have
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41 76 any significant variation with temperature.
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49 78 Idicula et al [2006] investigated the thermo-physical properties of banana /sisal hybrid
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51 79 fibre reinforced polyester composites. It was found that hybridization with glass fibre
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53 80 increased the heat transport ability of the composite. In another study involving
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1 81 hybridization, the thermal diffusivity and conductivity of sisal and glass fibre reinforced
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3 82 polyethylene composites were reported by Kalaprasad et al [2000].
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8 84 The objective of this investigation was to determine the thermophysical properties of
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10 85 flax reinforced polypropylene composites at room temperature. The fibre loading of the
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12 86 composites was varied from 20% to 40%. The effects of zein coating on the thermo-
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14 87 physical properties were investigated. DSC studies were carried out to obtain
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16 88 information on heat flow and crystallization effects in composites. Dielectric
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18 89 measurements of the composites were also carried out to look into the variation of
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20 90 dielectric constant with fibre content and modification.
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26 92 **2. EXPERIMENTAL**

27 93 **2.1 Materials**

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30 94 Flax fibres (grown in South Africa) were cottonised on Temafa Cottonization line by
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32 95 processing them through 1 pass in pre-opener (at speed 680 rpm) and 1 pass Cottonizer
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34 96 (at 1470 rpm) to produce needle-punched nonwovens. The needle-punched nonwoven
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36 97 from 100% cottonised flax fibres with an area weight of 200 g/m² was used in this
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38 98 study. Polypropylene in sheet form (6 mm thickness), with a density of 0.9g/cc and melt
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40 99 flow index of 1.5g /10 min was procured from Ampaglas SA. Zein was obtained from
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42 100 Scientific Polymer Product Company, Ontario, NY. All other chemical reagents used in
43
44 101 this study were of analytical grade.
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52 103 **2.2 Chemical Modification of Nonwovens**

53 104 ***2.2.1 Zein modification of flax nonwovens***

1 105 Zein belongs to the characteristic class of proteins known as prolamines which occur
2
3 106 specifically in cereals. The protein products from corn wet milling are corn gluten meal
4
5 107 (CGM) and corn gluten feed (CGF) and zein is obtained as a by-product from corn
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8 108 gluten meal [Momany et al. 2006; Shukla & Cheryan 2001; Wang et al. 2004].
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12
13 110 Varying concentrations of zein solution was prepared by mixing the required weight of
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15 111 zein with an ethanol/water mixture in the ratio of 80/20. The flax nonwovens were
16
17 112 immersed in this solution and were allowed to stand for 2 hours. The ethanol/water
18
19 113 mixture was drained out and the nonwovens were dried in air and then in an oven at
20
21 114 110°C until completely dry. These nonwovens were used to prepare the modified
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23 115 composites.
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29 117 **2.2 Preparation of composites**

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31 118 Composites were prepared from nonwoven flax and polypropylene on the basis of
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33 119 varying fibre content. The flax nonwoven mats were cut into small uniform squares (30
34
35 120 cm x 30 cm) and then dried in an air oven at 110°C for 7 h. The dried nonwoven mats
36
37 121 were placed between weighed polypropylene sheets. This was wrapped in Teflon[®]
38
39 122 sheets and sandwiched between two aluminium plates. Subsequently these two plates
40
41 123 were placed between the two platens of compression moulding press and cured under a
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43 124 pressure of about 35 bars at 210°C for 20 minutes, followed by cooling under pressure
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45 125 for 3 minutes.
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53 54 127 **3. ANALYSIS**

128 **3.1 Thermophysical properties**

129 A periodical method was used to estimate thermal conductivity, diffusivity and specific
130 heat of polymer composite materials at room temperature (Figure 1). This method is
131 based on the use of a small temperature modulation in a parallelepiped-shape sample
132 (44mm × 44mm × 2.5 mm) and allows obtaining all the thermophysical parameters in
133 only one measurement with their corresponding statistical confidence bounds
134 [Boudenne et al. 2004]. The composite sample is fixed between two metallic plates. The
135 front side of the first metallic plate is heated periodically using a sum of five sinusoidal
136 signals and the temperature is measured with thermocouples placed inside both front
137 and rear metallic plates [Boudenne et al. 2006]. The thermophysical parameters of the
138 sample are identified by comparison of the experimental and theoretical heat transfer
139 functions. The system under study is modeled with one-dimensional quadrupoles
140 theory. The experimental heat transfer function is calculated at each excitation
141 frequency as the ratio between the Fourier-transform temperatures of the front and rear
142 plates. A parameter estimation technique is then applied to estimate simultaneously both
143 thermal conductivity (λ) and diffusivity (a).

144 The identification of the set of thermophysical parameters is a non-linear optimization
145 problem that is solved iteratively: starting with sufficiently accurate initial guesses for
146 the unknown parameters, we successively refine the estimates by using the Levenberg–
147 Marquardt method.

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149 The specific heat capacity (C_p) values of the composite samples were determined using
150 thermal conductivity (λ) and diffusivity (a) values and knowing the density ρ :

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$$Cp = \frac{\lambda}{\rho a} \quad (1)$$

152 The pycnometer method was adopted for measuring density of the composites. The
153 measurements are carried out with a balance and a pycnometer for small quantities of
154 different composites. The density of the sample is obtained by using the following
155 equation:

156
$$\rho = \frac{m_1}{m_2 - m_3 + m_1} \rho_{\text{water}} \quad (2)$$

157 where m_1 is the sample weight, m_2 is the weight of the pycnometer filled with water and
158 m_3 is the weight of the pycnometer containing the sample and filled with water. The
159 density of the composites is reported in Table 1. The uncertainty on the density
160 measurement is calculated from the following equation:

161
$$u(\rho) = \rho \sqrt{\frac{u^2(m_1)}{m_1^2} + \frac{u^2(m_T)}{m_T^2} + \frac{u^2(\rho_{\text{water}})}{\rho_{\text{water}}^2}} \quad (3)$$

162 Where: $m_T = m_2 - m_3 + m_1$ and $u^2(m_T) = u^2(m_1) + u^2(m_2) + u^2(m_3)$

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164 3.2 Dielectric permittivity measurement

165 The permittivity measurements were performed at room temperature on the samples by
166 fixing between two copper plates of thickness $t = 9$ mm. In that case, samples constitute
167 a capacitor with an electrical capacitance noted C (See Figure 2). The effective
168 capacitance of samples was measured with a RCL meter using 4 electrodes in order to
169 reduce the effect of the impedance of connectors and cables. The AC voltage applied on
170 samples was fixed to 2V RMS and the measurements of the electrical capacitance were
171 performed using a large frequency range ($50 \text{ Hz} < f < 10^6 \text{ Hz}$) without using guarded

1 172 electrodes. A correction of experimental values was performed in order to take into
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3 173 account the presence of edge effects according to the procedure described in a previous
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5 174 paper [Cecen et al. Submitted]. Considering the geometry of samples used for dielectric
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7 175 measurements, the maximum correction obtained is about 5%. Then relative dielectric
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9 176 permittivity ϵ_r is computed as follows:

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$$\epsilon_r = \frac{C e}{\epsilon_0 D^2} \quad (4)$$

18 178 where ϵ_0 is the vacuum dielectric permittivity ($\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$), C the
19 179 capacitance, e the thickness of samples and D the area of sample under electrode.
20
21 180 Relative dielectric permittivity measurements have shown a negligible dependence of
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23 181 permittivity in the whole frequency range of measurements. Besides, there is no
24
25 182 significant evolution of the shape of $\epsilon_r(f)$ curves upon filler loading. In the case where
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27 183 the shape of $\epsilon_r(f)$ curves is conserved whatever the filler loading, all curves at different
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29 184 fibres concentration must superimpose with the curve of the polypropylene matrix. This
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31 185 allows determining the increase or decrease in dielectric permittivity with respect to the
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33 186 polypropylene matrix.
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44 188 For each sample, five successive experiments were performed and an average value
45 189 reported. Uncertainties were computed considering the standard deviation of
46 190 experimental values of dielectric permittivity and uncertainties of the measurement
47 191 device and on samples dimensions.
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55 193 **3.3 Differential scanning calorimetry studies (DSC)**
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194 The melting and crystallisation behaviour of flax reinforced polypropylene composites
195 were studied using a Perkin Elmer DSC thermal analyser at a heating rate of 10°C/min
196 in a nitrogen atmosphere. Temperature range used was from 30°C to 200 °C.

197 The thermal properties such as crystallization temperature (T_c), melting temperature
198 (T_f), heat of fusion (ΔH_f), and percentage of crystallinity (X_c) obtained from DSC
199 studies has been analysed. The crystallinity of the PP component was determined by
200 using the relationship:

$$201 \quad X_c (\% \text{ crystallinity}) = \frac{\Delta H_f 100}{\Delta H_f^0 w} \quad (5)$$

202 Where $\Delta H_f^0 = 138\text{J/g}$ was taken for 100% crystalline isotactic PP and w is mass fraction
203 of PP in the composite.

205 **4. RESULTS AND DISCUSSION**

206 **4.1 Thermophysical properties**

207 ***4.1.1 Effect of fibre loading***

208 Heat transport in non-metals is majorly dependent on conduction of phonons through
209 the polymer matrix and fibres while electrical transport depends on conduction of
210 electrons by percolation mechanism. The phonon scattering that occurs at the interfaces
211 between the fibres [Nakamura & Iji, 2009] influences the thermal properties as well.
212 Therefore, in polymers, crystal or amorphous boundary, defects, the ends and
213 entanglements of the molecular chains can scatter phonons and interfere with the
214 thermal transmittance. The thermo-conductive properties of nonwoven reinforced
215 polymer composites also depend on the nature and fineness of fibres, pore size,

1 216 distribution of fibres in composites and overall material bulk density [Yachmenev et al.
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3 217 2006].
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8 219 The thermal conductivity and diffusivity of the samples based on fibre loading is
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10 220 presented in Table 1. It can be seen that the incorporation of flax nonwovens in PP
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12 221 matrix results in lowering of thermal conductivity and diffusivity. However as fibre
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14 222 loading increases it can be seen that both thermal conductivity and diffusivity register a
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16 223 slight increase.
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22 225 At 30% loading, thermal conductivity decreases by almost 20% compared to
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24 226 polypropylene. The flax nonwovens used in the composites tend to be highly porous
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26 227 containing pockets of air which have low thermal conductivity ($\lambda_{\text{air}}=0.0245 \text{ Wm}^{-1}\text{K}^{-1}$).
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28 228 Moreover natural fibres have a hollow cylindrical structure encompassing a cavity
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30 229 (referred to as lumen) and act as insulating materials which reduces the heat transport
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32 230 characteristics of the composites. Similar behaviour for thermal conductivity has been
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34 231 reported by Paul et al [2008], Li X et al [2008] and Idicula et al [2006] for natural fibre
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36 232 composites. The thermal diffusivity values follow the same trend; fibre reinforced
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38 233 composites exhibit lower values than matrix. This indicates that composites containing
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40 234 flax fibres require longer time to heat or cool than polypropylene.
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49 236 The slight increase in thermal properties with fibre loading can be attributed to the fact
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51 237 that at higher fibre loadings the compressive forces during molding decreases the
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53 238 presence of these air pockets (thermal contact resistance) and that may lead to a slight
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55 239 increase of thermal transport properties. It is to be noted that the relative thermal
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1 240 diffusivity uncertainties are more significant than those noted for thermal conductivity.
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3 241 The specific heat capacity does not show any significant trend upon addition of flax
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5 242 nonwovens (See Table 1). However at 40% flax fibre weight, the specific heat capacity
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8 243 of composites decreases by almost 10%.
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12 13 14 245 ***4.2.2. Effect of chemical modification***

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16 246 The effect of coating nonwovens with zein on the thermo-physical properties are given
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18 247 in Table 1. It can be seen that thermal diffusivity and conductivity of treated composite
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20
21 248 decreases compared to untreated. The amino acid composition of zein [Di Gioia et al.
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23 249 2000] shows the presence of a number of polar and non-polar constituents. In a model
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26 250 proposed by Argos et al [1982] the structure of zein is composed of helical segments
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28 251 which are arranged in a ring of "pencils" held together, side-by-side, by hydrogen bonds
29
30
31 252 and linked at each end by glutamine-rich turns or loops. The exterior of the helical
32
33 253 segments forming the lateral faces have a hydrophobic character, whereas the top and
34
35
36 254 bottom surfaces containing the glutamine-rich loops are hydrophilic. Therefore, zein is
37
38 255 amphiphilic in nature having affinity for both polar and non-polar groups. This
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41 256 characteristic allows it to bind itself between the polar flax nonwovens and non-polar
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43 257 matrix and results in enhanced interfacial adhesion which results in reduction of the
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45 258 thermal contact resistance and consequently thermal properties.

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50 260 Thermal diffusivity and conductivity [Kotkata et al. 1986] are related to velocity and
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52 261 mean free path of phonons as shown in the following equations [Fujishiro et al, 1997;
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55 262 Yamanaka, 2005].
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$$a = \frac{1}{3} \nu l \tag{6}$$

264
$$\lambda = \frac{1}{3} C \nu l \tag{7}$$

265 where a is the thermal diffusivity, λ the thermal conductivity, ν the velocity of
266 phonons, l is the mean free path of phonons (distance travelled by the phonons between
267 two consecutive collisions) and C the heat capacity per unit volume.

268 It is apparent from equations 6 and 7 that any factor that reduces the velocity and the
269 mean free path of phonons lowers the thermal diffusivity and conductivity. The stronger
270 adhesion in treated composites results in tighter packing within the polypropylene-flax
271 network, which means that mean free path and velocity of the phonons decreases and
272 consequently results in lowering of thermal properties.

273
274 Another interesting observation is that as the concentration of zein increases, the
275 thermal properties register an increase. This can be attributed to the differences in
276 interfacial adhesion in the composites which affects the mean free path and
277 consequently thermal properties of the composites. The superior mechanical properties
278 obtained for flax-PP composites when using a concentration of 2% zein has been
279 reported earlier.

280
281 The better adhesion in 2% zein treated composites is also evident from the scanning
282 electron micrographic studies. Figures 3a, b and c shows the tensile fracture surface of
283 untreated, 2% treated and 4% treated composites at 30% loading. The presence of
284 cavities is clearly visible in Figure 3a. This indicates that the level of adhesion between
285 the fibers and the matrix is poor, and when stress is applied, it causes the fibers to be

1 286 pulled out from the polypropylene matrix easily, leaving behind gaping holes. In Figure
2
3 287 3b, we can see the presence of a number of short, broken fibers projecting out of the
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5 288 polypropylene matrix. This indicates that the extent of adhesion between the fibers and
6
7
8 289 the matrix is greatly improved, and when stress is applied, the fibers break and do not
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10 290 wholly come out of the matrix. Figure 3(c) shows the presence of resin on the fibres
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13 291 indicating interfacial interactions.

14 292 ***4.2.2. Theoretical thermal conductivity models***

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16 293 Many theoretical models have attempted to explain the thermal conductivity of two-
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18 294 phased composites [Meredith and Tobias, 1962; Cheng and Vachan, 1969; Hamilton and
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21 295 Crosser, 1962; Agari and Uno, 1986]. Several factors, such as solids loading, particle
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24 296 size or shape, and homogeneity of the dispersed phase in the matrix, etc., were taken
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27 297 into account in heat conduction models. But these models have not always been well
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30 298 correlated with the experimental results.

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32 299 The simplest alternatives would be with the materials arranged in either parallel or
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35 300 series with respect to heat flow (see Figure 4), which gives the upper or lower bounds of
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38 301 effective thermal conductivity. For the parallel conduction model:

$$39 302 \lambda = \varphi\lambda_f + (1 - \varphi)\lambda_m \quad (8)$$

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42 303 and for series conduction model:

$$43 304 \frac{1}{\lambda} = \frac{1 - \varphi}{\lambda_m} + \frac{\varphi}{\lambda_f} \quad (9)$$

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46 305 where, λ , λ_m and λ_f are the thermal conductivities of the composite, the matrix and the
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49 306 filler, respectively and φ is the volume fraction of filler.

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52 307 Hashin and Shtrikman [1962] developed models based on macroscopical isotropy and
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55 308 quasi-homogeneity of the composite, where the shape of the reinforcement is not a
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1 309 limiting factor. The model initially assumes a homogeneous and isotropic reference
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3 310 material in which the constituents are dispersed. The upper and lower bounds are
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6 311 calculated as:

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$$\lambda_l = \lambda_m + \frac{\varphi}{\frac{1}{\lambda_f - \lambda_m} + \frac{(1-\varphi)}{d \lambda_m}} \quad (10)$$

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$$\lambda_u = \lambda_f + \frac{(1-\varphi)}{\frac{1}{\lambda_m - \lambda_f} + \frac{\varphi}{d \lambda_f}} \quad (11)$$

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19 314 The indices “*u*” and “*l*” refer to the upper and lower bounds, respectively. The
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22 315 parameter *d* is the dimension of the system and defines the form of the fillers (*d* = 2 in
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24 316 the case of fibres).

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29 318 Figure 5 presents a comparison between the experimental values of thermal
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32 319 conductivity of the composites and some theoretical models. All data are plotted as a
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34 320 function of filler volume fraction. Computations were performed using the theoretical
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37 321 thermal conductivity value of the polypropylene matrix and those of the fillers ($\lambda_{\text{flax}} =$
38
39 322 $0.035 \text{ W.m}^{-1}.\text{K}^{-1}$ and $\lambda_{\text{pp}} = 0.24 \text{ W.m}^{-1}.\text{K}^{-1}$ [Shackleford and Alexander, 2001]). As it is
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41
42 323 seen in Figure 5, the experimental values are close to the parallel model and the upper
43
44 324 bound of Hashin and Shtrikman model. This result is foreseeable because the thermal
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47 325 conductivity was measured in the parallel direction to the plane of the composite plate.
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49 326 So, in this case, the composite can be seen as a stacking of several fibre layers separated
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52 327 by polymeric matrix.

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55 56 329 **4.2 DSC and dielectric measurements**

57 58 59 330 ***4.2.1 Effect of fibre loading and chemical modification***

1 331 Table 2 presents thermal properties of composites. It is clear that the addition of flax
2
3 332 fibres to polypropylene results in an increase in the crystallization temperature (T_c) of
4
5 333 the polymer matrix. In the presence of 40% weight fraction of incorporated fibres, the
6
7 334 T_c of neat PP increased from ca. 116°C to 120°C. This effect can be explained by the
8
9 335 assumption that the fibres act as efficient nucleating agents for the crystallization of PP
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11 336 and consequently increase its crystallization growth rate during the cooling from the
12
13 337 molten state. With regard to the melting temperature of the different samples, the
14
15 338 addition of the fibres in the PP matrix causes only a marginal effect ($\pm 1^\circ\text{C}$), and no
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17 339 essential correlation of the results with the fiber content can be established. However, a
18
19 340 comparison of crystallinity (X_c) of neat PP, calculated according to equation (5) for the
20
21 341 PP component in the composites, yielded slightly higher values for the 40% flax
22
23 342 composite samples than for unfilled PP. This observation can again be explained by the
24
25 343 fact that the surface of the flax fibre acts as nucleation sites for the crystallization and
26
27 344 partial crystalline growth in PP. It may be assumed that the nucleating effect of the fibre
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29 345 surfaces considerably contributes to the occurrence of transcrystalline layers around the
30
31 346 fibres resulting in an increase of the achieved percentage of crystallinity. On comparing
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33 347 the untreated system to the 2% zein treated composites, it can be observed that the
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35 348 crystallinity of the treated composite increases due to the increased nucleating ability of
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37 349 chemically modified fibres. Similar results have been reported by other researchers
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39 [Joseph et al. 2003].
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352 ***4.2.2 Dielectric permittivity measurements***

353 The dielectric constant (dielectric or static permittivity) of a material depends upon the
354 polarizability of the molecules. The polarizability of non-polar molecules arises from

1 355 electronic polarization (in which the application of applied electric field causes a
2
3 356 displacement of the electrons relative to the nucleus) and atomic polarization (in which
4
5 357 the application of applied electric field causes a displacement of the atomic nuclei
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8 358 relative to one another). In the case of polar molecules a third factor also comes into
9
10 359 play which is orientation polarization (in which the application of applied electric field
11
12 360 causes an orientation of dipoles) [Jacob et al. 2006]. The dependence of the relative
13
14 361 dielectric permittivity (ϵ_r) of composites with fibre weight fraction is presented in
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17
18 362 Figure 6. It can be observed that the reinforcement of polypropylene matrix with flax
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20 363 nonwovens induces an increase of the relative dielectric permittivity. This is because of
21
22 364 the fact that polypropylene is a non polar material and has only instantaneous atomic
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24 365 and electronic polarization to account for. The presence of flax nonwovens in
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26
27 366 polypropylene leads to the presence of polar groups giving rise to dipole or orientation
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29 367 polarizability. The over all polarizability of a composite is therefore the sum of
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31 368 electronic, atomic and orientation polarization giving rise to higher dielectric constant.
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35 369 Hence the dielectric constant increases with the increase in fiber loading. The use of
36
37 370 zein coating tends to decrease the dielectric constant even if the magnitude of this effect
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39
40 371 is small. Zein coating results in formation of linkages between hydroxyl groups of fibres
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42 372 and amine groups in zein which leads to reduction in mobility of free polar groups. This
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44 373 resultant decrease of hydrophilicity of the fibres leads to lowering of orientation
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47 374 polarization and subsequently the dielectric constant.
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51 376 **5. CONCLUSIONS**

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54 377 Composites were prepared from flax nonwovens and polypropylene matrix. The
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57 378 thermophysical properties of the composites were measured as a function of nonwoven
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1 379 content and chemical modification. The chemical modification employed was a zein
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3 380 coating on the flax fibres which had the additional advantage of being a biodegradable
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5 381 coupling agent. The increase of fibre content in polypropylene matrix resulted in a
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8 382 decrease of thermal conductivity and thermal diffusivity of the composites. Chemical
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10 383 treatment decreased thermal conductivity and diffusivity of the composite compared to
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12 384 untreated composite. This was attributed to increased adhesion leading to decrease in
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14 385 velocity and mean free path of phonons. Further evidence was found in the dielectric
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16 386 studies which revealed a reduced dielectric constant due to lower mobility of polar
17
18 387 groups for zein treated composites. DSC studies revealed increase in crystallinity of
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20 388 fibre reinforced composites. This was attributed to the surface of the flax fibres acting
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22 389 as nucleation sites for the crystalline growth. The dielectric constant of the composites
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24 390 increased with fibre content due to increase in orientation polarization brought about by
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26 391 the polar hydroxyl groups present in natural fibres.
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Table 1: Experimental values of thermal conductivity (λ), thermal diffusivity (a), and specific heat capacity (Cp) for flax reinforced polypropylene composites

Fibre weight fraction (%)	λ (W.m⁻¹.K⁻¹)	a (m².s⁻¹) .10⁻⁸	Cp (J Kg⁻¹ K⁻¹)
0	0.240 ± 0.008	16.60 ± 0.40	1731 ± 85
20	0.190 ± 0.003	9.81 ± 0.56	1960 ± 231
30	0.192 ± 0.004	10.80 ± 0.37	1683 ± 135
40	0.193 ± 0.003	11.13 ± 0.71	1567 ± 205
2% zein	0.172 ± 0.004	9.72 ± 0.55	1654 ± 203
4% zein	0.181 ± 0.003	10.36 ± 0.26	1629 ± 97
6% zein	0.203 ± 0.003	10.70 ± 0.27	1658 ± 103

Table 2: Melting temperature, crystallisation temperature, enthalpy of fusion and crystallisation of composites

Sample	1 st Cooling curve		1 st Heating curve		X _c (%)
	T _c (°C)	ΔH _c (J/g)	T _m (°C)	ΔH _f (J/g)	
PP	116.5	-56.6	150.1	23.1	16.7
20%	118.5	-41.0	150.7	17.5	15.8
30%	119.8	-37.8	151.5	16.2	16.7
40%	120.2	-36.1	152.5	15.8	19.1
2% Zein (30%)	120.4	-41.1	153.5	18.1	18.7

Figure

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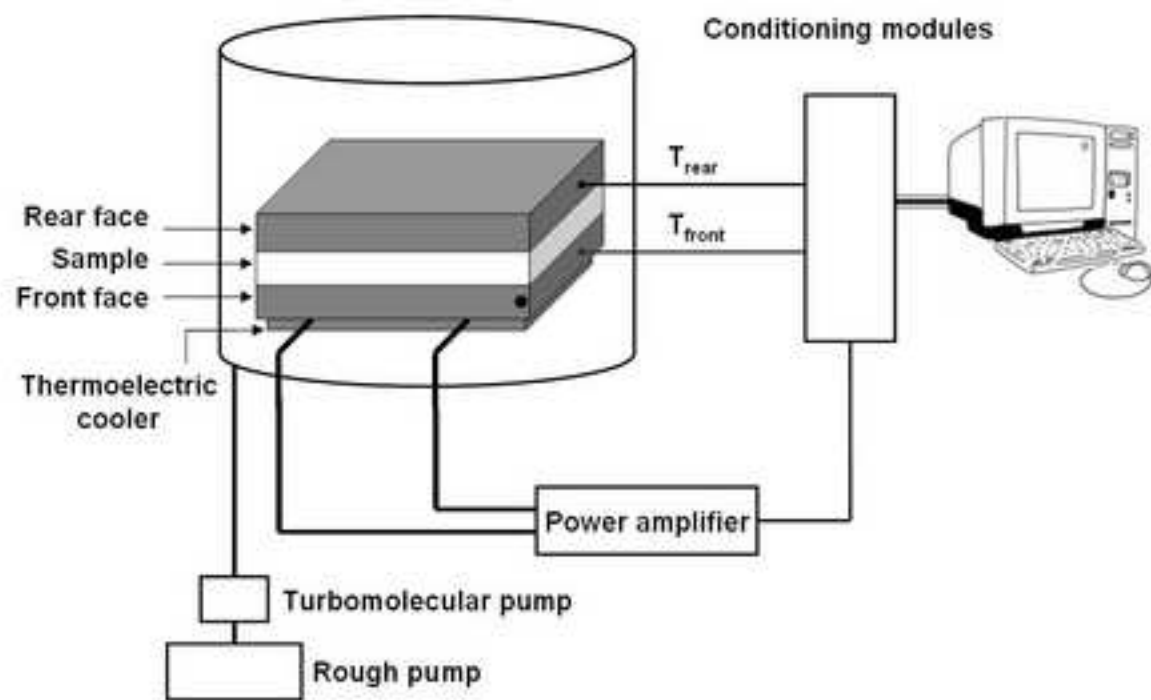
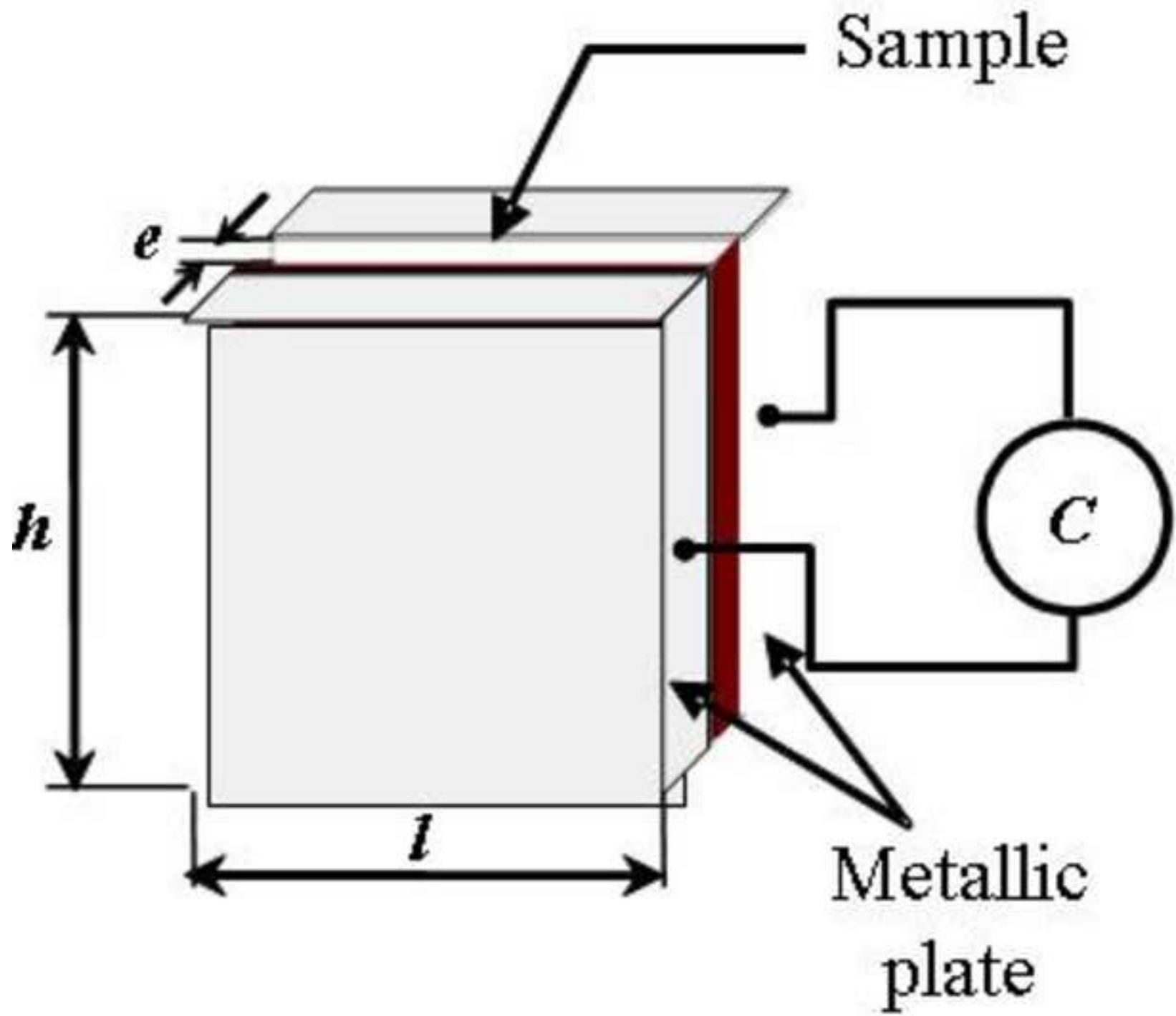


Figure 1

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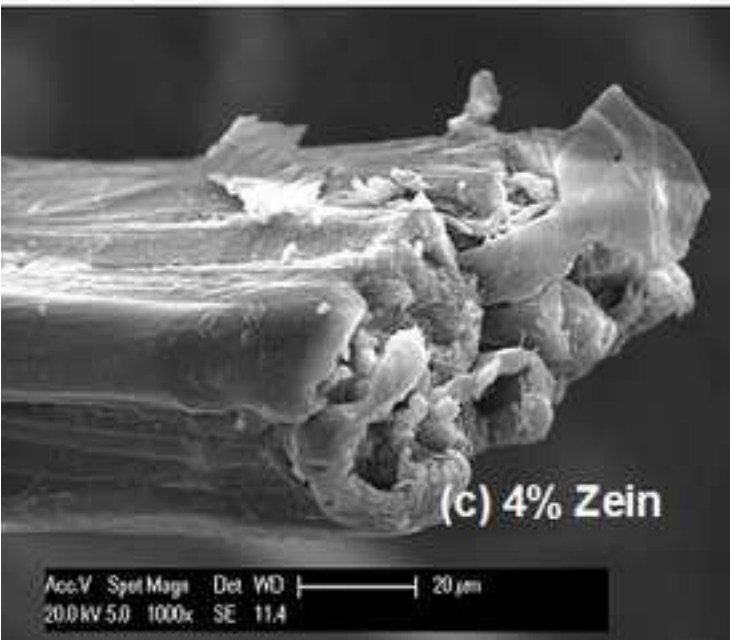
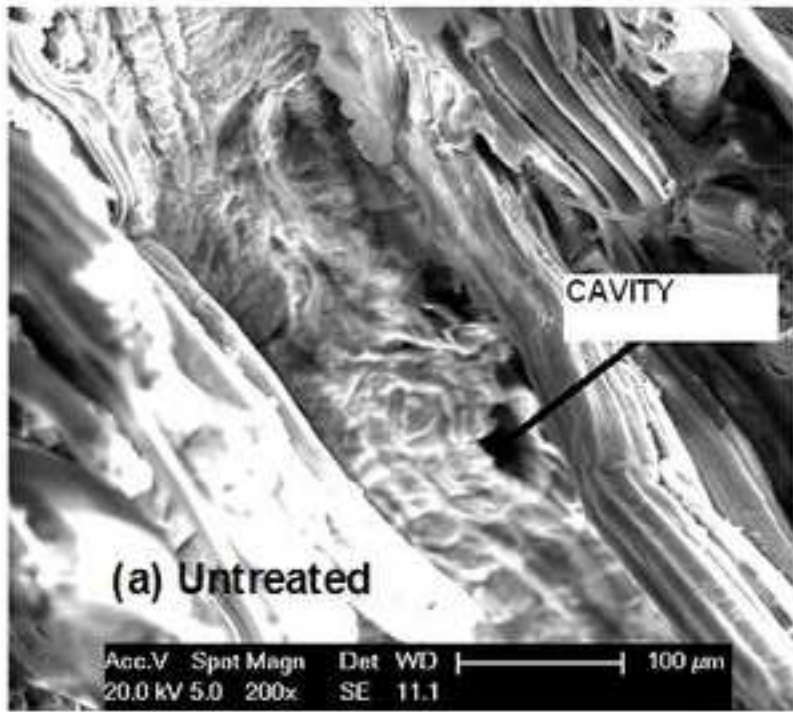


Figure 3 (a,b & c)

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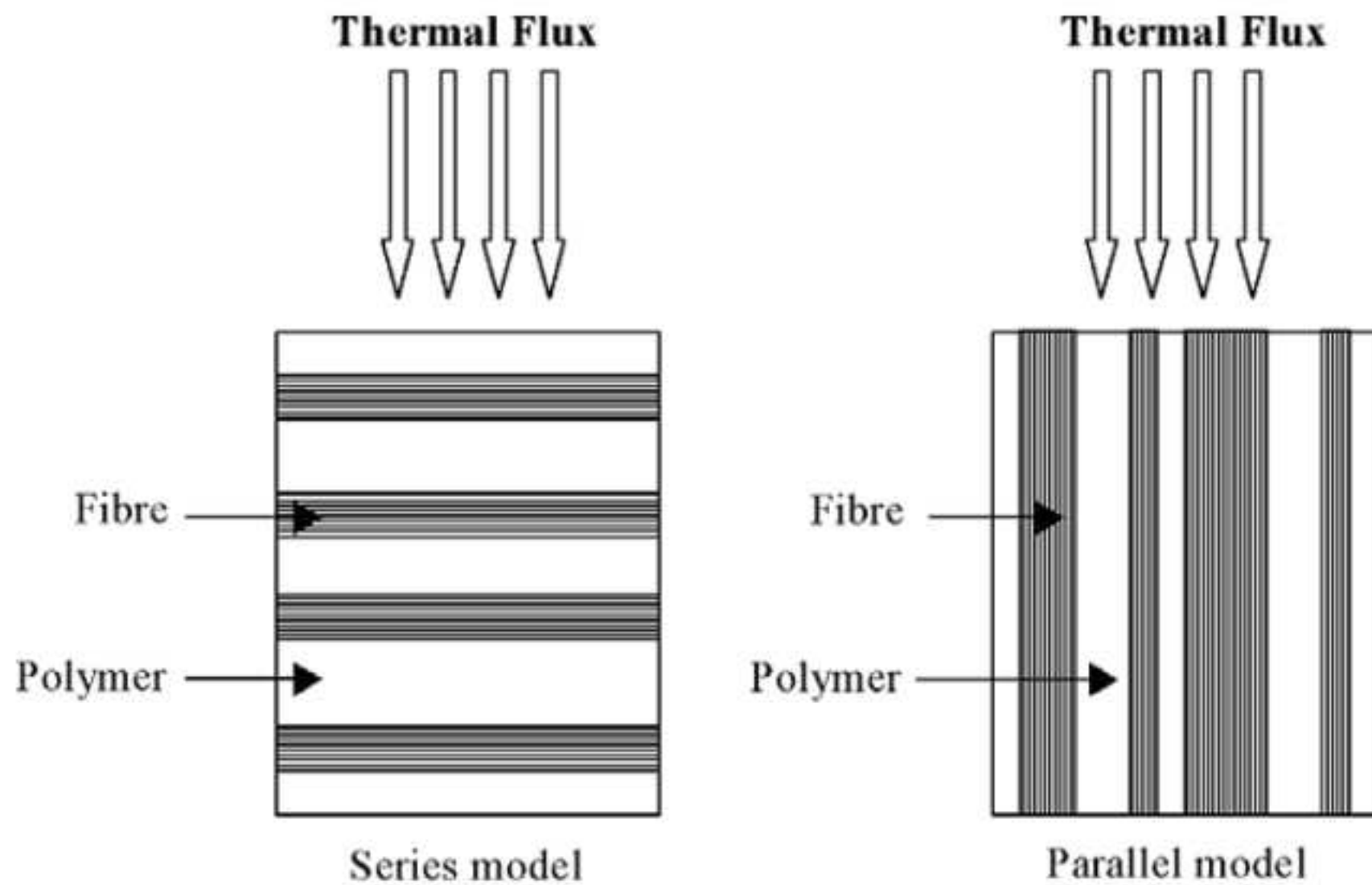


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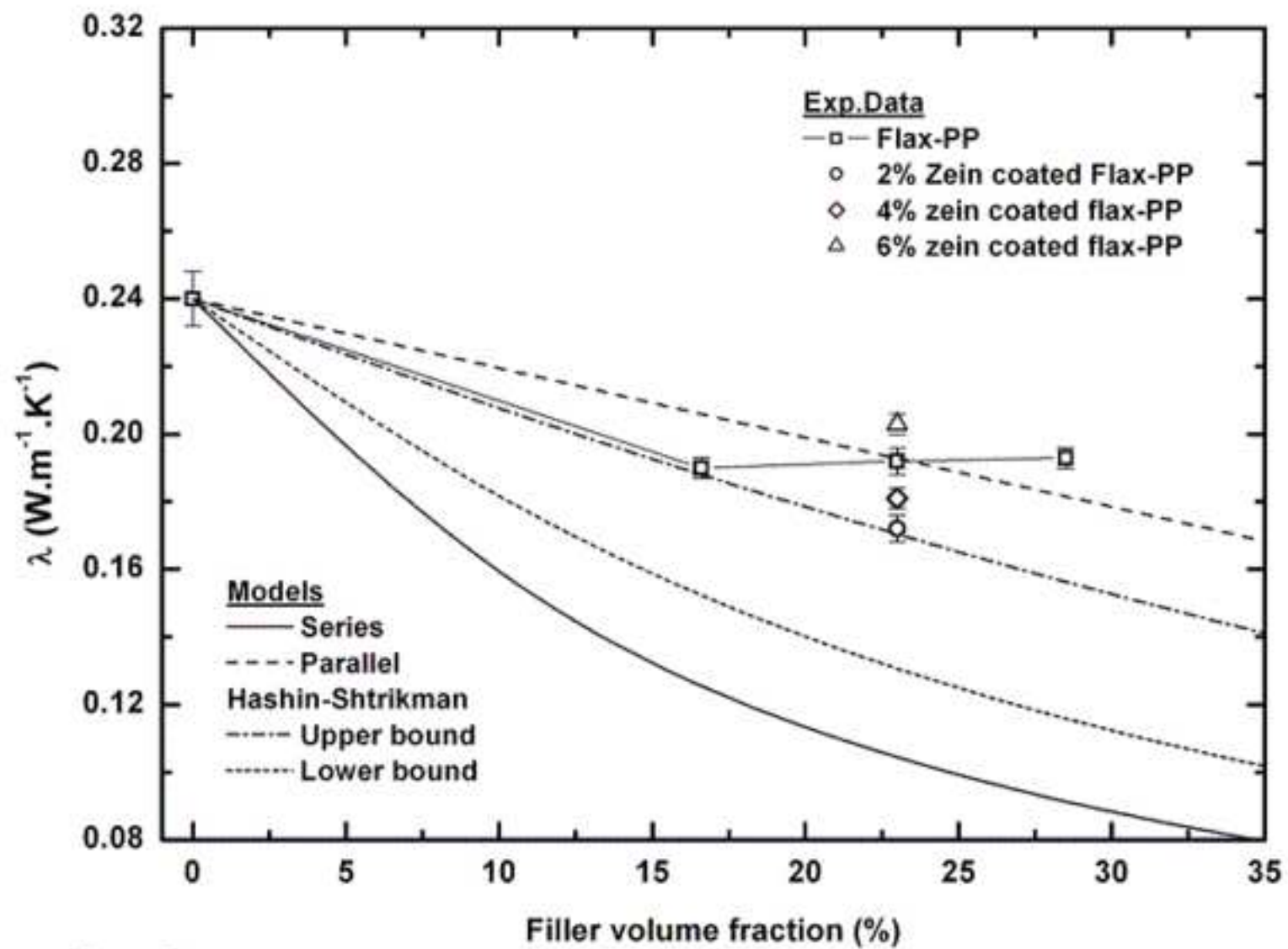


Figure 5

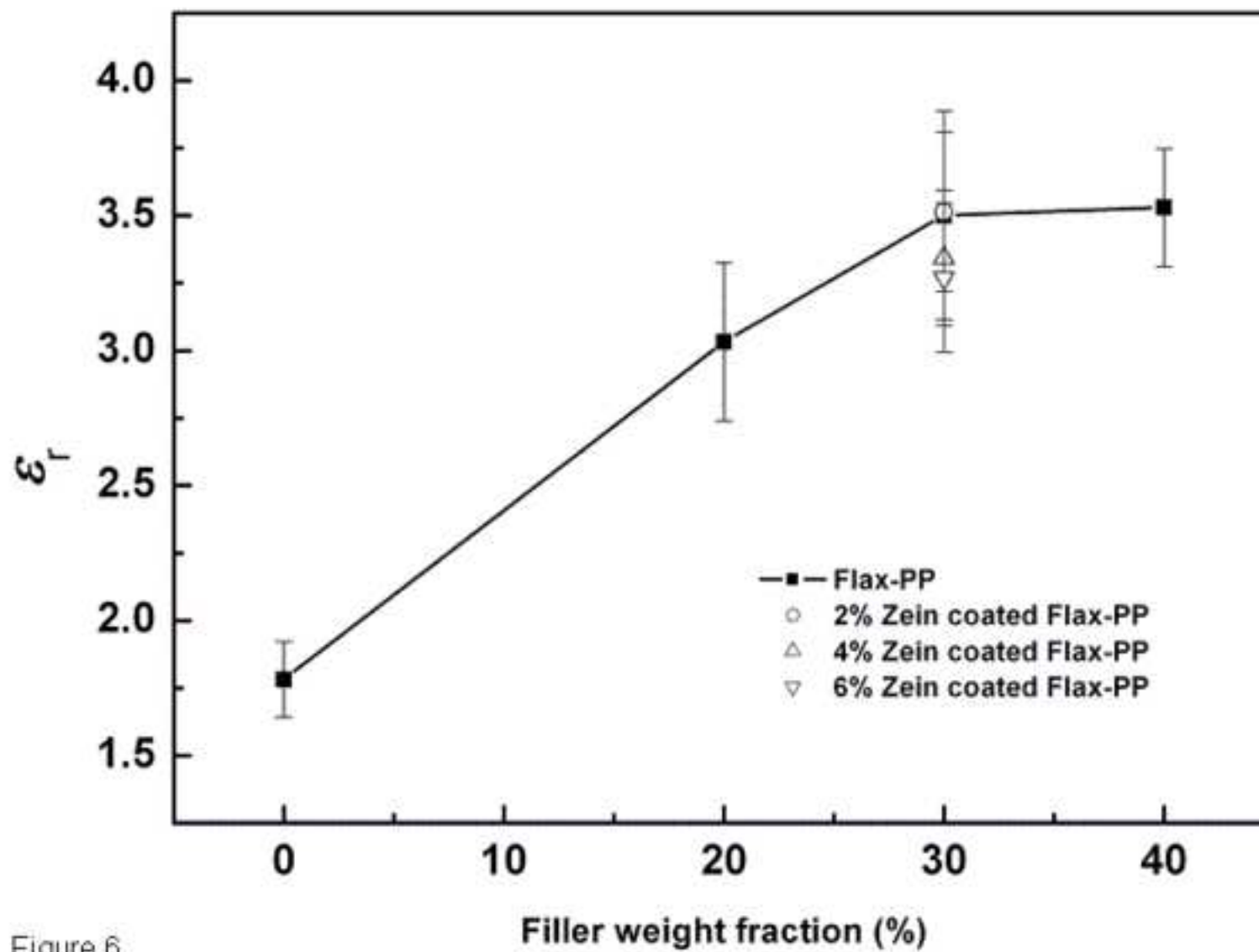


Figure 6