Preparation of Functional LLDPE/LDPE/TiO₂ Membranes

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ABSTRACT
Nano-scaled TiO₂ is being used in the polymer industry owing to its promising properties as a light catalyst and in UV light shielding. Functional LLDPE/LDPE/TiO₂ membranes were manufactured successfully in this study. To solve the poor dispersion of TiO₂ in polyethylene, TiO₂ was introduced into blow-forming LLDPE/LDPE as a master batch. The nano-TiO₂ had an induced nucleation effect on the crystallization of polyethylene; with the introduction of TiO₂, the size of the crystal spheres decreased, as their numbers increased. TiO₂ was dispersed randomly throughout the membrane, with an average size of about 100 nanometers. This excellent dispersion gave rise to the UV absorption by the membranes. Moreover, the visible light transmittance of the membrane changed slightly with the introduction of TiO₂. In conclusion, the resulting membranes had the desired properties plus a UV absorption function. Such membranes will have many applications in agriculture and food packing owing to the anti-bacterial effect induced by the UV absorption.

Key Words: TiO₂, membranes, crystallization, nucleation, UV adsorption

1. INTRODUCTION
Nano-scaled TiO₂ is being used in the polymer industry owing to its promising properties as a light catalyst and in UV light shielding[1-3]. The anti-bacterium function of TiO₂ comes from its photo-induced reaction. Due to the high oxidation of radicals produced in the reaction, the organic compounds, such as protein and ester, will be attacked, and the remainder will be then degraded. The function of anti-bacterium will be fairly beneficial to the membranes used in agricultural application and food packing.

Linear Low Density Polyethylene (LLDPE) and Low Density Polyethylene (LDPE) are chosen as the matrix of the membranes in our research. Since they are both crystalloid polymers, the transparency of the produced membranes will be great influenced by the degree of crystallinity of polymers. The exhibition of the special functions of TiO₂ in the final products is also determined by its dispersion conditions in the polymer matrix. In this paper, it was presented the preparation of LLDPE/LDPE/TiO₂ membranes and the comprehensive studies focused on the crystallinity of polyethylene and the dispersion of TiO₂.

2. EXPERIMENTS
LDPE (type 150L, Dow Chemical Co LTD, USA) and LLDPE (type 7042, Yangzi Petro-Chem Co LTD, China) were used as the row polymer of membrane. TiO₂ (Qingdao Haier-QUEST Nano Technology Company, China) possessed an average primary particle size of 80nm and 80% anatase crystal structure. A low molecular weighted polyethylene named as LDPE1 (type 800, Modern Chemical, Korea) was used as the polymer matrix of the master batch containing TiO₂.

TiO₂ was dried for 8 hr at 100°C, and then subjected to the high speed mixing with LDPE1. The mixture was then extruded in two-screw extruder (ZKS-25 type, Krupp Werner & Pfleiderer Gmbh, Germany) to yield LDPE1/TiO₂ granules. The so-prepared master batch with 20% TiO₂ in
weight was blow-formed with LLDPE/LDPE at a single-screw blow-forming system (Laiwu Plastics Machinery Company, China) where the weight ratio of LLDPE to LDPE was 3:1. The dosage of TiO$_2$ in the final membrane was adjusted by the ratio of master batch to polyethylene.

The melt point and enthalpy of the LLDPE/LDPE membrane were measured on NETZSCH Thermal Analysis DSC Cell with temperature increasing rate of 10K/min from room temperature to 180°C.

The dispersion of TiO$_2$ in polyethylene was observed in Electron microscope (JEM-2000EX type, Japan Electron Co.). The light absorption of membranes was measured in Ultraviolet radiation-Visible light absorption spectrum instrument (Cary 500, Varian Instrument, U.S.A). The transparency of LLDPE/LDPE membranes was measured in photo-behavior tester (HAZE-GARD puls, BYK Gurder, Germany).

3. RESULTS AND DISCUSSIONS

3.1 Dispersion of TiO$_2$ and its Nucleation Effect on PE Crystallization

The dispersion of TiO$_2$ in the final LLDPE/LDPE/TiO$_2$ membrane was directly observed under an optical microscopy. Rarely could the dark regions be found in the visual field. The microscopic observation was carried out in SEM. Figure 1 indicated a random dispersion of nano-scaled TiO$_2$ in the polymer matrix, where the average diameter of the dispersed phase was less than 100 nanometers. The complementary application of optical microscopy and SEM confirmed the even and uniform dispersion of TiO$_2$ in LLDPE/LDPE when introduced in the form of master batch of low molecular weighted LDPE.

Figure 1. SEM photo of an LLDPE/LDPE membrane with 0.5 wt% TiO$_2$

Figure 2. Polarized images of membranes (a) 0, (b) 0.25, and (c) 0.5 wt% TiO$_2$ (scale bar 100 µm)
LLDPE and LDPE were both crystalloid polymers, and their different molecular structures resulted in the different crystallization behaviors. In general, LLDPE exhibited a greater capacity in crystallization due to its linear structure. Observed in the polarized microscopy, the crystalline of LLDPE was about 380 micrometers in diameter, which was much larger than the 110 micrometers of LDPE. The polarized image of LLDPE/LDPE was shown in (a) of Figure 2, the sizes of the crystalline differed much from each other, most of which ranged from 200 micrometers to 300 micrometers. However the appearance of a minority of crystalline with diameter about 100 micrometers indicated the separated crystallization of LLDPE and LDPE, which was further confirmed by two separated crystallization peaks in DSC curves shown in Figure 3.

### 3.2 UV absorption behaviors and transparency of the membranes

The good dispersion of TiO$_2$ in the polyethylene matrix provided the probability of an efficient UV absorption of the LLDPE/LDPE membrane. The experimental result shown in Figure 4 indicated the special UV absorption of the membrane after the introduction of 0.5% TiO$_2$ in weight. The curve (1) of pure LLDPE/LDPE membrane leveled off almost in the whole range of wavelength, while curve(2) of LLDPE/LDPE with 0.5% TiO$_2$ in weight exhibited an remarkable absorption in the UV region with wavelength ranging from 200 to 400 nanometers. This phenomenon indicated an anti-bacterium function induced by the consequent photochemical reaction.

![Figure 3. DSC curves of primary LLDPE/LDPE membranes, with [1.1] for LLDPE/LDPE membrane; [2.1] for membrane with 0.5wt% TiO$_2$.](image)

![Figure 4. UV absorption spectrum of LLDPE/LDPE membrane s showing the adsorption from 200 to 400 nm; line 1-pure membrane and line 2-membrane with 0.5 wt% TiO$_2$.](image)

The introduction of TiO$_2$ into LLDPE/LDPE system changed much the size of crystalline. As shown in (b) and (c) of Figure 2, the diameters of LLDPE/LDPE varied much with each other, however most of crystalline were less than 200um after the introduction of 0.25% TiO$_2$ in weight. When content of TiO$_2$ was 0.5% in weight, the polarized microscopic image was similar but with an arising of the number of the crystalline in the visual field. The induced nucleation effect of TiO$_2$ could be confirmed by the polarized microscopic images.

Being used as packaging material or agricultural membrane, the transparency was the most important property of LLDPE/LDPE, which, however, might be lessened by the induced nucleation of TiO$_2$. As shown in Figure 5, the transparency of the membrane decreased with the dosage of TiO$_2$, however the decline was so slight that could be ignored. This result was a bit surprising, especially accounting for the induced nucleation effect of TiO$_2$. The DSC determination revealed that the degree of crystallinity changed little with the introduction of TiO$_2$. As shown in Figure 3, the
membranes processed two melting peaks at about 121°C for LLDPE and 108°C for LDPE respectively, which proved the crystallization of LLDPE and LDPE occurred independently, while the introduction of TiO₂ led the peak of LDPE more distinguishable. Killer and Hill put forward the concept of liquid-liquid phase separation based on the similar phenomenon observed in HDPE/LDPE system [4], and it was believed that the separation should be regards as a common separation in metastable phase[5], which could be influenced by the molecular weight, the branched chains of the polymers. In our study, the phase separation emerged in the rheological behaviors of LLDPE/LDPE as a big deviation from the pseudo-plastic flow, which would be reported later. Here, the combination of DSC with the polarized microscopic observation revealed the independency in the crystallization of LLDPE/LDPE system.

![Graph showing Transparency of LLDPE/LDPE membranes](image)

Though the melt point of polyethylene was little changed, the relative height of these two peaks differed with the introduction of TiO₂, which indicated the influence of TiO₂ on the crystallization of polyethylene. The total areas under the curves, however, were almost the same. So, no loss in transparency of the membrane could be attributed to the crystallinity of polyethylene. The slight decline in transparency could be resulted from the difference between the refraction indexes of polyethylene and TiO₂. After all, the measurement confirmed that the transparency of LLDPE/LDPE membranes could satisfy the request in common applications after the introduction of TiO₂.

In summary, TiO₂ was successfully introduced into LLDPE/LDPE system in the form of master batch, and the membrane manufactured exhibited a special UV absorption while maintaining its transparency. The result indicated a new application of nano-scaled TiO₂ in functional membrane material.

4. CONCLUSIONS

In the present paper, LLDPE/LDPE membrane with special UV absorption was successfully prepared by the introduction of TiO₂. Several points could be concluded as below through the discussion and analysis:

1. The crystallization behavior of polyethylene was great influenced by the introduction of TiO₂ in nano-scale, which could provide a remarkable induced nucleation. As the result, the size of the crystalline of polyethylene decreased while the number of the crystalline increased. However the degree of crystallinity remained almost unchanged, therefore the introduction of TiO₂ changed the transparency of LLDPE/LDPE membranes only a bit.

2. TiO₂ was well dispersed in LLDPE/LDPE membrane with the average diameter less than 100 micrometers after introduced in the form of master batch, which consequently resulted in the remarkable UV adsorption of the membrane.

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