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Utilization of industrial waste in producing natural fiber reinforced green composites

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Abstract

Oil-palm fibers (OPF) were treated with acrylic acid and Toulene Diisocynate (TDIC) and were used as reinforcement in resin matrix. Differential Scanning Calorimeter (DSC) was used to evaluate activation energy of crystallization, crystallization temperature and glass transition temperature. Rate of crystallization has been explained using the term thermal stability. Thermal diffusivity and effective thermal conductivity (ETC) of the composites was measured by Transient Plane Source Technique (TPS). A comparative study of model and experimental results has been done. Scanning electron microscopy (SEM) has been used for Surface study of composites.

Keywords: Oil-palm fiber, phenol-formaldehyde resin, acrylic acid, TDIC, transient plane source (TPS), thermal conductivity, DSC, crystallization kinetics.

Introduction

It's a noble duty of mankind to preserve natural resources and look for alternatives, as only a small fraction of such resources are remaining. Moreover the present scenario necessitates the utilization of man created waste in a constructive manner. Empty fruit bunches of palm, an industrial waste of oil mills, has been used to obtain ligno-cellulosic natural fibers. The fruit bunches are industrial waste created in oil mills. This waste is a heaven for pests and insecticides and poses severe environmental damage and health risks. It's use in composite fabrication is beneficial from all dimensions. On one hand natural fibers are abundant and inexpensive. The natural fiber composites (NFC) so formed will have low density, high strength, thermal insulation properties along with good mechanical strength[1-3].

Moreover, the utilization of OPF in the composite fabrication can help in protecting the environment as fibers are biodegradable[4]. NFC has been used as packaging material, building materials, and in automobile industries[5]. Hydrophilic nature is associated with strongly polarizing nature of –OH group in lingo-cellulosic fibers leading to the compatibility issues[6]. Which in-turn causes inappropriate wetting of the filler by the resin[7].

It's a general feature to optimize the interfacial interaction of lingo-cellulosic fiber and matrix for good performance of the composite[10-12]. Interfacial bonding can be enhanced by chemical treatments, coupling agents and radical induced adhesion on the fiber surface[13-15]. This paper is an attempt to study and explore enthalpy released, thermal stability, activation energy, thermal diffusivity and ETC of chemically treated composites.

Composition of Oil-palm fiber can be seen in our previous publications. Scanning Electron Micrograph (SEM) of OPEFB fiber surface reveals the presence of micro-pores (Figure-1) and pithy material.

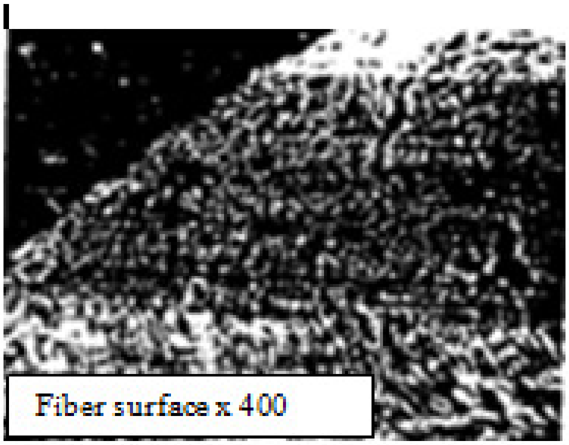


Figure-1: SEM of oil-palm fiber.

Materials and methods

Acrylation: OPEFB fibers were treated with 10% NaOH and were kept for 30 min at 27^{0}C. The solution was discarded and fibers were treated with acrylic acid of varying concentrations. This treatment lasted for about 1h at 50^{0}C. A mixture of water and alcohol was used to wash the OPEFB fibers and then dried. Figure-2 represents the acrylated surface of fiber. The reaction takes place:

$\text{Fiber} - OH + CH_2 = CH\text{-}COONa \rightarrow \text{Fiber} - O - CH_2\text{-}CH_2\text{-}COOH$

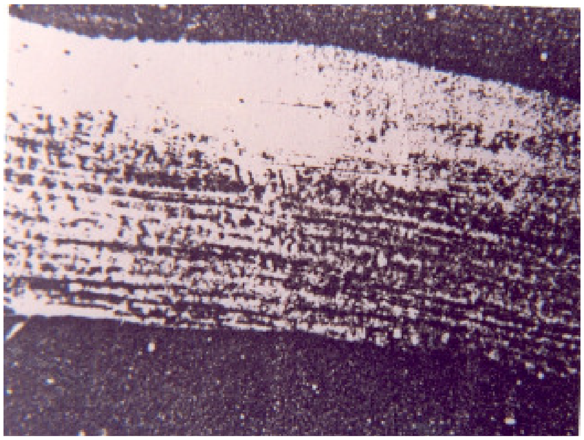
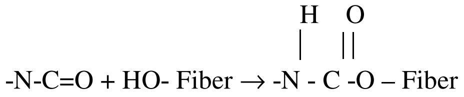


Figure-2: SEM (×400) of acrylated fiber.

Toluene di-isocyanate treatment (TDIC): Fibers were kept at room temperature for two days in 5% NaOH solution, washed and dried. Fibers were then dipped in $CHCl_3$ containing dibutyl tin dilaurate catalyst. TDIC solution was added drop-wise onto the fibers. Figure-2 represents the TDIC treated surface of fiber. The following reaction takes place for 2h with constant stirring. Fibers were refluxed with acetone, washed and dried.



$$-N-C=O + HO\text{- Fiber} \rightarrow -\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-\text{Fiber}$$

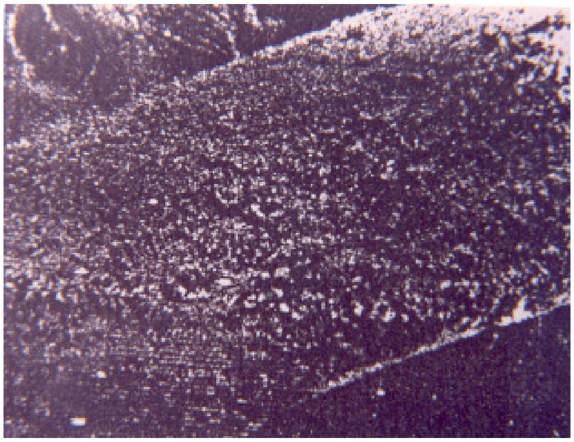


Figure-3: SEM (×400) of TDIC treated fiber.

Measurements: Details about the DSC measurements, materials used and composite preparation are available in reference[16]. For TPS studies the sample size taken was $1.3x1.3x0.3cm^3$. Theory of TPS experimental setup and measurements is given in reference[17].

Results and discussion

Modified Kissinger's equation and Matusita's equation have been used for activation energy of crystallization, which are iso-conversional methods[18-19]. Typical DSC thermograms of acrylated and TDIC treated composites are shown in Figure-4 and 5 respectively. A well-defined peak of crystallization is visible for both the composites. It's very interesting to observe a second peak of crystallization in TDIC treated composite.

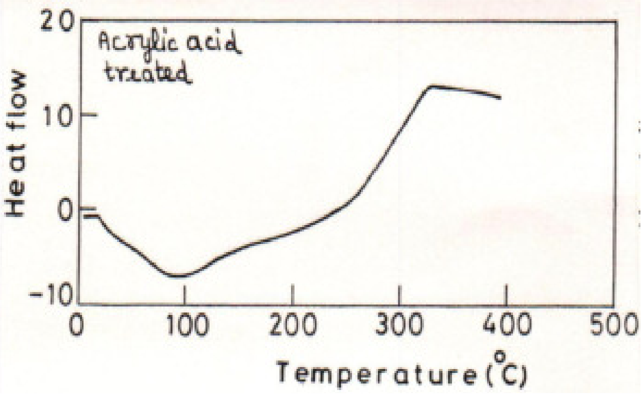


Figure-4: DSC thermogram of acrylic acid treated composite.

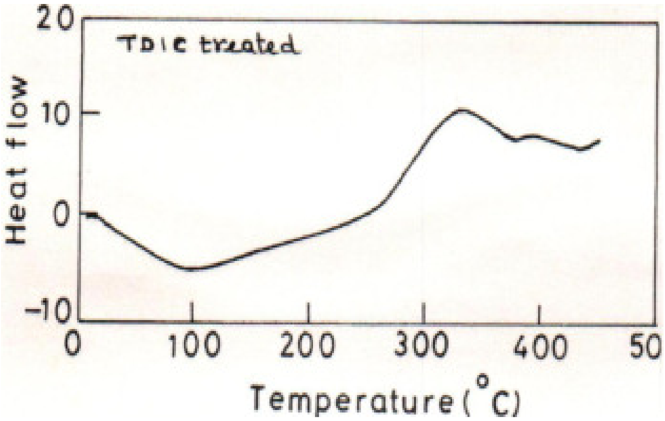


Figure-5: DSC thermogram of TDIC treated composite.

Activation energy (m/n)Ec has been obtained from the slope of Figure-6, using Kissinger's equation[18,20].

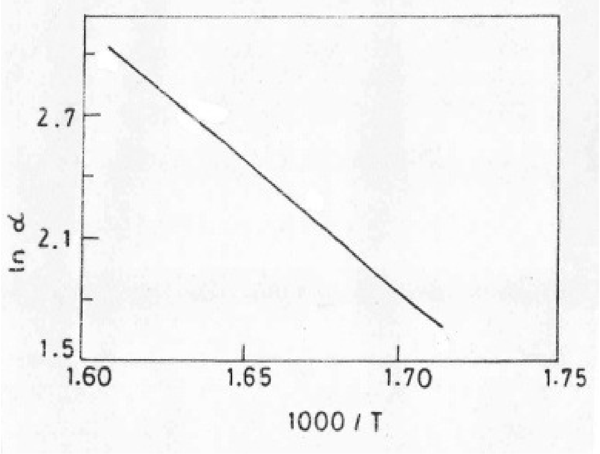


Figure-6: ln α versus 1/Tp curve for untreated composite.

Activation energy using Matusita's equation has been obtained by Figures 7a and 7b for acrylated and TDIC treated composites respectively[19].

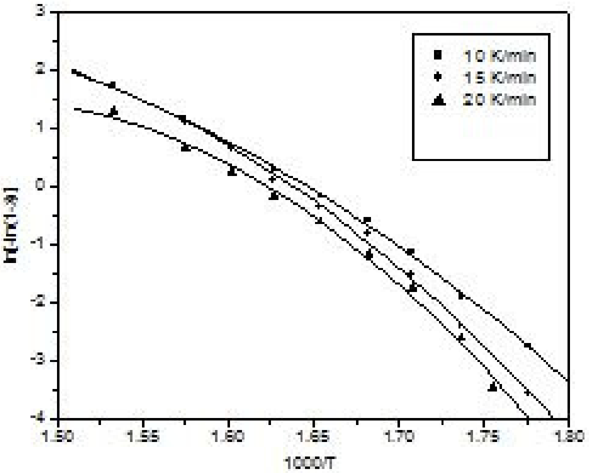


Figure-7a: ln[ln(1-x)] versus 1000/T curve for acrylated composite.

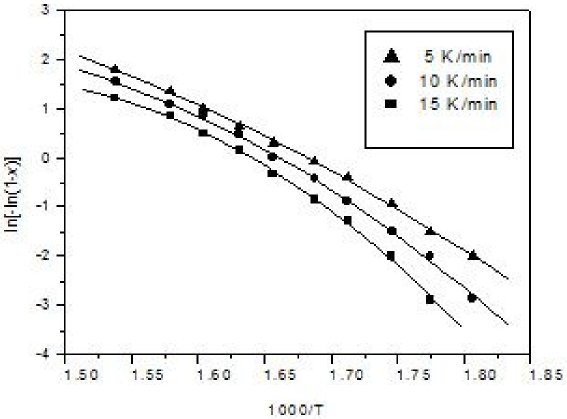


Figure-7b: ln[ln(1-x)] versus 1000/T curve for TDIC treated composite.

Avrami exponent (n) has been deduced Figure-8a and Figure-8b for acetylatd and TDIC treated composites respectively. Activation energies evaluated by both models are listed in Table-1. A slight variation in the calculated activation energy is attributed to different approximations used in equations. A small variation in the Ec values with respect to heating rates is with-in acceptable error range. Avrami's exponent and the dimensionality of growth can be derived from Matusita's equation. Avrami's exponent (n) evaluated is approximately equal to one for treated and untreated composites, concluding that surface nucleation with 1-D growth is present in the composites.

Activation energy and rate of crystallization are inter-related. Higher the activation energy, slowest is the rate of crystallization. Hurby number is related to T_c , T_g and enthalpy released[21]. The difference between the crystallization temperature and the glass transition temperature determines thermal stability of the composite. Hence the thermal stability of acrylated composite is maximum and that of untreated composite is minimum. Hurby number inversely proportional to the enthalpy released. Enthalpy released is maximum for untreated composite and minimum for acrylated composite.

The TPS results of the study are listed in Table-2. Thermal conductivity of untreated fibers has been evaluated[16,21-25]. Results so obtained are in excellent agreement. λ_f of treated fiber has been summarized in Table-2.

Model Calculations of ETC of Treated composites: Effective thermal conductivity of composites obtained from Maxwell[26], Babanov[27], Brailsford and Major[28], Verma et. al.[29], Hamilton and Crosser model[30] are listed (Table-3) respectively. Q. Z. Que model[31] enables to evaluate the ETC of the nano-filler reinforced composites. This model does not include any characteristic of nanofillers. Hence Q. Z. Que model[31] should be applicable to any binary composite. ETC of the treated composites using this model has been listed in column 6 of Table-3.

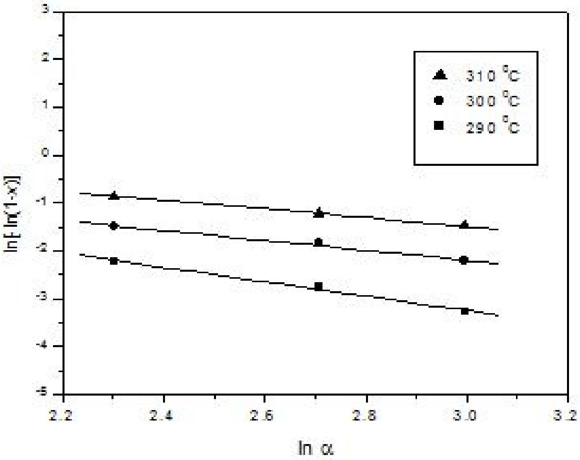


Figure-8a: ln[ln(1-x)] versus ln α plot for acrylated composite.

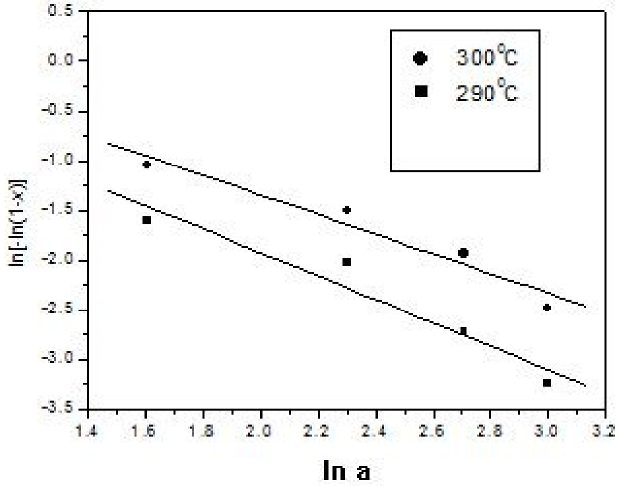


Figure-8b: ln[ln(1-x)] versus ln α plot For TDIC treated composite.

Table-1: Evaluated activation energy values.

Composite	Activation energy (KJ/mol)				Enthalpy released (mcal/mgK)	$(T_c - T_g)$ ^0C
	Kissinger's Eq^n (Ec)	Matusita's Equation				
		n	m	E_c		
Untreated	130.4	1.29	1	144.86	735.6	228.0
Acrylated	181.43	1.14	1	148.39	433.05	244.14
TDIC treated	159.39	1.08	1	128.63	583.35	239.29

Table-2: Effective Thermal conductivity (λ_e), λ_f, χ and ρC_p values of treated composites.

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
Acrylated	0.335	0.321	0.160	2.093
TDIC treated	0.347	0.345	0.193	1.797

Table-3: Theoretically Evaluated values of ETC and TPS 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	TPSR ES
Untreated		0.303	0.292	0.292	0.289	0.292	0.293
Acrylic acid	0.335	0.336	0.335	0.335	0.335	0.335	0.335
TDIC	0.346	0.348	0.347	0.347	0.346	0.346	0.347

There is an increase in thermal conductivity of fibers/composites after chemical treatment. Introduction of higher thermal conductivity fiber in comparison to the matrix increases the ETC of the composites and vice-versa[32]. This seems to be justified for the treated composites. From the SEM (Figure-2) slight fibrillation is visible which facilitates the coupling of fiber with matrix resin[33]. This modified surface encourages the fiber matrix adhesion due to uneven surface topology. Fiber surface morphology is a deciding factor for fiber matrix adhesion. Enhanced adhesion contributes to increased ETC of the composite.

The –N=C=O- group of TDIC reacts with the –OH group of the fiber and reduces the hydrophilic nature of fiber. Major changes like formation of irregular fiber surface due to mass like substance deposition on the fiber is visible in Figure-3. The deposition is an outcome of the reaction of isocyanate group with cellulose and lignin present content of the fiber. The deposition gives rise to rough surface and hence leads to strong interaction between fiber and matrix resin. . It has been reported that sisal fiber's surface become irregular and rough after TDIC treatment[33].

Conclusion

Activation energies evaluated by Kissinger's and Matusita's equation are in good agreement. Little deviation is attributed to the approximations involved. Chemical treatment does not affect the nucleation mechanism appreciably. Surface nucleation with 1-D growth is present in the composites. Composite having maximum enthalpy released has minimum value of (Tc –Tg). Chemical treatments have enhanced the thermal stability of composites. Acrylated composite has minimum value of enthalpy released, least rate of crystallization and hence highest stability. A second peak of crystallization has also been obtained in TDIC treated composite. Chemical treatments have changed the surface of fibers. Thermal conductivity of the fibers has enhanced as a result of chemical treatment. ETC of the treated composites have increased than that of ETC of the untreated fiber.

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