Mechanical performance of GNP/PLA nanocomposite under varied SPS process parameters

Mechanical performance of GNP/PLA nanocomposite under varied SPS process parameters

OT Adesina [1]. T Jamiru [1]. ER Sadiku [2]. MO Durowoju[3]. OF Ogunbiyi [1]

[1]Department of Mechanical Engineering, Mechatronics and Industrial Design, Tshwane University of Technology, Pretoria South Africa
[2]*Institute of NanoEngineering Research (INER) and Department of Chemical Metallurgy and Materials Engineering, Tshwane University of Technology Pretoria, South Africa*
[3]*Department of Mechanical Engineering, Ladoke Akintola University of Technology, Nigeria.*
Corresponding author*. Tel (+27) 651073608
E-mail: oluwagbengaadesina@yahoo.com

Abstract
The study examines the mechanical performance of GNP/PLA nanocomposite developed under varied SPS process parameters. The samples were fabricated using a novel Spark Plasma Sintering technique. In this research, the effect of sintering process in terms of sintering pressure and temperature has been studied by focusing on the mechanical properties of GNP/PLA nanocomposites. The densification of the samples was obtained via the Archimedes' principle while hardness results was obtained using the micro hardness tester. The results show that the density and hardness increased with increasing sintering temperature and pressure. The samples were prepared under uniaxial pressure of 20 MPa and 30 MPa. The sintering temperature of 135 $^{\circ}$C and 160 $^{\circ}$C was used in developing the samples. The synergetic influence of these process parameters and graphene inclusion was significant in obtaining above 99% densification and with a concurrent enhancement in the hardness property of the developed composite.

Keywords: polylactic acid, graphene, nanocomposite, densification, hardness

1. Introduction

The ecological and environmental friendliness of bio-based composite has attracted major researchers in recent times. This is in a bid to mitigate the implication of petroleum based material on human, environment and ecological lives. In addition to the need to reduce the over dependency on petroleum resources that is continuously depleting. The use of bio degradable polymer plays an important role in solving public hazards of polymer materials and maintaining ecological balance [1]. However, the application of polylactic acid can be found in packaging, textiles, engineering and biomedical applications, hereby rising to the second place in terms of global demand after starch based plastics in the bio-based plastic category [2].
Poly(lactic) acid is a fully bio-based polymer sourced via the fermentation of agricultural products such as corn, potato and sugar beets. Its basis of attractiveness is own to its biodegradability, recyclability

and composability. Its production also consumes carbon dioxide [3,4 &5]. In addition, its requires 25-55% less energy to produce compare to the petroleum based polymers [6]. It is known for its good mechanical properties, excellent barrier capacity and ease of processing in numerous applications. However, it high brittleness, low impact strength, weak thermal stability and water uptake are major drawback for its extended commercial applications [7,8]. The modification and enhancement in the mechanical, physical and thermal properties of poly(lactic) acid is made possible via the use of fibres and fillers as reinforcement in the poly(lactic) acid matrix [9]. The incorporation of nano-sized reinforcement within a polymer matrix produces a nanocomposite material. A polymer nanocomposite refers to multi-phase materials where at least one of the constituent phase which is mostly nano-filler has one dimension in nanoscale range [10,11]. The synergetic effect of reinforcing a biodegradable polymer with nano-fillers compensate for the limitation of the polymer matrix.

The promotion of biopolymer can be viewed in three aspects in terms of its performance, processing and cost. The performance and processing are major issues affecting biodegradable polymers [1]. According to Norazlina et al. [2], the physical, mechanical and barrier properties of PLA depends on the solid state morphology and its crystallinity. The low crystallisation rate and low crystallinity of PLA serves as a major limitation for its extended applications like automotive and electronics [12]. The use of organic or inorganic fillers for reinforcement in polymer matrix serves as heterogeneous nucleating agents to elevate the crystallinity property of PLA [13]. Among the various fillers such as carbon nanotube, clay, graphene(GN) as heterogeneous nucleation is found to be more effective [14,15].

According to the review on the research progress on the preparation of bio-degradation PLA/ Graphene nanocomposites by Li et al. [16], it was inferred that the manufacturing process, technique and appropriate content ratio of graphene played a major influence in improving the properties of the nanocomposites.

Sintering refers to the process of firing and consolidating powders at temperatures lower than their melting point, where diffusional mass transport leads to bonding between particles and the formation of a dense body. Sintering process engages the external pressure and electric field simultaneously to enhance the densification of the powder compact. In SPS, a pulsed direct current is allowed to pass through a conducive die and through the sample. The pulsed direct current produces an electric field during the sintering process [18]. This process is advantageous in producing a highly densified compact within the shortest time, low energy consumption and nano-sized powder can be sintered without considerable grain growth. The stages of SPS occur under applied pressure, increasing temperature and holding time within a short duration of (5-25 min), thereby making control of the microstructure and grain growth achievable mostly in nanostructured materials [17]. The simultaneous application of temperature and pressure in SPS leads to high densification and low porosity can be achieved. This results in outstanding mechanical properties such as strength and hardness [18].

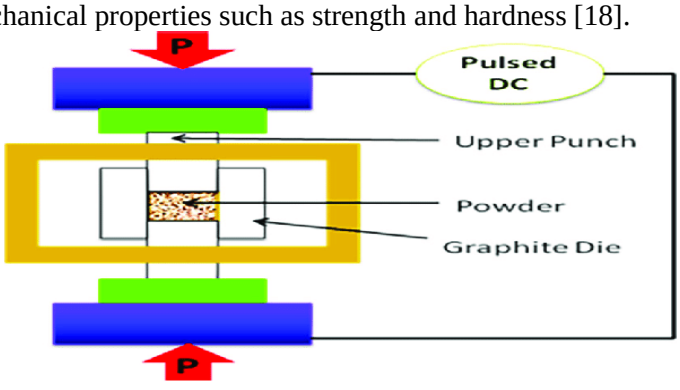

Figure 1: Schematic diagram of spark plasma sintering technique [23]

Several studies on the spark plasma sintering of polymers and polymer composites have emphasised the role of applied pressure and temperature on the mechanical property of sintered compact. Tanaka et al. [19] investigated the wear property of polyimide filled with carbon and diamond particle. The composites were developed using SPS technique. The pressure was set at 50 MPa and a temperature

220°C. At elevated sintering temperature, cracks were noticed and anti- wear properties of the sintered compart deteriorated. Schwertz et al. [20] also worked on the consolidation of polyimide and polyetheretherketone using Spark Plasma sintering technique. Relative densities above 99% was reached for PI at temperature as low as 320 °C and 200 °C for PEEK. The sintered samples show enhancement in the compression strength and hardness property.
This study investigates the influence of process parameters of novel SPS technique on the mechanical performance of graphene reinforced poly(lactic) acid nanocomposite. The parameters of influence in this study are the pressure and temperature while the properties investigated are the density and hardness properties.

2 Experimental Procedure

2.1 Materials
Polylactic acid powder, a Micro Powders, Inc., was used in this study. According to the supplier the melting point was 150-160 °C and the density of 1.23-1.25 g/cm^3. Graphene nanoplatelet from Sigma Aldrish with an average diameter of 5μm and average thickness of 15nm was used. Both materials were used without any further modification or purification.

2.2 Preparation of samples
The sample containing the blend of graphene (GNP) and polylactic acid (PLA) was mixed in a dry environment using Turbula Shaker Mixer T2F for 6hrs for homogeneity and with 5% weight composition of graphene nanoplatelets. The appropriate amount of mixed powders required to produce cylindrical specimen of 10mm thick and 30mm diameter were poured into the graphite die. Graphite sheet were inserted between the graphite die, powders and plungers for easy removal of sintered compact. The admixed powder is then sintered using the Spark Plasma sintering (SPS) machine from FCT Systeme GmbH (Raustein Germany) under varied process parameters. Details can be found in our previous work [21]. GNP/PLA samples were sintered at temperature of 135 °C and 160 °C each under a pressure condition of 20MPa and 30MPa. Figure 2 shows a typical sample of the sintered nanocomposite. This is to investigate the effect of pressure and temperature variation on the density and hardness property of the nanocomposite.

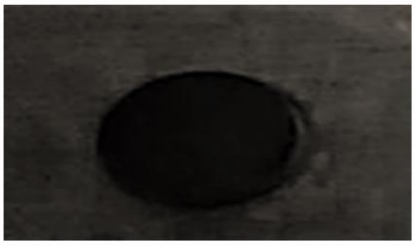

Figure 2: The developed SPSed 30mm diameter and 10 mm thick GNP/ PLA nanocomposites.

2.3 Characterisation
The densities of the sintered samples were determined via the Archimedes principle. The Vickers micro hardness (Hv) at room temperature was measured by the micro hardness tester (Future-tech) at a load (P) 0f 100gf(1.0N) and a dwell time of 15 sec. Arithmetic mean of six successful indentation recorded to ensure accuracy of the data.

3. Experimental results and discussion.
The selection of the temperature values used in this study is based on our previous work [21] where it was observed that below 135 °C, the admixed powders are not consolidated and above 160 °C, the powder melted out of the die in the SPS chamber. In accordance with the information provided by the manufacturer's data sheet, PLA has a melting temperature within the range of (150-160) °C. Also, the sintering of powders must be below the lowest melting point of the powders in the admixture.

Table 1: Density and hardness value of sintered GNP/PLA nanocomposite under different operating parameters

Process Parameters	Notation	Density(g/cm^3)	Hardness(HV)
135 °C, 20 MPa	A	1.278	235.94
135 °C, 30 MPa	B	1.282	243.31
160 °C, 20MPa	C	1.285	257.42
160 °C, 30 MPa	D	1.288	265.00

From the results provided Table 1, for both temperatures (135 and 160) °C, an increase in pressure results in the enhancement in densification which consequently increases the hardness value of the sintered compact. More so, at both pressure conditions, the effect of temperature increase is observed with an increase in both the densification and hardness value of the sintered nanocomposite compact.
The increase in densification is as a result of compressive stress created by the increase pressure which results in improved contacts between the powder particles and a decrease in porosity level due to increase in compaction. Increasing pressure breaks agglomeration, enabling the re arrangement of particles. Thereby removing pores spaces with homogeneous and limited grain growth facilitating increased packing [18,22]. Furthermore, the presence of graphene nanocomposite enhanced the crystallinity property of polylactic acid there improving its hardness property.

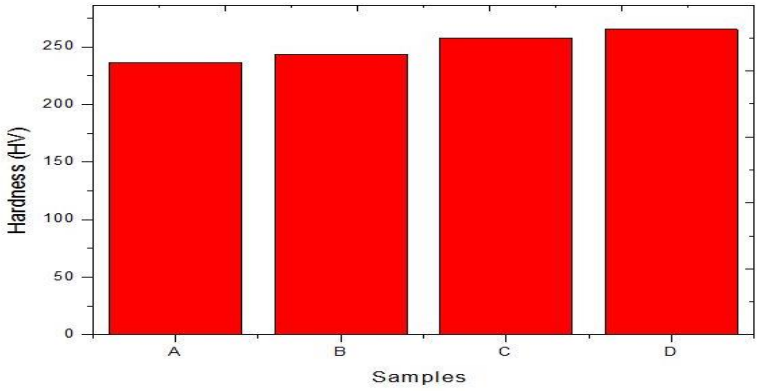

Figure 3: shows the increasing trend of hardness value with respect to varying process parameters.

4. Conclusion

GNP/PLA nanocomposite had been synthesized by Spark plasma sintering technique. The influence of temperature and pressure variation was examined on the density and hardness property of the nanocomposite. The results can be concluded as follows;

1. The density and hardness increases with increase in sintering temperature and pressure within the range of 135-160° C and 20-30 MPa
2. The densification of above 99% were obtained for all the developed nanocomposite which implies a minimal porosity in the material.
3. A developed nanocomposite is of high relevance automobile application based on its light weightiness and eco friendliness. This will help mitigate the rate of carbon emission and other greenhouse gases.
4. The inclusion of graphene nanoplatelets acts as nucleating agent increasing the crystallinity property of the polylactic acid for better mechanical property such as hardness.
5. The process parameters have a major influence on the mechanical performance of the sintered compact.

5. References

[1] Sun, J., Shen, J., Chen, S., Cooper, M., Fu, H., Wu, D. and Yang, Z., 2018. Nanofiller reinforced biodegradable PLA/PHA composites: Current status and future trends. *Polymers*, *10*(5), p.505.

[2] Norazlina, H. and Kamal, Y., 2015. Graphene modifications in polylactic acid nanocomposites: A review. *Polymer Bulletin*, *72*(4), pp.931-961.
[3] Sawyer, D.J., 2003, October. Bioprocessing–no longer a field of dreams. In *Macromolecular symposia* (Vol. 201, No. 1, pp. 271-282). Weinheim: WILEY-VCH Verlag.
[4] Gruber, P.R., Drumright, R.E. and Henton, D.E., 2000. Polylactic acid technology. *Adv. Mater*, *12*, pp.1841-1846.
[5] Dorgan, J.R., Lehermeier, H.J., Palade, L.I. and Cicero, J., 2001, October. Polylactides: properties and prospects of an environmentally benign plastic from renewable resources. In *Macromolecular symposia* (Vol. 175, No. 1, pp. 55-66). Weinheim: WILEY-VCH Verlag GmbH.
[6] Vink, E.T., Rabago, K.R., Glassner, D.A. and Gruber, P.R., 2003. Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. *Polymer Degradation and stability*, *80*(3), pp.403-419.
[7] Bajpai, P.K., Singh, I. and Madaan, J., 2013. Tribological behavior of natural fiber reinforced PLA composites. *Wear*, *297*(1-2), pp.829-840...
[8] Lee, J.T., Kim, M.W., Song, Y.S., Kang, T.J. and Youn, J.R., 2010. Mechanical properties of denim fabric reinforced poly (lactic acid). *Fibers and Polymers*, *11*(1), pp.60-66.
[9] Huda, M.S., Drzal, L.T., Mohanty, A.K. and Misra, M., 2008. Effect of fiber surface-treatments on the properties of laminated biocomposites from poly (lactic acid) (PLA) and kenaf fibers. *Composites science and technology*, *68*(2), pp.424-432.
[10] Hussain F, Hojjati M, Okamoto M, Gorga RE. Review article:polymer–matrix nanocomposites, processing, manufacturing, and application: an overview. Journal of Composite Materials 2006;40:1511–75.
[11] Laoutid F, Bonnaud L, Alexandre M, LopezCuesta JM, Dubois P. New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. Materials Science and Engineering:R 2009;63:100–25.
[12] Rasal, R.M., Janorkar, A.V. and Hirt, D.E., 2010. Poly (lactic acid) modifications. *Progress in polymer science*, *35*(3), pp.338-356..
[13] Yang, B., Wang, D., Chen, F., Su, L.F., Miao, J.B., Chen, P., Qian, J.S., Xia, R. and Liu, J.W., 2019. Melting and Crystallization Behaviors of Poly (Lactic Acid) Modified with Graphene Acting as a Nucleating Agent. *Journal of Macromolecular Science, Part B*, pp.1-15.
[14] Aoyama, S.; Park, Y. T.; Ougizawa, T.; Macosko, C. W. Melt Crystallization of Poly(ethylene Terephthalate): Comparing Addition of Graphene vs. Carbon Nanotubes. Polymer 2014, 55, 2077–2085
[15] Wu, D., Cheng, Y., Feng, S., Yao, Z. and Zhang, M., 2013. Crystallization behavior of polylactide/graphene composites. *Industrial & Engineering Chemistry Research*, *52*(20), pp.6731-6739.
[16] LI, S.H., LIU, J.C., WANG, D.Y., CHEN, Y.W., WEI, H.Z., QIN, Z.M. and JIA, H.M., 2016. Research Progress on Preparation and Performance of Bio-Degradation PLA/Graphene Nanocomposites. *DEStech Transactions on Materials Science and Engineering*, (amst).
[17] KubotaM(2007) Properties of nano-structured pure Al produced by mechanical grinding and spark plasma sintering. J Alloys Compd 434:294–297
[18] Cavaliere, P., Sadeghi, B. and Shabani, A., 2019. Spark Plasma Sintering: Process Fundamentals. In *Spark Plasma Sintering of Materials* (pp. 3-20). Springer, Cham.
[19] Tanaka A, Umeda K, Takatsu S (2004) Friction and wear of diamond-containing polyimide composites in water and air. Wear 257(11):1096–1102.
[20] Schwertz M, Lemonnier S, Barraud E, Carradò A, Vallat MF, Nardin M (2014) Consolidation by spark plasma sintering of polyimide and polyetheretherketone. J Appl Polym Sci 131(18).
[21] Adesina, O.T., Sadiku, E.R., Jamiru, T., Ogunbiyi, O.F., Beneke, L.W. and Adegbola, A.T., 2019. Optimization of SPS processing parameters on the density and hardness properties of graphene reinforced polylactic acid nanocomposite. *The International Journal of Advanced Manufacturing Technology*, pp.1-12.
[22] Munir, Z.A., Anselmi-Tamburini, U. and Ohyanagi, M., 2006. The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. *Journal of Materials Science*, *41*(3), pp.763-777.

Acknowledgement
The authors would like to extend appreciation to Tshwane University of Technology, Pretoria, South Africa for the financial support given through bursary support.