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Characteristics of Bio Thermoplastic Composite Pellets Based on Modified Cassava Starch and Glucomannan in Variations of Synthetic Polymers

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Abstract: The research aims to determine the appropriate type and concentration of synthetic polymers in production of biothermoplastic composite pellets from modified cassava starch and glucomannan (BTC-MCS/GM). This research used a factorial randomized block design experiment. Factor 1: type of synthetic polymer consisting of PCL (polycaprolactone), PLA (poly lactic acid), PE (polyethylene), and PP (polypropylene) while factor 2: concentration of synthetic polymer with levels of 40, 50, 60% w/w, thus there are 12 treatment combinations grouped into 3 pellet making process times, so there are 36 experimental units. The data obtained were analyzed for diversity and continued with the Duncan test. Variables measured were tensile strength, elongation at break, Young's modulus, density, water vapor transfer rate (WVTR), oxygen transfer rate (O_2TR), swelling, melting point/temperature (Tm), melt flow rate (MFR), crystallinity and time biodegradation, surface profile, and functional groups. The research results show that the type and concentration of synthetic polymer have a very significant effect on the average tensile strength, elongation at break, Young's modulus, density, WVTR, O_2TR, swelling, Tm, MFR, crystallinity, and biodegradation time of BTC-MCS/GM pellets. BTC-MCS/GM pellets that use PCL, PLA, PE, and PP almost all meet SNI 7818:2014 and international standards. However, the best is BTC-MCS/GM pellets using PLA (BTC-MCS/GM/PLA) with characteristics of tensile strength 23.56 MPa, elongation at break 7.18%, Young's modulus 1548.34 MPa, density 1.22 g/ml, WVTR 179.76 g/m^2.day, O_2TR 199.67 ml/m^2.day, swelling 120.58%, Tm 152.47^{o}C, MFR 0.62 g/10 minutes, crystallinity 0.62%, biodegradation time 11.67 days. The longitudinal surface profile of the BTC-MCS/GM/PLA pellets shows smooth spots that are evenly distributed on all surfaces, while the transverse surface profile shows the presence of small, regular wavy lumps. BTC-MCS/GM/PLA pellets contain OH alcohol functional groups at wave numbers of 2144.94, 2884.67, 3100.7, 3283.95, 3601.25 cm^{-1}, C≡C (alkyne) at wave numbers of 1937.58 cm^{-1}, C=O at wave number of 1719.61cm^{-1}, C=C at wave number of 1663.68 cm^{-1}, C=C (aromatic rings) at wave number of 1553.73 cm^{-1}, C-O at wave number of 1052.21, 1112.97 and 1248 cm^{-1}, C-H at wave number of 707.91 and 923.94 cm^{-1}, (CH_2)n at wave number of 380.96 and 453.29 cm^{-1}. Thus, it has great potential to be used as raw material for ecofriendly bags.

***Keywords*: **pellets, biothermoplastic composites (BTC), modified cassava starch (MCS), glucomannan (GM), types and concentrations of synthetic polymer

1. Introduction

The development of environmentally friendly plastic bags using the casting method on a widespread and commercial basis has many obstacles. According to Moshood et al. [1], the casting method only develops environmentally friendly bags on a laboratory scale with a small capacity. Developing environmentally friendly bags using the casting method on a wider scale requires a lot of time, equipment, and costly therefore, it is not efficient [2].

The explanation above indicates the need for an alternative development of environmentally friendly bags using other methods. According to Nasir et al. [2], the blowing method is one way to develop environmentally friendly plastic bags. The development of environmentally friendly plastic bags using the blowing method requires semi-finished materials in the form of biothermoplastic composite pellets, which are a mixture of natural polymer based materials and synthetic polymers [3]. The natural polymer base material that has potential and has been proven capable of forming environmentally friendly plastic bags according to SNI 7818:2014 is a mixture of modified cassava starch (MCS) and glucomannan (GM) [4]. Biothermoplastic pellets from a mixture of different natural and synthetic polymers will produce different biothermoplastic pellet characteristics, especially regarding the compatibility of the two constituent polymers, which has an impact on reducing physical and mechanical properties [5, 6]. Similarly, differences in concentrations of natural polymers and synthetic polymers will produce different biothermoplastic pellet characteristics [7]. The higher the concentration of synthetic polymer (the lower the concentration of natural polymer), the biodegradation properties will decrease, the lower the concentration of synthetic polymer (the higher the concentration of natural polymer), the mechanical properties will increase [8, 9]. The success of developing biothermoplastic pellets for environmentally friendly plastic bags is influenced by many factors, including the type and concentration of natural and synthetic polymers used [10]. Waryat et al. [6] showed that pellets made from a mixture of thermoplastic starch (TPS) with 76% HDPE produced a tensile strength of 15.8 MPa and an elongation at break of 305.6%. Bullatovic et al. [11] showed that TPS mixed with 35% PCL and 15% PLA produced pellets with an MFR of 12 g/minute. Wang et al. [8] explained that pellets made from 50% TPS, 30% PE, and 20% anhydrous maleic acid (AMA) produced higher mechanical characteristics than pellets with other treatments. Phothisarattana et al. [7] showed that pellets from a mixture of 27% acetylated starch, 9% glycerol,4% titanium oxide, and 60% poly (butylene adipate-co-terephthalate) produced characteristic tensile strength of 12.5 MPa and Young's Modulus of 53.4 MPa and WVTR is 8.8 g.mm/ m^2.day.atm. The description above shows that the type and concentration of synthetic polymer used greatly influence the characteristics of the BTC pellets produced. A related issue is that BTC pellets are made from MCS and GM base materials mixed with synthetic polymers, but there has been no specific research regarding the type and concentration of synthetic polymers included. Therefore, it is necessary to investigate the type and concentration of synthetic polymers mixed with BTC, especially those made from MCS and GM in making the pellets. The research aims to determine the appropriate type and concentration of synthetic polymers in making BTC-MCS/GM pellets that meet SNI 7818:2014 and international standards as raw materials for environmentally friendly plastic bags.

2. Materials and method

2.1. Materials

Materials used: modified cassava starch (amylopectin MW : 2.4x106 Da and amylose MW: 5.2x108 Da) and glucomannan (MW : 198 KDa) from CV Nura Jaya), glycerol (MW: 92.09 g/mol) and distilled water (CV Brathacem), polycaprolactone/PCL (CAPA-6800, MW: 80,000 g/mol) biodegradable medical grade (CV Kilau Sejati), polylactic acid/PLA (MW: 23289,83) pro analysis (CV Maxlab), pure polyethylene/PE (HDPE SF5007: density of 0.948-0.951g/cm3 and medium load melt index /MLHI of 0.8-1.2) and pure polypropylene/PP (trilen HI10H0, density : 0,855 g/cm 3, melting point : 154oC) from PT. Infofilam and anhydrous maleic acid (MW:98.06 g/mol, density: 1.314 g/m3, melting point 60oC from CV Sukses Makmur.

2.2 Method

2.2.1 Experimental design

The experimental design in this research was a factorial randomized block design. Factor I is a type of synthetic polymer including polycaprolactone (PCL), polylactic acid (PLA), polyethylene (PE), and polypropylene (PP).

Factor II is the synthetic polymer concentration including 40, 50, and 60% w/w. Therefore, there are 12 combination treatments. Each treatment combination was grouped into 3 based on the time of the pellet making process which was carried out on 3 different days so there were 36 experimental units.

2.2.2. Research implementation

The making of the pellets is divided into 2 stages, namely 1) making biothermoplastic composites (BTC) from modified cassava starch (MCS) and thermoplastic glucomannan (GM), 2) making BTC-MCS/GM pellets with synthetic polymers. The stages are described as follows.

The weighing of the ingredients for making thermoplastic MCS (dough 1) include 2.5 kg glycerol, 1.5 kg distilled water, and 10 kg MCS. The weighing of the ingredients for making thermoplastic GM (dough 2) includes 0.83 kg glycerol, 0.5 kg distilled water, and 3.33 kg GM. The making of dough 1: glycerol and distilled water are mixed and then stirred until homogeneous. The homogeneous solution was added to MCS gradually until it was finished while being stirred using a mixer at a speed of 240 rpm for 10 minutes. The flat dough is aged for 8 days. The making of dough 2: glycerol and distilled water are mixed and then stirred until homogeneous. The homogeneous solution is added to GM gradually until it is finished while being stirred using a mixer at a speed of 240 rpm for 10 minutes. The flat dough is aged for 8 days. The dough that had been aged for 8 days was mixed at a temperature of 90 ºC with a rotation speed of 50 rpm for 15 minutes with the result being chunks of both thermoplastic MCS and thermoplastic GM. The two chunks were ground separately with a grinder and then sieved with 100 mesh size.

The weighing of thermoplastic MCS 10 kg and thermoplastic glucomannan weighed 3.33 kg. The two ingredients are mixed and stirred until homogeneous using a mixer at 240 rpm speed for 10 minutes to produce BTC-MCS/GM which will be used to prepare the experimental unit. Preparation is carried out with the composition as in Table 1.

Table 1. Composition of ingredients for making BTC-MCS/GM pellets with synthetic polymers

Treatment	BTC-MCS/GM (g)	Synthetic polymer (g)	Anhydrous maleic acid (g)	Total (g)
Polycaprolactone (PCL); 40%	52,5	40	7,5	100
Polycaprolactone (PCL); 50%	42,5	50	7,5	100
Polycaprolactone (PCL); 60%	32,5	60	7,5	100
Polylactic acid (PLA); 40%	52,5	40	7,5	100
Polylactic acid (PLA); 50%	42,5	50	7,5	100
Polyalactic cid (PA); 60%	32,5	60	7,5	100
Polyethylene (PE); 40%	52,5	40	7,5	100
Polyethylene (PE); 50%	42,5	50	7,5	100
Polyethylene (PE); 60%	32,5	60	7,5	100
Polypropylene (PP); 40%	52,5	40	7,5	100
Polypropylene (PP); 50%	42,5	50	7,5	100
Polypropylene (PP); 60%	32,5	60	7,5	100

The pellet material which has been weighed according to the composition above is then mixed and stirred with a mixer at a speed of 240 rpm for 10 minutes then fed into the screw extruder machine, and the extrusion process continues with a barrel temperature profile of 130-130-130-130-140ºC with a rotor speed of 75 rpm. The extrusion results are then formed into pellets using a pellet molding machine with a hole diameter of 0.5 cm.

2.3. Observation variables and measurement procedures

2.3.1 Observation variables

The variables observed were tensile strength, elongation at break, young modulus, density, WVTR, O_2TR, swelling, Tm, MFR, crystallinity and biodegradation time, surface profile, and functional groups.

2.3.2. Variable measurement procedures

The pellets produced in each experimental unit, some prepared for test samples are in the form of film sheets and some remain in pellet form. Test samples in the form of film sheets were made by hot pressed pellets at a temperature of 110oC with a thickness of 0.5 mm. The film sheets were then tested for tensile strength and elongation at break following the SNI 7818: 2014 procedure, Young modulus following the ASTM D638 procedure, swelling following the EN317 procedure, WVTR following the ASTM F1249 procedure, O2TR following the ASTM D3985 procedure. Meanwhile, the test sample was in pellet form, the density test was carried out following the ASTM D792-91 procedure, the melting temperature (Tm) followed the ASTM E324 and melting flow rate (MFR) followed the ISO 1133-2 procedure, the biodegradation time followed the EN 14995 (2006) procedure. These tests were carried out 3 times each.

Equipment used: screw extruder, rheomix 3000, hydraulic hot press, mixer, grinder, autograph-shidmazu mechanical testing equipment based on ASTM D638, scanning electron microscopy/SEM (Low vacuum electron microscope, type: JSM - IT 200, brand: JEOL, sample: solid, sample size: 1 cm x 1cm, filament voltage: 1.5 kV, sensors: secondary electron detector), FTIR spectrometer (Brand : Shimadzu IR Prestige – 21, type : 206-73600-36, series: A21005002919, sample shape: solid, sample size: small pieces measuring 0.5 cm x 0.5 cm, measurement mode: % transmittance, anodization: happ-genzel, resolution: 2.0/cm, wave number range: 340 - 4700 cm-1, beam: internal, detector: standard, mirror speed: 2.8 ms, IFG noise: 1, IFG similarity:1, IR range: mid), Thermal Gravimetry Analyzer/TGA (sample size: 20 mg, dry N2 flow speed: 140 ml/minutes, operational temperature: 25 – 500oC, temperature speed: 10oC/min), X-Ray Diffractometer/XRD (brand: MAXima tipe XRD-7000, diffractometer type: 0000000011063758, sample: powder, sample size: 1 mg, anode material: Cu, radiation of CuKα (λ=1,54 Å), relative intensity at 2Ɵ: 10-80o, K-A2/K-A1 ratio: 0.500, goniometer radius: 240 mm, measurement temperature: 25oC, voltage: 40 kV, electric current: 40 mA), WVTR tester, Oxygen TR tester, Melting Point Analyzer.

2.4. Data analysis

The data obtained was analyzed of variant (Anova) and continued with the Duncan Multiple Range Test using the SPSS 25.0 program

Results and discussions

3.1. Tensile strength, elongation at break and young's modulus

Analysis of variant shows that the type and concentration of synthetic polymer have a very significant effect on the average tensile strength, elongation at break, and Young's modulus of BTC-MCS/GM pellets. The average tensile strength ranges from 15.78– 23.56 MPa, the average elongation at break ranges from 7.18– 148.89%, and the average Young's modulus range from 145.17– 1548.34 MPa, as shown in Table 2.

Table 2. Average tensile strength, elongation at break, and young modulus of BTC-MCS/GM pellets with synthetic polymers

Treatment	Average tensile strength (MPa)	Average elongation at break (%)	Average Young modulus (MPa)
Polycaprolactone; 40%	15.78 ± 0.011^{c}	110.34 ± 0.061^{a}	145.17 ± 0.161^{b}
Polycaprolactone; 50%	16.56 ± 0.011^{bc}	124.62 ± 0.071^{a}	157.67 ± 0.193^{b}

Polycaprolactone; 60%	17.40 ± 0.0113^{b}	148.89 ± 0.092^{a}	171.34 ± 0.201^{b}
Polylactic acid (PLA); 40%	17.56 ± 0.011^{b}	10.49 ± 0.011^{c}	1234.98 ± 1.191^{a}
Polylactic acid (PLA); 50%	19.65 ± 0.012^{ab}	9.13 ± 0.011^{c}	1357.79 ± 2.123^{a}
Polyalactic cid (PA); 60%	23.56 ± 0.013^{a}	7.18 ± 0.011^{c}	1548.34 ± 2.521^{a}
Polyethylene; 40%	18.12 ± 0.011^{ab}	43.67 ± 0.041^{b}	189.39 ± 0.264^{b}
Polyethylene; 50%	19.23 ± 0.012^{ab}	50.48 ± 0.050^{b}	201.45 ± 0.344^{b}
Polyethylene; 60%	21.26 ± 0.013^{a}	53.56 ± 0.049^{b}	223.76 ± 0.367^{b}
Polypropylene; 40%	19.34 ± 0.012^{ab}	50.67 ± 0.51^{b}	202.65 ± 0.234^{b}
Polypropylene; 50%	20.67 ± 0.013^{a}	52.78 ± 0.043^{b}	237.98 ± 0.314^{b}
Polypropylene; 60%	22.14 ± 0.013^{a}	56.45 ± 0.051^{b}	240.67 ± 0.374^{b}

Note: The same notation behind the averages in the same column shows that they are not significantly different at the 5% error level.

The high average tensile strength (20.56– 23.14 MPa) is possessed by BTC-MCS/GM pellets which use PLA 60%, PE 60%, PP 50%, and PP 60%, this value is not significantly different from the average tensile strength from BTC-MCS/GM pellets which use 50% PLA, 40% PE, 50% PE and 50% PP. Meanwhile, the lowest average tensile strength (15.78 MPa) was possessed by BTC-MCS/GM pellets which used 40% PCL, which was not significantly different from the average tensile strength of BTC-MCS/GM pellets which used 50% PCL. Similar results were produced by Jeziorska et al [12], the higher the synthetic polymer content or the lower the TPS, the higher the tensile strength value. According to Kim and Lee [13], the increase and decrease in mechanical properties including the tensile strength of biodegradable composites depend on the interfacial surface interaction between TPS and synthetic plastic. This is also influenced by the type and characteristics of the synthetic polymer added) [14]. Meanwhile, Dome et al. [15] explain that tensile strength is greatly influenced by the presence of a mixture of other materials and the degree of crystallinity of these materials. The average value of tensile strength above, although it is lower than the tensile strength of TPS/PLA-HDPE composites with a value of 27.4 MPa and TPS/PLA-PP with a value of 35.9 MPa [16] and also PLA/MPLA/TPS composites with a value of 33.0 MPa [12], but has complied with SNI 7818:2014 which sets a minimum tensile strength value of 13.7 MPa.

The high average elongation at break (110.34– 148.89%) of BTC-MCS/GM pellets using PCL 40, 50, and 60% is significantly different from the others. Meanwhile, the average elongation at break is low (7.49– 10.49%) for BTC-MCS/GM pellets which use 40 and 50% PLA, which is significantly different from the others. Similar results were produced by Wang et al. [9] which showed that the higher the PLA content of TPS, the lower the average elongation at break of biothermoplastic composites. This seems to be in accordance with the opinion of Kim and Lee [13] and Hwang et al. [14] who explain that mixtures of thermoplastic materials and synthetic polymers are greatly influenced by the surface interaction ability of the materials mixed. This is also influenced by the type, concentration and characteristics of the polymer material mixed [9, 17]. Meanwhile, according to Zhong and Kang [18], elongation at break that is too high or too low occurs due to disruption of compatibility and homogeneity, resulting in an imbalance of functional groups caused by the material concentration ratio and process temperature being too extreme. This has an impact on molecular dispersion which affects mechanical properties including elongation at break. The average value of elongation at break value above is lower than the elongation at break of the TPS/PLA-HDPE composite with a value of 237.7% and TPS/PLA-PP with a value of 645.9% [16], but higher than the composite PLA/MPLA/TPS with a value of 4% [12] and does not meet SNI 7818:2014 which sets a minimum value of 400 – 1120%.

A high average Young's modulus (1234.98– 1548.34 MPa) was found in BTC-MCS/GM pellets using 40, 50 and

60% PLA, which was significantly different from the others. This Young's modulus value is in line with the results of measuring the tensile strength of BTC-MCS/GM pellets with PLA. According to Muller et al. [19] Young's modulus is the ability of a material to return to its original shape when pressure is applied. Therefore, Young's modulus is highly dependent on tensile strength and elongation at break. This is supported by the opinion of Wang et al [9], Hwang et al [14], Kim and Lee [13] who explain that the mechanical properties of biothermoplastic composites including Young's modulus are greatly influenced by the type, concentration and characteristics of the polymer material mixed because it will affect the interaction ability surface of the composite material [17]. The average value of Young's modulus above are mostly lower than the Young's modulus of TPS/PLA-HDPE composites with a value of 1300 MPa and TPS/PLA-PP with a value of 1700 MPa [16], except for TPS/PLA 50% and 60% with values of 1357.79 MPa and 1548.34 MPa respectively. However, all of them have a Young's modulus value lower than PLA/MPLA/TPS with a value of 3264 MPa [12].

3.2. Density, WVTR, O_2TR and swelling

Analysis of variant shows that the type and concentration of synthetic polymer have a very significant effect on the average density, WVTR, O_2TR, and swelling of BTC-MCS/GM pellets. The average density ranges from 1.01 – 1.22 g/ml, the average WVTR ranges from 6.67– 231.02 g/m^2.day, the average O_2TR ranges from 184.45– 211.34 ml/ m^2.day, as shown in Table 3.

Table 3. Average density, WVTR, O2TR, and swelling of BTC-MCS/GM pellets with synthetic polymers

Treatment	Average density (g/ml)	Average WVTR (g/m^2.hari)	Average O_2TR (ml/m^2.hari)	Average swelling (%)
Polycaprolactone; 40%	1.03 ± 0.001^{de}	219.06 ± 0.311^{a}	211.34 ± 0.323^{a}	152.15 ± 0.291^{a}
Polycaprolactone; 50%	1.05 ± 0.001^{cd}	207.77 ± 0.291^{a}	209.64 ± 0.411^{a}	149.87 ± 0.312^{a}
Polycaprolactone; 60%	1.08 ± 0.001^{bc}	192.71 ± 0.283^{a}	201.45 ± 0.311^{b}	136.98 ± 0.316^{ab}
Polylactic acid (PLA); 40%	1.17 ± 0.002^{ab}	231.02 ± 0.333^{a}	207.16 ± 0.323^{ab}	148.06 ± 0.291^{a}
Polylactic acid (PLA); 50%	1.19 ± 0.002^{ab}	210.63 ± 0.322^{a}	200.78 ± 0.299^{b}	137.65 ± 0.322^{ab}
Polyalactic cid (PA); 60%	1.22 ± 0.002^{a}	179.76 ± 0.219^{a}	199.67 ± 0.281^{b}	120.58 ± 0.291^{ab}
Polyethylene; 40%	1.05 ± 0.001^{cd}	10.7 ± 0.011^{b}	200.56 ± 0.295^{b}	95.23 ± 0.123^{bc}
Polyethylene; 50%	1.04 ± 0.001^{de}	9.73 ± 0.012^{b}	198.45 ± 0.284^{b}	80.59 ± 0.091^{c}
Polyethylene; 60%	1.03 ± 0.001^{de}	7.97 ± 0.011^{b}	192.67 ± 0.310^{bc}	78.45 ± 0.092^{c}
Polypropylene; 40%	1.03 ± 0.001^{d}	8.89 ± 0.011^{b}	191.78 ± 0.343^{bc}	79.51 ± 0.071^{c}
Polypropylene; 50%	1.02 ± 0.001^{e}	7.65 ± 0.011^{b}	188.1 ± 0.298^{c}	72.63 ± 0.082^{c}
Polypropylene; 60%	1.01 ± 0.001^{e}	6.67 ± 0.012^{b}	184.45 ± 0.314^{c}	67.43 ± 0.079^{d}

Note: The same notation behind the averages in the same column shows that they are not significantly different at the 5% error level.

The highest average density (1.22 g/ml) was owned by BTC-MCS/GM pellets using 60% PLA, which was not significantly different from the average density of BTC-MCS/GM pellets using 40 and 50% PLA. Meanwhile, the low average density (1.01- 1.02 g/ml) of BTC-MCS/GM which uses PP 50 and 60% is not significantly different from the average density of BTC-MCS/GM pellets which use PE. 50 and 60% and PCL 40%. The highest average density of BTC-MCS/GM pellets using 60% PLA showed results similar to the density of biothermoplastic composites from TPS/PBSA/PLA with values between 1,224 – 1,228 g/ml [9]. Meanwhile, the density of LLDPE/TPS ranges between 0.9003-1.0466 g/ml, and HDPE/TPS ranges between 0.9539-1.0160 g/ml [5], while the density of PP with bamboo fiber and sugar cane fiber ranges from 0.844 – 0.846 g/ ml [20].

The high average WVTR (179.76 – 231.02 g/m^2.day) was possessed by BTC-MCS/GM pellets which used PCL 40, 50, 60% and PLA 40, 50, 60%, which was significantly different from the others. BTC-MCS/GM pellets with PLA and PCL have a higher WVTR value than the WVTR of PBS biocomposite reinforced with 3% NCC with a value between 49.4 – 83.8 g/m^2.day [21]. However, the PBS biocomposite reinforced with 3% NCC has a higher WVTR value than BTC-MCS/GM with PE and PP. Lin and Razali [21], explained that composites formed with a hydrophobic-hydrophilic pattern will affect the WVTR properties. This is likely due to differences in adhesion between synthetic plastic surfaces and thermoplastic materials [22]. According to Wang et al. [9], the hydroxyl and carboxyl groups of PLA establish a good interfacial binding effect with TPS through intermolecular hydrogen bonds, which causes TPS to be dispersed into PBSA. When the PLA content is optimal, PLA has the best compatibility with PBSA. However, when the PLA content is increased, the compatibility between PLA and PBSA decreases, resulting in a decrease in system performance which impacts the WVTR characteristics. According to Ferreira et al. [23], the properties of WVTR are influenced by the materials that make up a biothermoplastic composite. This can also affect the ability of biocoating or biopackaging to exchange gas and water vapor. The higher the WVTR value, the higher the water vapor permeability. The high average O_2TR (209.64 - 211.34 ml/m^2.day) was found in BTC-MCS/GM pellets using 40 and 50% PCL, which was not significantly different from the average O_2TR from BTC-MCS/GM pellets with PLA. Meanwhile, the low average O2TR (184.45– 188.16 ml/m^2.day) was owned by BTC-MCS/GM which used PP 50 and 60% which was not significantly different from the average O_2TR from BTC-MCS/GM pellets which used PP 40% and PE 60%. The average of O_2TR above shows a lower value than the O2TR from PBS bicomposite reinforced with 3% NCC with a value of 280 ml/m^2.day [24]. According to Surendren et al.[22] and Wang et al. [9], differences in interfacial adhesion between thermoplastic and synthetic plastic materials will cause differences in system performance and have an impact on differences in O_2TR [25]. According to Chauhan et al. [26], blending between TPS and synthetic polymers causes oxygen diffusion through long, winding paths due to increased crystallinity. Such a crystal structure creates a twisting path for oxygen molecules across the film, thereby leading to low oxygen permeability [27]. However, the ability to transfer oxygen is greatly influenced by the characteristics of the polymer that makes up the composite and the presence of a plasticizer that acts as an oxygen trap [28]. The high average swelling (148.06– 152.15%) was owned by BTC-MCS/GM pellets using PCL 40, 50 and PLA 40%, which was not significantly different from the average swelling of BTC-MCS/GM pellets with PCL 50 and PLA 50, 60%. Meanwhile, the lowest average swelling (67.43%) was possessed by BTC-MCS/GM which used PP 60% which was significantly different from the others. The average swelling value above is higher than the swelling of PLA/PTS/nanoclay composites with a range of 30 - 35% [12]. Basically, biothermoplastic composites formed with a hydrophobic-hydrophilic pattern will affect the swelling properties [21]. According to Aslam et al. [29], differences in swelling characteristics between composites are caused by differences in the types and ratios of constituent materials, manufacturing processes, and chemical modifications carried out in composite synthesis. Chemical modification will change the chemical, physical, and mechanical properties if one of the main functional groups such as the hydroxyl group undergoes a reaction. Reactions that can occur include acetylation, etherification, esterification, and carbonation [30]. According to Harsojuwono and Arnata [31], the hydroxyl group causes a compound to be polar, because the electronegative oxygen atom can attract electrons. If the electrons come from water molecules, it will facilitate the dissolution of compounds containing hydroxyl groups.

3.3. Melting point/temperature (Tm), melt flow rate (MFR), degree of crystallinity, and biodegradation time

Analysis of variant shows that the type and concentration of synthetic polymer have a very significant effect on the average Tm, MFR, crystallinity, and biodegradation time of BTC-MCS/GM pellets. The average Tm ranges from 41.91– 152.47°C, the average MFR ranges from 0.39– 0.63g/10 minutes, the average degree of crystallinity ranges from 0.59– 57.24%, the average biodegradation time ranges from 7.00– 49.33days as shown in Table 4.

Table 4. Melting point, flow rate, and biodegradation time of biodegradable plastic pellets

Treatment	Average Tm (°C)	Average MFR (g/10 minute)	Average degree of crystallinity (%)	Average biodegradation time (Hari)
Polycaprolactone; 40%	41.91 ± 0.041^{c}	0.51 ± 0.001^{ab}	39.36 ± 0.051^{a}	7.00 ± 0.011^{c}
Polycaprolactone; 50%	52.72 ± 0.063^{c}	0.59 ± 0.001^{a}	48.23 ± 0.064^{a}	7.33 ± 0.011^{c}
Polycaprolactone; 60%	59.13 ± 0.059^{c}	0.63 ± 0.001^{a}	57.24 ± 0.072^{a}	7.33 ± 0.011^{c}
Polylactic acid (PLA); 40%	139.34 ± 0.32^{ab}	0.47 ± 0.001^{ab}	0.59 ± 0.001^{c}	11.33 ± 0.013^{b}
Polylactic acid (PLA); 50%	145.26 ± 0.454^{a}	0.58 ± 0.001^{a}	0.74 ± 0.001^{c}	11.33 ± 0.012^{b}
Polyalactic cid (PA); 60%	152.47 ± 0.419^{a}	0.62 ± 0.001^{a}	0.85 ± 0.001^{c}	11.67 ± 0.012^{b}
Polyethylene; 40%	117.32 ± 0.332^{b}	0.3 ± 0.0019^{c}	7.83 ± 0.011^{b}	45.67 ± 0.064^{a}
Polyethylene; 50%	119.47 ± 0.299^{b}	0.42 ± 0.001^{b}	9.54 ± 0.012^{b}	46.67 ± 0.067^{a}
Polyethylene; 60%	121.92 ± 0.417^{ab}	0.51 ± 0.001^{ab}	11.18 ± 0.019^{b}	48.67 ± 0.071^{a}
Polypropylene; 40%	140.67 ± 0.578^{a}	0.40 ± 0.001^{b}	19.87 ± 0.031^{ab}	46.33 ± 0.063^{a}
Polypropylene; 50%	143.18 ± 0.498^{a}	0.45 ± 0.001^{b}	24.45 ± 0.042^{ab}	47.67 ± 0.061^{a}
Polypropylene; 60%	148.32 ± 0.541^{a}	0.5 ± 0.0012^{ab}	29.13 ± 0.044^{ab}	49.33 ± 0.071^{a}

Note: The same notation behind the averages in the same column shows that they are not significantly different at the 5% error level.

The average high melting point (140.67– 152.47°C) is possessed by BTC-MCS/GM pellets which use 50 and 60% PLA and 40, 50, 60 % PP, which is not significantly different from the average Tm of BTC-MCS/ GM uses PLA 40 and PE 60%. Meanwhile, the average Tm was low (41.91– 152.47°C) for BTC-MCS/GM pellets using PCL 40, 50, and 60%, which was significantly different from the others. According to Greco and Ferrari [32], the Tm of biothermoplastic composites will decrease compared to the original polymer. Siracusa and Blanco [33] explained that the chemical structure, molecular weight, type of polymer, and degree of crystallinity of the mixed materials cause differences in Tm. Chauhan et al. [26] show that the Tm of TPS/PLA composites ranges from 148–154 °C. Akesson et al. [16] show that the melting point of TPS/PP is between 161.2 – 161.5 °C and TPS/HDPE is around 132.1 – 132.3 °C. Gajdosova et al. [34] showed that the melting point of TPS/PCL ranges between 120 -135 °C depending on the ratio of materials mixed in forming the biocomposite. Gharibshahian et al. [35], explained that PCL composites in additive manufacturing technology have a melting point of 59 - 64 °C. Meanwhile, Estrada-Monje et al. [36] explained that the decrease in melting point is related to the compatibility between PCL and plasticized starch, as confirmed by the shift in infrared absorption in the mixture of the two materials.

A high average MFR (0.39– 0.63g/10 minutes) possessed by BTC-MCS/GM pellets using 50 and 60% PCL and 50 and 60% PLA, which was not significantly different from the average MFR of BTC- MCS/GM which uses PCL 40%, PLA 40%, PE 60% and PP 60%. Meanwhile, the lowest average MFR (0.30 g/10 minutes) was possessed by BTC-MCS/GM pellets which used 40% PE, which was significantly different from the others. According to Wang et al. [9], at a fixed TPS concentration, the average MFR of the composite decreases with increasing PLA concentration. Rogovina and Aleksanyan [37] and Eaysmine et al [25] show that increasing the concentration of synthetic polymer further reduces the average MFR of composites using a TPS matrix. This is very advantageous when composites with optimal composition are blown during film making [9]. Waryat et al. [5] showed that the MFR of LLDPE/TPS (60/40) was 0.12 – 0.61 g/10 minutes, meanwhile Zaman and Beg [38] showed that the MFR of TPS/LDPE ranges from 2.42 – 2.71 g/10 minutes. Composite of PLA/TPS with 25% TPS using 1% the epoxydized soybean oil (ESO) has average MFR of 7.39 g/10 minutes. Addition of ESO content up to 2% resulted in a reduction in MFR to 5.26 g/10 minutes Przybytek et al. [39]. This seems to be related to differences in the type, characteristics, and concentration of the materials that make up the composition [40].

A high average degree of crystallinity (0.59– 57.24%), is owned by BTC-MCS/GM pellets using PCL 40, 50, and 60%, which is not significantly different from the average degree of crystallinity of BTC-MCS/GM using PP 40, 50, and 60%. The average low degree of crystallinity (0.59 – 0.85%) is owned by BTC-MCS/GM pellets using 40, 50, and 60% PLA, which is significantly different from the others. This difference in the degree of crystallinity is due to differences in the type and concentration of materials making up the composite [41]. A similar opinion was expressed by Zhang et al. [42] who explained that in composite systems there is a strong interaction between the polymer materials that make up the composite. This condition occurs due to the breaking of intermolecular and intramolecular hydrogen bonds during the composite formation process, resulting in damage to the crystal structure of the constituent polymers [43]. This causes the polymer to be easily dispersed even without a solvent [44]. Guang-Mei et al. [41] reported that the degree of crystallinity of the PCL/hydroxyapatite nanoparticles composite ranges from 39-55% which depends on the PCL content. Meanwhile, Trinh et al. [45] showed that increasing the ST/PLA concentration in the TPS/PLA matrix caused a decrease in the crystallinity of the biothermoplastic composite. According to Tsioptsias et al. [46], the degree of crystallinity of PP composites and antioxidants with various fillers ranges from 40-50%. Meanwhile, Kasmi et al. [47], showed that the PLA/Hytrel composite had a degree of crystallinity ranging from 1.9 – 6.6%, while the TPS/LLDPE composite reinforced with banana fiber had a degree of crystallinity ranging from 18.06 – 31.63% [48]. According to Estrada-Monje et al. [36], the tapioca composite with PCL has a crystallinity degree of 38%, while the corn starch composite with PCL has a crystallinity degree of 62%.

The long average biodegradation time (45.67- 49.33 days) was experienced by BTC-MCS/GM pellets using PE and PP 40, 50, and 60%, which was significantly different from the others. Meanwhile, the short biodegradation time (7.00– 7.33 days) for BTC-MCS/GM pellets using PCL 40, 50, and 60% is not significantly different from the average biodegradation time for BTC-MCS/GM pellets using PLA 40, 50, and 60 %. All BTC-MCS/GM pellets made using PCL, PLA, PE, and PP, comply with SNI 7818:2014. The standards set a maximum biodegradation time for biothermoplastic composites of 60 days [4]. Meanwhile, according to ISO 20200:2006, the biodegradation time is set at a maximum of 75 days when the biocomposite has been destroyed by 90% [49]. According to Jha et al. [50], the rate of biodegradation generally depends on the interfacial adhesion of fiber-matrix interactions and the hydrophilicity of the polymer matrix. Apart from that, it also depends on the presence of biological materials as components of biothermoplastic composites [31]. Basically, the biodegradation begins with chemical degradation, namely oxidation of molecules which produces micromolecules, and continues with decomposition by microorganisms which break them down into very simple molecules and minerals [6]. According to Kumar and Thakur [51], biopolymer degradation will produce simple compounds such as CO_2, and H_2O.

3.4. Surface profile

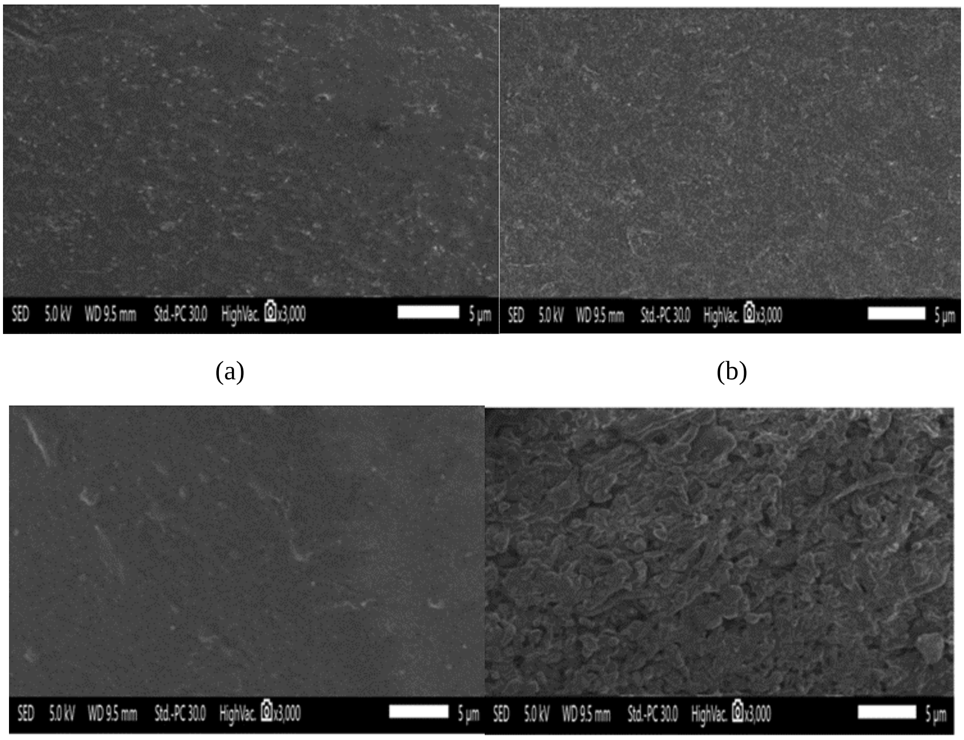
The surface profile of BTC-MCS/GM pellets using PCL, PLA, PE, and PP in the longitudinal position is shown in Figures 1a, 1b, 1c, and 1d. Meanwhile, the surface profile of BTC-MCS/GM pellets using PCL, PLA, PE, and PP in the transverse position is shown in Figure 2a, 2b, 2c dan 2d.

The longitudinal surface profile of BTC-MCS/GM pellets using PCL shows the presence of evenly distributed small spots with a few small bubbles. This is similar to the results of research from Jha et al (2021) [50], which shows that the TPS/PCL composite contains graphite grains with clearly visible pores.

Meanwhile, the longitudinal surface profile of BTC-MCS/GM pellets using PLA shows the presence of fine spots evenly distributed on all surfaces. This result is similar to TPS/PLA composites that display smooth fracture surfaces [45]. According to Nazrin et al. [24], increasing TPS levels cause cracks to become smaller and only small cavities are visible. This indicates the presence of undisturbed starch grains in the PLA matrix. This means that the fine fracture surface is very similar to pure PLA with smaller agglomerations.

The longitudinal surface profile of BTC-MCS/GM pellets using PE shows a smooth surface with relatively large bubbles. This result is similar to the TPS/PE composite which shows the presence of lumps on the inner surface of the particles [52]. Meanwhile, Waryat et al. [5] showed that the biothermoplastic composite TPS/LLDPE (40:60) had a less smooth surface structure. This is characterized by starch collecting at several points/spots and not spreading evenly.

Meanwhile, the longitudinal surface profile of BTC-MCS/GM pellets using PP shows large lumps that are almost evenly distributed on all surfaces. Meanwhile, Matondang et al. [53] produced a surface profile of a mixture of PP, maleic acid and sago starch which showed the presence of small granules that could not interact with PP-g-MA. However, the granules are micron-sized, which is very small, so it can be said that the surface is flat and there is a good interaction between PP-g-MA and palm oil sago starch.



(a) (b)

(c) (d)

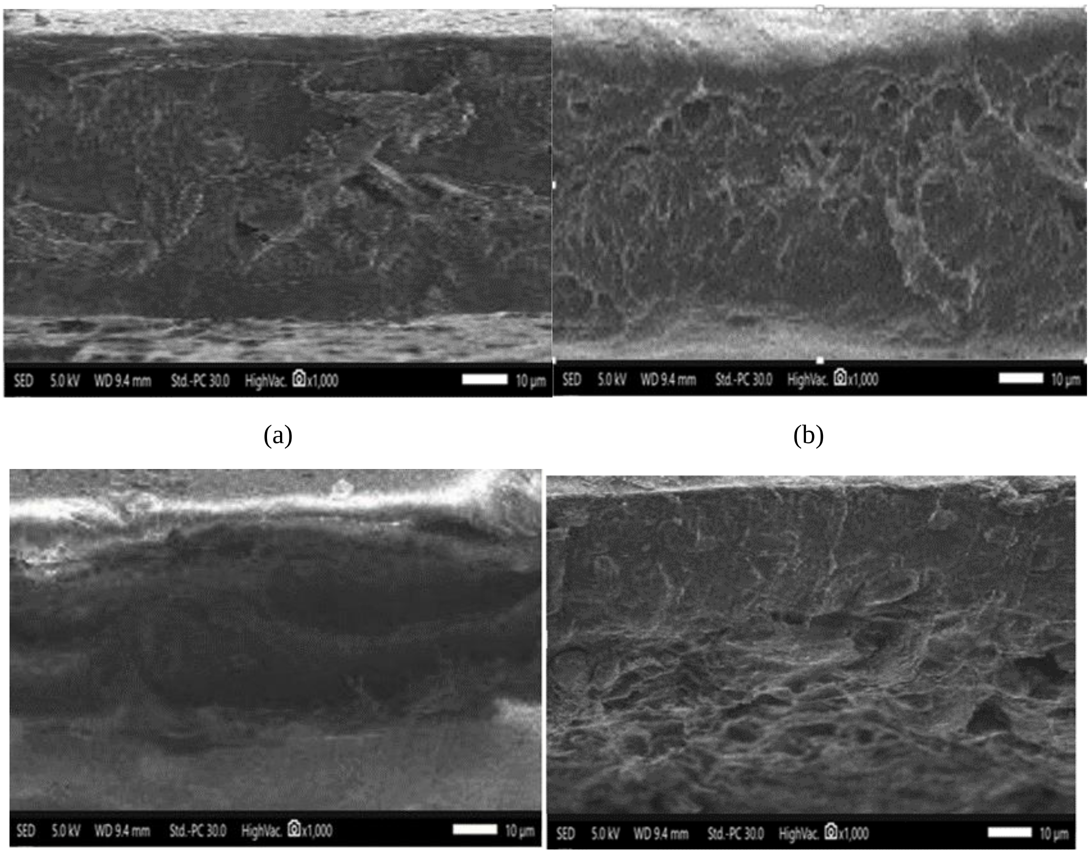
Figure 1. Surface profile of BTC-MCS/GM pellets using a) PCL, b) PLA, c) PE, d) PP in the longitudinal position

The transverse surface profile of BTC-MCS/GM pellets using PCL shows the presence of large irregular wavy lumps. This result appears to be different from the composite formed between urea thermoplastic starch (UTPS) and PCL which shows the presence of cryogenic fracture surfaces from this mixture. When the UTPS content increases in the UTPS-PCL mixture, the morphology changes from a spherical to an elliptical shape [54]. Gajdosova et al. [34] explained that TPS particle size decreased with an increasing concentration ratio of TPS components to PCL, although most mixtures showed the opposite trend. This difference also seems to be due to differences in the type and concentration of materials that form the composite.

Meanwhile, the transverse surface profile of BTC-MCS/GM pellets using PLA shows the presence of small, regular wavy lumps. This is similar to the research results of Jeziorska et al. [12] which showed that a mixture of PLA and TPS with MPLA compatibilizer, containing individual starch granules formed a dispersed phase in the PLA matrix, thus forming a continuous and porous morphology. According to Gisario et al. [27], most of the starch is well dispersed and distributed within the polyester matrix and there is no interface cleavage between polyester and starch.

The transverse surface profile of BTC-MCS/GM pellets using PE shows the presence of lumps with very large waves with a smooth surface. These results are in accordance with the results of Hammache et al. [55], explaining that blending TPS with a PP/HDPE mixture causes an increase in homogeneity, resulting in a composite with a smooth surface.

Meanwhile, the transverse surface profile of BTC-MCS/GM using PP appears to have a mixture of small lumps with regular and irregular waves. According to Wu et al. [56], this occurs due to tensile cracks caused by PP and other components dispersed in the TPS in the form of multidirectional orientations, which can block crack propagation.



(a) (b)

(c) (d)

Figure 2. Surface profile of BTC-MCS/GM pellets using a) PCL, b) PLA, c) PE, and d) PP in the transverse position

3.5. Functional groups

Wave number analysis of BTC-MCS/GM pellets using PCL, PLA, PE, and PP as shown in Figures 3a, 3b, 3c, and 3d. Meanwhile, the alleged functional groups contained in BTC-MCS/GM pellets which use PCL, PLA, PE, and PP are shown in Tables 5a, 5b, 5c, and 5d.

Based on Figure 3a and Table 5a, show that the BTC-MCS/GM pellets using PCL contain the OH alcohol functional group at wave numbers of 2936.75 and 3302.27 cm^{-1}, C=O at wave number of 1721.54 cm^{-1}, C-O ether, carboxylate at wave number of 1721.54 cm^{-1}, C-O ether, carboxylate at wave number of 1721.54 cm^{-1}. 1034.85 cm^{-1} and C-H at wave number of 939.37 cm^{-1}. This result is similar to the research results of Hernandez [57] which showed an increase in the band at wave number of 3330 cm^{-1} which corresponds to the hydroxyl group (–OH) along with increasing TPS content. The results of research by Hernandez [57] on the TPS/PCL composite ratio 50/50 found the hydroxyl O–H strain of starch at 3331 cm^{-1}, the carbonyl C=O stretch of the ester group at 1724 cm^{-1}, and the C–O–C glycosidic bond strain, at 1043 cm^{-1}. These results show that there is a shift in absorption, according to Estrada-Monje et al. [36], a greater shift in the infrared absorption band due to the presence of amylopectin in TPS.

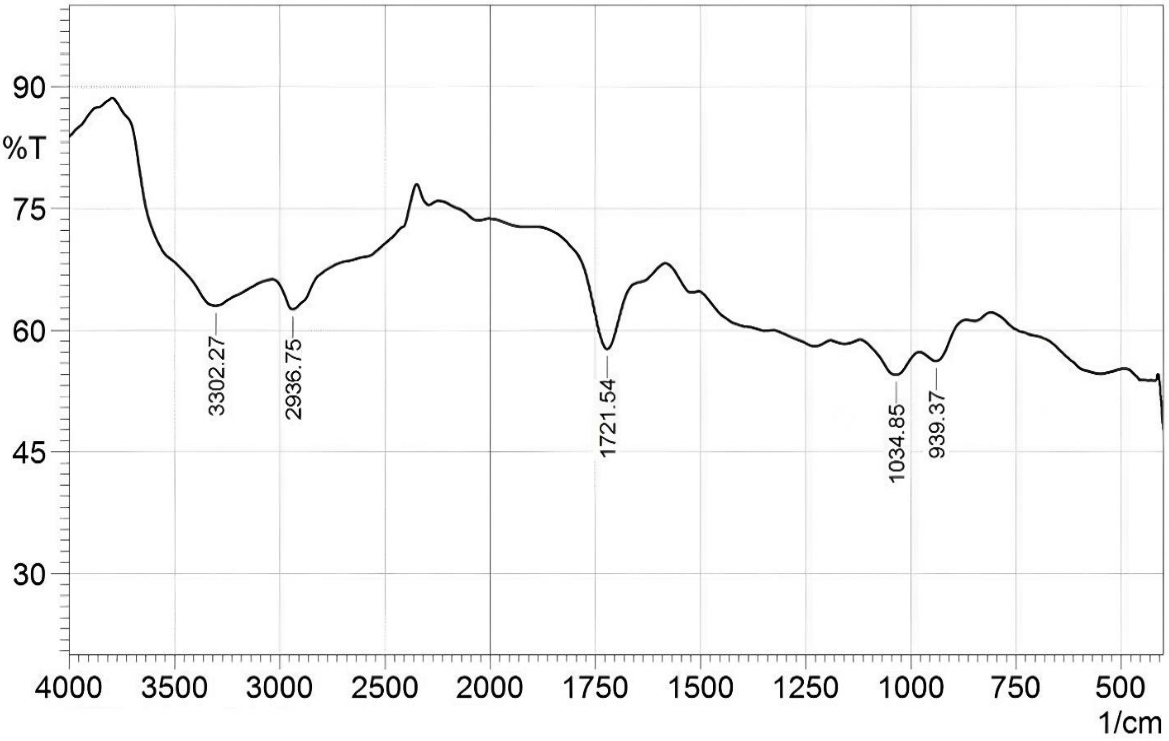


Figure 3a. Wavenumber spectrogram of BTC-MCS/GM pellets with PCL

Table 5a. Wave numbers and functional groups contained in BTC-MCS/GM pellets using PCL

Standard wave number area (cm^{-1}) (Gable, 2014)	Standard functional group (Gable, 2014)	Wave number of the pellet BTC-MCS/GM with PCL (cm^{-1})	Functional groups in pellets - MCS/GM with PCL
2000 - 3600 1690 - 1760 1025 - 1200 650 – 1000	O-H alcohol C=O	2936.75, 3302.27 1721.54 1034.85 939.37	O-H alcohol C=O

	C-O ether, carboxylate C=H		C-O ether, carboxylate C=H

Based on Figure 3b and Table 5b, it shows that BTC-MCS/GM pellets using PLA contain OH alcohol functional groups at wave numbers of 2144.94, 2884.67, 3100.7, 3283.95, 3601.25 cm-1, C=C (alkyne) at wave numbers of 1937.58 cm -1, C=O at wave number of 1719.61cm-1, C=C at wave number of 1663.68 cm -1, C=C (aromatic rings) at wave number of 1553.73 cm -1, C-O at wave number of 1052.21, 1112.97 and 1248 cm-1, C-H at wave number of 707.91 and 923.94 cm -1, (CH2)n at wave number of 380.96 and 453.29 cm-1. These results are largely similar to the research results of Nazrin et al. [24] which showed that the O-H functional group experienced a shift in wave number indicating weak inter- and intramolecular hydrogen bonds in starch chains. This reflects that mixing PLA with starch hinders the hydrogen bonding of starch molecules. The higher the TPS/PLA ratio causes the peak to shift towards lower wave numbers [58].

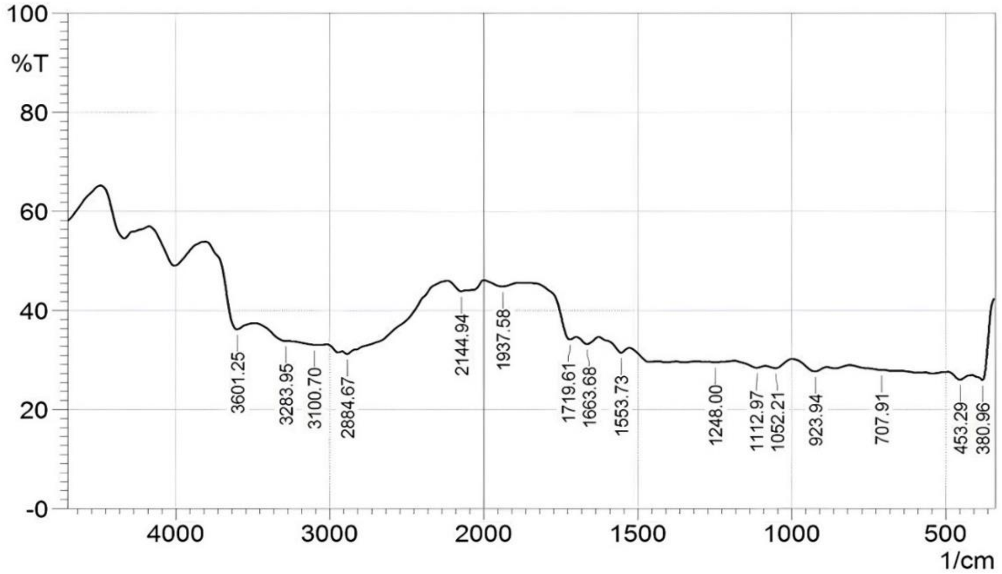


Figure 3b. Wavenumber spectrogram of BTC-MCS/GM pellets with PLA

Table 5b. Wave numbers and functional groups contained in BTC-MCS/GM pellets using PLA

Standard wavenumber area (cm^{-1}) (Gable, 2014)	Standard functional group (Gable, 2014)	Wave number of the pellet BTC-MCS/GM with PLA (cm^{-1})	Functional groups in pellets BTC-MCS/GM with PLA
2000 - 3600	O-H alcohol	2144.94, 2884.67, 3100.7,3283.95, 3601.25	O-H alcohol
1900 - 2260		1937.58	
1690 – 1760	C≡C (alkyne)	1719.61	C≡C (alkyne)
1610 - 1680	C=O	1663.68	C=O
1500 – 1600		1553.73	

1050 – 1300 650 - 1000 < 722	C=C C=C (aromatic rings) C-O C=H $(CH_2)_n$	1052.21, 1112.97, 1248 707.91, 923.94 380.96, 453.29	C=C C=C (aromatic rings) C-O C=H $(CH_2)_n$

Based on Figure 3c and Table 5c, it shows that the BTC-MCS/GM pellets using PE contain the OH alcohol functional group at wave numbers of 2930.00 and 2038.85 cm-1, C=O at wave number of 1702.58 cm-1, C-O ether, carboxylate at wave number of 1702.58 cm-1, C-O ether, carboxylate at wave number of 1702.58 cm-1. 1034.85 cm-1, and C-H at wave numbers of 929.73, 843.89 cm-1. This functional group profile is similar to the research results of Smail and Chaoui [59] which showed that the TPS/LDPE composite had characteristic saccharide bands located at 921 and 1160 cm-1. These peaks are characterized by the C-C and C-O band stretching vibrations present in amylose and amylopectin. The wideband localized between 3100 and 3600 cm-1 corresponds to the vibration of the O-H group [60].

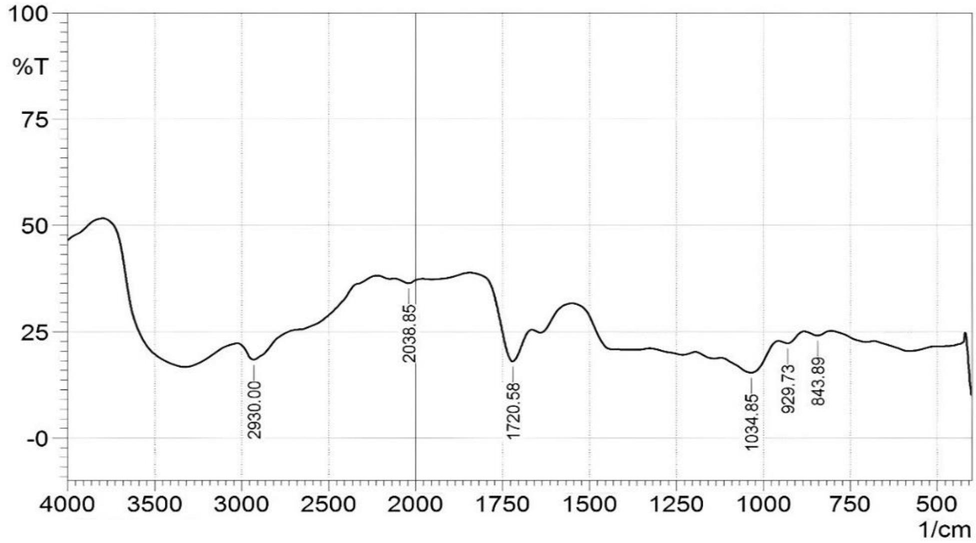


Figure 3c. Wavenumber spectrogram of BTC-MCS/GM pellets with PE

Table 5c. Wave numbers and functional groups contained in BTC-MCS/GM pellets using PE

Standard wavenumber area (cm^{-1}) (Gable, 2014)	Standard functional group (Gable, 2014)	Wave number of the pellet BTC-MCS/GM with PE (cm^{-1})	Functional groups in pellets BTC-MCS/GM with PE
2000-3600	O-H alcohol	2930.00, 2038.85	O-H alcohol
1690-1760	C=O	1702.58	C=O
1025-1200	C-O ether, carboxylate	1034.85	C-O ether carboxylate
650 – 1000	C=H	929.73, 843.89	C=H

Based on Figure 3d and Table 5d, show that BTC-MCS/GM pellets using PP contain the OH alcohol functional group at a wave number of 2940.61 cm-1, C=O at a wave number of 1724.44 cm-1, C-H bending at a wave number of 1446.67 cm-1, C-O ether, carboxylate at wave number of 1030.03 cm-1 and C-H at wave number of 840.04 cm-1. This result is similar to the research results of Matondang et al. [53], which showed that the OH group band in the PP-g-MA composite blended with sago starch experienced a shift from 3459 cm−1 to 3942 cm−1. Meanwhile, Tsioptsias et al. (2022) [46], informs that C=O vibrations occur at wave numbers 1,780-1,713 cm-1in the compatibilizer spectrum caused by symmetric stretching of C=O in the the anhydride and carboxylic acid groups.

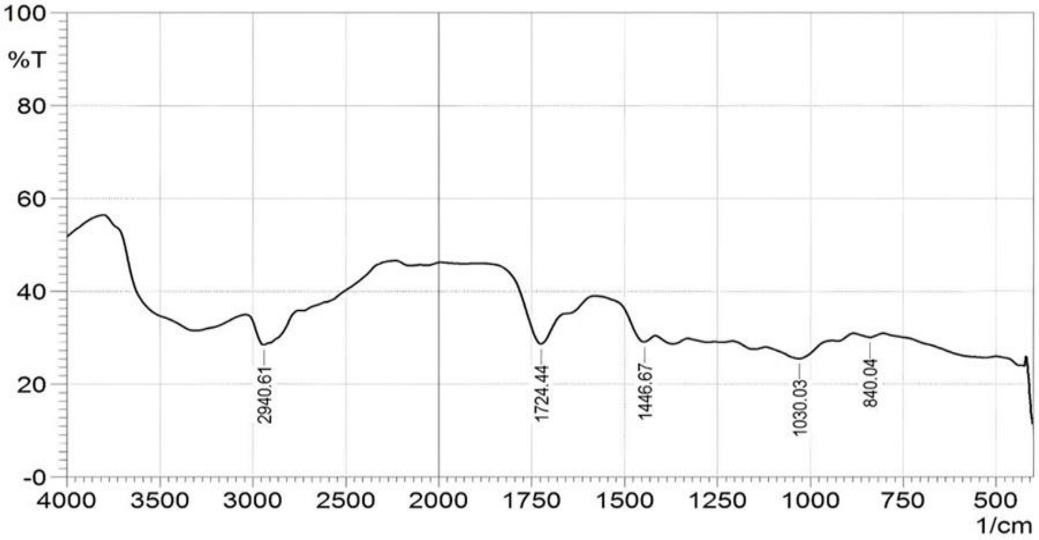


Figure 3d. Wavenumber spectrogram of BTC-MCS/GM pellets with PP

Table 5d. Wave numbers and functional groups contained in BTC-MCS/GM pellets using PP

Standard wavenumber area (cm^{-1}) (Gable, 2014)	Standard functional group (Gable, 2014)	Wave number of the pellet BTC-MCS/GM with PP (cm^{-1})	Functional groups in pellets BTC-MCS/GM with PP
2000-3600 1690-1760 1300-1475 1025-1200 650 – 1000	O-H alcohol C=O C-H bending C-O ether, carboxylate C=H	2940.61 1724.44 1446.67 1030.03 840.04	O-H alcohol C=O C-H bending C-O ether carboxylate C=H

4. Conclusion

The type and concentration of synthetic polymer have a very significant effect on the average tensile strength, elongation at break, young modulus, density, WVTR, O_2TR, swelling, Tm, MFR, crystallinity, and biodegradation time of BTC-MCS/GM pellets with synthetic polymers. BTC-MCS/GM pellets that use PCL, PLA, PE, and PP almost all meet SNI 7818:2014 and international standards, but the best is the BTC-MCS/GM pellets that use PLA with tensile strength characteristics of 23.56 MPa, elongation at break 7.18%, Young modulus 1548.34 MPa, density 1.22 g/ml, WVTR 179.76 g/m^2.day, O_2TR 199.67 ml/m^2.day, swelling 120.58%, Tm 152.47°C, MFR 0.62 g/10 minutes, crystallinity 0.62%, biodegradation time 11.67 days. The longitudinal surface profile using PLA shows smooth spots that are evenly distributed on all surfaces, while the transverse surface profile shows the presence of small, regular wavy lumps. Apart from that, BTC-MCS/GM pellets which are blended with PLA, contain the OH alcohol functional groups at wave numbers of 2144.94, 2884.67, 3100.7, 3283.95, 3601.25 cm^{-1}, C=C (alkyne) at wave numbers of 1937.58 cm^{-1}, C=O at wave number of 1719.61cm^{-1}, C=C at wave number of 1663.68 cm^{-1}, C=C (aromatic rings) at wave number of 1553.73 cm^{-1}, C-O at wave number of 1052.21, 1112.97 and 1248 cm^{-1}, C-H at wave number of 707.91 and 923.94 cm^{-1}, (CH2)n at wave number of 380.96 and 453.29 cm$^{-1.}$

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Conflict of interest

There are no conflicts of interest between the authors or with other parties.

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