

Study of Nucleation Activity and Application of a Nucleating Agent to Copolypropylene

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ABSTRACT: The influences of nucleating agent content on crystallization peak temperature, crystallization curve shape, crystallization onset temperature, and crystallinity of a copolypropylene were studied in detail by differential scanning calorimetry. The results showed that crystallization onset temperature and crystallization peak temperature increased 17°C–22°C and 15°C–19°C, respectively, with increasing nucleating agent content. The behavior of the nucleating agent showed excellent efficiency. But the shape of the crystallization curve broadened with increasing nucleating agent content, and the crystallinity came to an extremum when the nucleating agent content was 0.2%. These results generally differed from those for crystallization of i-PP by a nucleating agent. Modification of copolypropylene was

studied by use of a nucleating agent, and the characteristics of the effects of the nucleating agent on copolypropylene were mastered. The results showed that the hardness of a copolypropylene improved observably. So the abrasion resistance of biaxially oriented polypropylene (BOPP) film for cigarette packaging was improved by adopting the modified copolypropylene as the skin-layer heat-seal material of BOPP film. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3915–3919, 2006

Key words: nucleating agent; crystallization; copolypropylene; biaxially oriented polypropylene film; abrasion resistance

INTRODUCTION

In recent years the promotion and application of polypropylene (PP) have been extended greatly. PP has had the speediest development of all the polyolefin resins,^{1–3} because PP can be a substitute material for common synthetic materials such as PA, PET, PE, PVC, PS, and ABS in the film, nonwoven fabric, rigid packaging, domestic appliance, automobile, and carpet markets. With the development of high-performance PP, the application of PP will be broadened further. Modification of PP mainly has been achieved by adding a nucleating agent, which may improve the mechanical, optical, and thermal properties of PP. However, the relevant research has focused on the development and application of i-PP,^{4–11} ignoring a corresponding study of the application of a nucleating agent in copolypropylene, which has a wide application in the fields of film, domestic appliances, and automobiles because of its favorable properties of impact resistance toughness and low temperature.^{12–14} In this article, the influence of a sorbol nucleating agent on the crystallization process of copolypropylene is discussed. The industrial application of copolypro-

pylene modified by a nucleating agent was investigated in order to improve the abrasion resistance of BOPP film for cigarette packaging.

EXPERIMENTAL

Materials

Copolypropylene (terpolymer), EP3C37F, and homopolypropylene, HP420J, came from the Montell Company (Belgium); the nucleating agent CHJ-2 came from the Guangzhou Chenghe Science & Technology Company (China); and the functional master batches for BOPP, P.T.A., came from the Schulman Plastics Company.

Equipment

The twin-screw extruder, TE-65, came from Nanjing Keya Company (China), the BOPP film line from the Brückner Company (Germany), and the differential scanning calorimeter (DSC), TG-7, from the P-E Company.

Thermal analysis method

The nucleating agent and copolypropylene were extruded into pellets with the twin-screw extruder. Thermal analysis was carried out on a DSC by pro-

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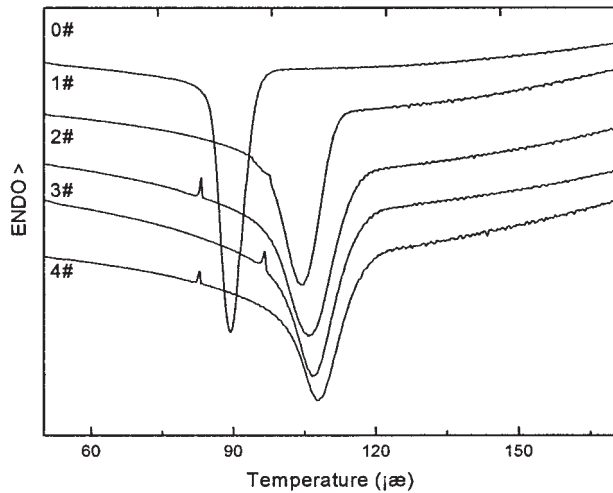


Figure 1 DSC cooling curves of copolypropylene.

tecting N_2 . The heating rate was 10 K/min from 25°C to 200°C. The temperature was maintained at 200°C for 3 min and then cooled to 25°C at the rate of 10 K/min.

RESULTS AND DISCUSSION

With nucleating agent contents of 0%, 0.15%, 0.20%, 0.25%, and 0.30%, DSC curves 0, 1, 2, 3, and 4, respectively, were obtained, as shown in Figure 1. Analysis of these crystallization DSC curves and the activity of nucleating agent are discussed in detail.

Effect of nucleating agent on crystallization peak temperature

Crystallization peak temperature, which represents the formation and growth ability of the crystal nucleus, can be gained when the rate of crystallization reaches the highest value. The formation of the crystal nucleus includes homogeneous nucleation and hetero-

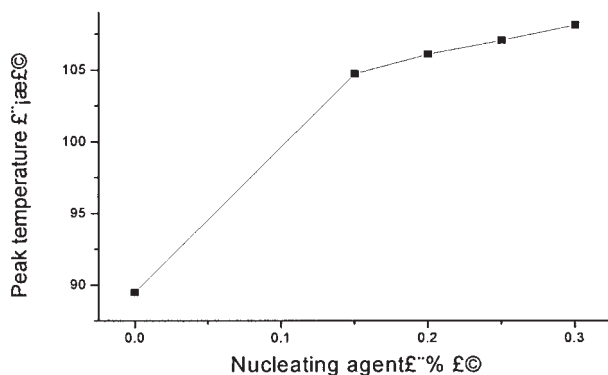


Figure 2 Relationship of crystallization peak temperature and content of nucleating agent.

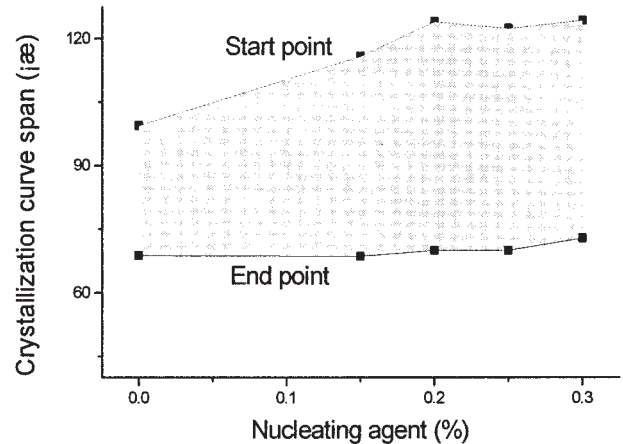


Figure 3 Effect of nucleating agent on crystallization curve span.

ogeneous nucleation. Homogeneous nucleation mainly depends on the ordered arrangement of the chain segment during the process of decreasing the temperature. At higher temperature homogeneous nucleation can be destroyed easily by the thermal motion of molecular. Only at lower temperature can homogeneous nucleation form; therefore, the crystallization peak temperature of homogeneous nucleation is lower. However, during heterogeneous nucleation with the addition of a nucleating agent, a large number of crystal nuclei were formed at a higher temperature. As shown in Figure 2, a little of the nucleating agent was able to enhance the crystallization peak temperature greatly.

With the nucleating agent content increasing, the crystallization peak temperature showed a rising trend. By adding a nucleating agent the crystallization peak temperature of heterogeneous nucleation was increased 15°C–19°C efficiently, compared with that of homogeneous nucleation.

Effect of nucleating agent on crystallization curve shape and peak width

Crystallization peak width is the span from the start point to the end point crossed by the crystallization curve and the baseline. As shown in Figure 3, the nucleating agent greatly increased the start point temperature, and when the content of nucleating agent was above 0.2%, it increased smoothly, whereas the

TABLE I
Crystallization Curve Shape Coefficient

Nucleating agent content (%)	0.00	0.15	0.20	0.25	0.30
Curve shape coefficient	2.053	1.389	1.262	1.204	1.204

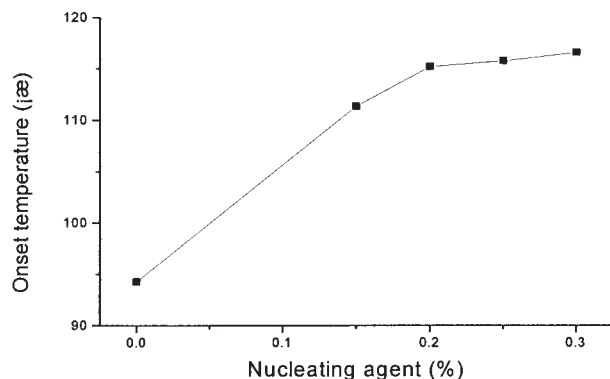


Figure 4 Effect of nucleating agent on crystallization onset temperature.

end point temperature always increased smoothly. Hence, with nucleating agent content increasing, the crystallization peak width increased to a maximum when the nucleating agent content was 0.2%; subsequently, the peak width began to decrease.

The crystallization curve shape can be directly observed from the DSC curve. The crystallization curve shape factor is defined as the ratio of crystallization enthalpy to crystallization peak width. The value of this factor is bigger, the peak is narrower, and contrarily the peak is broad. Heat liberation during crystallization reflects the degree of crystallinity, and at a certain rate of cooling the crystallization peak width substantially reflects crystallization time; thus, the crystallization curve shape factor corresponds to average crystallization rate. Table I shows that with an increasing nucleating agent content, the crystallization curve shape factor decreased gradually, the crystallization peak widened, and the average crystallization rate decreased, which was different from the relation between the crystallization curve shape of i-PP and the nucleating agent.

Effect of nucleating agent on crystallization onset temperature and crystallinity

Because the melting point of the nucleating agent was higher than that of PP, in the cooling process the nucleating agent, as heterogeneous crystal nucleus, accelerated the crystallization to start at a higher temperature. As shown in Figure 4, the crystallization onset temperature was enhanced 17°C–22°C by the

TABLE II
Gap Between Crystallization Peak Temperature and Onset Temperature

Nucleating agent content (%)	0.00	0.15	0.20	0.25	0.30
Gap	4.77	6.60	9.11	8.66	8.45

TABLE III
Effect of Nucleating Agent Content on Crystallinity

Content of nucleating agent (%)	0.00	0.15	0.20	0.25	0.30
ΔH (J/g)	62.93	65.51	68.08	63.01	61.92
Crystallinity (%)	30.11	31.34	32.57	30.15	29.63

nucleating agent. In the synthesis of copolypropylene, the copolymerization of ethylene, propylene, and butylenes destroys the structural regularity of PP chains; therefore, homogeneous nucleation needs a higher degree of supercooling, whereas homogeneous nucleation can make crystallization reach its maximum temperature sooner than can heterogeneous nucleation. Table II lists the differences in values between crystallization peak temperature and onset temperature. It shows that when the nucleating agent content was 0.2%, the gap between crystallization peak temperature and onset temperature reached its maximum, which corresponded to the calculated crystallinity. Crystallinity, listed in Table III, can be calculated by the formula $X_c = -\Delta H/\Delta H_0$, where ΔH_0 is the melting enthalpy of the crystallization district of i-PP.

Crystallinity was improved by adding a nucleating agent but not by the direct ratio to the nucleating agent content. Dramatically, with the same nucleating agent content, 0.2%, crystallinity reached the maximum. The probable reason for this is that at a fixed rate of cooling, proper nucleating agent content may not only maintain the formation ability of the crystal nucleus and the crystallization rate, but also may afford enough crystallization time before the peak value is reached in order to form a perfect crystal structure. Nevertheless, when the nucleating agent content was above 0.2%, crystallization onset temperature and peak temperature improved, but the degree of crystallinity decreased. With a 0.3% content, crystallinity was even lower than that of copolypropylene without nucleating agent. Therefore, the speedy formation of a crystal nucleus at a higher temperature did not neces-

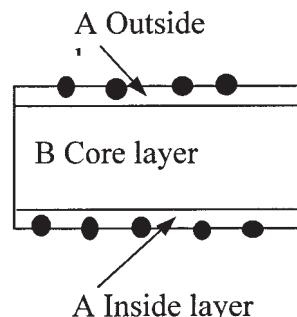


Figure 5 ABA structure schematic representation of BOPP film for cigarette.

TABLE IV
Effect of Nucleating Agent Content on Hardness

Nucleating agent content (%)	0.00	0.15	0.20	0.25	0.30
Hardness (%) (Shore D)	44.0	47.6	54.0	53.8	53.4

sarily improve the crystallization rate and crystallinity, which are obviously different from the classical crystallization theory and the crystallization rule of i-PP. the mechanism of this kind of nucleating agent and the crystallization rule of copolypropylene await further research.

Effect of nucleating agent the abrasion resistance of biaxially oriented polypropylene (BOPP) film

It is necessary for the biaxially oriented polypropylene film used in cigarette packaging to resolve the surface abrasion resistance during the transportation and packaging of cigarettes. Therefore, in this study, the effect of a nucleating agent on the surface hardness of the BOPP film was investigated. As shown in Figure 5, which is a schematic representation of the BOPP film used for cigarette packaging, BOPP film is made of three parts: the outside surface, the inside surface, and the core layer.

The outside surface and inside surface layers of BOPP film were made of copolypropylene, and the core layer was made of homopolypropylene. The antiblock agent of silicon dioxide was introduced into the outside and inside layers, which resulted in roughness of the BOPP film surface. Subsequently, surface scraping was unavoidable during the transportation and packaging because of the hard particles of silicon

dioxide standing out from the skin layer. For this reason, the nucleating agent CHJ-2 was introduced into the copolypropylene to improve the hardness of the BOPP film. The effect of the nucleating agent content on the hardness of the copolypropylene is shown in Table IV. It can be seen that the hardness of the copolypropylene improved by more than 20% when the nucleating agent content was 0.2%. This indicates that the introduction of the nucleating agent was effective in improving the hardness of the copolypropylene. Subsequently, the copolypropylene modified by this nucleating agent was used for producing the BOPP film as the outside and inside layers. The properties are listed in Table V.

As shown in Table V, for BOPP film there were no obvious differences in the index of performance including mechanical strength, the optical property, the heat shrinkable rate, the frictional property, and heat seal strength.¹⁵ To investigate the abrasion resistance property, two sheets of BOPP film were prepared. One was fixed on the flat, and the other weighed a poise glided to and fro at a speed of 50 mm/s. The haze was measured after 20 circular times, which is shown in Table V. It can be seen that in the BOPP film modified with the nucleating agent (sample B) there was less haze than that in the original film (sample A). This shows there was obvious improvement in the abrasion resistance of the modified BOPP film.

CONCLUSIONS

The nucleation activity of this kind of nucleating agent, CHJ-2, for copolypropylene performed very efficiently. The results showed that the crystallization

TABLE V
Effect of Nucleating Agent on Properties of BOPP Film

Property		Film A	Film B	
Tensile strength	MD	190	190	
	TD	295	308	
Yield strength	MD	93	94	
	TD	245	244	
Elongation rate at rupture	MD	165	168	
	TD	68	74	
Heat-shrinkable rate	MD	4.9	5.0	
	TD	4.1	4.3	
Friction coefficient	25	Static dynamic	0.36	0.35
			0.26	0.27
			0.72	0.70
50	Static dynamic	0.43	0.43	
		94.6	94.5	
		3.4	3.4	
Heat seal strength	N/15 mm	2465	2590	
		MPa		
Elasticity modulus	Before scraping	1.2	1.2	
	After scraping	2.6	2.1	

A represents unmodified BOPP film, B represents BOPP film modified with a nucleating agent, MD represents machine direction, and TD transverse direction.

temperature increased markedly even though the nucleating agent content was low. And the crystallization behavior of copolypropylene by CHJ-2 was very different from that of homopolypropylene. The hardness of copolypropylene modified by the nucleating agent improved more than 20%. The modified copolypropylene was used as the skin-layer heat-seal material of BOPP film for cigarette packaging. An obvious improvement in the abrasion resistance of the BOPP film was achieved by measuring the change of haze after the surface scraping test.

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