

MELT DRIPPING AND FLAMMABILITY BEHAVIOUR OF BIODEGRADABLE NATURAL FIBRE – REINFORCED THERMOPLASTIC COMPOSITES

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Abstract

This work reports the fabrication of jute fibre-reinforced polypropylene (PP) and polylactic acid (PLA) composites using a novel patented nonwoven technology. The water absorption, physical, mechanical and flammability properties of these partially (jute/PP) and fully biodegradable (jute/PLA) composites have been studied and compared with similarly produced glass-fibre reinforced composites with a view to enabling their use in automotive applications. The fibre reinforcements in composites reduced the rate and propensity of burning compared to respective neat resins. There was no melt/flame dripping observed in any of the fibre-reinforced composites.

1 Introduction

There is an increasing need for more environmentally-friendly composites, both in terms of the raw materials used and the end of life disposal methods. The automotive industry is a key example as the demand for greener vehicles and less scrap material to go to landfill is high. This has led to the use of biodegradable natural fibres as a replacement of glass fibres in fibre-reinforced polymer composites. Natural fibres from plant origins (lignocellulosic fibres) have certain advantages over glass fibres, in particular low density, low abrasive wear, availability worldwide, renewable and biodegradable nature. Their production is economical and they can be easily recycled. There are however, some disadvantages of using natural fibres such as low compatibility with hydrophobic polymer matrices, thermal sensitivity at the temperature of compounding processes, moisture absorption and flammability. Natural fibres such as flax, hemp, jute, etc. have been reported in literature to be used as reinforcement for both thermoplastic and thermoset matrices [1-6]. The choice of matrix material however, is limited by the thermal sensitivity of natural fibres at temperatures above 200°C [4-6]. Thermoplastic composites are processed by melt blending/pressing at the softening/melting temperature of the polymer. Examples of available thermoplastics that have suitable processing temperatures are polyethylene (M pt = 137-146 °C), polypropylene (M Pt = 160 - 220 °C), polystyrene (M Pt = 177-277 °C), and polyvinyl chloride (M pt = 177-212 °C). Out of these polymers, polypropylene is a more popular choice for natural fibre-reinforced composite, especially in automotive applications [3,4]. Besides petroleum based synthetic polymers, biopolymers are

an attractive alternative material for the matrix in order to achieve fully bio-degradable composites [1,7,8]. One promising and the most suitable matrix material is polylactic acid (PLA), with melting temp = 173-178°C [9].

For the usage of natural fibre composites in the transport and construction industries, it is essential to assess the fire risk associated with the application. All products have to conform to certain specified regulations for particular applications. This work assesses the flammability of jute fibre-reinforced PP and PLA composites as compared to similarly produced glass composites.

2 Materials and testing methods

2.1 Materials

Jute and glass fibres in woven fabric form were used as reinforcements for the thermoplastic composites. Jute fabric of 174 g/m² area density was sourced from the National Institute of Textile Technology Research and Design (NITTRAD), Bangladesh. E-glass fabric of 280 g/m² area density was supplied by Glasplies, UK. Polypropylene and biodegradable polylactic acid fibres were used as matrix materials. The length of polypropylene fibre was 50 mm and the fibre linear density was about 3.3 dtex, the length of biodegradable polylactic acid fibre was 40 mm and the fibre linear density was about 2.2 dtex.

2.2 Composite preparation

For the preparation of jute fibre –reinforced composites, jute fabric was needle-punched with PP and PLA fibre webs to produce base fabrics using our previously patented procedure [10]. For this, firstly nonwoven webs of PP or PLA fibres were produced by using Automatex laboratory nonwoven line. In the second step, each nonwoven web and the reinforcing fabric were fed together for needlepunching. The woven fabric/thermoplastic fibre ratio was kept as 40:60 (w/w). Composite materials were produced from these jute/PP(40/60) and jute/PLA(40/60) base fabrics by using a hot press. Eight layers of each base fabric were placed between two aluminium plates and heated at 190°C for 2.5 min under 20 kg/cm² pressure. After that the composite sample containing plates were cooled in another press operated under cooling conditions for 2 minutes at 10 kg/cm² pressure. The properties of the composites are given in Table 1.

For glass fibre-reinforced composites, base fabrics similar to jute/PP or jute/PLA could not be obtained due to needles breakage while processing the glass fabric. The composites were prepared by using alternate eight layers of each of glass woven fabric and PP or PLA nonwoven webs, following the similar procedure as above. PP and PLA cast resin samples were prepared by melt pressing their nonwoven webs using similar procedure as those for the respective components.

Sample	Fabric area density of reinforcing fabric (g/m ²)	Composite composition		Thickness (mm)	Flexural modulus, E (GPa)
		Fibre (wt-%)	Polymer (wt-%)		
PP	-	-	100	2.7	0.6 ±0.08
PLA	-	-	100	2.5	1.8 ±0.16
Jute/PP	174	42	58	3.2	2.6 ±0.36
Jute/PLA	174	39	61	3.0	6.0 ±0.37
Glass/PP	280	40	60	3.5	6.6 ±0.62
Glass/PLA	280	40	60	3.2	12.4 ±0.9

Table 1. Physical and mechanical properties of polymer matrices and composites

2.3 Mechanical and physical testing

The flexural moduli of all test specimens before and after immersion in water were determined using a three-point bending mode test rig using a 100 N load cell Instron 3369 tensometer with a load and displacement control, at a cross-head speed of 1 mm/min.

Water absorption of the composites was carried out by dipping the samples in water at 25°C for three weeks. Specimens were dried at 50°C for 24 h and weighed before immersing in water. After set period of times, the samples were removed from the water bath, air dried and weighed. These samples were dried again at 50°C for 24 h and weighed again. Water uptake was determined by measuring the increase in sample weight as:

$$W_{abs} = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_t is the weight of the sample after t min exposure to water and W_0 is the weight of the sample before exposure to water.

2.2 Thermal and flammability testing

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of fibres, polymeric matrices and composites were performed on an SDT 2960 simultaneous DTA–TGA instrument from room temperature to 700 °C using 15 ± 1 mg samples heated at a constant rate of 10 °C/min in air flowing at 100 ± 5 mL/min.

A Fire Testing Technology Limiting Oxygen Index Tester was used to carry out limiting oxygen (LOI) test. Flame spread tests were done by a modified UL-94 test on matrix and composite samples (length = 120 mm, width = 10 mm) to observe their burning behaviour in both horizontal and vertical orientations. The first 10 mm of sample burning was not taken into account and so times of burning were recorded once the flame had reached a line drawn 10 mm from the edge against which flame of 30 mm was applied for 10 s as specified in the test. A video film was taken of the burning of each sample from which times to reach 50 (t_1) and 100 mm (t_2) marks and/or to achieve flameout were noted. Two replicate specimens of each sample were burnt and results averaged. The burning behaviour of each sample was observed and noted.

A Fire Testing Technology cone calorimeter was used according to ISO 5660 / ASTM E1354 standard to perform experiments on horizontally oriented samples of 75 mm x 75mm dimensions at 35kW/m² external heat flux. All experiments were conducted in triplicate and results were reproducible to $\pm 10\%$.

3 Results and Discussion

3.1 Physical and mechanical characterisation

To establish the potential usefulness of each composite in terms of a semi load-bearing structural component the flexural properties were measured in a three point bending mode. The results presented in Table 1 show that PLA polymer (matrix) has a higher flexural modulus than PP, with a similar trend shown by jute and glass fibre – reinforced composites; jute/PLA=6.0 GPa, jute/PP =2.6 GPa. Other researchers have also shown that PLA has higher mechanical properties than PP [3,11,12]. The moduli of jute-composites are 50% less than those of similarly produced glass fibre – reinforced composites.

3.2 Water uptake

Figure 1(a) shows the weight gain results from water absorption test for jute/PP and jute/PLA composites. It can be seen that the pattern for water absorption is typical for jute fibres, i.e., water absorption in initial stages is very rapid and then it becomes slower and static with time. Moreover, the results for jute/PP and jute/PLA composites are very similar. Both PP and PLA are hydrophobic, whereas jute due to its cellulosic nature is hydrophilic in nature. The elementary unit of cellulose is anhydro-D-glucose, which contains three hydroxyl groups, which account for the strong hydrophilic nature of jute. In composites, most of the water absorption occurs through the fibres exposed along the sides of the specimens or through the micropores or cracks in the matrix or by capillary action along the fibre/matrix interface. When these fibres were dried, all absorbed water was desorbed and the initial weight of these composites could be attained. The water absorption however, disturbs the mechanical integrity of the composites affecting the fibre strength, matrix strength and fibre-matrix interface simultaneously. Even when the water is desorbed, the mechanical integrity of the components and the composite is not restored. This can be seen from results in Figure 1(b), where it can be seen that after 3 weeks of immersion in water, the flexural moduli of jute/PP and jute/PLA composites were reduced by 31.3% and -24.3%, respectively. There was no change in this behaviour after drying the laminates.

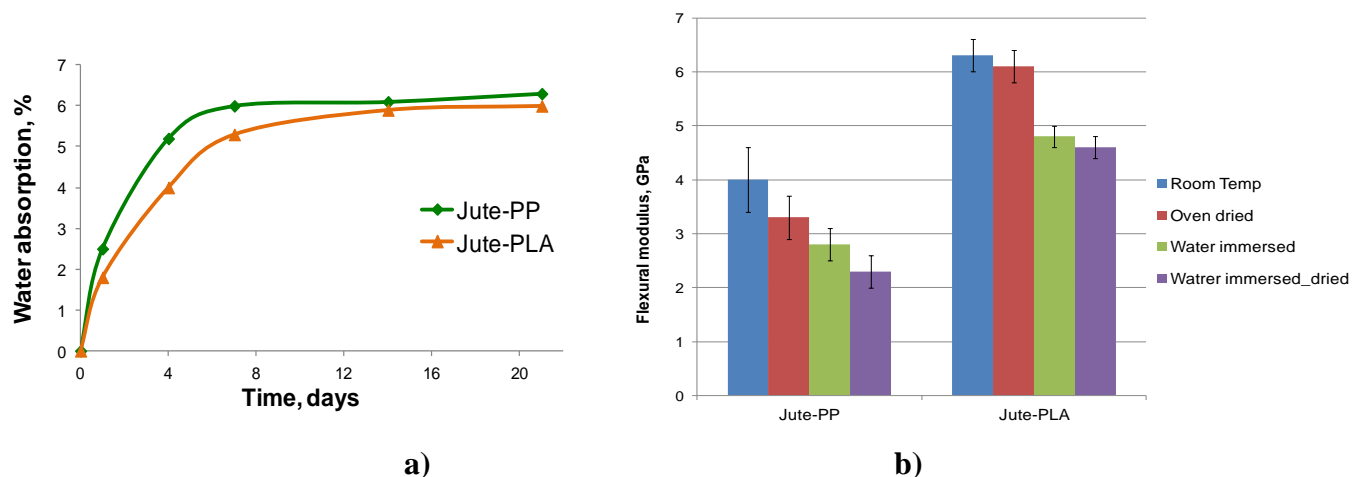


Figure 1. a) Water uptake of jute/PP and jute/PLA composites as function of time: b) flexural moduli of jute/PP and jute/PLA samples tested at ambient conditions, oven dried (50°C for 24h, followed by keeping in a desiccator for 24h), after immersion in water for 3 weeks tested at ambient conditions and oven dried.

3.3 Thermal analysis

To understand the thermal decomposition behaviour of composites and whether there is any interaction between the two components of the composite at the processing stage, thermal analysis of neat polymers, fibre and composites were performed in flowing air. All results are presented in Table 2 and selected results shown in Figure 2. The onset of decomposition temperature of jute is 235 °C, which is higher than the melting point of PP or PLA (Table 2). TGA curve shows that it decomposes in two stages leaving no char residue above 480 °C, which is typical behaviour of lignocellulosic materials. These two stages are corroborated by two exothermic peaks in DTA (see Table 2) representing decomposition and char oxidation reactions for the jute fibres.

PP curve in Figure 2(a) shows 98% mass loss in the temperature range 197 – 395 °C, representing decomposition stage, followed by 2% mass loss between 395 - 480 °C, representing oxidation of combustible products. No char is left at the end of the test. The TGA curve of PLA in Figure 2(b) shows that the onset of decomposition occurs at 296 °C and 97% mass loss occurs up to 385 °C, followed by 3% up to 465 °C. On comparing TGA and DTA curves of PP and PLA, the PLA seems to be more thermally stable than PP.

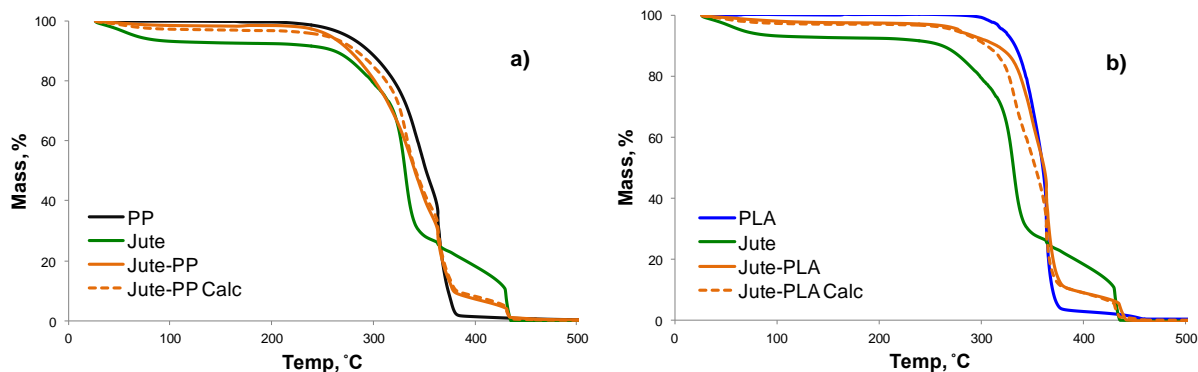


Figure 2. Thermogravimetric curves of Jute, PP, PLA, jute/PP and jute/PLA composites. The dashed lines are calculated curves from sum of individual components.

The thermal analytical behaviour of jute/PP and jute/PLA composites is a combination of their respective components. The detailed analysis is given in Table 2, while the calculated TGA curves from the respective curves of individual components are shown in Figure 2. The calculated and experimental curves are very similar, indicated that both components are decomposing individually and there is no chemical interaction between them at this stage. In glass fibre – composites the mass loss shown is for pure polymer and the residual mass left after the test represents the glass content in the composite. In general, jute fibre- composites are less thermally stable in terms of mass loss compared to respective glass composites.

Sample	DTA analysis		TGA analysis			
	Melting endotherm (°C)	Decomposition peaks* (°C)	DTG peak maxima (°C)	T ₁₀ (°C)	T ₅₀ (°C)	Char (%)
PP	169	382, 423	381, 418	299	360	0.2
PLA	58, 169	342 (En), 362, 376, 455	363, 453	332	360	0.4
Jute fibre	-	348, 459	333, 453	260	334	0
Jute/PP	167	380, 439	352, 442	279	344	0.3
Jute/PLA	58, 169	355 (En), 383, 467	358, 453	315	356	0
Glass/PP	163	277, 377, 416	371, 418	292	-	52.1
Glass/PLA	58, 169	344 (En), 371, 394	361, 394	323	-	44.6

Note: * All peaks are exothermic in nature except for those denoted as En, endothermic.

T₁₀ = Temp. at 10% mass; T₅₀ = Temp. at 50% mass;

Table 2. TGA-DTA data for polymer matrices and composites

3.4 Flammability of composites

The LOI values of neat polymers and composites are given in Table 3. LOI is the minimum concentration of oxygen in a mixture of oxygen and nitrogen that will just support flaming

combustion of a material. PLA samples (matrix and composites), have slightly higher LOI values than PP samples, indicating that PLA is less flammable than PP. For all samples immersed in water for 3 weeks and then dried, there was no effect on LOI values.

Rate of flame spread of the neat polymers and composites was studied using a modified UL-94 test, igniting the sample and recording times taken to reach 50 (T₁) and 100 mm (T₂) marks in both horizontal and vertical modes and the results are presented in Table 3. In the horizontal mode PP sample melted and burned with flaming drips. The dripping was very fast and it was difficult to count the number of drops. In vertical mode, rate of burning was much faster and dripping was less compared to the horizontal mode as the samples burn more easily. In PLA polymer, the dripping was much less and slow compared to PP and the sample burned more steadily. In both jute and glass fibre – composites, no melt dripping was observed. Jute/PP burned slowly in horizontal mode compared to the vertical mode. In both cases water immersed samples burned a little bit more slowly compared to the control samples. This shows that moisture helps in reducing the flammability, though the effect is very low. The rate of flame spread for glass composites was lower than for respective jute composites, which is as expected.

Sample	LOI (%)	Horizontal burn				Vertical burn			
		T ₁ (s)	T ₂ (s)	RB (mm/s)	No. of MD	T ₁ (s)	T ₂ (s)	RB (mm/s)	No. of MD
PP	17.4	68	128	0.76	~1000	14	44	2.93	~600
PLA	20.0	72	138	0.71	388	20	49	2.29	194
Jute/PP	18.7	115	222	0.45	0	22	55	2.02	0
Jute/PP – Water**	18.9	120	240	0.42	0				
Jute /PLA	19.8	80	173	0.60	0	34	73	1.42	0
Jute-PLA-Water**	19.9	84	183	0.56	0				
Glass/PP	*	187	370	0.27	0	22	52	2.13	0
Glass/PLA	*	122	247	0.41	0	23	52	2.05	0

Note : T₁ = time to 50mm; T₂ = time to 100mm; RB = rate of burning; No. of MD = number of melting drips

* = Test not performed

** = Samples after immersion in water for 3 weeks and then oven dried.

Table 3. LOI and flame spread results of polymer matrices and composites

Neat polymers and composite laminates were also tested by a cone calorimeter at 35 kW/m² heat flux. Heat release rate and mass loss vs time curves are shown in Figure 3 and derived results are presented in Table 4. Both samples ignited between 28 – 30 sec. PP showed peak heat release rate (PHRR) 1699 kW/m² and total heat release (THR) 95.4 MJ/m². For PLA the values are much lower, PHRR = 663 kW/m² and THR = 49.8 MJ/m². The effective heat of combustion of PLA (18.2 MJ/kg) is also much lower than for PP (42.9 MJ/kg). PLA produces negligible smoke compared to PP as shown in Table 4. This study shows that although PLA is combustible, it poses less of a fire hazard as it releases less heat during combustion.

As can be seen for results of jute fibre-reinforced composites that the fibres had minimal effect on time-to ignition (TTI) of PP or PLA matrix. Jute fibre reinforcement reduced the PHRR of PP from 1699 kW/m² to 675 kW/m², which is 60% reduction. However, glass fibres displayed more reduction, ie 70%, which is expected as glass fibre is non-flammable, whereas jute is flammable. However, the THR increased for jute fibre – reinforced composite. It is

well known that natural fibre-reinforced composites burn slowly but for a longer time, producing more total heat and smoke.

Sample	TTI (s)	FO (s)	PHRR (kW/m ²)	THR (MJ/m ²)	Hc (MJ/kg)	Smoke (m ² /m ²)	Char (%)
PP	30	160	1699	95.4	42.9	1302	0
PLA	28	180	663	49.8	18.2	0.7	3.0
Jute/PP	33	290	675	95.5	31.7	1121	3.3
Jute/PLA	38	300	393	60.7	16.1	0.9	4.4
Glass/PP	25	260	506	79.7	38.1	1308	50.9
Glass/PLA	27	280	275	46.4	16.6	0.1	43.9

Table 4. Cone calorimetric results of PP, PLA and jute and glass fibre-reinforced composites at 35kW/m² external heat flux.

In the case of PLA composites, glass fibres helped in reducing the PHRR by 58% in comparison to pure PLA and jute by 40%. This reduction is much less than that seen for PP composites. THR for Jute/PLA sample is increased, whereas smoke production in all samples is minimal.

On comparing the results for PP and PLA composites, the difference between any one type of fibre containing composites was similar to that seen for the two matrices in Figure 3.

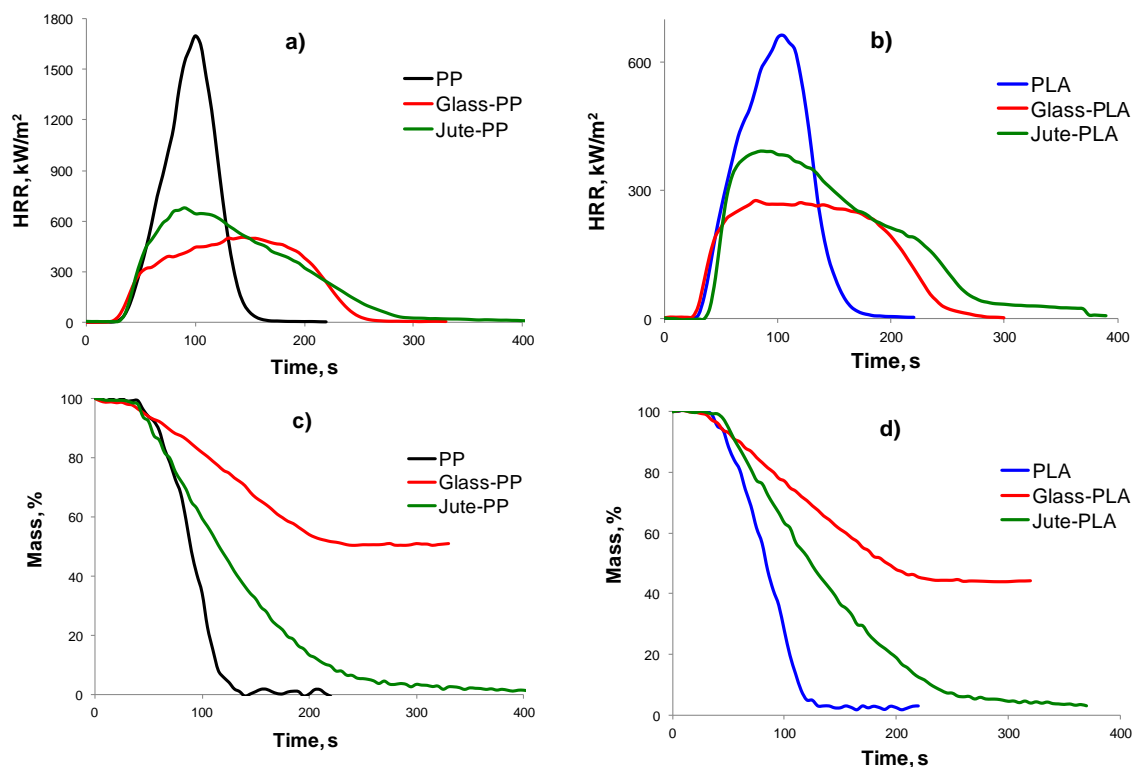


Figure 3. HRR and mass loss vs time curves for PP, PLA matrices and jute and glass fibre-reinforced composites exposed to 35kW/m² heat flux.

4 Conclusions

This work has shown that natural fibres, when used as reinforcement for PP or PLA, reduce their melt dripping and flammability. Jute/PLA composites showed better mechanical and flammability properties compared to jute/PP composites. Moisture absorption helps in reducing the flammability, though the effect is very low. Jute fibre composites though had inferior mechanical and flammability properties than their glass counterparts, the properties are significant for their usage in semi-structural composites. These composites can be easily used for automotive industry, which has less stringent fire regulations. However, for these composites to be used in other sectors such as marine, aerospace or construction, they will have to pass commercial fire tests, such as UL-94, flame spread etc. For this some sort of flame retardant treatment is required.

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