

Preliminary Study on the Characteristics of Isotactic Polypropylene with Nucleating Agent Swollen by Supercritical Carbon Dioxide*

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Abstract Impregnation of isotactic polypropylene (iPP) with nucleating agent (NA21) using supercritical carbon dioxide as the swelling agent at different temperature and pressure and its non-isothermal crystallization kinetics were investigated. The results showed that NA21 was dispersed at a nanometer-scale in the PP matrix, resulting in the formation of different types of crystal phases of iPP and the enhancement of its mechanical properties.

Keywords supercritical carbon dioxide, polypropylene, nucleating agent, mechanical performance

1 INTRODUCTION

Polypropylene (PP) has been one of the most rapidly growing engineering plastics in recent years due to its intrinsic properties such as low density, high melting point, high tensile strength, rigidity, stress crack resistance, abrasion resistance, low creep and a surface which is relatively resistant to chemical attack. Nowadays, it has been widely used in the field of automobile industry, home appliance manufacturing, packaging as well as other new applications. Nucleating agents allow the polymer to crystallize at higher temperature during processing and the size of polymer spherulites to be adjusted. Therefore, the use of nucleating agents is of great importance for processing PP with high mechanical and optical performances. The state of dispersion of nucleating agents in a PP matrix can affect both the growth of spherulites and subsequent processing^[1,2].

Supercritical fluids (SCFs) are unique solvents for polymer processing. Among them, supercritical CO₂ (SC-CO₂) is the most widely used because it is nonflammable, nontoxic, and relatively inexpensive. Moreover, its critical conditions are moderate ($T_c = 31.1^\circ\text{C}$ and $p_c = 7.37\text{ MPa}$) and thus are relatively easy to implement^[3]. SC-CO₂ is usually a very weak solvent for polymers except for some fluoropolymers and silicones^[4]. However, it is a good swelling agent for most polymers and can dissolve many small

molecules^[5–9]. The dissolving of a SCF can be tuned continuously from gaslike to liquidlike by manipulation of the temperature and pressure. This provides the ability to control both the degree of swelling in polymers^[5–12] and the partitioning of small molecule penetrants between swollen polymer and the fluid phase^[12–14]. The low viscosity and zero surface tension of a SC-CO₂ allow for rapid mass transfer of penetrants into swollen polymers. In addition, CO₂ is a gas at ambient pressure, making its removal from the final products facile.

In this paper, the nucleating agent was impregnated into isotactic PP (iPP) by using supercritical CO₂, and this work aimed at studying the effect of pressures and temperature on the impregnation behavior of iPP with a nucleating agent. The non-isothermal crystallization kinetics of the impregnated iPP films and the mechanical performance of the impregnated iPP granules after twin screw extrusion and injection molding were also investigated.

2 EXPERIMENTAL

2.1 Materials

The isotactic PP (iPP) pellets with a number average diameter of 3–4 mm were kindly provided by the Plastics Department of Shanghai Petrochemical Company. The mass-average molar mass (M_m) of iPP was $188700\text{ g}\cdot\text{mol}^{-1}$. Its polydispersity index was

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5.1. 15 g of the isotactic PP was melt in an oven at 200°C and then pressed into a film with thickness of 0.3 mm with a pressure of 10 MPa. The film was then cut into standard specimen with dimensions of 1 mm×3 mm×0.3 mm. It was refluxed with acetone for 24 h to remove impurities and then annealed at 100°C for 2 h. The nucleating agent, NA21, an organic derivative of phosphate salt, was kindly supplied by Asahi Denka Kogyo K.K. (Japan).

2.2 Apparatus

The experimental apparatus used is sketched in Fig. 1. All the metallic parts in contact with the chemicals were made of stainless steel. The apparatus was tested up to 35 MPa. The total volume of the system was 500 ml.

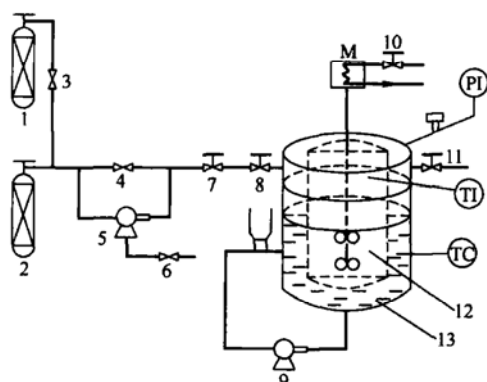


Figure 1 Schematic diagram of the penetration process

- 1—N₂ cylinder; 2—CO₂ cylinder;
3—N₂ valve; 4—gas booster valve;
5—gas booster; 6—gas booster release valve;
7,8—shutoff valve; 9—circulation pump;
10—cooling water valve; 11—purge valve;
12—high pressure reactor; 13—electrical heating

2.3 Dissolution of NA21 in SC-CO₂

A high-pressure visualized cell with two quartz windows was made by our laboratory^[15]. The dissolubility of NA21 in SC-CO₂ was determined with the cell for observing the dissolution process of the NA21. About 1 g of NA21 was placed on the quartz window. A digital camera was used to observe the dissolution process. The cell was firstly cleaned by low pressure CO₂, and then pressurized to a prescribed pressure, usually above the critical pressure of CO₂. Thereafter

it was heated up using a heating tape that surrounded it outside.

2.4 Impregnation procedures

The impregnation system was cleaned thoroughly using low pressure CO₂ and then dried under vacuum at ambient temperature. Isotactic PP films marked from one to twelve were placed in the pressurized cell together with 1% NA21 powder (by mass). The system was then purged with CO₂. After it had reached the desired temperature CO₂ was charged till the desired pressure was attained. The impregnation process lasted for 4 h. Thereafter the pressurized cell was rapidly depressurized. It was then cooled down, opened up and the specimens were taken out for subsequent characterization by different techniques. A series of experiments were carried out at 7.58 MPa and 16.88 MPa and different temperatures ranging from 60°C to 120°C, respectively.

2.5 Gravimetric characterization

A gravimetric technique^[6] was used to measure the change in mass of the iPP film. A blank test was first carried out to check whether or not the mass of the film would change with time after it was taken out from the system. It showed that 48 h later almost no mass change of film occurred, which means all CO₂ had released from the PP film after depressurization. Then the amount of NA21 incorporated into the iPP matrix was calculated through the subtraction of the film's mass 48 h after the impregnation process from its original one. The mass of the film was measured by a high precision balance (Sartorius BP211D) with an accuracy of within ±0.01 mg.

3 RESULTS AND DISCUSSION

3.1 Dissolution process of NA21 in SC-CO₂

All the experiments were to be conducted under the conditions under which NA21 can be dissolved in SC-CO₂ completely, as confirmed by the qualitative test on the dissolution process of the NA21 in SC-CO₂ in a cell with two quartz windows (see Fig. 2). Initially, the NA21 powder adhered to the quartz window of the cell. Upon pressurization with CO₂, NA21 began to dissolve. After a certain period of time, it was completely dissolved.

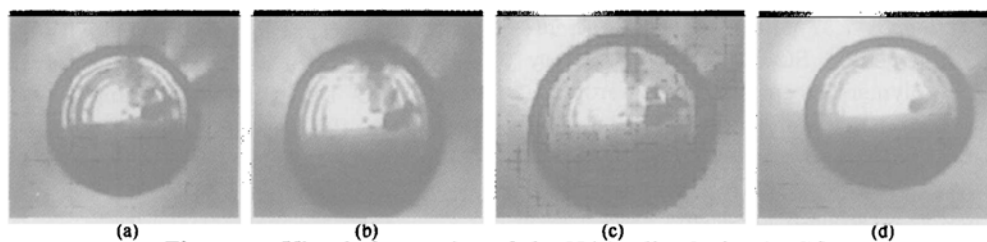


Figure 2 Visual observation of the NA21 dissolution in CO₂
(a) atmospheric pressure; (b) 0 min, 7.6 MPa; (c) 30 min, 10.0 MPa; (d) 55 min, 13.0 MPa

It was important to distinguish two different mechanisms that might operate in the impregnation processes. The first involved the deposition of a substance soluble in supercritical fluid into the polymer matrix upon depressurizing the cell containing the supercritical fluid solution. In that mechanism, even a solute that had low affinity to the polymer matrix could be trapped therein. However, the solute often re-crystallized within the polymer matrix and thus was unable to be dispersed in the molecular level. The second mechanism used a supercritical fluid solution in which a solute having high affinity with the polymer matrix was dissolved. This could result in a high partition coefficient of the solute between the polymer and fluid phase. In addition, specific interactions between the solute and the polymer matrix prevented the solute from self-association and resulted in its dispersion at the molecular level within the polymer matrix. The second mechanism which was based on the affinity of the solute to the polymer matrix had a tremendous potential for supercritical fluid impregnation of additives into polymer matrices.

Kazarian *et al.*^[16] showed that incorporation of dye molecules into a polymeric matrix could be effective if the partition coefficient of the dye between the polymer and SC-CO₂ phase was high, even though the solubility of the dye in SC-CO₂ solution was low. High partition coefficients resulted from high affinity of dye molecules to the polymer matrix through, *e.g.*, H-bonding. The solubility of NA21 in SC-CO₂ was low. Nevertheless it could be effectively impregnated into the iPP matrix owing to its high partition coefficient between the polymer and SC-CO₂ phase.

3.2 Dispersion of NA21 in the iPP matrix

NA21 was migrated into the iPP matrix owing to its high partitioning coefficient between the SC-CO₂ and the iPP phase. Fig. 3 shows the size distribution of the initial NA21 particles measured with a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK). The number-average particle size was 4.0 μm . After its incorporation into the iPP matrix through the above described impregnation process, the NA21 particles were homogeneously dispersed in the iPP matrix with a number average size of 50 nm to 100 nm (Fig. 4).

3.3 Effects of pressure and temperature

Figure 5 shows the effects of pressure and temperature on the amount of NA21 that was incorporated into the iPP matrix.

Since the impregnation process included the dissolution of the solid (NA21) in supercritical CO₂ and then partitioning between the CO₂ and the iPP, high pressure or high temperature were expected to favor the mass uptake due to increased solubility with increasing pressure or temperature. From Fig. 5, the

experimental results showed that high temperature is favorable to the impregnation process, while the mass uptake decreased at high pressure. This maybe explained as the low partitioning of solute in polymer phase at high pressure.

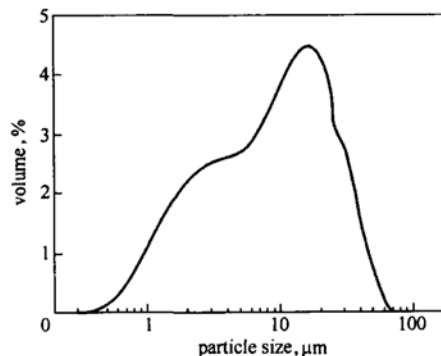
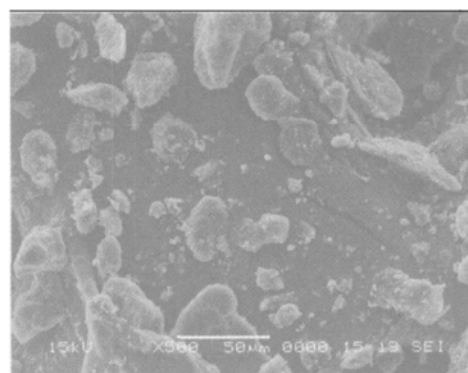
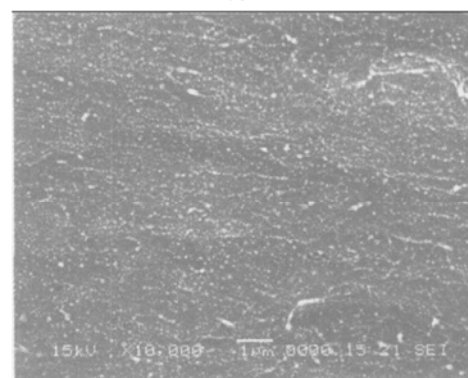


Figure 3 Size distribution of the NA21 particles before its incorporation in the iPP matrix



(a)



(b)

Figure 4 SEM GRAPHS of (a) the original NA21 particles and (b) its dispersion in iPP matrix with SC-CO₂

3.4 DSC analysis

The DSC analysis was carried out with NETZSCH DSC 200 PC. The sample was heated to 200 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$, and was annealed at that temperature for 5 min to remove the heat history. After annealing, the system was cooled to 60 $^{\circ}\text{C}$ at a

rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and was kept at that temperature for 5 min before it was heated up again to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The melting temperature, T_m , and the crystallinity were taken in the second heating cycle. Fig. 6 compares the DSC curves between a pure iPP specimen used in the experiment and an iPP impregnated with NA21 under CO_2 (7.58 MPa and $100\text{ }^{\circ}\text{C}$) with an average mass uptake of 0.5%. There were three peaks located at $145.8\text{ }^{\circ}\text{C}$, $154.0\text{ }^{\circ}\text{C}$, $161.0\text{ }^{\circ}\text{C}$, respectively, in the DSC curve of the NA21 impregnated iPP. They corresponded to the α , β , γ phases of the iPP, respectively.

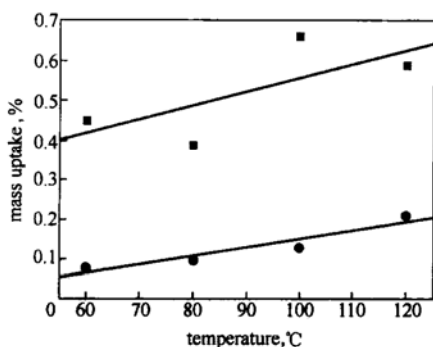


Figure 5 Variation of the amount of NA21 incorporated into the iPP matrix as a function of temperature and pressures
p, MPa: ■ 7.58; ● 16.55

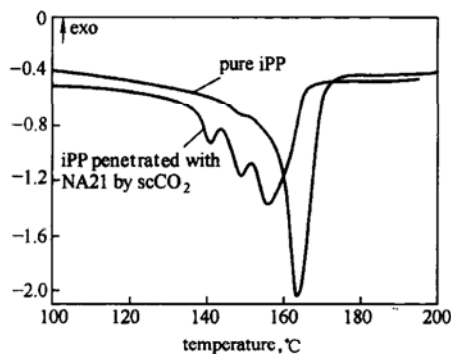


Figure 6 DSC curve of a NA21 penetrated iPP film sample

From the above DSC results, the nano-scale dispersion of NA21 promoted the formation of β phase compared with the pure iPP. It also promoted the formation of the γ phase. The latter is often formed at elevated pressures up to 500 MPa from high molecular weight homopolypropylene^[17,19].

3.5 Non-isothermal crystallization kinetics of NA21 impregnated iPP films

The Jeziorny method, which applies the Avrami equation to the analysis of isothermal DSC curves, was used to explain the non-isothermal crystallization kinetics of NA21 impregnated iPP films^[18].

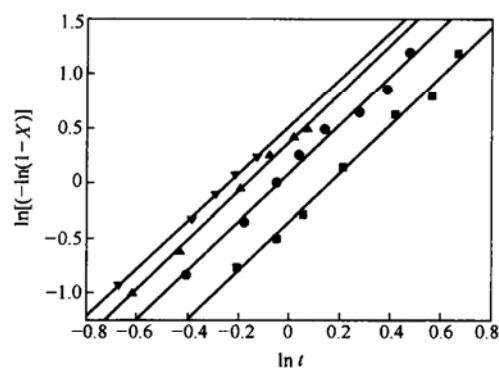
The Avrami equation is

$$\ln[-\ln(1-X)] = \ln Z + n \ln t \quad (1)$$

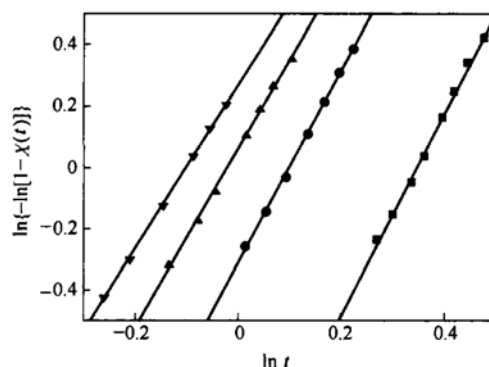
The parameters n , Z in the above equation could be obtained through the plot of $\ln[-\ln(1-X_c)]$ against $\ln t$. Considering the effect of the cooling rate, Z should be amended by the following formula:

$$\ln Z_c = \frac{\ln Z}{\phi} \quad (2)$$

Fig. 7 shows the plots of $\ln[-\ln(1-X_c)]$ vs. $\ln t$, from which the values of the non-isothermal crystallization parameters were obtained in Table 1.



(a) Pure iPP



(b) NA21 impregnated iPP

Figure 7 Plots of $\ln[-\ln(1-X_c)]$ vs. $\ln t$ for the recrystallization kinetics
cooling rate, $\text{K}\cdot\text{min}^{-1}$: ■ 5; ● 10; ▲ 15; ▼ 20

Table 1 Values of the non-isothermal crystallization parameters of the pure and NA21 impregnated iPP

Cooling rate $\text{K}\cdot\text{min}^{-1}$	Neat iPP			iPP+NA21		
	n	Z	Z_c	n	Z	Z_c
5	2.22	0.4399	0.849	3.30	0.0722	0.591
10	2.22	1.250	1.023	3.16	0.487	0.931
15	2.23	2.356	1.059	2.91	1.155	1.010
20	2.17	3.341	1.062	2.62	1.806	1.030

The kinetic rate constant, Z , increased with the cooling rate, implying that the recrystallization rate

increasing. When the iPP crystallized without NA21, the value of the Avrami exponent n remained virtually constant, regardless of the cooling rate. This is because the iPP crystals grew in two dimensions. When it was impregnated with the NA21 under SC-CO₂, the value of the Avrami exponent n decreased with the increasing cooling rate. This implies that the iPP crystal grew in multiple directions at low cooling rates.

3.6 Enhanced mechanical performances of iPP's

A larger autoclave with a volume of 2 L was used to prepare a large amount of the NA21 impregnated iPP (about 500 g). Its mechanical properties were tested after extrusion and injection molding and are shown in Table 2. The mechanical performances were greatly enhanced by the growth of small sized spherulites with the nano-sized distributed nucleating agent as nuclei.

Table 2 Enhanced mechanical properties of iPP's by NA21 impregnation under SC-CO₂

	Tensile strength MPa	Tensile modulus MPa	Bending strength MPa	Bending modulus MPa
pure iPP	31.52	1162	37.09	1014
iPP + NA21 by extrusion	33.95	1166	39.48	1076
iPP + NA21 by impregnation under SC-CO ₂	35.91	1523	43.21	1236

4 CONCLUSIONS

The nucleating agent, NA21, was successfully dispersed as nano-sized particles into an isotactic polypropylene (iPP) under SC-CO₂ and the mass uptake of NA21 was investigated with a gravimetric technique. There are three phases of iPP, that is α , β , γ phase respectively, emerged in the crystallization process of iPP and the mechanical performances of iPP were enhanced after it was incorporated with NA21 by using SC-CO₂.

NOMENCLATURE

n	Avrami constant
p	pressure, MPa
T	temperature, K
t	crystallization time, s
X	crystallinity, %
Z	rate constant
ϕ	cooling rate, K·min ⁻¹

Subscripts

m	melting
c	crystallization

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