



Original article

Synthesis and characterization of starch based bioplastics using varying plant-based ingredients, plasticizers and natural fillers

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ABSTRACT

With the ever-increasing demand of plastics in the world and their consequent disastrous effects on environment, a suitable environmental-friendly substitute like bioplastics/biodegradable plastics is the need time. This study centers on green-production of a variety of bioplastic samples from (1) banana peel starch (BPP) and (2) a composite of banana peel starch, cornstarch and rice starch (COM) with varying amounts of potato peel powder and wood dust powder as fillers, respectively. Two different plasticizers – Glycerol and Sorbitol – have been utilized separately and in a 1:1 combination. A total of 12 samples of each of two types of bioplastics were made using multiple amounts and combinations of the fillers and plasticizers, to test the differences in the physical and chemical characteristics (moisture content, absorption of water, solubility in water, solubility in alcohol, biodegradation in soil, tensile strength, Young's modulus and FT-IR) of the produced samples due to their different compositions. The differences in the properties of the bioplastic samples produced make them suitable for usage in many different applications. All 24 of the samples produced were synthesized using natural and environmentally safe raw material and showed biodegradation, thus proving to be a good alternative to the conventional plastics. © 2020 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Plastics are everywhere around us, being used for a plethora of purposes as they are cheap, easily available and perdurable (Narissara and Shabbir, 2013). In totality around 8.3 Billion metric tons of plastics has been created till now, while around 6.3 thousand metric tons of plastic waste has been produced. Only 9% of that waste plastic was recycled, 12% incinerated and the leftover 79% is cumulated in the sanitary landfill or in the environment. It is estimated that by 2050, 12 thousand metric tons of wasted plastics will get cumulated in the sanitary landfill or in open environment (Geyer et al., 2017). Due to the current growing production and disposal trends as well as the low percentage of waste being recycled by year 2050 the sea is projected to have a load of plastic greater than the fish (Sardon and Dove, 2018).

The disadvantages of plastics are many as they have a variety negative impacts, such as:

- Plastics do not degrade in nature thus stay in the environment for ages (Sanyang et al., 2016)
- Plastic production requires a lot of energy (Avérous et al., 2012)
- Plastics are a menace for the environment (Jones et al., 2013)

Furthermore, the increasing dependency of human beings on plastics is leading to plastic waste cumulating in landfills which becomes the cause of various negative effects such as groundwater pollution and dangers to the health of living organisms (Al-Salem et al., 2017).

Plastic pollution in the oceans is not only hazardous for human health but also for the marine animals which get entangled in that waste plastic (Rochman et al., 2013; Gregory, 2009). Humans get exposed to plastic particles through seafood, fresh water and air (Gasperi et al., 2015; McCormick et al., 2014; Galloway, 2015), which can cause a myriad of problems for human health such as toxicity or pathogenic diseases (Vethaak and Leslie, 2016). In addition to that another global concern is the high carbon footprint of petroleum plastics. The ever increasing price of the nonrenewable crude oil is pushing researchers to try and find suitable alternatives

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of it (Ismail et al., 2016), the best of which is bioplastics, an environmental friendly and harmless alternative (Reddy et al., 2013).

Polysaccharides being the most abundant macromolecules in flora and fauna, is one of the most suitable raw material for bioplastics in the form of starch, which is not only renewable and sustainable but is also plentiful and cheap. Starch also has favorable thermoplastic properties and is biodegradable (Thakur and Thakur, 2016; Imre and Pukánszky, 2015; Jiménez et al., 2012; Zhang et al., 2014). Starch is mainly made up of two kinds of glucose macromolecules, amylose and amylopectin (Pérez and Bertoft, 2010), however functional and structural dissimilarities are present between different types (Carpenter et al., 2017), thus the efficiency of starch as a raw material for bioplastics depends upon its specific structure and composition (Pfister et al., 2016).

The area of bioplastic research is fairly new thus research is still deficient in this field. Agricultural waste has been voiced as the cheap and renewable raw material alternative (Jain and Tiwari, 2015). Many techniques are used to step-up the use of starch as a biopolymer for creating bio-degradable materials which can be employed in various applications (Guimaraes et al., 2010; Yun et al., 2008). This study is centered on the use of renewable waste from natural agricultural sources like banana peels and a composite of banana peel starch, cornstarch and rice starch, for the production of bioplastics. This can be instrumental in reducing the hazards and issues of conventional plastics, as well as the meliorations of the mechanical characteristics of them by using readily available, abundant, biodegradable and renewable natural waste as reinforcing fillers.

2. Materials and methodology

Three types of starch were used, from banana peels, rice and corn. Reinforcement was done using waste products as fillers, like potato peel powder and sawdust.

2.1. Chemicals and fillers preparations

Ethanol, Analytical grade Glacial Acetic acid, Sorbitol, Glycerol 5 ml of acetic acid was poured carefully into 95 ml distilled water and stirred properly.

Pretreatment of fillers was done using slightly modified two similar methodologies of Darni et al., (Darni et al., 2017) and Moro et al., (Moro et al., 2017). Both the potato peels and wood shavings were reduced in size using scissors, followed by drying in oven at 90 °C for 5–6 h and then powdered in a blender. The powdered filler was then passed through a sieve of size 63 µm to get uniform powder size.

2.2. Production of bioplastics

2.2.1. Bioplastics from banana peel starch (BPP)

Banana peel bioplastic (BPP) was produced using slightly modified methods of (Astuti and Erprihana, 2014; Astuti and Erprihana, 2014) and (Yaradoddi et al., 2016; Yaradoddi et al., 2016).

Peels were washed properly and then reduced in size using scissors followed by boiling in water for 30 min. The water was stained and thrown away, while the peels were kept to dry. When dry the peels were made into a paste using a blender.

Aqueous acetic acid (5%) solution, plasticizers and water are the main ingredients. A total of 12 samples were produced (BPP1 - BPP12), varying the amount of the main ingredients such as plasticizer content (glycerol, sorbitol and their 1:1 combination) and potato peels powder filler content in (0:100, 5:95 and 10:90% w/v) to produce a variety of different samples, the composition of which is given in the (Table 2).

In order to synthesize the bioplastic samples, the required amount of paste of banana peels, 5 ml aqueous acetic acid (5%) solution and 5 ml/5 g of plasticizer as well as the required amount of reinforcement filler were added in a beaker, and stirred thoroughly. The mixture was boiled at 220 °C for 15 min while continuously being stirred. Then the cooked mixture was spread into a petri dish lined with aluminium foil and allowed to dry at room temperature for 24 h, followed by heating again in oven at 85 °C for 2 h. The bioplastic was again allowed to cool down properly before removing it from the foil.

2.2.2. Bioplastics from banana peel, cornstarch and rice starch composite (COM)

Bioplastics from a banana peel, cornstarch and rice starch composite (COM) was produced using slightly modified methods of Sujuthi and Liew (Sujuthi and Liew, 2016) and Sultan and Johari (Sultan and Johari, 2017).

Banana peel paste was prepared using the method mentioned above. Cornstarch solution (20% w/v) was obtained through dissolution of 20 g of cornstarch powder in required quantity of distilled water and then addition of more distilled water till the volume became exactly 100 ml; while the rice starch solution was obtained through boiling rice in water for 30 min, filtering the starchy water and then boiling it to reduce its volume to 50%.

These three ingredients, paste of banana peels (16 ml), Cornstarch solution (20% w/v) (12 ml) and rice starch solution (12 ml) were mixed in a ratio 40:30:30 respectively to get a 40 ml composite. Aqueous acetic acid (5%) solution, plasticizers and water are the other main ingredients. A total of 12 samples were produced (COM1 - COM12), varying the amount of the main ingredients such as plasticizer content (glycerol, sorbitol and their 1:1 combination) and sawdust powder filler content in (0:100, 5:95 and 10:90% w/v) to produce a variety of different samples, the composition of which is given in the (Table 3).

In order to synthesize the bioplastic samples, the required amount of composite starch solution, 5 ml aqueous acetic acid (5%) solution and 5 ml/5 g of plasticizer as well as the required amount of reinforcement filler were added in a beaker, and stirred thoroughly. The mixture was boiled at 220 °C for 15 min while continuously being stirred. Then the cooked mixture was spread into a petri dish lined with aluminium foil and allowed to dry at room temperature for 24 h, followed by heating again in oven at 85 °C for 2 h. The bioplastic was again allowed to cool down properly before removing it from the foil.

2.3. Characterization methods

2.3.1. Moisture content

Bioplastic samples of size 1.5 cm² were weighed to measure the initial weight (W_1). The samples were dried in an oven at 85°C for 24 h. The samples were weighed once more to measure the final weight (W_2). The moisture content was then determined using the following formula (Sanyang et al., 2016):

$$\text{MoistureContent}(\%) = \frac{(W_1 - W_2)}{W_1} \times 100$$

2.3.2. Absorption of water

Absorption of Water of the bioplastics was found out from slightly modified ASTM D570-98 method. Bioplastic samples with size 1.5 cm² were first dried in oven at 85 °C for 24 h to allow measuring its dry weight (W_1), followed by placing them in a beaker of 50 ml distilled water at room temperature for 24 h. After 24 h the bioplastic was obtained by filtering the water, and then its weight was measured to find its final weight (W_2). The absorption of water was found using the following formula:

Table 1
Composition of different bioplastic samples.

| Sample Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---------------|----|----|----|-----|----|----|----|-----|----|----|----|-----|
| Starch (ml) | 40 | 40 | 40 | 40 | 38 | 38 | 38 | 38 | 36 | 36 | 36 | 36 |
| Glycerol (ml) | 0 | 5 | 0 | 2.5 | 0 | 5 | 0 | 2.5 | 0 | 5 | 0 | 2.5 |
| Sorbitol (g) | 0 | 0 | 5 | 2.5 | 0 | 0 | 5 | 2.5 | 0 | 0 | 5 | 2.5 |
| Filler (g) | 0 | 0 | 0 | 0 | 2 | 2 | 2 | 2 | 4 | 4 | 4 | 4 |

Table 2
Physical and chemical properties of Banana Peel Bioplastic (BPP) Samples.

| Bioplastic Sample | Moisture Content % | Absorption of Water % | Solubility in Water % | Solubility in Alcohol % | Biodegradation % |
|-------------------|--------------------|-----------------------|-----------------------|-------------------------|------------------|
| BPP-1 | 5.58 | 218.39 | 42.53 | 39.02 | 12.07 |
| BPP-2 | 37.63 | 104.48 | 85.57 | 77.22 | 81.41 |
| BPP-3 | 11.88 | 85.66 | 83.67 | 72.2 | 70.25 |
| BPP-4 | 21.34 | 98.86 | 85.17 | 74.44 | 69.96 |
| BPP-5 | 5.5 | 198.7 | 28.14 | 29.63 | 49.48 |
| BPP-6 | 21.28 | 106.31 | 72.26 | 59.96 | 62.61 |
| BPP-7 | 9.51 | 94.08 | 67.91 | 56.43 | 58.39 |
| BPP-8 | 14.35 | 101.55 | 70.19 | 59.54 | 57.66 |
| BPP-9 | 1.46 | 210.06 | 25.35 | 23.46 | 53.19 |
| BPP-10 | 20.24 | 122.36 | 62.98 | 51.25 | 69.8 |
| BPP-11 | 7.11 | 113.37 | 59.41 | 49.38 | 67.63 |
| BPP-12 | 9.37 | 114.56 | 59.9 | 50.59 | 65.32 |

Table 3
Physical and chemical properties of COM samples.

| Bioplastic Sample | Moisture Content % | Absorption of Water % | Solubility in Water % | Solubility in Alcohol % | Biodegradation % |
|-------------------|--------------------|-----------------------|-----------------------|-------------------------|------------------|
| COM-1 | 6.54 | 215.79 | 10.53 | 8.62 | 29.59 |
| COM-2 | 35.52 | 94.19 | 67.65 | 60 | 79.09 |
| COM-3 | 10.31 | 87.9 | 65.32 | 52.21 | 78.4 |
| COM-4 | 17.67 | 91.39 | 65.57 | 57.5 | 66.02 |
| COM-5 | 5.07 | 163.89 | 10.19 | 8.61 | 31.94 |
| COM-6 | 18.52 | 97.09 | 54.61 | 49.31 | 65.03 |
| COM-7 | 6.97 | 91.13 | 54.19 | 49.01 | 56.37 |
| COM-8 | 13.51 | 93.57 | 54.5 | 49.02 | 44.59 |
| COM-9 | 4.65 | 215.69 | 8.97 | 8.05 | 34.76 |
| COM-10 | 17.03 | 125.07 | 44.14 | 37.89 | 66.92 |
| COM-11 | 5.52 | 110.56 | 40.99 | 37.24 | 66.56 |
| COM-12 | 11.23 | 112.88 | 43.59 | 37.53 | 60.34 |

$$\text{WaterAbsorption}(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

2.3.3. Solubility in water

Bioplastic samples of size 1.5 cm² were first dried in oven at 85 °C for 24 h to allow measuring its dry weight (W₁), followed by placing them in a beaker of 50 ml distilled water at room temperature for 24 h. After 24 h the bioplastic residue was obtained by filtering the water and again dried in an oven at 85 °C for 24 h and then weighed to find final weight (W₂). The solubility was found using the following formula (Sanyang et al., 2016):

$$\text{SolubilityinWater}(\%) = \frac{(W_1 - W_2)}{W_1} \times 100$$

2.3.4. Solubility in alcohol

Bioplastic samples of size 1.5 cm² were first dried in oven at 85 °C for 24 h to allow measuring its dry weight (W₁), followed by placing them in 3 ml ethanol in test tubes with caps on at room temperature for 24 h. After 24 h the bioplastic residue was obtained by filtering the water and again dried in an oven at 85 °C for 24 h and then weighed to find final weight (W₂). The solubility was found using the following formula (Sanyang et al., 2016):

$$\text{SolubilityinAlcohol}(\%) = \frac{(W_1 - W_2)}{W_1} \times 100$$

2.3.5. Biodegradability test

Bioplastic samples of size 1.5 cm² were weighed to measure the initial weight (W₁). The samples were buried under 2 cm of moist garden soil contained in Styrofoam cups and kept for 5 days at room temperature. The soil was kept moist for 5 days, after which the bioplastic residue was collected from the soil, followed by washing with water and drying in an oven at 85 °C for 24 h and then again weighed to measure the final weight (W₂). The biodegradability was measured from the following formula (Tan et al., 2016):

$$\text{Biodegradability}(\%) = \frac{W_1 - W_2}{W_1} \times 100$$

2.3.6. FT-IR

FT-IR technique was utilized to out the functional groups present in the bioplastic samples, using 4000–650 cm⁻¹ wavenumber range and 2 cm⁻¹ resolution. Beam splitter: Germanium-coated KBr for Middle IR (Standard). The spectrum data in graphic form was analyzed in results. Fourier Transform Infrared Spectrophotometer (FT-IR) Instrument = IRTracer-100, Shimadzu Corporation.

2.3.7. Mechanical properties

Universal testing machine was used to measure the tensile strength as well as the Young's modulus of the samples, with 10 mm/min as crosshead speed and 40 mm length and 15 mm width of gauge.

2.3.8. Statistical analysis

After completion of the characterization of the samples, the results of the physio-chemical properties were analyzed, tabulated and represented graphically. These results were analysed statistically utilizing Microsoft Excel 2013.

3. Results

3.1. Preparation of starch based bioplastic samples

Twelve samples of each starch based bioplastic samples were synthesized using different amounts and combinations of plasticizers and fillers. The amount of Acetic Acid (5%) was kept constant for all samples, i.e., 5 ml. Control sample 1 were synthesized without any filler or plasticizer (Table 1.).

3.2. Physical and chemical properties of the samples

The properties of the banana peel starch (BPP) bioplastic samples (Fig. 1) can be seen in (Table 2); whereas the properties of Banana Peel/Cornstarch/Rice Starch Composite (COM) samples (Fig. 4) can be seen in (Table 3) given below.

3.2.1. Moisture content

The values for the moisture content of both BPP (Fig. 3) and COM (Fig. 6) bioplastics were noted to increase when plasticizer was added. The control (sample 1) has the lowest value of moisture content. Bioplastic samples with glycerol had the highest values of moisture content, while those with glycerol-sorbitol had values lower than them and bioplastics with sorbitol had the lowest value. This has been explained in a previous study that glycerol comprises of hydroxyl group which has an affinity for water molecules that allowing them to make hydrogen bonds and contain water in the structure (Cerqueira et al., 2012), while sorbitol forms substantial hydrogen bonds with the starch molecules, thus reducing the affinity for water molecules (Sanyang et al., 2016). In both the bioplastic (BPP and COM) samples moisture content was

observed to decrease with increasing the amount of filler added (Fig. 2 and Fig. 5). Such results were also observed in research undertaken by (Mohan et al., 2016; Mohan et al., 2016).

3.2.2. Absorption of water

The values of absorption of water were highest for the control samples (sample 1) of both the BPP and COM bioplastics (Fig. 7). The reason for this is that the hydroxyl group in starch has an affinity for water molecules and the gelatinisation also breaks up starch granules which lets water diffuse in (Azahari et al., 2011). Many studies have shown that absorption of water is directly proportional to the quantity of starch (Sujuthi and Liew, 2016; Azahari et al., 2011; Aranda Garcia et al., 2015). Thus addition of plasticizer decreases absorption of water. Of the samples plasticized, the ones with glycerol had the highest absorption of water, followed by glycerol-sorbitol and then sorbitol respectively. Glycerol has a higher attraction to water molecules as compared to sorbitol molecules (Sanyang et al., 2016; Cerqueira et al., 2012).

3.2.3. Solubility in water

The values for solubility of water was seen to increase upon adding plasticizer in both BPP (Fig. 3) and COM (Fig. 6) bioplastics. This can be explicated by examining the starch molecules' crystalline structure which consists of hydrogen bonds, which results in starch granules being insoluble in cold water (Sarker et al., 2013). As with moisture content retention and absorption of water, the solubility of starch based bioplastics in water was also seen to be highest in samples with glycerol as a plasticizer and lowest in samples with sorbitol, while the samples with the glycerol-sorbitol combination were in between the two. This can be explicated with the fact that glycerol has a greater attraction to water than sorbitol, and its molecular weight is also lighter which lets the water molecules penetrate easily into polymer chains (Ghasemlou et al., 2011). Previous studies have also shown that plasticizer type affects a bioplastic's solubility in water (Chiumarelli and Hubinger, 2014).

Solubility of water was observed to decrease upon adding fillers in both BPP (Fig. 2) and COM (Fig. 5) bioplastics. This is because both the fillers, potato peel powder and wood dust are very slightly soluble or insoluble in water as potato peel is mainly made of starch (Arapoglou et al., 2010) and starch granules demonstrate water insolubility at normal room temperature (Alcázar-Alay and Meireles, 2015), while wood dust is composed of cellulose

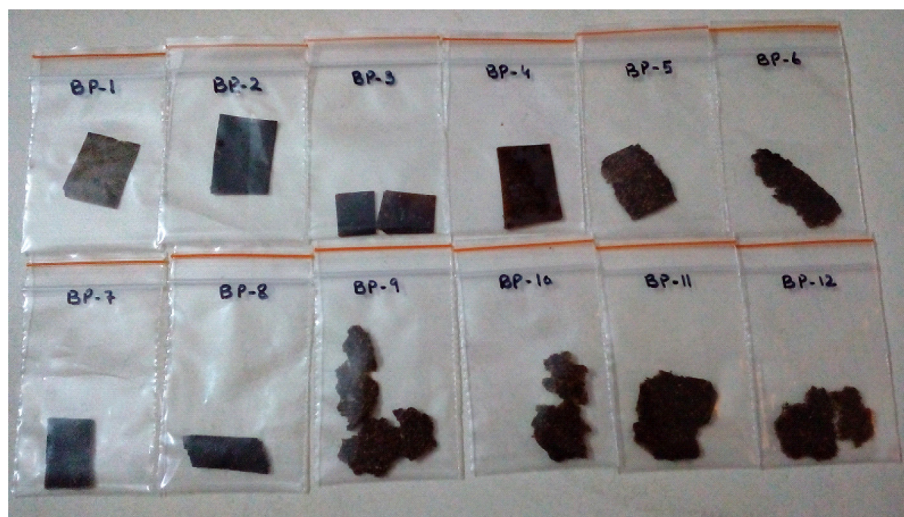


Fig. 1. Showing the twelve different banana peel starch based bioplastic samples produced.

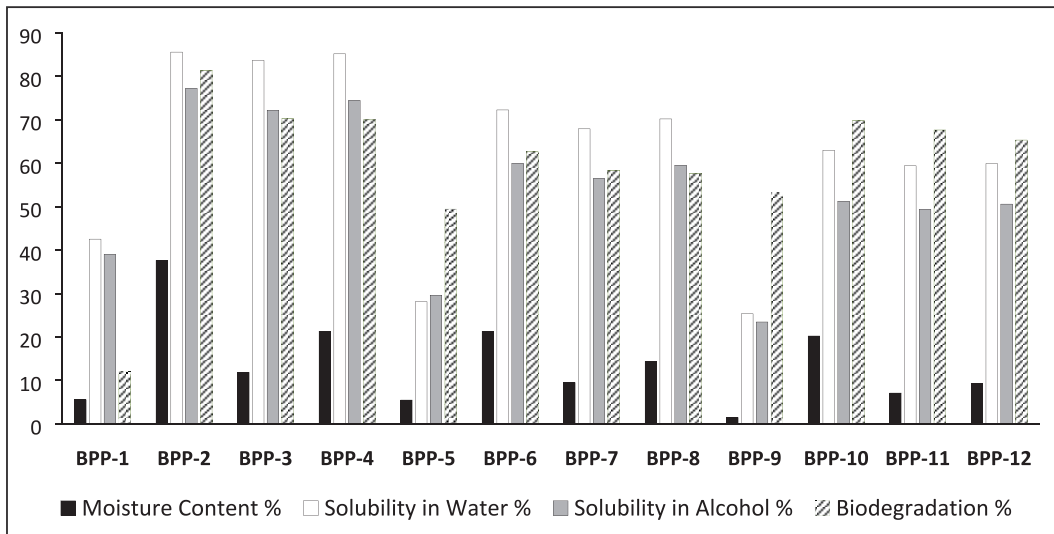


Fig. 2. Impact of filler amount on properties of BPP samples.

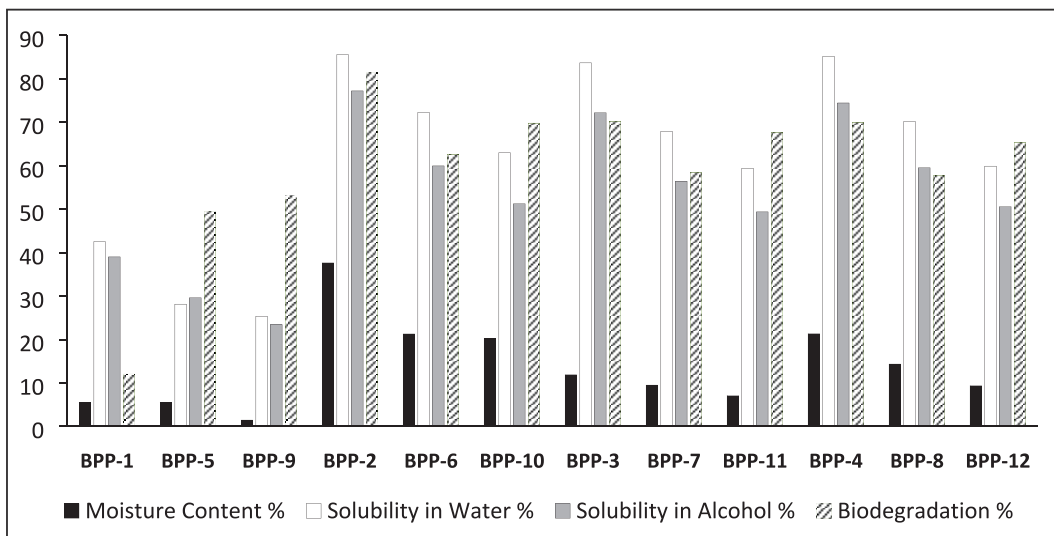


Fig. 3. Impact of plasticizers on properties of BPP samples.



Fig. 4. Showing the twelve different COM samples produced.

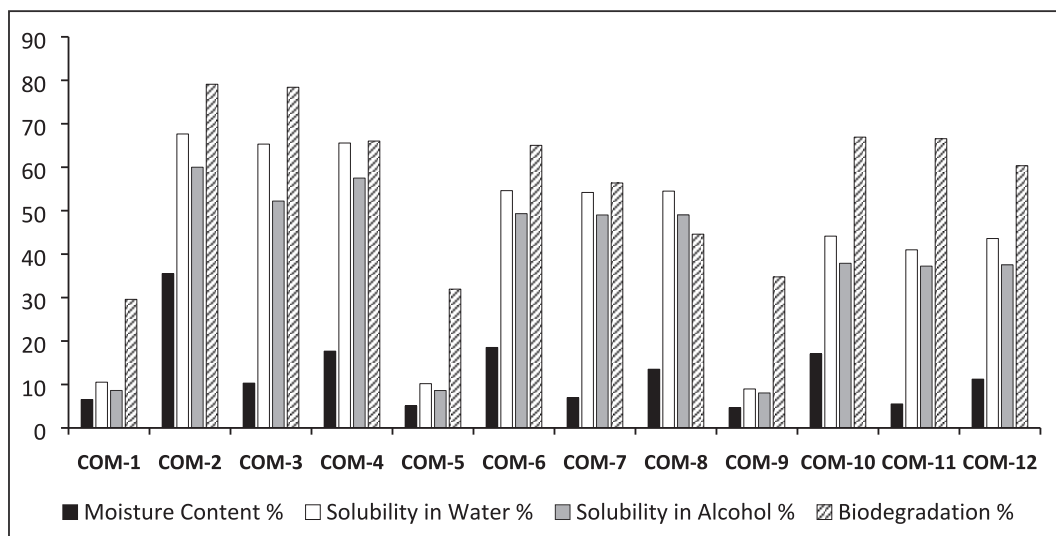


Fig. 5. Impact of filler amount on properties of COM bioplastics.

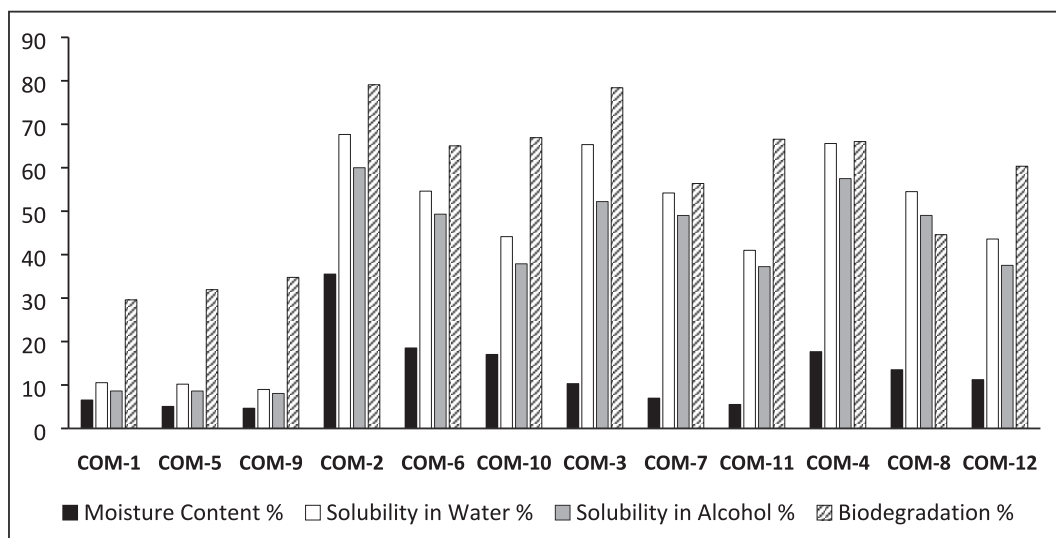


Fig. 6. Impact of plasticizers on properties of COM bioplastics.

(Shulga et al., 2007) which also exhibits water insolubility (Chen et al., 2015a, 2015b).

3.2.4. Solubility in alcohol

Solubility in Alcohol increased when plasticizer was added in both BPP (Fig. 3) and COM (Fig. 6) bioplastics. Following the trend of moisture content, absorption of water and solubility in water of starch based bioplastics was also seen to be highest in samples with glycerol as a plasticizer and lowest in samples with sorbitol, while the samples with the glycerol-sorbitol combination were in between the two. Starch is not soluble in alcohol at normal room temperature, and sorbitol is very slightly soluble in comparison to water (O’Neil, 2006). Addition of filler decreased the solubility in alcohol, as both fillers used, powdered potato peels and powdered wood dust for both types of bioplastics BPP (Fig. 2) and COM (Fig. 5) respectively are very slightly or completely insoluble in alcohol because they are mainly made up of starch and cellulose respectively which are insoluble in alcohol as reported by (Chen et al., 2015a, 2015b; O’Neil, 2006).

3.2.5. Biodegradation

Physiochemical properties like chemical structure, molecular weight, affinity to water and surface area etc. of the bioplastics determine their biodegradation ability (Tokiwa et al., 2009). In BPP bioplastics (Fig. 3), control was observed to have the lowest biodegradation. Adding plasticizer was detected to increase the biodegradation of the bioplastics samples, while adding fillers (5% w/v) was detected to reduce biodegradation ability in plasticized samples and improve it in unplasticized sample (Fig. 2). Yet, increasing the filler quantity from 5% w/v to 10% w/v was detected to increase the biodegradation for both plasticized and unplasticized bioplastic samples. Adding plasticizer improving the biodegradation of samples can be attributed to better water absorption capacity of the samples which is because of the affinity of both the plasticizers (glycerol and sorbitol) towards water. Samples with glycerol exhibited the highest level of biodegradation, followed by samples with sorbitol as plasticizer and glycerol-sorbitol combination as plasticizer, respectively. The exact same trend was noticed for COM samples (Fig. 5 and Fig. 6).

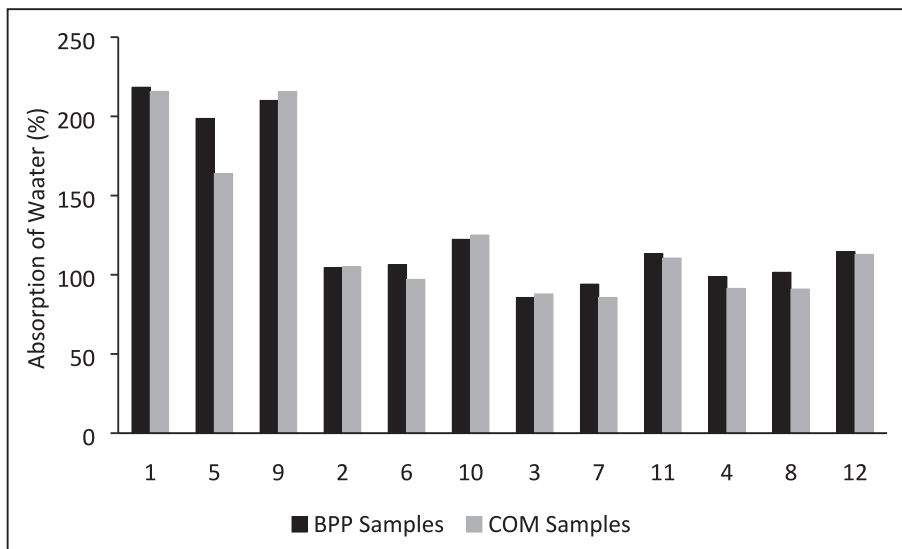


Fig. 7. Effect of plasticizers on absorption of water capacity (%) of BPP and COM bioplastics.

3.2.6. Tensile strength and Youngs modulus

Observing the mechanical properties of bioplastics is essential to find their usability (Azahari et al., 2011; Spiridon et al., 2013). Tensile strength and Youngs Modulus of various bioplastics produced were tested in the study using Universal testing machine. Plasticizers were seen to have the same effect in both types of bioplastics (BPP and COM), with samples with glycerol having the lowest values for tensile strength and Youngs Modulus and samples with sorbitol having the greatest values, while samples with a combination of glycerol-sorbitol used as plasticizer showed results in between the two (Fig. 9 and Fig. 10). Similar results with similar trends for glycerol and sorbitol plasticized biofilms have been previously reported in studies (Tapia-Blácido et al., 2013; Ooi et al., 2012). The greater plasticization ability of Glycerol over sorbitol can be attributed to the former having a smaller molar mass (almost half) than the latter, thus allowing the molecules of glycerol and starch to interact more efficiently. However in sample where a combination of the two plasticizers is added, both of them

impact the bioplastic tensile strength and Youngs modulus simultaneously (Sanyang et al., 2016).

3.2.7. Fourier Transform Infrared Spectroscopy (FTIR)

Functional groups and any potential chemical alterations upon addition of plasticizers and fillers were observed using the FTIR analysis. It allows for quick, authentic and efficient determination of functional groups (Pavia et al., 2001). Characteristic peaks between 2925 and 3011 cm^{-1} signifying = C-H stretching, because of the presence of starch, were noticed in all analyzed samples of both kinds of bioplastics (Fig. 11 and Fig. 12). Similar peaks in starch based bioplastic samples have been observed before as well (Yin et al., 2005). Peaks signifying O-H functional group between 3290 and 3316 cm^{-1} were observed in plasticized samples. This is because both plasticizers used, glycerol and sorbitol, are polyols (Ano et al., 2017) which contain a huge number of O-H groups, causing broad peaks between 3600 and 3200 cm^{-1} to be observed (Chen et al., 2015a, 2015b). Similar peaks between 3200 and

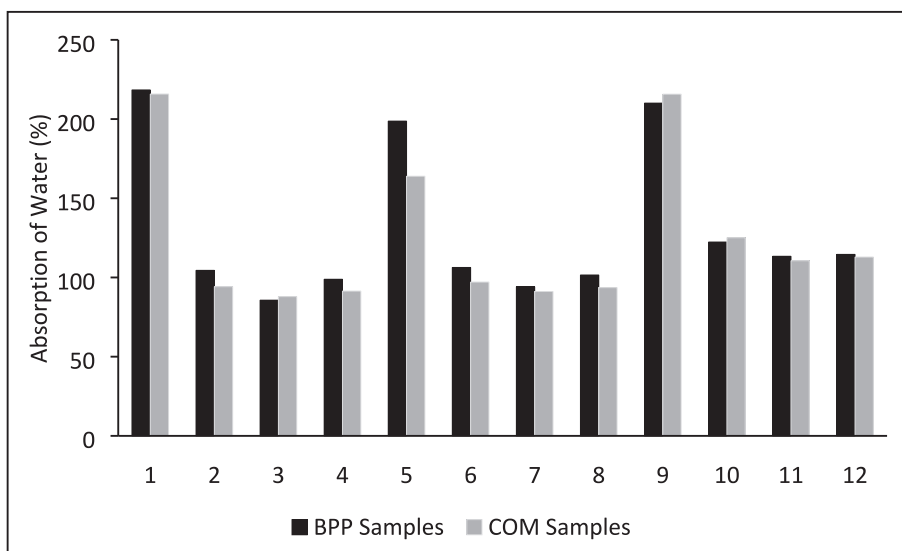


Fig. 8. Effect of filler amount on absorption of water capacity (%) of BPP and COM bioplastics.

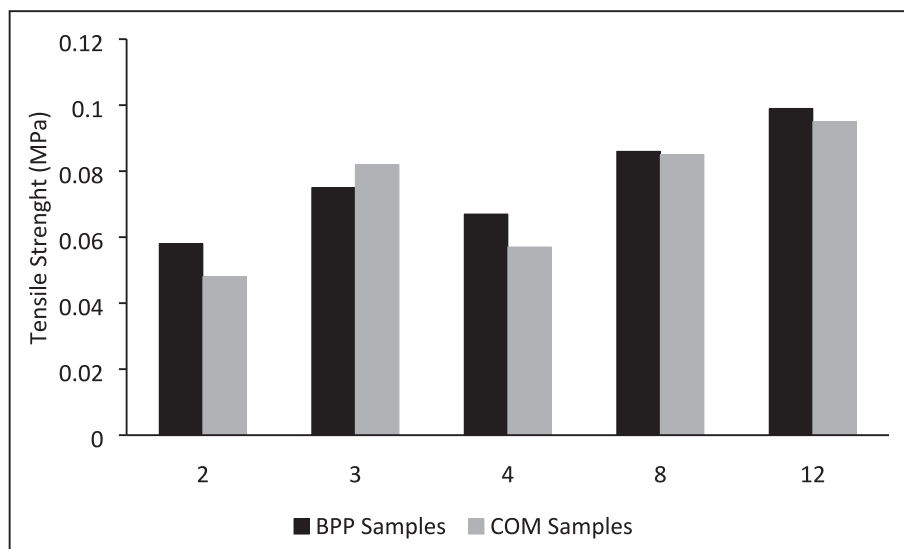


Fig. 9. Impact of plasticizer and filler on Tensile Strength of BPP and COM bioplastics.

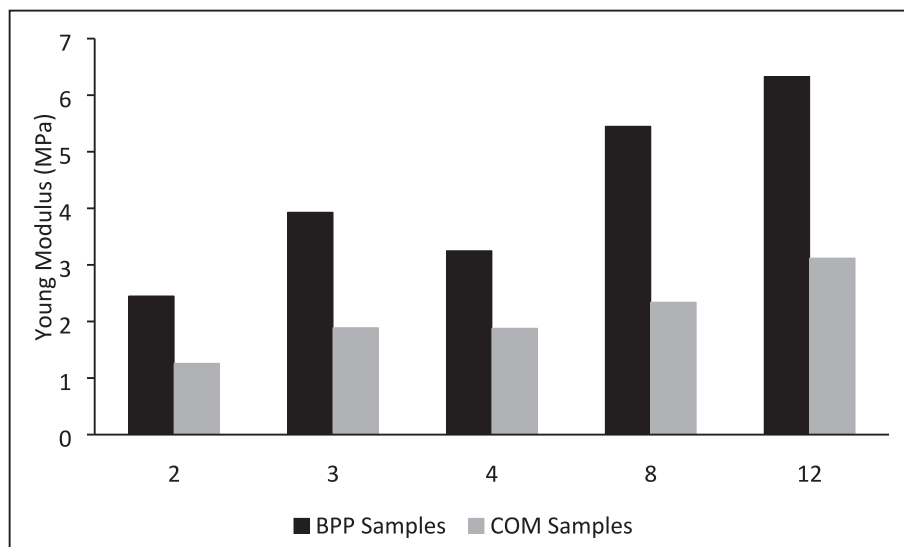


Fig. 10. Impact of plasticizer and filler on the Young Modulus of BPP and COM bioplastics.

3600 cm^{-1} for O-H stretching were also noticed by Cao *et al.*, (Cao *et al.*, 2008). A few peaks between 900 and 1033 cm^{-1} signifying C-O-H group and 1075–1155 cm^{-1} signifying C-O-C group were noticed in all unplasticized and plasticized samples of COM bioplastics, while they were absent in unplasticized BPP bioplastics, where these specific functional groups were only noticed in plasticized samples (Fig. 11). This can be explicated by keeping in consideration the quantity of water utilized while preparing the samples, as water itself can behave as a plasticizer (Juansang *et al.*, 2015; Kuo *et al.*, 2016). BPP samples had very small amount of water added to them in comparison to COM bioplastics, which may have resulted in the absence of these specific functional groups in unplasticized BPP sample. In a previously conducted study by (Abolibda, 2015; Abolibda, 2015), plasticized bioplastics also demonstrated three to four peaks between 1200 and 900 cm^{-1} . Addition of filler was not found to add any new functional groups to the samples. In a similar former study on starch-based bioplastics, adding filler was also not found to add any new functional groups (Darni *et al.*, 2017).

4. Discussion

Absorption of water was observed depend upon the nature of filler used and its amount. Both BPP and COM bioplastics (Fig. 8) with powdered potato peels and wood dust as filler respectively presented similar results where samples with no filler added (except control) demonstrated the lowest absorption of water capacity whilst addition of filler demonstrated a steady increase in the water absorbance capacity. In a study by Darni *et al.*, (Darni *et al.*, 2017), similar results were also noticed in which absorption of water was seen to increase when sorghum stalks filler was added into a sorghum starch based bioplastic. This can be attributed to sorghum stalks comprising of cellulose, and cellulose being hydrophilic. Pine wood dust consists of 58.2% cellulose by weight (Shulga *et al.*, 2007), thus our results are justified. Increasing amount of cellulose based filler also increases absorption of water because of the intramolecular hydrogen bonding (Maulida *et al.*, 2016). The increase in the absorption of water capacity of BPP bioplastic samples can also be due to the presence of powdered potato

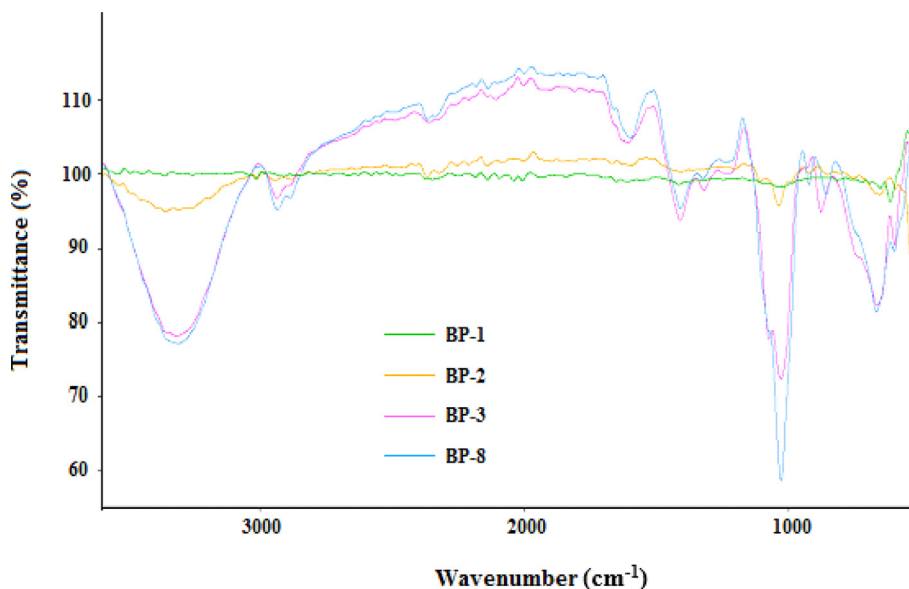


Fig. 11. FTIR spectra of BPP bioplastic samples.

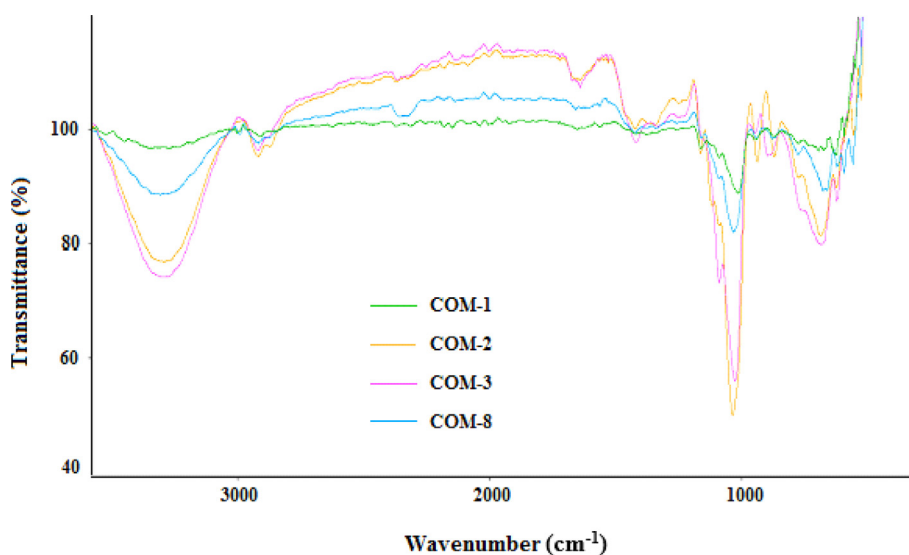


Fig. 12. FTIR spectra of COM bioplastic samples.

peel filler. Potato peel contains 52.14% starch by dry weight (Arapoglou et al., 2010). Starch is hydrophilic in nature (Lu et al., 2009) so increasing the amount of the powdered potato peel filler in BPP bioplastic samples no doubt increases the capacity of absorption of water. In other studies, Bogoeva-Gaceva et al., (Bogoeva-Gaceva et al., 2006) also noticed an increase in water absorption capacity by jute fiber filled polypropylene on increasing the quantity of jute fiber, while the results demonstrated by (Ewulonu and Igwe, 2012; Ewulonu and Igwe, 2012) were also similar as they detected enhanced absorption of water capacity of oil palm fruit bunch fiber filled high density polypropylene as the filler amount was increased. The two main ways in which water can diffuse into the structure of the bioplastics: the empty spaces between the bioplastic matrix and added filler let water diffuse into the bioplastic, or the interfacial fissures of the bioplastic with added filler can cause capillary action. Water that has been absorbed into the bioplastic is mainly of two kinds: (a) free water

– water that move in or out from the spaces in the matrix or (b) bound water molecules – water that is dispersed through the bioplastic and has an affinity for the polar groups present within.

In a study by Mohan et al., (Mohan et al., 2016) the adding filler to cornstarch bioplastics was seen to reduce biodegradation. Nevertheless, the phenomenon of increase in the filler quantity causing meliorated biodegradability can be explicated by keeping in consideration the fact that the presence of filler provides a huge surface contact area through which degrading agents can enter the polymer (Rutkowska et al., 2002). Thus, natural fillers do not only help in biodegradation but in oxidation too. The biodegradation of bioplastic samples improving proportionally upon adding filler was observed by Kim et al., (Kim et al., 2006) who noticed biodegradation (percentage weight loss) of biocomposites increasing upon increase in the quantity of rice husk flour filler. Natural filler have also formerly been proven to have the ability to accelerate the biodegradation of bioplastics by Kumar and Sekaran,

(Kumar and Sekaran, 2014) and Egute *et al.*, (Egute *et al.*, 2009). Fillers demonstrate hydrophilic properties and microorganisms can easily absorb them, resulting in enhanced adhesiveness of microorganisms to the surface of the polymer (Shah *et al.*, 2008). This helps in the adhesion of microorganisms to the surface of the polymer and its resultant biodegradation. The physical and chemical characteristics of fillers define the biodegradation of polymer (Mastalygina *et al.*, 2016). The fact that powdered potato peels and powdered wood dust are used as fillers in BPP and COM bioplastics also helps explain the obtained results because according to Mastalygina *et al.*, (Mastalygina *et al.*, 2017) existence of wheat and wood flour in low-density polyethylene matrix improves the growth of fungus. Fillers that contain protein or easily soluble and hydrolyzed components improve biodegradation ability.

Addition of fillers was seen to enhance the tensile strength and Youngs modulus of both types of bioplastic samples proportionally (Fig. 9 and Fig. 10). Similar results have also been reported in a formerly conducted study on the tensile strength of starch based bioplastics (Maulida *et al.*, 2016) as well as Youngs Modulus (Liang, 2013; Dawale and Bhagat, 2018). Azahari *et al.*, (Azahari *et al.*, 2011) comment that enhancement of these properties be attributed to the fact that better interfacial adhesiveness can lead to the creation of stronger hydrogen bonds amongst starch matrix and the filler.

5. Conclusion

This study shows that starches from different natural sources can be used, individually or combined, with and without the addition of different plasticizers, and kinds and amounts of natural fillers to produce a variety of different kinds of bioplastics boasting different physical and chemical characteristics. The differences in these properties will allow the bioplastics to be suitable for varying applications. All the bioplastics produced were biodegradable and environmental-friendly, thus being a good substitute of petroleum-based plastics, and an efficacious way to alleviate the problem of plastic pollution.

6. Recommendations

- Bioplastics can be synthesized from a huge variety of renewable organic raw materials from faunal, floral, algal and microbial sources that are inexpensive, occur in huge quantity and do not compete with food and feed production, so further efforts to identify suitable raw materials to synthesize biodegradable biopolymers have to be made by experimenting and testing different sources of renewable organic material.
- A plethora of different kinds of materials are discarded as waste in all sectors around the world which can be used as fillers in bioplastics. Thus, different kinds of waste materials need to be researched upon to determine their efficiency as reinforcing filler in bioplastics. Using inexpensive raw materials for the synthesis of bioplastics can also make them economically feasible.
- Poor resistance of bioplastics to moisture impede their growth and use on a larger scale, thus research needs to be done on agents that can impart hydrophobic properties to them to improve their resistance against moisture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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