Synthesis of LDPE/Nano TiO_2 Nanocomposite for Packaging Applications

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Abstract:

Improving barrier properties through the use of nanocomposites is an important area of research, especially for the food packaging industry. In this work, Titanium dioxide (TiO_2)/Low density Poly Ethylene (LDPE) nanocomposites were synthesized as the oxygen barrier layers through the co-extrusion process. The Oxygen permeability of the nanocomposite with 4% of TiO_2 decreased for about 16% compared to the pristine LDPE. Furthermore, the rancidity of almonds in the packaging which is made of the former is about 78% less than the latter. Therefore, from the data obtained from the permeation, mechanical and degradation experiments, it can be concluded that these nanocomposites provide promising applications as O_2-barrier and anti-degradation agents in food packaging.

***Keywords**: Nanocomposite, TiO_2 nanoparticle, packaging, permeability.*

1. INTRODUCTION

In the past decade, polymer nanocomposites have emerged as a new class of materials and attracted considerable interest and investment in research and development worldwide. This is largely due to their new and often much improved mechanical, thermal, electrical and optical properties as compared to their macro- and micro-counterparts. In general, polymer nanocomposites are made by dispersing inorganic or organic nanoparticles into either a thermoplastic or thermoset polymer. Nanoparticles offer enormous advantages over traditional macro- or micro-particles (e.g., talc, glass, carbon fibers) due to their higher surface area and aspect ratio, improved adhesion between nanoparticle and polymer, and lower amount of loading to achieve equivalent properties [1].

Recently, considerable efforts have been made to extend the application of nanocomposites to packaging industries. Nanocomposites represent a good candidate to produce food packaging because of their good barrier and mechanical properties [2-5]. Indeed, the preservation of the desired qualities of the products, e.g. organoleptic properties in food industries, depends on the ability for controlling gas, vapor and flavours' transports through the packaging material [6].

In most researches concerning nanocomposites, the barrier properties are examined by using gas [7-10]. Such improvements in the gas barrier properties of nanocomposite materials are attributed to two separate phenomena resulting from the addition of the inorganic phase. Firstly, the inclusion of the inorganic phase results in modifications of the polymer chain flexibility and in the arrangement of the polymeric matrix itself, which ultimately lowers the penetrate mobility in the nanocomposite and changes the solubility parameters. Moreover, the impermeable inorganic phase represents a physical barrier to diffusing molecules, which are forced to a more tortuous path through the polymer. It is specifically on the latter effect that several modeling works have been carried out to relate structural and transport properties [6, 10].

Experimental studies on the morphology and mechanical properties of nanocomposites have also attracted noticeable attention in the past decade [11-19]. It has been reported that reinforcement of polymers with nanostructures results in an increase in the Young's modulus, ultimate tensile strength and apparent yield stress, as well as a decrease in elongation at break [4, 20].

The techniques and methods used to prepare nanocomposites are also very important in terms of structural organization. Melt processing has proven to be one of the more attractive and preferred methods to produce nanocomposites for commercial use which is due to some reasons: First, it is environmentally acceptable due to the absence of organic solvents. Second, it is compatible with current industrial processes, such as extrusion and injection molding. And finally, due to the possibility of modifying the nanocomposite structure by altering the melt blending conditions [4, 8, 21, 22].

However, although different approaches have been developed in the last few years for the purpose of increasing the gas barrier property of polymer films, most of these methods are devoted to the nanocomposites made by the addition of organoclays (formed from montmorillonite) to thermoplastics [1, 7-12]; while in this study, TiO_2 was utilized instead of organoclay. That is due to its better chemical & thermal stability together with innocuity comparing to montmorillonite. In these experiments, uniform polyethylene/ TiO_2 nanocomposites with improved barrier and mechanical performance were fabricated.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

In order to measure the effects of adding nanoparticles of 70-80nm size to the base material for at least four different concentrations (1% - 4% wt), a total amount of 150gr of TiO_2 Nanopowder (Rutile Grade) was used. A total of 10kg of granular low density polyethylene (LDPE) was also used with commercial grade of LF0200, melt flow index of about 2gr/10min and density of $0.92 gr/cm^3$, which was obtained from Bandar-Imam petrochemical complex.

An amount of 7.5kg of this material was used to make five samples each of which containing concentration of TiO_2 and the remaining 2.5kg was used for starting and cleaning up processes before each run. Polyethylene pellets were dried in a vacuum oven at 80°C for at least 12hr before melt blending. That is due to avoid the presence of water during melting.

2.2. Synthesizing procedure

The TiO_2/LDPE samples were prepared by melt compounding of the nanoparticles and the polymer using a DO-CORDER C3 twin screw extruder (L/D =36). The screw speed (which was increased before increasing feed flow rate and entering the feed into the hopper) was set to 60rpm proportionate to feed flow rate and the thermal zones of 150, 160, 170 and 180°C respectively from the feed inlet. Finally, the samples were pelletized by granulator. As the feed flow rate increases - when molten polymer

Table 1: *Nanocomposite Samples' Specification*

Sample	1	2	3	4
Master Batch (gr)	150	300	450	600
Pure LDPE for Dilution (gr)	1350	1200	1050	900
TiO_2 in Final Sample (%)	1%	2%	3%	4%

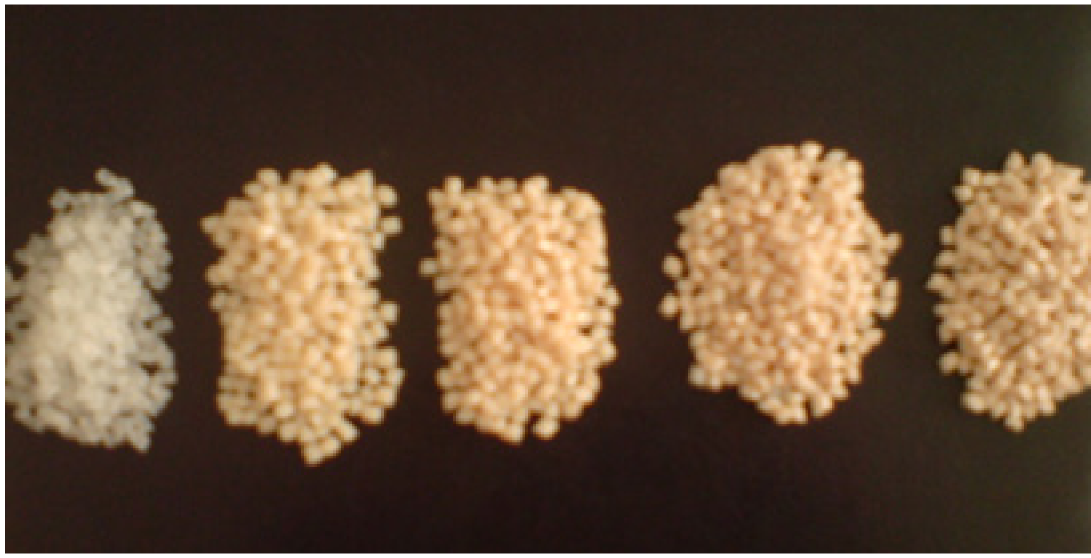

Figure 1: *The granulated nanocomposite (From left to right: Pristine PE, nanocomposites with 1, 2, 3 & 4% of TiO_2 nanoparticles)*

reaches the granulator unit - speed of granulator motor varies to protect granule size in permitted region. Moreover, for the purpose of comparison, pure LDPE was also prepared using the above procedure without adding the TiO_2.

In order to gain a better homogeneity and decrease nanoparticles' loss, a master batch (with composition of 1.5 kg LDPE and 150 gr TiO_2) was first synthesized as a prototype and then all intended samples were prepared by diluting it with pure LDPE. Table 1 and Figure 1; show the specifications and the image of the four samples, respectively, which clearly shows the variation of the samples color by increasing the TiO_2 nanofiller. At the final stage, nanocomposite films with a thickness of about 60±5μm were obtained by blowing into the molten nanocomposite with Clextral E20T equipment with blow up ratio of 2.

Tensile testing of the film samples was carried out in the machine direction (MD) according to ASTM Standard D882-02 on an Instron 1130 equipped with a 200lb load cell. The gauge length of the test samples was 50.8mm, and the width of the samples was 13.8mm. The crosshead speed of the test was maintained at 50mm/min during the duration of each test. Ten samples of each film were tested & averages were reported.

3. RESULT AND DISCUSSION

The images obtained by scanning electron microscopy (SEM), clarify the morphological characterization of nanocomposites. One of which is shown in Figure 2 when 1% TiO_2 is applied to the base fluid. It is quite clear that the nanoparticles are well dispersed within the polymer matrix.

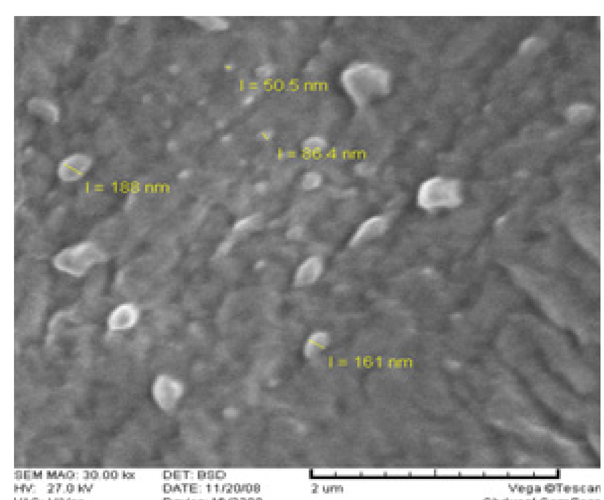

Figure 2: *SEM image of LDPE/TiO_2 nanocomposite with 1% TiO_2 nanopowder*

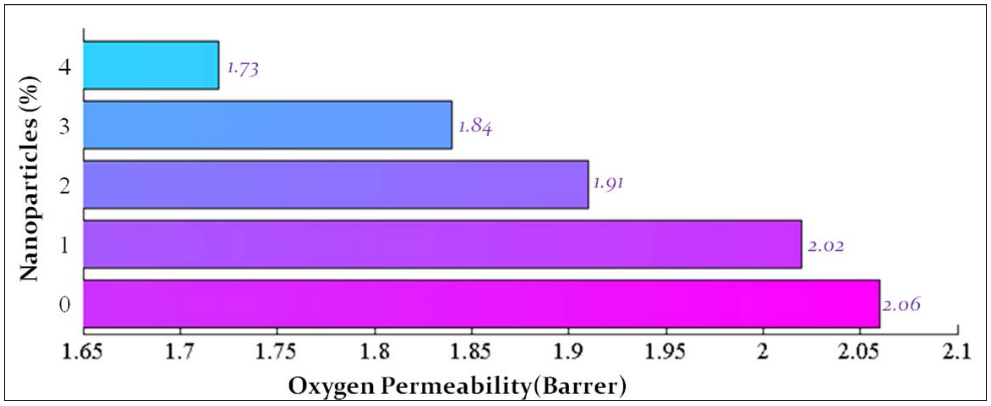

Figure 3: *Variations of the O_2 permeability (barrer) as a function of TiO_2 nanoparticle (percentage)*

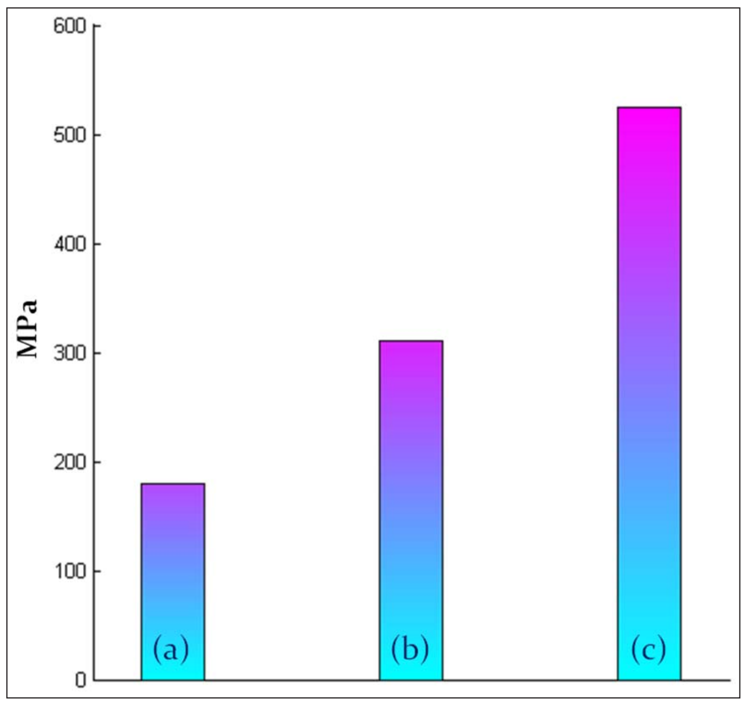

Figure 4: *Variation of Young's modulus (Pa) for (a) LDPE (b) Nanocomposite containing 2% nanoparticles (c) Nanocomposite containing 4% nanoparticles*

Gas permeability experiments were carried out by using the constant-pressure technique according to ASTM 1434 in a permeability apparatus at 298 K. Figure 3 represents that the O_2 permeability decrease from 2.05 barrer for pristine LDPE to below 1.75 barrer for the nanocomposite with 4% nanoparticles. Results show that Oxygen permeability of nanocomposites decrease significantly as the nanoparticle content increase in polymer matrix.

Figure 4 shows the Young's modulus determined from tensile tests for pure LDPE and the nanocomposite containing 2% nano TiO_2. It can be seen that the Young's Modulus increase by the nanoparticle addition.

In order to investigate the improvement of retention time in nanocomposite packages, 95 grams of pistachio and almond were packaged in pure LDPF and nanocomposite with 4%wt TiO_2. Then, to increase the degradation rate, the samples were put in oven at 45°C for a month. Unsaturated nut oils oxidize quickly on exposure to heat, light and air, creating rancidity that causes unfavorable smell and taste. In this process the long-chain fatty acids are degraded and short-chain compounds are formed.

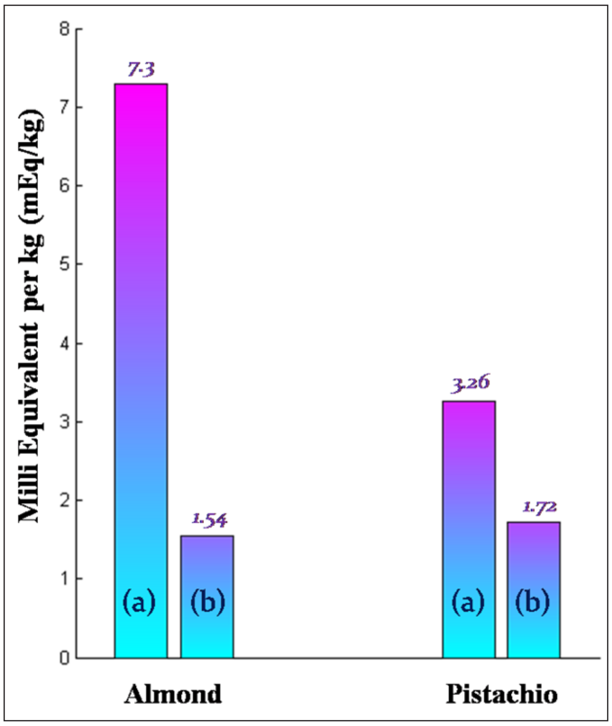

***Figure 5:** Rancidity of pistachio & almond in (a) pure LDPE and (b) nanocomposite packages at 45°C after 1 month*

It is seen in Figure 5 that the rancidity in nanocomposite package decreases dramatically for both almond and pistachio samples.

4. CONCLUSION

In this work, high oxygen barrier films were successfully produced by utilizing TiO_2/LDPE nanocomposite. Analysis of these film's oxygen barrier properties revealed that oxygen permeation of the LDPE films decrease significantly as the nanoparticle content increase in polymer matrix. Furthermore, the increase of the nanoparticle in the polymer film significantly affected mechanical properties such as Young Modulus. The ultimate modulus of the films increased when the neat LDPE was substituted with the TiO_2/LDPE nanocomposite. Similar improvements were observed when the rancidity of two kinds of nuts was tested in the nanocomposite packages. It was found that the degradation rate in nanocomposite films is much slower due to the reduction in O_2 permeation.

The reported results indicate that these nanocomposite films are of high potential to use in food packaging industry because of their extended shelf-life specifications.

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