Materials

Effect of Cooling Rate on Morphology and Oxygen Permeability of Polypropylene

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Abstract: The influence of different cooling rates on the morphology and oxygen permeability of polypropylene containing ferrocene has been investigated. The spherulitic crystalline size and structure, which can affect the oxygen permeability, are dependent upon the heating temperature, annealing time and cooling rate. The modulus of the composite was measured by dynamic mechanical analysis.

Key Words: polypropylene; oxygen permeability; cooling rate

For food packaging or barrier films, low oxygen permeability is very important for keeping the food fresh. Polypropylene is widely used in food or beverage containers. Polypropylene is typical of most crystalline thermoplastics, consisting of a polycrystalline mosaic of close packed spherulitic structures bounded by multiple facets and amorphous region between the grain boundaries. The size and perfection of each spheruite is influenced by its thermal history and composition. Nucleating agents are commonly employed to regulate the number and size of the spherulites, in which the cooling rate is important since annealing or quenching of the molten polymer can influence the size and lamellar perfection of the radial crystallites which generate spherulites during the cooling stage. The amorphous regions have lower densities and greater free volume, defects and impurities [1–7] so that oxygen tends to diffuse more rapidly through the amorphous regions. Fick's law can be used to determine the gas permeability of the composite [8].

In present work, the influence of polypropylene morphology on the oxygen permeability was measured after various thermal treatments.

1 Experimental

Polypropylene (Himont Profax 6401 homopolymer, Melt Flow 6.5 g/min) was melted in a Brabender Plasticorder equipped with roller blades at different temperatures (170, 180, 190, 200 ℃). The speed of the roller blades was adjusted to 80 r/min in the electrically heated chamber and after 12 min each sample was removed from the mixer. Approximately 5 g of the polypropylene mixture was pressed into a thin film be-

tween Mylar films at 185 ℃ for 2 min without stop at 30 t pressure in a heating platen press. The film was cooled rapidly under pressure using water to cool the cored platens from 185 ℃ to 75 ℃ at 60 ℃/min, and then cooled more slowly using compressed air from 75 ℃ to 50 ℃ under continuous 30 t pressure. To examine the morphology, small samples of each mix were placed between two microscope slides and after being heated in an oven, the sample was squeezed into a film and allowed to cool. The cooling rates were carried out in three ways: by allowing them to cool naturally in air;by slow cooling in an oven,or by quenching in tap water. The specimens were then observed under a microscope (Olympus Metallurgical Microscope equipped with polarizer, heated stage and camera, Model BH SM - NL).

An OX-Tran 100 Oxygen Permeability instrument (Modern Controls Inc.) was employed to measure the oxygen transmission rate of the pressed films (see **figure 1**). The instrument was carefully deaerated with nitrogen before each series to establish a reproducible baseline. Equilibrium conditions were usually established after 4 h of operation. The OX-Tran consists of single 100 cm² diffusion cell with a metal clamp for securing the test film over the detection chamber. Commercial grade oxygen was introduced into the upper chamber and a dilute concentration of hydrogen (99 nitrogen:1 hydrogen) into the lower chamber on the other side of the test film. The flow rate was adjusted to 10 cm³/min at 25 ℃. Each gas was saturated with water vapour by passing it through a bubbler. The detector signal reached equilibrium after about 4 h. The oxygen permeability is proportional to the distance between the equilibrium trace and the predetermined baseline re-
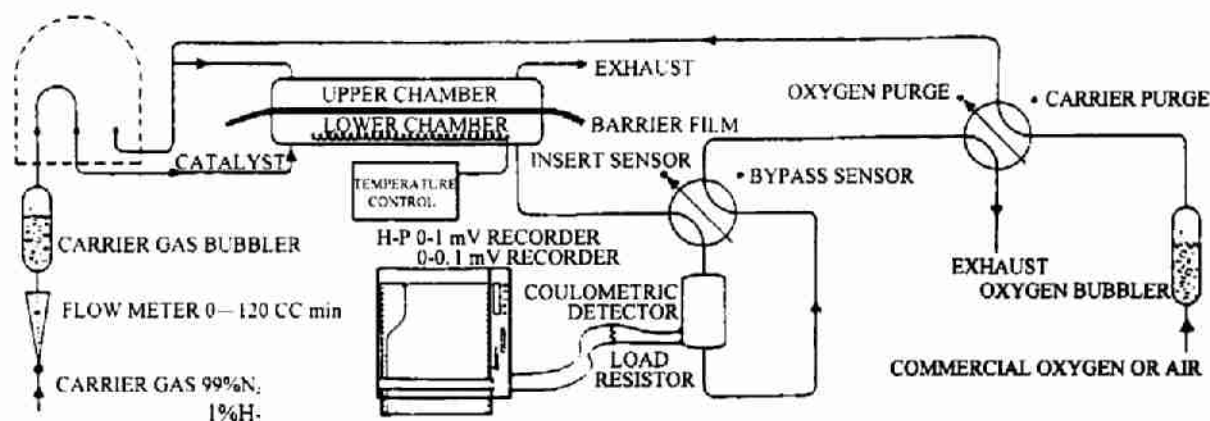
Figure 1 Flow diagram of gases during operation

sponse. The chart reading was calibrated with a standard PET film provided by the OX-Tran manufacturer (Trade literature. Ox-Tran 100 Modern Controls inc.).

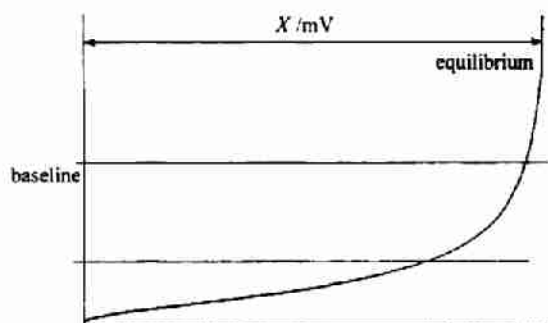Figure 2 shows the characteristic chart of an oxygen permeability test with an Ox-Tran load resistor of 5.3

Figure 2 Characteristic chart of an oxygen permeability test

Ω:

$1 mV = 100$ cc mil/m²/day/ atm.

Thus for a sample of Y mils thick, the permeability is

$P = X \cdot Y \times 100$ cc mil/m²/day/atm,

where X is the equilibrium value of oxygen permeation.

The dynamic modulus analysis was used to determine the modulus after different cooling rates.

2 Results and Discussion

Figures 3–8 are the pictures of the samples after heating at 170, 180, 190 and 200 ℃ and then oven cooling (i.e. annealing, followed by slow cooling). From these photographs, we can see that most are α-type (see figure 3 and 4) and some of them are β-type (see figure 5, 7, 8), depending upon the treatment. The black cross in the spherulite crystals is attretriled to the anisotropic

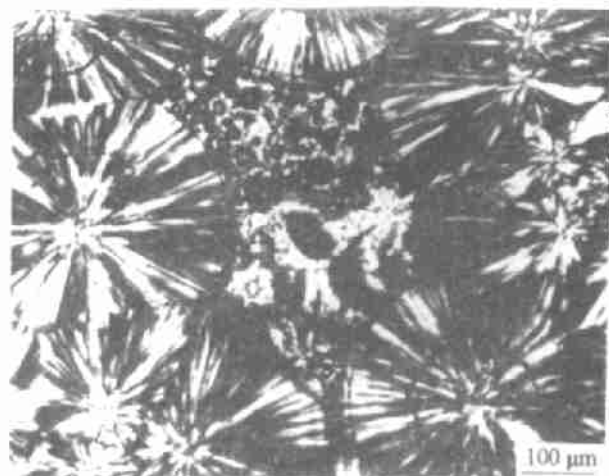
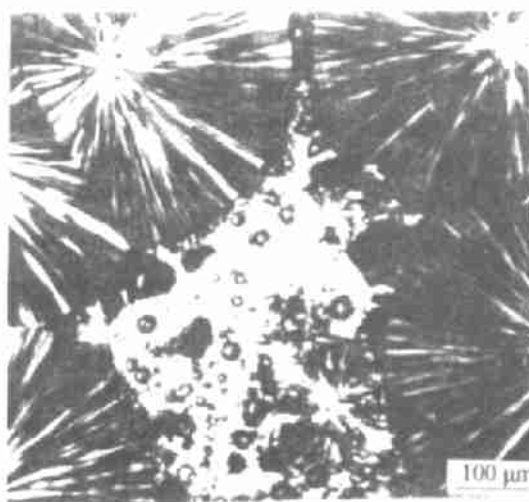Figure 3 Morphology of polypropylene after slow cooling from 170 ℃ in an oven

Figure 4 Morphology of polypropylene after slow cooling from 180 ℃ in an oven

nature of the spherulites. The greater the initial temperature, the larger the resulting spherulites. The average size of the spheroidal crystal is less than 300 μm above 170 ℃ to more than 600 μm below 200 ℃. Since
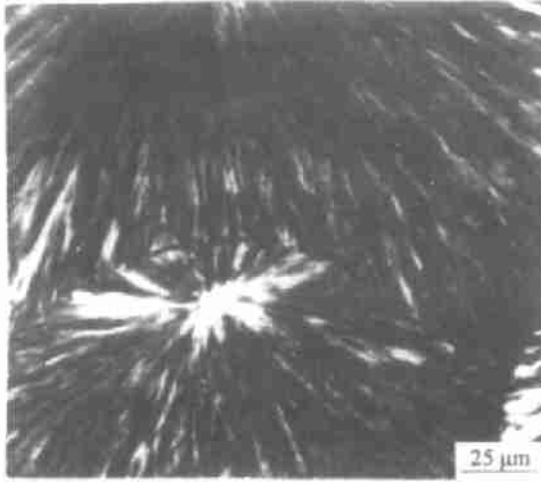
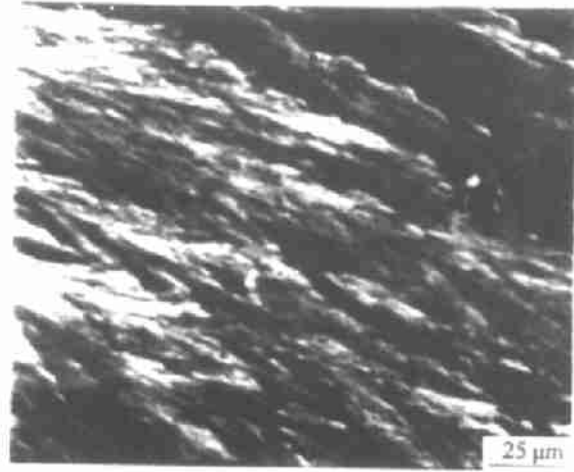Figure 5 Morphology of polypropylene after slow cooling from 190 ℃ in an oven

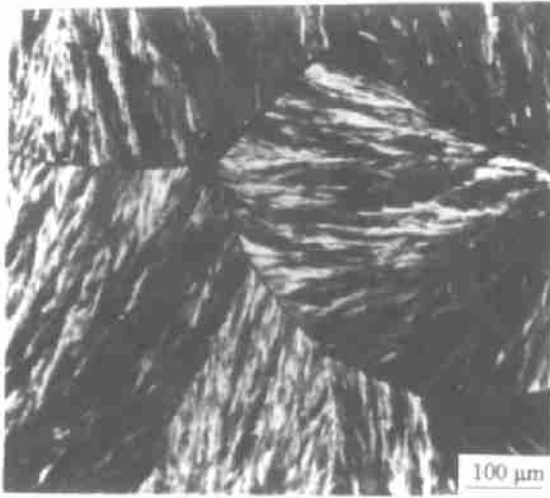Figure 8 Morphology of feathered growth of polypropylene after cooling in an oven

resulting in a broad distribution of spherulite sizes. The morphology of PP at 170 ℃ after annealing shows imperfect spherulitic crystals because the heating temperature is not high enough and there are many cracks inside the crystals. Since the formation of the nuclei is quite different, the grain boundary is also different. Figures 7 and 8 show that some resulting morphologies inside the spherulites exhibit a feather growth from the center of the spherulite and form between the lamellae. Some crystals produce branches and end at the spherulite boundary.

When the samples are cooled in air or in water (shown in **figures 9–12**), a faster cooling rate with much

Figure 6 Morphology of polypropylene after slow cooling from 200 ℃ in an oven

Figure 9 Morphology of polypropylene after quenching in water, the initial temperature is 180 ℃
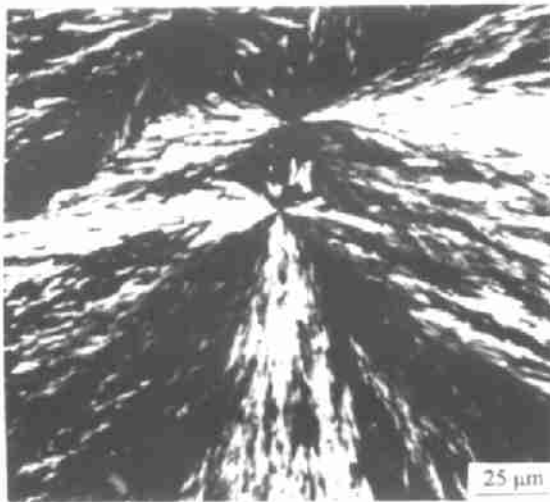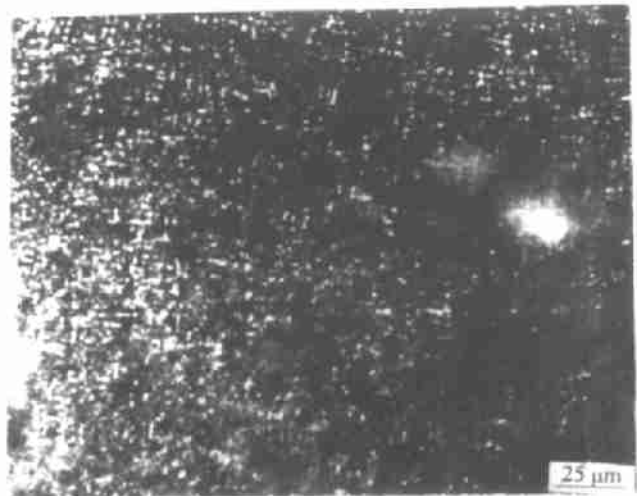

Figure 7 Morphology of feathered growth of polypropylene after slow cooling in an oven

the sample cools continuously, only a few nuclei can be formed above the melting point, so that a number of the secondary nuclei will form and grow simultaneously,

smaller crystals can be obtained. The tiny spherulitic crystals can not be observed clearly at 400 magnification after quenching in water, but do possess short-range order. When the same sample is cooled in air, larger crystals are obtained which can be observed at 100
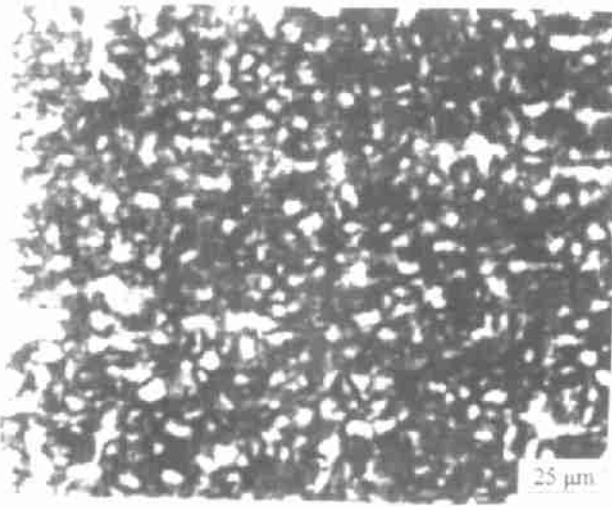
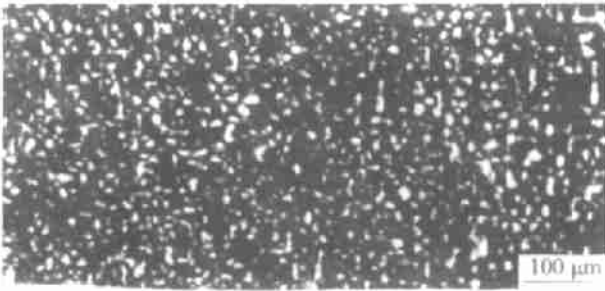Figure 10 Morphology of polypropylene after quenching in water, the initial temperature is 190 ℃

Figure 11 Morphology of polypropylene after cooling in air from 180 ℃

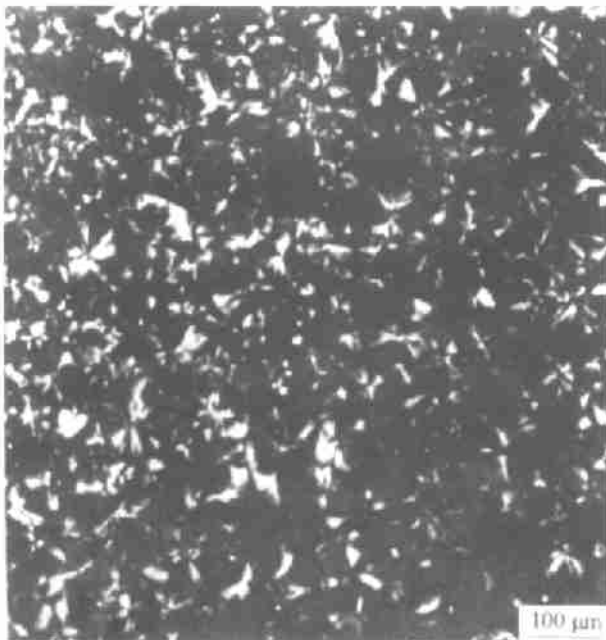

Figure 12 Morphology of polypropylene after cooling in air from 200 ℃

magnification. The average size of these spherulites is more than two orders of magnitude smaller than those obtained after slow annealing in the oven.

Figure 13 and **table 1** give the oxygen permeability of polypropylene at different cooling rates. The oxygen
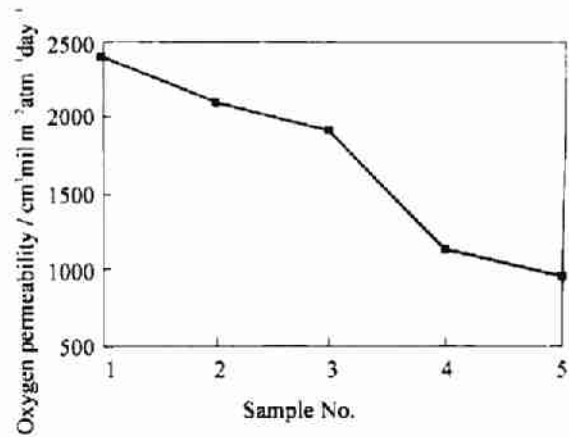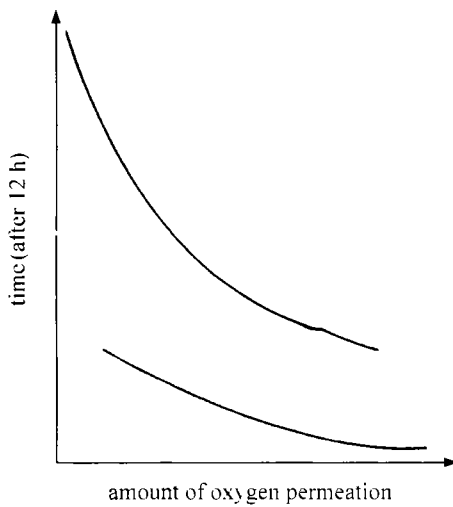

Figure 13 Oxygen premeability of polypropylene with different cooling rate, 1– polypropylene; 2– polypropylene after quenching in water; 3– polypropylene after cooing in air; 4– polypropylene after cooling in oven under pressure; 5– polypropylene after cooling in oven without pressure.

permeability of polypropylene annealed in oven is approximately 40% less than the control cooling rate 60 ℃/min from 185 ℃ to 75 ℃ and then using compressed air, cool more slowly from 75 ℃ to 50 ℃. The quenched sample gave lower oxygen permeability than the control also. Perhaps the diffusive path is longer than that of the control. All samples have the typical asymplotic curve as shown in figure 2, except the annealed sample (**figure 14**) which gave the lowest oxygen permeability at equilibrium. It appears to have large oxygen permeability before reaching equilibrium, for reasons, which are not clear. Oxygen can diffuse passing through the spherulitic crystals and noncrystals between the grain boundaries, but it is easier to pass through the noncrystals because they have lower density and voids. Therefore, any method, which can decrease the noncrystals region and increase the size of the spherulites, may decrease the oxygen permeability. The spherulites are much larger after annealing (*i.e.* slow oven cooling) than cooling in air or water, the larger spherulites have less oxygen permeability. Thus the oxygen permeability is dependent upon both the microstructure and spherulite size.

The dynamic modulus, the phase angle of polypropylene annealing in the oven is less than that of the water quenched polypropylene, it means the former has less amorphous content than the quenched sample, so the oxygen permeability of the annealed sample is less than that of the quenched sample (see **figure 15**).

Table 1 Oxygen permeabilities of polypropylene films after treatment at different cooling rates

Samples	Cooling condition	Average thickness /10^{-2}mm	Permeability/cm^3mil m^{-2}atm^{-1}day^{-1}	Average	Ratio %
PP1		28	2 300		
PP2		25	2 400	2 400	100
PP3		30	2 500		
PW1	quenching in water	34	2 124		
PW2	quenching in water	30	1 944	2 097	87.3
PW3	quenching in water	35	2 205		
P1	cooling in air	25	1 626		
P2	cooling in air	34	2 204	1 915	79.7
P1a	annealing in oven	28	1 102	cooling with pressure	
P2a	annealing in oven	35	1 171	1 125	46.9
P3a	annealing in oven	28	1 102	cooling without pressure	
P4a	annealing in oven	25	787	944	39.3

Figure 14 Oxygen permeability of polypropylene after cooling in oven with and without pressure

Figure 15 DMA results, P_a– polypropylene after cooling in oven; P– after cooling in air; P_w– after cooling in water.
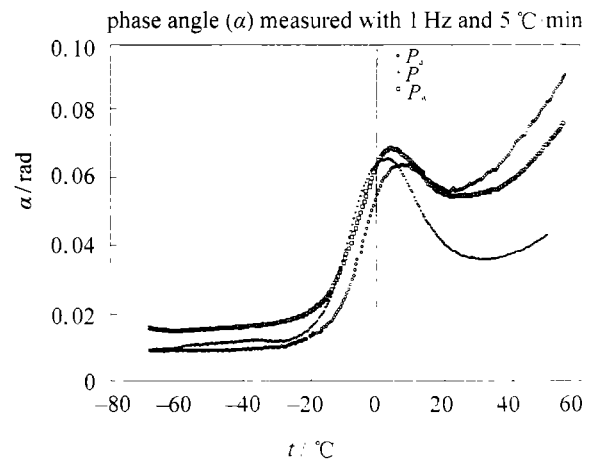
3 Conclusions

(1) The cooling rate has a major influence on spherulite size, morphology and oxygen permeability.

(2) Using slow cooling rates the size and the perfection of spherulites are greater and the oxygen permeability is much less than the quenched specimens.

(3) The greater the initial temperature, the larger the resulting spherulites with corresponding reduced oxygen permeability.

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