Mechanical properties of Biodegradable Composite Developed by Modification of Poly lactic Acid with Orange Peel Powder

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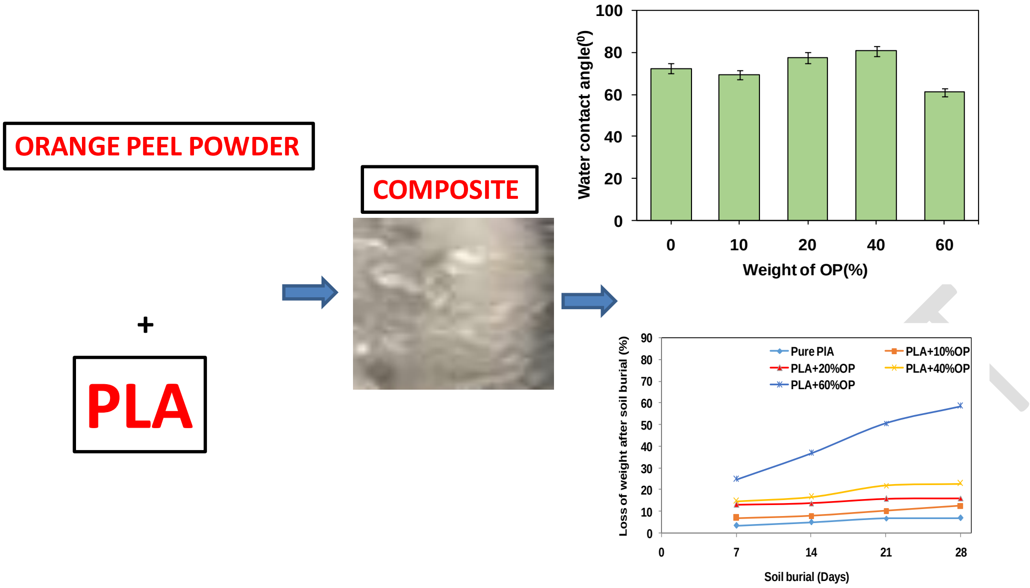
Graphical Abstract



Abstract

One of the biggest environmental issues has been the use and disposal of traditional fossil-based plastic, which is not biodegradable and uses a lot of energy in its production. Poly lactic acid (PLA) has received a lot of attention as an environmentally friendly substitute due to the fact that it is a renewable polymer made from natural sources with qualities equivalent to traditional plastics and minimal environmental cost. Orange peel waste is abundantly produced and contains many important components, but its prospective uses in fortifying the PLA matrix have received little attention. Synthesized from dried orange peel waste, orange peel powder (OP) was added to PLA solution in this investigation. Finally, thin films were produced using the solution casting method from PLA/OP solutions with varying OP loadings (0, 10, 20, 40, and 60 wt%). The addition of OP to PLA has reduced its tensile strength and Young's modulus, but has increased its elongation at break by 49–737%, as shown by tensile test results. Analyses of water contact angles reveal that hydrophilic OP has altered the hydrophobicity of PLA's surface, with contact angles ranging from 70.12^{0} to 88.18^{0}: nevertheless, greater loadings result in a reduction in surface energy. After 28 days, the

PLA/60 wt% OP composite has the highest biodegradation performance, with a weight loss of 59.43%. This suggests that the inclusion of OP enhances the biodegradability of PLA.

Keywords: Composites, Morphology, Orange powder, Soil degradation, Strength.

1. Introduction

Plastic is a material that is strong, cheap, and light. It can be used for many things, from food containers to computer goods. Every year, more than 381 million tons of plastic are made, and it was said that about 55% of that was for one-time use only, 25% was burned, and 20% were reused (Geyer *et al.,* 2017). Most people use standard petroleum-based plastic, which doesn't break down very well and pollutes the environment and uses up resources that can't be replaced (Moshood *et al.*, 2022). The process of making plastic goods uses a lot of energy, and the most popular ways to get rid of plastic waste, like putting it in landfills, burning it, or throwing it into the ocean, are bad for the environment (Acquavia *et al*., 2021). Plastic waste in the environment can reduce the amount of land available because it can take up to a few hundred years for plastic goods to break down fully in landfills (Chamas *et al*., 2020). If plastic garbage were burned instead of thrown away, its amount could be cut by 80 to 95% (Acquavia *et al*., 2021). But when plastics are burned, poisonous heavy metals and dangerous gases are released into the air (Royer *et al.*, 2018). Recent studies (Mohammed and Meincken, 2021) have shown a lot of interest in biopolymer because of growing worries about plastic waste. Environmentally friendly biopolymers originating from renewable sources or capable of decomposing spontaneously are favoured as safer alternatives (Balart *et al*., 2021, Mahmud *et al*., 2021). Poly(lactic acid), also called Polylactide, is a polymer that can be made over and over again. It is made by esterifying lactic acid, which is made by fermenting sugar (Singhvi *et al*., 2019). PLA got a lot of attention because it was seen as the most likely biopolymer to replace plastic made from oil. It has good mechanical properties, can be made into different products, and has a low carbon footprint. But PLA can't be used for everything because it is very weak and doesn't have good barrier qualities (Bassani *et al*., 2019). PLA may be decomposed in a few days to several months under regulated and precise industrial composting conditions, however it can take hundreds of years to disintegrate in landfill. Also, getting rid of orange waste has been hard because there is a lot of it but not enough use for it. (Raimondo *et al*., 2018) proposed that about 31.2 million tons of citrus fruits are processed every year, and that 50 to 60% of the total weight ends up as waste. Citrus trash can't be put in a landfill because it has a low pH, which can make the earth salty and hurt ruminants in other ways (Bátori *et al.,* 2017). Orange peel is a kind of fruit trash that has a lot of useful things in it, like pectin and cellulose fibers. Pectin that gels well and cellulose fibers that give goods strength could be used as new building blocks. Cellulose breaks down naturally when microbes eat it. People are interested in these benefits of orange peel trash because they could be used to strengthen traditional petrochemical or biobased materials. People think that adding orange peel powder to reusable PLA can make the biobased polymer more biodegradable and improve its mechanical qualities, such as its flexibility. Bassani *et a.*, did study on how to use an extract of antioxidants from orange peels to make a new type of active packing made of PLA. One of the good things about orange peels is that they contain phenolic chemicals, which are good antioxidants (Rafiq *et al.,* 2018). So, more study needs to be done on how to combine orange peel powder and PLA to make biocomposites. In this work, orange peel powder is added to pure PLA to make it break down faster in nature while keeping its good physical properties. The unaltered orange peel garbage is reduced to a fine powder and combined with PLA in varying proportions in a chloroform solution. With the solution casting method, a smooth hybrid film is made by pouring the uniform solution onto a flat surface. Researchers test how quickly the biocomposite film breaks down by placing it in the ground for 28 days.

2. Materials and Methods

2.1. Materials

Nature Tech India Private Limited, Chennai, India, supplied PLA (PLA 4043D). Oranges were purchased from a local grocery in Chennai. Merck International in India supplied the chloroform, hydrochloric acid, and sodium hydroxide. The compounds are used without being purified or treated further.

2.2. Pre-Treatment and Synthesis of Orange Peel Powder

The gathered sweet orange peel washed off with regular water to eliminate surface contaminants. According to (Farahmandfar *et al.,* 2020), orange peel was sun dried for 20 hours before being dried in an oven for 18 hours at 60^0C. Then, using a pestle and mortar to decrease the size of the dried orange peel, an electric blender was used to ground the peel into a fine powder. The grinded powder was then sieved in 100µ m size for uniformity and stored in room temperature.

2.3. Synthesis of Composite Films

PLA pellets were allowed to dissolve in chloroform for 1 hour at room temperature under constant stirring to generate a 10% PLA solution. Weight of 0.5g of OP was mixed with PLA solution for the process of producing PLA with 10% wt of orange powder (OP). It was then agitated for one hour in constant speed. After mixing the solution was poured on to the glass plate and petri dishes. It's then allowed to dry at room temperature for 24 hours. The same procedure was adopted by altering the quantity of orange powder used to generate PLA/OP solutions comprising 20%, 40%, and 60% OP.

2.4. Properties of composite

A stereoscopic microscope was used to capture the morphology of the film. Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the sample functional groups. A 2x2 cm^2 pure PLA sample was put on the FTIR. The same size PLA sheet was put on a goniometer for water contact angle analysis. A single drop of deionized water was dispensed from the syringe on top onto the surface of the specimen. The angle formed by the surface of the specimen and the edge of the water drop was measured. Mechanical strength study was performed with a universal testing machine. Blank PLA sheet was cut into dumbbell shapes in accordance with the ASTM D638 standard. While the sample was inserted into the 5 kN Universal Testing Machine's grip, the software was used to record the sample's dimensions, including its breadth, gauge length, and thickness. The grip separation was initiated and continued at a steady speed of 5 mm/min until the sample was broken. The graph obtained was used to analyze the various strength of the sample.

2.5 Biodegradability Test

The initial weight (Winitial) of PLA-free and PLA/OP composite samples cast in an 8-centimeter-diameter Petri dish was determined by weighing PLA-free and PLA/OP samples of varying concentrations. Each sample was interred in a container with 2 centimetres of moist garden soil for 28 days in an open environment. The method of conducting biodegradability test has been modified from investigations done by (Park *et al.*, 2003). A sufficient quantity of water was sprayed to keep the soil moist. The samples were monitored for period of four weeks at 7 days interval. Before weighing the degraded specimens from the soil, the samples were cleaned with water to remove the soil over the sample. Then it is allowed to dry in oven for 30 minutes at 40^0C .Then the weight of the samples were taken and recorded as (Wfinal). The amount of degradation was calculated using Equation 1.

Percentage of biodegradability = ((Wfinal − Winitial)/ Winitial) × 100 ---------(1)

2.6 Swelling Test

From each composite, three 4x4 cm^2 samples were prepared and weighted to determine the respective initial weight, Wdry. The dry samples were immersed in the solution (0.1M HCL, NaOH, distilled water) (Gunathilake *et al.*, 2020). The samples were taken out from the solution after one hour and the excess solution on the sample were wipped off. Then the samples weight were recorded after immersion in the solution.(Wfinal). The swelling index was computed using Equation 2.

Swelling index (%) = ((Wfinal – Wdry)/ Wdry) × 100 -----------------(2)

3. Results

3.1. Morphology, Functional Groups and Contact Angle

The PLA film (Figure 1a) exhibited high transparency and a smooth, glossy surface despite its lack of color. With an addition of orange powder at 10 and 20% wt, the composites (Figure 1b,c) took on a yellowish hue but retained the characteristics of PLA where the surface remained glossy and transparent. When the OP loading was increased to 40 and 60 wt%, a more pronounced difference was observed; the composite appeared as vivid orange coatings and lost its surface gloss. In addition, the higher amount of OP resulted in a roughening of the composites' surfaces.

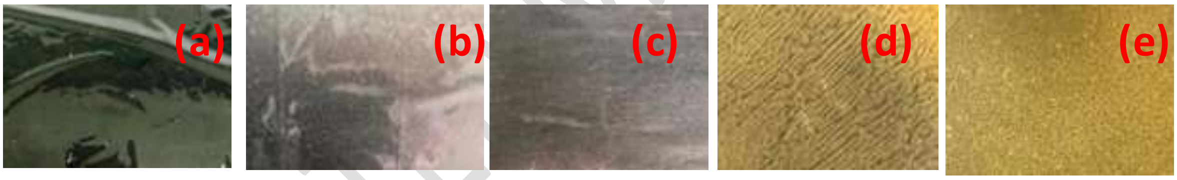


Figure 1. Composite of (a) PLA, PLA with (b)10%OP (c)20%OP (d)40%OP (e) 60%OP

A FTIR analysis was performed to determine the functional groups present in the PLA matrix before and after OP incorporation. Figure 2 depicts the FTIR spectra from 4000 $cm^{-1}$to 550 cm^{-1} in wave number. The minor peaks at 2956 to 2986 cm^{-1} are ascribed to the CH stretching vibration.

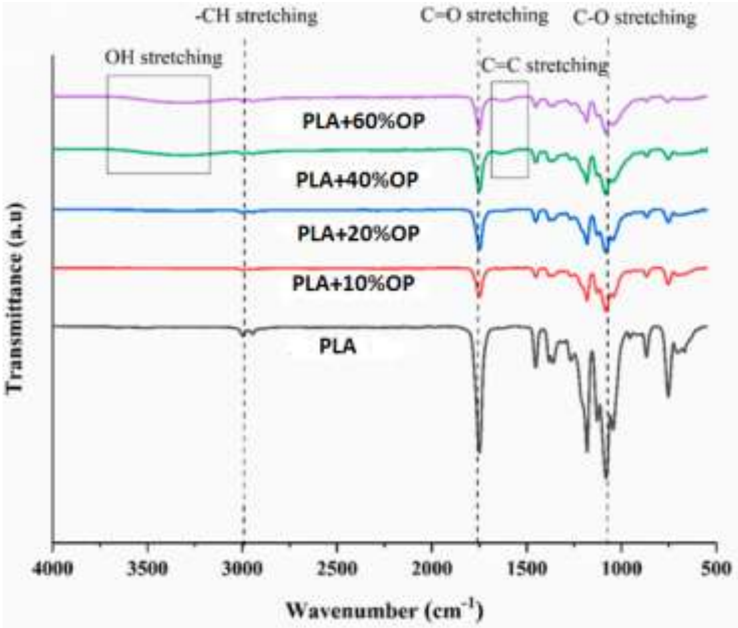


Figure 2. Samples FTIR spectra

To investigate the hydrophobicity or surface wettability of a composite film, the water contact angle between a water droplet and the surface of the film was measured. Figure 3 is a bar graph depicting the water contact angle (^{0}) for each film. The PLA film reveals an angle of 73.82^0, which corresponds to its hydrophobic nature, which has a static contact angle between 60 and 85^0 (Baran and Erbil 2019). This value is also near to the measured angle of blank PLA film (67.27°) prepared using the same solution casting method as (Alakrach *et al.*, 2018) reported.

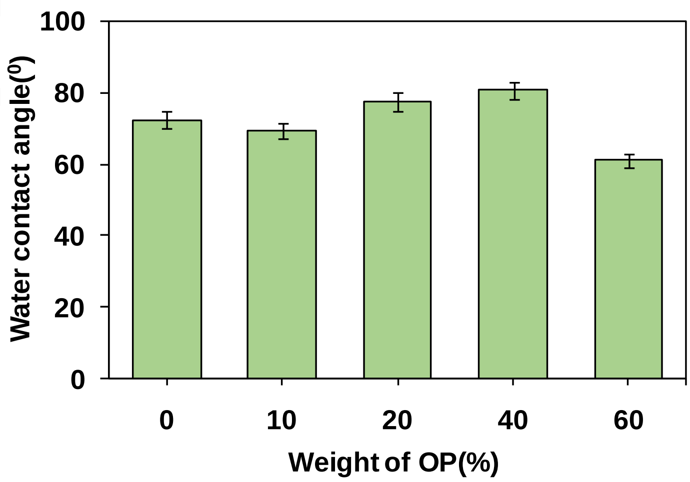
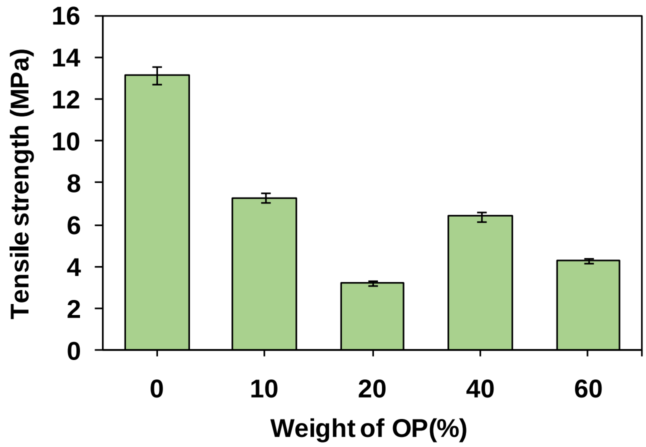
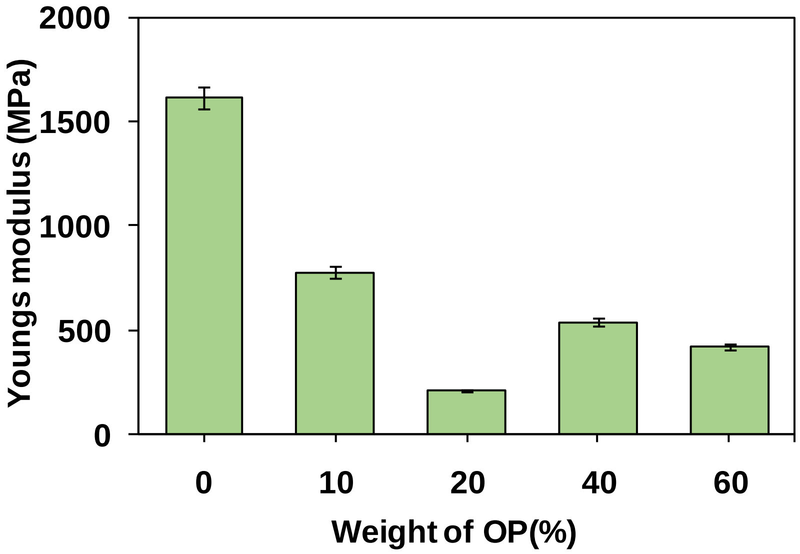


Figure 3. Composites water contact angle

3.2 Mechanical Properties

When compared to the pure PLA film, the integration of OP in the PLA matrix decreased its mechanical characteristics as shown in Figure 4. PLA film's initial tensile strength and modulus are 13.21 MPa and 1586 MPa, respectively. The PLA/OP composites of all loadings exhibit a decrease in tensile strength between 2.89 and 6.7 MPa and a decrease in modulus between 145 and 642 MPa. On the other hand, the elongation at break has significantly improved. PLA/20 wt% OP, PLA/40 wt% OP, and PLA/60 wt% OP composites exhibit greater elongation than PLA film without additives.





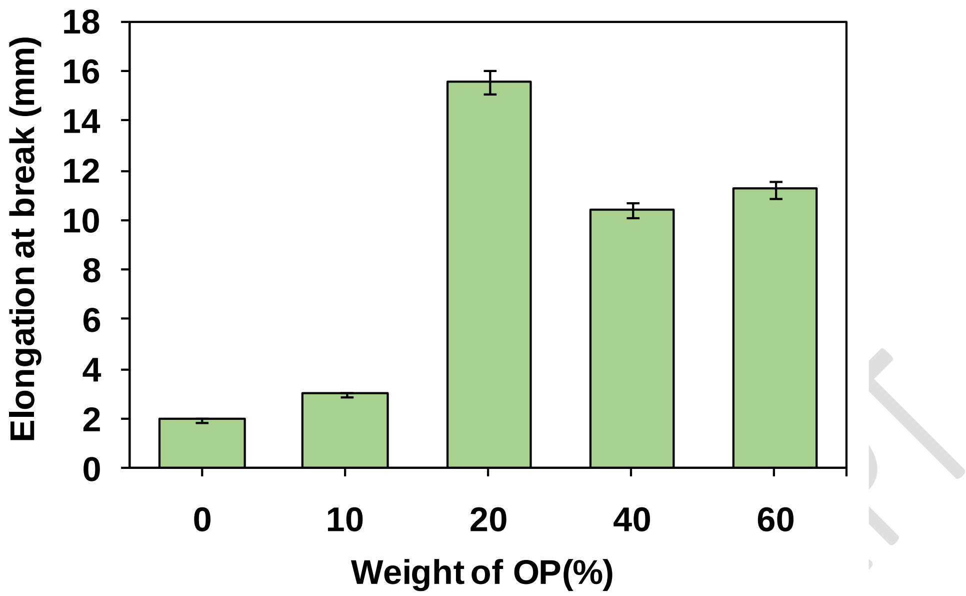


Figure 4. Mechanical property strength of composites

3.3 Degradation

Experiment with soil burial was tested for a total of 28 days, with samples extracted, weighed, and observed every seven days. Figure 5 depicts a graph of the percentage of weight loss for each film versus the number of days after soil burial.

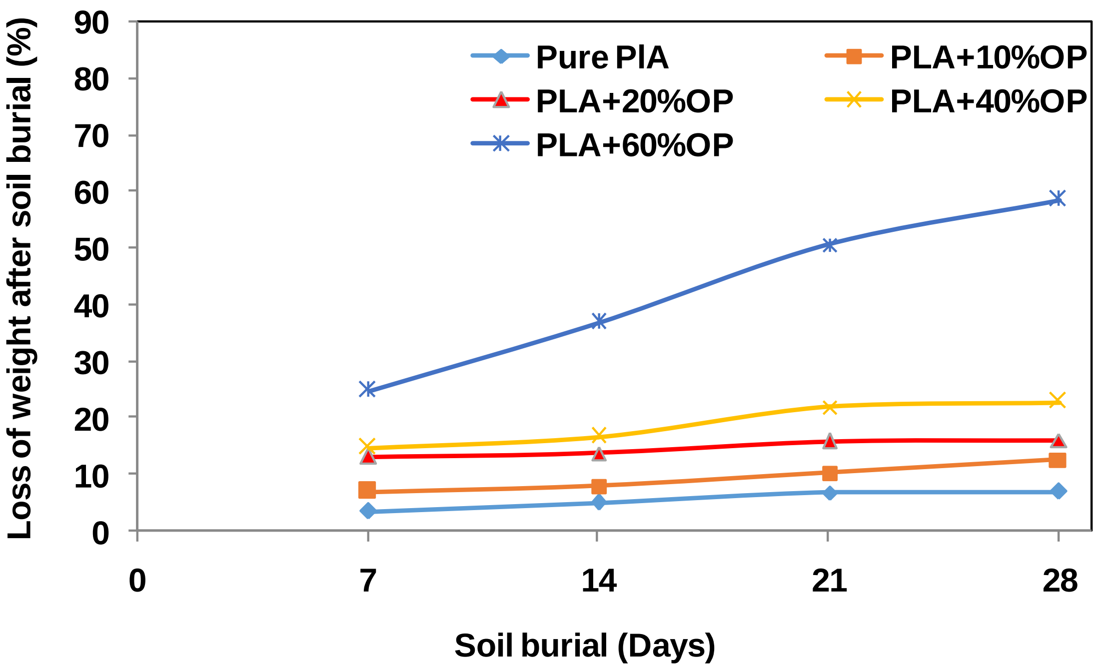
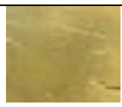
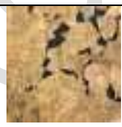


Figure 5. Weight loss percentage after soil burial

Table 1. Appearance of composites- Soil burial

Composite	**PLA**	10%OP	20%OP	40%OP	60%OP
Before soil burial					
7 days					
14 days					
21 days					
24 days					

Throughout the soil burial experiment, the blank PLA film had the least weight loss, with a low percentage ranging from 3.53 to 5.75%. Due to its hydrophobic nature and sluggish degradation rate, it can be seen in Table 1 that the plain PLA film undergoes very few changes in appearance. (Lertphirun and Srikulkit 2019) obtained a similar result for their PLA degradation study in a soil burial test. As the percentage of OP in PLA increases, so does the trend of weight loss and degradation in the composites. The PLA/60 wt% OP composite exhibits the greatest weight loss, with a range of 25.03 to 60.43%, which is eight to twelve times greater than that of PLA film. In addition, Table 1 demonstrates that after soil burial, OP composites develop surface fissures, cavities, and fungal growth, and become more brittle. All composites exhibit an increase in these characteristics over time, but PLA/OP composites with higher loadings exhibit the most pronounced modifications.

3.4 Swelling

The rate of swelling (%) is calculated by comparing the weight of each composite sample before and after immersion in acidic, alkaline, and neutral distilled water at pH 1, 13, and 7, respectively. From Figure 6, it can be seen that, independent of the solution's pH, the enlargement percentage of samples increases with increasing OP loadings. The PLA film with no additives exhibits the lowest swelling rate of all samples, which is consistent with its hydrophobic nature (Lertphirun and Srikulkit 2019). The swelling percentage increases significantly with the addition of increase in percentage of orange powder.

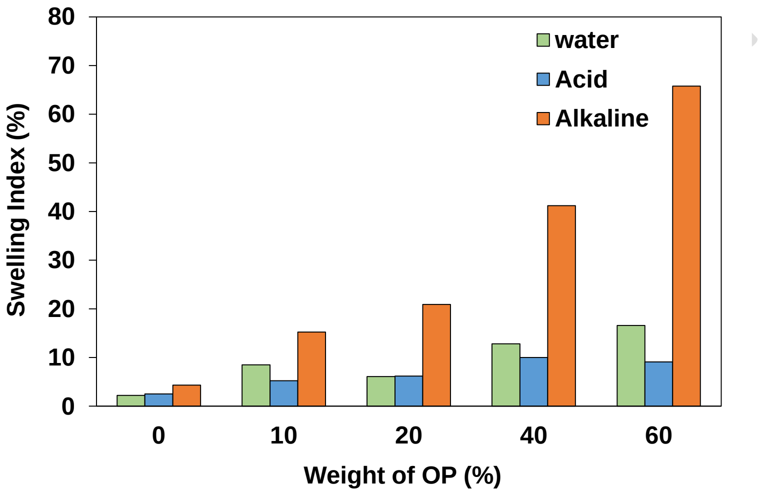


Figure 6. Swelling percentage of all composites in different solution

4. Discussion

As shown in Figure 1b and 1c, an excellent and uniform dispersion of OP particles in PLA matrix was obtained at relatively modest loadings of 10 and 20% by weight. When the OP dosage reached 40 wt%, it was evident that the OP particles were no longer evenly distributed on the surface, as agglomeration and a few aggregates were observed in the upper right corner of the film (Figure 1d). At the greatest amount of 60 wt% OP, the entire composite became denser, with almost no interstitial space visible (Figure 1e). A broad peak in the high energy region (2944.72 to 3309.94 cm^{-1}) in Figure 2 FTIR spectra indicates the presence of a hydroxyl group, which is only observed in PLA/OP composites with higher loadings. This is due to the large quantity of OH groups present in the orange peel's carbohydrates and lignin and is more apparent when the OP loadings are high and the fiber content is increased. Due to the presence of unsaturated aromatic compounds in orange peel (Dey *et al.*, 2021), a similar trend is observed for the C=C stretching at 1608 cm^{-1}. Lastly, the peaks between 1081.31 and 1183.32 cm^{-1} in all spectra indicate the presence of C-O stretching (Shen *et al.*, 2018). The addition of cellulose-rich hydrophilic infill OP has marginally modified the hydrophobic nature of PLA. The decreased contact angle (70.12^0) indicates that the PLA/10 wt% OP composite is now more hydrophilic. The presence of OH groups in OP increases the composite film's polarity and surface energy. A surface with a high surface energy generates a strong attractive force, allowing water droplets to spread out more evenly on the surface, thereby exhibiting excellent wettability. However, at 20, 40, and 60 wt% OP loadings, the water contact angle increases to 78.4, 81.72, and 88.18, respectively, indicating that the hydrophobic character of the composites has been restored. Due to the large loadings of OP in the PLA matrix, the surface roughness is increased, which in turn reduces the surface energy (Alakrach *et al.*, 2018), causing the composites to become mildly hydrophobic. It is observed that the cellulose components of OP have contributed to the modification of the material's durability by increasing its elongation. Due to the hydrophilic nature of OP and the hydrophobic nature of PLA, inadequate interfacial adhesion between cellulose fibres and polymer can result in agglomerations, leading to low tensile strength and modulus. While the addition of OP appears to counteract the brittleness of PLA by increasing elongation at break (Figure 4c), this is not the case. Similar decreases in tensile strength and increases in elongation at break were observed in previous studies that modified PLA with cellulose as fillers (Paul *et al.*, 2021), where the addition of cellulose can interlock with the PLA matrix and ease the movement of the composite under stress, thereby increasing the elongation. In addition, the optimal loading is obtained at 20 wt% OP, which results in the highest elongation at break and provides the polymer with sufficient ductility so that it does not break readily. Nonetheless, at even greater OP loadings (40 wt% and 60 wt%), all three mechanical attributes, i.e. tensile strength, Young's modulus, and elongation at break, are observed to decrease once more. This is likely due to the excessive OP loadings that result in poor distribution and agglomeration of filler particles, resulting in composites that are brittle. The mechanical strength results are comparable to those of (Singh *et al.,* 2020) whereas high cellulose loading in PLA decreased tensile strength and modulus while increasing elongation at break. The orange peel powder may function as a plasticizer to increase the ductility of a material, as indicated by an increase in elongation at break of 49 to 97 percent, typically at the expense of tensile strength and rigidity. Other contributors to the decrease in tensile strength and modulus include the imperfect distribution of orange peel powder and the feeble adhesion between orange peel powder and PLA. The addition of OP containing hydrophilic cellulose fibres has resulted in a higher absorption or enlargement rate due to the affinity of OH groups for water molecules. Comparing the three distinct pH solutions, the composites expand the most in alkaline NaOH, with the PLA/60 wt% OP composite achieving the maximum rate of 80.22%. Moreover, after 1 hour of immersion in the alkaline solution, fracture was observed. Due to the presence of a greater quantity of cellulose, an increase in OP loadings has improved the biodegradability of the composites. The high cellulose content (9.19 to 22%) of orange rind has promoted biodegradation via hydrolysis and microbial activity (Ayala *et al*., 2021).

5. Conclusions

In this investigation, a biobased, biodegradable polymer was created by incorporating orange peel granules into PLA. The presence of a hydroxyl group in the high energy region and a C=C functional group at a wave number of 1608 cm^{-1} demonstrates that OP has been incorporated into the PLA matrix. In addition, it was discovered that the incorporation of OP into PLA decreases the tensile strength and modulus, whereas modest OP loadings result in a substantial increase in elongation. It was hypothesized that the OP containing a high proportion of cellulose fibres modified the composites' durability and improved their ductility. Analysis of the water contact angle revealed that the hydrophilic OP substantially altered the surface hydrophobicity of PLA, with higher OP loadings resulting in an uneven surface and low surface energy for composites. The presence of OP improved the biodegradability of PLA, as determined by a 28-day soil burial test. With increasing concentrations of OP, biodegradability improved.

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