Nigerian Research Journal of Engineering and Environmental Sciences 7(1) 2022 pp. 1-8
p ISSN: 2635-3342; e ISSN: 2635-3350

Nigerian Research Journal of Engineering and Environmental Sciences
Journal homepage: www.rjees.com

Original Research Article

Differential Scanning Calorimetry Analysis of Untreated and Treated Poly (Lactic Acid)/Guinea Corn (*Sorghum bicolor*) Husk Particulate Bio-Composites

***[1,2]Shehu, U., [2]Mat Taib, R., [3]Ishiaku, U.S., [1]Aponbiede, O. and [1]Ause, T.**

[1]Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria, Nigeria.
[2]School of Materials and Mineral Resources Engineering, Engineering Campus Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
[3]Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria, Nigeria.
*mrshehu53@gmail.com

http://doi.org/10.5281/zenodo.6720046

ARTICLE INFORMATION

Article history:
Received 12 Apr, 2022
Revised 07 Jun, 2022
Accepted 10 Jun, 2022
Available online 30 Jun, 2022

Keywords:
Poly (lactic acid)
Guinea corn husk particulate
Differential scanning calorimetry
Glass transition temperature
Melting temperature

ABSTRACT

In response to the environmental concerns posed by synthetic non-degradable polymeric packaging materials, efforts are being devoted to developing bio-degradable packaging materials that are based on green and sustainable resources. As a class of green materials, poly (lactic acid) (PLA) has received extensive attention. In this work, PLA was filled with guinea-corn (Sorghum bicolor) husk particulates (GHP) to produce biocomposites, and thereafter analysed by differential scanning calorimetry (DSC). The plain PLA was plasticized by Biomax strong (PLABM). Formulations of the composites were produced with untreated GHP and those treated with sodium hydroxide, 3-aminopropyltriethoxysilane and a combination of both treatments varying the filler composition from 10 to 40 wt% at 10 wt% interval. This was achieved by melt-mixing using extrusion and pelletizing followed by injection moulding. The composites produced were subjected to DSC thermal analysis. Result of the analysis reveals that the glass transition temperature (Tg) of PLABM was 60 °C and its melting temperature (Tm) was 150 °C. The degree of crystallinity was found to be 12.66%. It was also observed that percentage GHP loading of the composite does not substantially affect its processing temperature. The composites produced were bio-degradable and suitable for short-term use or indoor application.

1. INTRODUCTION

Synthetic polymeric packages have been extensively used globally because of their desirable chemical, physical and mechanical properties (Singhvi *et al*., 2019). They are widely used in various forms and serve

many vital roles in virtually all spheres of human endeavor; which makes day-to-day life without them almost impossible to imagine (Shehu, 2015; Domínguez *et al*., 2018; Beleška *et al*., 2019).

A close observation of the environment today, presents the various forms of these plastic-package wastes, which are scattered almost everywhere. Some of these items include packaged-water sachets, take-away packs, disposable-plastic cups and spoons, empty plastic-containers for water and soft drinks. These polymeric materials all have one thing in common, which is; they are all used and discarded immediately. Efforts to control the menace of these pollutants in the environment by adopting the 3Rs (recycle, reuse and remove) have not been very effective (Navalgund, 2020). There is therefore, the need to find a lasting solution to the problems posed by these materials that are used for a short period of time and discarded almost immediately after use. The reason these materials constitute nuisance to the environment after they are used and discarded is because they are derived from non-bio-degradable petroleum resources that persist for many years in the environment after their disposal; thereby raising concern of negative impact on the environment (Shehu, 2015).

To salvage the situation, research effort is directed towards the development of bio-based materials. One of the most interesting bio-based polymers is poly (lactic acid) (PLA). It is an aliphatic polyester which is made from plants and is readily bio-degradable. It was developed to serve as an alternative to conventional polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) (Nofar *et al.*, 2018; Hamad *et al.*, 2018; Djukić-Vuković *et al.*, 2019; Gavril *et al.*, 2019). In general, PLA is synthesized by ring-opening polymerization of lactide and lactic acid monomers, which are obtained from the fermentation of sugar beet, corn, sugarcane and potato (Singhvi *et al*., 2019; Djukić-Vuković *et al*., 2019; Kalelkar and Collard, 2020).

Agricultural crop residues such as corn-cob, oil-palm leaves, palm-kernel shell, coconut coir and shell, pineapple leaf, banana leaves, sugarcane bagasse, rice husk, guinea corn husk/stalk, wheat straw and empty fruit bunch are produced in billions of tonnes around the world (Kamusoko *et al*., 2019). They can be obtained in abundance, low cost and are renewable sources of biomass. Among these large amount of residues, only a small quantity is applied as household fuel or fertilizer while another little portion is consumed by animals and the rest which is the major portion of the residues is either left to rot on the farmlands or burned in the field (Shehu, 2015). As a result, it gives a negative effect on the environment due to the air pollution it generates (Pasukphun, 2018). The vital alternative to solve this problem is to use the agricultural residues as reinforcement in the development of polymer composites. A viable solution is to use the entire residues as natural fillers/fibers and combine them with polymer matrices derived from petroleum or renewable resources to produce a useful product for daily applications (Shehu, 2015).

Guinea corn is a cereal crop which is grown in different parts of the world such as the United States, India, Nigeria, Argentina, China and Ethiopia (Mundia *et al*., 2019). Nigeria is the largest sorghum producer in West Africa, accounting for about 71% of the total regional sorghum output (Toyin *et al.*, 2017). Nigeria's sorghum production also accounted for 35% of the African production in 2007 (Garba *et al*., 2017). The country is the third largest world producer after the United States and India (Adeola *et al*., 2017). However, 90% of sorghum produced by United States and India is used as animal feed, making Nigeria the world leading country for food grain sorghum production. In Nigeria, sorghum is the third cereal in terms of production after maize and millet (Mundia *et al*., 2019) with about 6.9 million tonnes harvested in 5.4 million hectares annually (Ahmad Yahaya et al., 2022). It is the primary food crop in virtually all the Northern part of the Nigeria (Maiadua *et al*., 2017).

Thermal analysis of polymers is an important technique used to understand the structure–property relation and mastering the technology for industrial production of different polymeric materials, especially fiber-reinforced composites. Moreover, it is a useful technique to determine the thermal stability of the materials, especially with the processing conditions in mind (Sheng *et al*., 2019; Demarest *et al*., 2020). It is a group of techniques in which the physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program (Durowoju *et*

al., 2017). Differential scanning calorimetry (DSC) is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. A number of important physical changes in a polymer may be measured by DSC. These include the glass transition temperature (Tg), the crystallization temperature (Tc), the melt temperature (Tm) and the degradation or decomposition temperature (TD). This work is aimed at the DSC analysis of biodegradable composite referred to as green composites or bio-composites based on PLA and GHP.

2. MATERIALS AND METHODS

2.1. Materials and Equipment

The materials used during the course of this research include poly(lactic acid) grade 3051D from Nature works (USA), Guinea corn husks particles (GHP) from Zaria, Nigeria, 3-Aminopropyltriethoxysilane (3-APS) cat.44,014-0 Lot: 12100 from Sigma Aldrich, Germany, Sodium hydroxide (NaOH) BP pellets, Acetic acid (glacial) 100% AOS, ISO, methanol, Plastic containers, Laboratory trays, Hand gloves, Nose masks, Biomax strong 100 from Nature Works (USA), Laboratory sized mini-crusher, Precision weighing balance (0.00001g), Brabender Single Screw Extruder model 837420, Granulator (Pelletizer) model 881207, Injection Moulding Machine model BOY 22M, Binder Humidity Chamber model KBF240 and Mettle Toledo Differential Scanning Calorimeter.

2.2. Methods

2.2.1. Preparation of guinea corn husks particulates

The Guinea corn stalk (after the removal of the edible cereals) were gathered from the local farmers in Zaria, Kaduna State, Nigeria after the harvest period (November -December, 2020) and the husks removed manually. The husks were then washed thoroughly with water and detergent solution to remove all forms of dirt including stones, dried and subsequently ground in a mini crusher having a sieve of 0.5mm attached to its outlet. The particulates were then oven dried at 105 °C for 24 h and then stored before embarking on further processes. To remove volatile materials, the particulates were soaked in hot water for 24 h, washed and dried in air and subsequently oven dried at 105°C for 24 h. The particulates were designated as untreated (UNTRD). The untreated particulates were treated with sodium hydroxide (NaOH) solution, 3-Aminopropyltriethoxysilane (3-APS) coupling agent and a combination of both treatments.

2.2.2. Alkali (ALK) treatment

The untreated particulates were treated with 5% sodium hydroxide solution for 24 h at room temperature after which it was washed with distilled water until all the NaOH was eliminated (Shehu, 2015). A little quantity of acetic acid was added to help in the quick neutralization process. This was confirmed by using a pH meter which showed neutral state of 7.2. After washing, the particulates were kept in air for 2 days to dry before oven drying at 105 °C for 6 h.

2.2.3. Silane (SIL) treatment

The untreated particulates were also treated with 3% of 3-Aminopropyltriethoxysilane silane coupling agent. This was achieved by first hydrolysing the silane coupling agent in a methanol/water mixture in the ratio 50/50. The pH of the mixture was adjusted to 4.5 by adding a small quantity of acetic acid. The whole mixture was stirred before introducing the particulates into the mixture and left for 3 h. The particulates were then removed, washed and kept in air for 2 days before oven drying at 105 °C for 6 h.

2.2.4. Combination of alkali and silane (ALKSIL) treatment

The untreated particulates were first treated with sodium hydroxide solution as described earlier in the alkali treatment section, followed by treatment with silane coupling agent as described in the silane treatment section. After the treatments, the particulates were placed in plastic bags, sealed and stored in a desiccator before further processing.

2.2.5. Compounding of composite materials

Four formulations were prepared for compounding; the PLA was first blended with Biomax strong 100 (BM) plasticizer of about 5% by weight. The Guinea-corn husks particulates (GHP) (untreated and treated) were oven dried at 80 °C for 6 h, the blended PLA were dried at 55 °C for 4 h. The compositions of GHP were varied from 10 – 40 wt.% in an interval of 10 wt.%. The compounding was accomplished for all the formulations using a Brabender single screw extruder with the following temperature profiles from hopper to nozzle:

PLA/Biomax (PLABM)/GHP: 160°C/ 175°C/ 175°C/ 165°C; screw speed 40rpm

The mixture of resin and particulates were introduced into the hopper of the extruder for compounding and subsequently extruded as long strands. The extrudates were collected in a water tank with continuous flow of water which served as a cooling medium. The extrudates were then pelletized using a Brabender granulator.

2.2.6. Injection moulding

The pellets were introduced into a BOY 22M injection moulding machine to produce the standard test samples. The temperature profiles used for the formulations were as follows:

PLA/Biomax(PLABM)/GHP: 145°C /180°C /180°C /165°C

Injection speed was 45: 53: 29 mm/s, injection pressure was 50bar, back pressure was 5 bar, mould temperature was 30 °C and cooling time was 30 s. After moulding, all the test samples were conditioned in a Binder KBF240 Humidity chamber for 40 h at 23 °C and 50% relative humidity prior to testing.

2.2.7. Differential scanning calorimetry

A Perkin-Elmer DSC 6 differential scanning calorimeter was the DSC instrument used to characterize the samples. The instrument was computer-controlled and the calculations were performed using Star^e software. All the analyses were performed under nitrogen flow (20 ml/min). The PLABM/GHP Composite samples were analysed from 25 to 200 ºC at a rate of 10°/min. The samples were heated, cooled, and reheated under the same conditions. Only the second heating scan was used to determine the melting enthalpies and temperatures. The % crystallinity (%Xc) of PLABM and its composites was evaluated using the following equation:

$$\%Xc = \left(\frac{\Delta Hm}{\Delta H^{\circ}\left(1-\frac{\%\, wt.filler}{100}\right)}\right) \times 100 \quad (1)$$

where ΔHm is the melting enthalpy (from second heating scan), ΔH° is the melting enthalpy of a 100% crystalline PLA (93.0J/g) (Battegazzore *et al.*, 2014) and % wt. filler is the filler weight percentage.

3. RESULTS AND DISCUSSION

The DSC curves of PLABM and its composites are shown in Figures 1 – 5 and the DSC data are summarized in Table 1. From Figures 1 – 5, it could be seen that addition of GHP did not affect the glass transition temperature (Tg) and melting temperature (Tm) as there was no substantial changes observed. Similar observation was reported previously (Erbas Kiziltas *et al.*, 2016; Thomas *et al.*, 2019). It was also observed that the peaks of the crystallization temperature (Tc) were most pronounced with the SIL treated composites (Figure 4) while these peaks were almost absent in the ALKSIL treated composites (Figure 5). On a general note, the Tc broadened, decreased in peak size and shifted to higher temperatures with GHP loading.

Table 1 showed that the Tg of PLABM was 60 °C and Tm was 150 °C and the degree of crystallinity was 12.66%. The low degree of crystallinity exhibited by PLABM could be either because the PLA was amorphous or that the plasticizer used may have decreased the molecular segmental mobility of PLA thereby reducing the ability of PLA to crystallize during processing (Razavi and Wang, 2019; Pascual-Jose *et al.*, 2021). The melting temperature of Biomax strong was not observed in the DSC curves probably because the

heat flow associated with the melting of the plasticizer was too low to be detected by the equipment. This was also the observation made by (Srithep and Pholharn, 2017).

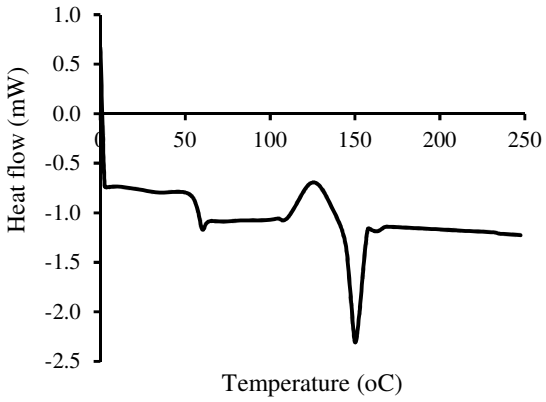

Figure 1: DSC thermogram for unreinforced PLABM

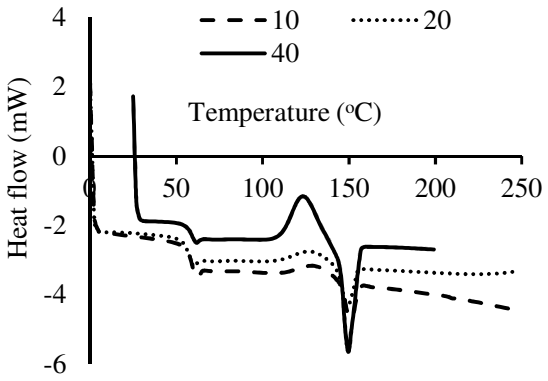

Figure 2: DSC thermogram for UNTRD PLABM/GHP composites

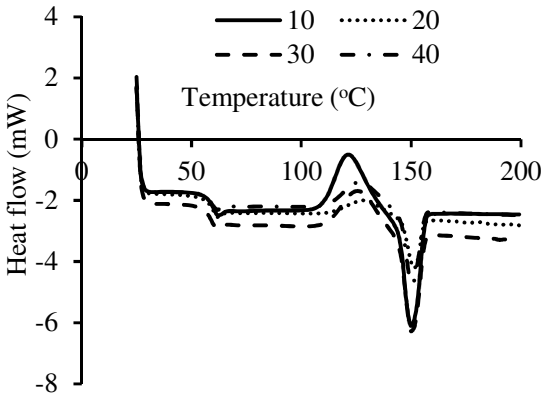

Figure 3: DSC thermogram for ALK treated PLABM/GHP composites

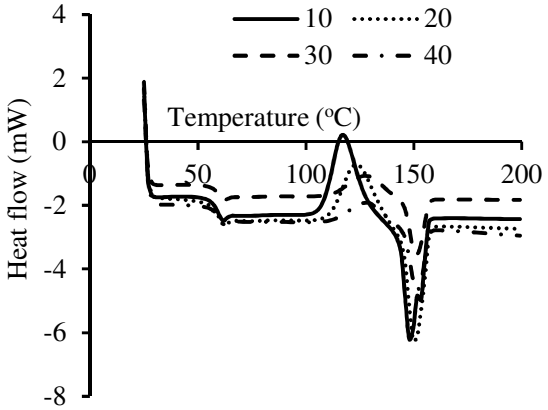

Figure 4: DSC thermogram for SIL treated PLABM/GHP composites

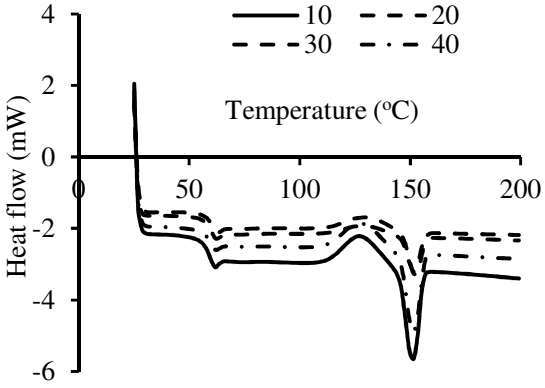

Figure 5: DSC thermogram for ALKSIL treated PLABM/GHP composites

Generally, as observed from Table 1, the degree of crystallinity for treated composites were higher than those for the untreated ones which is also reported by Sang *et al*. (2016). The increase in crystallinity could be ascribed to the enhancement of nucleating effect from the GHP contents due to improved interfacial bonding between the constituents (Sang *et al*., 2016). Fillers are responsible for the increase in PLA crystallinity but the low values obtained in this study could be as a result of interference from the Biomax strong that was used as a plasticizer and the low Xc values indicated less crystallites (Battegazzore *et al*., 2014; Kuciel *et al*., 2019).

Table 1: Summary of DSC data for PLABM/GHP Composites

Specimen	Tg (°C)	Tc (°C)	Tm (°C)	Xc (%)
PLABM	60.00	127.50	150.01	12.66
PLABM/10UGHP	62.50	132.51	150.01	4.46
PLABM/20UGHP	60.00	130.01	150.01	5.25
PLABM/30UGHP	60.00	130.01	150.01	4.03
PLABM/40UGHP	61.67	124.01	149.68	20.66
PLABM/10AGHP	61.67	122.18	149.68	20.56
PLABM/20AGHP	61.67	129.51	149.68	8.88
PLABM/30AGHP	61.67	127.68	151.51	18.66
PLABM/40AGHP	61.67	127.68	149.68	18.98
PLABM/10SGHP	61.67	118.51	149.68	24.20
PLABM/20SGHP	61.67	124.011	147.85;153.35	22.32
PLABM/30SGHP	61.67	129.51	149.68	9.18
PLABM/40SGHP	63.53	129.51	151.51	14.19
PLABM/10ASGHP	61.67	127.68	151.51	11.42
PLABM/20ASGHP	61.67	129.51	151.51	6.04
PLABM/30ASGHP	63.50	131.34	151.51	8.29
PLABM/40ASGHP	61.67	129.51	151.51	15.60

U: Untreated; A: Alkali-treated; S: Silane treated; AS: Alkali and Silane treated; GHP: Guinea-corn husk particulate; PLABM: PLA/Biomax strong

4. CONCLUSION

The research focused on the DSC analysis of PLA/GHP composites produced using single screw extruder for compounding and injection moulding for production. At the end of the study, the following conclusions were drawn based on the results obtained:

1. PLA/GHP composites of different formulations were successfully produced.
2. The glass transition temperature (Tg) of PLABM was found to be 60°C.
3. The melting temperature (Tm) of PLABM was 150°C.
4. The percentage crystallinity of PLABM was found to be 12.66%
5. The melting temperature of biomax strong was not observed in the DSC curves.
6. The addition of GHP to PLABM did not substantially affect the Tg and Tm of the composites.
7. The degree of crystallinity of the treated composites were higher than those of the untreated ones.
8. The composites produced were stable at their processing temperatures during compounding and injection moulding processes.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

Adeola, A.A., Shittu, T.A., Onabanjo, O.O., Oladunmoye, O.O. and Abass, A. (2017). Evaluation of nutrient composition, functional and sensory attributes of sorghum, pigeonpea and soybean flour blends as complementary food in Nigeria. *Agronomie Africaine*, 29(2), pp. 47 – 58.

Ahmad Yahaya, M., Shimelis, H., Nebie, B., Ojiewo, C. O. and Danso-Abbeam, G. (2022). Sorghum production in Nigeria: opportunities, constraints, and recommendations. *Acta Agriculturae Scandinavica, Section B—Soil & Plant Science*, *72*(1), pp. 660-672.

Battegazzore, D., Bocchini, S., Alongi, J. and Frache, A. (2014). Plasticizers, antioxidants and reinforcement fillers from hazelnut skinand cocoa by-products: Extraction and use in PLA and PP. *Polymer Degradation and Stability*, 108, pp. 297-306.

Beleška, K., Valeika, V., Jankauskaite, V. and Valeikiene, V. (2019). Properties of films prepared as packaging plastics from blends of synthetic polymer and biopolymer. *Defect and Diffusion Forum*, 394, pp. 85–89.

Demarest, S. J. and Frasca, V. (2020). Differential scanning calorimetry in the biopharmaceutical sciences. In *Biophysical characterization of proteins in developing biopharmaceuticals*, pp. 311–332.

Djukić-Vuković, A., Mladenović, D., Ivanović, J., Pejin, J. and Mojović, L. (2019). Towards sustainability of lactic acid and poly-lactic acid polymers production. *Renewable and Sustainable Energy Reviews*, 108, pp. 238–252.

Domínguez, R., Barba, F. J., Gómez, B., Putnik, P., Bursać Kovačević, D., Pateiro, M. and Lorenzo, J. M. (2018). Active packaging films with natural antioxidants to be used in meat industry: A review. *Food Research International*, 113, pp. 93–101.

Durowoju, I. B., Bhandal, K. S., Hu, J., Carpick, B. and, Kirkitadze, M. (2017). Differential scanning calorimetry — A method for assessing the thermal stability and conformation of protein antigen. *Journal of Visualized Experiments*, 121, pp. 1 – 8.

Erbas Kiziltas, E., Yang, H.-S., Kiziltas, A., Boran, S., Ozen, E. and Gardner, D. J. (2016). Thermal analysis of polyamide 6 composites filled by natural fiber blend. *BioResources*, 11(2), pp. 4758 – 4759.

Garba, M.H., Makun, H.A., Jigam, A.A., Muhammad, H.L. and Patrick, B.N. (2017). Incidence and toxigenicity of fungi contaminating sorghum from Nigeria. *World Journal of Microbiology*, 4(2), pp. 105 – 114.

Gavril, G.L., Wrona, M., Bertella, A., Świeca, M., Râpă, M., Salafranca, J., Nerín, C. (2019). Influence of medicinal and aromatic plants into risk assessment of a new bioactive packaging based on polylactic acid (PLA). *Food and Chemical Toxicology*, 132, pp. 110662.

Hamad, K., Kaseem, M., Ayyoob, M., Joo, J. and Deri, F. (2018). Polylactic acid blends: The future of green, light and tough. *Progress in Polymer Science*, 85, pp. 83–127.

Kalelkar, P. P. and Collard, D. M. (2020). Tricomponent Amphiphilic Poly(oligo(ethylene glycol) methacrylate) Brush-Grafted Poly(lactic acid): Synthesis, nanoparticle formation, and in vitro uptake and release of hydrophobic dyes. *Macromolecules*. 53(11), pp. 4274–4283.

Kamusoko, R., Jingura, R. M., Parawira, W. and Sanyika, W. T. (2019). Comparison of pretreatment methods that enhance biomethane production from crop residues-a systematic review. *Biofuel Research Journal*, *6*(4), pp. 1080.

Kuciel, S., Mazur, K. and Jakubowska, P. (2019). Novel biorenewable composites based on poly (3-hydroxybutyrate-co-3-hydroxyvalerate) with natural fillers. *Journal of Polymers and the Environment*, 27, pp. 803–815.

Maiadua, U., Suhasin, K., Jainuddin, S.M. and Sadiq, M.S. (2017). Acreage response of sorghum to price and non-price factors in Nigeria: an evidence from Nerlove adjustment model. *SKUAST Journal of Research.* 19(1), pp. 115 – 120

Mundia, C. W., Secchi, S., Akamani, K. and Wang, G. (2019). A regional comparison of factors affecting global sorghum production: The case of North America, Asia and Africa's sahel. *Sustainability*, 11(7), pp. 2135.

Navalgund, R. (2020). Reduce, reuse and recycle: an environmental law approach to long-term sustainability of outer space. *Air and Space Law*, *45*(3), pp. 285 – 308.

Nofar, M., Sacligil, D., Carreau, P. J., Kamal, M. R. and Heuzey, M.C. (2018). Poly (lactic acid) blends: Processing, properties and applications. *International Journal of Biological Macromolecules*, 1, pp. 1 – 12.

Pascual-Jose, B., Badia, J. D., Múgica, A., Addiego, F., Müller, A. J. and Ribes-Greus, A. (2021). Analysis of plasticization and reprocessing effects on the segmental cooperativity of polylactide by dielectric thermal spectroscopy. *Polymer*, *223*, pp. 123701.

Pasukphun, N. (2018). Environmental health burden of open burning in northern Thailand: A review. *PSRU Journal of Science and Technology*, 3(3), pp. 11-28.

Razavi, M. and Wang, S. Q. (2019). Why is crystalline poly (lactic acid) brittle at room temperature? *Macromolecules*, *52*(14), pp. 5429-5441.

Sang, L., Wang, Y., Chen, G., Liang, J. and Wei, Z. (2016). A comparative study of the crystalline structure and mechanical properties of carbon fiber/polyamide 6 composites enhanced with/without silane treatment. *RSC Advances*, 6(109), pp. 107739–107747.

Shehu, U. (2015). Development and characterisation of poly (lactic acid) (PLA)/guinea corn (sorghum bicolor) husks particulate (GHP) composites, Unpublished Doctoral Thesis, Ahmadu Bello University, Zaria. pp. 14 – 33.

Sheng, M., Valco, D., Tucker, C., Cayo, E., Lopez, T. (2019). Practical use of differential scanning calorimetry for thermal stability hazard evaluation. *Organic Process Research and Development*, 23 (10), pp. 2200–2209.

Singhvi, M. S., Zinjarde, S. S. and Gokhale, D. V. (2019). Polylactic acid: synthesis and biomedical applications. *Journal of applied microbiology*, *127*(6), pp. 1612-1626.

Srithep, Y. and Pholharn, D. (2017). Plasticizer effect on melt blending of polylactide stereocomplex. *e-Polymers*, 17(5), pp. 1 – 9.

Thomas, S., Shumilova, A. A., Kiselev, E. G., Baranovsky, S. V., Vasiliev, A. D., Nemtsev, I. V. and Volova, T. G. (2019). Thermal, mechanical and biodegradation studies of biofiller based poly-3-hydroxybutyrate biocomposites. *International Journal of Biological Macromolecules*, 155, pp. 1373-1384.

Toyin, B. A., Opeyemi, E. A., Abdoulaye, T. and Ada Ojoko, E. (2017). Analysis of the impact of selected economic variables on sorghum prices in Nigeria. *Journal of Agribusiness and Rural Development*, 46(4), pp. 723–729.