

Moisture Absorption Behaviour of Biopolymer Polycaprolactone (PCL) /Organo Modified Montmorillonite Clay (OMMT) biocomposite films

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Abstract: Bio composite materials were fabricated using mixing biodegradable polymer polycaprolactone (PCL) and Organo Modified Montmorillonite Clay (OMMT) through solution casting. Various samples of bio composite films were prepared by varying the OMMT wt% composition by 0.1%, 0.5%, 1% and 1.5%. Thereafter, the density and water absorption of the composites were investigated with respect to immersion time in water. The moisture absorption results show that with an increase in weight percentage (from 0.1 to wt 1.5%) of OMMT within the bio polymer films, the absorption value of bio-nanocomposite films reduced rapidly from 34.4% to 22.3%. The density of hybrid composites also increased with increase in weight percentage of OMMT. The swelling characteristic of PCL increased with increasing % of OMMT clay. These results indicate that the optimized composition of constituents in composite membrane could effectively reduce the anhydrous conditions of bio-composite film.

Keywords: Nano clay, PCL, water absorption and density

1. Introduction

The use of biopolymer materials for packaging has been increased in the past few years owing to consumer awareness. Recently, there have been developments in fabrication as well as applications of biopolymer based plastic films which were earlier being obtained through the petroleum derived raw materials [1-3]. Polycarbonate (PCL) based biodegradable materials have been used in various applications like automobiles, packaging, food packaging, industry application and drugs delivery because Polycaprolactone (PCL) is a fully biodegradable non-toxic biopolymer [4-7]. However, poor mechanical properties of PCL have limited its large-scale manufacture as a proxy of traditional polymers [8]. Many authors have reported last few years that the properties of fully biodegradable polymer such as Polyhydroxybutyrate (PHB), Polyhydroxyalkanoate (PHA), Polylactic acid (PLA) and Polycaprolactone (PCL) can be modulated like increment of thermal and mechanical properties through mixing with nano fillers (Nano clay, carbon nanotubes, OMMT clay etc.) and [9,10]. Among different fillers, OMMT clay is now considered the most promising fillers for the development of high performance materials. PCL is a fully biocompatible, biodegradable and nontoxic to living organisms. In fact, PCL has good resistance to oil, solvents and water. The unique properties of PCL give it high potential in biomedical fields, and it has been used in the development of controlled packaging, food



Industry, drug delivery systems and other resorbable fixation devices. These polymer nano-composites have been demonstrated superior properties. For example, OMMT clay based polymer nano-composites have shown better thermal, mechanical, gas barrier, electrical and flame retardant properties, compared to the pristine polymer [11-13]. OMMT clay based fillers have been found to have unique properties such as yield strength, high aspect ratio, fracture toughness, elastic modulus and thermal conductivity. These properties make them appropriate for application in the development of advanced green polymer bio-nanocomposites [14]. The superior properties of OMMT clay compared to polymers are reflected in OMMT clay based polymer composites. Recently, OMMT clay has gained tremendous attention in the field of bio polymer-based nano-composites due to its great potential for enhancing, thermal, mechanical, electrical and gas barrier properties of host polymers. In the present study, the preparation and characterization of the PCL/ OMMT clay nano bio-composites is reported. The density and water absorption of the composites are investigated with respect to immersion time in water. The swelling characteristic of PCL with increasing % of OMMT are also reported in this paper.

2. Materials

The PCL (3001D) ($M_n = 89141$ g/mol and $M_w = 158480$ g/mol, density = 1.24 g/cm³) was purchased from Nature works[®] LLC, USA. OMMT clay powder was purchased by Sigma Aldrich., and all the chemicals were purchased by Merck.

3. Characterization techniques

3.1 Determination of Moisture absorption

A small cut piece of the bio nano composites film samples were vacuum dried in oven at 70°C for overnight. Thereafter, all the samples were taken out from the oven and kept into desiccator to make it dry. The specimens were weighed and subsequently immersed into a beaker containing distilled water at room temperature. Water absorption values of the samples were measured after every 4 hrs. Weights were measured till the saturation point. Water absorption of the prepared PCL/OMMT clay bio composite films was ascertained according to the Eq.1:

$$\text{Moisture absorption values (\%)} = (W_{\text{wet}} - W_{\text{dry}})(100)/W_{\text{dry}} \quad (1)$$

where W_{wet} represents the weights of wet bio composite films and W_{dry} is the weight of the own dry PCL films at time.

3.2 Measurement of the Density

The specimens were weighed and subsequently immersed into a beaker containing distilled water at room temperature. Subsequently the weight of the wet samples were measured. Samples of dimensions $30 \times 30 \times 30\text{mm}$ (width \times length \times thickness) were taken for the study. Densities of five specimens were measured and averaged for each sample. The volume was calculated for the measured dimension. The density for all samples are represented in Fig. 1. The density is then calculated using following formula (Eq. 2):

$$\text{Density (D)} = \text{Mass (m)} / \text{Volume (V)} \quad (2)$$

3.3 Determination of Swelling ratio

A cut piece of dimension $2 \times 2 \text{ cm}^2$ from bio composite films, was first dried at 70°C under vacuum. The thicknesses were measured by a thickness gauge. Thereafter, they were subsequently immersed into beakers containing distilled water for proper dousing. After leaving undisturbed for 24 h, respective cut pieces of each sample were taken out, and their thicknesses were once again measured in order to determine their swelling extent. Respective swelling ratios of the prepared membranes were calculated from the following equation (3):

$$\text{Swelling ratio (\%)} = (T_{\text{wet}} - T_{\text{dry}}) (100) / T_{\text{dry}} \quad (3)$$

where T_{wet} represents the respective thicknesses of wet membranes soaked in distilled water for 24 h, and T_{dry} is the respective thicknesses of dry membranes.

4. Result and Discussion

4.1 Water absorption

Water absorption properties were analyzed on the developed bio-composites. Fig. 1 shows percentage (%) of moisture absorption of a PCL or PCL/ OMMT clay bio-composites. Water absorption significance was observed to be increased with the expanding of OMMT clay stacking for PCL bio-composites. Fig. 1. demonstrates that the water absorption of PCL/OMMT clay composites were 1.15, 3.13, 4.23, 6.11, 7.13, 7.69 % for 0, 0.1, 0.5, 1 and 1.5% of (% w/w) PCL substance. The maximum expansion of weight up to 50% resulted due to water absorption in OMMT/PCL composite. It clearly indicates that OMMT/PCL samples has a tendency to absorb more moisture than pristine PCL sample. Conversely, the lower water absorption of 10/90 PCL/OMMT clay composite may be credited to some hydrophilic nature of OMMT clay which has cellulose and lignin containing free hydroxyl in its structure. Comparable perceptions done by [15] reveals that hydroxyl group (OH) of PCL reduces its water absorption properties.

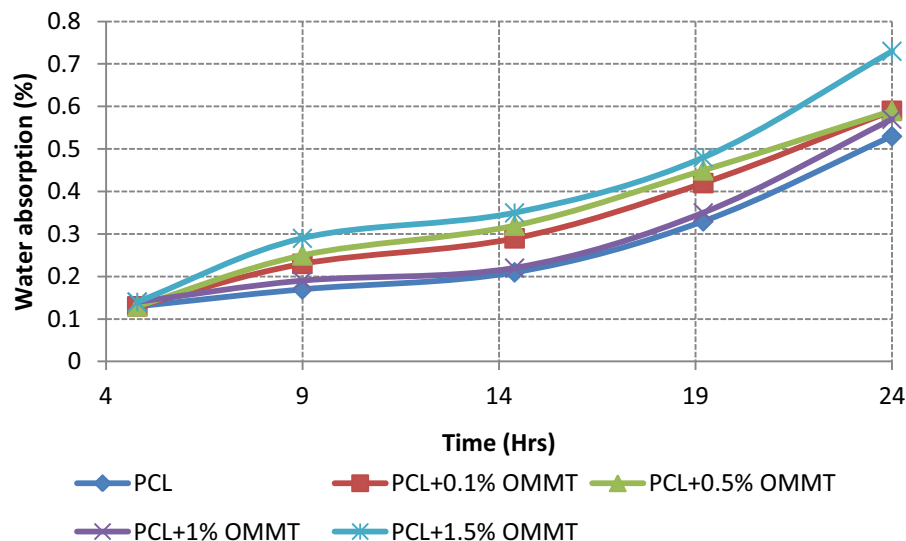
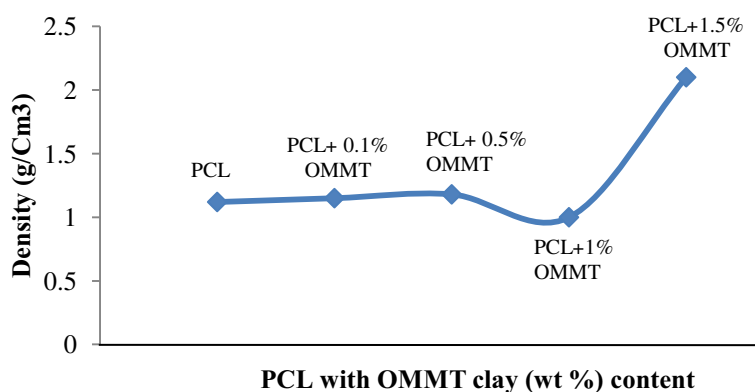


Figure:1 Water absorption (%) of bio-composite films

4.2 Density

Fig.2, shows that the density of bio composites increases with increasing % of OMMT clay. The increasing % of OMMT reduces the wetting properties of bio polymer (PCL) which results in void formation inside core of the composites. The presence of these voids at the nano clay filler matrix interface, within the OMMT and in the bio polymer PCL matrix affects the OMMT/PCL composite properties and decreases the density. The density of PCL matrix is 1.12 g/cm^3 and that of PCL and OMMT clay is 1.0 g/cm^3 . The particle sizes of OMMT clay into the PCL matrix enhance the bio-composites density since the PCL matrix is lower than OMMT clay. On the other hand, the density increases as the amount of SPF increases. This is mainly due to the lower density of the bio-composites of 1.0 g/cm^3 compared with PCL matrix of about 2.1 g/cm^3 . The result indicates that the 1% of OMMT clay does affect the properties of PCL bio-composites.

Figure:2 Density(g/Cm³) (%) of bio-composite films

4.3 Analysis of swelling ratio

The PCL/OMMT clay based bio composite films exhibit swelling behaviour that is sensitive to the aqueous media. Table 1. displays the Swelling ratios with increase in percentage of PCL/OMMT clay bio composite films in deionized water. The equilibrium-swelling ratio increases with increasing OMMT content at room temperature. It was experimentally observed that the swelling ratio of PCL/OMMT (1% wt) sample is more than two times that of pure PCL bio-polymer film for all the tested aqueous media. This is due to the dramatic increase in the hydrophilic groups in the PCL/OMMT bio composite films system. Nevertheless, all the PCL/OMMT bio composite films samples survived in all the tested aqueous media, acidic or basic. Similarly, the swelling ratio analyses revealed that the sample 1% exhibited the maximum swelling, followed by the sample 0.1%. Both these samples showed swellings higher than PCL bio polymer.

Table: 1 Swelling ratio of PCL with PCL/OMMT (% wt) clay bio composites

| S.No | Composition of PCL with wt % OMMT clay | Swelling ratio |
|------|--|----------------|
| 1 | PCL | - |
| 2 | PCL+0.1% OMMT | 3% |
| 3 | PCL+0.5% OMMT | 3% |
| 4 | PCL+1% OMMT | 8% |
| 5 | PCL+1.5% OMMT | 5% |

5. Conclusion

The effect of OMMT clay in PCL based bio composite films increased its water absorption and density values. This was mainly due to presence of more hydrophilic sites available for water absorption. Water absorption lead to a build-up of moisture in the PCL biopolymer walls, which adversely affected the dimensional stability. The swelling ratio was also found to be increasing with the increase in % of OMMT clay. Overall conclusion was that the optimized composition of constituents in composite membrane could effectively reduce the anhydrous conditions of bio-composite film.

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7. References

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