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Thermal studies of lingo-cellulosic palm fiber reinforced hybrid green composites

Richa Agrawal[1*] and N.S. Saxena[2]
[1]G.N. Khalsa College, Matunga, Mumbai, MS, India
[2]Polymer Science Lab, University of Rajasthan, Jaipur, Rajashthan, India
jainricha_agarwal@yahoo.com

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Abstract

Thermal properties of the hybrid composites have been explored by differential Scanning Calorimeter (DSC) and Transient Plane Source (TPS) technique. Hybrid composites have been prepared by reinforcing lingo-cellulosic oil palm fibers and glass fibers in phenol formaldehyde resin matrix. Non-isothermal crystallization kinetics has been studied by Differential Scanning Calorimeter. Parameters like enthalpy released and thermal stability of the composites have been evaluated using the DSC data. Activation energy of the composites has been evaluated by two different methods and compared. TPS technique has been employed to measure the effective thermal diffusivity and thermal conductivity of the composites. Thermal conductivity of the fibers has been evaluated by a theoretical model and compared.

Keywords: Acetophenone, Aldehyde, Metal complexes, Spectral analysis, Antimicrobial activity.

Introduction

The crises of solid waste management and un-utilized industrial waste have generated the need for the production of environmental friendly materials. Bio-degradable composite have attracted considerable attention in last two decades due to their use as green materials contributing to less environmental pollution. Hence the utilization of lingo-cellulosic material apart from wood in fabricating composites has been a keen area of research. Significant efforts have been made by researchers to utilize the abundant and renewable material like sisal, banana, pineapple, coir and oil-palm fibers[1-3] as reinforcement in resins to produce fiber reinforced composites (FRC). Natural fibers being non abrasive, non-hazardous, strong, light-weight, abundant and inexpensive have been advantageously used in the fabrication of composites. These natural fiber reinforced composites (FRC) are beneficial due to excellent mechanical properties[4,5] and thermal performance. Moreover, these fibers are environment friendly and bio-degradable. Oil-palm (Elaeis Guineensis) was originated in tropical forests of West Africa and presently are cultivated in Malaysia and India[6,7]. Chemical composition of Oil palm fiber shows the presence 19% lignin (ASTM D 1106), 65% holo-cellulose (ASTM D 1104) 2% ash. Many million tons of oil-palm fibers are thrown by oil mills throughout the world as industrial waste. This industrial waste creates a good habitat for insects and pests, which causes severe environmental problems. Utilization of oil palm fiber in composites protects the environment and leads to new composite material. Oil –palm fiber (OPF) has been used as an excellent reinforcing agent in brittle plastics[8] such as phenol-formaldehyde (PF), which lies in the category of thermosetting resins. Brittleness of PF can further be reduced by the suitable combination of OPF with other fibers. Inclusion of two or more fibers in a single matrix leads to the fabrication of hybrid composites[9,10]. Careful selection of the fibers and matrix may lead to a tailor made composite with desired set of properties, which cannot be attained by a lone fiber. In the fabrication of the hybrid composite, each fiber is selected to off-set the poor qualities of the other fiber. Glass fiber has been proved to be a good reinforcing agent along with the natural fibers in resin matrices. Reinforcement of the glass fiber leads to high strength, light weight, less corrosive and dimensionally stable composite with improved performance. Properties of the hybrid composites mainly depend upon the type of fiber, reinforcement, fiber length, intermingling and the orientation of the fibers in the matrix. Fiber matrix adhesion is an important factor for the overall performance of the composite.

FRC have been widely used electronic systems, automotive and aerospace industries. In these applications ample heat is produced which must be dissipated to keep the elements at appropriate temperature for their reliable operation. About 10 ^{0}C increase in the temperature half's the mean life-time of the element[11]. Therefore the thermal parameters of FRC are very important for their appropriate application. Keeping this in mind hybrid composites have been prepared by reinforcing OPF and glass fiber in PF matrix. This paper is an attempt to study and explore the thermal properties such as enthalpy released, thermal stability, activation energy, thermal diffusivity and effective thermal conductivity of the hybrid composites.

Materials and methods

Oil-palm empty fruit bunches were procured from Oil Palm India Ltd., Kottayam, India. Phenol-formaldehyde resole type resin was obtained from West Coast Polymers Pvt. Ltd, Kannur, Kerala, India. The solid content of resin was (50 + 1%). Caustic soda was used as the catalyst during manufacture. Glass fiber mats were procured from Ceat India Limited, Hyderabad. Fibers from oil-palm empty fruit bunches were processed by retting process. The pithy material was removed and the fibers were washed, dried at 60^0 C and chopped. Randomly oriented mats were prepared using the chopped fibers. Mould was coated with resin. Glass fiber mats and oil palm fiber mats were arranged in such a manner so as to get maximum intermingling. PF resin was brushed onto the reinforcing material and the process was repeated till the desired thickness was obtained. All the composites prepared have a 40% fiber loading by weight. Seven Composites having volume percentage (oil palm fiber: glass :PF) 0.49:0.02:0.49, 0.45:0.04:0.51, 0.41:0.06:0.53, 0.31:0.11:0.57, 0.0.20:0.17:0.63, 0.07:0.24:0.69, 0:0.25:0.75 have been prepared and will be addressed as composite 1 to composite 7 in the further text.

Measurements: Differential scanning calorimeter (DSC) study was performed on a Rigaku 8230 B model attached to a thermal analysis station (TAS 100) at different heating rates. The temperature precision of the instrument is + 0.1 K with an average standard error of about ±0.01K in the measured values. The DSC equipment was calibrated prior to measurements, using high purity standards Pb, Sn and In with well known melting points. Samples of approximately 15 mg have been weighed using a high performance Sartorius balance with an accuracy of 0.1µg. Samples were taken in standard aluminum pans and heated from room temperature to 450^0C at the heating rates of 5, 10, 15 and 20 K/min. Simultaneous measurements of effective thermal conductivity and diffusivity were made at room temperature and normal pressure with the TPS method[12]. Details about the TPS can be seen in reference 12. The sample dimensions used for the TPS study are 1.4 x 1.4 x 0.4 cm^3. Thermal diffusivity and thermal conductivity of the samples measured by TPS method are reproducible within 2-2.5%.

Results and discussion

A large number of methods are available in literature to study the crystallization kinetics. These methods can be divided into two categories namely as iso-conversional methods and iso-kinetic methods. Iso-conversional methods are further classified as integral conversional methods and differential methods. Iso-conversional methods being model free are considered to give accurate values of the kinetic parameters. Starink's[13] analysis has shown integral conversional methods are more accurate than the iso-kinetic methods. We have used modified Kissinger's[14] equation and Matusita's[15] equation for the evaluation of the activation energy of crystallization, which fall under iso-conversional methods. Figure-1 show typical DSC thermo-grams of hybrid composites at the heating rate of 10 K/min. The figure shows a well-defined peak of crystallization for all the composites. The activation energy for crystallization has been determined using Kissinger's equation given as

$$\ln (\alpha^n / T_p^{\ 2}) + \ln K = - mE_c / RT_p \qquad (1)$$

Where: K is a constant, containing factors depending on the thermal history of the samples, n and m are constants having values between 1 and 4 depending upon the morphology and growth[15] of a composite, α represents the heating rate and T_p is the peak crystallization temperature. The values of the activation energy $(m/n)E_c$ can be determined from the slope of a $\ln \alpha$ versus $1/T_p$ curve as shown in Figure-2. Values of the activation energy obtained from such curves are listed in Table-1, for all the composites.

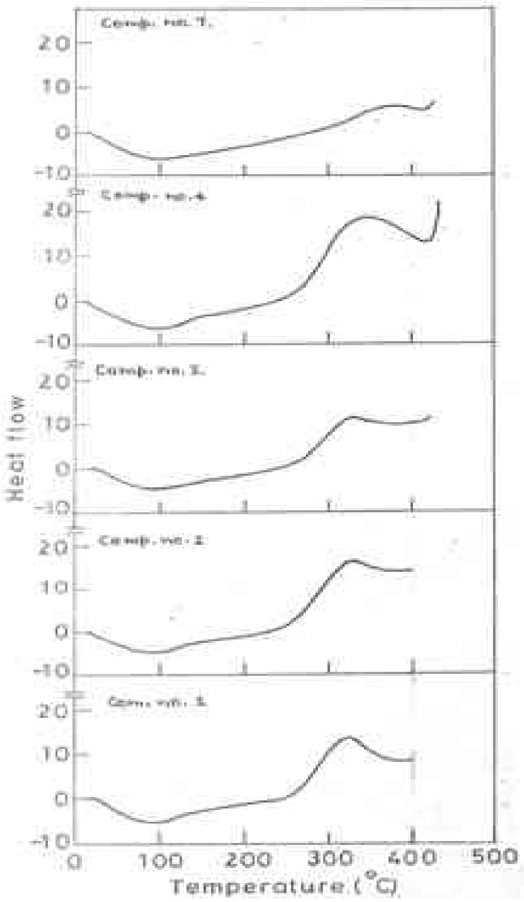

Figure-1: DSC thermo-grams of hybrid composites at the heating rate of 10 K/min.

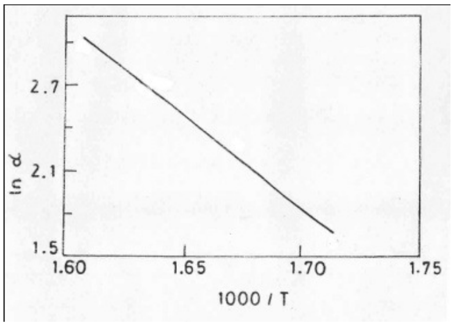

Figure-2: Plot of ln α as a function of $1/T_p$ for the evaluation of activation energy of crystallization for composite 2.

Table-1: Activation energy and kinetic parameters for hybrid composites.

Composite			Activation energy (E_c) (kJ/mol)				Enthalpy released (mcal/mgK)	($T_c - T_g$) (K)
			Kissinger's Equation (E_c)	Matusita's equation				
S.no.	v_p(%)	v_g(%)		n	m	E_c		
1.	0.49	0.02	113.34	1.06	1	127.29	552.1	249.2
2.	0.45	0.04	134.11	1.09	1	129.56	513.1	250.6
3.	0.41	0.06	137.87	1.19	1	131.19	357.7	253.8
4.	0.31	0.11	147.02	1.215	1	136.19	239.8	254.9
5.	0.00	0.25	176.53	1.217	1	170.54	186.2	282.2

Matusita's[15] equation for a non-isothermal crystallization process can be written as

$$\ln[-\ln(1-x)] = -n\ln(\alpha) - 1.052\, mE_c/RT + \text{constant} \qquad (2)$$

Where x is the fraction crystallized at a uniform heating rate, factors n and m are dependent on the process of nucleation. The slope of a $\ln[-\ln(1-x)]$ versus $1/T$ curve at different heating rates has been utilized for the evaluation of activation energy of crystallization for all the composites. These curves are shown in Figure-3a and 3b for the composite numbers 1 and 7 respectively. An average value of mE_c has been taken as this quantity is weakly dependent on the heating rate. The value of the Avrami exponent (n) can be evaluated by the slope of a $\ln[-\ln(1-x)]$ versus $\ln\alpha$ curve. Figure-4a and 4b show data for composite numbers 1 and 7 respectively at different temperatures.

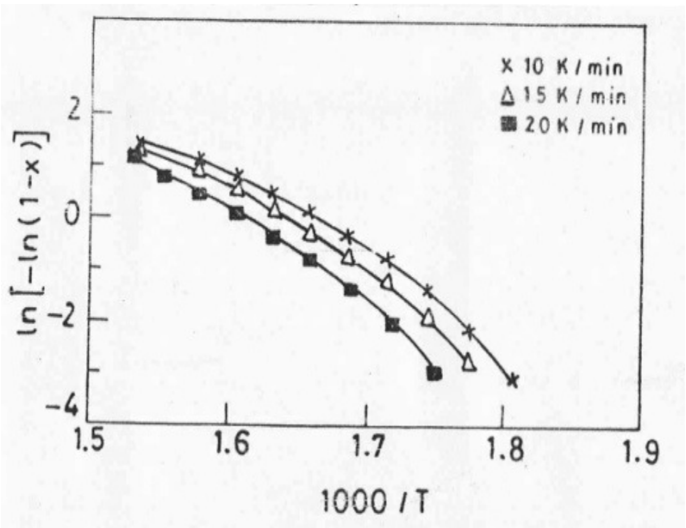

Figure-3(a): A plot of $\ln[-\ln(1-x)]$ versus $1/T$ at different heating rates for composite 1.

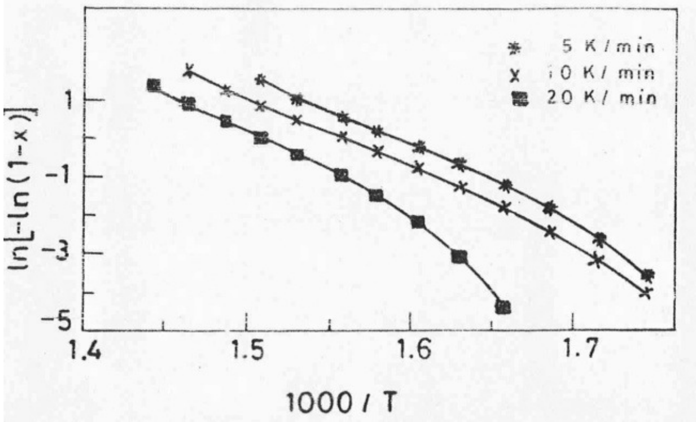

Figure-3(b): A plot of $\ln[-\ln(1-x)]$ versus $1/T$ at different heating rates for composite 7.

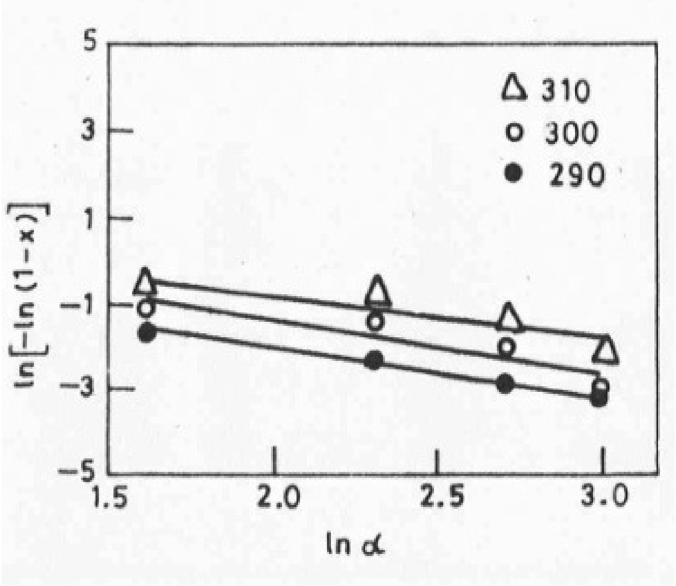

Figure-4(a): A plot of $\ln[-\ln(1-x)]$ versus $\ln\alpha$ for composite 1 at different temperatures.

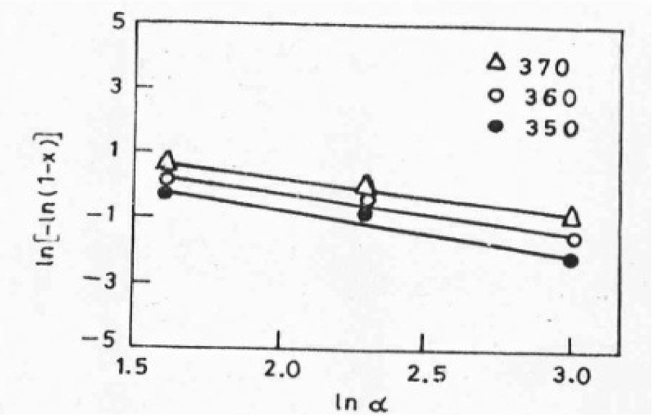

Figure-4(b): A plot of ln[-ln(1-x)] versus ln α for composite 7 at different temperatures.

Activation energies evaluated by both models are listed in Table-1. The difference in activation energy as calculated with said equations may be attributed to different approximations used in these models. The Kissinger's equation basically gives the variation of peak crystallization temperature with heating rate. According to Kissinger's equation, transformation under non-isothermal condition is represented by a first order ($n = 1$) reaction, although, the concept of nucleation and growth has not been included in Kissinger's equation. Matusita[15] *et al* have developed the equation on the basis that crystallization does not advance by nth order reaction but by nucleation and growth process. They emphasized that different crystallization mechanisms such as bulk crystallization (bulk nucleation followed by two or three dimensional growth) or surface crystallization (surface nucleation followed by linear growth) should be taken into account for evaluating E_c. Matusita's equation is not dependent on the heating rate. The slight variation in the values of E_c at different heating rates is with-in the error range. In addition to activation energy, Matusita's equation provides information about the Avrami exponent and the dimensionality of growth. Avrami's exponent (n) evaluated using Matusita's equation comes out to be approximately equal to one for hybrid composites. This is an indication that surface nucleation with one-dimensional growth is dominant in these composites.

Dependence of activation energy on the crystallization rate concludes, that the composite containing 0.25 % of glass fiber has slowest rate of crystallization. The crystallization temperature increases as the volume percentage of glass fiber increases in the composites states that the system moves towards greater thermal stability. Particular combination of fibers in the composites 0.020:0.17:0.63 and 0.07:0.24:0.69 do not show any exothermic peak in the thermo-grams, indicating that for these composites the thermal stability[16] is so high that no crystallization takes place. Activation energy calculations for these composites could not be performed. Enthalpy released is related to the difference between the crystallization temperature and the glass transition temperature[17]. Enthalpy released for the composite having only glass fiber is found to be minimum.

Experimental values of the effective thermal conductivity (ETC) and thermal diffusivity of the glass oil-palm fiber reinforced composites are listed in Table-2. ETC of the samples is plotted as a function of volume percentage of the fibers is shown in Figure-5. Effective thermal conductivity of the composite depends upon the conductivity of the individual fibers as well as on the thermal conductivity of the matrix. So the thermal conductivity of the fibers has been evaluated using Y. Agari model[18,19]. Figure-6 and Figure-7 show the curve of log λ (thermal conductivity) as a function of volume percentage of glass fiber (v_g) and of log λ (thermal conductivity) as a function of volume percentage of oil-palm fiber (v_p) respectively. Thermal conductivity of glass fiber (λ_g) and oil-palm fiber (λ_p) came out to be 0.373 W/mK and 0.243 W/mK respectively using the Y. Agari model. Experimental value of thermal conductivity of the matrix is 0.348 W/mk. Authors[11] have found a good agreement in the λ_p values obtained from binary composites and for hybrid composites. Effective thermal conductivity of the composites is a reflection of the thermal conductivity of its constituents[11]. The Initial decrease in the ETC of the composite is attributed to partial replacement of PF resin by the fibers. When the volume percentage of the fibers is comparable (v_g = 0.17 and v_p =.02) and matrix contribution (v_m=0.63) is more ETC starts picking up. At the point where percentage of the glass fiber dominates the oil-palm fiber with increasing amount of PF the ETC increases. The SEM of the oil-palm surface (Figure-8) shows the presence pores of about 0.07 mm. diameter giving rise to an uneven surface. A waxy layer is also present on the fiber surface due to the presence of fatty acids. The fact that no combination of the fibers and matrix could increase the ETC of the composite beyond the matrix value is attributed to the waxy layer and the smooth surface of the synthetic glass fibers. The waxy layer on oil-palm fiber reduces the fiber matrix adhesion forces due to the poor wetting of the fiber by the matrix resin. Due to some practical problems thermal conductivity data for composite 4 could not been obtained.

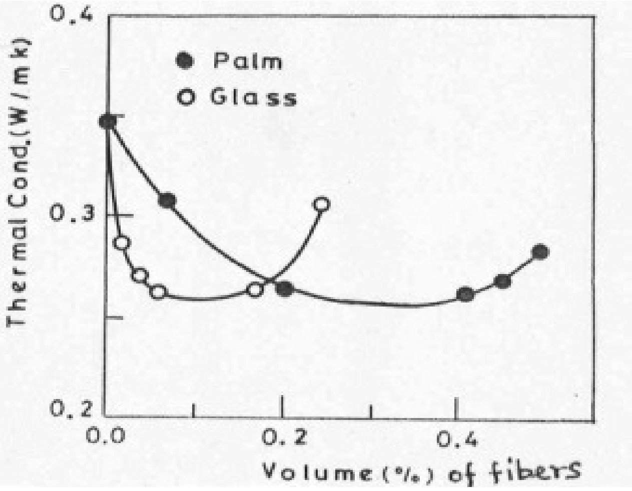

Figure-5: ETC as a function of volume percentage of fibers at 303 K.

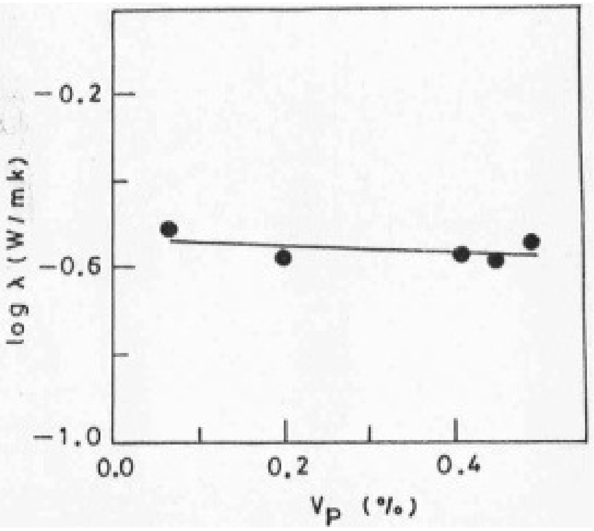

Figure-6: Logarithmn of ETC as a function of volume percentage of glass fiber.

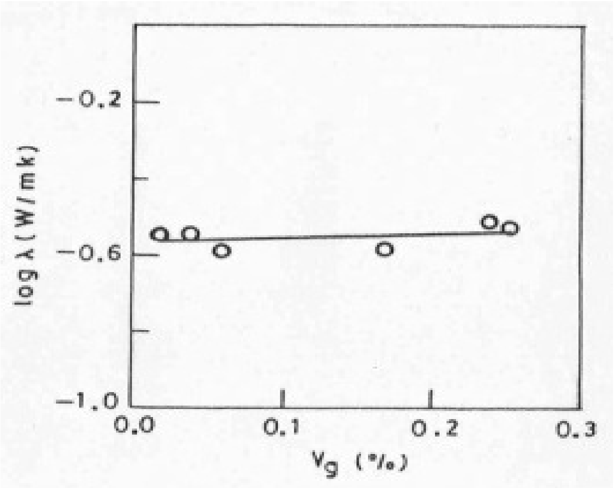

Figure-7: Logarithmn of ETC as a function of volume percentage of oil-palm fiber.

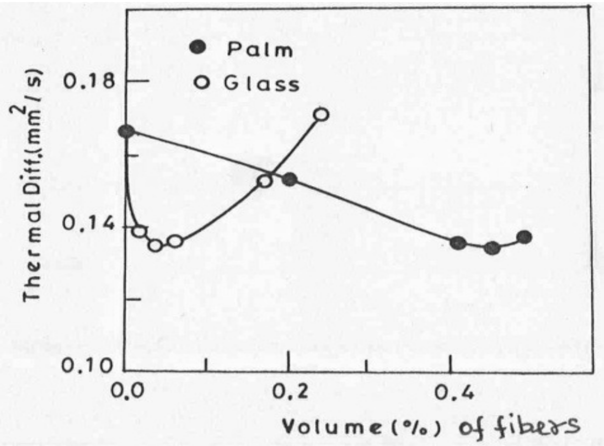

Figure-8: Thermal diffusivity as a function of volume percentage of fibers at 303 K.

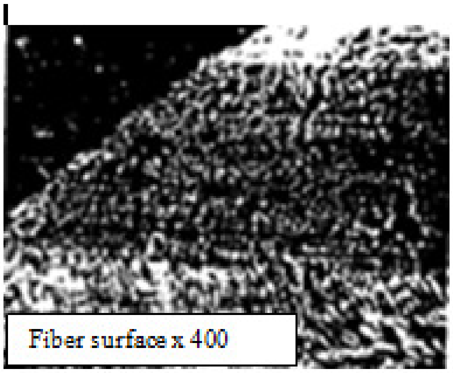

Figure-9: Scanning electron micrograph of oil-palm fiber surface (× 400).

Table-2: Effective thermal conductivity and thermal diffusivity of hybrid composites.

v_p (%)	v_g(%)	$\lambda_{e(}$ (W/mK)	K (mm^2/s)
0.49	0.02	0.285	0.139
0.45	0.04	0.270	0.135
0.41	0.06	0.263	0.137
0.20	0.17	0.265	0.154
0.70	0.24	0.308	0.172
0.00	0.25	0.304	0.173

Conclusion

Crystallization parameters and crystallization temperature show weak dependance on the heating rate for hybrid composites.

The analysis of crystallization exo-therms using Kissinger’s and Matusita’s equation reveals that activation energies evaluated by both the equations are in good agreement. The little difference in the values of activation energies is attributed to approximations taken in the derivation of these equations.

Nucleation mechanism is unaffected for various combinations of oil-palm and glass fiber. Nucleation with one-dimensional growth is present in all the composites.

There is a gradual increase in the (T_c –T_g) values with the increasing percentage of the glass fiber, indicating reinforcement of glass fiber leads to more thermally stable composite.

Composite having maximum enthalpy released has minimum value of (T_c –T_g).

Thermal conductivity of the matrix and oil-palm fibers, obtained by Y. Agari model is found to match with those obtained from binary composites study. Factors responsible for the overall performance of the composites are the relative percentages and conductivity of individual fiber. Fiber surface morphology is a deciding factor for fiber matrix adhesion.

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