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#### Controlled Crystallization of Isotactic Polypropylene Based on α/β Compounded Nucleating Agents: From Theory to Practice

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#### 1. Introduction

Isotactic polypropylene (iPP) is one of the most important thermoplastic polymers owing to its low manufacturing cost and versatile properties. Moreover, iPP exhibits a very interesting polymorphic behavior (Awaya, 1988; Busse et al., 2000; Lotz et al., 1996; Vagar, 1992). At least five modifications: monoclinic  $\alpha$  form, trigonal  $\beta$  form, orthorhombic  $\gamma$  form,  $\delta$  and smectic phase have been reported. The  $\alpha$  form is the best known and most stable in commercial grades of iPP being found in most melt crystallized specimens, especially those being added  $\alpha$  Nucleating agents (NA) (Labour et al., 1999; Vagar, 1986). The  $\beta$  form is metastable thermodynamically and is obtained under some special conditions such as a high degree of supercooling, temperature gradient, shear-induced crystallization or addition of  $\beta$ nucleating agents (Fillon et al., 1993; Ismail & Al-Raheil, 1998). The  $\gamma$  form occurs in lowmolecular-weight iPP or under high pressure and the mesomorphic form results from quenching (Meille et al., 1990; Lotz et al., 1986). Different crystalline form of iPP leads different properties like optical and mechanical properties.

NA as one of the additives presents a role of increasing the nucleation density of polymer greatly and enhancing the nucleation rate dramatically so as to have a great impact on the mechanical properties of polymer (Kristiansen et al., 2003; Romankiewicz et al., 2004; Tenma & Yamaguchi, 2007). So far, two kinds of NAs,  $\alpha$  phase and  $\beta$  phase NAs discriminated by the form of iPP they induce have been widely put into use in modifying iPP. The  $\alpha$  phase NA can improve the stiffness and optical properties of iPP while decrease its toughness (Gui et al., 2003; Zhang G.P. et al., 2003; Zhang Y.F. & Xin, 2006). The  $\beta$  phase NA will induce  $\beta$ -iPP during crystallization, which can improve toughness and heat distortion temperature of iPP while decrease its stiffness (Tordjeman et al., 2001; Zhao et al., 2008). Thereby, it is well expected to balance the iPP's stiffness and toughness. Xin's research group firstly proposed the idea of compounding  $\alpha/\beta$  NAs. However, whether compounding  $\alpha, \beta$  NAs will enhance stiffness and toughness simultaneously or not and what influence will  $\alpha/\beta$  compounded NAs take on the crystallization kinetics, crystallization morphologies, and mechanical proprieties of iPP call our eye.

In this work, three kinds of well studied  $\alpha/\beta$  compounded NAs, Phosphate/Amide, Sorbitol/Amide, and Phosphate/Carboxylate were selected to review. This short review aims to present some conclusions of  $\alpha/\beta$  compounded NAs and to lay the foundation for compounding  $\alpha$  and  $\beta$  NAs afterwards.

#### 2. Crystallization kinetics of iPP nucleated with $\alpha/\beta$ compounded NAs

Crystallization process of semi crystalline polymers such as polypropylene can have a dramatic impact on the mechanical properties. Thus, we studied the crystallization kinetics of iPP nucleated by  $\alpha/\beta$  compounded NAs first.

Isothermal crystallization kinetics of iPP nucleated with Phosphate/Amide compounded NA, NA40/NABW was studied by Zhang et al. (Zhang & Xin, 2007). The results showed that Avrami equation, as shown below, was quite successful for analyzing the experimental data of the isothermal crystallization kinetics.

$$1 - X_t = \exp(-Z_t t^n) \tag{1}$$

where  $X_t$  is the relative crystallinity at time t, n is Avrami exponent, a constant whose value depends on the mechanism of nucleation and on the form of crystal growth, and  $Z_t$  is a constant containing the nucleation and growth parameters. The addition of NA40/NABW could shorten crystallization half-time  $(t_{1/2})$  and increase crystallization rate of iPP greatly. Consequently the molding cycle time of iPP would be reduced obviously, which has great importance for polymer processing. The Avrami exponents of iPP and nucleated iPP were close to 3, indicating that the addition of nucleating agents did not change the crystallization growth patterns of iPP under isothermal conditions and the crystal growth was heterogeneous three-dimensional spherulitic growth. The Caze method was applied to study on the non-isothermal crystallization kinetics of nucleated iPP by Phosphate/Amide compounded NA, NA11/DCHT (Zhao & Xin, 2010). It can be seen from the results that the addition of the  $\alpha/\beta$  compounded NAs can obviously shorten  $t_{1/2}$  of iPP, especially at lower cooling rates. When the cooling rate  $\Phi$  is 2.5°C/min, t<sub>1/2</sub> of nucleated iPP was 104.9s, while that of pure iPP was 135.4 s. The Avrami exponent n for nucleated iPP indicated that the  $\alpha/\beta$  compounded NA acted as heterogeneous nuclei followed by three-dimensional spherical growth during non-isothermal crystallization. Therefore, the type of nucleation of iPP was significantly changed in the presence of the  $\alpha/\beta$  compounded NAs while the geometry of crystal growth of iPP did not change.

Bai et al. investigated the isothermal crystallization kinetics of nucleated by Sorbitol/ Amide compounded NA, DMDBS/TMB-5 (Bai & Wang, 2009). The crystallization kinetics parameters suggested that compounded NA accelerated the crystallization process of iPP greatly.  $t_{1/2}$  of iPP/DMDBS/TMB-5 was much smaller than iPP, indicating the faster crystallization process by the addition of compounded NA. For all the samples, the Avrami exponent value n ranges from 2 to 3, which means spherulite development arose from an athermal heterogeneous nucleation. The fold surface free energy of virgin iPP and nucleated iPP was also calculated from the crystallization kinetics. Samples with addition of compounded NA resulted in smaller values. That means interfacial surface free energy of iPP was reduced with the presence of compounded NA. Similar results were obtained by

the study on the non-isothermal crystallization kinetics of iPP nucleated by Sorbitol/Amide compounded NA, 3988/DCHT (Zhao & Xin, 2010).

Except for Amide NA, Carboxylate NA is proved to be another highly effective  $\beta$  NA for iPP. Xu gave us the picture of non-isothermal crystallization kinetics of iPP nucleated by Phosphate/Carboxylate compounded NA, NA40/H-Ba (Xu, 2010). From the point view of crystallization temperature, the addition of NA40/H-Ba enhanced the crystallization rate of iPP. Judging from the Avrami exponent, the spherulite of iPP grew in the way of three-dimensional during non-isothermal crystallization with the presence of NA40/H-Ba, which was in accordance with the other two  $\alpha/\beta$  compounded NAs.

	Compounded NAs	T <sub>C</sub> /℃	t <sub>1/2</sub> /s	n	$\overline{n}$
		123	42	2.70	
	iPP	125	66	2.58	2.85
		127	108	2.84	
		129	197	3.10	
		131	428	3.04	
Phosphate/Amide		133	24	2.76	
	NA40/NABW	135	47	2.61	2.77
		137	78	2.77	
		149	141	2.99	
		141	252	2.72	
		124	180	2.44	
		126	306	2.43	
	iPP	128	516	2.6	2.54
		130	840	2.63	
Sorbitol/Amide		132	1356	2.58	
		134	30	2.65	
	DMDBS/TMB-5	136	54	2.90	2.96
		138	102	3.00	
		140	204	3.30	

Table 1. Isothermal crystallization kinetics parameters of pure iPP and nucleated iPP (Bai & Wang, 2009; Zhang & Xin, 2007)

	Compounded NAs	Cooling rate Φ/ (°C/min)	T <sub>C</sub> /°C	$t_{1/2}/s$	n
		2.5	121.4	135	
Phosphate/Amide		5	118.8	78	
	iPP	10	115.9	44	3.75±0.03
		20	112.7	23	
		40	108.9	14	
		2.5	133.7	104	
		5	131.2	60	
	NA11/DCHT	10	128.5	25	3.66±0.11
		20	125.6	16	
		40	121.7	8	
		2.5	121.4	135	
		5	118.8	78	
	iPP	10	115.9	44	3.75±0.03
		20	112.7	23	
		40	108.9	14	
Sorbitol/Amide		2.5	128.7	121	
		5	124.6	69	
	3988/DCHT	10	120.2	43	2.88±0.25
		20	115.4	27	
		40	111.9	17	
		2.5	127.8	127	
		5	124.7	124	
	iPP	10	121.6	121	3.67±0.09
		15	119.8	119	
Phosphate/Carboxylate		20	118.4	118	
		2.5	137.9	115	
		5	135.3	60	
	NA40/H-Ba	10	132.6	33	4.52±0.04
		15	130.8	23	
		20	129.7	18	

Table 2. Non-isothermal crystallization kinetics parameters of pure iPP and nucleated iPP (Xu, 2010; Zhao & Xin, 2010)

Isothermal and non-isothermal crystallization kinetics of iPP nucleated by three kinds of  $\alpha/\beta$  compounded NAs were reviewed in this section. It can be concluded that compounded

NAs will increase the crystallization temperature of iPP, shorten the crystallization halftime. Consequently the molding cycle time of iPP will be reduced obviously, which has great importance for polymer processing. The obtained Avrami exponents indicated that the type of nucleation of iPP is changed from homogeneous to heterogeneous in the presence of the  $\alpha/\beta$  compounded NAs while the geometry of crystal growth of iPP remains threedimension spherical growth.

#### 3. Crystallization morphologies of iPP nucleated with $\alpha/\beta$ compounded NAs

The spherulite size of iPP can be decreased by cooperation with any kinds of NAs. But the morphology of nucleated iPP largely depends on the types of NA. The  $\alpha$  NA will only induce  $\alpha$  form iPP while  $\beta$  form iPP can be obtained by incorporating with  $\beta$  NA. Then what about the morphologies of iPP nucleated by  $\alpha/\beta$  compounded NAs?

Polarized optical microscope was used to investigate the crystallization morphologies of iPP nucleated with Phosphate/Carboxylate compounded NA, NA40/H-Ba by Xu et al. (Xu et al., 2011). As shown in Fig.1, in nucleated iPP, a large number of nuclei would be produced due to the existence of NAs. Therefore the spherulites cannot grow large enough to overlap, the size of spherulites in nucleated iPP would be much smaller than those in pure iPP. But as to the morphologies of the samples, iPP nucleated with NA40/H-Ba showed no sign of bright and colorful  $\beta$  crystals, appeared much close to the morphology of iPP induced by NA40 individually.

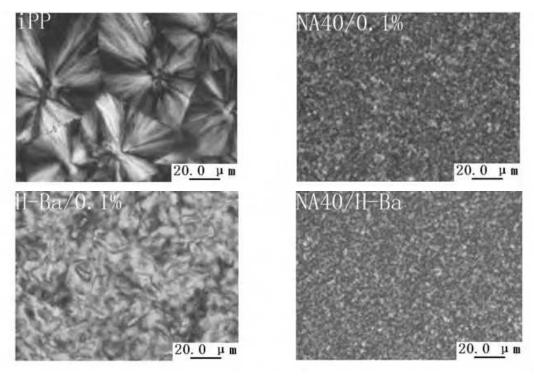


Fig. 1. Polarized light microphotographs for pure iPP and nucleated iPP samples crystallized at 135 °C (Xu et al., 2011)

The crystallization morphologies of pure iPP and iPP induced by Sorbitol/Amide compounded NA, 3988/DCHT were shown in Fig.2 (Zhao & Xin, 2010). From figure, it can be seen that with the addition of the  $\alpha/\beta$  compounded NA, the spherulite size decreased

significantly. Different from iPP with NA40/H-Ba,  $\beta$  form iPP became the majority in the morphology of iPP nucleated with 3988/DCHT. It can be considered that DCHT played a leading role during crystallization. The same conclusion was drew by investigating of iPP cooperation with 3988/NABW (Xu, 2010). The morphology of nucleated iPP was close to that incorporation with NABW individually. In addition, Bai et al. directly observed the crystallization morphologies of iPP nucleated with Sorbitol/Amide compounded NA, DMDBS/TMB-5 by SEM (Bai et al., 2008). Pure iPP showed the growth of well developed a spherulites with 30~50um in diameter. The size of iPP spherulites was also reduced with addition compounded NA. Similarly  $\beta$  form iPP dominated in the morphology of PP/0.1DM/0.1TM.

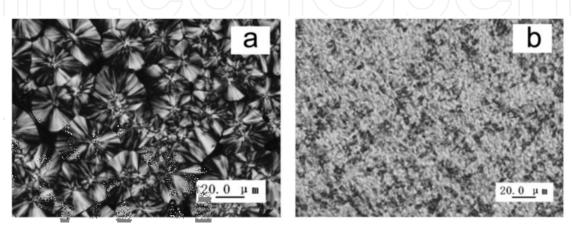


Fig. 2. Polarized light microphotographs for pure iPP and nucleated iPP samples crystallized at 140 °C (Zhao & Xin, 2010) (a) pure iPP, (b) iPP/ (3988/DCHT)

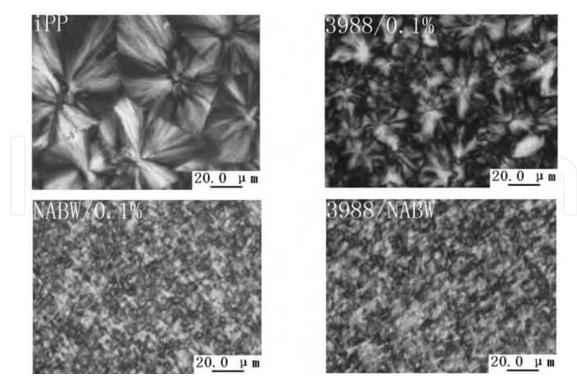


Fig. 3. Polarized light microphotographs for pure iPP and nucleated iPP samples crystallized at 135 °C (Xu, 2010)

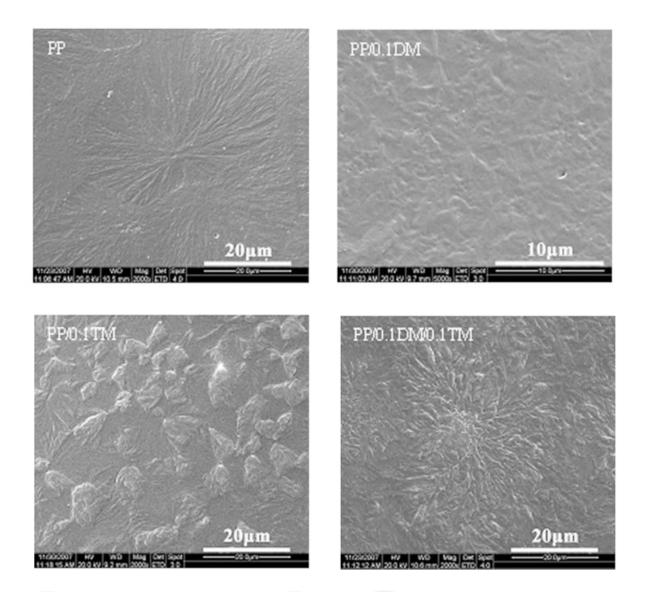


Fig. 4. SEM for pure iPP and nucleated iPP samples (Bai et al., 2008)

However, it was interesting that totally different results could be gained when the DCHT compounded with different  $\alpha$  NAs. Zhao et al. found the nucleation effect of NA11/DCHT compounded NA was between that of iPP/NA11 and iPP/DCHT. It can be seen from Fig.5, the spherulites of pure iPP showed the typical characteristic of  $\alpha$  crystal, which had a large size and clear boundaries (Zhao & Xin, 2010). By adding compounded NA, the spherulite size greatly reduced, indicating that compounded NA played a role of heterogeneous nuclei during crystallization. The content of bright and colorful  $\beta$  form iPP was less than that of iPP/DCHT, but was higher than iPP/NA40, which means at this condition the crystallization morphology of iPP was affected by both NAs within the compounded NA. The same result was got through the study on crystallization morphologies of iPP nucleated with Phosphate/Amide compounded NA, NA40/NABW by Xu, as shown in Fig.6 (Xu, 2010).

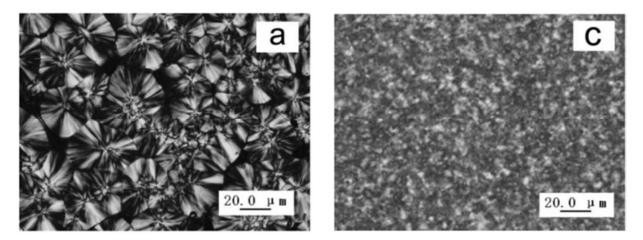


Fig. 5. Polarized light microphotographs for pure iPP and nucleated iPP samples crystallized at 140 °C (Zhao & Xin, 2010) (a) iPP, (c) iPP/ (NA11/DCHT)

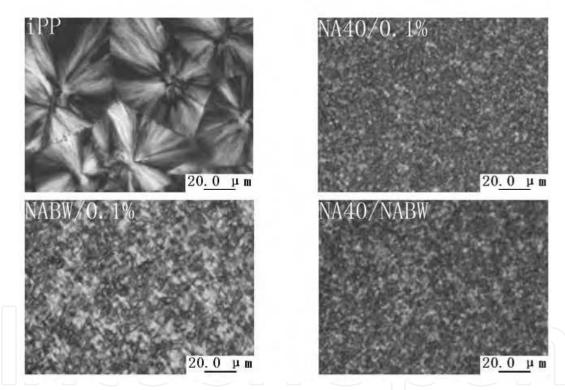


Fig. 6. Polarized light microphotographs for pure iPP and nucleated iPP samples crystallized at 135 °C (Xu, 2010)

All studies showed that the size of spherulites in nucleated iPP appeared much smaller than that of in pure iPP. However, iPP nucleated by different  $\alpha/\beta$  compounded NAs showed different crystallization morphologies. The morphology of iPP nucleated Phosphate/Carboxylate compounded NA, NA40/H-Ba was close to iPP nucleated by NA40 individually, while iPP nucleated by Sorbitol/Amide compounded NA, 3988/DCHT showed the similar morphology of iPP/DCHT. IPP nucleated with Phosphate/Amide NA40/NABW compounded NA presented a crystallization morphology that combined both NAs' within the compound system.

#### 4. Mechanical properties of iPP nucleated with $\alpha/\beta$ compounded NAs

The effects of different NAs on the crystallization process of polymer reflect on its mechanical properties finally, which determines on the use value of the polymer. Mentioned in the introduction, the  $\alpha$  NA can improve the stiffness and optical properties of iPP while decrease its toughness. The  $\beta$  NA will induce  $\beta$ -iPP during crystallization, which can improve toughness and heat distortion temperature of iPP while decrease its stiffness. Will it come true that we can balance the iPP's stiffness and toughness by compounding two kinds of nucleating agents?

Xu et al. investigate the effect of Phosphate/Carboxylate  $\alpha/\beta$  compounded NA, NA40/HB on the mechanical properties of iPP (Xu et al., 2011). As shown in Tab.3, tensile strength (ASTM D-638) and flexural modulus (ASTM D-790) of iPP were improved with the presence of NA40 while the impact strength (ASTM D-256) decreased. On the contrary, the impact strength of iPP could increase to 3.4 times to that of pure iPP but tensile strength and flexural modulus was reduced as always by adding HB. Numerically the mechanical properties of iPP nucleated with NA40/HB were close to that iPP/NA40, which showed no sign of enhancing the toughness of iPP.

	Compounded NA	Tensile strength / MPa	Flexural modulus / MPa	Impact strength /(J/m)
	iPP	29.8	1223	33.8
Phosphate/Amide	NA11 (0.1 wt %)	34.5	1770	30.2
	DCHT (0.1 wt %)	27.9	1143	74.0
	NA11/DCHT (1:1)	34.2	1669	49.7
	iPP	29.8	1223	33.8
Sorbitol/Amide	3988 (0.1 wt %)	31.5	1297	30.9
	DCHT (0.1 wt %)	27.9	1143	74.0
	3988/DCHT (1:1)	27.6	1108	73.4
Phosphate/Carboxylate	iPP	33.1	1052	35.6
	NA40 (0.1 wt %)	36.2	1562	33.2
	HB (0.1 wt %)	28.8	1025	158.2
	NA40/HB (1:1)	36.3	1521	34.2

Table 3. Mechanical Properties of Pure iPP and iPP Nucleated with Individual  $\alpha$ ,  $\beta$  and  $\alpha/\beta$  Compounded NAs (Xu et al., 2011; Zhao & Xin, 2010)

Similar to the effect on crystallization morphologies, different mechanical properties of iPP would be reached when the DCHT compounded with different  $\alpha$  NAs. Incorporation with Sorbitol/Amide compounded NA, 3988/DCHT can significantly improve the impact

strength of iPP, but was not benefit to the stiffness like tensile strength, flexural modulus (Zhao & Xin, 2010). It is exciting that the goal of enhancing the stiffness and toughness of iPP simultaneously can be reached by compounding DCHT with another  $\alpha$  NA, NA11. The tensile strength, flexural modulus and impact strength of iPP nucleated with NA11/DCHT was higher than those of pure iPP.

Mechanical properties such as tensile strength, flexural modulus and impact strength of iPP nucleated with three kinds of  $\alpha/\beta$  compounded NAs were investigated. The similar results to the study on crystallization morphologies were obtained. Incorporation with Phosphate/Carboxylate compounded NA, NA40/H-Ba only enhanced the stiffness of iPP, while with Sorbitol/Amide compounded NA, 3988/DCHT increased the toughness of iPP, which was close to iPP nucleated by DCHT individually. Compounding NA40 and DCHT could reach a good balance between stiffness and toughness of iPP. Then, what factor plays a dominant role when compounding  $\alpha$ ,  $\beta$  two kinds of nucleating agents?

#### 5. Optimization method for compounding $\alpha$ , $\beta$ NAs

Through reviewing on the crystallization kinetics, crystallization morphologies, and mechanical proprieties of iPP nucleated by  $\alpha/\beta$  compounded NAs, it can be noticed that some  $\alpha$ ,  $\beta$  NAs can induce iPP during crystallization respectively when they are compounded, hence improve the stiffness and toughness simultaneously. While some  $\alpha$  or  $\beta$  NA will play a leading role when it compounds with another NA. Thus the nucleating effect of the compounded NA appears close to the leading one, which goes against original intention of compounding  $\alpha$  and  $\beta$  NA. So find out the key factor of affecting the effect of  $\alpha/\beta$  compounded NAs is the precondition of successfully compounding  $\alpha$  and  $\beta$  NA.

From the traditional crystallization point of view, the overall crystallization rate depends on two stages: nucleation and growth. In the nucleation process, the formation of nucleus relies on the molecular movement in the molten spontaneously. Once the nucleus came into existence, the crystal grows in the form what nucleus is. So nucleation is the precondition for crystallization. The role of NA is to provide a large number of nuclei before the self-nuclei formed, which results in changing the homogeneous nucleation into a heterogeneous one. Furthermore, several studies on crystallization kinetics show that the NA has little impact on the growth stage of crystallization (Cai et al., 2010; Huang et al., 2005; Zhao & Xin, 2010). Accordingly, we believe that the crystallization form of polypropylene depends on the NA which comes into effect first in the nucleation stage. This sequence can be judged by the crystallization temperature (Tc) of polypropylene nucleated with NA individually. The NA with higher Tc means earlier the NA nuclei could be "accepted" by polypropylene and consequently comes into effect first in compounded system. So Tc is considered as the key factor of affecting the effect of  $\alpha/\beta$  compounded NAs.

Zhao et al. confirmed that the effect of compounded NA depends on which NA come into effect first during the nucleation stage (Zhao & Xin, 2010). The Tc of iPP induced by different NA individually was illustrated in Fig.7. It can be seen that Tc of iPP induced by DCHT was much higher than that of 3988. According to the mentioned assumption, when DCHT compounds with 3988, DCHT would play a leading role. Refers to the results in section 3 and section 4, it is clear that the nucleating effect such as crystallization morphologies and mechanical properties of Sorbitol/Amide compounded NA, 3988/DCHT appeared close to

that of DCHT. It can be noticed from Fig.7 that Tc of NA11 showed little difference to that of DCHT. During crystallization competitive nucleation takes place between two NAs, which results in the combined crystallization morphology and simultaneously increasing tensile strength, flexural modulus and impact strength of iPP. Xu et al. came to the same result by investigating Phosphate/Carboxylate compounded NA, NA40/H-Ba (Xu et al., 2011). NA40, the one with higher Tc plays a leading role in the crystallization while H-Ba showed no effect on inducing iPP. Therefore Tc is proved to be the key factor of affecting the effect of  $\alpha/\beta$  compounded NAs.

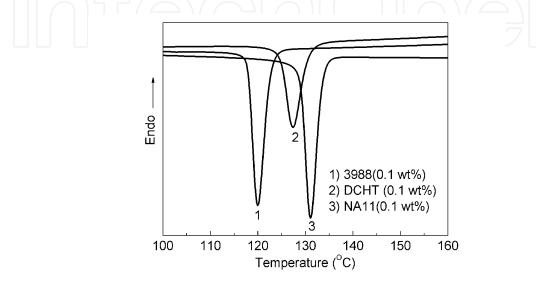


Fig. 7. DSC melting curves of iPP nucleated with individual α or β NAs (Zhao & Xin, 2010)

Sample	Т <sub>С</sub> / °С		
iPP	121.6		
NA40/iPP	130.2		
HB-a/iPP	125.1		

Table 4. Crystallization temperature of iPP nucleated with different NAs (Xu et al., 2011)

The key factor of affecting the  $\alpha/\beta$  compounded NAs was summarized in this part. That is the crystallization temperature of polypropylene nucleated with NA individually. The NA with higher Tc plays a leading role in the crystallization process. Consequently the mechanical properties, crystallization properties and crystallization morphologies of iPP appear close to it. Competitive nucleation will occur when the difference of Tc between the two NAs is not significant.

According to this, Tc becomes the one we can adjust that controls the crystallization behaviors of iPP based on  $\alpha/\beta$  compounded NA. It can be easily conclude that the principle of compounding  $\alpha$  and  $\beta$  NA is to make Tc of two NAs as close as possible, so as to let competitive nucleation happen. As known to all, the Tc of a NA depends on not only the species but the content of it as well. That is to say various addition amount of the same NA leads different Tc. Then, method for compounding  $\alpha$  and  $\beta$  NAs can be developed according

to this: First, we shall obtain Tc of iPP nucleated with different addition amounts of  $\alpha$  and  $\beta$  NAs individually by DSC. Then list T<sub>C  $\alpha$ </sub> and T<sub>C  $\beta$ </sub> at each ratio of compounded  $\alpha/\beta$  with a fixed concentration. The ratio which contains T<sub>C  $\alpha$ </sub> = T<sub>C  $\beta$ </sub> will be the optimal compounded ratio of these two  $\alpha$  and  $\beta$  NAs at this concentration. In this context, competitive nucleation will occur during crystallization.

#### 6. Practice of adjusting the stiffness and toughness of iPP based on $\alpha/\beta$ compound NAs

Here an example of adjusting the stiffness and toughness of isotactic polypropylene based on different of  $\alpha/\beta$  compound NAs was employed. Shi et al. studied the different ratios  $\alpha/\beta$ compounded NAs on mechanical properties of iPP (Shi & Xin, 2011). It was found that stiffness and toughness of iPP could be adjusted and enhanced simultaneously by changing the ratio of  $\alpha$  and  $\beta$  nucleating agents, as shown in Fig.8. Comparing to the others, the absolute value of difference of crystallization peak temperature between two kinds of NAs at optimal compounded ratio was the smallest. It verifies that the key factor summarized before can also be applied to different ratios  $\alpha/\beta$  compounded NAs. Then relying on the established method, the optimal compounded ratios of NA40/H-Ba and NA40/PA-03 (PA-03, Carboxylate  $\beta$  NA for iPP) were obtained, at which there appeared T<sub>C  $\alpha$ </sub> = T<sub>C  $\beta$ </sub> as shown in Fig.9. Refer to Fig.10, the calculated results were proved to be valid by the investigation of the effect of NA40/H-Ba and NA40/PA-03 with different ratio on mechanical properties of iPP, which means the method is applicable for compounding any NAs. Furthermore compounded NAs could enhance stiffness and toughness of iPP simultaneously with these ratios, as can be seen from Tab.5.

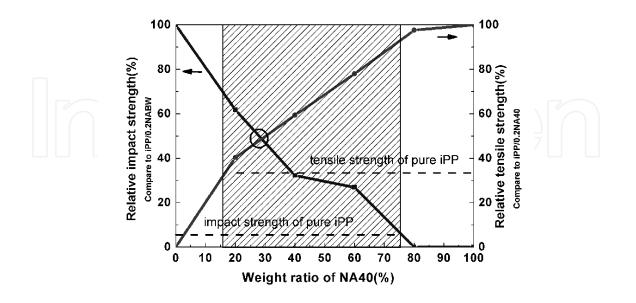


Fig. 8. Effect of NA40/NABW compounded NAs with different ratio on mechanical properties of iPP (addition amount 0.2wt %) (Shi & Xin, 2011)

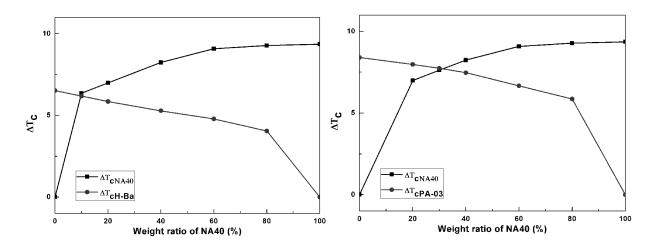


Fig. 9.  $T_{C\alpha}$  and  $T_{C\beta}$  at different ratio of NA40/H-Ba and NA40/PA-03 compounded NAs (addition amount 0.2 wt %)

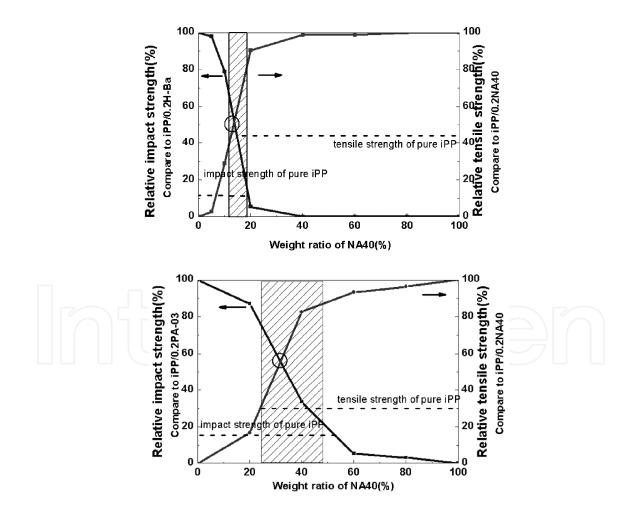


Fig. 10. Effect of NA40/H-BA and NA40/PA-03 compounded NAs with different ratio on mechanical properties of iPP (addition amount 0.2wt %) (Shi & Xin, 2011)

Nucleating agents	Compound ratio	Tensile strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
iPP	-	29.9	1171	31.7
NA40	-	32.9	1616	27.1
NABW	-	25.4	1031	98.2
NA40/NABW	1:3	31.1	1443	58.0
H-Ba		26.9	1018	93.6
NA40/H-Ba	1:9	30.8	1309	79.0
PA-03	-	27.1	1022	103.7
NA40/PA-03	3:7	31.0	1344	64.0

Table 5. Mechanical Properties of iPP Nucleated with different NAs (addition amount 0.2 wt %) (Shi & Xin, 2011)

#### 7. Conclusions

Nowadays  $\alpha/\beta$  compounded NAs for polypropylene have attracted more and more attention. This short review summarized the research on  $\alpha/\beta$  compounded NAs in recent years. Three kinds of well studied  $\alpha/\beta$  compounded nucleating agents (NAs), Phosphate/Amide, Sorbitol/Amide, and Phosphate/Carboxylate were selected to review their influence on the crystallization kinetics, crystallization morphologies, and mechanical proprieties of isotactic polypropylene (iPP). The results showed that  $\alpha/\beta$  compounded NAs could not only increase the crystallization temperature of iPP but also shorten the crystallization half-time, consequently reduce molding cycle time of iPP more obviously. The obtained Avrami exponent indicated that the type of nucleation of iPP could be changed while the geometry of crystal growth of iPP remains. The size of spherulites in nucleated iPP appeared much smaller than that in pure iPP. However, iPP nucleated by different  $\alpha/\beta$  compounded NAs showed different morphologies. The same result was obtained by the investigation of the mechanical properties of iPP. Some  $\alpha/\beta$  compounded NAs were able to enhance stiffness and toughness of iPP simultaneously while the other  $\alpha/\beta$  compounded NAs could only devote to one aspect. It was summarized that the key factor of affecting the  $\alpha/\beta$  compounded NAs is the crystallization temperature of iPP nucleated with NA individually (T<sub>C</sub>). The NA with higher Tc plays a leading role in the crystallization process. Consequently the mechanical properties, crystallization properties and crystalline microstructure of iPP appear close to it. Competitive nucleation will occur when the difference of Tc between two NAs is not pronounced. According to this rule, the optimization method for compounding a and  $\beta$  NAs was developed. That is to find out the ratio of  $\alpha$  and  $\beta$  NAs with T<sub>C  $\alpha$ </sub> = T<sub>C  $\beta$ </sub> so as to let competitive nucleation occur during crystallization. Then the method was applied to an example of adjusting the stiffness and toughness of iPP based on different of  $\alpha/\beta$  compound NAs. Rely on it the optimal ratios of  $\alpha/\beta$  compounded NAs can be easily determined by calculation T<sub>C</sub> at different ratios instead of testing them on mechanical properties. Sequentially it makes more effective to enhance stiffness and toughness of iPP based on  $\alpha/\beta$  compounded NAs.

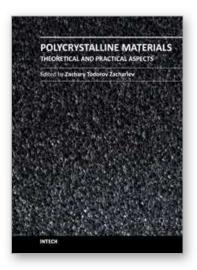
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