

## **EFFECT OF HOLDING TIME DURING HOT COMPRESSION MOULDING ON MECHANICAL PERFORMANCE OF POLY(3- HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE)**

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**ABSTRACT:** Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biopolymer known for its biodegradable and non-toxic properties. In this study, the PHVB was subjected to various holding times to investigate the influence of thermal exposure on the mechanical performance, crystallinity and morphology of the PHBV. The compression pressure of 25 000 psi at the optimum temperature of 175 °C was used while the holding time was set to 18, 23 and 28 minutes. The results indicate that holding time influences the formation of pores, uniformity of polymer melting, crystallinity, and tensile and flexural properties of the PHVB. The highest tensile strength (22.01 MPa) and Young's modulus (4.9 GPa) and flexural strength and modulus at 70.82 MPa and 21.6 GPa, respectively were obtained when 23 minutes of holding time were used. Morphological analysis through SEM shows the presence of pores and crack propagation, emphasising the impact of holding time on plastic deformation. The study concludes that selecting appropriate

processing conditions is crucial for optimising the performance of PHBV, addressing challenges associated with its narrow processing window.

**KEYWORDS:** *Compression Moulding; Holding Time; Tensile Properties; Degree of Crystallinity; PHVB*

## 1.0 INTRODUCTION

In recent years, a growing interest has been in making environmentally friendly plastic, moving away from the traditional synthetic-based polymer. Biopolymers were invented in the early 1990s as an eco-friendly replacement for petroleum-based polymers, which are produced by microorganisms. Biopolymers are also known as polymeric biomolecules, which are large molecules composed of monomers linked together in a chain-like manner [1]. Biopolymers, such as polyhydroxyalkanoates (PHAs) and polylactic acid (PLA), are derived entirely from sustainable sources [2-4] and are naturally degradable through the enzymatic activity of microorganisms, owing to the presence of oxygen and nitrogen atoms within their chemical composition. Today, the naturally friendly features of PHAs have begun to attract researchers' interest, especially due to their flexibility, which enhances their relevance for various manufacturing applications [5-7]. Among PHAs, polyhydroxybutyrate (PHB) is one of the homopolymers considered the most promising materials currently being produced and assessed. PHB possesses properties similar to those of petroleum-based polymers such as polyethylene (PE) and polypropylene (PP) [6,8]. However, PHB faces significant limitations, including high manufacturing cost, low yield, susceptibility to degradation due to its narrow processing temperature window, and difficulties in microorganism extraction [6-7]. Moreover, PHB has a high crystallinity structure and is thermally unstable, resulting in a stiff and brittle structure [9]. To mitigate this issue,  $\beta$ -hydroxyvaleric acid (HV) was added as a second monomer to PHB aimed to improve its brittleness and stiffness, creating a copolymer known as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). This copolymer exhibits lower crystallinity and improved processability, making it ideal for advanced manufacturing applications.

Despite these improvements, the narrow thermal processing window of biopolymers remains a significant obstacle to replacing synthetic polymers. While PHBV has lower crystallinity compared to PHB, it has better crystallinity and slower nucleation rates compared

to synthetic polymers [10]. However, PHBV is known to rapidly crystallise upon reaching its melting point, particularly at higher temperatures. Due to its rapid crystallisation characteristic, an intrinsic fragility behaviour of PHBV was observed when prolonged exposure to high temperatures [10]. Fabrication parameters, such as processing factors, including temperature, pressure, and processing time, may significantly impact the properties of the polymer in the final products [12-16]. Elevated temperatures or prolonged processing time may result in thermal degradation of the polymer and weaken its strength [17]. While there were a few studies about the manufacturing conditions for PHVB-based products [9-11], however, the data on correlation between the holding time and prolonged thermal exposure on mechanical performance the PHVB PHVB-based materials are still limited.

Thus, this study aims to address this gap by investigating the impact of the holding period under compression pressure and thermal exposure on the mechanical performance of PHBV. This research assesses the performance of the PHBV through physical and mechanical testing as well as their degree of crystallinity upon exposure to high temperatures. By focusing on the holding period, this study aims to enhance PHBV's performance, offering a new option for utilising biopolymers in advanced manufacturing.

## **2.0 MATERIALS AND METHODS**

### **2.1 Materials**

The PHBV powder with 3 mol% of 3-(hydroxyvalerate) (HV) content under the trade name of Enmat Y1000P (TianAn Biopolmer, China) with a density of 1.25 g/cm<sup>3</sup> is used in this study. The melting point of Enmat Y1000P was determined to be 175° through Differential Scanning Calorimetry (DSC) following the guidelines specified in ASTM D3418-12. The Polymers were dried in a drying oven at 60° for at least 4 hours before processing.

### **2.2 Sample Preparation**

The PHBV sample was prepared by placing 75 g powdered PHBV in a closed aluminium mould with dimensions of 200 mm × 100 mm × 3 mm and compressed moulded using a hot press (Carver, USA). The moulding temperature was set at 175°C. The mould was heated from

room temperature and the pressure was increased gradually (Figure 1). At the maximum temperature of 175°C, the compression pressure was maintained under 25 000 psi and the mould was held at different holding times of 18, 23, and 28 minutes (Table 1). The initial 18 minutes of soaking time was used with the reference to [18]. Afterwards, the platen was cooled down to room temperature with the aid of a water-quenching and the samples were kept in a dry cabinet to avoid any humidity.

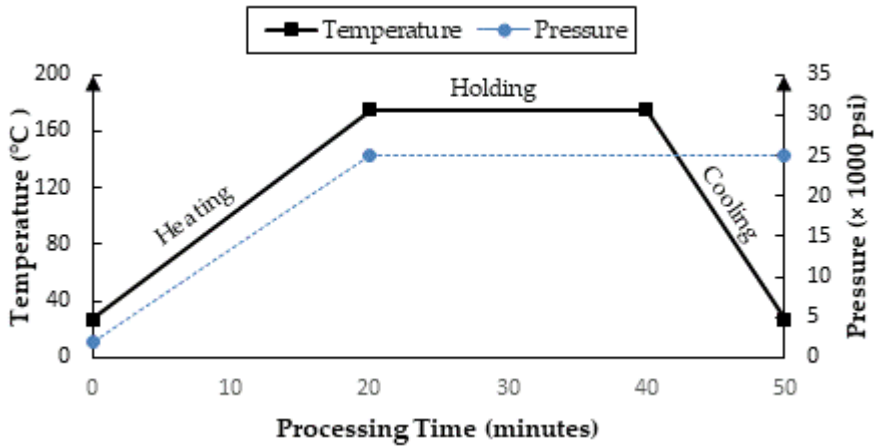


Figure 1: Temperature-time and pressure-time process diagram for fabricated PHBV composite.

Table 1: The sample identification and holding time.

| Samples | Holding Time (min) |
|---------|--------------------|
| PHBV1   | 18                 |
| PHBV2   | 23                 |
| PHBV3   | 28                 |

### 2.3 Degree of Crystallinity Analysis

The crystallinity analysis was carried out using X-ray diffraction (XRD) (Rigaku Miniflex, Japan) on the PHBV sample before and after being subjected to thermal processing. The analysis was conducted using an X-ray beam with a wavelength,  $\lambda$  of 1.5406 Å (0.15406 nm) using Cu-K $\alpha$  radiation sources at 40 kV and 15 mA. The diffraction angles for the scans were run from a  $2\theta$  value of 3° to 90° at a scan speed of 0.01°

### 2.4 Mechanical Testing

The tensile test was carried out following ASTM D3039 using a Universal Testing Machine (UTM, AGS-X Shimadzu) with a 20 kN load cell at a crosshead speed of 2 mm/min. An 80 mm of gauge length between the upper and lower clamps and 20 mm of gripping length was used. Flexural test was carried out according to ASTM D790-03. The test method utilised a three-point loading system and crosshead speed was set to 1.28 mm/min using sample dimensions of 72 mm x 12.7 mm x 3 mm with a 48 mm support span for each sample. Both the load and the flexural displacement are measured throughout the entire test. Before testing, all samples were subjected to a 24-hour conditioning period at room temperature ( $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ) and a relative humidity of  $51 \pm 1\%$ . Five samples were repeated for each of the test parameters.

## **2.5 Morphological Analysis**

The morphology analysis of the PHVB tensile-tested fractured surface was carried out using a Zeiss EVA 50 scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Before the analysis, the surface of the samples was coated with gold.

## **3.0 RESULTS AND DISCUSSION**

### **3.1 Crystallinity**

The degree of crystallinity of the PHBV samples at different holding times is shown in Figure 2. The diffraction peaks of the unprocessed PHBV powder and thermal subjected PHBV samples both appeared at  $13.32^{\circ}$ ,  $16.71^{\circ}$ ,  $21.35^{\circ}$ ,  $22.33^{\circ}$ , and  $25.34^{\circ}$ . The intensity peaks of PHBV correspond to (020), (110), (111), (121), and (040) crystalline planes, respectively. The XRD pattern of the thermal subjected samples showed a new peak at  $19.96^{\circ}$  (crystalline plane = 021), indicating the formation of new crystalline phases. The intensity of thermal subjected peaks is much higher than the unprocessed PHBV owing to the thermal processing at  $175^{\circ}\text{C}$ . The first peak of all PHBV samples slightly shifted to  $13.16^{\circ}$ ,  $13.14^{\circ}$ , and  $13.25^{\circ}$  for PHBV1, PHBV2, and PHBV3, respectively. The longer holding time promotes PHBV crystallisation, resulting in higher peak intensity at a lower degree of crystallinity than the unprocessed PHBV powder. The highest peak intensity can be observed for PHBV2, which represents the high crystallinity and may contribute to the improved mechanical properties of the polymer compared to amorphous or less crystalline counterparts as reported by

Ponjavic et al. [19].

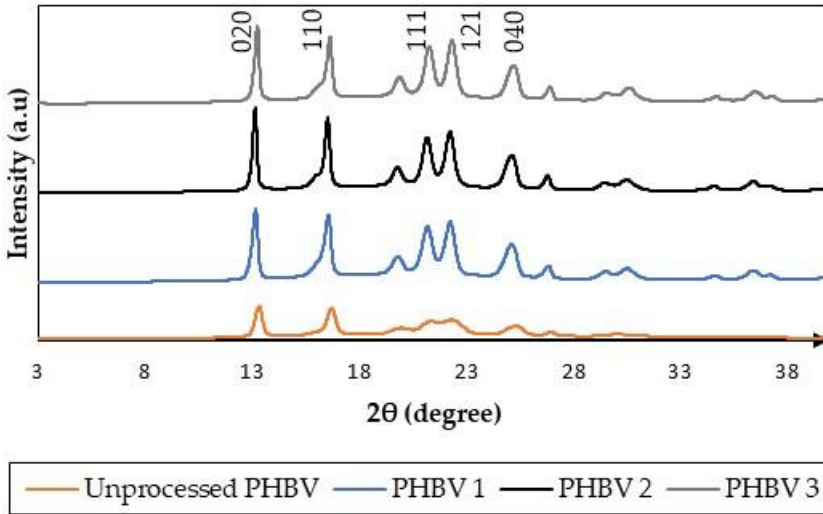


Figure 2: XRD spectra for unprocessed PHBV and thermally subjected PHBV.

### 3.2 Physical Properties

All specimens of PHBV with various holding times are shown in Figure 3. Based on Figure 3(a), the agglomeration of unmelt polymer and air bubbles within the specimen is visible through the naked eye. However, with a longer holding time (23 minutes), the incomplete melting of polymer particles appeared reduced (Figure 3b). In Figure 3(c), the absence of white particles on the specimen's surface indicates a complete melting has achieved. These results indicate that the PHBV polymer is fully processable at 175°C with 25000 psi compression pressure.

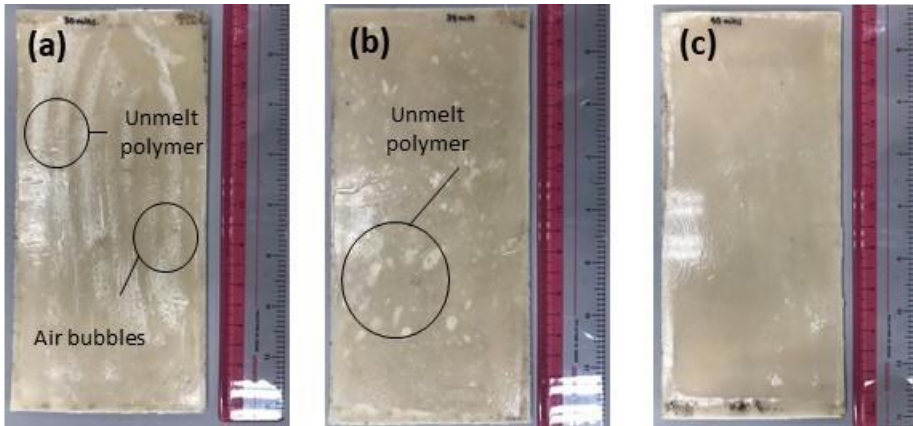


Figure 3: The physical appearance of (a) PHBV1, (b) PHBV2, and (c) PHBV3 plate as function of holding time under hot compression pressure

### 3.3 Mechanical properties

The effect of the holding temperature on the mechanical properties of the PHVB is shown in Table 2. It can be observed that the highest tensile flexural strength of the PHVB was produced when using 23 minutes of holding time. On another hand, the PHVB1 and PHVB3 recorded approximately 7% lesser strength than those prepared for PHBV2. The modulus values of the samples suggested that the sample with under- or over-processing time may result in less stiffness, making it more brittle compared to the sample processed for PHBV2.

Table 2: Mechanical properties of PHBV as a function of holding time under hot compression pressure

| Samples | Holding Time (min) | Tensile        |            |               | Flexural       |            |               |
|---------|--------------------|----------------|------------|---------------|----------------|------------|---------------|
|         |                    | Strength (MPa) | Strain (%) | Modulus (GPa) | Strength (MPa) | Strain (%) | Modulus (GPa) |
| PHBV 1  | 18                 | 20.29          | 5.24       | 3.89          | 62.77          | 2.78       | 18.4          |
| PHBV 2  | 23                 | 22.01          | 4.52       | 4.90          | 70.82          | 2.15       | 21.6          |
| PHBV 3  | 28                 | 20.31          | 5.23       | 3.89          | 62.20          | 2.24       | 14.9          |

The difference in mechanical strength of composite may resulted from the small processing window of PHBV. Bossu et al. [11] reported that the strength of the polymer was affected by the unique crystallisation behaviour of PHBV and its high sensitivity to temperature changes during processing, similarly observed in this study. Insufficient

holding time for PHBV1 at 18 minutes resulted in lower tensile and flexural strength of biopolymer as there is non-uniform temperature distribution leading to non-uniform crystallinity as well as non-uniform polymer melting patterns, which may cause pore formation within the structure as concurred by Zhu et al. [20]. Consequently, it can be seen that PHBV1 exhibits lower tensile strength, which could be corresponds to its crystalline behaviour. Meanwhile, prolonged exposure to high temperature for PHBV3 for 28 minutes holding time resulted in a brittle polymer, as the prolonged heating of thermosetting polymers can help release adsorptive inter-layer bonds and volatile group, which can modify the polymer structure and potentially increase brittleness, as reported by Korolev et al. [21]. The breakdown of chemical bonds within the polymer chains and changes in the degree of crystallinity due to thermal degradation as a result of overheating may lead to a reduction in molecular weight and changes in the physical and mechanical properties of the polymer.

Similar behaviour was observed for the flexural properties of PHBV. The stiffening of neat PHBV could be the reason for the decrease in flexural strength for PHBV3. The polymer stiffens when fast crystallisation occurs causing the monomer of PHB and HV to different degrees of solidification, such as amorphous or semi-crystalline solids [11]. Thus, the flexural strength of PHBV1 is notably lower compared to PHBV2 due to non-uniformity in the crystalline phase.

### **3.4 Mechanical properties**

Figure 4 shows the surface morphology of the tensile-tested PHVB. Rough fracture surface and pores were observed for PHVB1 (Figure 4a) which may contribute to their lower strength compared to PHVB2 as previously mentioned. The insufficient holding time resulted in incomplete polymer melting, forming irregular pores due to the trapped air inside the powdered PHBV. Previous studies have reported that the irregular pores formed during the processing stage of the polymer may reduce the stiffness and strength of polymer samples [22-23]. The pore disrupts the stress distribution within the sample, causing it to have lower strength compared to the other two samples. In addition, PHBV is a semi-crystalline polymer that may exhibit higher porosity volume than amorphous composites due to rapid recrystallisation during the cooling process [24-25].

With the increase of the holding time, the fracture surface of the PHVB appears to be smother and the presence of cracks was observed (Figure



4b and 4c). While sufficient thermal exposure may allow a complete melting of the polymer during fabrication, prolonged exposure may contribute to thermal degradation and cause the polymer to be more brittle. This observation is similar to those reported by Garcia-Garcia et al. [26].

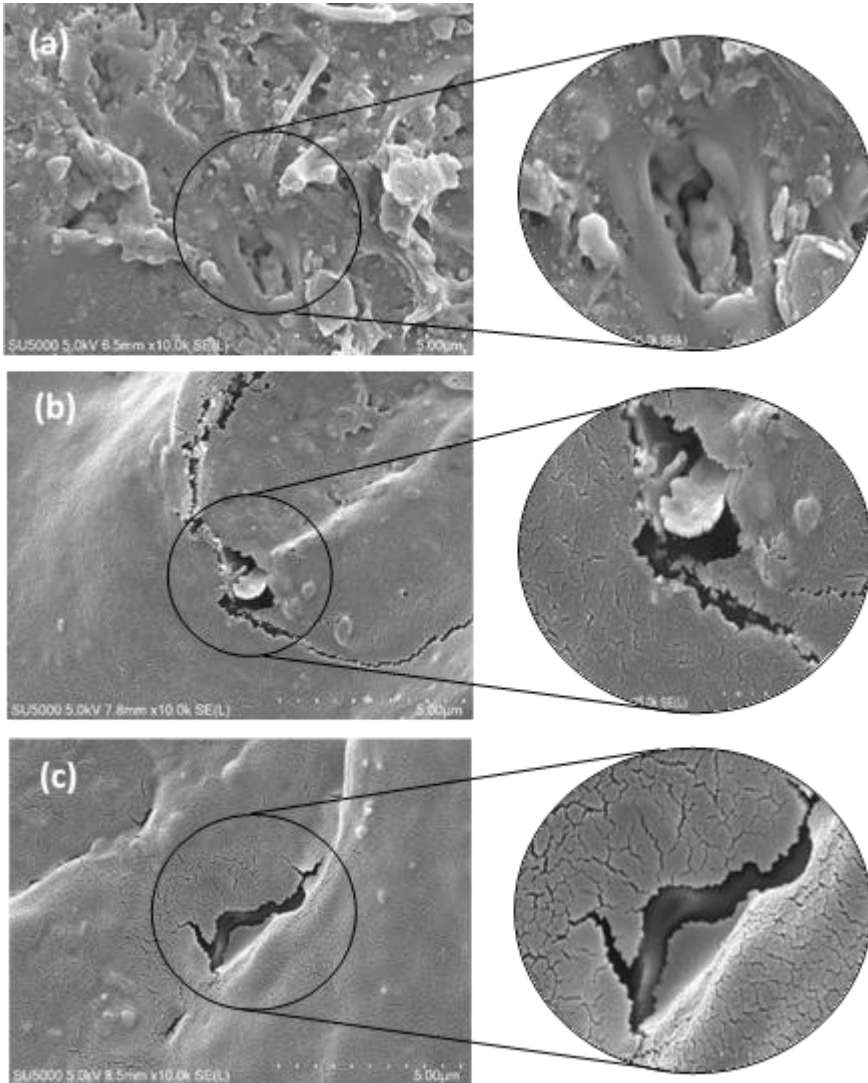


Figure 4: Microstructural image of (a) PHBV1, (b) PHBV2, and (c) PHBV3, respectively, at 10,000X magnification.

#### 4.0 CONCLUSION

The mechanical and morphological properties of PHBV samples processed at various holding times were analysed. The thermal exposure duration during polymer composite processing has proven to influence the formation of pores, the strength of materials, and the uniformity of polymer melting. The optimum tensile strength and Young's modulus were obtained at 23 minutes holding time, 22.01 MPa and 4.9 MPa, respectively. Similar patterns were observed in flexural properties with optimum flexural strength and modulus are 70.82 MPa and 21.6 GPa, respectively. The morphological analysis also showed the presence of pores and cracks in the polymer at various stages indicating the influence of the thermal exposure conditions during the processing on their properties. The polymer becomes weaker and brittle with prolonged holding time indicating a narrow processing window of PHBV should be carefully monitored to avoid any thermal degradation during the processing. Thus, this study concluded that selecting appropriate processing conditions positively impacts the performance of biopolymers. In the future, the performance properties of PHBV can be further observed with the present reinforcement such as with nanofillers or natural fibres.

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## **AUTHOR CONTRIBUTIONS**

A. S. Amirah: Writing-Original Draft, Methodology, Data curation; Z. Mustafa: Validation, Writing-Reviewing and Editing, Supervision, Funding acquisition; S. Y. Chang: Validation, Writing-Reviewing and Editing; S. H. S. M. Fadzullah: Validation, Writing-Reviewing and Editing, Funding acquisition. Q. Ahsan: Validation, Writing-Reviewing. All authors approved the final version of the manuscript.

## **CONFLICTS OF INTEREST**

The manuscript has not been published elsewhere and is not under consideration by other journals. All authors have approved the review,

agree with its submission and declare no conflict of interest on the manuscript.

## REFERENCES

- [1] J. Baranwal, B. Barse, A. Fais, G. L. Delogu and A. Kumar, "Biopolymer: A Sustainable Material for Food and Medical Applications", *Polymers*, vol. 14, no. 5, pp.1-22, 2022.
- [2] Z. Mustafa, A.S. Razali, A.A.A. Sappa, S.H.S.M. Fadzullah, S.D. Malingam and T. Ratanawilai, "Water absorption behaviour and its effect on mechanical and thermal properties of continuous unidirectional pineapple leaf fibre reinforced polylactic acid composites", *Journal of Advanced Manufacturing Technology*, vol. 17, no. 2, pp. 105-118, 2023.
- [3] D. Vicente, D. N. Proença and P. V. Morais, "The Role of Bacterial Polyhydroxyalkanoate (PHA) in a Sustainable Future: A Review on the Biological Diversity", *International Journal of Environmental Research Public Health*, vol. 20, no. 4, pp.1-21, 2023.
- [4] S. A. Acharjee, P. Bharali, B. Gogoi, V. Sorhie, B. Walling and Alemtoshi, "PHA-Based Bioplastic: a Potential Alternative to Address Microplastic Pollution", *Water Air Soil Pollution*, vol. 234, no. 21, pp. 1-31, 2023.
- [5] N. Tomano, T. A. Osswald, P. Potiyaraj, O. Boondamnoen and C. Aumnate, "Toughened Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/Epoxidized Natural Rubber Blends Fabricated by Dynamic Vulcanization and Interfacial Compatibilization", *Journal of Polymer Environment*, pp. 1-11, 2024.
- [6] B. McAdam, M. Brennan Fournet, P. McDonald and M. Mojicevic, "Production of Polyhydroxybutyrate (PHB) and Factors Impacting Its Chemical and Mechanical Characteristics", *Polymers*, vol. 12, no. 12, pp. 1-20, 2020.
- [7] P. Sedlacek, I. Pernicova, I. Novackova, X. Kourilova, M. Kalina, A. Kovalcik, M. Koller, J. Nebesarova, V. Krzyzanek, K. Hrubanova and J. Masilko, "Introducing the Newly Isolated Bacterium *Aneurinibacillus* sp. H1 as an Auspicious Thermophilic Producer of Various Polyhydroxyalkanoates (PHA) Copolymers–2. Material Study on the Produced Copolymers", *Polymers*, vol. 12, no. 6, pp. 1-18, 2020.
- [8] M. Ali, N. Idayu, M. Salleh, S. Sivaraos and M. Yamaguchi, "Optimization of Injection Machine Parameters on High Tensile Strength of Polypropylene/Fibreglass", *Journal of Advanced Manufacturing Technology*, vol. 16, no. 3, pp. 69-80, 2022.
- [9] M. Kervran, C. Vagner, M. Cochez, M. Ponçot, M. R. Saeb and H. Vahabi, "Thermal degradation of polylactic acid (PLA)/polyhydroxybutyrate (PHB) blends: A systematic review," *Polymer Degradation and Stability*, vol. 201, pp. 1-17, 2022.
- [10] P. Feijoo, K. Samaniego-Aguilar, E. Sánchez-Safont, S. Torres-Giner, J.M. Lagaron, J. Gamez-Perez and L. Cabedo, "Development and

- Characterization of Fully Renewable and Biodegradable Polyhydroxyalkanoate Blends with Improved Thermoformability," *Polymers*, vol. 14, no. 13, pp. 1-24, 2022.
- [11] J. Bossu, N. Le Moigne, P. Dieudonné-George, L. Dumazert, V. Guillard and H. Angellier-Coussy, "Impact of the processing temperature on the crystallization behaviour and mechanical properties of poly[R-3-hydroxybutyrate-co-(R-3-hydroxyvalerate)]", *Polymer*, vol. 229, pp. 1-12, 2021.
- [12] N. Jamil, M. Selamat, R. Hasan, M. Daud and M. Tahir, "Optimization of Compression Moulding Parameters for Multi Filler Polymer Composite Using Taguchi Method", *Journal of Advanced Manufacturing Technology*, vol. 12, no. 2, pp. 1-10, 2018.
- [13] O. Edynoor, A. Warikh, S. Yahaya, M. Salleh and T. Moriga, "Study on Performance of Kenaf Fibre/Epoxy Reinforced Aluminium Laminates (KeRALL) Via Compression Moulding Technique", *Journal of Manufacturing Technology*, vol. 14, no. 3, pp.1-15, 2020.
- [14] N. H. Kamarudin, M. H. I. Ibrahim, R. Asmawi, R. L. Muhamud and M. H. Ibrahim, "Parameter Optimization of Injection Moulding Using High-Density Polyethylene-Pineapple Leaf Fibre", *Journal of Advanced Manufacturing Technology*, vol. 15, no. 1, pp. 69-82, 2021.
- [15] S.U. Gwon, S.H. Lee, U.S. Youn, J.S. Roh, "Effect of Pressure and Holding Time during Compression Molding on Mechanical Properties and Microstructure of Coke-Pitch Carbon Blocks", *Applied Science*, vol. 14, pp.1-5, 2024.
- [16] M. Mansor, M. Taufiq, Z. Mustafa, R. Jumaidin, M. Mastura, H. Firdaus and B. Basori, "Thermal and mechanical behaviour of recycled polypropylene/polyethene blends of rejected unused disposable diaper", *Journal of Advanced Manufacturing Technology*, vol. 13, no. 3, pp. 13-23, 2019.
- [17] K. Pielichowski, J. Njuguna and T. M. Majka, *Thermal Degradation of Polymeric Materials*. Elsevier, 2023.
- [18] M. J. John, "Biobased alginate treatments on flax fibre reinforced PLA and PHBV composites", *Current Research in Green and Sustainable Chemistry*, vol. 5, pp.1-6, 2022
- [19] M. Ponjavic, I. Malagurski, J. Lazic, S. Jeremic, V. Pavlovic, N. Prlainovic, V. Maksimovic, V. Cosovic, L.I. Atanase, F. Freitas, M. Matos and J. Nikodinovic-Runic, "Advancing PHBV Biomedical Potential with the Incorporation of Bacterial Biopigment Prodigiosin", *International Journal of Molecular Sciences*, vol. 24, no. 3, pp. 1-16, 2023.
- [20] Z. Zhu and C. Majewski, "Understanding pore formation and the effect on mechanical properties of High-Speed Sintered polyamide-12 parts: A focus on energy input", *Materials and Design*, vol. 194, pp. 1-16, 2020.
- [21] A. Korolev, M. Mishnev, N. I. Vatin and A. Ignatova, "Prolonged Thermal Relaxation of the Thermosetting Polymers", *Polymers*, vol. 13, no. 23, pp.1-16, 2021.
- [22] A. Y. Al-Maharma, S. P. Patil and B. Markert, "Effects of porosity on the mechanical properties of additively manufactured components: a critical review", *Materials Research Express*, vol. 7, no. 12, pp. 1-27, 2020.

- [23] M. Černý, J. Petruš and I. Chamradová, "The Influence of Porosity on Mechanical Properties of PUR-Based Composites: Experimentally Derived Mathematical Approach", *Polymers*, vol. 15, no. 8, pp. 1-19, 2023.
- [24] O. Adeniran, N. Osa-uwagboe, W. Cong and M. Ramoni, "Fabrication Temperature-Related Porosity Effects on the Mechanical Properties of Additively Manufactured CFRP Composites", *Journal of Composites Science*, vol. 7, no. 1, pp. 1-14, 2023.
- [25] L. Kaniuk and U. Stachewicz, "Development and Advantages of Biodegradable PHA Polymers Based on Electrospun PHBV Fibers for Tissue Engineering and Other Biomedical Applications", *ACS Biomaterials Science & Engineering*, vol. 7, no. 12, pp. 5339–5362, 2021.
- [26] D. Garcia-Garcia, L. Quiles-Carrillo, R. Balart, S. Torres-Giner and M. P. Arrieta, "Innovative solutions and challenges to increase the use of Poly(3-hydroxybutyrate) in food packaging and disposables", *European Polymer Journal*, vol. 178, pp. 1-20, 2022.