Compatibilization of PLA grafted maleic anhydrate through blending of thermoplastic starch (TPS) and nanoclay nanocomposites for the reduction of gas permeability

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**ABSTRACT**

Here, the effects of compatibilization and clay nanoparticles on the gas permeability of nanocomposites of poly-lactic acid (PLA)/thermoplastic starch (TPS)/nanoclay were discussed. TPS and compatibilized PLA/TPS were tailored in the first step. The starch with D-sorbitol as a plasticizer was mingled through the internal mixer. Afterward, the maleinization method was utilized on PLA to ameliorate the compatibilization of PLA and TPS. In this regard, maleic anhydrate (MA) has been grafted on PLA in the presence of L101 as a peroxide initiator via melt mixing to obtain PLA-g-MA. The optimum content of PLA-g-MA was about 4 phr, confirmed by DMTA and SEM. Noteworthy, the presence of PLA-g-MA has moderately improved the oxygen barrier. Then, the nanocomposites of PLA and TPS containing 1% of Cloisite-30B as well as the optimum compatibilizer (4phr), were produced by melt mixing in the masterbatch module leading to the formation of an extraordinary well-dispersed structure according to XRD patterns. The mixing order controlled the localization of nanosheets. It was concluded that the inclusion of 1% nanoclay in the PLA phase reduces the oxygen permeability by 55% compared to the pristine blend due to the tortuosity effect of nanosheets that are appropriately dispersed in the matrix.

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1. Introduction

Nowadays, using petroleum-based products has notably expanded and consequently posed a long-lasting risk to the ecosystem. Ubiquitous microplastics are announced as environmental pollutants due to their undegradable nature and sometimes emitting toxic substances [1]. In this regard, the replacement of synthetic polymers with bio-based and biodegradable ones is an appropriate strategy to tackle this issue [2]. One of the recently studied candidates is PLA, comparable to petroleum-based counterparts, in the case of performance, and can be synthesized via (I) polycondensation of lactic acid derived from the fermentation of different sources of starch or (II) ring-opening polymerization of lactide dimers [3,4]. Despite all of the PLA’s advantages, some features need tailoring and engineering. More importantly, the high production cost of PLA also affects the final products’ price, though blending PLA with other polymers has been introduced as a solution to overcome all these obstacles [5,6].

Starch is a natural, biodegradable, and abundant polymer with a much lower price than PLA; therefore, it seems to be a rational choice for blending with PLA. However, the point is that starch should be thermos-plastisized by means of a plasticizer to adjust its melting temperature and shift it to below the degradation temperature [7]. Over decades, a wide range of nonvolatile and small molecules known as plasticizers have been precisely introduced and performed on starch to fabricate TPS [8,9]. In this study, sorbitol has been selected owing to its accessibility and advantageous effect on increasing barrier features against oxygen reported by recent papers [10,11]. It is worth noting that the aforementioned blend has wide applications in film packaging.

Blending immiscible hydrophobic PLA with hydrophilic TPS requires a compatibilization method to enhance the interfacial adhesion of both phases [12–14], which leads to ameliorating the final properties of the PLA/TPS blend. Some of these methods were reviewed and categorized by Bing Zeng and Ang Li [15]. For instance, component modification in the way that one component generates more affinity to the other one has been studied by various chemical modifications on starch to exchange hydroxyl groups with more hydrophobic ones through oxidation, esterification, and etherification [16,17]. Another example is modifying PLLA with PEG as a middle block to be blended with TPS [18]. In some cases, according to the final application, it is recommended to connect two components through cross-linking as a way of making them compatible [19]. Using a transition phase between PLA and TPS, with better compatibility and interfacial adhesion to both phases, is another method known as interfacial transitioning [20], such as using polycaprolactone (PCL) in PLA/TPS blends, which has been reported to have a compatibilization effect [21,22]. Moreover, applying block copolymers of starch and PLA in PLA/TPS blends is meant as physical bridges to make the phases more compatible, known as the amphiphilic bridging method by researchers [23,24]. Also, in recent research for boosting compatibility, two or more beneficial tricks are combined. Poly(ethylene octane) grafted with glycidyl methacrylate (GPOE) is an example of suchlike compatibilizers for PLA/LDPE blend, which can be compatibilized through physical and chemical interactions at the same time [25]. Due to the complicated and excessive synthetic procedure of previous methods, forming chemical bonds between PLA and TPS is the frequently used strategy to boost their compatibility. In this scenario, initiators like benzoyl peroxide (BPO) and L101, as well as molecules containing unsaturated anhydrous bonds such as maleic
2. Materials and methods

Two different techniques were coupled here, namely solution casting and melt-mixing, to fabricate PLA/TPS/C30B nanocomposites. More specifically, the coupling technique contains 5 main steps; (I) preparation of TPS nanocomposites through an internal mixer, (II) fabrication of PLA-g-MA via melt mixing, (III) production of PLA/C30B masterbatches using solution casting method, (IV) forming a compatibilized blend of pure PLA and TPS through melt mixing procedure, and (V) fabrication of PLA/TPS/C30B nanocomposites.
It is worth noting that clay nanoplatelets were incorporated into the final nanocomposite specimens using two different approaches. In the first series of nanocomposites, clay nanoplatelets were included by incorporating PLA masterbatches, and in the second series of nanocomposites, C30B nanoparticles were added by incorporating TPS nanocomposites. Both of the mentioned series contains 4 phr PLA-g-MA after meticulous optimization of this compatibilizer. More details are provided in the below sections.

2.1 Raw materials

The poly (lactic acid) used in this study was type PLA 2003D having a melt flow index (MFI) of 6 g/(10 min) (at 210°C/ (2.16 Kg)), a density of 1.24 g/cm³ and weight average molecular weight ($M_w$) of 246,500 g/mol, which was supplied from Nature Works LLC (USA). Wheat starch (grade 111,685 of Merck Co.) has an amylose/amylopectin ratio of 75/25. D-Sorbitol (SB0491) (as a plasticizer) was purchased from Bio Basic Inc. (Canada). Nanoclay, with the trade name of Cloisite30B (C30B) that modified by a quaternary ammonium ion containing methyl tallow bis-2-hydroxyethyl, was supplied by Southern Clay Products, Inc. Maleic anhydride (Merck, Germany) and the initiator 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane with the trade name of Luperox 101 or L101 (Sigma-Aldrich Chemical Co, Germany) were utilized for the preparation of maleic anhydride grafted PLA. All chemical reagents were of analytical grade and were used without further purification.

2.2 Preparation of thermoplastic starch in nanocomposite

To obtain thermoplastic starch (TPS), starch and D-sorbitol were premixed at a ratio of 64/36 by weight. They were kept in the oven to be dehydrated for 24 hours prior to being melt-mixed in a counter-rotating internal mixer (Brabender, Germany) at 120°C and a screw speed of 80 rpm for 10 minutes. Nanoclay particles were added into TPS, and thereafter, TPS nanocomposite samples were fabricated, incorporating 4 wt% clay nanoplatelets to obtain 1 wt% PLA/TPS nanocomposite as TPS makes up 25 wt% of each sample, referring to Table 1 and Figure 1.

2.3 Preparation of PLA-g-MA

The grafting of MA on PLA molecule chains has been carried out by reactive functionalization of PLA. This procedure requires varied parameters to be optimized like the percentage of each of MA and L101 or even processing conditions like screw speed and exerted temperature. As there are numerous studies in this field, the most suitable percentages of components and processing conditions were used in this work. According to Figure 1, the first step was to keep PLA granules in a vacuum oven at 90°C for 5 hours. Next, they were soaked with 0.6wt% of L101 followed by mixing with 5 wt% of MA [44], both based on the PLA weight, in a zip-lock plastic bag [45]. Finally, they were fed into the internal mixer at 175°C and a screw speed of 60 rpm; the components were mixed for 10 minutes.
2.4 Preparation of nanoclay masterbatch with PLA

First of all, nanoclay was dispersed in chloroform by the ratio of 1 wt% and sonicated for 15 minutes using an ultrasonic probe processor to ensure uniform dispersion of clay; the sonication power was set at 100 W and the frequency of 40 Hz. Thereafter, the mixture was added to the 5 wt% PLA solution in chloroform. Eventually, the final solution was poured into Petri dish, and the solvent was allowed to evaporate to obtain membranes that were dried in an oven for residual evaporation of the solvent [46]. This procedure is demonstrated in Figure 1.

2.5 Preparation of compatibilized blends

Compatibilized blends resulted from melt mixing of PLA/TPS (in a weight ratio of 75/25 at 175°C and rotor speed of 60 rpm in the internal mixer) followed by incorporating 0–6 phr PLA-g-MA.

2.6 Preparation of PLA/TPS/Clay nanocomposites

In all of the nanocomposites, the total amount of clay nanoparticles (clay@total) was fixed to 1 wt%. Two other indicators, clay@PLA and clay@TPS, are attributed to the content of clay nanoparticles in PLA and TPS phases, respectively. Specimens in which clay was kept

| Sample code   | PLA (wt %) | TPS (wt %) | PLA-g-MA (phr) | clay@PLA (wt %) | clay@TPS (wt %) | clay@total (wt %) |
|---------------|------------|------------|----------------|----------------|----------------|------------------|
| p-PLA         | 100        | 0          | 0              | 0              | 0              | 0                |
| PLA/TPS0      | 75         | 25         | 0              | 0              | 0              | 0                |
| PLA/TPS2      | 75         | 25         | 2              | 0              | 0              | 0                |
| PLA/TPS4      | 75         | 25         | 4              | 0              | 0              | 0                |
| PLA/TPS6      | 75         | 25         | 6              | 0              | 0              | 0                |
| PLA/1%C       | 99         | 0          | 0              | 1              | 0              | 1                |
| PLA/TPS4/1%C  | 74         | 25         | 4              | 0              | 4              | 1                |
| PLA/1%C /TPS4 | 74         | 25         | 4              | 1.35           | 0              | 1                |

Figure 1. Schematic diagram of sample preparation stages.
in the PLA phase (PLA/C30B masterbatch) were incorporated with pure PLA simultaneously. Otherwise, clay was incorporated while preparing TPS nanocomposites in the first step, as shown in Figure 1. All sample formulations are summarized in Table 1.

The schematic diagram of all the aforementioned sample preparation procedure stages is depicted in Figure 1.

2.7 Characterizations

2.7.1 X-ray Diffraction (XRD)

In the case of nanocomposite specimens, the d-spacing between clay nanosheets, as well as gelatinization of starch through the thermo-plasticization process, has been studied using Equinox3000, Intel. Measurements were conducted under Cu Ka radiation (\(\lambda = 0.1540\) nm) at 40 kV and 30 mA.

2.7.2 Fourier Transform Infrared (FTIR) Spectra

FTIR spectroscopy was performed on PLA-g-MA and pure PLA to distinguish the grafting of MA on PLA in PLA-g-MA using a Bruker spectrometer with 2 cm\(^{-1}\) resolution. After keeping samples for 24 hours at a 130°C oven, equal amounts of each sample were weighed (0.5 gr) and examined. It should be mentioned that all the samples were washed by titration method according to Detyothin [47,48] to remove excess MA, which did not react with PLA chains, from samples prior to this test.

2.7.3 Degree of functionalization

With the purpose of determining how much MA has reacted to PLA molecule chains, the titration method has been utilized. In the first step, PLA-g-MA was washed to remove the unreacted MA from the substance, and then the sediment was dissolved in chloroform and titrated with 1 M KOH standard solution in the presence of 8–10 droplets of phenolphthalein. The endpoint of titration was distinguished using color and pH. PLA was also titrated under the same condition. The acidic number for both samples and functional degree for PLA-g-MA was calculated aiding below expressions:

\[
M = \frac{V_{KOH} \times N_{KOH}}{W} \times 56.1
\]

\[
G = \frac{M_s - M_b}{2 \times 561} \times 98.06
\]

Here, \(M\) is the acidic number (mgKOH/g). \(V_{KOH}\), \(N_{OH}\) and \(w\) are the volume (ml), the normality of the standard solution of KOH, and the mass of the specimen, respectively. \(G\) is the percentage of functionality. \(M_s\) and \(M_b\) correspond to the acidic number of PLA-g-MA and PLA, respectively.
2.7.4 Dynamic Mechanical Thermal Analysis (DMTA)
Glass transition temperature ($T_g$) of specimens containing varied contents of PLA-g-MA (0–4 phr) was assessed with the DMTA technique in order to measure the compatibility. Using a Diamond DMA Perkin Elmer, the prepared samples in a rectangular form of $1 \times 3$ cm$^2$ and 2 mm thickness were tested under the tensile mode, 1 Hz frequency, and a heating rate of 5°C per minute ranging from 0°C to 130°C.

2.7.5 Scanning Electron Microscopy (SEM)
To investigate the micro-scale morphology of the blends, SEM images were obtained from Quanta 200. Here, the rectangular samples were first fractured in liquid nitrogen, followed by etching and using distilled water to extract the TPS phase. On the next step, they were coated with a thin layer of gold using a Coxem machine at 25 kV, and the images were analyzed in Pixel Ferber software.

2.7.6 Differential Scattering Calorimetry (DSC)
Thermal analysis of samples has been carried out by Mettler Toledo DSC. Approximately 4 mg of each specimen was weighed and tested in an aluminum pan. In order to eliminate the prior thermal history of specimens, they were heated at a scanning rate of 10°C per minute under nitrogen purge from 25°C to 200°C and kept at the molten state for 2 minutes. Then they were cooled at a rate of $-10^\circ$C/min from 200°C to 25°C and again heated back at a rate of 10°C/min to 200°C. Indeed the second heating thermographs were used.

Crystal percentage ($X_c$) of each specimen was calculated using the equation below:

$$X_c = \frac{\Delta H_m}{\Delta H_m}$$

where, $\Delta H_m$ and $\Delta H_m$ represent melting enthalpy of sample and melting enthalpy for 100% crystalline PLA, respectively. $\Delta H_m$ equals to 93.7 J/g for PLA.

2.7.7 Thermogravimetric Analysis (TGA)
The decomposition temperature was measured using a thermogravimetric analyzer (TGA, Pyris 1 TGA, PerkinElmer) at temperatures ranging from 50°C to 600°C with a heating rate of 10°C/min under nitrogen purge with a rate of 50 ml per minute.

2.7.8 Oxygen Permeability
Permeability test of the specimens was performed by a device in Tarbiat Modares University at about 30°C and under constant pressure difference of 1 atm using oxygen gas regarding ASTM-D-1434 standard. This device was also used previously by Khalili et al. for the same purpose (oxygen permeability) [49]. Film samples of each blend, with a crude thickness of 150 ± 20 micron, were prepared using a hydraulic press at 190°C and under the pressure of 20 bar for approximately 2 minutes and put on the device’s chamber.
3. Results and discussions

3.1 Characterization of TPS and synthesized PLA-g-MA

In Figure 2, the XRD patterns against 2θ are demonstrated for native starch and TPS, including 36 wt% of D-sorbitol as the plasticizer. Indicative diffraction peaks at 15°, 17°, 18°, and 23° show a semi-crystalline native starch with an A-type crystal structure. The mentioned peaks are diminished and shifted to a more intensive peak at 20°, indicating the formation of V-type crystals in TPS [50]. This phenomenon is known as retrogradation due to the rearrangement of amylopectin chains through thermo-polymerization of starch, which is a sort of chain relaxation [51,52]. It is worth mentioning that choosing a suitable plasticizer is crucial; indeed, the driving force is the strength of chemical attraction between plasticizer and amylopectin chains, which should be more robust than the amylopectin chains themselves to obtain this property. In this case, the hydrogen bonds between OH groups of sorbitol and amylopectin chains are responsible for such a rearrangement and led to the formation of a well-thermo-polymerized starch.

The FTIR spectroscopy has been applied – as meant to assess the authenticity and analyze the functional groups of the synthesized compatibilizer (PLA-g-MA). In Figure 3, the spectrums of pure PLA and PLA-g-MA are illustrated. Results are similar to those reported by other literatures comparing PLA and PLA-g-MA [44,53,54]. According to them, in the case of pure maleic anhydrate's spectra, two diagnostic peaks exist; one intensive peak around 1760 cm\(^{-1}\) as well as a weak one around 1850 cm\(^{-1}\), which are attributed to symmetric and asymmetric stretching of carbonyl group (C = O), respectively [32,55]. Here, the weaker peak around 1850 cm\(^{-1}\) is not noticed due to the low concentration of MA in PLA-g-MA. The percentage of reacted MA was calculated at about 0.4 wt%. As

![Figure 2. X-ray diffraction patterns for native starch and TPS.](image-url)
a minor content of MA has reacted with PLA chains, maleic anhydrate grafted on PLA backbone is just proven by investigation and comparison of carbonyl peak of pure PLA and PLA-g-MA spectrums. Furthermore, the peak related to C = O groups of pure PLA has appeared at 1745 cm\(^{-1}\). These two distinctive absorptions are so close to each other that can be recognized by the clear increasing of intensity and a slight shift because the aforementioned peaks has somehow overlapped and consequently mixed with each other. This is why the distinctive peak of MA grafting appeared more intensive at 1753 cm\(^{-1}\) [30,56]. The deconvoluted peak with the aid of computerized curve fitting (Lorentzian equation) is demonstrated in Figure 3 (b). The aforementioned clues point out the well-grafted MA on PLA. Moreover, peaks observed at 1031, 1079, 1180, 1260 and 1850 cm\(^{-1}\) belong to the bending and stretching mode of c-o-c group. Carbocyclic group (C-COO) has shown a peak at 862 cm\(^{-1}\). Also, 1368 and 1448 cm\(^{-1}\) peaks are related to C-H and C-H\(_3\) vibrations, respectively.

3.2 Effect of compatibilizer (PLA-g-MA) on the properties of PLA75/TPS25 blend

3.2.1 Effect of compatibilizer (PLA-g-MA) on phase morphology of PLA75/TPS25 blend

Microstructure undoubtedly determines and controls various properties of blends. To investigate the dispersion of the TPS phase in PLA and the influence of compatibilizer on microstructure, the SEM images of the cryogenically fractured surface of PLA/TPS samples containing different amounts of PLA-g-MA (0–6 phr) are obtained and indicated in Figure 4. Black spots are attributed to the extracted TPS phase by an etching method, which is dispersed in the PLA matrix and has created a matrix-droplet microstructure that resembles those results reported by other researchers [27,44,57,58]. As observed, droplets are elliptical, which means the TPS phase tends to droplet breakup, and the melt blending has stopped before completion of the procedure. In order to statistically study the
morphology of these blends, the biggest ($D_1$) and smallest ($D_2$) diameters of droplets are measured using Pixel Ferber Software. Moreover, the numerical and weighted average of the resulting data were calculated and reported in Table 2. According to the provided information, by including more amount of compatibilizer from 0 to 4 phr, the ratio of average $D_1$ to $D_2$ increased, which visually means the droplets are more stretched, resulting from proper tension transfer between two phases. The interaction between the anhydrous ring of PLA-g-MA and hydroxyl groups of TPS is responsible for this attachment. Likewise, PDI as a quantitative variable for dispersion is declined; therefore, droplets’ size dispersion has improved up to 4 phr of PLA-g-MA. This phenomenon implies

| Sample name | Numerical average of the biggest diameter ($D_1$) µm | Weighted average of the biggest diameter ($D_1$) µm | PDI $D_1$ | Numerical average of the smallest diameter ($D_2$) µm | Weighted average of the smallest diameter ($D_2$) µm | PDI $D_2$ | $D_1/D_2$ |
|-------------|-------------------------------------------------|---------------------------------|-----------|-------------------------------------------------|---------------------------------|-----------|-----------|
| PLA/TPS0    | 10.112                                          | 15.545                          | 1.54      | 4.274                                           | 6.442                           | 1.51      | 2.36      |
| PLA/TPS2    | 10.665                                          | 16.407                          | 1.54      | 6.689                                           | 4.561                           | 1.43      | 3.59      |
| PLA/TPS4    | 10.380                                          | 15.435                          | 1.49      | 5.918                                           | 4.200                           | 1.41      | 3.65      |
| PLA/TPS6    | 10.456                                          | 17.588                          | 1.68      | 9.023                                           | 5.157                           | 1.75      | 3.41      |

Figure 4. SEM images of PLA/TPS (75/25 wt/wt) with different PLA-g-MAs; a) 0 phr b) 2 phr c) 4 phr d) 6 phr.
the amelioration of compatibility pertaining to TPS and PLA in the blends by incorporating PLA-g-MA, and the optimized content is chosen 4 phr. However, in regards to the concentration of 6 phr, the averaged dimensions and PDI have raised simultaneously, which point out sort of incompatibility due to rheological and chemical alteration of TPS phase that causes less desire to the other phase; therefore, the more the droplets are stable in larger sizes, the less they tend to have an interface with the matrix. To explain more, when two phases have fewer things in common, their tendency to share their boundaries decreases since their chemical sites are no longer attracted to each other. In this case, the over-usage of PLA-g-MA prevents OH groups of TPS from being exposed to the matrix by keeping TPS droplets in captivity. Also, from a rheological point of view, when the content of the compatibilizer exceeds an optimum point due to the lower viscosity of PLA-g-MA, the tension transfer loses its meaning. Therefore, TPS domains receive less tension during processing and consequently become stable in bigger sizes. This is what has happened regarding 6 phr of compatibilizer.

### 3.2.2 Effect of synthesized PLA-g-MA on the compatibility of polymeric blends

In general, compatibility means how close two substances’ characteristics are. One of these characteristics is glass transition temperature. When components of a binary blend are immiscible, as what we have studied in this work, observing two distinctive glass transitions attributing to each of the components is inevitable. The closer these peaks are, the more compatible they will be, as it means more similarity in their behavior on the molecular scale. For a more detailed discussion, $T_g$ is a criterion for chains’ dynamics; thus, any factor that influences it can definitely alter the temperature at which glass transition happens. In this case, different quantities of PLA-g-MA are used to impress both types of polymer chains (PLA and TPS) to have a more homogenous and compatible system. One of the predominantly used approaches to investigate the compatibility of polymeric blends is dynamic-mechanical-thermal analysis (DMTA). In the mentioned test, $\tan \delta_{\text{max}}$ corresponds to glass transfer temperature ($T_g$) in the graphs.

*Figure 5* reveals DMTA curves of pure PLA, TPS, and their blends containing various amounts of PLA-g-MA. As it is noticed, the graph related to TPS has demonstrated two peaks; one at about 17°C and the other at 70°C, which are caused by plasticizer-rich ($\beta$ transfer) and starch-rich (α transfer) domains [59–61]. By and large, in the blends’ diagram, the sharp peak around 60°C (T) is devoted to the PLA phase, and the exact temperature of the mentioned peak, as well as its deviation from that of pure PLA (p-PLA), were reported in *Table 3*.

Results represent that the more PLA-g-MA was incorporated into the blend (up to 4 phr), the more T shifted to lower temperatures, which means the inclusion of PLA-g-MA leads to more affinity between two phases, and this trend has been reported in recent researches [62,63]. Because of reacted functional groups on synthesized PLA-g-MA, there are more chemically and physically attractions among OH groups of TPS and functional groups of PLA-g-MA, which would consequently decrease TPS chains’ dynamic, though the relevant glass transition appears in higher temperatures. As discussed before, due to the maleination reaction on PLA chains, synthesized PLA-g-MA has a bulky structure; hence the chains’ free volume increases. Consequently, the chains’ dynamic expedites, leading to fewer energy consumptions for glass transition than pure PLA. The presence of
PLA-g-MA in the PLA phase provides more free volume for the matrix chains meaning less energy is needed for segmental transformation, and that is why T has shifted to lower temperatures up to 4 phr concentration of the compatibilizer.

A simple overview of what has happened in the microstructure is depicted in Figure 6. In regard to 6 phr concentration, not only PLA-g-MA no longer plays the compatibilizer role, as T was shifted to a higher temperature (the same as pure PLA), but also it seems to have the reverse effect on the blend due to the bimodal shape of the peak, which means PLA-g-MA was detected as a separate component; this is the definition of phase separation. However, it is expected from the glass transition of TPS phase to occur at a higher temperature. It can be interpreted that exceeded amount of PLA-g-MA has made heat transfer locally difficult, and TPS droplets find sufficient energy for their segmental movements at higher temperatures. This event goes along with the rheological differences observed in the morphology analysis of SEM images that prevents the tension from being transferred. As a result, morphology and DMTA assessments eventually elucidated that the optimum compatibilizer content among all specimens is 4 phr.

![Figure 5](image-url)  
**Figure 5.** DMTA curves of PLA, TPS, and their blends in the presence of various contents of compatibilizer (PLA-g-MA) from 0 to 6 phr.

| Sample name     | $T$ (°C) | $\Delta T$ |
|-----------------|----------|------------|
| P-PLA           | 60.8     | -          |
| PLA/TPS0        | 59.4     | 1.4        |
| PLA/TPS2        | 57.4     | 3.4        |
| PLA/TPS4        | 56       | 4.8        |
| PLA/TPS6        | 60       | 0.8        |

Table 3. Information obtained from DMTA graphs of PLA, TPS, and their compatibilized blends.
3.2.3 Thermal properties of PLA75/TPS25 blend (DSC)

In order to know how TPS and compatibilizers have influenced the thermal properties of their blends, DSC thermographs of pure PLA and its blends are shown in Figure 7(a). More detailed data are gathered in Table 4, wherein T_g, ΔH_m, ΔH_cc and X_c correspond to the glass transition temperature, melting enthalpy, cold crystallization enthalpy, and degree of crystallinity, respectively, and T_m is the melting temperature. These curves are the second heating of samples to eradicate the thermal history of the polymer.

First of all, in the case of T_g, a peak was obtained at ~60 °C for the p-PLA sample, the same as a result obtained from DMTA analysis. As exhibited in Figure 7(a), the mentioned peak was shifted to a lower temperature (62.39°C) for PLA/TPS0 sample; this peak transition is due to the amorphous nature of TPS that led to a better molecular movement of PLA chains. Moreover, the mentioned peak moved to lower temperatures by

![Figure 6. Schematic of the compatibilization effect of PLA-g-MA in PLA/TPS blends.](image)

![Figure 7. (a) DSC second heating thermographs of pure PLA, TPS, and their blends with and without compatibilizer. (b) PLA barriers and their blends.](image)
incorporating PLA-g-MA (PLA/TPS4). As mentioned in the DMTA section, the reason for the shift is related to the maleination reaction on PLA chains, resulting in a bulky structure of PLA-g-MA and increasing the chain’s free volume, which ameliorates the molecular mobility of PLA/TPS4 specimen as compared to p-PLA. The numerical results of the mentioned shifts are tabulated in Table 4.

Secondly, in all samples, a broad exothermic peak is observed at around 130°C, which is attributed to a prevalent phenomenon in PLA named cold crystallization and is the result of the slow dynamic of chains [64]. Whenever a chain is able to locate in the crystalline structure, but it does not have the adequate energy level to rearrange its segments, as soon as it finds the opportunity, it will contribute to a crystal cell. Unlike crystallization, cold crystallization occurs in heating just before melting. Here, the addition of TPS has remarkably intensified this phenomenon as well as the degree of crystallinity owing to the nucleating effect of TPS droplets compared to its absence in pure PLA. Also, the decrement in $T_m$ values might be correlated to minor migration of starch plasticizer. Incorporation of the optimum amount of PLA-g-MA (4 phr) has generated (I) a notable drop of crystallization percentage, but (II) an increase in cold crystallization. Both of the effects are associated with a reduction of chain mobility, which is a sign of the compatibilization effect of PLA-g-MA among the phases [65]. This is due to the fact that more chemical and physical bonds are created between PLA and TPS by incorporating PLA-g-MA, leading to a reduction of chain mobility, which is also confirmed in morphology and DMTA studies of the specimens.

### 3.2.4 Barrier properties against oxygen of PLA75/TPS25 film

Two pivotal variables that determine the gas barrier features of polymeric films are crystallinity and tortuosity [66]. In this study, the PLA crystallization factor has been omitted to some extent by the quenching technique, which was mentioned before in the DSC analysis section. In Figure 7 (b), a bar-chart of pure PLA barrierity compared to its blends with TPS in presence of different amounts of compatibilizer are portrayed. It is noticed that the incorporation of the TPS phase has increased the oxygen barrierity of the blend. This phenomenon denotes that TPS droplets played the role of obstacles against the pathway of oxygen molecules and somehow have lengthened their route, which is well-known as a tortuosity effect. According to the previous discussion on XRD patterns, the plasticizer changes the crystal type in TPS instead of disappearing them; therefore, the crystalline droplets act as blocks. The presence of plasticizer elicits more free volume in which diffused oxygen molecules would be trapped and prevented from exploring; also, this phenomenon was reported in previous researches [67]. According to reported data of DSC thermographs, the existence of TPS droplets has increased the degree of crystallinity pertaining to PLA itself due to the nucleating effect, albeit the blends are quenched and restricted from crystallization. Hence, the barrier effect of PLA crystals is inevitable.
Moreover, and as Figure 7 (b) reveals, incorporation of the compatibilizer seems to have minimal barrier impact against $O_2$, which can be related to the more interface attachment caused by the compatibilizer. Indeed, the compatibilizer reduces the micro-voids in the interface [62]. These are why oxygen barrier features of the blends have such a trend, but so far, this parameter of the blends is not persuasive; therefore, another technique is required to refine this feature. In this regard, the assimilation of nanoplatelets has been selected to provide the nanocomposite specimens.

3.3 Influence of mixing order on the properties of PLA/TPS blends with nano-clay

3.3.1 Influence of mixing order on dispersity of nano-clay in the blends

Small-angle x-ray diffraction (SAXD) is a prevalent method to distinguish whether the platelet nanoparticles like nanoclay and nanographene have been dispersed well or how much gap nanoplatelets have in polymeric nanocomposites. Figure 8 manifests XRD patterns of pure clay (C30B) compared to its nanocomposites. The diffraction pattern of pure clay indicated a reflection peak at $2\theta = 4.8^\circ$, from which the interlayer spacing was calculated 1.82 nm using Bragg’s law. Undoubtedly, it can be declared that nanoplatelets are well-dispersed in nanocomposites to some extent that can be announced as exfoliated; This result ties nicely with previous studies [37,43]. Thermodynamic and kinetic parameters principally determine the dispersion of nanoclays in a polymeric matrix. Hydrophobicity of nanoclay using different functional groups has been tuned and led to different clays [68]. C30B is a type of nanoclay that has been reported and proved to have an affinity to PLA and TPS [41,69]; therefore, that is a legitimate reason for such a significant dispersion in the nanocomposites. On the other hand, kinetic is a crucial parameter, especially for platelet-shaped nanoparticles, which can even confront

![Figure 8. XRD patterns of C30B and its nanocomposites with PLA and TPS.](image-url)
thermodynamics. Here, utilizing two-step processing methods seems to have an enormous impact on the dispersion of the nanoclay owing to the tremendous shear forces inducing the stacked structure of platelets to break up in PLA/TPS/1%C nanocomposite. In a sample named PLA/1%C/TPS, both solution and masterbatch techniques were used for the preparation of the specimen. In fact, the diffusion of PLAs chains into stacked platelets as well as sonication in solution state are responsible for a satisfactory dispersion in PLA/1%C and an excellent dispersion after the melt-mixing containing shear forces in PLA/1%C.

3.3.2 Influence of mixing order on thermal properties

In Figure 9 (a), DSC patterns of pure PLA (P-PLA) and PLA/1%C are represented to investigate the effect of 1% nanoclay C30B on thermal crystallization characteristics of PLA, and their detailed data are tabulated in Table 5. It is apparent from this table that cold crystallization has been intensified in the nanocomposite; this discrepancy could be attributed to two factors. Firstly, sparse aggregates of nanoparticles in PLA/1%C, which were recognized by the XRD method, can act as a nucleating agent; therefore, crystallization tendency undoubtedly enhances for such a matrix that has a cold crystallization. Secondly, due to the well-dispersion of the majority of nanoclays proved through the XRD technique, PLA chains have appropriately been exposed to nanoparticles and inevitably attached to them. This situation slows down segmental dynamics; therefore, cold crystallization would be more intensive than pure PLA because as soon as the chains find adequate energy, they enter crystal cells.

Table 5. Thermal properties of PLA and its nanocomposites with C30B extracted from DSC thermographs.

| Sample code          | $\Delta H_m$ (J/g) | $\Delta H_{cc}$ (J/g) | $X_c$ (%) | $T_m$ (°C) |
|----------------------|--------------------|-----------------------|-----------|------------|
| p-PLA                | -5.69              | +5.43                 | 6.08      | 152.30     |
| PLA/1%C              | -21.44             | 20.81                 | 22.91     | 150.24     |
| PLA/TPS4             | -15.08             | +14.25                | 16.11     | 150.88     |
| PLA/TPS4/1%C         | -22.66             | 21.57                 | 24.21     | 148.70     |
| PLA/1%C/TPS4         | -16.25             | 15.96                 | 17.36     | 150.46     |
Figure 9 (a) also indicates the influence of nanoclay in each phase of compatibilized PLA/TPS nanocomposites on thermal properties. The addition of nanoclays into the TPS phase initially leads to entanglement between clay nanoparticles and the starch chains. Thus, TPS droplets’ viscosity rises, which causes more shear force to be applied to them, droplets result after droplet breakup. Smaller TPS domains provide more nucleating agents and ease cold crystallization aptly. These tiny droplets are also able to rise enthalpy by enhancing PLA chains’ mobility. Moreover, the double melting point occurred at temperatures of 148°C and 154°C is attributed to the melting of two PLA crystal forms, α and α’ [70,71]. α’ structure corresponds to smaller and somehow disordered spherulites made up of shorter PLA chains hence tend to melt in lower temperature (148°C). Lamellar rearrangement or recrystallization during heating could be responsible for this phenomenon. This is what has happened in PLA/TPS/1%C. By including nanoclay in the PLA phase of PLA/1%C/TPS specimens, nanoplatelets’ dispersion was almost perfect, as it was mentioned in XRD patterns. This demonstrates that PLA chains are widely involved with nanoparticles. Consequently, the chains’ dynamics descend to some extent that they do not tend to contribute to crystal cells even via cold crystallization. Therefore, lamellar rearrangement has occurred merely in the shape of a slight shoulder in the melting peak. Furthermore, the observed cold crystallization peak is related to the nucleating effect of TPS droplets. That is how PLA/1%C/TPS4 and PLA/TPS4/1%C nanocomposites differentiate in thermal properties.

The thermal stability of specimens was investigated by the TGA technique in which their weight loss as a function of temperature is measured. As observed in Figure 9 (b), the pure PLA (p-PLA) showed a single-step decomposition procedure, starting around 290°C, while the other samples represent weight loss from lower temperatures. PLA/TPS4 had the least thermal stability among other ones. This is from one side due to the presence of TPS, which induced plasticizer migration and resulted in lower decomposition temperature compared to pure PLA. On the other side, incorporation of the 4 phr PLA-g-MA, which shows lower molecular weight compared to the pristine PLA because of going along maleinination with MA and L101, accelerated degradation. This is due to the smaller size of the chain and, consequently, lower energy required for breaking backbone bonds [45,56]. As expected, the inclusion of clay nanoplatelets delayed the decomposition of all nanocomposites compared to their counterparts in the absence of clay nanoparticles due to their excellent exfoliation and dispersion discussed in the XRD section and proper affinity between the modified surface of clay platelets and other components. This level of exfoliation means polymer chains are extensively exposed to nanoplatelets, and as clay mineral nanosheets have high heat capacity as well as heat conductivity, they consume and transfer heat energy. Through this mechanism, decomposition has shifted to higher temperatures. This effect compensates for the low thermal tolerance of TPS domains and PLA-g-MA somehow, which is more obvious in PLA/1%C/TPS and slowed down the degradation since nanoplatelets were located in the matrix [20,29,72–74].

3.3.3 Influence of mixing order on Oxygen Permeability of Nanocomposites

Figure 10 demonstrates the oxygen permeability of pure PLA compared to its nanocomposites. As pointed out in previous sections, the crystallization factor has been omitted by the quenching technique to investigate other ingredients’ effects. At first sight, it can be
seen that the addition of nanoparticles has beneficially reduced $O_2$ permeability. Nanocaly, with such an excellent dispersion, which is detected through XRD patterns as well as its high aspect ratio, eventually acts as nano-scale obstacles that prevent oxygen molecules from venturing their path. This phenomenon is called the tortuosity effect reported by other researchers [75,76]. By incorporating nanoclay in the PLA phase, PLA/1%C/TPS, this effect is more significant because PLA forms the majority of the nanocomposite. Thus, more proportion of the specimen is somehow protected. The role of dispersion is undeniable. All in all, most degree of dispersion has been observed in PLA/1%C/TPS based on XRD results; as expected, the least permeability is observed in PLA/1%C/TPS.

4. Conclusions

This work consists of two distinct phases in order to tune varied features of the PLA/TPS blend to be used as food packaging. In the first phase, PLA-g-MA was synthesized and included in various contents (0–6 phr) to the blend. Through investigating DMTA graphs and SEM images, 4 phr turned out to induce the maximum compatibilizing effect. Then in the next phase, the clay nanocomposite of the optimized formula (PLA/TPS4) was precisely designed with the purpose of achieving the highest level of dispersion. This target came true using two-step masterbatch dilution and has proven to be surprisingly effective via XRD analysis. Moreover, the localization of nanoplatelets was controlled by process sequence to observe how this feature influenced different properties. Finally, the sample
PLA/1%C/TPS4 demonstrated the least oxygen permeability due to (I) the perfect dispersion of nanoparticles in the matrix of the blend acting as a preventive shield, (II) the presence of TPS droplets as another barrier, and (III) smaller droplets of TPS as the result of compatibilizing effect of PLA-g-MA. All these factors take part in the tortuosity effect and make transferring of $O_2$ molecules harder.

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