Performance Improvement on Biopolymer Nanocomposites

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Abstract*— In this study, we investigated the effect of nano filler material on the mechanical and thermal property of biopolymer. For the preparation of specimens, solvent casting technique was used. Specimens are prepared using pure polylactic acid (PLA) with chloroform and Polylactic acid combined with nanoparticles (Clay). Moisture absorption results show that PLA Nanocomposite plays a great role in increasing the composite properties such as mechanical properties, since as the proportion of PLA Nanocomposite increase water uptake by the nano composite was less. nano composites produced by this method shows very good biodegradation behavior, which renders them advantageous in terms of environmental protection. OTR and WVTR test values show that PLA Nanocomposite plays a powerful role in increasing the gas barrier properties. Hence these PLA nanocomposites can be used for packaging to protect food from oxidation reaction and moisture.

Keywords-component; biopolymer, Polylactic Acid, nanoclay, chloroform, nanocomposite, Mechanical & Thermal Properties

I. INTRODUCTION

Poly lactic acid (PLA) has gained a considerable interest due to its biodegradability and biocompatibility. Poly lactic acid (PLA) is rigid thermoplastic polyester with a semi crystalline or completely amorphous structure depending on the stereo purity of the polymer backbone. Furthermore, its ability to be crystallized under stress, thermally crystallized, filled, and copolymerized, makes it suitable for a wide range of applications. The principal drawbacks of such a biodegradable polymer in terms of industrial application like food packaging are its poor thermal resistance, low mechanical and limited gas barrier properties. These properties can be improved by fillers, copolymerization techniques and by blending. However, the use of fillers appears to be the most attractive approach because of lower cost ease of Use.

Various candidate fillers for PLA are fiber-like natural fillers and other agricultural waste into polymeric matrix. Earlier studies have shown that presence of the natural fillers in biodegradable polymers may strongly accelerate biodegradation process. Moreover, presence of natural filler increases water absorption, which highly influences biodegradation process of the composites, in comparison to neat polymer. During the last decade, an increasing attention has been paid to biodegradable polymers because of environmental impact. Poly lactic acid (PLA) is a well-known green polymer produced from renewable resources that draws a lot of attention in the polymer industry. Several poly lactide properties such as mechanical strength, thermal stability and permeability need to be improved in order to enlarge its range of applications, especially in packaging, since PLA is too much brittle and permeable to gases for some purposes. The introduction of a few percent of nano fillers, such as layered alumino silicate clays, is known to enhance various polymer properties such as the stiffness/toughness balance.

Nano particle fillers

It has been reported that addition of nanoparticles to base polymers confers improved properties that make them usable in automotive, construction and medical areas. PLA nanocomposites have been shown to exhibit improved tensile strength and young's modulus compared to Pure PLA. Nanocomposites are a class of composites in which the dimensions of the reinforcing material are in the order of nanometers. Compared to conventional composites nano filler composites exhibit superior properties due to better interfacial bonding. Several nano filler materials such as calcium carbonate, ceramic, clay, graphite, kaolin, mica etc., have been tried out to obtain nano composite materials. Nano clay is a good candidate for use as a filler material due to its remarkable increase in rigidity (elastic modulus), thermal and dimension stability, good barrier properties to gases and vapours, toughness. Depending on the specific interactions between the polymeric matrix and the clay, different structures such as intercalated and exfoliated may be obtained. The clay layers may be well dispersed provided that a strong interaction can be developed between the clay and the polymeric matrix.

II. MATERIALS AND METHODS

PLA with a density of 1300 kg/m^3, melting point of 150-170 °C and molecular weight (M_W) of 197000 g/mol. PLA resins were dried in a vacuum oven at 60 °C for 24 hours before use. Organically modified fillers as Nano reinforcement, Solvents was used to dissolve PLA and to swell and disperse Nano reinforcement, Glycerol was used to grease the molds prior to casting

Method of preparation:

- In the first step of preparing the specimen, 10gms of PLA were dissolved in 100ml of chloroform solution and it is poured into a glass beaker.
- In the second step, the solution was stirred vigorously on a magnetic stirrer for dissolving the PLA into the solution for 5hrs. At the same time nano clay of 1gm was added into the solution mixture.
- In the third step, Dissolved solution was poured onto a greased glass molds and allowed to dry for 24hrs at room temperature

Preparation of films

PLA and PLA-based nanocomposites films were prepared using a solvent casting method as shown in fig 1. 10gms of PLA was dissolved in 100 mL of solvents while agitating vigorously for 5 hours at room temperature (25°C). The dissolved solution was poured onto greased glass molds and then allowed to dry for about 24 hours at room temperature. The manufactured film was removed from the casting surface. For the preparation of PLA nanocomposite films, a predetermined amount of fillers was dispersed in the solvent by vigorous stirring for 5 hours with a magnetic stirrer. They were then homogenized at 2,000 rpm for 45 min followed by sonication for 30 min at room temperature. The filler solutions were mixed with the previously prepared PLA solution and then stirred for 15 min with a magnetic stirrer. The solutions were homogenized at 2,000 rpm for 45 min and sonicated for another 30 minutes, then casted onto greased glass molds. The final film was obtained by the same procedure explained above for pure PLA films. After drying at room temperature for 24 hours, all PLA films were further dried at 60°C in a vacuum dryer to remove the remaining solvent to prevent its plasticizing effect.

Fig 1: PLA Film Preparation of size 200mmx150mm

Material Properties

Moisture absorption behavior

The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity, intimately relates to such composite properties as mechanical strength, dimensional stability and appearance. Though the poly(lactic acid) has been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties. Moisture absorption test was carried for all the ten composite films in which the PLA Nanocomposite and matrix polylactic acid are in the ratio of 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05. It was observed that as the percentage of PLA Nanocomposite increases, moisture absorption decreased. This behavior clearly reflects the presence of hydrophobic moieties onto the fibre surface increase in their resistance towards moisture.

Biodegradation in soil

Biodegradation of materials occurs in various steps. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to metabolization of the fragments. Either way, eventually the chain fragments become short enough to be converted by microorganisms.

The studies on biodegradation behavior are important for the application of biocomposites in environment. In this work, soil burial experiments were performed for all the ten ratio films. Table 1 shows present weight loss of various films as a function of biodegradation time. Note that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films, weight decreases for 2 days is average 3% and it decreases gradually as the time increase and after 18 days average weight decrease is 16%. The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained to herein reveal that the film composites would not cause any deleterious ecological impact.

Table1: Moisture absorption studies of ten (PLA Nanocomposite/PLA) film composites

No. of days	%wt. increase 10:90	%wt. increase 20:80	%wt. increase 30:70	%wt. increase 40:60	%wt. increase 50:50	%wt. Increase 60:40	%wt. increase 70:30	%wt. increase 80:20	%wt. increase 90:10	%wt. increase 95:05
2	2.9	2.7	2.7	2.4	1.9	1.7	1.7	1.5	1.4	1.4
4	5.1	4.9	4.8	4.4	3.9	3.6	3.6	3.1	2.9	2.8
6	7.2	6.9	6.7	6.2	5.6	5.1	5.0	4.5	4.3	4.2
8	9.0	8.7	8.4	7.8	7.1	6.5	6.4	5.9	5.6	5.5
10	10.6	10.3	9.7	9.0	8.2	7.5	7.3	6.8	6.4	6.2
12	12.3	12.0	11.0	10.1	9.3	8.6	8.2	7.7	7.2	6.9
14	13.9	13.5	12.2	11.3	10.4	9.6	9.1	8.6	8.0	7.6
14	13.9	13.5	12.2	11.3	10.4	9.6	9.1	8.6	8.0	7.6
16	15.7	15.3	14.5	12.5	11.4	10.7	10.1	9.4	8.7	8.2
18	17.2	16.7	15.8	13.6	12.5	11.8	11.0	10.2	9.5	8.9
20	18.6	18.1	17.1	14.8	13.6	12.9	11.9	11.1	10.2	9.5
22	20.1	19.5	18.3	16.0	14.7	13.9	12.8	12.0	11.0	10.1
24	21	20.3	19.5	17.2	15.7	14.9	13.8	12.8	11.7	10.6

Table 2: Biodegradable studies of ten (PLA Nanocomposite/PLA) film composites

No. of days	%wt. decrease 10:90	%wt. decrease 20:80	%wt. decrease 30:70	%wt. decrease 40:60	%wt. decrease 50:50	%wt. decrease 60:40	%wt. decrease 70:30	%wt. decrease 80:20	%wt. decrease 90:10	%wt. decrease 95:05
2	2.7	2.8	3.0	2.9	2.8	3.1	2.9	3.0	3.3	3.2
4	3.9	3.8	4.1	3.9	3.9	4.2	3.7	4.2	4.2	4.4
6	5.8	5.6	5.9	5.7	5.5	5.6	5.3	5.5	5.7	5.6
8	7.7	7.5	7.6	7.4	7.5	7.4	7.7	7.6	7.8	7.6
10	9.3	9.5	9.4	9.2	9.3	9.6	9.6	9.8	9.7	9.8
12	11.7	11.6	11.7	11.5	11.4	11.6	11.4	11.6	11.7	11.9
14	13.2	13.4	13.6	13.7	13.5	13.8	13.7	13.8	13.9	14.0
16	15.4	15.7	15.6	15.9	15.4	15.6	15.6	15.7	15.5	15.7
18	15.6	15.8	15.7	15.9	15.5	15.6	15.8	15.8	15.6	15.9

Oxygen permeability test

Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in a high elastic state. The gas permeability of crystalline polymer is much lower. The high molecular weight glassy polymers with rigid chains have very low gas permeability. With decreasing chain flexibility gas Permeability decreases. Closer packing of the molecules supports permeability resistance.

Table 3 shows represent OTR (Oxygen Transmission Rate) values for all the ten ratio films. Generally, hydrophilic polymeric films have shown good oxygen barrier property. As it can be observed in Figure 4.15, there was an improvement in oxygen barrier properties of the films as the percentage of PLA Nanocomposite increases. It was observed that there is a great decrease in oxygen transmission rate as the percentage composition of the PLA Nanocomposite increases. It is obvious that PLA Nanocomposite played a powerful role in improving the oxygen gas barrier properties. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of PLA Nanocomposite decreases because intermolecular bonding between fibre and matrix decreases. This resulted in a phase separation among the main components where the film could not be formed well, facilitating the oxygen permeation. So, it was more advantageous to improving the gas barrier properties by increasing the percentage of PLA Nanocomposite. This result indicates the potential of these films to be used as a natural packaging to protect food from oxidation reactions.

Table 3: OTR values of ten (PLA Nanocomposite/PLA) film composites

SL No	PLA Nanocomposite+ Pure PLA	OTR value; Cc/sqm/day/atm
1	10+90	1850
2	20+80	1698
3	30+70	1520
4	40+60	1423
5	50+50	1315
6	60+40	1220
7	70+30	1105
8	80+20	1090
9	90+10	980
10	95+5	823

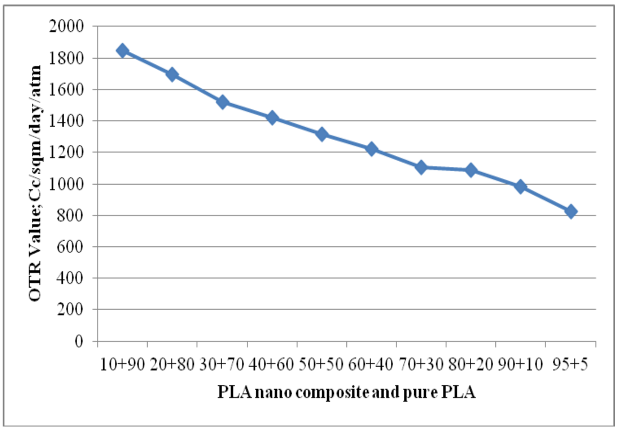

Figure 2: Oxygen permeation versus Parts per hundred PLA nanocomposites in a (PLA Nanocomposite/Pure PLA) blend

Water vapour permeability test

Table represents Water Vapour Transmission Rate values for all the ten ratio films. The water vapor permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. It was observed that there is a small decrease in water vapour transmission rate as the percentage composition of the PLA Nanocomposite increases. This is because as the percentage composition of PLA Nanocomposite increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. The comparison between OTR and WVTR indicates that PLA Nanocomposite is greatly effective in obstructing the oxygen permeation, but less effective in retarding the water vapour permeation. This results shows that these films may impede moisture transfer between the surrounding atmosphere and food, or between two components of a heterogeneous food product. This property is very much use full in packaging application.

Table 4: WVTR values of ten (PLA Nanocomposites/Pure PLA) film composites

SL NO	PLA Nanocomposite+PLA	WVTR value gm/sqm/day
1	10+90	6.532
2	20+80	5.842
3	30+70	5.023
4	40+60	4.492
5	50+50	4.12
6	60+40	3.658
7	70+30	2.98
8	80+20	2.845
9	90+10	2.059
10	95+5	1.234

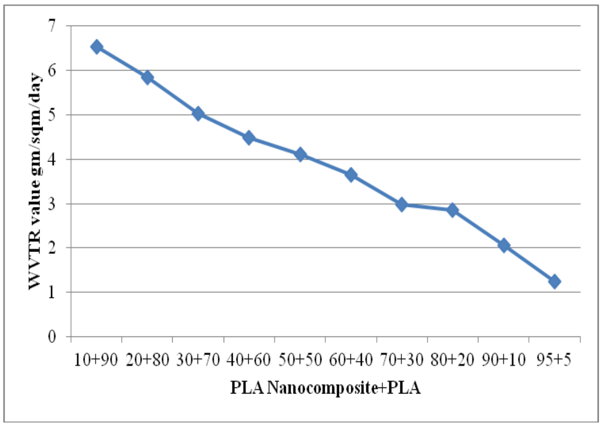

Figure 3: Water vapour permeation versus Parts per hundred PLA Nanocomposite in a (PLA Nanocomposite/PLA) blend

conclusion

- Moisture absorption results show that PLA Nanocomposite plays a great role in increasing the composite properties such as mechanical properties, since as the proportion of PLA Nanocomposite increase water uptake by the nano composite was less. nano composites produced by this method shows very good biodegradation behavior, which renders them advantageous in terms of environmental protection. The produced film composites possess higher tensile strength as the proportion of PLA Nanocomposite increases and higher elongation at break as the proportion of PLA increases. So PLA Nanocomposite plays a vital role in increasing the tensile strength of film composites.

- OTR and WVTR test values show that PLA Nanocomposite plays a powerful role in increasing the gas barrier properties. Hence these PLA nanocomposites can be used for packaging to protect food from oxidation reaction and moisture.

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