

Preparation and Characterization of Linear Low-Density Polyethylene/Low-Density Polyethylene/TiO₂ Membranes

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ABSTRACT: Because of their special functions, the application of nanoscale powders has recently attracted both industrial and theoretical interest. In this study, nanoscale TiO₂, which exhibited a special UV absorption and consequent antibacterial function, was added to a low-density polyethylene/linear low-density polyethylene hybrid by melt compounding to yield functional composite membranes. TiO₂ exhibited an apparent induced nucleation effect on the crystallization of polyethylene, and the size of the crystallites decreased while the number increased with the

introduction of TiO₂; however, the crystallinity of polyethylene changed little. Also, TiO₂ exhibited an ideal dispersion in the membrane with an average size less than 100 nm, and this excellent dispersion provided the membranes extra UV absorption; moreover, the transparency of the membranes was maintained to satisfy common requirements. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 216–221, 2005

Key words: crystallization; membranes; nucleation; polyethylene (PE)

INTRODUCTION

Nanoscale TiO₂ is now widely used in industry because of its promising properties in light catalysts and UV-light shielding. In the polymer industry, the antibacterial and self-sterilization functions of nano-TiO₂ have attracted special attention.^{1–3} The antibacterial function comes from the photoinduced reaction of TiO₂. When nano-TiO₂ is exposed to light radiation, pairs of electron cavities will be induced on the surface of TiO₂, and consequently, the oxygen and water absorbed on the surface will be radicalized.^{3,4} Because of the high oxidation of radicals containing oxygen, organic compounds, such as protein and ester, will be attacked, the proteins will lose their activity, and the remainder will then be degraded. Nano-TiO₂ has been industrially introduced to domestic electrical appliances,⁵ and *antibacterial plastic* is now becoming a fashionable term. The antibacterial function is also fairly beneficial to membranes used in agricultural applications and food packing. Moreover, the introduction of TiO₂ provides agricultural membranes a hydrophilic surface after UV radiation. Such a surface prevents the gathering of atmospheric dew. Until now, the appli-

cations of nano-TiO₂ in polymer membranes, however, have not been reported.

Linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) are the most common polymers used in agricultural membranes, and they were chosen for our research. They are both crystalline polymers, and so the transparency of produced membranes will be greatly influenced by the polymers' degree of crystallinity. Moreover, the difference between the refraction indices of TiO₂ and the polymer will undoubtedly result in a loss of transparency. Thus, the transparency of the final membranes is the first problem encountered in applications of TiO₂.

On the other hand, the exhibition of the special functions of TiO₂ in the final products is determined by the dispersion conditions in the polymer matrix, so the evolution of agglomerates of nano-TiO₂ in the melt flow becomes another important part of our research; both the processing properties and the formation of a nanodispersed structure during the melt-mixing process are involved. After all, the application of nano-TiO₂ is both considerably important to industry and theoretically interesting. In this article, we present the preparation of LLDPE/LDPE/TiO₂ membranes and comprehensive studies on the structure and properties of the membranes.

EXPERIMENTAL

LDPE (type 150L, Dow Chemical Co., Ltd., Midland, MI) and LLDPE (type 7042, Yangzi Petro-Chem Co.,

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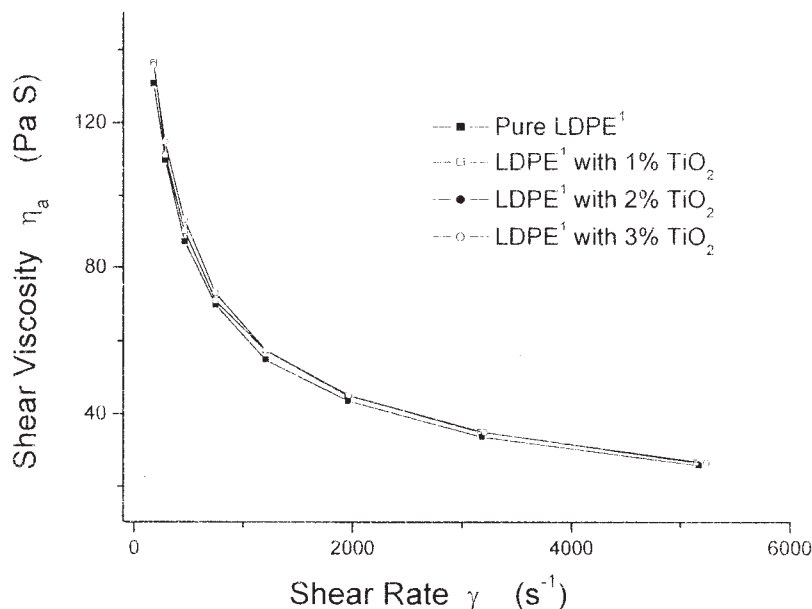


Figure 1 Flow curves of the LDPE¹/TiO₂ composites.

Ltd., Nanjing, China) were used as the row polymers of the membranes. TiO₂ (Qingdao Haier-QUST Nano Technology Co., Qingdao China) possessed an average primary particle size of 80 nm and an 80% anatase crystal structure. Another kind of polyethylene, named LDPE¹ (type 800, Modern Chemical, Seoul, Korea), was used as the polymer matrix of the master batch containing TiO₂.

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

The rheological behaviors of the materials were measured with a Rosand precision rheometer (Bohilin Instrument, Malvern, UK) in the double-bore experiment mode. The length/diameter ratio of the capillary in one bore was 16/1, and with the orifice die in the other bore, there was a zero-length capillary. The experiments were carried out at 170°C for LDPE¹/TiO₂ and at 180°C for LLDPE/LDPE. The experimental results were processed by software from Bohilin Instrument, and all the rheological data were Bagley and Rabinowitch calibrated.

The melting points and enthalpies of the LLDPE/LDPE membranes were measured with a Netzsch thermal analysis differential scanning calorimetry (DSC) cell (NETZSCH Geraetebau GmbH, Selb, Ger-

many); the heating rate was 10 K/min from room temperature to 180°C.

The dispersion of TiO₂ in polyethylene was observed with an electron microscope (JEM-2000EX type, Japan Electron Co., Tokyo, Japan). The light absorption of the membranes was measured with a UV-radiation/visible-light absorption spectrum instrument (Cary 500, Varian Instrument, Palo Alto, CA). As one of the most important properties, the transparency of the LLDPE/LDPE membranes was measured with a photobehavior tester (Haze-Gard puls, BYK Gurder, Geretsried, Germany).

RESULTS AND DISCUSSION

Rheological analysis and dispersion of TiO₂

Because of the huge difference between the polarities of polyethylene and TiO₂, the direct introduction of TiO₂ to the blow formation of LLDPE/LDPE could not yield a satisfying dispersion of TiO₂ in the membrane. Therefore, in our research, TiO₂ was introduced in the form of a master batch in which TiO₂ was predispersed in a low-molecular-weight LDPE (termed LDPE¹). Figure 1 shows the flow curves of LDPE¹/TiO₂ composites. The viscosities of the composites were little influenced by TiO₂, the concentration of which was less than 3 wt %. The non-Newtonian index curves of the composites had an intersection, as shown in Figure 2(a). The corresponding shear rate of the intersection was about 750 S⁻¹, before and after which TiO₂ exhibited different influences on the non-Newtonian indices. A similar phenomenon was previously found in an high impact polystyrene (HIPS)/TiO₂ sys-

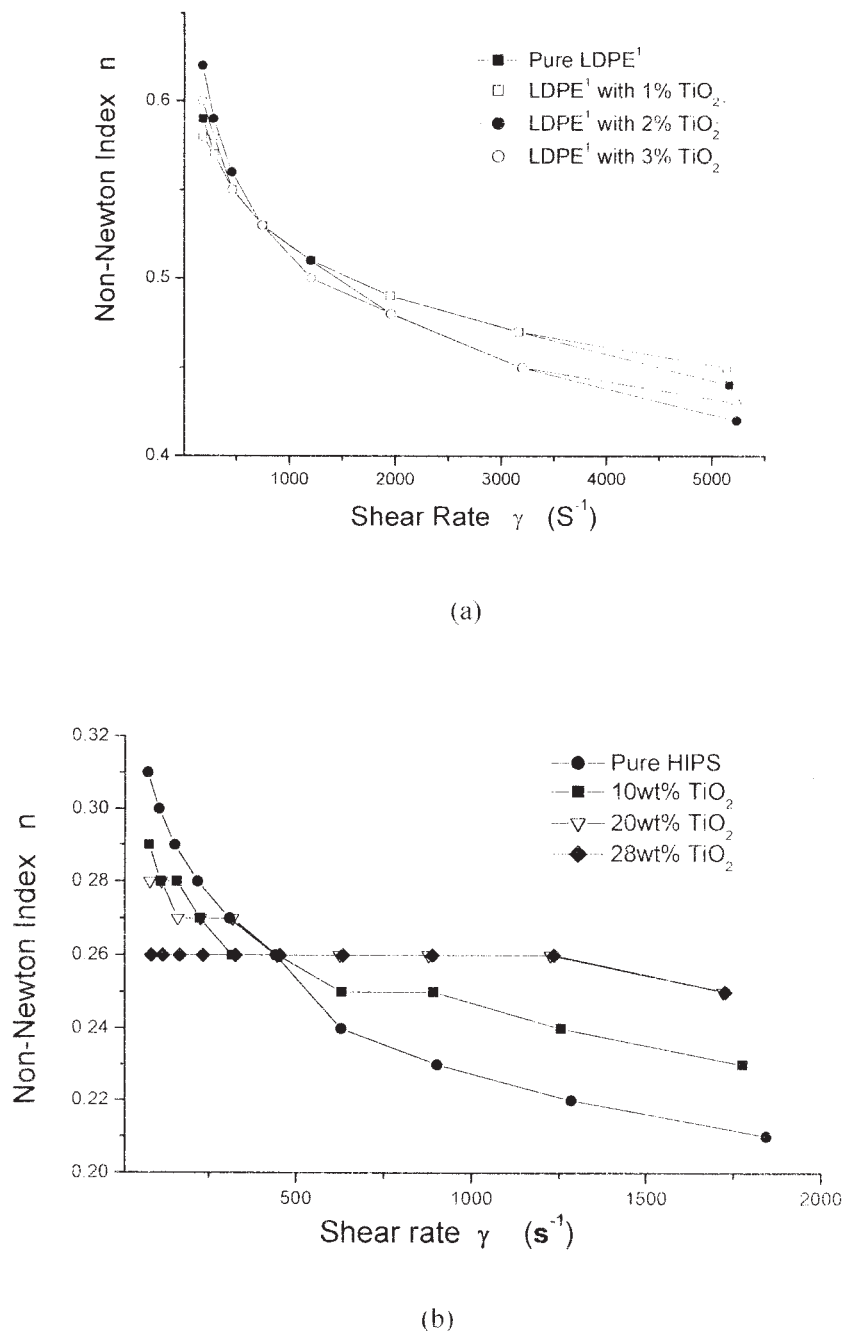


Figure 2 Non-Newtonian indices of the filled composites: (a) LDPE¹/TiO₂ and (b) HIPS/TiO₂.

tem, in which the intersection was regarded as an indication of the critical point of the segmentation of TiO₂ agglomerates. The relevant rheological analysis of the intersection is detailed in the literature.⁶ However, in HIPS-based composites, the intersection appeared under a lower shear rate at about 400 S^{-1} , as shown in Figure 2(b). The numerical difference between the two intersections could be attributed, at first glance, to the various polarity conditions of the LDPE/TiO₂ and HIPS/TiO₂ systems. The polarity difference in LDPE/TiO₂ was more than that in HIPS/

TiO₂, so its intersection, that is, the critical shear rate, was a bit larger.

However, the critical point at 750 S^{-1} was not a high shear rate in the blow-forming technique; thus, it was reasonable to expect a fine dispersion of TiO₂ if it was introduced as a master batch of LDPE¹/TiO₂ to the common membrane recipe. The dispersion of TiO₂ in the final LLDPE/LDPE/TiO₂ membrane was directly observed under an optical microscope. Rarely could the dark regions be found in the visual field. The microscopy observation was carried out with scanning

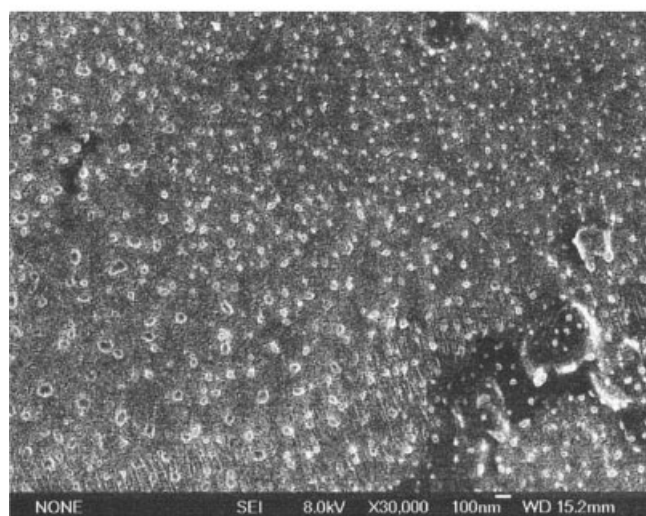
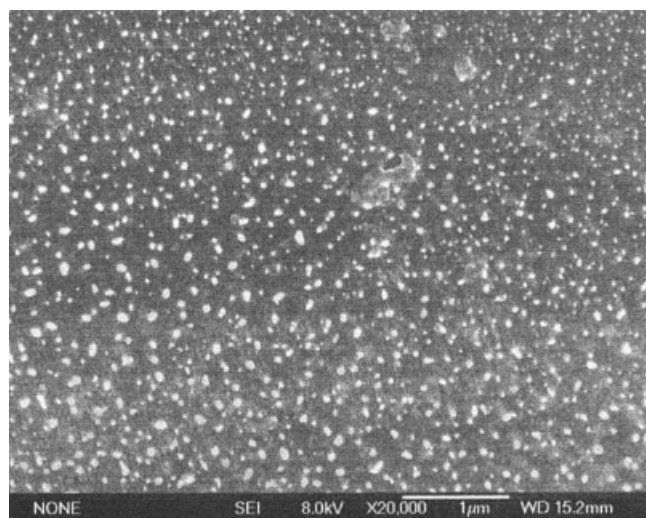


Figure 3 SEM photographs of an LLDPE/LDPE membrane with 0.5 wt % TiO₂.

electron microscopy (SEM). Figure 3 shows a fine dispersion of nanoscale TiO₂ in the polymer matrix; the average diameter of the dispersed phase was less than 100 μm. The complementary application of optical microscopy and SEM confirmed the even and uniform dispersion of TiO₂ in LLDPE/LDPE when it was introduced in the form of a master batch of low-molecular-weight LDPE¹.

Nucleation effect of TiO₂

LLDPE and LDPE are both crystalloid polymers, and their different molecular structures result in different crystallization behaviors. In general, LLDPE exhibits a greater capacity for crystallization because of its linear structure, whereas LDPE possesses more graft chains, and so its crystallizability is less than that of LLDPE. In Figure 4, polarized microscopy images of crystal-

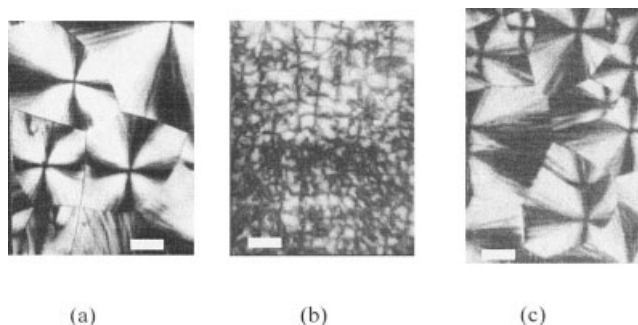


Figure 4 Polarized microscopy photographs (scale bar = 100 μm): (a) LLDPE, (b) LDPE, and (c) LLDPE/LDPE.

lites are compared. A remarkable dark cross appears in Figure 4(a), and the crystallites of LLDPE were about 380 μm in diameter. They were much larger than those of LDPE (110 μm) shown in Figure 4(b). A polarized image of LLDPE/LDPE is shown in Figure 4(c), and it appears somewhat similar to that of LLDPE. As LLDPE was the majority in the LLDPE/LDPE blend, the analogy was reasonable. The sizes of the crystallites of LLDPE/LDPE differed much from one another; most ranged from 200 to 300 μm. However, the appearance of a minority of crystallites with a diameter of about 100 μm indicated the separated crystallization of LLDPE and LDPE. As a result, large and small crystallites were formed together.

The introduction of TiO₂ into the LLDPE/LDPE system changed the size of the crystallites much. As shown in Figure 5, the LLDPE/LDPE diameters varied much with one another, but most crystallites were less than 200 μm after the addition of 0.25 wt % TiO₂. When the concentration of TiO₂ was 0.5 wt %, the polarized microscopy image was similar, but with an increase in the number of crystallites in the visual field. The induced nucleation effect of TiO₂ was confirmed by the previously shown polarized microscopy images.

UV absorption behavior and transparency of the membranes

The good dispersion of TiO₂ in the polyethylene matrix provided the probability of efficient UV absorp-

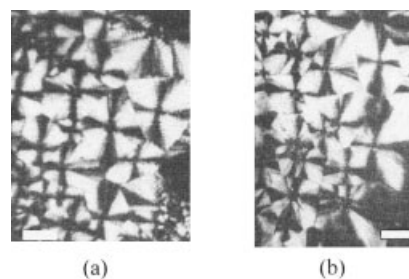


Figure 5 Polarized images of LLDPE/LDPE (scale bar = 100 μm) with TiO₂ concentrations of (a) 0.25 and (b) 0.5 wt %.

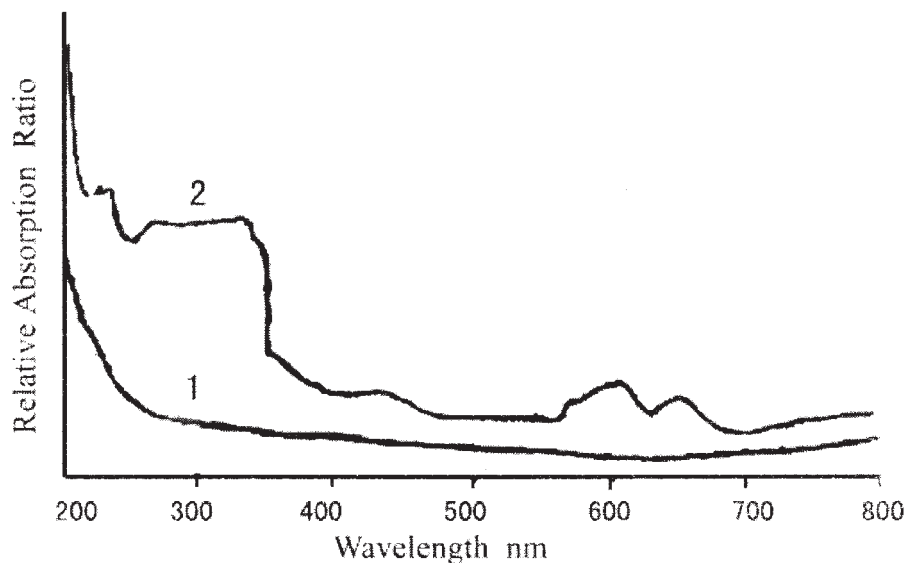


Figure 6 UV absorption spectra of LLDPE/LDPE membranes: (1) pure LLDPE/LDPE and (2) LLDPE/LDPE with 0.5 wt % TiO_2 .

tion of the LLDPE/LDPE membrane. The experimental results shown in Figure 6 indicate the special UV absorption of the membrane after the introduction of 0.5 wt % TiO_2 . Curve 1 of the pure LLDPE/LDPE membrane leveled off almost in the whole wavelength range, whereas curve 2 of LLDPE/LDPE with 0.5 wt % TiO_2 exhibited a remarkable absorption in the UV region with wavelengths ranging from 200 to 400 nm. This phenomenon indicated an antibacterial function induced by the consequent photochemical reaction. The details of the antibacterial functions of the membranes will be revealed by biochemical experiments in the future.

For use as packaging materials or agricultural membranes, transparency is the most important property of LLDPE/LDPE; however, it might be lessened by the induced nucleation of TiO_2 . As shown in Figure 7, the transparency of the membrane decreased with the dosage of TiO_2 , but the decline was so slight that it could be ignored. This result was a bit surprising, especially because of 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 8, the membranes processed two melting peaks at about 121°C for LLDPE and at 108°C for LDPE, and this proved that the crystallization of LLDPE and LDPE occurred independently, whereas the introduction of TiO_2 made the peak of LDPE more distinguishable. Hill et al.⁷ put forward the concept of liquid-liquid phase separation based on a similar phenomenon observed in a high-density polyethylene/LDPE system, and it is believed that the separation should be regarded as a common separation in a metastable phase,⁸ which can be influenced by the molecular weight and 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 pseudoplastic flow, which will be reported later. Here, the combination of DSC with polarized microscopy revealed the independence of the crystallization of the LLDPE/LDPE system.

Although the melting point of polyethylene was little changed, the relative height of these two peaks differed with the introduction of TiO_2 , and this indicated the influence of TiO_2 on the crystallization of polyethylene. The total areas under the curves, however, were almost the same. Lu et al.⁹ reported similar crystallization behaviors of LLDPE/LDPE blends, and both the induced nucleation effect and the alkaline of TiO_2 were used to interpret the crystallization behavior of the blends. However, the phase separation in the

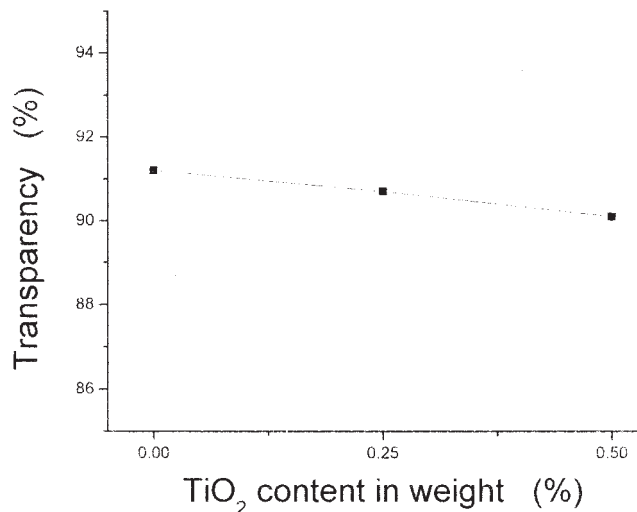


Figure 7 Transparency of LLDPE/LDPE membranes.

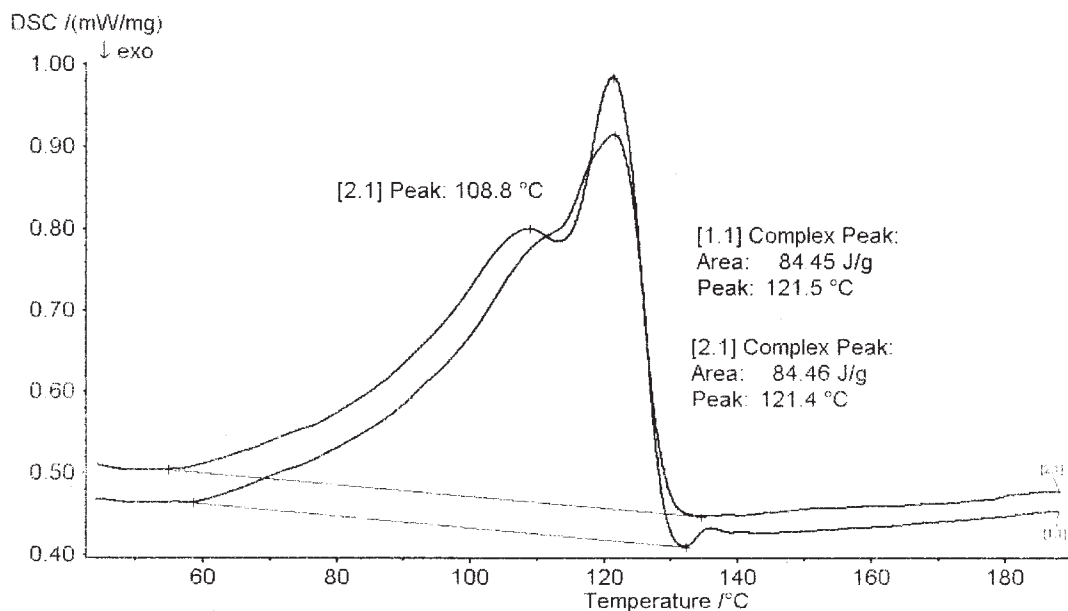


Figure 8 DSC curves of primary LLDPE/LDPE membranes: (1.1) LLDPE/LDPE membrane and (2.1) LLDPE/LDPE membrane with 0.5 wt % TiO₂.

flow was not explained in that research. The mechanism of crystallization was rather complicated and could only be revealed by a combination of rheology and crystallization investigations. Nevertheless, the experimental results showed clearly that no loss in transparency of the membrane could be attributed to the crystallinity of polyethylene. The slight decline in the transparency could have resulted from the difference between the refraction indices of polyethylene and TiO₂. After all, the measurements revealed that the transparency of LLDPE/LDPE could satisfy the requirements of common applications after the introduction of TiO₂.

In summary, TiO₂ was successfully introduced into the LLDPE/LDPE system in the form of a master batch, and the manufactured membrane exhibited special UV absorption while its transparency was maintained. The results indicated a new application of nanoscale TiO₂ in functional membrane materials.

CONCLUSIONS

An LLDPE/LDPE membrane with special UV absorption was successfully prepared by the introduction of TiO₂. Several points have been concluded from the discussion and analysis:

1. The crystallization behavior of polyethylene was greatly influenced by the introduction of TiO₂ on the nanoscale, which could provide a remarkable induced nucleation. As a result, the size of the crystallites of polyethylene decreased, whereas the number of crystallites increased. However, the degree of crystallinity remained almost unchanged, and so the introduction of TiO₂ changed the transparency of LLDPE/LDPE membranes only a bit.
2. TiO₂ was well dispersed in the LLDPE/LDPE membrane with an average diameter less than 100 μm after being introduced in the form of a master batch, and this consequently resulted in the remarkable UV adsorption of the membrane.

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