
Advancement in Packaging Film Using Microcrystalline Cellulose and TiO₂

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Abstract: The objective of this study is to study the effects of the addition of TiO₂ and microcrystalline cellulose on properties of packaging films based on biodegradable polymer blends. Biocompositions of Linear Low Density Polyethylene (LLDPE) - Microcrystalline Cellulose were prepared by Twin Screw Extrusion using of maleic anhydride grafted polyethylene as compatibilizer and TiO₂ as pro-oxidative additives. Polyethylene wax was used as processing aid to ease the blown film process. The presence of large amount of microcrystalline cellulose contents had a divergent effect on the tensile properties of Cellulose-PE blend. However, the addition of compatibilizer to the blends improved the interfacial bonding between the two materials. High amount of cellulose also was found to upsurge the rate of biodegradability of Cellulose-PE composite films. The burst strength and soil burry test of this composite film was also improved. It suggest that this film can be used for packaging film which can degraded up to certain extend.

Keywords: Microcrystalline Cellulose, Pro-Oxidative Additives, Compatibilizer, Bio Degradable, Packaging Film

1. Introduction

There are progresses of biodegradable plastics that can decrease the municipal wastes and this growth indirectly will prevent the world become waste disposal. Biodegradable polymers and plastics are material that was entirely decomposed when exposed and under attack to microorganism, either bacteria or fungi with suitable environmental state. Biopolymers from agronomic sources are becoming an interesting substitute for biodegradable films and other plastics materials. By combination of polymers and starch the tendency for the product to degrade is become higher. The blending of biodegradable polymer which is starch with inert polymers such as polyethylene has received considerable attention because of the probable application in the waste disposal of plastics [1]. Chief application of plastics is in packaging and this condition may contribute to serious environmental complications. Synthetic plastics such as polyethylene and polypropylene have a very low water Vapour transmission rate and most importantly, so that, they are absolutely non-biodegradable, and therefore

lead to environmental pollution, which pose serious environmental problems. Polyolefin are not degraded by microbes in the atmosphere, which contributes to their long lifetime of hundreds of years. There has been an increased attention in enlightening the biodegradability of synthetic plastics by blending them with low price natural biopolymers.

Recycle of products also has it restriction such as high cost of operation, besides, the technology of recycling are still under progress [2]. Many packaging materials do not lend themselves to recycling because of contamination, and the cleaning necessary prior to recycling can be very expensive. Biodegradable plastics are plastics that can undergo a degradation process known as biodegradation. They are defined as plastics with similar properties to conventional plastic but which can be decomposed after disposal to the environment by the activity of microbe. It is also defined as plastics with similar properties to conventional plastics, but it can be decomposed after disposal to the environment by the activity of microorganisms to yield end products of CO₂ and H₂O. Biodegradable plastics provide chances for reducing municipal solid waste through biological recycling to the

ecosystem and can replace the conventional synthetic plastic products. In addition, it is required that these biodegradable polymers come mainly from agronomic or other renewable resources for a justifiable environment.

Blending of low density polyethylene (LLDPE) with a economy natural biopolymer such as cellulose will increase the biodegradability of this material [3]. Incorporation of cellulose will accelerate the attack of microbes to LLDPE. Furthermore, cellulose is being a good choice since it is a plentiful and low cost material in the market, so, it will reduce the cost of production of LLDPE / cellulose biodegradable polymer for packaging industries. Numerous methods have been identified to enhance the interfacial bonding between the composite components. An adhesion promoter, based on a maleic anhydride modified polypropylene, was found to behave as a true coupling agent, i.e., impact, strength, and elongation values increased significantly while the elastic modulus remained practically unchanged [4]. The main objective of this research paper was to evaluate thermal, mechanical and biodegradable property of Cellulose - PE composite films for packaging applications.

2. Methodology

2.1. Materials

Linear Low Density Polyethylene (LLDPE) resin grade (F19010) provided by Reliance was used in this study. The density of the polymer was 0.918 g/cm³ according to ASTM D1505. It had a Melt Flow Index of 0.90 g/10 min according to ASTM D 1238. Microcrystalline Cellulose was supplied from Dariyal Polymers Pvt. Ltd. Pro-oxidative Additive Titanium Di Oxide (TiO₂) was delivered by Parshwanath group of industries and the grade PA101 (Anatase) was used. Maleic anhydride –grafted- polyethylene from Plus Polymers Pvt. Ltd was used as a compatibilizer of LLDPE / cellulose Mixture. Polyethylene wax flakes (M3300) from Triveni Interchem Pvt. Ltd. Changing the amount of these processing aids to the blending will be done to get the finest composition.

2.2. Processing

Linear Low-density polyethylene and microcrystalline cellulose were dehydrated in an oven for 24 hours at 80°C before pre-mixing and compounding to dry the moistness particularly for cellulose. The compounding of LLDPE / Microcrystalline cellulose was done using twin screw extruder (High speed Torque ZV 20, M/s Specific Engineering & Automats, India). The compounding process was carried out at a speed of 80 rpm and the temperature set at 140°C / 150°C / 160°C / 150°C. The extrudate was palletized using a pelletizer machine for each formulation. In the extrusion process, plastic pellets are first heated in a long barrel. A rotating screw then forces the heated plastics through a die opening of the preferred shape. As the continuous plastic form emerges from die opening, it is cooled and solidified, and the continuous plastic form is then

cut to the desired length.

The compounded samples were blown using Blow Film Machine (Monolayer Blown Film Plant - Standard Model, Konark Plastomech, India) to produce LLDPE / cellulose plastic film. This procedure will be carried out at temperature of 165°C / 160°C / 150°C / 140°C / 130°C / 120°C with drawer and screw speed of 50 rpm and 600 rpm respectively. Blow film extrusion is the process used to make plastic continuous film. This process works by extruding a hollow, sealed-end thermoplastic tube through a die opening. As compressed plastic tube emerges from die opening, air is driven inside the hollow tube to stretch and thin the tube to the preferred size and wall thickness. The plastic is then air-cooled and pulled away on take up rollers.

Table 1. Samples formulation.

Materials	C ₁₀ P ₁ (%)	C ₁₅ P ₂ (%)	C ₂₀ P ₃ (%)	C ₁₅ P ₀ (%)
LLDPE	85.75	80.75	75.50	81.00
Microcrystalline Cellulose	10	15	20	15
MAPE	3	3	3	3
PE Wax	1	1	1	1
TiO ₂	0.25	0.25	0.25	0

2.3. Characterization

2.3.1. Melt Flow Index

Melt Flow Index (MFI Tester, Saumya Machinerics Pvt. Ltd, India) was determined by Melt flow Indexer according to ASTM D1238. The temperature of 190°C and load of 2.16 kg will be used. The time taken for the break is one minute. The weight of extrudate will be measured and the melt flow of the samples was calculated. The MFI corresponds to the mass of polymers that passes through a standard capillary, in an interval of 10 min, at a given applied pressure.

2.3.2. Tensile Test

Tensile test will be carried out using an Instron machine Lloyd, India. The test will be done according to ASTM D 638. Gauge length will be set at 50 mm and the crosshead speed of testing will be fixed at 500 mm/min. Samples for tensile measurements was conditioned at 30±2% relative humidity for 24 hours before testing and ten samples was tested for each formulation. The conditioning of tensile specimens was followed accordingly as stated by the standard. Tensile modulus, tensile strength and elongation at break will be evaluated from stress-strain data.

2.3.3. Water Absorption Test

This test was carried out to study the water resistance of LDPE/cellulose films. Samples were dried at 80°C in a vacuum oven until a constant weight was achieved prior to absorption in water in a thermo stated stainless steel water bath at 30°C. Weight incensement of the samples was recorded by periodic removal of the samples from the water bath and weighing on a balance with a precision of 1 mg. The percentage of weight gain at 24hrs was taken; as a result of moisture absorption was determined by equation.

2.3.4. Differential Scanning Calorimetry (DSC)

Crystallinity studies were conducted using a Perkin-Elmer DSC 7 Thermal Analyser, United States under a nitrogen atmosphere based on ASTM D3418-03. 5 to 10 milligrams of samples were capsulated in aluminum pans and exposed to heating-cooling cycles. The samples were subjected to a first heating process to remove the patterns of their previous heating history. Then the samples were cooled to room temperature at a constant rate of 10°C / min to favour crystallization. Then, the second heating was set at 10°C / min in the temperature range of 30–175°C. The heat of fusion was calculated by fit in the areas under the endothermic curve.

2.3.5. Soil burry Test

Garden (agriculture) soil (1200 g) was taken in different vessels. A weighed amount (1 g) of each of the samples that is, PE, Cellulose-PE composite (composite and true graft separately) covered in synthetic net were placed in the beaker such that the soil covered the polymer from all the sides. The pots were covered with the aluminum foil and kept at room temperature. The weight of all the samples, PE and Cellulose-PE composite, were taken at regular interval of time (15 days) to check for any weight loss. Percent wt. loss as a function of number of days was determined.

2.3.6. Burst Strength

Burst Strength of Cellulose-PE composite was analyzed by Digital Burst Strength Tester, model EP 1100 (M/S P.S.I. sales Private Ltd). In this test, Place specimen without tension in the ring clamp and fasten securely. Start Burst Strength tester and continue until the specimen bursts and Record results. The bursting strength of paper or paperboard is a composite strength property that is affected by various other properties of the sheet, principally tensile strength and stretch. Generally, bursting strength depends upon the kind, proportion, and quantity of fillers present in the sheet, their method of preparation, their degree of beating and refining, upon sheet formation, and the use of additives.

3. Results and Discussion

3.1. Melt Flow Index

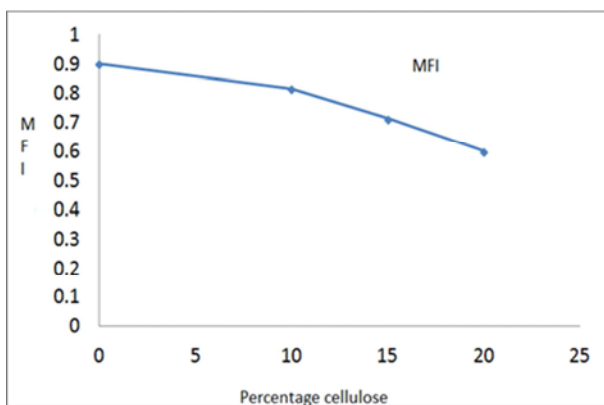


Figure 1. MFI values for Cellulose-PE composites.

The Melt Flow Index (MFI) values of LLDPE/Cellulose composites reduced as the content of cellulose increased. Decrease in MFI values indicate the viscosity of composite increased. This may be credited to the improved molecular motion, accessibility of larger free volume and also decreasing entanglement density and weaker intermolecular interaction between the polymer and filler as well. Thus, composite melts were able to flow easier at higher temperature leading to reasonably lower viscosity [5].

3.2. Tensile Test

Variations of Tensile stress–strain curve of Cellulose-PE composites films had been observed. The stress-strain relationship of Cellulose-PE composite is shown in Figure 2. LLDPE is a soft but tough plastic with low modulus but high elongation at break. With cumulative cellulose content, the tensile properties of the composites were noticeably altered. Similarity trend was also observed in composite films loaded with cellulose except for the tensile strength that showed an increased as the filler content increased [6]. This was expected due to cellulose acts as reinforcing fillers through the existence of crude fiber. Decrease in tensile strength was perhaps caused by less effective cross sectional area of LLDPE matrix toward globular particulates cellulose granules as the cellulose contents rise. Consequently resulting in reduce of tensile strength.

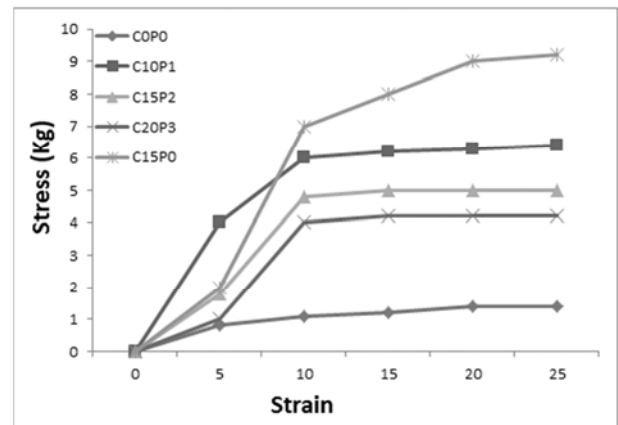


Figure 2. Tensile stress–strain curve for different Cellulose-PE composites.

3.3. Water Absorption Test

For virgin LLDPE films, a small amount of water uptake was detected. Cellulose based LLDPE tend to absorb water because the hydroxyl group in cellulose can form a hydrogen bond with water. Since the cellulose is hydrophilic, it has a highly attraction to water molecules. Hence, as cellulose content increased, the trend increases. Composite films contain high amount of Cellulose show high water uptake [7]. Meanwhile, composite films containing 10%, 15% and 20% of cellulose content differ somewhat from each other. This was predictable due to the low concentration of cellulose particles near to the composite surfaces while the rest were situated inter the matrix.

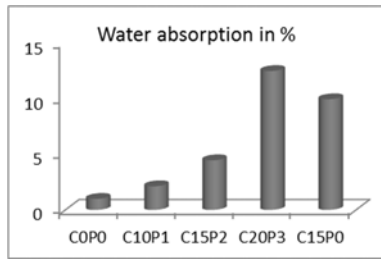


Figure 3. Water absorption percentage for Cellulose-PE composites.

The interior cellulose particles were not available to form hydrogen bonding with water molecules as they are trapped in LLDPE matrix. For higher loading of cellulose, cellulose particles filled and crowded the composites and resulted in higher concentration of cellulose near the composite surface.

Moisture uptakes in cellulose- LLDPE composites is mainly due to the cellulose particles, exposed cellulose granules or those at or near the surface absorb moisture faster than those interior. Cellulose-PE composites take months to equilibrate even completely immersed in water.

3.4. Differential Scanning Calorimetry (DSC)

Melting temperature (T_m) of the composite samples were obtained from the second heating curves in the DSC scanning, two endothermic melting peak was observed for all of the samples, which was actually a characteristic two forms of crystal with infinite crystal length. The melting peak occurred (T_m) at 120.40°C and 102.82°C for sample without TiO₂ while it varied from 118.38°C and 100.93°C for other TiO₂ based control composites.

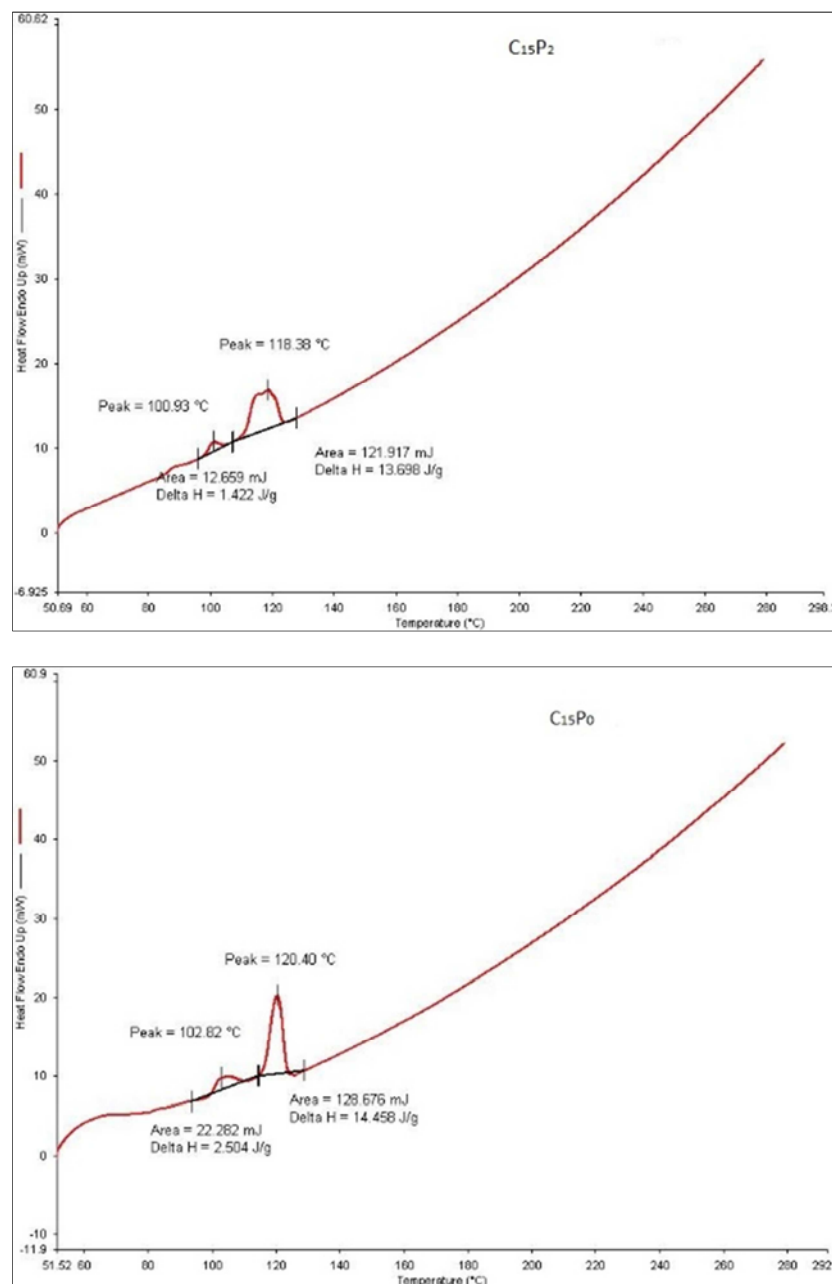


Figure 4. DSC curve of Cellulose-PE composites of pro-oxidant additives A) C₁₅P₂ and B) C₁₅P₀.

The presence of Pro-oxidative additive affects the thermal stability of the polymer. The thermal stability of polymer decreases with the presence of pro-oxidant additive. Pro-oxidant additive decreases the thermal stability which helps in bond breaking as a much simple phenomenon than without pro-oxidative. The % crystallinity was calculated using the DSC Standard Data Analysis software based on 276 J/g for a 100% crystalline material. In the presence of Microcrystalline Cellulose, LLDPE chains are difficult to form crystal due to the interfering chains alignment from the neighboring components [8].

Table 2. DSC data of Cellulose-PE composite.

Sample	Melt peak temperature	Enthalpy (J/g)	Crystallinity (%)
C ₁₅ P ₂	118.38°C	13.7	4.9
C ₁₅ P ₀	120.40°C	14.5	5.2

3.5. Soil Burial Analysis

Open-air agriculture soil burial is a bio-geophysical test that can provide a truthful atmosphere because soil moisture, temperature, and microbe types depend upon the season. Weight loss is one of the direct ways to measure the biodegradability of polymers. All Cellulose-PE composite samples were exposed to moist compost for a period of 15, 30, 45 days and weight loss was recorded. The samples were not discolored indicating that samples were not chemically interacted, but lessening in weight was detected. This is due to bleaching, dissolving or degradation of cellulose microbe attack. Pro-oxidative additive TiO₂ can be stimulated by absorbing UV light with wavelength lower than 390 nm and yield photo induced electrons and holes. Then, the electrons and the holes reacted with H₂O and O₂, making OH, OOH, and O₂ radicals. These highly reactive radicals can attack the LLDPE polymer chains to form carbon-centered radicals CHCH₂. Once the carbon centered radicals were hosted to the polymer chains, the consecutive reactions resulted in the cleavage of polymer chains with oxygen incorporation and producing species containing carbonyl groups. These carbonyl intermediates can be further photo catalytically oxidized to CO₂ and H₂O, leading to weight loss and decrease molecular weight [9].

The hydroxyl group (-OH) from the cellulose was chemically reacted with the anhydride group from PE-g-MA to form the strong ester bond. Thus, the cellulose was strongly attached to LLDPE with the presence of PE-g-MA as a compatibilizer [10]. This might contribute to the low susceptibility to microbe attack of the compatibilizer blends. The rates of biodegradation of Cellulose-PE composite are graphically shown in Figure. From the figure, it was noticed that the rate of biodegradation increases with increase in cellulose content in LLDPE matrix [11]. This may be attributed to the effect of microcrystalline cellulose in the blends, which absorbs moisture. This increases microbial attack, which produces defects in mechanical behavior. Therefore biodegradation occurs when microorganisms consume microcrystalline cellulose, leading to increased

porosity and voidness and decreased structural integrity of the matrix [12, 13, 14]. The percent weight loss increased with increase in cellulose content in LLDPE system.

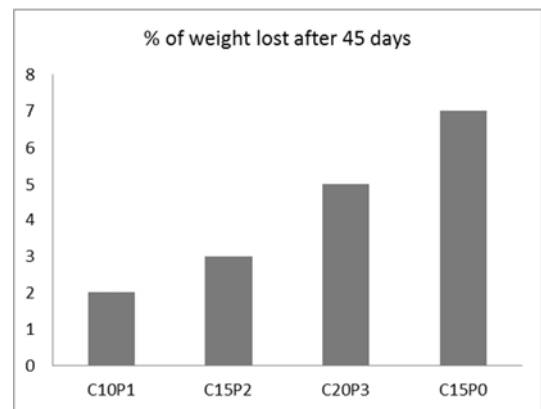


Figure 5. Weight loss of Cellulose-PE composites.

3.6. Burst Strength

The test specimen, held between annular clamps, is subjected to an increasing pressure by a rubber diaphragm, which is expanded by hydraulic pressure at a controlled rate, until the test specimen ruptures. The pressure reading at the instant of rupture is recorded as the bursting strength. The units of expression are pounds per square inch or "points". From the graph, it suggests that as microcrystalline cellulose increases burst strength increases. It shows optimum strength at 15% of cellulose content than after it decreases. It indicates that this film can be used for packaging with good strength [15].

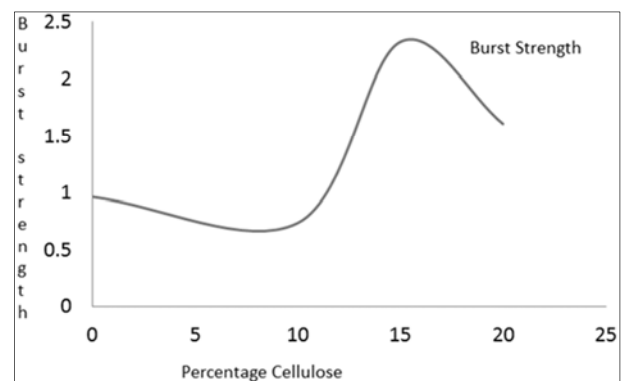


Figure 6. Burst Strength of Cellulose-PE composites.

4. Conclusions

The addition of microcrystalline cellulose in LLDPE films was productive by blown extrusion. Cellulose are strongly affected the physical, chemical, and mechanical properties of LLDPE / cellulose mixtures. Addition of cellulose has increased the biodegradability properties of LLDPE Biocomposites. Cellulose imparts an antagonistic effect upon the mechanical properties wherein decreased the tensile strength and elongation at break, while modulus increased.

This inefficiency is due to the hydrophilic nature of cellulose that is not compatible to hydrophobic nature of synthetic polymers that result in weakness of interfacial adhesion.

The existence of filler has an effect on its burst strength as the cellulose increases burst strength increases but after a certain percentage of loading the burst strength decreases. Apart of mechanical properties, this situation also contributes to decrease in Melt Flow Index (MFI), in such way that rigid particles restrict the flow of matrix. Burst strength of C15P2 is higher related to other composites. To know effect of pro-oxidative additives on thermal degradation, DSC graph of only C15P2 and C15P0 was taken in study and it found that, the LLDPE-TiO₂ is more vulnerable to thermal degradation and photo degradation than the other two composites. The pro-oxidant TiO₂ system enhances the thermal degradation and not the cellulose part, which might even retard the degradation. These biodegradable LLDPE/Cellulose blending have proved remarkable properties and thereby appeared as a new generation of composites, and beneficial features, that suitable to for many fields including consumer, agriculture and biomedical packaging industries.

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