



The reinforcing effect of montmorillonite on thermoplastic starch/low density polyethylene matrix nanocomposite

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ABSTRACT

In this research, composite nanofibers containing carbon nanotubes (CNT) were prepared. The need to replace the petroleum-based polymers with more environmentally friendly ones has been growing continuously over the past two decades. As a matter of fact, lower material costs, easy processing and environmental concerns are the major driving forces for using biodegradable polymers. On the contrary, low mechanical properties and high hydrophilicity are the main challenges of natural polymers. Consequently, recent research has focused on the composite preparation. One of the most effective approaches to reduce these limitations is the blending of thermoplastic starch (TPS) as a biodegradable polymer with the petroleum-based polymers and nanoclay to prepare a nanocomposite with satisfying mechanical properties. In this study, montmorillonite nanoclay was added as reinforcing agents to alloy the TPS/low density polyethylene (LDPE) by twin-extruder in presence of polyethylene grafted maleic anhydride (PE-g-MA). The addition of 5 phr (part per hundred) nanoclay increased the tensile strength and Young's modulus of the samples by 53% and 19% respectively in comparison to those that do not/without have PE-g-MA. The X-ray diffraction (XRD) was also implemented to investigate the intercalation and exfoliation phenomena. Soil burial biodegradation tests, carried out for samples and followed by CO₂ emitted measurements, revealed that biodegradation was enhanced for the hybrid materials in comparison to low density polyethylene.

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1. Introduction

In recent years, much of the chemicals used in the industry have been produced from natural materials. In the early twentieth century, with the development of the petrochemical industries, oil was converted from one product state to oil-based products. Using these materials, along with all the benefits, mounts big challenges. The challenges are their high stability in environment and long

time taken for decomposition that causes environmental pollutions [1]. Thus, In recent years, interest in using the remarkable advantages of "Green polymers" and biodegradable polymers –featuring low cost, wide abundance, renewable, and environment-friendly characteristics, to name but a few - in various applications such as packaging and medical industries which have been growing continuously [2]. Biodegradable polymers such as Starch-based polymers, which are made

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from raw materials of forest and agriculture land, are mostly used in food packaging.

Unfortunately, TPS has some disadvantages, such as poor mechanical properties and high water absorption, which are the most conspicuous ones [2]. In order to solve these problems, three main strategies have been used: the chemical modification of native starch [3], blending biodegradable polymers with petroleum-based polymers [4], and the preparation of composites with natural reinforcements [5]. As a result, starch-based composites naturally reinforced recently have been considered more for production. Due to high production, low cost, high biodegradability and being a renewable source, starch is the most used biodegradable polymer in the industry. However its low mechanical properties and high moisture absorption in comparison to oil-based polymers (e.g. polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET)) has limited the use of this material. One of the ways for overcoming these weaknesses is to mix the starch with petroleum based polymers. Accordingly various mixtures are produced from starching with PP and PE. The use of starch with these polymers has reduced their consumption and cost, and has increased their biodegradability rate [6-8]. Addition of nanoparticles to LDPE/TPS is also another way for improving the mechanical properties. Among the nanoparticles, most researchers have used clay nanoparticles such as Montmorillonite (MMT), because of its high specific surface, low cost and good properties. These particles have alternative layers of silicate, in about some nanometers thickness, with alkaline and/or alkaline earth cations between the layers. If the starch molecules would be able to penetrate into the space between the layers, nanocomposites having nanometric layers will be obtained (the best mechanical properties come from exfoliated state). The main challenge for researchers is to achieve the uniform distribution of nanometer silicate layers in starch matrix [9-11]. Schlemmer et al. [12] believed that in low proportion (below 5%) of reinforcement, exfoliation would be the dominant mechanism of distribution. But with increasing clay amount, the remained area in polymeric matrix would be limited and the clay distribution would be in intercalation mechanism. Results from mechanical properties tests of Montmorillonite (MMT) nanoparticles reinforcing nanocomposites with Na⁺ ions show that particles addition up to 30% (wt%) increases

the ultra-tensile strength and elastic modulus, and reduces the strain to fracture [13]. In these years, PE-g-MA is the most common compatibilizer and showed good efficiency in the case of PE/TPS blends. This improvement was attributed to the esterification reaction between maleic anhydride groups of PE-g-MA and hydroxyl groups of starch, and good interaction of its non-polar chain with the PE matrix. Reactive compatibilization decreases the interfacial tension and leads to finer morphology [14].

In this work the thermoplastic starch, as a biodegradable material, has been alloyed with polyethylene that has better mechanical properties. Afterwards, for improving mechanical properties, reducing permeability and being antibacterial, nanoclay was added to mixed TPS/PE with the PE-g-MA compatibilizer. As a result, the nanocomposite with a matrix of TPS/PE alloy was made.

2. Experimental Procedure

The used materials include 0075 low density polyethylene grades which was purchased from Bandar Imam Khomeini petrochemical, cornstarch (Glucose production-Iran-Qazvin), PE-g-MA was purchased from Exellor Company, Inc. Glycerol (Dr. Jalali brand-Iran-Tehran) and distilled water which was used for making thermoplastic starch. At first, Montmorillonite nanoclay was distributed in glycerol aqueous from the first batch with ultrasonic device (80kHz) for 5 minutes with the ratio of 1,3 and 5 phr. Corn starch was then added slowly to the above mixture and simultaneously the mechanical stirrer with 800-1400 rpm speed for preparing thermoplastic starch was used. The produced TPS composition was: 55% starch, 30% glycerol and 15% water plasticizers. The polymeric matrix also contains 40% thermoplastic starch and 60% LDPE. Finally, the mixture of LDPE and TPS was extruded with different amounts of nanoclay (1,3,5phr), in two screw extruder (L/D=20) in a temperature range of 180-200°C and with 12rpm rotation speed. The obtained strands were turned into granules by crushing machine and then were injected by plastic injection machine in a temperature range of 170-180°C (p=80bar). For mechanical properties analysis, the samples were tested according to ASTM D638 using stretch machine by 5 mm/min strain rate. Also for nanoclay distribution analysis in the polymeric matrix, low angle X-ray diffraction at angles below

10° was used. Biodegradation of TPS, TPS/LD and TPS/LD/PE-g-MA nanocomposites containing MMT were investigated by soil burial test and CO₂ emission from microorganism bioactivity measurement for four weeks. A pure LDPE specimen was used as a control.

3. Results and Discussion

According to table 1, by adding nanoclay to the specimens without compatibilizer, due to the presence of nanoclay in polymeric chains, Tensile strength has been reduced. Another reason for reduced strength is low polar adhesion between clay and LD/TPS matrix, which causes the polymeric chain to break.

Also in systems which have PE-g-MA, due to increased strength (Fig. 1), it is come out that MMT has good adhesion with LD/TPS matrix. In fact the MA group as a polar material has a tendency towards TPS and nanoclay, and the PE group has tendency to PE of matrix. So it causes the good compatibility between the system components. Also according to increasing modulus, it could be

deduced that distribution of nanoclay has become better.

According to impact test (Fig. 2), although by increasing compatibilizer the impact resistance has increased, but in the specimens with PE-g-MA, increasing nanoclay makes no change in impact resistance which is due to dominance of the increase in impact strength with regard to better softening properties of compatibilizer than of the nanoclay. This phenomenon can be seen clearly in specimens without compatibilizer, in which the impact resistance increases with a little change in reinforcement phase and increasing nanoclay.

According to XRD test (Fig. 3), the peak of montemorillonite was observed in $2\theta=4^\circ$ and d-spacing=22.07 Å. In 1Phr group, nanoclay without compatibilizer, the MMT's peak goes to slight angle ($2\theta=1.6^\circ$ and d-spacing=55 Å), that is indicative of intercalation, but with compatibilizer due to complete removal of peak and curve smoothing, exfoliation state and good distribution of nanoclay could be seen. It corresponds with the results of figure 2.

Table 1. Mechanical properties of samples

| Composition [phr] | Tensile Strength [MPa] | Strain at Break [%] | Young's modulus [MPa] |
|----------------------|---------------------------|------------------------|-----------------------|
| TPS/LD | 5.23 | 16.61 | 125.80 |
| TPS/LD/1 | 3.86 | 16.52 | 72.29 |
| TPS/LD/3 | 3.77 | 16.73 | 75.84 |
| TPS/LD/5 | 3.65 | 17.54 | 59.59 |
| TPS/LD/PE-g-MA | 5.24 | 22.90 | 70.68 |
| TPS/LD/PE-g-MA/1 | 4.50 | 17.64 | 71.58 |
| TPS/LD/PE-g-MA/3 | 5.72 | 23.31 | 83.64 |
| TPS/LD/PE-g-MA/5 | 8.00 | 36.17 | 150.00 |

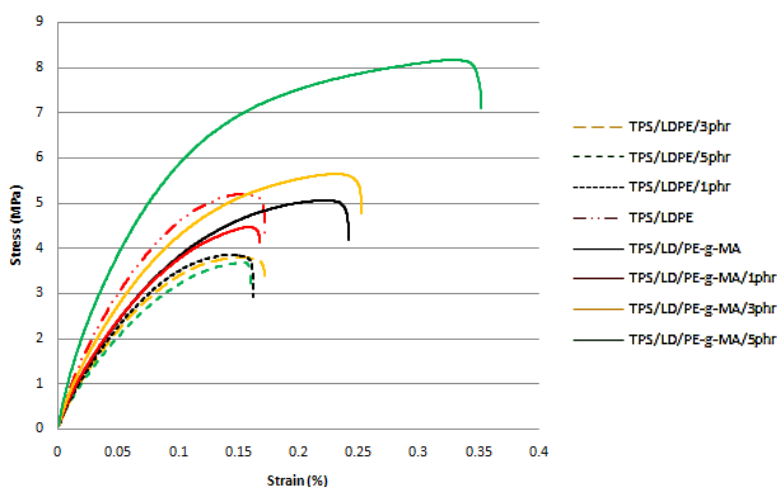


Fig. 1. The Stress-strain curves of TPS/LDPE and different mass MMT and PE-g-MA composites.

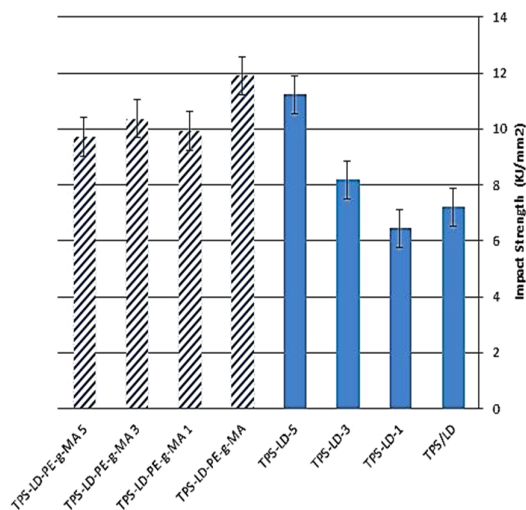


Fig 2. The Impact strength of TPS/LDPE and different mass MMT and PE-g-MA composites.

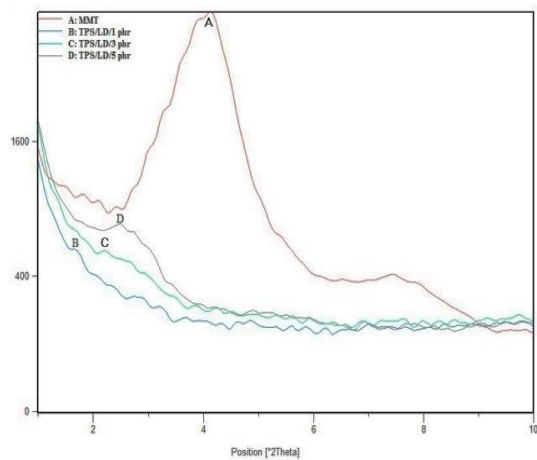


Fig 3: X-ray diffractograms in the at angles below 10° .

In the 3 and 5 Phrnanoclay specimens, the peak shifts to lower angle with $2\theta=2.2^\circ$ and 2.5° with d-spacing= 40.12 \AA and 35.31 \AA , Respectively. This indicates that by increasing the nanoclay, the system goes from exfoliation to the intercalation state. Although in these specimens with adding compatibilizer, due to XRD curve damping, better distribution of clays and diffusion of polymeric chains between the layers could be deduced, that are in accordance with mechanical tests.

Fig. 4 presents the average of CO_2 released in 4 weeks for all samples. In the end of test, TPS nanocompositecollections and control sample (LDPE) show the highest and lowest biological breathing, respectively. Compared to the control sample, the collection of TPS nanocomposites, TPS/LDPE

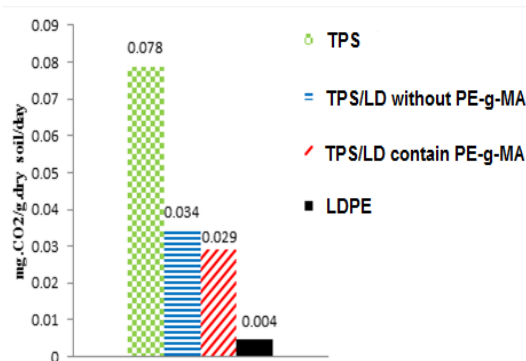


Fig. 4. CO_2 emissions by the end of the four-week average of each set of test.

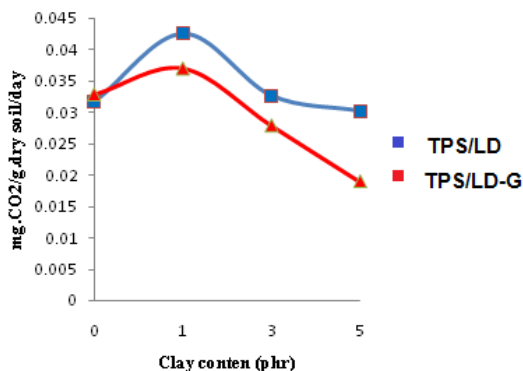


Fig. 5. Effect of clay content in CO_2 emission in presence or absence of PE-g-MA.

without PE-g-MA nanocomposites, TPS/LDPE contain PE-g-MA nanocomposites show 19.5 times, 8 times and 7.5 times increase, respectively, in CO_2 emission, biological breathing and biodegradability rate. It seems, this increase in biodegradability rate shows a significant potential in order to traditional packaging. The effect of MMT in biodegradability is illustrated in Fig. 5. Generally, the biological breathing reached the lowest value for 3 and 5 phr MMT. It can be claimed that increase of MMT reduced the rate of biodegradation. In fact, by adding MMT to system, due to the improved mechanical properties, the adhesion between the components is increased and the sample destroying by microorganism is harder.

4. Conclusion

Generally, in all specimens, mechanical properties have been increased by adding PE-g-MA compatibilizer, as the sample with compatibilizer had the increment about 67% in impact resistance, and the sample with 5 Phrnanoclay had 53% increment in tensile strength than LD/TPS matrix. Also the lower nanoclay caused more exfoliation

and by increasing the nanoclay, the distribution would be in intercalation state. Also, by using TPS in LDPE, the biodegradability rate increased which can be a significant potential for traditional packaging.

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