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Surface Modification of Plasticized PLA by N_2 Plasma to Improve the Barrier Properties

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ABSTRACT

Polylactic acid (PLA) is a kind of biopolymer made from non-conventional resources. It is biodegradable and has high mechanical properties. However, its use as the packaging material in the food-packaging sector is limited due to its brittleness and porosity. Therefore, to reduce the brittleness and improve the barrier properties, the compression-molded PLA/ESO films were surface treated with N_2 plasma. Water vapour permeability, migration and differential scanning calorimetry tests have been carried out to assess the surface barrier performance and thermal properties of the manufactured films. The surface-treated PLA/ESO showed better barrier properties than pure PLA and PLA/ESO. The water vapor transfer rate of surface-treated PLA/ESO was 3.35 % lower than the PLA/ESO. The improvement in barrier properties, as well as the reduction in glass transition temperature, could increase the potential of the material for packaging.

Keywords

Nitrogen (N_2) plasma, Water vapor permeability, Differential scanning calorimetry (DSC), Polylactic acid (PLA), Epoxidized soybean oil (ESO).

Introduction

It is essential in the food industry to choose the right food packaging to enhance endurance, preserve the quality of the products during storage, and transit [1]. The four most common materials used for food packaging are paper, plastic, glass and metal [1-3]. Global plastic consumption is anticipated to surpass 500 million tonnes by 2050, according to annual growth in plastics consumption, with single-use items being the dominant user [4,5]. In the plastic global sales, the food packaging industry consumes 84 percent of thermoplastics [6,7]. Because of their low weight, strong mechanical performance, and good barrier qualities, fossil polymeric materials were widely utilized in food packaging [2,8-10].

Packaging is the largest significant contributor to worldwide plastic garbage, accounting for about 50 % of global weight [11]. Methane is released when garbage is dumped in landfills, which is more powerful than CO_2 in terms of causing global warming by more than 2000%. [12]. Sustainability challenges, the insufficiency of conventional energy resources, and waste generated by existing petroleum plastics have sparked attention to the development of new ecologically acceptable materials [13]. The United Nations refers to the problems as 17 Sustainable Development objectives [13,14]. Biopolymers have been extensively researched to overcome these issues.

PLA is amongst the most commercially successful aliphatic plastics that are both bio-derived and biodegradable [15]. Because of its good thermoformability, moldability and additional characteristics such as outstanding transparency, chemical, UV resistance, oil, excellent flavor, aroma barrier, and satisfactory mechanical and thermal properties, it is getting prominence in the food-packaging sector [16]. However, PLA usage is restricted in the food packaging industry because of many difficulties, particularly brittleness, mediocre gas and low moisture barrier qualities [13,15,16]. One of the viable methods for enhancing PLA toughness and reducing brittleness is to use plasticizers, which may react chemically among polymers and improve interparticle separation along with

chain mobility [13,17-19]. Plasma surface treatment is one of the most effective methods for improving barrier qualities without affecting the substrate's bulk characteristics [20,21].

A plasticizing agent that can migrate lower and has minimal toxicity is more desirable as a replacement for phthalate esters. Research studies are becoming more and more on bio-derived plasticizers made of vegetable oils, esters of citric acid, and modified monosaccharides, which can be used to increase the flexibility of polymers. [22]. Because of the binding affinity of the epoxy moiety with the hydroxyl and carboxyl groups of PLA thermoplastic, epoxidized oils are considered reacting additives [23]. Epoxy plasticizers are created by epoxidizing the covalent bond between carbon atoms in oils and additives, which tends to result in negligible volatility and minimal migration [24,25]. Epoxidized soybean oil (ESO) is derived from renewable sources and is biodegradable. According to the findings, combining PLA with ESO improved viscosity and viscoelastic flow properties [26]. Both the elasticity and percentage elongation are improved by adding ESO to the PLA. PLA with a 6-weight% ESO content has been deemed to have a superior performance balance [26].
Plasma is comprised of a wide number of exciting reactive species that either are in charged or base states [1,27,28]. The plasma can be generated at varied processing temperatures and pressures. Thermal [29] or non-thermal [30] plasma is classified based on the excited state of charged particles and heavy plasma species [1]. Cold plasma is a type of partly or totally ionized gas. It has proved an effective treatment approach that is utilized in a range of industries and for a variety of purposes [1,31]. To significantly alter the characteristics of different polymer surfaces, oxygen (O_2), nitrogen (N_2), air, helium (He) and argon (Ar) are commonly used [1,32].

There have been no earlier reports on vacuum-assisted low-pressure plasma surface treatment of PLA/ESO. Therefore, the objective of this study is to determine the barrier and thermal characteristics of PLA/ESO sheets that have been surface-treated with N2 plasma. In this study, PLA/ESO was blended with an extruder and PLA; PLA/ESO sheets were made with a hydraulic press. PLA/ESO sheets were surface treated with N_2 plasma. The findings of the water vapor permeability (WVP) migration and differential scanning calorimetry (DSC) tests were properly stated.

Experimental Methods and Materials

PLA, which has a density of 1.24 g/cm^3 was provided by the OWL-Filament, Deutschland. Epoxidized soybean oil with a density of 0.99 - 1.01 g/cm^3 was kindly provided by TRAQUISA, Spain. Bioethanol was purchased from the Carl Warrlich GmbH.

Compounding

PLA pellets of 100 wt % were manually mixed with 6 wt % of ESO plasticizer in a tilting drum mixer, dried for 24 hours at 50°C, and then blended in a twin-screw extruder. The screw speed was set between 35 and 45 rev/min, and the barrel temperature was maintained between 150 and 180°C. The moistness of the pelletized material was removed by drying for 24 hours at 50°C.

Compression Molding

The films with an area of 120 cm^2 were prepared with PLA and PLA/ESO granules by using a hot press at 210°C. For the 10 minutes of pressure holding, the hot press's hydraulic pressure was maintained at 80 bar. To cool the mold and reach 40°C, a water-cooling system was used.

Plasma Treatment

For the surface treatment of PLA/ESO films, a low-pressure plasma system, PINK V6-G, was employed, as illustrated in Figure 1. This model has a plasma generator that works with a microwave power of 50 – 300 W and an excitation frequency of 2.45 GHz. The inlet pressure without a vacuum pump is 0.5 KVA and the power supply is 230 V with a frequency of 50/60 Hz. Samples were kept on specimen carriers for surfaces modification, and specific control parameters were utilized. The N_2 gas was supplied at a flow rate of 5 ml/min, and maintained the process pressure of 15 Pa and microwave power of 50W for 180 seconds.

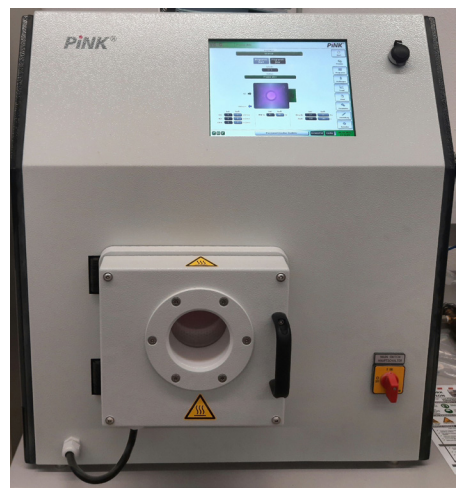

Figure 1. Pink V6-G plasma machine

Water Vapor Permeability Tests

According to the standard DIN EN 1279-1:2018, the water vapour permeability of PLA, PLA/ESO and surface-treated PLA/ESO were measured. At 50°C, the round specimens having a radius of 56.87 mm and a 0.5 mm thickness were dried for 24 hours in the oven. The individual film specimen was placed on the top of the tray filled with and without desiccant (dry silica gel) and fixed with wax as shown in Figure 2. A dummy sample (without desiccant) was also tested to compensate for evaporation and oxidation. Each test arrangement was weighed and stored at 23°C. The rotor speed was maintained at 100 rpm throughout the test to ensure constant circulation. Relative humidity in the test cabinet was > 94 % and in the test dish, it was < 5%. Samples were weighed periodically until a constant mass transfer occurred. The water vapor transmission rate and water vapor permeability were determined from the following equations (1) and (2).

$$Water\ vapor\ transmission\ rate\ (WVTR) = \frac{\Delta m}{(A * t)} \qquad (1)$$

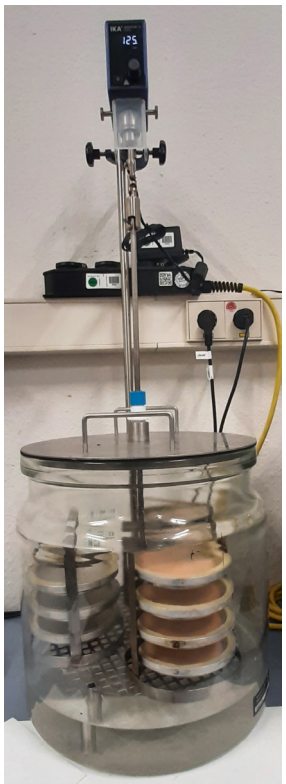

Figure 2. Experimental setup of water vapour permeability tests

Where Δm is the mass gain of water vapor from initial to final in g, A is the test area in m^2 and t is time in d [33].

$$Water\ Vapor\ Permeability\ (WVP) = \frac{WVTR}{P * (RH_1 - RH_2)} * h \quad (2)$$

In the above equation, P is the vapor pressure of water in Pa at temperature 23°C, h is the film thickness in m and RH_1-RH_2 are the moisture gradients [33].

Migration Tests

According to European regulation (EU) 10/2011, the permitted migration value for 1 dm^2 of the plastic film is 10 mg (although two surfaces of the material have been exposed to the foodstuff substitute, only a single surface is taken into account) [13]. The overall migration of surface-treated and untreated PLA/ESO samples were examined based on this standard. The 0.5 mm thickness films were cut into rectangular shape specimens with an 80 mm length and 30 mm width and dried for 3 days at 40°C. The samples were initially weighed and then place inside the glass bottles. Glass bottles were filled with food simulants (50% bioethanol and 50% of distilled water). The samples were stored for 10 days at 40 °C. After being exposed for that specified duration, the samples were removed and cleaned with water, then dried with the use of a towel. Then the sample mass was re-measured to quantify the absorption of the test liquid. The weight uptake was due to the absorption of food simulant. Samples were kept in the oven for 7 days at 60°C. The mass difference between before and after treatment was then used to determine the overall migration value by using equation (3).

$$Overall\ migration\ (OM) = \frac{(m_i - m_f)}{A} \quad (3)$$

Where m_i is the initial mass of the specimen before starting the migration test, m_f is the final mass of the specimen after migration test, in mg and A is the surface area of the specimen in dm^2 [34].

Solubility of surface-treated and untreated PLA/ESO samples were also determined from the migration tests [35]. The percentage of the total soluble matter was calculated by using equation (4).

$$Solubility\ (\%) = \frac{(m_i - m_f)}{m_i} * 100 \quad (4)$$

Differential Scanning Calorimetry Tests (DSC)

Perkin Elmer DSC 7 was used to conduct DSC testing in accordance with DIN EN ISO 11375 - 4. The ten-milligram samples were measured and sealed in aluminium pans. Sealed pans were put on the test side of the DSC and heated at a rate of 20 k/min from 30 to 200°C. The glass transition temperature, melting temperature, and cold crystallization temperatures were determined.

Results and Discussion

The water vapor transmission rate results are presented in Table 1. As shown in Figure 3, the pure PLA WVTR (6.19 g/m^2 d) was low compared to PLA/ESO due to its crystallinity. Crystallinity acts as a barrier to the transfer of water vapor molecules. ESO could significantly increase the PLA's chain mobility, allowing the water particles to permeate more quickly [13], which in turn increases the water vapor permeability (6.26 g/m^2 d) as shown in Figure 4. Another reason for the increase in WVP is the balance between the hydrophobic and hydrophilic characteristics of the mixture components and their interfacial properties. The greater the tension at the interface are, the larger are the interphase spaces, which favors water diffusion. The combination of the carboxy group from PLA with the epoxide of ESO might result in an interface of PLA with ESO [26]. Thus, a hydrogen bond could be formed between PLA and ESO. The WVTR of the plasma-treated films (6.05 g/m^2 d) was low due to the tortuous paths formed by the crosslinking of nitrogen molecules with carbon and hydrogen atoms on the film surface during plasma treatment.

Table 1: Results of water vapor permeability tests.

Specimen	Slope, Δm/t	WVTR	WVP
	[g/d]	[g/m^2 d]	[g/m d Pa] *10^{-8}
Pure PLA	0.063 (± 0.0096)	6.19	1.17
PLA/ESO	0.064 (± 0.00025)	6.26	1.18
Surface-treated PLA/ESO	0.061 (± 0.00052)	6.05	1.14

The overall migration results are depicted in Table 2. The migration value was the same for PLA/ESO and surface-treated PLA/ESO (15.76 mg/dm^2). However, the surface-treated specimens show a greater regularity than the untreated specimens (Figure 5). This is due to the uniform surface achieved by the plasma treatment. The results of solubility tests are depicted in Table 3. The solubility of the simulant value was also low for surface-treated PLA/ESO (0.058%).

Table 2: Results of migration tests.

Specimen	Migration in [mg/dm^2]
PLA/ESO	15.76 (± 0.00057)
Surface-treated PLA/ESO	15.76 (± 0.00026)

Table 3: Results of solubility tests.

Specimen	Initial mass in [g]	Final mass in [g]	Solubility in [%]
PLA/ESO	1.536	1.535	0.065
Surface-treated PLA/ESO	1.560	1.559	0.058

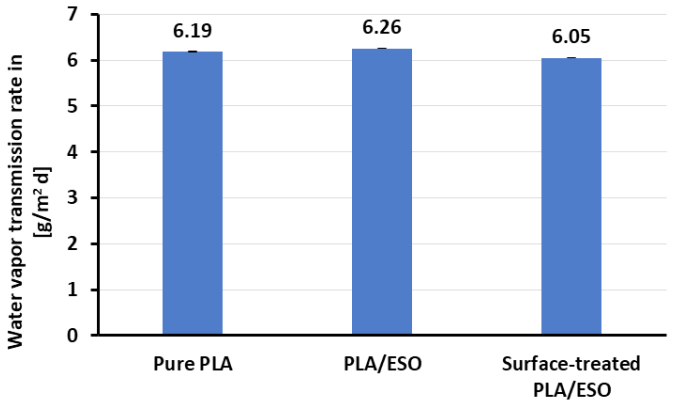

Figure 3: Water vapor transmission rate of pure PLA, PLA/ESO and surface-treated PLA/ESO

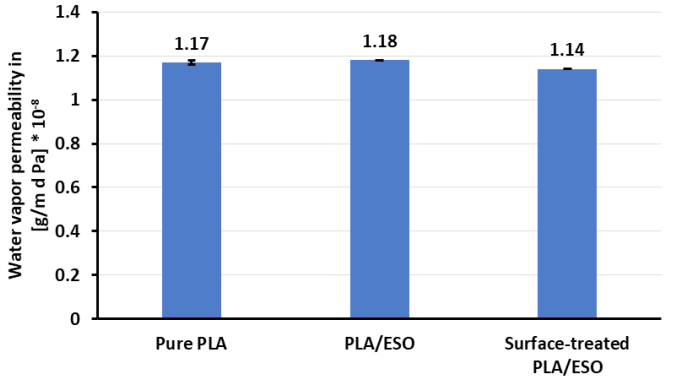

Figure 4: Water vapor permeability of pure PLA, PLA/ESO and surface-treated PLA/ESO

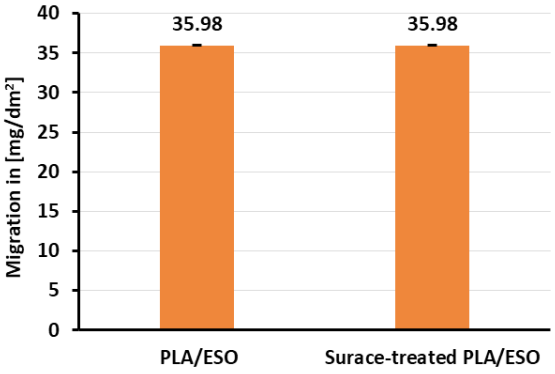

Figure 5: The migration values of PLA/ESO and surface-treated PLA/ESO

Table 4: Results of differential scanning calorimetry tests.

Specimen	Glass transition temperature, T_g in [°C]	Cold crystallization temperature, T_{cc} in [°C]	Melting temperature, T_m in [°C]	Specific heat capacity, C_p in [J/kg k]
Pure PLA	60.06 (± 0.47)	120.73	153.56	1304
PLA/ESO	58.73 (± 0.47)	112.23	155.23	310
Surface-treated PLA/ESO	58.90 (± 0.55)	107.56	156.40	1005

For the three types of materials, DSC curves showed a single glass transition and melting point. The T_g obtained from pure PLA is 60.06 °C, but it drops to 58.90°C for the surface-treated PLA/ESO specimens (Table 4). It might be owing to the higher miscibility caused by the PLA-ESO interaction. This affects the heat capacity, which was also reduced from 1304 J/ Kg K of pure PLA to 1005 J/ Kg K of surface-treated PLA/ESO. It was determined that adding ESO lowered the T_{CC} because plasticization could enhance the PLA chains branching flexibility [23].

Conclusions

In this research, WVP, migration and thermal properties of the pure PLA, PLA/ESO and surface-treated PLA/ESO were examined. The moisture barrier of surface-treated PLA/ESO was somewhat improved, and the glass transition temperature was decreased, increasing the likelihood of this material being used in food packaging. The surface modification had no effect on the migration barrier. To enhance the barrier and reduce migration, plasma coating with a silicon group would be better because it gives a layer with high density and more reaction groups. The required WVTR for packaging cheese and processed meat is 1 to 15.5 g/m^2 day and 3.1 to 7.75 g/m^2 day, respectively [13]. Therefore, the WVTR of surface-treated PLA/ESO is suitable for packaging both cheese and processed meat. Overall, to pack fruits, solid foods, vegetables and baked items, this material could also be utilized. In the future, plasma-coated objects with different monomers could be measured with different food simulants.

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