Received: 2 September 2020 | Revised: 18 September 2020 | Accepted: 22 September 2020
DOI: 10.1002/pc.25835

REVIEW ARTICLE

Polymer COMPOSITES
WILEY

Flame retardancy and thermal stability of agricultural residue fiber-reinforced polylactic acid: A Review

Vianney Andrew Yiga[1] | **Michael Lubwama**[1,2] | **Sinja Pagel**[3] | **Johannes Benz**[3] | **Peter Wilberforce Olupot**[1] | **Christian Bonten**[3]

[1]Department of Mechanical Engineering, Makerere University, Kampala, Uganda
[2]Africa Center of Excellence in Materials, Product Development and Nanotechnology, Makerere University, Kampala, Uganda
[3]Institut für Kunststofftechnik, University of Stuttgart, Stuttgart, Germany

Correspondence
Vianney Andrew Yiga, Department of Mechanical Engineering, Makerere University, Kampala, Uganda.
Email: vyiga@cedat.mak.ac.ug

Funding information
Volkswagen Foundation, Grant/Award Number: 96655

Abstract
Biocomposites containing natural fibers and biopolymers are an ideal choice for developing substantially biodegradable materials for different applications. Polylactic acid is a biopolymer produced from renewable resources and has drawn numerous interest in packaging, electrical, and automotive application in recent years. However, its potential application in both electrical and automotive industries is limited by its flame retardancy and thermal properties. One way to offset this challenge has been to incorporate natural or synthetic flame retardants in polylactic acid (PLA). The aim of this article is to review the trends in research and development of composites based on agricultural fibers and PLA biopolymers over the past decade. This article highlights recent advances in the fields of flame retardancy and thermal stability of agricultural fiber-reinforced PLA. Typical fiber-reinforced PLA processing techniques are mentioned. Over 75% of the studies reported that incorporation of agricultural fibers resulted in enhanced flame retardancy and thermal stability of fiber-reinforced PLA. These properties are further enhanced with surface modifications on the agricultural fibers prior to use as reinforcement in fiber-reinforced PLA. From this review it is clear that flame retardancy and thermal stability depends on the type and pretreatment method of the agricultural fibers used in developing fiber-reinforced PLA. Further research and development is encouraged on the enhancement of the flame retardancy properties of agricultural fiber-reinforced PLA, especially using agricultural fibers themselves as flame retardants as opposed to synthetic flame retardants that are typically used.

KEYWORDS
biofibers, biopolymers, composites, flame retardance, thermal properties

1 | INTRODUCTION

In the past decade, fiber-reinforced plastics have drawn much attention in automotive and aerospace applications because of their low mass forces, which reduce inertia.[1] In the meantime, fossil-based plastics derived from petroleum are less preferred for such applications because of their unsustainability and the severe environmental pollution challenges they pose.[2–4] As a result of this, there is continuous effort to produce plastic composites that are renewable, biodegradable, and produce less or no greenhouse gas emissions.[5,6] Significant research effort has been made on the so-called "biocomposite materials" as a result of increasing environmental problems and the growing eco-friendly consciousness.[7–9] The term "biocomposites" comprises of either composites of synthetic matrix and natural fibers, composites of bio-based matrix and synthetic fibers or composites of bio-based matrix and natural/agricultural fibers.[10] The application of biocomposites has been extended to multiple sectors. Fossil-based polymers or bio-based polymers reinforced with agricultural fibers are the most common in this respect, and their application is constantly growing.[11]

Agricultural fibers are of lignocellulosic nature and their annual global production is approximately 2×10^{11} tons.[12,13] They can be classified into seven major groups including stem, leaf, seed, fruit, stalk, grass, and wood.[14] These lignocellulosic materials can be potential materials for compositing because they are flexible, eco-friendly, renewable, and cheap compared to synthetic fibers like glass and carbon fiber.[2] Significant literature exists on the use of agricultural fibers in polymer matrix. This increasing trend in using agricultural residues as reinforcements in plastics is due to their flexibility during processing, highly defined solidity, easy accessibility, biodegradability, high toughness, low cost on a volumetric basis, and eco-friendliness.[2,4,8,10,15–18] More research is, however, required in replacing synthetic fiber reinforcements in composites so as to establish new value chains for particular crops and add economic benefits to the farmers. Actually, ongoing research in the field of natural fiber reinforced plastics has shown that their mechanical properties like tensile strength and Young's moduli are comparable to those of glass fiber-reinforced composites.[19–22] This means that natural fiber reinforced plastics can be used to produce structural components for automotive applications like doors, panels, roofs, and covers. As such, companies like Mercedes Benz, Toyota, and Daimler Chrysler are already using natural fiber composites.[23,24]

To produce fully bio-based composites, both polymer matrix as well as reinforcement must be derived from renewable resources.[25] This is the best way to combat the challenges of conventional petroleum-based plastics like environmental unsustainability.[26] As a result, polylactic acid (PLA) has received much attention in past decades because it is fully bio-based and biodegradable under certain conditions, especially in industrial compositing plants.[27–30]

Bioplastics currently account for about 1% of the more than 359 million tons of plastic produced annually and the focal products in terms of production volumes are PLA and starch-based plastics.[31] PLA is derived from renewable resources and possesses good mechanical properties compared to other bioplastics, making it an ecologically friendly material for composite applications.[32–35] However, compared to most fossil-based plastics, PLA has inferior mechanical properties. PLA is getting worldwide attention because of its attractive compostability, nontoxicity during incineration, availability at competitive prices and recyclability.[36,37] Another reason for this attention is that the production of PLA requires 25 to 55% less energy, compared to petroleum-based polymers, which in turn leads to the release of less greenhouse gases.[38,39] These attributes are important for sustainability of a product during its use in specific applications. Table 1 identifies some typical properties of agricultural fibers as well as applications of agricultural fiber-reinforced PLA composites.

As much as PLA is the most promising in the bio-based polymer family, its use can be constrained by its limitations in polymer formulation, its inherent brittleness, poor toughness, its slow degradation rate, its low flame retardancy and thermal stability as well as processing difficulties.[60–63] These are the major reasons why PLA has not been fully utilized, especially in the transport sector.[64] In order to overcome the limitations of PLA, it is necessary to reinforce it with different filler materials. The most common fillers used in bio-composite reinforcements are from plants.[65] This is because plant reinforcements offer advantages of abundance, high specific strength, low density and non-abrasiveness over inorganic fillers like clay. One main disadvantage of plant fibers is that their properties can vary depending on the season and hydrogeological condition.[66] Other disadvantages with plant fibers are their hydrophilicity and poor compatibility with polymer matrices, especially of petroleum nature, which often leads to weak interfacial adhesion and therefore results to poor mechanical properties of the composites.[10,17] PLA, being a biopolymer, can easily be combined with agricultural fibers.[67] This usually improves its mechanical properties like tensile and impact strength because these fibers have large surface area and can therefore be utilized in load bearing composites.[68] Additionally, because both PLA and agricultural fibers come from renewable resources that are compostable, agricultural fiber-reinforced plastics are "green" and eco-friendly materials that can therefore be easily recycled.[69] The extent however, to which agricultural fiber reinforced plastics can be used depends on their eco-friendliness and wide material applications.

Recently developed agricultural fiber-reinforced PLA plastics have favorable mechanical properties but a major disadvantage to their application is their low flame retardancy and thermal stability. Low flame retardancy and thermal stability are attributed to the fact that

TABLE 1 Bio-chemical, mechanical, and physical properties of typical agricultural residue fibers and their applications in fiber reinforced PLA

	Bio-chemical properties			Mechanical properties			Physical properties				
Agricultural fiber	**Cellulose (wt%)**	**Hemicellulose (wt%)**	**Lignin (wt%)**	**Tensile strength (MPa)**	**Young's modulus (GPa)**	**Elongation at break (%)**	**Density (g/cm^3)**	**Length (mm)**	**Diameter (μm)**	**Application**	**Author**
Abaca	56-63	20-25	7-9	430-980	31.1-33.6	2.9	1.5	2-4	150-260	Automotive, aerospace	[21,40]
Bamboo	73-83	12.49	10.15	262	9.8	2.7	—	2.7	14	Electronics, packaging	[14,21,41–43]
Banana	63-68	5-10	4.6	355	33.8	5.3	1.35	0.17	13.16	Disposable	[14,21,44]
Coir	32-43	0.15-0.25	40-45	220	6	15-25	1.25	0.3-1	100-460	Biomedical	[14,45,46]
Cotton	85-90	0.7-1.6	0-1	287-597	6-12	3-10	1.5-1.6	15-56	12-35	Automotive	[14,21,47]
Elephant Grass	45.6	—	17.7	185	7.4	2.5	0.82	—	70-400	Automotive	[45,48,49]
Flax	71-78	2.2	0.9-1.7	800-1500	60-80	2.7-3.2	1.4	10-65	5-38	Structural	[14,21,50]
Hemp	68	15	10	550-900	70	1.6	1.48	5-55	10-51	Automotive	[14,51,52]
Jute	64.4	12	11.8	400-800	10-30	1.8	1.46	0.8-6	5-25	Architectural, biomedical	[14,53,54]
Kenaf	53.4	33.69	21.2	295	40-53	2.7-6.9	1.2	1.4-11	12-36	Electronics	[14,55]
Pineapple	81	18.8	12.7	170-1672	82	1-3	1.5	3-9	20-80	Automotive	[14,51,56]
Ramie	68.6-76.2	13-16	0.6-0.7	500	44	2	1.5	40-250	18-80	Automotive, aerospace	[14,21,57]
Sisal	65	12	9.9	600-700	38	2-3	1.33	0.8-8	7-47	Electronic, automotive	[14,51,58]
Sugarcane bagasse	55.2	16.8	25.3	20-290	19.7-27.1	1.1	1.2	0.8-2.8	10-34	Automotive	[14,51,59]

agricultural fibers have poor thermal properties compared to synthetic fibers. This reduces the aromaticity of the polymer matrix which would otherwise decompose into an insulating surface layer of carbonaceous char. Decreasing aromaticity fastens conduction into composite and increases flammable gas emissions. This hinders their application in industry especially in automotive industry.[70] It is therefore extremely important to study the flame retardancy and thermal stability of agricultural fiber-reinforced PLA. The main goal of this review is to create a better understanding of the role of flame retardancy and thermal stability properties for successful utilization of PLA and agricultural fiber-reinforced PLA to increase their potential application in different technical fields.

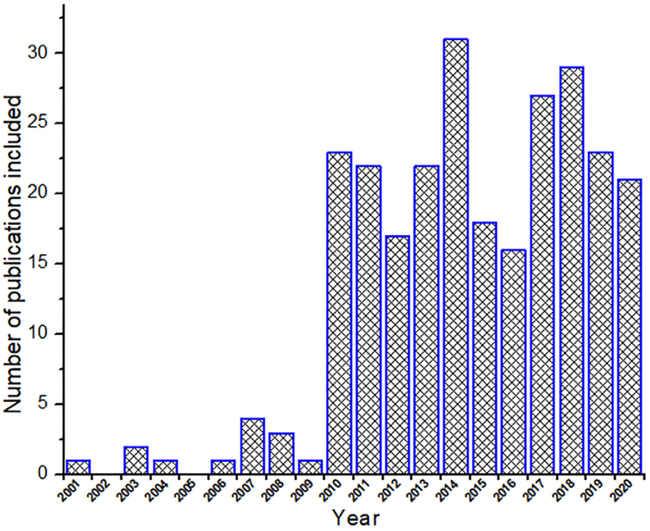

FIGURE 1 Yearly publication numbers used in the review [Color figure can be viewed at wileyonlinelibrary.com]

2 | METHODOLOGY

This review detailed original research and review articles on composites based on agricultural fibers and PLA in the past decade (2010-2020). The review process followed an iterative search process where search terms were updated as the review progressed. Selection of literature was based on peer reviewed scientific articles and reviews as well as peer reviewed conference proceedings. The searches were done from online scientific databases including Scopus and ScienceDirect. The search was expanded to Google Scholar to include peer reviewed conference proceedings and other sources that may not be available in Scopus and ScienceDirect. The searches were conducted using keywords including; (i) PLA, (ii) agricultural fiber-reinforced PLA, (iii) PLA composites, (iv) natural fiber reinforced PLA, (v) flame retardancy, (vi) thermal properties, and (vii) thermal stability. The last three keywords (v-vii) were searched in conjunction with the first four keywords (i-iv). A total of 262 references were used in this review (see Figure 1). Articles from 2001 to 2009 were used to explain property results in the review. Based on the institutional affiliation of the first author, most articles were from Asia (59%), followed by Europe (25%), then Africa (6%), and the Americas (6%). Articles from Australia had the least appearance at 4%.

3 | FIBER-REINFORCED PLA

3.1 | Thermal degradation of agricultural fibers

Agricultural fibers mainly consist of hemicellulose, cellulose and lignin.[13] These are extremely important in understanding flammability and thermal stability of agricultural fibers and agricultural fiber-reinforced composites. Thermogravimetric analysis (TGA) is used to study thermal degradation of agricultural fibers.[71,72] According to Cabeza et al,,[73] TGA is a slow pyrolysis process in which the mass variation of a given sample under experiment is recorded as temperature increases from room temperature. Hemicellulose primarily contributes to the thermal stability, cellulose to the Arrhenius parameters, and lignin to the final stage of the weight loss curve.[74]

The thermal degradation of agricultural fibers during TGA begins with the vaporization of liquid phases. Moisture evaporates at around 100°C and oil between 100 and 300°C. At 200°C, lignin begins to decompose, breaking its weaker parts and enhancing the reaction of hemicellulose and cellulose. Between 250 and 275°C, hemicellulose reacts and at around 300°C, it disappears completely. This promotes the decomposition of cellulose. Between 300 and 350°C, further degradation occurs and only lignin, inert substances and char residues remain of the fibers. Lignin depletes at about 500°C and char residues remain thereafter.[73]

3.2 | Heat transfer in PLA

PLA is a thermoplastic polymer derived from renewable lignocellulosic material, mainly corn and sugarcane.[75,76] Other source materials include sugar beet, cassava, wheat straw and wood chips.[68] The chemistry of PLA involves processing and polymerization of lactic acid monomer. PLA's synthesis path is shown in Figure 2. Lactic acid is a

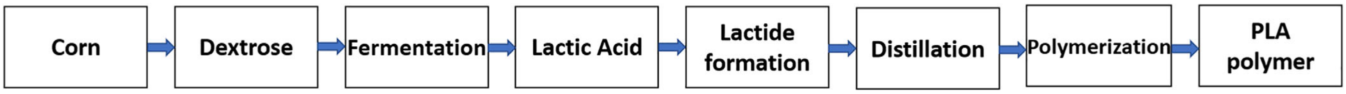

FIGURE 2 PLA's synthesis path (adapted from ref.[21]) [Color figure can be viewed at wileyonlinelibrary.com]

simple chiral molecule that exists as L- and D-lactic acid.[32,77] D-lactide content strongly influences the thermal properties of PLA and high D-lactide contents increase amorphousness of PLA.[32] The two different molecular structures of the PLA chain are presented in Figure 3.

TGA of PLA and its composites can be used to quantify the threshold for the initial mass, above which heat transfer effects are significant.[79] TGA involves combustion of a sample using either oxygen or air to ascertain its decomposition as temperature increases.[80] According to Richter and Rein,,[79] a sample undergoing a TGA experiment should be sufficiently small for heat transfer effects to be negligible, so that the degradation of a polymer is purely kinetically controlled. TGA has been noted to provide specific data on char residues, mean reactivities, and peak temperatures, which can critically be used to understand heat transfer during combustion of PLA and its composites.[80,81]

One way to retard heat transfer in PLA and its composites is by incorporation of flame retardants. Char residues have been noted to increase with incorporation of flame retardants and therefore heat transfer is delayed during combustion, hence, improving the flame retardant property.[82] Additionally, char residues have been noted to increase with incorporation of agricultural fibers like rice husks in polymer matrices, signaling prevention of heat transfer due to the inherent silica compositions manifested during combustion of rice husks.[83]

3.3 | Flammability of PLA

PLA is a flammable polymer with the LOI value of about 19. Not much literature entails the flame retardancy of PLA. This is possibly because earlier applications of PLA were mainly limited to disposable materials and semi-durable materials like textiles. One main application of PLA for example, is the production of single-use dishes. These did not really require focus on flame retardancy. Current trends in the market show demands for more enduring materials and substitutes for petroleum-based thermoplastic polymers by PLA in sectors such as transportation and electronics. In these sectors, protection from fire hazards is important and flame retardancy is an important property to consider. Therefore, development of flame retardancy of PLA or its blends has become a significant issue.[84]

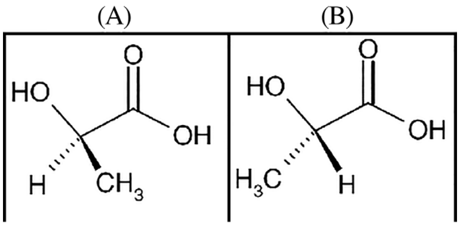

FIGURE 3 PLA, A, L-lactic acid, B, D-lactic acid[78]

Flammability of PLA and its blends is becoming important because current trends in the plastics industry necessitate a shift from petroleum-based materials to bio-based materials. PLA, being flammable, burns readily and produces less visible smoke than other nonflame retardant materials so visibility hazards in a fire are decreased. Actually, the peak energy release rate of burning PLA is 60% less than PET's. When exposed to fire, PLA and its blends may quickly ignite and combust releasing CO_2, water and large amounts of heat. The release of large quantities of heat creates a challenge to their applications in advanced engineering fields especially in automotive industry, since they are potential fire hazards and can pose security-related risks. Consequently, there is need to investigate possible cost effective ways of improving reaction-to-fire properties of PLA and its blends.[84–87]

Fire retardancy is a phenomenon whereby a polymeric material may be rendered less likely ignitable with the use of nanoscale additive materials, termed flame retardants. In case a material is ignitable, the presence of flame retardants should encourage such a material to burn less efficiently. Fire/flame retardancy may be accomplished by chemical and physical treatments of polymeric materials. The physical approach of fire retardancy may be exemplified by the use of flame retardant fillers, such as carbon-based materials like bio-char.[85] Flammability of PLA and its blends may be improved using additives including clays, graphite, aluminium hypophosphite, and glass fiber.[88–91]

3.4 | Methods used in producing and characterizing fiber-reinforced PLA

Fiber-reinforced PLA plastics are produced mainly by extrusion and compression molding techniques. Selection

TABLE 2 Typical mechanical characterization methods of agricultural fiber-reinforced PLA composites

Fiber-reinforced PLA				Results		
Agricultural Fiber	**Fiber loading**	**Processing technique**	**Characterization**	**Tensile strength (MPa)**	**Young's modulus (MPa)**	**Author**
Wheat	20, 30 wt%	Compression molding	Tensile test, SEM, three point bending test	25.23-32.41	—	[92]
	20, 30 wt%		Tensile test	26.8-34.48	1470-1190	[93]
	10, 20, 30, 40 wt%	Extrusion	Optical microscopy, SEM, XRD, tensile test, flexural test	60-70	1750-4000	[94]
	30 wt%		SEM, tensile test, flexural test, impact test, water absorption	56-69	2800-5000	[95]
Banana	10,20,30 wt%	Extrusion	Hardness test, Stereo-microscope analysis, FTIR, XRD, tensile test, flexural test, impact test, SEM	12-58	1400-1600	[96]
	10, 20, 30, 40 wt%		Tensile test, impact test, SEM	56-68	1800-5625	[97]
	10-40 wt%		FTIR, tensile test, flexural test, impact test, SEM, water absorption	56-67	1958-5577	[98]
	10, 20, 30, 40 wt%		Tensile test, impact test, SEM, FTIR	27.12-49.19	2540.8-4128.7	[99]
	10, 20, 30, 40 wt%	Compression molding	Tensile test, impact test, biodegradation, water absorption	7.76-38	3546-4705	[100]
Kenaf	20 wt%	Extrusion	Atomic force microscopy, SEM, cells analysis, water absorption, tensile test	2-19	—	[101]
	40 wt%	Compression molding	FTIR, universal testing, SEM	36.18-50.00	846.11-1200	[102]
	10, 40 wt%		SEM, tensile test	50-62	700-1500	[103]
Abutilon straw	1, 3, 5 wt%	Extrusion	FTIR, rheology test, impact test, SEM, tensile test	37-57	—	[104]
	1, 3, 5 wt%		FTIR, SEM, tensile test	30-50	420-480	[105]
	40 wt%		Tensile test, flexural test, impact test, SEM	32.9-35.7	1720-2110	[106]
Bamboo	40 wt%	Extrusion	FTIR, XRD, SEM, tensile test, flexural test, impact test	29.39-39.51	1710-2170	[107]
	2.5, 5, 7.5, 10 wt%		Flexural test, impact test, tensile test, SEM, hardness test, XRD, water absorption, UV absorptance and transmission	36-50	2900-4000	[108]
	50 wt%	Compression molding	Tensile test, SEM, XRD, XRD	10.7-16	745.8-586.8	[109]
Hemp	10, 30, 50 wt%	Extrusion	SEM, tensile test, flexural test, impact test,	50-60	—	[110]
	10, 20, 30, 40 vol.-%		Tensile test, hardness test, wear test	43-64	1400-3200	[111]
	10, 15, 20, 30 wt%			50.7-67.2	—	[112]

TABLE 2 (Continued)

Fiber-reinforced PLA				Results		
Agricultural Fiber	**Fiber loading**	**Processing technique**	**Characterization**	**Tensile strength (MPa)**	**Young's modulus (MPa)**	**Author**
			Interfacial strength test, tensile test, toughness test, microscopy			
	0, 10, 20, 30, 40 wt %		FTIR, SEM, tensile test, flexural test, impact test	51.9-72.1	700-2400	[113]
	10, 20, 35, 45 wt%	Compression molding	Tensile test, SEM	30-65	3600-6500	[114]
	6, 20 wt%		Tensile test, impact test, SEM	59-70	2500-3500	[115]
	10, 20, 30 wt%		Tensile test, impact test, fracture roughness test, SEM	50.5-75.5	3500-8200	[116]
	5, 10, 15, 20, 25, 30, 35, 40 wt%		SEM, tensile test	43-102	3600-9700	[117]
	48 wt%		Tensile test, shear test, molecular weight measurement	10-32	3600-3900	[118]
	30, 40 wt%		Optical light microscopy, SEM, impact test, flexural test	42-49	4500-9000	[119]
	30 wt%		Tensile test, impact test, optical light microscopy, SEM, XRD, FTIR, hydrothermal ageing	36-81	2500-10 500	[120]
	30 wt%		Tensile test, flexural test, impact test, fracture toughness test, optical light microscopy, FTIR, SEM, XRD, accelerated weathering test	11.5-85	1125-11 250	[121]
Wood	15, 20, 25, 30, 35 wt%	Extrusion	Tensile test	—	3400-6550	[122]
	25 wt%		Thickness test, color test, SEM, tensile test	38.4-52.2	4911-6758	[123]
	30, 40 wt%		XRD, TEM, SEM, tensile test, flexural test, impact test	44.65-65.21	3750-7080	[124]
Ramie	30 wt%	Extrusion	FTIR, tensile test, flexural test, impact test, SEM	45.2-64.3	2300-4500	[125]
	10 wt%		Water absorption, aging, gel permeation chromatography, tensile test, flexural test, SEM	5-60	—	[126]
	30 wt%		SEM, tensile test, flexural test, impact test	46.1-56.4	—	[127]
	9, 16, 24, 38 wt%	Compression molding	Tensile test, flexural test, impact test, XRD	29.4-76.1	944.6-1800	[128]
	30 wt%		Tensile test, impact test	30-75	2500-3500	[129]
	30, 50, 50 wt%		Tensile test, FTIR, SEM, degradation	38-75	1000-1700	[130]

(Continues)

TABLE 2 (Continued)

Fiber-reinforced PLA				Results		
Agricultural Fiber	**Fiber loading**	**Processing technique**	**Characterization**	**Tensile strength (MPa)**	**Young's modulus (MPa)**	**Author**
Sisal	7.5, 15 wt%	Compression molding	Tensile test, flexural test, XRD, polarizing microscopy, SEM	47.7-54.4	1334.9-2264.2	[131]
	30 wt%	Extrusion	Stereo microscopy, tensile test, flexural test, impact test, SEM	40-55	3500-7250	[132]
	30 wt%		Tensile test, flexural test, impact test, SEM	27.88-60.52	—	[133]
Basalt	5, 10,15, 20, 30,40 wt%	Extrusion	Tensile test, flexural test, impact test, SEM	100-200	3000-8400	[134]
	10, 20, 30, 40 wt%		Tensile test, flexural test, impact test, SEM	40-110	—	[135]
Coir	1, 3, 5, 7 wt%	Extrusion	Tensile test, impact test, SEM	60.57-71.23	—	[136]
	1, 3, 5, 7 wt%		Tensile test, impact test, SEM	55-71.5	1480-1825	[137]
	15, 30, 45, 60 wt%	Compression molding	Tensile test, FTIR, SEM	25-55	2500-3700	[138]
	5, 10, 20, 30 wt%		Tensile test, flexural test, SEM, Biodegradation	2.5-24	300-1470	[70]
Manicaria Saccifera	40 wt%	Extrusion	TGA, tensile test, impact test, flexural test, SEM	54.36-68.45	3230-4890	[139]
	-		Tensile test, SEM	57.6-123.36	3540-7810	[140]
Miscanthus	20, 30, 40 wt%	Compression molding	X-ray photoelectron spectroscopy, SEM, X-ray tomography, Tensile test	50.6-59.1	2354-3184	[141]
	20, 30, 40 wt%	Extrusion	X-ray photoelectron tomography and spectroscopy, SEM, tensile test	50.6-59.1	2354-3184	[141]
Jute	50 wt%	Extrusion	Tensile test, impact test, SEM, X-ray micro-tomography	28.0-90.7	2800-12 300	[142]
	50 wt%	Compression molding	Tensile test, impact test, SEM, biodegradation	155-210	5280-7300	[143]
Paddy straw	5, 10, 15 wt%	Compression molding	Tensile test, FTIR, SEM, biodegradation	4.52-52.42	1445.6-4034.1	[144]
Flax	30 wt%		FTIR, SEM, tensile test, XRD, x-ray photoelectron microscopy	55.4-59.1	2155-2908	[145]
Pineapple	10 wt%		Tensile test, flexural test	4-59.1	—	[146]
Jute, flax, cotton	65 wt%		Tensile test	59.9-106.9	—	[147]
Kraft, Stone, wood, Fluff	15, 20, 25, 30, 35 wt%	Extrusion	Tensile test, SEM	49.85-68.8	—	[148]
Arundo donax	10, 40 wt%		SEM, density, tensile test, flexural test	31.5-48.9	3220-4470	[149]
Argan nut shell	8, 15 wt%		SEM, FTIR, tensile test, hardness test, dynamic contact angle, water absorption	42-52	1650-2000	[150]

TABLE 2 (Continued)

Fiber-reinforced PLA				Results		
Agricultural Fiber	Fiber loading	Processing technique	Characterization	Tensile strength (MPa)	Young's modulus (MPa)	Author
Abaca, jute	30 wt%		Tensile test, impact test, SEM,	63.5-92	3400-9600	[151]
Fir, poplar, wood, wheat, bamboo	50 wt%		FTIR, XRD, SEM, water absorption, flexural test, TEM, impact test, tensile test	11.6-32.1	930-2400	[152]
Olive	10, 20,30 wt%		SEM, tensile test	55-85	1100-2320	[153]
Poplar	20 wt%		FTIR, tensile test, impact test, flexural test, SEM, surface wettability	38.5-50	840-1680	[154]
Rice, wheat	10, 20, 25 wt%		Energy dispersive X-ray microanalysis, SEM, tensile test, impact test	47-70	3573-5026	[155]
Hazelnut shell	20 wt%		Tensile test, impact test, flexural test, hardness test, SEM	15.3-45.0	590-1019	[156]
Bamboo, vetiver, coconut	10, 20, 30, 40 wt%		Tensile test, SEM	28-60	3750-10 000	[157]
Olive pit	5, 10, 15, 20 wt%		Particle size analysis, density, SEM, tensile test	55-62	3500-4100	[158]

of a suitable processing technique depends on different agricultural fiber properties and different applications of the developed composites. Other production methods include: pultrusion, resin injection molding, hand lay-up, and fiber spraying.[1] Majority of the work, basing on the two processing techniques, is done on mechanical characterization of agricultural fiber-reinforced PLA (see Table 2).

3.4.1 | Compression molding

Compression molding is a technique of molding where the molding material is preheated by melt blending before introduction of fibers and proceeding further melt blending.[159] After melt blending of the matrix and fibers, the composites are removed and cooled. The composites are then placed in a press for compressing under pressure to produce biocomposite sheets.[102] This process is shown in Figure 4.

3.4.2 | Extrusion

Extrusion process is used by the plastics industry to modify polymers into plastics and also in the continuous production of semifinished components. Single-screw extruders are used when mixing effect does not have to be high while twin-screw extruders are used for compounding respectively to modify plastics.[1] A twin-screw extruder has a drive section and a processing section (see Figure 5).

3.5 | Analysis of flammability and thermal stability tests

3.5.1 | Flammability

The application of PLA in industry can be limited by its flammability and dripping combustion.[160] Flammability is a very important parameter because often, biopolymers behave poorly and become unsafe when exposed to high temperatures.[161] This, however, can be improved by incorporating agricultural fibers, even though these are more flammable than synthetic fibers.[48] The flammability of agricultural fibers is determined by their biochemical composition.[48] Higher cellulose contents in agricultural fibers enhance their mechanical properties but induce higher flammability while higher lignin contents result in higher char formulation hence retarding flame propagation.[81,162] In fact, lignin increases the resistance of agricultural fibers to hydrolisis as well as chemical and biological degradation.[163,164] Studies on

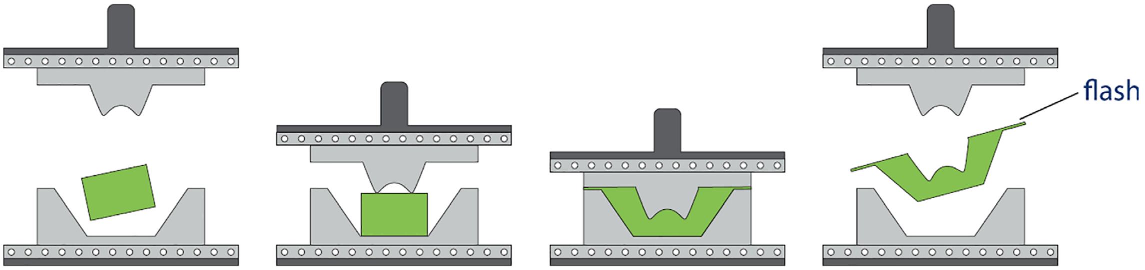

FIGURE 4 Compression molding process[1] [Color figure can be viewed at wileyonlinelibrary.com]

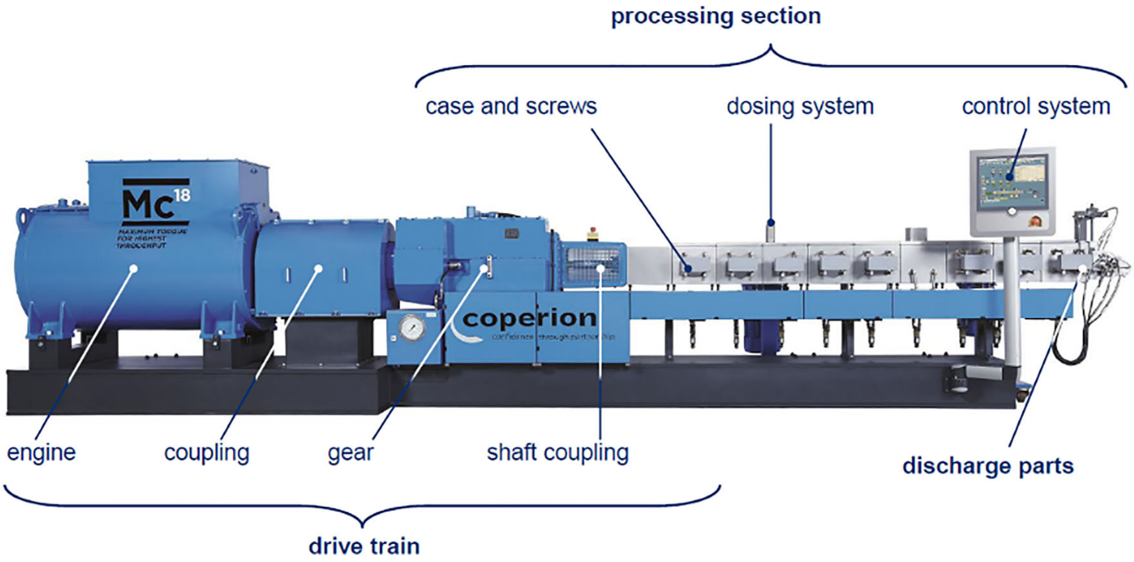

FIGURE 5 Twin screw extruder—general structure (adapted from ref.[1]) [Color figure can be viewed at wileyonlinelibrary.com]

flame retardancy are necessary on fiber-reinforced PLA composites to ascertain and boost their durability. Flame retardancy of fiber-reinforced PLA can be studied using Limiting Oxygen Index (LOI), Heat Release Rate (HRR), UL94 Horizontal, and Vertical burning tests.[165] Recent works on these typical flame retardancy properties of agricultural fiber-reinforced PLA are shown in Table 3.

3.5.2 | Thermal stability

Many studies in the literature have attributed good thermal stability of fiber reinforced PLA to the constituent agricultural fibers incorporated in the biocomposites. These biocomposites have also been recognized to provide low-density and low-cost materials.[48] Because PLA possesses low thermal stability, knowledge of the thermal behavior of mixtures based on agricultural fiber materials and PLA is extremely important to produce plastics of suitable thermal properties. Thermal properties of fiber-reinforced PLA can be studied using TGA, Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), and Thermo-Mechanical Analysis (TMA). Recent works on these typical thermal properties of fiber-reinforced PLA are shown in Table 3.

3.5.3 | Kenaf fiber-reinforced PLA

Kenaf fiber, PLA, and azodicarbonamide (ADC) were mixed evenly into fiber-reinforced PLA by Hassan et al,.[101] Addition of ADC slightly delayed decomposition, thus enhancing thermal stability of the developed composites. Additionally, ADC led to an improvement in softness and elasticity of the developed composites. In a dissimilar manner, Tawakkal et al,,[103] Han et al,,[188] and Yussuf et al,[189] noted decreasing trends with increasing kenaf contents. This is because portions of PLA get replaced with the less thermally stable kenaf fibers, owing to low lignin compositions (see Table 1). Lignin in enhances flame retardancy properties because it degrades at very high temperature.[83]

The effect of APP flame retardant and alkali pre-treatment of kenaf fibers on thermal properties of fiber-

TABLE 3 Thermal stability and flame retardancy characterization of agricultural residue fiber-reinforced PLA

Fiber-reinforced PLA			Results						
Agricultural fiber	Fiber loading	Characterization	Onset temperature (°C)	Char residues (%)	Glass transition Temperature (°C)	Crystallization Temperature (°C)	LOI (%)	HRR (kW/m^2)	Author
Kenaf	20 wt%	TGA	246-273	5.4-9.7	—	—	—	—	[101]
	10, 30, 50 wt %	DSC	—	—	61-62	79.4-89.7	—	—	[110]
	25 wt%	TGA, LOI	280-312	9.7-22.7	—	—	27.6-31.6	—	[161]
Wood	40 wt%	DSC, TGA	280.7-338.3	0-40	59.8-62.5	95.2-102.6	—	—	[166]
	20, 30, 40 wt %	TGA	260-270	0-17	—	—	—	—	[167]
	20 wt%	DSC, TGA, DMA	185-310	1.16-12.1	36.38-62.19	91.16-123.8	—	—	[168]
	20, 30 wt%	DSC, DMA	—	—	59.1-60.3	98.8-109.5	—	—	[169]
	50 wt%	DSC, TGA	224.1-306	10-15	55.1-66.2	77.1-89.7	—	—	[170]
	25 wt%	DSC	—	—	50.0-54.4	109.5-121.9	—	—	[123]
	30, 40 wt%	TGA, DSC	387.6-408.8	0.5-9	51.1-52.3	130	—	—	[124]
Banana	10,20,30 wt%	TGA, DMA	275-285	0-5	68-69	—	—	—	[96]
	10, 20, 30, 40 wt%	TGA	274-295	0-9.55	—	—	—	—	[97]
	10-40 wt%	DMA, DSC	—	—	57-59	101-109	—	—	[98]
	10, 20, 30, 40 wt%	TGA, DSC, LOI, UL94	223-261.3	0-10	56.6-62.7	95.94-108	24-34	—	[44]
	30 wt%	TGA, DSC, DMA, LOI,UL94	223-261.3	0-10	57.38-62.64	89.83-114.41	24-34	—	[171]
	10, 20, 30, 40 wt%	DMA, TGA, DSC	223-263	0-3	56.6-60.5	105.79-113.35	—	—	[172]
	10, 20, 30, 40 wt%	DSC, TGA	223-263	0-3	56.6-60.5	105.79-113.35	—	—	[100]
	10, 20, 30, 40 wt%	TGA, DSC, DMA	226.42-400	0-9	55.17-58.56	101-124.09	—	—	[99]
Bamboo	40 wt%	DSC, TGA	291-319	5-10	57.78-59.35	—	—	—	[106]
	40 wt%	TGA, DSC	270.7-296.3	5-10	57.78-61.52	97.42-108.97	—	—	[107]
	25 wt%	DSC, TGA	354-365	0-9	58.3-63.4	98.7-112.1	—	—	[173]
	30, 40, 50 wt %	TGA, DSC	230	2.8	66.52-72.15	—	—	—	[174]

(Continues)

TABLE 3 (Continued)

Fiber-reinforced PLA			Results						
Agricultural fiber	Fiber loading	Characterization	Onset temperature (°C)	Char residues (%)	Glass transition Temperature (°C)	Crystallization Temperature (°C)	LOI (%)	HRR (kW/m²)	Author
Hemp	20, 30, 40 vol.-%	TGA, DSC	250-300	0-9	—	—	—	—	[175]
	20, 30, 40 vol.-%	TGA	322.6-350.2	1-11	—	—	—	—	[176]
	10, 20, 35, 45 wt%	DSC, DMA	—	—	54.03-57.18	97.58-112	—	—	[114]
	30, 40 wt%	DSC	—	—	61.0-62.2	109.89-115.92	—	—	[119]
	30 wt%	DSC	—	—	48-61	81.0-111.3	—	—	[120]
	30 wt%	DSC	—	—	42-61	—	—	—	[121]
	30 vol.-%	TGA, HRR	322-337	1-13	—	—	—	265-485	[177]
Sisal	30 wt%	TGA, DSC	235.9-265.2	3.2-5.4	46.52-55.5	105.9-123.8	—	—	[178]
	9 wt%	DSC, TGA	322.4-344.6	0-4	57.6-63.5	100.9-110.5	—	—	[179]
	7.5, 15 wt%	DSC, TGA	328.5-360.6	0-9	63.5-66.9	110	—	—	[131]
	10, 20, 30 wt %	DSC	—	—	55.3-59.2	91.3-108.7	—	—	[180]
	5, 10, 15, 20, 25 wt%	TGA	130.5-322	0.3-8	—	—	—	—	[181]
Ramie	30, 50, 50 wt %	TGA, DMA	335.5-366.7	0.3-0.43	—	—	—	—	[130]
	5 wt%	DSC, DMA	—	—	58.3-62.7	97.6-129.5	—	—	[182]
	9, 16, 24, 38 wt%	DSC, DMA	—	—	85-105	108.4-110.8	—	—	[128]
	30 wt%	DSC, DMA, TGA	331-313	0.1-4.88	57.07-60.68	92.54-104.43	—	—	[125]
	30 wt%	DMA,DSC,TGA	200-328	0-3	—	—	—	—	[183]
	30 wt%	TGA, DMA, LOI, UL94	240-300	8.85-21.9	—	—	19.1-35.6	—	[127]
Flax	30 wt%	TGA, DMA,LOI, UL94,HHR	311-331	0-9	69-71	—	19.1-26.1	396-407	[145]
	22 wt%	DSC, DMA	—	—	58-62	19.5-36	—	—	[184]
	34 wt%	DMA, DSC, TGA	221-270	0-9	60.8-61.3	78.4-105.2	—	—	[185]

TABLE 3 (Continued)

Fiber-reinforced PLA			Results						
Agricultural fiber	Fiber loading	Characterization	Onset temperature (°C)	Char residues (%)	Glass transition Temperature (°C)	Crystallization Temperature (°C)	LOI (%)	HRR (kW/m^2)	Author
	15, 25, 40 wt %	TGA, DSC	282-340	—	59-62	93-99	—	—	[186]
	25 wt%	TGA, LOI, UL94, HHR	200-253	30-46.5	—	—	21-33	149-774	[187]
Kanaf	10, 40 wt%	TGA	321-323	0-10	—	—	—	—	[103]
	20, 30, 40 wt %	DSC, TGA	348.1-370.8	0-4	93	92.54-113.21	—	—	[188]
	20 wt%	TGA	305-323	0-4	—	—	—	—	[189]
	10, 20 wt%	DMA, DSC	—	—	60-63	121-125	—	—	[190]
Coir	1, 3, 5, 7 wt%	DMA, DSC, TGA	250-302	0-9	63.33-64.83	96.83-101.17	—	—	[136]
	1, 3, 5, 7 wt%	DMA, DSC, TGA	200-300	0-5	64-67	92-94	—	—	[137]
Basalt	5, 10,15, 20, 30,40 wt%	DSC, DMA	—	—	50-55	60-80	—	—	[134]
	10, 20, 30, 40 wt%	DSC	—	—	—	131.44-133.85	—	—	[135]
Rice	5, 10, 15 wt%	DSC	—	—	—	88.12-111.05	—	—	[144]
	7, 8, 9 wt%	DSC, TGA	309-324	12.2-16.4	58.8-59.4	96.7-105.3	—	—	[61]
	20 wt%	TGA	305-323	0-4	—	—	—	—	[189]
	20, 30, 40 wt %	DSC, TGA	220-333	0-4	46.4-59.1	98.6-126.9	—	—	[191]
Wheat, rice	20 wt%	TGA	340-360	0-8	—	—	—	—	[192]
	10, 20, 25 wt %	TGA, DSC	280	0-10	61.56-63.56	114.39-129.64	—	—	[155]
	30 wt%	DMA,DSC,TGA	200-250	0-10	58-61	97-110	—	—	[95]
	40 wt%	TGA	212-250	15-18	—	—	—	—	[193]
Coconut/jute	15, 30, 45, 60 wt%	DSC, TGA	250-300	0-10	57.7-63.3	114.8-115.5	—	—	[138]
	35 vol.-%	TGA	211-296	0.5-11.5	—	—	—	—	[194]

(Continues)

TABLE 3 (Continued)

Fiber-reinforced PLA			Results						
Agricultural fiber	Fiber loading	Characterization	Onset temperature (°C)	Char residues (%)	Glass transition Temperature (°C)	Crystallization Temperature (°C)	LOI (%)	HRR (kW/m^2)	Author
Hazelnut shell	20 wt%	DSC, TGA, DMA	317-339	11-13	58.7-66.5	102.4-105.3	—	—	[156]
	10, 20, 30, 40 wt%	DSC, TGA	306-345	0.8-16.3	66.5	111.5-104	—	—	[195]
Abutilon	1, 3, 5 wt%	DSC, TGA, DMA	230-251	~20	—	132-141	—	—	[104]
Olive pit	10, 20,30 wt%	TGA, DSC	200-225	0-3	51.6-57	109-117	—	—	[153]
Argan nut shells	8,15 wt%	TGA	272-294	0-5	—	—	—	—	[150]
Pennisetum purpureum	10, 20, 30 wt %	TGA	295.01-301.63	0.663-7.006	—	—	—	—	[22]
Sawdust, hazelnut, flax, corn cob	10, 20, 30 wt %	TGA, DSC	222-320	1-10	55-61	103-126	—	—	[196]
Olive pit	5, 10, 15, 20 wt%	TGA, DSC	248-306	1.4-8.1	62.2-66.9	121-127.3	—	—	[158]
Grewia optiva, nettle, sisal	20 wt%	TGA	306-326	0.24-2.7	—	—	—	—	[197]
Oil palm MCC	1, 3, 5 wt%	TGA	259.93-341.46	0-2.4	—	—	—	—	[198]
Bamboo, wood, coconut	2 wt%	DMA, DSC	—	—	58.8-61	92.5-93.9	—	—	[199]
Miscanthus	20, 30, 40 wt %	TGA, DMA	350-365	—	66.9-71.4	80-110	—	—	[141]
Spartium junceum L.	30 wt%	TGA, HRR	328-354.1	0-4.9	—	—	—	280.9-475.1	[200]
Jute, Sisal, Elephant grass	5, 10, 20, 25 wt%	TGA	240.5-322	0.3-8	—	—	—	—	[201]
Potato starch	2.5, 5, 10 wt%	TGA, LOI, HRR	259-328	0.2-22.2	—	—	20-41	97-398	[202]
Milkweed floss	1 wt%	DMA, DSC	—	—	63	96	—	—	[63]
Poplar	20 wt%	TGA, DSC, DMA	250-259	3-6	61.3-61.9	106.9-109.4	—	—	[154]
Manicaria Saccifera	40 wt%	TGA	338-361	1.6-11.1	—	—	—	—	[139]
Arundo donax	10, 40 wt%	DSC	—	—	58-61	104-119	—	—	[149]

reinforced PLA was studied by Shukor et al,.[161] At the start of the TGA experiment, increase in APP flame retardant decreased the temperatures at which 15% weight losses occurred, owing to APP pyrolysis and advance decomposition of fibers caused by acid release from APP decomposition. Shukor et al,[161] noted increasing LOI values from 27.6 to 31.6 with incorporation of APP, confirming enhanced flame retardancy. In their discussion, they highlighted that APP acted as the acid source, blowing agent and carbonizing agent as well, thus acid species catalyzed the dehydration reaction of the carbonizing agent. This led to the formation of a carbonaceous layer which created an insulation that prohibited flammability by increasing the reaction and contents of lignin composition in the developed composites.[81] Similar results have been obtained by other researchers that worked on incorporating different flame retardants in fiber-reinforced PLA.[202–204] Additionally, Hassan et al,[101] noted that increase in APP contents led to an increase in resulting char residues at the maximum temperature. At the start of the TGA experiment, thermal stability of the developed fiber-reinforced PLA was increased as shown by the increase in the temperatures at which 15% of the weight losses occurred. However, at higher temperatures (600°C), alkali pretreatment of the kenaf fibers led to decreasing char residues (showing decrement in formation of carbonaceous char) with increasing alkali pretreated fiber loading in PLA. In fact, Shukor et al,[161] presented that alkali pretreatment of kenaf fibers led to a reduction in LOI values of the developed fiber-reinforced PLA from 29.4 to 28 because during alkali pretreatment, lignin was removed from the fiber surface. In a related study, Woo and Cho,[205] investigated the effects of aluminum Trihydroxide (ATH) on flame retardancy of kenaf/PLA composites. ATH adequately retarded flammability of the developed composites. The 40 wt% kenaf fiber-reinforced PLA composite exhibited an LOI value of 23.9, and the LOI was increased up to 39.7 after adding 50 wt% of ATH flame retardants, confirming enhanced flame retardancy in the latter.

As regards DSC, Tawakkal et al,[103] noted no change in glass transition temperature with increase in kenaf fiber loading unless when plasticizer is used. Their submission was contrary to a study by Anuar and Zuraid,[190] who found that glass transition temperature and cold-crystallization enthalpy increases with kenaf content. Similar to the submission by Anuar and Zuraid,,[190] Han et al,[188] noted a single melting peak observed at about 150°C in case of neat PLA which shifted to lower temperatures with increasing kenaf loading. They also noted a second minor peak appears in a 135 to 140°C range which also shifted to lower temperatures with increasing kenaf loading.

3.5.4 | Wood fiber reinforced PLA

Ozyhar et al,[166] revealed that addition of wood fiber in PLA shifts the onset point to lower temperatures. These temperatures were further decreased by incorporation of calcium carbonate because it has high thermal conductivity. These results are in agreement with those of Liu et al,[170] and Battegazzore et al,[196] who reported reducing onset point temperatures with increasing amounts of organo-montmorillonite (MMT) contents and wood fiber compositions respectively. Meng et al,[124] also reported decreasing onset point temperatures with incorporation of wood fibers and attributed this trend to low degradation temperatures and moisture traces introduced by wood fibers. The low degradation temperatures of wood fibers are possibly due to their low lignin compositions. Another study by Petchwattana et al,[168] also presented decreasing onset point of degradation to lower temperatures as well as lower char residues with incorporation of wood fibers as and increasing tributyrin plasticizer contents. The onset point for neat PLA reduced from 310°C to 250°C due to incorporation of 20 wt% wood fibers, thereafter decreasing steadily to 185°C at the highest plasticizer content (15%). These reducing amounts are due to decomposition of low molecular weight compositions in composites. Sun et al,[167] reported increasing char residues with increasing wood fiber loading which signals improved thermal stability. This is because wood fibers themselves emit more char residues when combusted and therefore their incorporation in neat PLA leads to a parallel behavior in the developed composites.

Ozyhar et al,[166] carried out DSC to elucidate the effect of mineral additives on wood fiber-reinforced PLA. Addition of wood fiber as well as mineral additives led to decreasing crystallization and melting temperatures of the developed fiber-reinforced PLA. From the DSC analysis carried out by Petchwattana et al,,[168] neat PLA had a glass transition temperature of 62.19°C and it reduced to 61.53°C with the addition of wood fiber. Addition of plasticizer led to further reductions in the glass transition temperature of the developed composites to the lowest temperature of 36.38°C at the maximum plasticizer loading, attributed to the segmental mobility enhancement induced by the tributyrin plasticiser. The crystallization temperature of neat PLA was found to significantly reduce from 123.8 to 118.2°C due to incorporation of 20 wt% wood fibers, thereafter decreasing steadily to 91.16°C at 15% plasticizer content. This result indicated good compatibility between PLA and wood fibers as well as between PLA, wood fibers, and plasticizer. The results obtained are in agreement with those of Liu et al,[170] who showed reducing glass and crystallization temperatures with increasing organo-MMT contents. Other studies also noted decreasing crystallization and melting temperatures of fiber-reinforced PLA.[206,207]

3.5.5 | Banana fiber reinforced PLA

Injection molding and compression molding were used by Komal et al,[96] to process banana/PLA composites. They utilized TGA and DMA to study thermal behaviours of the composites. The developed fiber-reinforced PLA lost 5, 25, 50, and 75% of their weight at the temperature ranges of 275-285, 315-320, 350-355, and 620-625°C, respectively. Maximum thermal degradation was observed between 250 and 350°C. The choice of processing techniques did not contribute a significant influence on the thermal degradation behavior of the developed banana fiber-reinforced PLA. From works of Jandas et al,,[100] TGA showed that incorporation of banana fibers in PLA matrix led to a reduction in degradation temperature as compared to neat PLA. This reduction was ascribed to the low thermal stability of banana fibers that possibly enhanced deformation of the crystalline structure of PLA at higher temperatures. A similar reduction trend in degradation temperatures with increasing banana fiber loading has also been obtained by other researchers.[171,172,208] Contrally to these however, Majhi et al,[99] found out that incorporation of banana fiber enhanced the thermal stability of the developed fiber-reinforced PLA. Actually, Jandas et al,[44] reported that incorporation of banana fibers increased LOI values from 24% to about 27%. Meanwhile neat PLA could not be classified using vertical burning test (UL94) as it showed very poor fire retarding properties. Incorporation of banana fibers in PLA matrix showed better fire characteristics categorized under V2 classification. The increasing resistance to flammability is linked to the sufficient lignin compositions in banana fiber (5-10 wt%), which create a prolonged char layer that prohibits further combustion. The developed composites showed lower burning rate with a total flaming combustion of around 135 seconds. These results were further confirmed by Jandas et al,.[171]

Another study by Sajna et al,[97] reported that incorporation of banana fiber and nanoclay increased the degradation temperature of neat PLA. The initial and final degradation of untreated banana fiber-reinforced PLA composite occurred at around 284 and 372°C, respectively, compared to the initial degradation (274°C) and final degradation (357°C) temperatures for neat PLA. Interestingly, Sajna et al,[98] found that incorporating banana fibers resulted in enhanced thermal stability and led to higher char residues. Additionally, adding clay further improved the composites' thermal stability because of clay's barrier effect. Clay acted as a flame retardant. Thermal stability of neat PLA can further be enhanced by silane treatment of banana fibers because of increase in molecular weight by cross-linking reaction between PLA and fibers or molecular chain extension between PLA itself that tends to increase thermal degradation temperatures.[100,172]

DMA results by Jandas et al,[100] reported that an increase in pretreated banana fiber led to a shift of the glass transition temperature to higher temperatures compared to raw banana fiber-reinforced PLA which indicated enhanced interfacial adhesion between banana fibers and the PLA matrix. Increasing fiber contents were also reported by Jandas et al,[172] and Kaiser and Anuar,[209] to increase the glass transition temperature of developed composites. DSC thermograms from the study by Jandas et al,[100] revealed an increase in melting transitions, revealing effective banana/PLA matrix interface. DSC analysis showed double melting peaks wherein silane pretreated fiber reinforced PLA exhibited higher glass transition, crystallization and melting temperatures. Increasing crystallization temperatures were also obtained by Majhi et al,[99] with increased banana fiber loading. Jandas et al,[172] reported that neat PLA had a glass transition temperature of 59.5°C, reducing to 56.6°C with incorporation of banana fibers, indicating a change in plasticization degree. Conversely, when silane treated banana fibers were used as filler, PLA's glass transition temperature increased by 1.7%, confirming efficient adhesion between the fiber and PLA matrix. Meanwhile, from the works of Jandas et al,[44] and Jandas et al,,[171] neat PLA had a glass transition temperature of 57.3°C, while the incorporation of banana fibers to led to a decrease in glass transition temperature to 56.6°C. This attributed to increased mobility and free volume of the PLA matrix chains by loose packing of banana fibers within the matrix due to less interaction between them. Similar decreases in glass transition temperatures of PLA composites with increasing banana fiber were obtained by Sango et al,.[210]

3.5.6 | Flax fiber-reinforced PLA

Zhang et al,[145] used TGA and DMA to study the thermal degradation of flax fiber-reinforced PLA. Neat PLA underwent a one-stage degradation from 331°C and obtained its highest degradation at 372°C, with no char residues at the end of the experiment (700°C). Very few studies explain the true meaning of char residues yet they have a positive correlation with thermal stability of fiber-reinforced PLA. Incorporation of flax fiber onset thermal degradation earlier at about 311°C owing to the fact that raw flax degradation occurred between 270 and 360°C. In fact, lower thermal stability was confirmed with reducing LOI values with incorporation of flax fibers in PLA matrix. Pure PLA had a 20% LOI while addition of 30 wt % flax fibers decreased to 19.1% thus increasing flammability of the developed composites. This was because of the scaffolding effect where molten decomposition products from polymer matrix were held in contact with the flame by the fibers. Chemical pretreatment of flax fiber using iron phosphate reduced the flammability of the developed composites as the LOI increased to 26.1%. This pretreatment method could have led to an increase in lignin compositions in the flax fibers, a characteristic that delays combustion.[13] Pretreatment also reduced the peak heat release rate of the developed fiber-reinforced plastics by 16% down from 497 kW/m^2 rates for the plastics made with raw flax fiber. In similar study by Bocz et al,,[187] it was reported that incorporation of flax fibers in PLA matrix led to a decrease in the LOI value. When flame retardant was applied in combination with the pretreatment of flax fibers, a 30% reduction was achieved in PHRR compared to the phosphorus-free reference fiber-reinforced PLA composites. The flame retardant ability exerted by the Phosphorous content of only the plasticizer and the fiber modifier (approximately 0.65 wt%) was insufficient to provide self-extinguishing character to the developed composites. However, the addition of as few as 10 wt% of APP was sufficient to achieve a V0 rating and a 33% LOI value.

TGA results by Zhang et al,[145] were in disagreement with Teymoorzadeh and Rodrigue,[186] which showed an increase in decomposition temperature from 282°C for neat PLA to 340°C for composites with 40 wt% flax fiber. This was because increase in flax content led to increased lignin which increased degradation temperatures. It is important to note that in the study by Zhang et al,,[145] chemical pretreatment of flax fiber using iron phosphate improved the thermal stability of the developed fiber-reinforced PLA because at the end of the experiment, more char residues were obtained compared to untreated flax fiber-reinforced PLA. On a similar note, Foruzanmehr et al,[185] reported that incorporation of TiO_2 oxidized flax fibers led to an improvement in the thermal stability of the developed composites. In another study by Kumar et al,,[211] introduction of MMT did not have a clear effect on thermal stability of the developed composites. This was attributed to the low contents of MMT (2.5%), at which intercalation dominated, but the amount of intercalated silicate layers was not sufficient to promote any significant improvement in thermal stability.

When compared to pure PLA, Zhang et al,[145] submitted that glass transition temperatures of raw flax fiber-reinforced PLA and treated flax fiber-reinforced PLA increased from 69°C by 4 and 2°C, respectively, indicating a better deformational heat resistance of the developed flax fiber-reinforced PLA. Similar increases in glass transition temperature of were recorded by Li et al,[133] because of chemical pretreatment of fibers. In disagreement, Georgiopoulos et al,[184] found that glass transition and melting temperatures of PLA composites are not significantly affected by flax fiber presence. Arias et al,[212] also revealed that the glass transition temperature of neat PLA was not affected by inclusion of flax fibers as the values were close to 60°C in all cases. Another study by Teymoorzadeh and Rodrigue,[186] reported that glass transition, crystallization, and melting temperatures decreased with addition of flax fiber to PLA. Foruzanmehr et al,[185] reported that incorporation of TiO_2 grafted flax fibers with and without cellulose oxidation led to an increase in glass transition temperatures of the developed composites from 60.8 to 61.3°C and 61.1°C, respectively.

3.5.7 | Coir fiber-reinforced PLA

Thermal properties of coir fiber-reinforced PLA were investigated by Sun et al,.[137] In contrast to the submission by Zhang et al,,[136] DMA results by Sun et al,[137] revealed that increase in amounts of coir fibers reduced glass temperatures of the developed composites. This reduction indicates increased mobility with free volume of PLA matrix chains by loose packing of coir fiber within the matrix due to poor adhesion between the matrix and fibers. The onset crystallization temperatures also slightly shifted to lower temperatures with increasing coir fiber, thus inducing cold crystallization earlier than neat PLA samples. TGA demonstrated that the thermal stability of coir fiber-reinforced PLA was reduced by the incorporation of treated coir fiber. This was observed by the shift of the peak temperatures to lower temperature regions. This is in agreement with findings from Dong et al,[70] who reported that increasing the fiber content decreases thermal stability of the developed coir fiber-reinforced PLA. This was attributed to the lower degradation temperatures of coir fibers as compared to PLA. In a similar finding by Zhang et al,,[136] neat PLA showed a degradation peak at 388°C, while addition of 1, 3, 5, and 7 wt% coir fibers lowered the temperatures to 379, 379, 377, and 363°C. It was evident that increasing coir fiber content led to decreased thermal stability of the developed composites. These findings are also in agreement with characteristics of phormium fiber-reinforced PLA.[213]

DSC results by Zhang et al,[136] showed that addition of coir fibers led to an increase in glass transition temperature and degree of crystallinity while the crystallization temperature decreased relative to the temperature at which neat PLA crystalizes (110°C). The increasing degree of crystallinity indicated that addition of coir fibers was favorable for crystallization of neat PLA. Meanwhile, Sun et al,[137] noted only a minor effect of the treated coir fiber on thermal behavior of PLA resin. Similarly, an analysis of DSC results by Dong et al,[70] showed that addition of coir fibers in PLA matrix does not affect the glass transition and melting temperatures of the developed fiber-reinforced PLA. The cold crystallization temperatures however decreased with increasing fiber content. This showed that the coir fibers play an effective nucleating role in accelerating the PLA crystallization process, thus improving crystal growth rate. Reducing cold crystallization temperatures with increasing fiber loading were also reported by other researchers.[149,214]

3.5.8 | Sisal fiber-reinforced PLA

Zhu et al,[131] reported that neat PLA had higher thermal stability than sisal fiber/PLA composites. The weight of neat PLA and its composites rapidly dropped between 340 and 360°C, attributable to the degradation of constituent materials. A second transition began between 360 and 380°C when the thermal decomposition started. Neat PLA had higher initial pyrolysis temperature (360.6°C), temperature of maximum pyrolysis rate (378.4°C), and final pyrolysis temperature (390.4°C) than sisal fiber-reinforced PLA composites. As an explanation for the behaviour of the developed fiber-reinforced PLA, they noted that during the preparation process, sisal fibers and PLA matrix experienced heat and friction which resulted in the thermal degradation, hence reducing the thermal stability of the developed composites compared with that of neat PLA. These findings are in agreement with those from Tengsuthiwat et al,[179] in which neat PLA started to decompose at 344.6°C while decomposition of sisal fiber-reinforced PLA started to decompose at 334°C. A study by Bajpai et al,[197] also reported that incorporation of sisal fibers led to a reduction in the degradation temperature of developed composites. In another study by Rajesh et al,,[181] untreated sisal/PLA composite showed intermediary thermal stability compared to that of neat PLA and treated sisal/PLA composites. Alkali treatments on coir fiber reduced the thermal stability of the composite compared to neat PLA and untreated sisal/PLA composites.

DSC results from Zhu et al,[131] reported the degree of crystallinity of neat PLA, alkaline treated sisal fiber-reinforced PLA and hybrid sisal fiber-reinforced PLA to be 19.4%, 24%, and 31.4%, respectively. Addition of sisal fibers therefore improved the crystallinity of PLA because of the nucleation effect of sisal fibers. They submitted that the glass transition temperature of the developed sisal fiber-reinforced PLA composites was similar to neat PLA's (66.9°C). Addition of sisal fibers did not affect the molecular structure but the aggregation structure of the matrix and had a slight influence on glass transition temperature. Similar findings were reported by Ahmad and Luyt,[215] and Gil-Castell et al,.[216]

3.5.9 | Bamboo fiber-reinforced PLA

Hu et al,[173] reported that thermal degradation of untreated bamboo fiber-reinforced PLA composites showed a single stage at 354°C which was lower than that of the neat PLA (365°C) due to the degradation that occurred in the processing progress of the composites by the two rollers counter rotating mixer. Surface modification of bamboo fibers however was noted to increase thermal stability of the developed fiber-reinforced PLA composites. This increasing thermal stability was ascribed to the reduction in the number of hydroxyl groups of neat PLA which had been reacted with coupling agent. Surface modification of bamboo fibers has also been reported by Zhang et al,[106] and Lin et al,[107] to increase thermal stability of neat PLA. Zhang et al,[106] attributed the increase in thermal stability to two reasons. The first was that surface modification prevented heat transfer; and the second reason was that surface modifications improved cross-linking density of PLA matrix, thereby strengthening the molecular structure of PLA. Some studies, however, have found that surface treatments on bamboo fibers led to a decrease in degradation temperatures, signifying weakened thermal stability of fiber-reinforced PLA.[217,218]

Compared with neat PLA, bamboo fiber-reinforced PLA composites in the study by Hu et al,[173] had higher glass transition temperatures and melting temperatures. This was because the bamboo fibers could limit the thermal motion of the molecular chain of PLA matrix. Surface modification of the bamboo fibers significantly increased the glass transition and melting temperatures of the developed composites because of surface treatments improved the interfacial compatibility between PLA and bamboo fibers. Their results were contradictory to those from Lin et al,[107] who showed that the glass transition temperature was not affected by surface modification of the bamboo fibers. In the study by Hu et al,,[173] surface modification was reported to lead to a decrease in crystallinity, compared to neat PLA. On the contrally, a study by Zhang et al,[199] reported that while melting temperatures did not show much difference, incorporation of fibers led to improvement in the degree of crystallinity of PLA matrix. Masruchin et al,[174] reported that glass transition and melting temperatures decreased with incorporation of bamboo fiber in PLA matrix because bamboo fiber in this case acted as a plasticizing component in the developed composites. Tisserat et al,[123] and Scaffaro et al,[219] also showed that incorporation of *Posidonia oceanica* fibers and Paulownia elongata fibers respectively increased the degree of crystallinity of neat PLA matrix. This degree of crystallinity is extremely important because higher degrees result into better mechanical properties of fiber-reinforced PLA.[70] Another closely related study by Qian et al,[220] reported that glass transition, melting and crystallization temperatures of bamboo/PLA composites were decreased by coupling agent treatment. When 4% content was used, they decreased from 45.6 to 30.6°C, 96.2 to 88.4°C, and 164.3 to 154.2°C, respectively. This was interpreted in terms of increasing molecular mobility attributed to an under cross-linked or plasticized matrix in the bamboo fibers vicinity.

3.5.10 | Wheat fiber-reinforced PLA

A study by Tran et al,[155] reported that thermal stability was not significantly different between neat PLA and the wheat/PLA composites although the latter had lower thermal degradation temperature compared to the former's. In agreement, studies by Nyambo et al,[95] and Fan et al,[193] reported that wheat straw fiber-reinforced PLA composites exhibited lower thermal stability than neat PLA because wheat fibers are less thermally stable and increase thermal degradation reactions occurring during processing. In order to enhance thermal stability of wheat fiber-reinforced PLA, Tran et al,[192] suggested hybrid surface modification of silane and alkaline on wheat fibers. This is because alkali treatment cleans the surface of wheat husks and actives the hydroxyl groups, which consequently react with the silanes more easily than the hydroxyl group on the surface of untreated wheat husks.

Tran et al,[155] reported that neat PLA had a glass transition temperature of 61.56°C. Addition of husks did not have any notable effect on the glass transition temperature. Neat PLA had a crystallisation temperature of 129.64°C and addition of wheat husk fibers decreased the crystallization temperature to 114.39°C for composites with 25% wheat husk. They explained the decrease in crystallization temperature by two reasons: (a) the viscosity of the composite mixture increased with the addition of wheat husks, which hindered the migration and diffusion of PLA molecular chains in the composite and (b) the decrease of the average molecular weight of PLA matrix after extrusion with husks. Nyambo et al,[95] reported that addition of wheat straw fibers did not significantly influence glass transition and melting temperatures of PLA, which were around 60 and 170°C, respectively. The composites showed decreased crystallization temperature, reduced enthalpy of crystallization and increased degree of crystallinity than neat PLA possibly due to the nucleating activity of wheat straw fibers. The obtained DSC data from their study are in agreement with observations reported by Lezak et al,[221] in which the addition of sugar beet pulp fibers nucleated PLA and increased its degree of crystallinity. Their results are also in agreement with those from Yang et al,[94] in which crystallinity of fiber-reinforced PLA composites with 30% wheat straw content reached 39.8%, while that for neat PLA was 0.7%. This finding indicated that the well-dispersed hemicellulose, lignin and cellulose nanofibrils from wheat straw can consequently act as a highly effective nucleating agent in promoting crystallinity of PLA matrix.

3.5.11 | Ramie fiber-reinforced PLA

Yu et al,[183] conducted TGA analysis of ramie fiber-reinforced PLA and found lower degradation temperature of untreated ramie fiber-reinforced PLA as compared to neat PLA. These results are in agreement with those by Shumao et al,.[127] The study suggested that due to decrease in molecular weight of PLA during processing, incorporation of ramie fibers and interfacial bonding might be responsible for this changed thermal degradation behavior of the developed composites. Chen et al,[222] reported that addition of APP flame retardant during composites processing reduced their thermal stability as observed by the significant reduction in the starting decomposition temperature as well as the two significant mass loss stages. The reduction in thermal stability was reported to be due of APP pyrolysis at the first mass loss stage and advance decomposition of ramie fibers caused by acids released from APP decomposition. Shumao et al,[127] and Chen et al,[222] also reported increasing char residues at high temperatures when APP flame retardant was incorporated, compared to fiber-reinforced PLA processed without flame retardants. The increase in char residues is because APP enhances the charring process for the developed ramie/PLA composites. Shumao et al,[127] actually reported that APP led to increase in LOI values by over 86% from a 19.1 value obtained in the control sample (composite that did not incorporate flame retardant). The control sample is more flammable because of two reasons; (a) a continuous mass path can form for contact of the filled agricultural fibers, speeding the flammable mass to the burning area; (b) the ramie agricultural fibers have a larger heat conduction coefficient and are more flammable than PLA. The heat can easily transmit to the fiber-reinforced PLA composite below the burning region. This is the "candlewick effect".[223] A study from Debeli et al,[130] also reported increasing char residues in ramie fiber-reinforced PLA compared to neat PLA. Neat PLA had 0.07% char residues at 450°C while incorporation of ramie fibers increased the value to 0.4%. However, alkali treatment, silane treatment and alkali-silane treatments increased the value increased to 0.43%, 0.36%, and 0.3%, respectively.

Chen et al,[128] reported that glass transition, crystallization and melting temperatures of the developed ramie fiber-reinforced PLA composites did not show much difference from those of neat PLA. Meanwhile, DSC analysis from Yu et al,[182] revealed that addition of compatibilizing agent (diisocyanates) increased the glass transition temperatures of the developed composites because of formation of cross-linked structures, which results in decreased mobility of the PLA matrix chain. Crystallization temperatures also shifted to high temperature by adding diisocyanates, which indicated that the composites' crystallization rate became more rapid in nonisothermal processes. The increase in crystallization temperatures was due to the nucleation effect of diisocyanates. The degree of crystallinity of the composites was deceased by addition of diisocyanates due to the strong interfacial interaction between PLA matrix and ramie fibers which resulted into confining polymer chain orientation.

3.5.12 | Hemp fiber-reinforced PLA

Oza et al,[175] investigated effects of surface treatment on thermal stability of hemp fiber-reinforced PLA biocomposites. Their results showed that addition of acetic-anhydride-treated hemp resulted in higher thermal stability than alkali or silane-treated fibers because the former significantly reduced the hygroscopic nature of the fibers. Meanwhile, Masirek et al,[224] had earlier showed that degradation of hemp fiber reinforced PLA starts earlier than that of neat PLA, signaling a reduction in thermal stability with increasing hemp fiber loading in PLA. A study by Lu and Oza,[176] reported that degradation of both treated and untreated hemp fibers occurs earlier than that of neat PLA, but there was a delay of 20°C in degradation temperature for treated fibers in comparison to that of untreated fibers. Hapuarachchi and Peijs,[177] developed bio-based flame-retardant hemp/PLA composites with multiwalled carbon nanotubes and sepiolite nanoclay as flame retardants. Cone calorimeter test results showed that compared with the PLA matrix, the peak heat release rate (PHRR) was reduced from 485 to 265 kW/m^2 for the PLA/MWNTs/Sep ternary nanocomposite; however, incorporating hemp fibers into the PLA ternary nanocomposites increased the PHRR value to 340 kW/m^2. This indicated a slightly better flame retardancy than hemp fiber-reinforced PLA composites that showed a PHRR of 361 kW/m^2. Similar increases in PHRR were obtained by Wang et al,.[202] LOI values were further increased by increases in amount of APP flame retardant in the processing stage. Additionally, increase in starch fiber loading led to higher rating in the UL-94 test, showing that starch fiber is an effective carbonization agent for PLA, which can promote formation of protective char layer to prohibit flammability.

Islam et al,[119] revealed that incorporation of hemp in PLA matrix decreases glass transition, crystallisation, and melting temperatures. Additionally, incorporation of hemp fiber into PLA led to an increase in percentage crystallinity of the PLA matrix. This was explained by the nucleating ability of hemp fiber, allowing the crystallization of PLA. Crystallinity of hemp fiber-reinforced PLA was further increased by surface modification of hemp fibers. This result was similar to those obtained from Islam et al,[120] and Islam et al,[121] in which alkaline pretreatment was effected on hemp fibers prior to fiber-reinforced PLA production. A study from Sawpan et al,[116] similarly reported that crystallinity of hemp/PLA composites increased with increased fiber content, attributable to increased availability of nucleation sites leading to the formation of increased transcrystallinity. The increase of crystallinity was smaller as fiber content increased from 20 to 30 wt% because of the decrease of PLA content. Alkaline and silane surface modifications were reported to increase crystallinity of PLA because impurities like wax and pectin were removed from the hemp fibers after surface modification, thereby increasing the number of nucleating sites of the fibers.

3.5.13 | Pennisetum purpureum fiber-reinforced PLA

TGA results from Revati et al,[22] revealed that incorporation of Pennisetum purpureum fibers into PLA enhanced thermal stability of the developed composites. From their study, it was clear that increase in fiber content reduced onset of degradation but led to increases in final degradation temperatures. This then led to an increase in char residues of the developed composites. These char residues are a depiction of increasing thermal insulation.[162] In fact, several other researchers also reported that when Pennisetum purpureum fibers are incorporated in PLA matrix, they provide a barrier layer, which prohibits oxidation during combustion of the developed fiber-reinforced PLA. Increase of fiber proportion in fiber-reinforced PLA was said to lower the permeability of volatile degradation products, which further extended the thermal degradation process.[225–227] Gunti et al,[201] reported that initial degradation occurred at 322°C for neat PLA. Most degradation occurred in the temperature range of 322 to 430°C and the char residues after combustion were 0.3%. In the case of Pennisetum purpureum fiber-reinforced PLA, incorporation of Pennisetum purpureum fiber in PLA matrix significantly affected the thermal degradation temperature. Initial degradation temperature for untreated Pennisetum purpureum fiber-reinforced PLA was 264.5°C which is 17.85% less compared to neat PLA. These results were explained by a decrease of relative molecular mass of PLA.

3.5.14 | Abutilon fiber-reinforced PLA

TGA results from a study by Wang et al,[104] revealed that thermal degradation of the developed abutilon fiber-reinforced PLA composites started earlier than that of neat PLA. This was because of the inferior thermal stability of the abutilon fibers compared with PLA matrix. Addition of abutilon fibers did not significantly affect the degradation process, as the curves for composites with increasing fiber weights did not show significant differences.

From DSC results presented by Wang et al,,[104] addition of abutilon fiber to PLA increased the crystallization temperature. The composites with 1, 3, and 5 wt% fiber recorded crystallization temperatures of 137, 132, and 141°C, respectively. Additionally, the melting peaks did not change with addition of 1 and 3 wt% of abutilon fiber to the PLA matrix, but addition of 5 wt% of abutilon fiber to PLA matrix led to a higher melting point. Another study by Wang et al,[105] reported that with addition of abutilon straw fiber, the peak related to glass transition temperature in PLA disappeared completely in DSC thermographs. This was related to hydrolysis and removal of the amorphous phase of PLA. Additionally, addition of abutilon fiber did not significantly increase the melting temperature of the developed fiber-reinforced PLA but the slight increase was reported to be due the strong interaction adhesion between the abutilon fiber and PLA. From TGA, they found that an increased content of abutilon in PLA resulted in decreasing decomposition temperatures, indicating reduced thermal stability of PLA.

3.5.15 | Hazelnut shell fiber-reinforced PLA

In a study by Balart et al,[195] TGA curves of hazelnut shell fiber-reinforced PLA composites showed a slight decrease in onset degradation temperature, changing from 345°C for neat PLA up to values in the range 306 to 331°C for the developed composites. The initial degradation stage of the developed composites is related to the degradation of hazelnut shell fibers themselves. In another study, Balart et al,[156] developed hazelnut shell floor fiber-reinforced PLA with constant filler loading (20 wt%) while varying the epoxidized linseed oil plasticizer content. Thermal stability increased with increasing plasticizer content in the developed fiber-reinforced PLA as shown by the shift to the right in degradation temperatures.

DSC results by Balart et al,[195] showed that addition of hazelnut shell fiber does not change glass transition temperature from neat PLA's (66.5°C), due to lack of interaction between hazelnut shell and PLA matrix. Georgiopoulos and Kontou,[169] and Battegazzore et al,[196] also reported that addition of fibers did not affect glass transition temperature of fiber-reinforced PLA composites. Georgiopoulos and Kontou,[169] presented constant glass transition temperatures at around 59°C. Balart et al,[195] reported that crystallization temperature for neat PLA was about 111.5°C. Addition of hazelnut shell fibers led to a decrease to 104°C because hazelnut shells enable early crystallization. Balart et al,[156] reported that increasing plasticizer amount led to a decrease in glass transition temperature. Orue et al,[178] noted similar decreases due to the plasticization effect of epoxidized linseed oil because its presence promotes chain mobility. Meanwhile, he presence of plasticizer did not affect the melting process.

3.6 | Flame retardants used in fiber-reinforced PLA

Few studies have been published on flame retardancy of agricultural fiber-reinforced PLA, even though the flammability and high smoke emissions restrict their applications in automotive components and electronic devices.[145] The major limitation of fiber-reinforced PLA is its thermal sensitivity at the temperatures of compounding processes and flammability.[145] These often conflict with safety requirements and as such, improvement of their flame retardancy is increasingly gaining traction.[51,127] One method used to impart flame retardancy in fiber-reinforced PLA is incorporation of flame retardants (.[48,145,228,229] Flame retardants should be resistant to high temperatures so that fiber-reinforced PLA remain intact during processing and should not contain components that produce toxic gases.[230] It is worthy to note however, that halogen (bromine, chlorine, fluorine, and iodine) flame retardants are not preferred because of the ability to produce toxic and corrosive gasses as well as migrate out of the plastic to the surface.[231–235] Flame retardancy enhancement using flame retardants can be achieved in three ways: (a) blending PLA matrix with flame retardants and then compounding with agricultural fibers, (b) treating agricultural fibers with flame retardants and then compounding with PLA, and (c) treating both agricultural fibers and PLA with flame retardants and then compounding into fiber-reinforced PLA.[127] Some studies using flame retardants for enhancing flame retardancy of fiber-reinforced PLA are shown in Table 4.

3.6.1 | Modes of action of flame retardants

Flame retardants can be divided into gas-phase-active and condensed-phase-active although sometimes they act in the condensed phase and in the gas phase at the same time.[228,236,237] Flame retardants' modes of action are based on slowing down combustion processes by physical or chemical action in the solid, liquid, or gas phase.[228]

Gas-phase-active modes

In the gas phase, action of flame retardants involves interference of the combustion processes, resulting in the reduction in the flame propagation in a given material. In this mode, flame retardants disrupt the combustion in the flame and act by physical or chemical mechanisms. Reduction in flame propagation during the gas phase involves inert gas dilution and chemical quenching of active radicals. The gas dilution effect is caused by the release of noncombustible vapors or gases such as H_2O, CO_2, and NH_3 during combustion, diluting the oxygen supply to the flame or diluting the fuel concentration to a point below the flammability limit.[238] Chemical quenching involves stopping the combustion process by releasing specific radicals, for example, Cl*, Br*, and P*. These radicals can react with highly reactive species, such as H* and OH* to form less reactive or even inert molecules.[228]

Condensed-phase-active modes

Flame retardants often act in the condensed phase as acid precursors, leading to polymer breakdown and char formation by esterification and dehydration.[237] When a flame-retardant acts in the condensed phase, less fuel is produced, resulting in a significant decrease of heat release.[238] The action of flame retardants in this mode is conclusively presented by Pereira and Martins,.[228]

3.6.2 | Phosphorus-containing flame retardants

The structure of phosphorus based flame retardants varies from organic to inorganic forms. The phosphorus element mainly has 0, +3, and + 5 oxidation states.[239] Their disadvantage is that high filling grades are required.

Intumescent flame retardants

Intumescent flame retardant (IFR) is a promising halogen-free flame retardant additive because of its advantages of low smoke, low toxicity, low corrosion, high efficiency, and no molten dropping during a burning.[240,241] These halogen-free flame retardants have been widely presented in literature.[161,202,240,242,243] IFRs loading ratios in composites can go up to 30%.[202] An IFR system includes an acid source, a carbonization agent, and a blowing source/agent. The blowing source is typically nitrogen-containing compounds like urea, melamine, dicyandiamide, and polyamide. The acid source decomposes at elevated temperatures, generating inorganic strong acid, which can promote dehydration of the carbonizing agent to produce a char layer, forming an

TABLE 4 Flame retardants used to enhance flame retardancy of fiber-reinforced PLA

Fiber	Fiber loading	Flame retardant	Author
Kenaf	25 wt%	Ammonium polyphosphate	[161]
Flax	25 wt%	Ammonium polyphosphate	[187]
Potato starch	2.5, 5, and 10 wt%	Ammonium polyphosphate	[202]
Ramie	30 wt%	Ammonium polyphosphate	[127]
Coconut/jute	35 vol%	Diammonium phosphate	[194]
Hemp	30 vol%	Sepiolite nanoclay and multiwalled nanotubes	[177]

intumescent effect.[236,244] Apart from this effect, IFRs can lead to a radical trapping effect which enhances flame retardancy and thermal stability of the composites in which they are used.[245,246]

Organic phosphorus compounds

Organic phosphorus flame retardants can be categorized as phosphate esters, phosphinates, and phosphonates.[239,247] Organic phosphorus can be classified into monomers and oligomers. Monomeric organic phosphorus has high volatility and relatively low fire retardancy effectiveness compared to oligomeric organic phosphorus. The latter have much higher thermal stability and are normally used in engineering thermoplastics like PA-6 and ABS. Combining volatile and nonvolatile organic phosphorus flame retardants can enhance flame retardancy effect because of the combination role played in both condensed and vapor phases. Organic phosphorus compounds flame retardant loading ratios in composites can be as high as 25%.[248] One notable issue is that the use of organic flame retardants in fiber-reinforced PLA can produce toxic products after thermal decay and combustion.[248,249]

Inorganic phosphorus compounds

The two typical inorganic phosphorus flame retardants typically used in engineering applications are Ammonium polyphosphate (APP) and Melamine polyphosphate (MPP). MPP has higher thermal stability and lower water sensitivity than APP. Generally, long-chain APP and short-chain APP starts to degrade at a temperature of slightly above 300 and 150°C, respectively, generating ammonia and polyphosphoric acid. This means the choice for APP flame retardants depends on the processing temperature of the individual materials that constitute a given composite.[239] Inorganic phosphorus flame retardant loading ratios in composites can go up to 25%.[222] APP is widely used in retarding flame during burning of fiber-reinforced PLA because APP is usually associated with char-forming agents and nitrogen containing components at high temperatures caused by the release of polyphosphoric acid.[127,250,251]

Red phosphorus

Red phosphorus has the highest content of phosphorus among phosphorus-based flame retardants.[239] For this reason therefore, its loading levels in fiber-reinforced PLA are typically below 10%. Red phosphorous is highly active in both condensed and gas phases and is effective for both oxygen-containing polymers (eg, polyesters, polyamides, and polyurethanes) and nonoxygenated polymers (eg, polypropylene and polyethylene).[252] The disadvantages of red phosphorus are evolution of highly toxic phosphine through reaction with moisture, poor thermal-stability and lack of compatibility with synthetic resins.[248] Another disadvantage is that their application leads to an undesired colour change of the parts in which it is used.[253]

3.6.3 | Metal hydroxide flame retardants

Metallic hydroxide additives as flame retardants are increasingly gaining focus because they are environmentally safe.[234,249] They offer an attractive alternative because of their low toxicity, low corrosion and low smoke emission during processing and combustion.[239] Aluminum hydroxide ($Al[OH_3]$) and magnesium hydroxide ($Mg[OH]_2$) are the most widely used metal hydroxide flame retardants for fiber-reinforced PLA.[51,222,254] Their mode of action is by releasing water vapour through endothermic decomposition, leaving a thermally stable inorganic residue. Their use in polymer composites causes dilution of combustible polymer decomposition products with water, cooling the condensed phase through the endothermic dehydration. Chemical reactions through which aluminum hydroxide and magnesium hydroxide decompose are shown in Equations (1) and (2), respectively.[255] A disadvantage of metal hydroxide flame retardants is that very high filling grades are needed.[228] For example, to generate a sufficient flame retardancy, up to 60 wt% of aluminum hydroxide or magnesium hydroxide has to be added to a given composite, which can lead to decreasing mechanical characteristics.[254–257]

$$2\mathrm{Al(OH)_3} \rightarrow \mathrm{Al_2O_3} + 3\mathrm{H_2O}\ \Delta\mathrm{H} = 20\,\mathrm{cal/g} \tag{1}$$

$$\mathrm{Mg(OH)_2} \rightarrow \mathrm{MgO} + \mathrm{H_2O}\ \Delta\mathrm{H} = 328\,\mathrm{cal/g} \tag{2}$$

3.6.4 | Nanoscale flame retardants

Based on the chemical structure and geometry, nanoscale flame retardants can be classified as particulate (zero-dimensional), fibrous (one-dimensional), and layered (two-dimensional) additives.[239] Fibrous nanoscale flame retardants contain single/multiwalled carbon nanotubes, halloysite, sepiolite, and so on while layered nanoscale flame retardants include inorganic nanoclay (eg, MMT), layered hydroxides, expanded graphite, and graphene.[258] For fibrous nanoscale flame retardants, the formulation of a three-dimensional physical network forms a compact layer, which acts as thermal insulation barrier and thus effectively protect the underlying polymer matrix.[239] Because of their physical barrier effects, layered nanoscale flame retardants such as clay have been found to modify the flame retardancy properties of fiber reinforced PLA when blended at low filler levels (<5 wt%).[259] Nanofillers form a silicate char surface layer that acts as a flame barrier and thus protect the underlying polymer matrix of the general developed fiber-reinforced PLA plastic.[177]

3.6.5 | Silicon-containing flame retardants

Silicon-containing flame retardants include silicones, silicas, organosilicates, silsesquixanes, and silicates. Silicone flame retardants are considered to be eco-friendly additives since they have no harmful impacts to the environment.[260] They have excellent thermal stability, high heat release rates, and very low release of toxic gases like carbon monoxide (CO) during thermal degradation. According to Fu et al,,[239] their superior flame retardancy is primarily attributed to the excellent dispersion in polymer matrices and migration toward the material surface during combustion followed by the formation of a highly flame retardant char layer. Silicas (SiO_2) also have various types, including silica gel, fumed silica, and fused silica. They can even be obtained from the combustion of agricultural materials like rice husks.[83] Their effectiveness mainly depends on factors such as pore size, particle size, surface area, density, and viscosity.[85] Silica flame retardants have reduced heat release rates and mass loss rates because of the physical action of the silica in the condensed phase.[85,260]

3.6.6 | Chitosan flame retardants

Chitin, the second most abundant natural polysaccharide is a major constituent of some living organisms. It can be found in the cell wall of fungi and yeasts, in the shell of crustaceans and in exoskeletons of arthropods. Chitosan is a deacetylated form of chitin.[261] Chitosan is an amino polysaccharide with multi-hydroxyl groups, which is produced by alkaline deacetylation of Chitin.[262] Chitosan acts as a carbon source because of its carbohydrate structure containing hydroxyl groups and therefore promotes char formation at high temperature.[250,261]

4 | CONCLUSIONS

This article presents an overview on flame retardancy and thermal properties of fiber-reinforced plastics of agricultural fiber reinforcement and PLA polymer. Biocomposites from PLA and agricultural fibers have gained researchers' interest because of reduction of finite resources and growing environmental awareness on climate change. Fiber-reinforced PLA plastics in particular are widely being developed due to the improved mechanical properties they possess compared to neat PLA plastics. Their challenges often include low thermal stability and inherent flammability, which tend to hinder application in industry. Efforts to improve thermal stability and flame retardancy of fiber-reinforced PLA are therefore very important to ensure safety during applications in which they are required. This article gives an extensive review on the flame retardants usually used to enhance flame retardancy of fiber-reinforced PLA. These studies show that the body of work involving agricultural residue fiber-reinforced PLA is relatively small compared to the number of studies involving agricultural residues in other polymers like PP and PE. An overview of the processing techniques that are typically used for production of fiber-reinforced PLA is provided. Typical methods used in ascertaining flame retardancy and thermal properties of fiber-reinforced PLA are presented. From the discussions in this article, the following conclusions can be drawn;

Agricultural fiber-reinforced PLA plastics have been shown to be an alternative to synthetic fiber reinforced PLA plastics due to the renewable nature and excess availability of agricultural fibers. More research on agricultural natural fibers as reinforcement for plastic composites is required to widen the scope of materials that can reduce greenhouse gas emissions during their lifecycle.

Flame retardancy and flammability of fiber-reinforced PLA is influenced by variables like origin of the agricultural fiber, pretreatment of agricultural fiber, and processing technique of fiber-reinforced PLA. These variables therefore have to be taken into consideration in the production of agricultural fiber-reinforced PLA.

Many works in literature focus on characterizing agricultural fiber-reinforced PLA and most of these works show that the properties of fiber-reinforced PLA often depend on the properties of the constituent agricultural fibers used as reinforcement. This article has provided details on bio-chemical, mechanical, and physical properties of typical agricultural fibers usually used as reinforcement in fiber-reinforced PLA. Surface modification has been noted to affect the flame retardancy and the thermal stability properties of the agricultural fibers. However, the extent of the property change greatly depends on the type of surface modification used.

Flame retardants retard flammability of agricultural fiber-reinforced PLA. Flame retardancy using flame retardants can be achieved by: (a) blending PLA with flame retardants and then compounding with agricultural fibers, (b) treating agricultural fibers with flame retardants and compounding with PLA, and (c) treating both agricultural fibers and PLA with flame retardants and compounding into fiber-reinforced PLA.

Coir fibers are the most promising fibers for use as fiber-reinforced PLA as regards flame retardancy and thermal stability while ramie fibers are the least promising fibers. This is because the former has the most lignin compositions while the latter has the least lignin compositions (see Table 1).

Metal hydroxide flame retardants are most preferred in retarding flammability because they release water vapour through endothermic decomposition, leaving a thermally stable inorganic residue. Their use in agricultural fiber-reinforced PLA can therefore cause dilution of the combustible polymer decomposition products with water, thereby cooling the condensed phase through endothermic dehydration.

Most of the work is done on thermal stability properties of fiber-reinforced PLA (Table 3). More research toward flame retardancy is required because as much as flame retardants are effective in retarding flammability, agricultural fibers themselves produce flame retardancy properties at specific temperatures during processing or combustion. This is because the inherent lignin in agricultural fibers acts as a natural flame retardant. Lignin is thermally stable because of crosslinking between monomer units, therefore high amounts of lignins in agricultural fibers increase their resistance to hydrolysis and degradation.

ACKNOWLEDGMENT

This work was supported by the Volkswagen Foundation under grant no. 96655 entitled “Enhanced flame retardancy of bio-composite plastics developed with rice husks and clay fillers.”

AUTHOR CONTRIBUTIONS

Vianney Andrew Yiga: conceptualization, writing-original draft, writing-review, and editing. **Michael Lubwama:** conceptualization, writing-original draft, and supervision. **Sinja Pagel:** Writing-original draft, writing-review and editing, and investigation. **Johannes Benz:** conceptualization, writing-review, and editing. **Peter Wilberforce Olupot:** writing-review and editing, and investigation. **Christian Bonten:** conceptualization, writing-review, and editing, supervision.

ORCID

Vianney Andrew Yiga https://orcid.org/0000-0002-9753-3684

Michael Lubwama https://orcid.org/0000-0001-7984-262X

REFERENCES

[1] C. Bonten, *Plastics Technology. Introduction and Fundamentals*, Hanser, Müncher **2019** ISBN 978-1-56990-767-2.

[2] R. Siakeng, M. Jawaid, H. Ariffin, S. M. Sapuan, *Polym. Compos.* **2019**, *40*, 2000.

[3] N. Jain, A. Verma, V. K. Singh, *Mater. Res. Exp.* **2019**, *6*, 105373.

[4] A. Verma, A. Gaur, V. K. Singh, *Mater Perform Charact* **2017**, *6*, 500.

[5] L. He, F. Song, D. F. Li, X. Zhao, X. L. Wang, Y. Z. Wang, *ACS Sustain. Chem. Eng.* **2020**, *8*, 1573.

[6] B. Wu, P. Xu, W. Yang, M. Hoch, W. Dong, M. Chen, H. Bai, P. Ma, *J. Polym. Sci.* **2020**, *58*, 500.

[7] M. H. M. Hamdan, J. P. Siregar, M. R. M. Rejab, D. Bachtiar, J. Jamiluddin, C. Tezara, *Int. J. Prec. Eng. Manufact.-Green Technol.* **2019**, *6*, 113.

[8] A. Verma, P. Negi, V. K. Singh, *Polym. Compos.* **2019**, *40*, 2690.

[9] A. Verma, P. Negi, V. K. Singh, *Adv. Civil Eng. Mater.* **2018**, *7*, 538.

[10] A. Verma, P. Negi, V. K. Singh, *J. Mech. Behav. Mater.* **2018**, *27*, 1.

[11] T. H. Mokhothu, M. J. John, *Carbohydr. Polym.* **2015**, *131*, 337.

[12] S. S. Todkar, S. A. Patil, *Comp., Part B* **2019**, *174*, 106927.

[13] V. A. Yiga, M. Lubwama, P. W. Olupot, *J. Nat. Fibers* **2019**, 1. https://doi.org/10.1080/15440478.2019.1642824.

[14] M. H. P. S. Jawaid, H. A. Khalil, *Carbohydr. Polym.* **2011**, *86*, 1.

[15] S. Chen, N. Hori, M. Kajiyama, A. Takemura, *J. Appl. Polym. Sci.* **2020**, *137*, 48981.

[16] K. N. Bharath, P. Madhu, T. G. Gowda, A. Verma, M. R. Sanjay, S. Siengchin, *Polym. Compos.* **2020**, 1.

[17] A. Verma, C. Singh, V. K. Singh, N. Jain, *J. Compos. Mater.* **2019**, *53*, 2481.

[18] A. Verma, V. K. Singh, *J. Test. Eval.* **2019**, *47*, 1193.

[19] S. Rastogi, A. Verma, V. K. Singh, *Mater. Perform. Character.* **2020**, *9*, 151.

[20] A. Ali, K. Shaker, Y. Nawab, M. Jabbar, T. Hussain, J. Militky, V. Baheti, *J. Ind. Text.* **2018**, *47*, 2153.

[21] Getme, A. S., & Patel, B. *Mater. Today: Proceed* **2020**.

[22] R. Revati, M. A. Majid, M. J. M. Ridzuan, M. Normahira, N. M. Nasir, A. G. Gibson, *Mater. Sci. Eng., C* **2017**, *75*, 752.

[23] R. Mishra, J. Wiener, J. Militky, M. Petru, B. Tomkova, J. Novotna, *Fiber. Polym.* **2020**, *21*, 619.

[24] M. P. Westman, L. S. Fifield, K. L. Simmons, S. Laddha, T. A. Kafentzis, *Natural Fiber Composites: A Review* (No. PNNL-19220, Pacific Northwest National Lab.(PNNL), Richland, WA **2010**.

[25] A. Verma, K. Joshi, A. Gaur, V. K. Singh, *J. Mech. Behav. Mater.* **2018**, *27*, 1.

[26] J. M. Raquez, Y. Habibi, M. Murariu, P. Dubois, *Prog. Polym. Sci.* **2013**, *38*, 1504.

[27] J. Gu, P. Xiao, P. Chen, L. Zhang, H. Wang, L. Dai, T. Chen, *ACS Appl. Mater. Interf.* **2017**, *9*, 5968.

[28] S. H. Park, S. G. Lee, S. H. Kim, *Comp. Part A: Appl. Sci. Manufact.* **2013**, *46*, 11.

[29] E. F. Santos, R. V. Oliveira, Q. B. Reiznautt, D. Samios, S. M. Nachtigall, *Polym. Test.* **2014**, *39*, 23.

[30] B. H. Tan, J. K. Muiruri, Z. Li, C. He, *ACS Sustain. Chem. Eng.* **2016**, *4*, 5370.

[31] European Bioplastics, **2020**. Bioplastics market data, https://www.european-bioplastics.org/market/ (accessed: May 2020).

[32] Murillo Castellón, S., Standau, T., Altstädt, V., and Bonten, C. *Proc. 35th Int. Conf. Polym. Process. Society (PPS-35)*, AIP Publishing LLC **2020**, *2205*, 20068.

[33] M. Abhilash, D. Thomas, Biopolymers for biocomposites and chemical sensor applications. in *Biopolymer Composites in Electronics*, Elsevier, United states **2017**, p. 405.

[34] Göttermann, S., Standau, T., Altstädt, V., and Bonten, C. *Proc. Techn. Conf. Exhib. Anaheim, California, USA, May 8–10, 2017: Soc. Plast. Eng*. 452–456. AIP Publishing LLC **2019**, *2055*, 020003.

[35] L. Sha, Z. Chen, Z. Chen, A. Zhang, Z. Yang, *Int. J. Polym. Sci.* **2016**, *2016*, 1.

[36] M. P. Arrieta, E. Fortunati, F. Dominici, E. Rayón, J. López, J. M. Kenny, *Polym. Degrad. Stab.* **2014**, *107*, 139.

[37] S. Göttermann, T. Standau, S. Weinmann, V. Altstädt, C. Bonten, *Polym. Eng. Sci.* **2017**, *57*, 1242.

[38] S. Farah, D. G. Anderson, R. Langer, *Adv. Drug Delivery Rev.* **2016**, *107*, 367.

[39] T. Mukherjee, N. Kao, *J. Polym. Environ.* **2011**, *19*, 714.

[40] J. A. Delicano, *Comp. Interf.* **2018**, *25*, 1039.

[41] K. Zhang, F. Wang, W. Liang, Z. Wang, Z. Duan, B. Yang, *Polymer* **2018**, *10*, 608.

[42] V. Kumar, N. K. Sharma, R. Kumar, *J. Reinf. Plast. Compos.* **2013**, *32*, 42.

[43] N. F. M. Rawi, K. Jayaraman, D. Bhattacharyya, *Polym. Compos.* **2014**, *35*, 1888.

[44] P. J. Jandas, S. Mohanty, S. K. Nayak, *J. Cleaner Prod.* **2013**, *52*, 392.

[45] K. M. M. Rao, A. R. Prasad, M. R. Babu, K. M. Rao, A. V. S. S. K. S. Gupta, *J. Mater. Sci.* **2007**, *42*, 3266.

[46] O. P. Gbenebor, R. A. Atoba, E. I. Akpan, A. K. Aworinde, S. O. Adeosun, S. A. Olaleye, Study on polylactide-coconut fibre for biomedical applications. in *TMS Annual Meeting & Exhibition*, Springer, Cham **2018**, p. 263.

[47] N. Graupner, A. S. Herrmann, J. Müssig, *Comp. Part A: Appl. Sci. Manufact.* **2009**, *40*, 810.

[48] R. Siakeng, M. Jawaid, H. Ariffin, S. M. Sapuan, M. Asim, N. Saba, *Polym. Compos.* **2018**, *40*, 446.

[49] W. Liu, A. K. Mohanty, P. Askeland, L. T. Drzal, M. Misra, *Polymer* **2004**, *45*, 7589.

[50] E. Bodros, I. Pillin, N. Montrelay, C. Baley, *Comp. Sci. Technol.* **2007**, *67*, 462.

[51] L. Mohammed, M. N. Ansari, G. Pua, M. Jawaid, M. S. Islam, *Int. J. Polym. Sci.* **2015**, *2015*, 1.

[52] A. Pappu, K. L. Pickering, V. K. Thakur, *Indust. Crops Prod.* **2019**, *137*, 260.

[53] Gupta, N., Vishwakarma, A., Jain, A. K., & Asokan, P. *AIP Conf. Proceed.* AIP Publishing LLC **2019**, Vol. 2158, No. 1, p. 020036.

[54] M. M. Rahman, S. Afrin, P. Haque, M. Islam, M. S. Islam, M. Gafur, *Int. J. Chem. Eng.* **2014**, *2014*, 1.

[55] S. Serizawa, K. Inoue, M. Iji, *J. Appl. Polym. Sci.* **2006**, *100*, 618.

[56] B. V. Ramnath, C. V. Krishna, S. Karthik, K. Saravanan, V. M. Manickavasagam, C. Elanchezhian, Evaluation of the flexural properties of pineapple reinforced polymer composite for automotive and electrical applications. in *Advanced Materials Research*, Vol. 893, Trans Tech Publications Ltd, Germany **2014**, p. 271.

[57] Y. Du, N. Yan, M. T. Kortschot, The use of ramie fibers as reinforcements in composites. in *Biofiber Reinforcements in Composite Materials*, Woodhead Publishing, Sawston, Cambridge **2015**, p. 104.

[58] S. Chaitanya, I. Singh, *Polym. Compos.* **2018**, *39*, 4310.

[59] S. M. Luz, A. Caldeira-Pires, P. M. Ferrão, *Resour. Conserv. Recycl.* **2010**, *54*, 1135.

[60] P. Ovlaque, M. Foruzanmehr, S. Elkoun, M. Robert, *Comp. Interf.* **2020**, *27*, 495.

[61] L. Qin, J. Qiu, M. Liu, S. Ding, L. Shao, S. Lü, X. Fu, *Chem. Eng. J.* **2011**, *166*, 772.

[62] Y. Zhao, J. Qiu, H. Feng, M. Zhang, L. Lei, X. Wu, *Chem. Eng. J.* **2011**, *173*, 659.

[63] T. Zhu, J. Guo, B. Fei, Z. Feng, X. Gu, H. Li, J. Sun, S. Zhang, *Cellulose* **2020**, *27*, 2309.

[64] A. Bouzouita, D. Notta-Cuvier, J. M. Raquez, F. Lauro, P. Dubois, Poly (lactic acid)-based materials for automotive applications. in *Industrial Applications of Poly (lactic acid)*, Springer, Cham **2017**, p. 177.

[65] M. J. John, S. Thomas, *Carbohydr. Polym.* **2008**, *71*, 343.

[66] S. Kalia, K. Thakur, A. Celli, M. A. Kiechel, C. L. Schauer, *J. Environ. Chem. Eng.* **2013**, *1*, 97.

[67] L. Nickels, *Reinf. Plastics* **2017**, *61*, 332.

[68] K. Immonen, P. Lahtinen, J. Pere, *Bioengineering* **2017**, *4*, 91.

[69] O. Faruk, A. K. Bledzki, H. P. Fink, M. Sain, *Macromol. Mater. Eng.* **2014**, *299*, 9.

[70] Y. Dong, A. Ghataura, H. Takagi, H. J. Haroosh, A. N. Nakagaito, K. T. Lau, *Comp. Part A: Appl. Sci. Manufact.* **2014**, *63*, 76.

[71] M. Lubwama, V. A. Yiga, *Renewable Energy* **2018**, *118*, 43.

[72] M. Lubwama, V. A. Yiga, *Renewable Energy* **2017**, *111*, 532.

[73] A. Cabeza, F. Sobrón, F. M. Yedro, J. García-Serna, *Fuel* **2015**, *148*, 212.

[74] H. L. Ornaghi Jr., F. G. O. R. M. Neves, F. M. O. Bianchi, *Cellulose* **2020**, *27*, 4949.

[75] Shakoor, A., Azam, K., Khan, S. W., & Ullah, A. (**2013**). Toughening PLA composites with natural fibers and enR. SPE Automotive Composites Conference & Exhibition at Troy, Michigan, USA from 11th to 13th September, 2012.

[76] H. He, Z. Duan, Z. Wang, *Comp. Part A: Appl. Sci. Manufact.* **2020**, *128*, 105676.

[77] A. Sharif, S. Mondal, M. E. Hoque, Polylactic Acid (PLA)-Based Nanocomposites: Processing and Properties. in *Bio-based Polymers and Nanocomposites*, Springer, Cham **2019**, p. 233.

[78] B. Gupta, N. Revagade, J. Hilborn, *Prog. Polym. Sci.* **2007**, *32*, 455.

[79] F. Richter, G. Rein, *Front. Mech. Eng.* **2018**, *4*, 18.

[80] Yiga, V. A., Lubwama, M., & Olupot, P. W. *5th Therm. Fluids Eng Conf.* ASTFE Digital Library. Begel House Inc **2020**. https://doi.org/10.1615/TFEC2020.cbf.032093.

[81] Yiga, V. A. and Lubwama, M. *14th HEFAT conference*, Dublin, Ireland **2019**.

[82] S. Yu, H. Xiang, J. Zhou, M. Zhu, *Prog. Nat. Sci.: Mater. Int.* **2018**, *28*, 590.

[83] V. A. Yiga, S. Pagel, M. Lubwama, S. Epple, P. W. Olupot, C. Bonten, *J. Thermoplast. Compos. Mater.* **2020**, *33*, 1269.

[84] S. Bourbigot, G. Fontaine, *Polym. Chem.* **2010**, *1*, 1413.

[85] M. E. Mngomezulu, M. J. John, V. Jacobs, A. S. Luyt, *Carbohydr. Polym.* **2014**, *111*, 149.

[86] S. Chapple, R. Anandjiwala, S. S. Ray, *J. Therm. Anal. Calorim.* **2013**, *113*, 703.

[87] S. Chapple, R. Anandjiwala, *J. Thermoplast. Compos. Mater.* **2010**, *23*, 871.

[88] L. Lin, C. Deng, G.-P. Lin, Y.-H. Wang, *Polym.-Plast. Technol. Eng.* **2014**, *53*, 613.

[89] G. Tang, X. Wang, W. Xing, P. Zhang, B. Wang, N. Hong, L. Song, *Ind. Eng. Chem. Res.* **2012**, *51*, 12009.

[90] E. Gallo, B. Schartel, D. Acierno, P. J. E. P. J. Russo, *Eur. Polym. J.* **2011**, *47*, 1390.

[91] K. Fukushima, M. Murariu, G. Camino, P. Dubois, *Polym. Degrad. Stab.* **2010**, *95*, 1063.

[92] W. Li, L. Zheng, D. Teng, D. Ge, F. I. Farha, F. Xu, *J. Indust. Text.* **2020**, 1.

[93] L. Y. Wu, F. J. Xu, P. W. Zhao, Y. P. Qiu, Fabrication, Tensile and Bending Properties of Wheat Straw/Polylactic Acid Green Composites. in *Advanced Materials Research*, Vol. 627, Trans Tech Publications Ltd, Germany **2013**, p. 715.

[94] S. Yang, S. Bai, Q. Wang, *Comp. Sci. Technol.* **2018**, *158*, 34.

[95] C. Nyambo, A. K. Mohanty, M. Misra, *Macromol. Mater. Eng.* **2011**, *296*, 710.

[96] U. K. Komal, M. K. Lila, I. Singh, *Composites, Part B* **2020**, *180*, 107535.

[97] V. P. Sajna, S. Mohanty, S. K. Nayak, *Int. J. Plastics Technol.* **2016**, *20*, 187.

[98] V. P. Sajna, S. Mohanty, S. K. Nayak, *J. Reinf. Plast. Compos.* **2014**, *33*, 1717.

[99] S. K. Majhi, S. K. Nayak, S. Mohanty, L. Unnikrishnan, *Int. J. Plastics Technol.* **2010**, *14*, 57.

[100] P. J. Jandas, S. Mohanty, S. K. Nayak, H. Srivastava, *Polym. Compos.* **2011**, *32*, 1689.

[101] N. A. A. Hassan, S. Ahmad, R. S. Chen, D. Shahdan, *Constr. Build. Mater.* **2020**, *240*, 117884.

[102] Kamarudin, S. H., Abdullah, L. C., Aung, M. M., & Ratnam, C. T. (**2018**). *IOP Conf. Ser.: Mater. Sci. Eng.* IOP Publishing **2018**, Vol. 368, No. 1, p. 012011.

[103] I. S. Tawakkal, M. J. Cran, S. W. Bigger, *Indust. Crops Prod.* **2014**, *61*, 74.

[104] H. Wang, E. Hassan, H. Memon, T. Elagib, F. Abad AllaIdris, *Processes* **2019**, *7*, 583.

[105] H. Wang, H. Memon, E. A. Hassan, T. H. Elagib, F. E. A. Hassan, M. Yu, *Int. J. Polym. Sci.* **2019**, *2019*, 1.

[106] K. Zhang, J. Lin, C. Hao, G. Hong, Z. Chen, Z. Chen, et al., *BioResources* **2019**, *14*, 1694.

[107] J. Lin, Z. Yang, X. Hu, G. Hong, S. Zhang, W. Song, *Polymer* **2018**, *10*, 403.

[108] M. P. Ho, K. T. Lau, H. Wang, D. Hui, *Composites, Part B* **2015**, *81*, 14.

[109] F. Wang, S. Zhou, M. Yang, Z. Chen, S. Ran, *Polymer* **2018**, *10*, 401.

[110] J. W. Park, J. H. Shin, G. S. Shim, K. B. Sim, S. W. Jang, H. J. Kim, *Polymer* **2019**, *11*, 349.

[111] Y. Nishitani, T. Kajiyama, T. Yamanaka, *Materials* **2017**, *10*, 1040.

[112] K. L. Pickering, M. A. Sawpan, J. Jayaraman, A. Fernyhough, *Comp. Part A: Appl. Sci. Manufact.* **2011**, *42*, 1148.

[113] Y. Song, J. Liu, S. Chen, Y. Zheng, S. Ruan, Y. Bin, *J. Polym. Environ.* **2013**, *21*, 1117.

[114] B. Baghaei, M. Skrifvars, L. Berglin, *Composites Part A: Appl. Sci. Manufact.* **2013**, *50*, 93.

[115] Y. S. Song, J. T. Lee, D. S. Ji, M. W. Kim, S. H. Lee, J. R. Youn, *Composites, Part B* **2012**, *43*, 856.

[116] M. A. Sawpan, K. L. Pickering, A. Fernyhough, *Comp. Part A: Appl. Sci. Manufact.* **2011**, *42*, 310.

[117] K. L. Pickering, M. A. Efendy, *Indust. Crops Prod.* **2016**, *84*, 139.

[118] S. Kobayashi, K. Takada, *Adv. Compos. Mater* **2015**, *24*, 509.

[119] M. S. Islam, K. L. Pickering, N. J. Foreman, *Comp. Part A: Appl. Sci. Manufact.* **2010**, *41*, 596.

[120] M. S. Islam, K. L. Pickering, N. J. Foreman, *J. Polym. Environ.* **2010**, *18*, 696.

[121] M. S. Islam, K. L. Pickering, N. J. Foreman, *Polym. Degrad. Stab.* **2010c**, *95*, 59.

[122] M. Delgado-Aguilar, F. Julián, Q. Tarrés, J. A. Méndez, P. Mutjé, F. X. Espinach, *Composites, Part B* **2017**, *125*, 203.

[123] B. Tisserat, N. Joshee, A. K. Mahapatra, G. W. Selling, V. L. Finkenstadt, *Ind. Crops Prod.* **2013**, *44*, 88.

[124] Q. K. Meng, M. Hetzer, D. De Kee, *J. Compos. Mater.* **2011**, *45*, 1145.

[125] T. Yu, N. Jiang, Y. Li, *Comp. Part A: Appl. Sci. Manufact.* **2014**, *64*, 139.

[126] T. Yu, F. Sun, M. Lu, Y. Li, *Polym. Compos.* **2018**, *39*, 1098.

[127] L. Shumao, R. Jie, Y. Hua, Y. Tao, Y. Weizhong, *Polym. Int.* **2010**, *59*, 242.

[128] X. Chen, J. Ren, N. Zhang, S. Gu, J. Li, *J. Reinf. Plast. Compos.* **2015**, *34*, 28.

[129] H. Y. Choi, J. S. Lee, *Fibers Polym.* **2012**, *13*, 217.

[130] D. K. Debeli, Z. Qin, J. Guo, *J. Natural Fibers* **2018**, *15*, 596.

[131] Z. Zhu, H. Wu, C. Ye, W. Fu, *J. Natural Fibers* **2017**, *14*, 875.

[132] S. Chaitanya, I. Singh, *Mater. Manuf. Processes* **2017**, *32*, 468.

[133] Z. Li, X. Zhou, C. Pei, *Int. J. Polym. Sci.* **2011**, *2011*, 1.

[134] T. Tábi, A. Z. Égerházi, P. Tamás, T. Czigány, J. G. Kovács, *Comp. Part A: Appl. Sci. Manufact.* **2014**, *64*, 99.

[135] T. Liu, F. Yu, X. Yu, X. Zhao, A. Lu, J. Wang, *J. Appl. Polym. Sci.* **2012**, *125*, 1292.

[136] L. Zhang, Z. Sun, D. Liang, J. Lin, W. Xiao, *BioResources* **2017**, *12*, 7349.

[137] Z. Sun, L. Zhang, D. Liang, W. Xiao, J. Lin, *Int. J. Polym. Sci.* **2017**, *2017*, 1.

[138] K. S. Chun, S. Husseinsyah, H. Osman, *J. Polym. Res.* **2012**, *19*, 9859.

[139] A. Porras, A. Maranon, I. A. Ashcroft, *Comp. Part A: Appl. Sci. Manufact.* **2016**, *81*, 105.

[140] A. Porras, A. Maranon, I. A. Ashcroft, *Comp. Struct.* **2016**, *140*, 692.

[141] M. Ragoubi, B. George, S. Molina, D. Bienaimé, A. Merlin, J. M. Hiver, A. Dahoun, *Comp. Part A: Appl. Sci. Manufact.* **2012**, *43*, 675.

[142] Y. Arao, T. Fujiura, S. Itani, T. Tanaka, *Composites, Part B* **2015**, *68*, 200.

[143] B. K. Goriparthi, K. N. S. Suman, M. R. Nalluri, *Polym. Compos.* **2012**, *33*, 237.

[144] N. D. Yaacob, H. Ismail, S. S. Ting, *BioResources* **2016**, *11*, 1255.

[145] L. Zhang, Z. Li, Y. T. Pan, A. P. Yáñez, S. Hu, X. Q. Zhang, D. Y. Wang, *Composites, Part B* **2018**, *154*, 56.

[146] R. F. Munawar, N. H. Jamil, M. K. Shahril, S. A. Rahim, S. Muhammad, Z. Abidin, K. T. Lau, Development of green composite: pineapple leaf fibers (palf) reinforced polylactide (pla). in *Applied Mechanics and Materials*, Vol. 761, Trans Tech Publications Ltd, Germany **2015**, p. 520.

[147] A. Rubio-López, A. Olmedo, A. Díaz-Álvarez, C. Santiuste, *Comp. Struct.* **2015**, *131*, 995.

[148] L. A. Granda, F. X. Espinach, Q. Tarrés, J. A. Méndez, M. Delgado-Aguilar, P. Mutjé, *Composites, Part B* **2016**, *99*, 514.

[149] V. Fiore, L. Botta, R. Scaffaro, A. Valenza, A. Pirrotta, *Comp. Sci. Technol.* **2014**, *105*, 110.

[150] S. A. Laaziz, M. Raji, E. Hilali, H. Essabir, D. Rodrigue, R. Bouhfid, A. el kacem Qaiss, *Int. J. Biol. Macromol.* **2017**, *104*, 30.

[151] A. K. Bledzki, A. Jaszkiewicz, *Comp. Sci. Technol.* **2010**, *70*, 1687.

[152] R. Liu, M. Liu, S. Hu, A. Huang, E. Ma, *Holzforschung* **2018**, *72*, 735.

[153] M. Khemakhem, K. Lamnawar, A. Maazouz, M. Jaziri, *Polym. Compos.* **2018**, *39*, E152.

[154] Z. Yang, X. Feng, M. Xu, D. Rodrigue, *Polymer* **2020**, *12*, 729.

[155] Tran, T. P. H., Bénézet, J. C., & Bergeret, A. *The 19 th Int. Conf. Comp. Mater. July 28 to August 2, 2013 in Montreal, Canada* **2013**.

[156] J. F. Balart, V. Fombuena, O. Fenollar, T. Boronat, L. Sánchez-Nacher, *Composites, Part B* **2016**, *86*, 168.

[157] W. Sujaritjun, P. Uawongsuwan, W. Pivsa-Art, H. Hamada, *Energy Procedia* **2013**, *34*, 664.

[158] A. F. Koutsomitopoulou, J. C. Bénézet, A. Bergeret, G. C. Papanicolaou, *Powder Technol.* **2014**, *255*, 10.

[159] K. Oksman, M. Skrifvars, J. F. Selin, *Comp. Sci. Technol.* **2003**, *63*, 1317.

[160] X. W. Cheng, J. P. Guan, R. C. Tang, K. Q. Liu, *J. Indus. Text.* **2016**, *46*, 914.

[161] F. Shukor, A. Hassan, M. S. Islam, M. Mokhtar, M. Hasan, *Mater. Des. (1980–2015)* **2014**, *54*, 425.

[162] V. A. Yiga, M. Lubwama, *MRS Adv.* **2020**, 1. https://doi.org/10.1557/adv.2019.485.

[163] Zhao, J. *Doctoral dissertation*, The Ohio State University **2013**.

[164] Y. Zheng, J. Zhao, F. Xu, Y. Li, *Prog. Energy Combust. Sci.* **2014**, *42*, 35.

[165] A. Basu, M. Nazarkovsky, R. Ghadi, W. Khan, A. J. Domb, *Polym. Adv. Technol.* **2017**, *28*, 919.

[166] T. Ozyhar, F. Baradel, J. Zoppe, *Comp. Part A: Appl. Sci. Manufact.* **2020**, *132*, 105827.

[167] C. Sun, C. Li, H. Tan, Y. Zhang, *Energy Convers. Manage.* **2019**, *202*, 112212.

[168] N. Petchwattana, P. Naknaen, B. Narupai, *Int. J. Sustain. Eng.* **2019**, 1. https://doi.org/10.1080/19397038.2019.1688422.

[169] P. Georgiopoulos, E. Kontou, *J. Appl. Polym. Sci.* **2015**, *132*, 1.

[170] R. Liu, Y. Peng, J. Cao, *Polym. Compos.* **2016**, *37*, 1971.

[171] P. J. Jandas, S. Mohanty, S. K. Nayak, *J. Therm. Anal. Calorim.* **2013**, *114*, 1265.

[172] P. J. Jandas, S. Mohanty, S. K. Nayak, *J. Polym. Environ.* **2012**, *20*, 583.

[173] G. Hu, S. Cai, Y. Zhou, N. Zhang, J. Ren, *J. Reinf. Plast. Compos.* **2018**, *37*, 841.

[174] N. Masruchin, S. S. Munawar, S. Subyakto, *Jurnal Ilmu dan Teknologi Kayu Tropis* **2017**, *9*, 1.

[175] S. Oza, H. Ning, I. Ferguson, N. Lu, *Composites, Part B* **2014**, *67*, 227.

[176] N. Lu, S. Oza, Effect of Surface Treatment of Hemp Fibers on the Thermal Stability of the Hemp-PLA (Poly lactic acid) Composites. in *Advanced Materials Research*, Vol. 651, Trans Tech Publications Ltd, Germany **2013**, p. 499.

[177] T. D. Hapuarachchi, T. Peijs, *Comp. Part A: Appl. Sci. Manufact.* **2010**, *41*, 954.

[178] A. Orue, A. Eceiza, A. Arbelaiz, *Indus. Crops Prod.* **2018**, *112*, 170.

[179] J. Tengsuthiwat, S. Siengchin, R. Berényi, J. Karger-Kocsis, *J. Therm. Anal. Calorim.* **2018**, *132*, 955.

[180] J. D. Badia, E. Strömberg, T. Kittikorn, M. Ek, S. Karlsson, A. Ribes-Greus, *Polym. Degrad. Stab.* **2017**, *143*, 9.

[181] G. Rajesh, A. R. Prasad, A. V. S. S. K. S. Gupta, *J. Reinf. Plast. Compos.* **2015**, *34*, 951.

[182] T. Yu, C. Hu, X. Chen, Y. Li, *Comp. Part A: Appl. Sci. Manufact.* **2015**, *76*, 20.

[183] T. Yu, J. Ren, S. Li, H. Yuan, Y. Li, *Comp. Part A: Appl. Sci. Manufact.* **2010**, *41*, 499.

[184] P. Georgiopoulos, A. Christopoulos, S. Koutsoumpis, E. Kontou, *Composites, Part B* **2016**, *106*, 88.

[185] M. Foruzanmehr, P. Y. Vuillaume, S. Elkoun, M. Robert, *Mater. Des.* **2016**, *106*, 295.

[186] H. Teymoorzadeh, D. Rodrigue, *J. Renew. Mater.* **2014**, *2*, 270.

[187] K. Bocz, B. Szolnoki, A. Marosi, T. Tábi, M. Wladyka-Przybylak, G. Marosi, *Polym. Degrad. Stab.* **2014**, *106*, 63.

[188] S. O. Han, M. Karevan, I. N. Sim, M. A. Bhuiyan, Y. H. Jang, J. Ghaffar, K. Kalaitzidou, *Int. J. Polym. Sci.* **2012**, *2012*.1.

[189] A. A. Yussuf, I. Massoumi, A. Hassan, *J. Polym. Environ.* **2010**, *18*, 422.

[190] H. Anuar, A. Zuraida, *Malaysian Polym J* **2011**, *6*, 51.

[191] B. S. Ndazi, S. Karlsson, *Exp. Polym. Lett.* **2011**, *5*, 119.

[192] T. P. T. Tran, J. C. Bénézet, A. Bergeret, *Indus. Crops Prod.* **2014**, *58*, 111.

[193] Q. Fan, G. Han, W. Cheng, H. Tian, D. Wang, L. Xuan, *Polymer* **2018**, *10*, 896.

[194] N. P. G. Suardana, M. S. Ku, J. K. Lim, *Mater. Des.* **2011**, *32*, 1990.

[195] J. F. Balart, D. García-Sanoguera, R. Balart, T. Boronat, L. Sánchez-Nacher, *Polym. Compos.* **2018**, *39*, 848.

[196] D. Battegazzore, J. Alongi, A. Frache, *J. Polym. Environ.* **2014**, *22*, 88.

[197] P. K. Bajpai, I. Singh, J. Madaan, *Wear* **2013**, *297*, 829.

[198] M. M. Haafiz, A. Hassan, Z. Zakaria, I. M. Inuwa, M. S. Islam, M. Jawaid, *Carbohydr. Polym.* **2013**, *98*, 139.

[199] Q. Zhang, L. Shi, J. Nie, H. Wang, D. Yang, *J. Appl. Polym. Sci.* **2012**, *125*, E526.

[200] Z. Kovacevic, S. Bischof, M. Fan, *Composites, Part B* **2015**, *78*, 122.

[201] R. Gunti, A. V. Ratna Prasad, A. V. S. S. K. S. Gupta, *Polym. Compos.* **2018**, *39*, 1125.

[202] X. Wang, Y. Hu, L. Song, S. Xuan, W. Xing, Z. Bai, H. Lu, *Ind. Eng. Chem. Res.* **2011**, *50*, 713.

[203] C. H. Ke, J. Li, K. Y. Fang, Q. L. Zhu, J. Zhu, Q. Yan, Y. Z. Wang, *Polym. Degrad. Stab.* **2010**, *95*, 763.

[204] H. Zhu, Q. Zhu, J. Li, K. Tao, L. Xue, Q. Yan, *Polym. Degrad. Stab.* **2011**, *96*, 183.

[205] Y. Woo, D. Cho, *Adv. Compos. Mater* **2013**, *22*, 451.

[206] B. Nekhamanurak, P. Patanathabutr, N. Hongsriphan, *Energy Proced.* **2014**, *56*, 118.

[207] K. Piekarska, P. Sowinski, E. Piorkowska, M. M. U. Haque, M. Pracella, *Comp. Part A: Appl. Sci. Manufact.* **2016**, *82*, 34.

[208] Y. F. Shih, C. C. Huang, *J. Polym. Res.* **2011**, *18*, 2335.

[209] Kaiser, M. R., & Anuar, H. *Int. Conf. Chem. Eng. (ICChE 2011)* **2011**, pp. 29–30.

[210] T. Sango, G. Stoclet, N. Joly, A. Marin, A. M. C. Yona, L. Duchatel, et al., *Eur. Polym. J.* **2019**, *112*, 466.

[211] R. Kumar, M. K. Yakabu, R. D. Anandjiwala, *Comp. Part A: Appl. Sci. Manufact.* **2010**, *41*, 1620.

[212] A. Arias, M. C. Heuzey, M. A. Huneault, *Cellulose* **2013**, *20*, 439.

[213] I. M. De Rosa, A. Iannoni, J. M. Kenny, D. Puglia, C. Santulli, F. Sarasini, A. Terenzi, *Polym. Compos.* **2011**, *32*, 1362.

[214] Y. Du, T. Wu, N. Yan, M. T. Kortschot, R. Farnood, *Composites, Part B* **2014**, *56*, 717.

[215] E. E. M. Ahmad, A. S. Luyt, *Polym. Compos.* **2012**, *33*, 1025.

[216] O. Gil-Castell, J. D. Badia, T. Kittikorn, E. Strömberg, A. Martinez-Felipe, M. Ek, et al., *Polym. Degrad. Stab.* **2014**, *108*, 212.

[217] S. Qian, K. Sheng, K. Yu, L. Xu, C. A. F. Lopez, *J. Mater. Sci.* **2018**, *53*, 10920.

[218] K. Sheng, S. Zhang, S. Qian, C. A. F. Lopez, *Composites, Part B* **2019**, *165*, 174.

[219] R. Scaffaro, F. Lopresti, L. Botta, *Comp., Part B* **2018**, *139*, 1.

[220] S. Qian, K. Sheng, *Comp. Sci. Technol.* **2017**, *148*, 59.

[221] E. Lezak, Z. Kulinski, R. Masirek, E. Piorkowska, M. Pracella, K. Gadzinowska, *Macromol. Biosci.* **2008**, *8*, 1190.

[222] L. Chen, Y. Z. Wang, *Polym. Adv. Technol.* **2010**, *21*, 1.

[223] W. Chen, P. Liu, Y. Liu, Q. Wang, *Polym. Chem.* **2015**, *6*, 4409.

[224] R. Masirek, Z. Kulinski, D. Chionna, E. Piorkowska, M. Pracella, *J. Appl. Polym. Sci.* **2007**, *105*, 255.

[225] Z. Lei, W. Xing, J. Wu, G. Huang, X. Wang, L. Zhao, *J. Therm. Anal. Calorim.* **2014**, *116*, 447.

[226] S. J. Sheng, F. Wang, Q. Y. Ma, X. Hu, *J. Therm. Anal. Calorim.* **2015**, *122*, 1077.

[227] F. Wang, G. Guo, Q. Ma, M. Gu, X. Wu, S. Sheng, X. Wang, *J. Therm. Anal. Calorim.* **2013**, *113*, 1113.

[228] C. M. C. Pereira, M. S. S. Martins, Flame retardancy of fiber-reinforced polymer composites based on nanoclays and carbon nanotubes. in *Polymer Green Flame Retardants*, Elsevier, United states **2014**, p. 551.

[229] A. Verma, V. K. Singh, M. Arif, *Res. Rev.: J. Mater. Sci.* **2016**, *4*, 1.

[230] M. R. Y. Hamid, M. H. Ab Ghani, S. Ahmad, *Indus. Crops Prod.* **2012**, *40*, 96.

[231] A. Dumitrascu, B. A. Howell, *Polym. Degrad. Stab.* **2012**, *97*, 2611.

[232] T. R. Hull, R. J. Law, Å. Bergman, Environmental drivers for replacement of halogenated flame retardants. in *Polymer Green Flame Retardants*, Elsevier, United states **2014**, p. 119.

[233] M. Kannan, S. Thomas, K. Joseph, *J. Vinyl Addit. Technol.* **2017**, *23*, E72.

[234] M. Si, J. Feng, J. Hao, L. Xu, J. Du, *Polym. Degrad. Stab.* **2014**, *100*, 70.

[235] F. Yang, Fire-retardant carbon-fiber-reinforced thermoset composites. in *Novel Fire Retardant Polymers and Composite Materials*, Woodhead Publishing, Sawston, Cambridge **2017**, p. 271.

[236] V. Cádiz, J. C. Ronda, G. Lligadas, M. Galià, Polybenzoxazines with Enhanced Flame Retardancy. in *Handbook of Benzoxazine Resins*, Elsevier, United states **2011**, p. 556.

[237] S. Rabe, Y. Chuenban, B. Schartel, *Materials* **2017**, *10*, 455.

[238] K. A. Salmeia, J. Fage, S. Liang, S. Gaan, *Polymer* **2015**, *7*, 504.

[239] S. Fu, P. Song, X. Liu, Thermal and flame retardancy properties of thermoplastics/natural fiber biocomposites. in *Advanced High Strength Natural Fibre Composites in Construction*, Woodhead Publishing, Sawston, Cambridge **2017**, p. 479.

[240] M. Gao, S. Yang, *J. Appl. Polym. Sci.* **2010**, *115*, 2346.

[241] J. Zhan, L. Wang, N. Hong, W. Hu, J. Wang, L. Song, Y. Hu, *Polym.-Plast. Technol. Eng.* **2014**, *53*, 387.

[242] W. P. Lim, M. Mariatti, W. S. Chow, K. T. Mar, *Composites, Part B* **2012**, *43*, 124.

[243] K. Wu, Y. Zhang, W. Hu, J. Lian, Y. Hu, *Comp. Sci. Technol.* **2013**, *81*, 17.

[244] L. T. Sin, *Polylactic Acid: PLA Biopolym. Technol. Appl.*, William Andrew, Oxford, UK **2012**.

[245] Z. Guo, L. Zhao, Z. Fang, *Fire Mater.* **2017**, *41*, 916.

[246] Y. Q. Pan, Z. H. Guo, S. Y. Ran, Z. P. Fang, D. Gao, Y. F. Cai, H. Y. Shen, Y. He, *Exp. Polym. Lett.* **2019**, *13*, 835.

[247] I. Van der Veen, J. de Boer, *Chemosphere* **2012**, *88*, 1119.

[248] B. Wang, H. Sheng, Y. Shi, W. Hu, N. Hong, W. Zeng, et al., *Polym. Degrad. Stab.* **2015**, *113*, 96.

[249] Q. T. Shubhra, A. K. M. M. Alam, M. A. Khan, M. Saha, D. Saha, M. A. Gafur, *Comp. Part A: Appl. Sci. Manufact.* **2010**, *41*, 1587.

[250] C. Chen, X. Gu, X. Jin, J. Sun, S. Zhang, *Carbohydr. Polym.* **2017**, *157*, 1586.

[251] G. Marosi, P. Anna, I. Csontos, A. Márton, G. Bertalan, New reactive additives for interface modification in multicomponent polyolefin systems. in *Macromolecular Symposia*, Vol. 176, No. 1, WILEY-VCH Verlag GmbH, Weinheim **2001**, p. 189.

[252] O. Faruk, A. K. Bledzki, H. P. Fink, M. Sain, *Prog. Polym. Sci.* **2012**, *37*, 1552.

[253] M. Rakotomalala, S. Wagner, M. Döring, *Materials* **2010**, *3*, 4300.

[254] H. Lu, L. Song, Y. Hu, *Polym. Adv. Technol.* **2011**, *22*, 379.

[255] L. A. Hollingbery, T. R. Hull, *Polym. Degrad. Stab.* **2010**, *95*, 2213.

[256] L. A. Hollingbery, T. R. Hull, *Thermochim. Acta* **2010**, *509*, 1.

[257] N. H. Huang, Z. J. Chen, C. H. Yi, J. Q. Wang, *Exp. Polym. Lett.* **2010**, *4*, 227.

[258] Lim, S. H., Lee, M. W., Teo, W. S., Juay, Y. K., & Dasari, A. (**2011**). On the flame retardancy of PLA-based nanocomposites. SIM Tech technical reports (STR_V12_N2_01_FTG) *12*, 48–53.

[259] S. Solarski, M. Ferreira, E. Devaux, G. Fontaine, P. Bachelet, S. Bourbigot, R. Delobel, P. Coszach, M. Murariu, A. Ferreira, M. Alexandre, P. Degee, P. Dubois, *J. Appl. Polym. Sci.* **2008**, *109*, 841.

[260] S. Zhang, A. R. Horrocks, *Prog. Polym. Sci.* **2003**, *28*, 1517.

[261] L. Costes, F. Laoutid, S. Brohez, P. Dubois, *Mater. Sci. Eng.: R: Rep.* **2017**, *117*, 1.

[262] Y. Xiao, Y. Zheng, X. Wang, Z. Chen, Z. Xu, *J. Appl. Polym. Sci.* **2014**, *131*, 1.

How to cite this article: Yiga VA, Lubwama M, Pagel S, Benz J, Olupot PW, Bonten C. Flame retardancy and thermal stability of agricultural residue fiber-reinforced polylactic acid: A Review. *Polymer Composites*. 2020;1–30. https://doi.org/10.1002/pc.25835