

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary investigation on the effect of nucleating agent types on mechanical properties of PP/EPR blend

It is generally known that polypropylene (PP) can crystallize to give more than one crystalline forms, i.e., α and β -forms. Its prevalent form depends on the nucleating agent type added. The prime objective of this experiment is to investigate the effect of various nucleating agents on mechanical properties of PP/EPR blend. Table 4.1 shows the mechanical properties of PP/EPR blend filled with Ca-Pim, NaBz, DMDBS or talc in comparison with those reported for unfilled PP/EPR blend.

Table 4.1 Mechanical properties of PP/EPR blends filled with different nucleant types at 0.1 %wt.

PP/EPR blends filled with	Tensile strength (MPa)	%Elongation at yield	Flexural modulus (MPa)	Izod impact strength (J/ m)
None	25.50 \pm 0.05	9.07 \pm 0.05	1,080 \pm 7.07	175.4 \pm 3.21
0.1%wt Ca-Pim	26.37 \pm 0.18	8.36 \pm 0.07	1,216 \pm 5.85	196.1 \pm 4.67
0.1%wt DMDBS	24.63 \pm 0.12	8.30 \pm 0.06	1,167 \pm 7.53	178.3 \pm 2.55
0.1%wt NaBz	31.15 \pm 0.15	7.40 \pm 0.08	1,500 \pm 9.49	95.4 \pm 2.12
1%wt Talc.	25.34 \pm 0.12	6.85 \pm 0.06	1,615 \pm 8.94	108.5 \pm 1.86

PP/EPR blend filled with 0.1 %wt. of two-component nucleator, the mixture of calcium stearate and pimelic acid (Ca-Pim), exhibits the highest Izod impact strength with a slight increase in the flexural strength, in comparison with the properties of the unfilled blend. In contrast, PP/EPR blend filled with 1%wt talc gives the highest flexural strength but quite low impact strength. While PP/EPR blend filled with 0.1%wt sodium benzoate (NaBz) imparts both high tensile strength and flexural strength but exhibits the lowest impact resistance. In the case of PP/EPR filled with 0.1%wt dimethyl dibenzylsorbital (DMDBS), the mechanical properties of the blend are similar to the one without any nucleating agent. It should be noted that both NaBz and talc, of which melting or decomposition temperatures are well above the processing temperatures of 210 to 250°C used to process the PP/EPR blend in this study at 400 and 900°C, respectively, are melt-insensitive nucleating agents. They can therefore act as single point nucleation sites within the matrix and could cause the crystallization of the polymer on these compounds. However, lattice matching between the oriented grown polymers and this type of nucleators is very important. The results showed that PP/EPR blend filled with either NaBz or talc exhibited much lower Izod impact strength than the one without the nucleators. The sudden drop of the impact strength is probably caused by the addition of these nucleators which could easily induce crazes. DMDBS, on the other hand, melts at 270°C, the temperature close to the processing temperatures. In contrast to Ca-Pim-filled PP/EPR blend, DMDBS-filled PP/EPR blend did not show an improvement in its mechanical properties, as compared to those of the unfilled blend.

The facts that the Ca-Pim-filled PP/EPR blend showed the best improvement on its Izod impact strength among all of the systems studied and that Shi and his co-workers [45-46] reported that β -form PP exhibited much higher impact resistance as compared to α -form PP led us to believe that the reason for the

highest impact strength observed in Ca-Pim-filled system was the result of the formation of the β -phase in the PP/EPR blend. Further investigations will be conducted in order to verify the hypothesis drawn.

4.2 Combined effect of talc and Ca-Pim on mechanical properties and morphology of PP/EPR blend

In previous section, it was found that talc-filled PP/EPR blend offered much higher flexural modulus than the other systems, whilst its Izod impact strength value was much lower, with the NaBz-filled PP/EPR exhibited the lowest value. On the other hand, the Ca-Pim-filled PP/EPR blend showed that the greatest value of Izod impact strength, as shown in Table 4.1. It should therefore be very interesting to see if it is possible to improve both Izod impact strength and flexural modulus at the same time by filling talc and Ca-Pim into both PP and PP/EPR blend simultaneously. The blended resins were molded for mechanical property testing, morphology study and thermal analysis.

4.2.1 Effect of talc loading on mechanical properties of PP/EPR blend

Talc is one of the well-known materials to be used commercially as reinforcing filler for improving the mechanical behavior of PP composites. McCenerty and Hooper [53] reported that formation of β -crystalline form can be taking place by adding various filler types such as calcium carbonate, wollastonite or talc. Indeed, most of fillers especially talc has been used to fulfill various industrial functions, e.g. upgrading flexural modulus or tensile strength of the final products. For this reason, it is interesting to investigate further whether talc influences the

formation of α -crystalline or β -crystalline form. This is very important since it has been reported that β -form PP offers greater impact strength and elongation properties in end-used products than does the α -form.

Specimens used in this study were prepared by blending talc with PP and PP/EPR blend at various percent loadings, either with or without the inclusion of 0.1%wt of Ca-Pim, respectively. This is to verify whether an increase in talc loading results in the reduction in the Izod impact strength (see Section 4.1) and whether inclusion of 0.1wt% Ca-Pim can compensate for such a decrease (due possibly to the formation of the β crystals formed as a result of the Ca-Pim addition. It should be noted that a solid evidence on the behavior of Ca-Pim as a β -nucleator can be found later in Section 4.2.4. Tables 4.2 and 4.3 illustrate the mechanical properties of talc-filled and Ca-Pim-filled PP/EPR and PP, respectively.

Table 4.2 Mechanical properties results of talc-filled and Ca-Pim-filled PP/EPR blend

Sample code	Nucleator contents (%wt)		Tensile strength (MPa)	Elongation at yield (%)	Flexural modulus (MPa)	Izod impact strength (J/m)
	Talc	Ca-Pim				
HC0	-	-	25.50 \pm 0.33	9.07 \pm 0.04	1,080 \pm 6.28	175.4 \pm 1.29
HC1	30	-	25.16 \pm 0.03	4.20 \pm 0.11	2,258 \pm 4.72	64.8 \pm 0.36
HC2	40	-	24.83 \pm 0.21	3.60 \pm 0.05	2,611 \pm 6.89	57.9 \pm 0.20
HC3	30	0.1	24.98 \pm 0.09	4.30 \pm 0.03	2,155 \pm 7.03	57.7 \pm 0.47
HC4	40	0.1	24.83 \pm 0.30	3.30 \pm 0.08	2,505 \pm 5.22	54.2 \pm 0.64

According to Table 4.2, the flexural modulus values of talc-filled PP/EPR blend at talc loading of 30 and 40 %wt., HC1 and HC2 samples, are more than twice as much as those of the unfilled PP/EPR blend. Somehow, the result showed more than two-fold in magnitude drop in the impact strength as compared to the unfilled system. The increase in the flexural modulus of talc-filled PP/EPR blend was in good agreement with the finding by Liu and Gilbert [54] who reported that talc generally imparts greater stiffness with creep resistance to the PP composites than other particulate fillers because of its platelike structure. Recently, Liu *et al.* [55] reported that talc-filled PP at loading contents up to 40%wt showed small amount of β -crystalline phase (ca. 1.8%), while the addition of wollastonite at 17.7%wt to PP could increase the amount of β -form (ca. 37%). After studied, it is widely accepted that talc behaves normally, i.e., as a result of its platelike nature, talc imparts stiffness even more than a carbonate filler, but it also degrades impact properties of PP specimens. In addition, Martinatti and Ricco [39] reported that the tensile yield stress of α -PP specimens tended to increase slightly with increasing talc content. This is due to the alignment of the lamellar shaped talc particulates in the drawing direction. Furthermore, Alonso *et al.* [43] indicated that talc acted as a heterogeneous crystallization nucleus, which markedly enhances the existence of the α -modification in the PP and suppresses the formation of the β -modification.

From all above investigations, talc performs majority on stiffness enhancement instead of impact strength improvement. Anyway, it needs to confirm the effect of talc if it is applied to our PP/EPR blend resin. Basically, PP/EPR blend resin used in this study has been specially designed to improve the impact strength in order to serve some specific applications, i.e. industrial sectors and automotive sectors which general PP can not. Shi and Zhang [45-46] who studied the effect of a β -nucleator (e.g. 0.1wt% quinacridone dye) on mechanical properties of PP found

that both elastic modulus and impact toughness of PP specimens were improved. Again, it has been proven elsewhere in this thesis that Ca-Pim is a β -nucleator (see Section 4.2.4).

According to Table 4.2, it appeared that the impact and flexural modulus values were nearly unchanged for the β -PP containing up to 30 and 40%wt. of talc. This implies that formation of the β -form in talc-filled PP/EPR blends could not offer impact strength enhancement. On the contrary, it would explain to the incorporation of talc filler onto β -PP that possibly caused the inferior performance. Besides, the other properties like tensile strength value was not significantly difference between filled and unfilled compositions. Eventhough the percentage of elongation of both filled and unfilled compositions exhibited almost two times lower that of conventional PP/EPR blend (HC0), it was not critical for industrial uses and still well-accepted in that range.

4.2.2 Effect of talc loading on mechanical properties of PP

It should be noted that studies on effect of talc on PP were designed to single out the possible “contamination” effect due to the presence of EPR copolymer in the PP/EPR blend (see Table 4.1). Tjong and Li [42] have already reported a study on the effect of talc on mechanical behavior of filled PP. In an attempt to verify their results, it was observed that 30wt%-talc-filled and 40wt%-talc-filled PP samples, HM1 and HM2, produced a large increase in the flexural modulus and slightly exhibited higher tensile strength (at yield) at an expense of the percent elongation (at yield) which exhibited a two-fold decrease in its values as compared with the unfilled sample (HM0) (see Table 4.3). This is in accordance with the results reported by Tjong and Li [42].

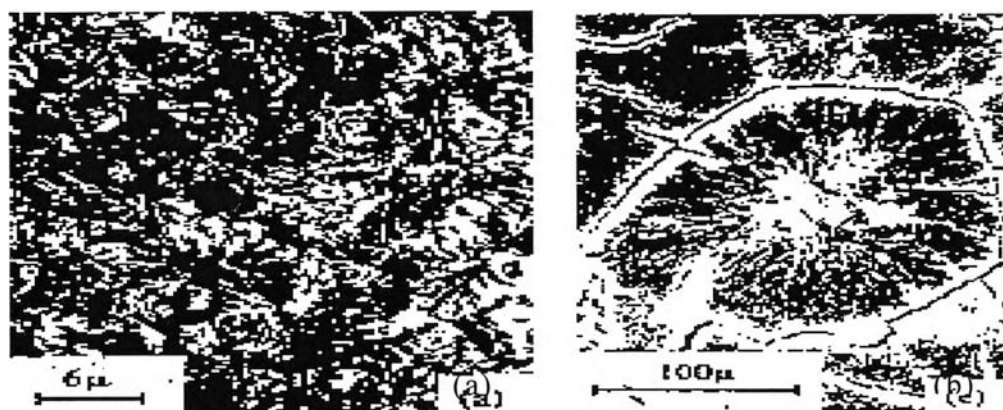
Table 4.3 Mechanical properties results of talc-filled and Ca-Pim-filled homopolymer PP.

Sample code	Nucleator contents (%wt)		Tensile strength (MPa)	Elongation at yield (%)	Flexural modulus (MPa)	Izod impact strength (J/m)
	Talc	Ca-Pim				
HM0	-	-	32.80 ±0.06	11.84 ±0.05	1,275 ±7.47	33.4 ±0.08
HM1	30	0.1	32.43 ±0.04	5.70 ±0.04	2,689 ±5.42	30.7 ±0.05
HM2	40	0.1	33.65 ±0.24	5.50 ±0.06	2,993 ±5.20	29.15 ±0.07

The impact strength was found to decrease slightly with increasing talc loading (see Table 4.3). This could be a result of the fact that talc is known to be the type of nucleating agent which mainly generates α -crystalline form rather than the β -crystalline form which can enhance the impact strength of the product.

4.2.3 Morphological study of talc-filled PP and PP/EPR blend based on SEM

In order to further support the results shown in Sections 4.2.1 and 4.2.2, scanning electron microscopy (SEM) technique was used to identify α and β crystalline structures. It is generally known that the spherulitic crystal structure plays a key role in controlling fracture behavior and mechanical properties of polymer specimens. For a morphological study of β -form spherulites, all PP molded plates were etched with an aqueous solution of $\text{KMnO}_4/\text{H}_2\text{SO}_4.\text{H}_3\text{PO}_4.\text{H}_2\text{O}$ for at least 5 hours then the samples were washed, dried and plated with gold prior to the SEM observations. The recent work of Tjong *et al.* which presented the spherulitic morphology of the α -form in mixing with predominant fine β -crystalline form of PP is shown in Figures 4.1 (a) and the morphology of α -spherulites in Figures 4.1 (b).



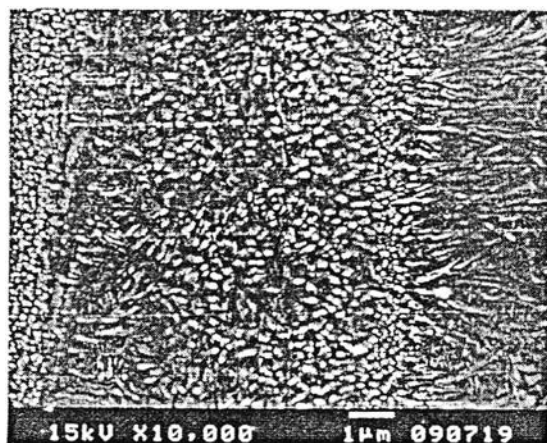
Figures 4.1 SEM micrographs of (a) predominant fine β -crystallines with few α -crystallines, (b) morphology of α -crystalline form

Theoretically, homopolymer PP normally gives majority of α -crystalline form but Figure 4.2 (a) belonged to unfilled PP that could not evidently show the distinguished α -form boundaries as Norton mentioned. Somehow, Figures 4.2 (b) and (c) revealed two boundaries of both crystalline forms. Different crystals nucleate separately with developing their distinct boundaries during crystallization. The basis of crystalline form of talc used in this study was a lamellae shape [6] the same as employing in commercial applications. It implies to offer a majority of the α -form. This is probably the reason that small amount of Ca-Pim addition was unable to induce the β -crystalline form. Another reason could be used to explain the observation. If the growth of the α -form spherulites nucleated at a higher temperature was accelerated to an adequate speed by the addition of talc, they could grow to impingement before the β -spherulites nucleated and began to crystallize at a lower temperature. Thus, the growth of the β -form was repressed. It would further link to impact strength of PP specimens dropped, whilst the flexural strength raised up.

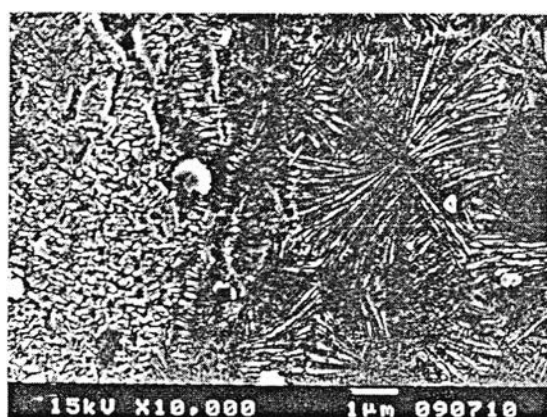
By all means, Figures 4.3 (a)–(e) could elucidate using the same concepts as mentioned above. Additionally, the X-ray diffraction analysis is one of the most efficient technique to examine β -crystalline form. All results including details were continued to be presented in section 4.2.4



(a) HM0



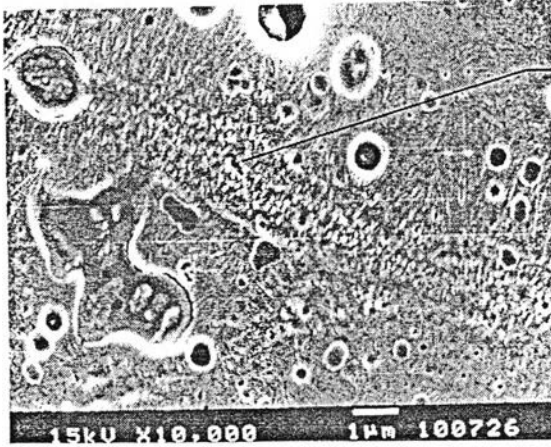
(b) HM1



(c) HM2

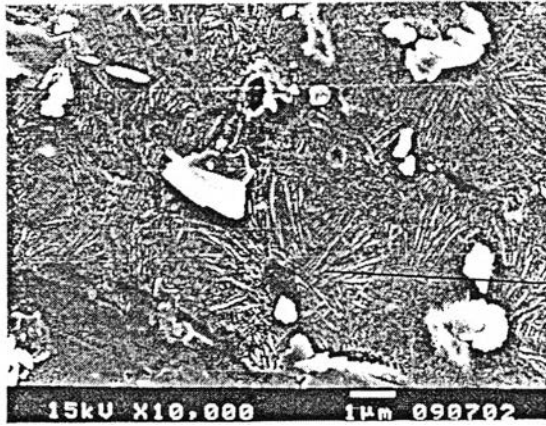
Figure 4.2 SEM micrographs of talc-filled β -homopolymer PP:

(a) unfilled, (b) 30%wt of talc and 0.1%wt of Ca-Pim, (c) 40%wt of talc and 0.1%wt of Ca-Pim



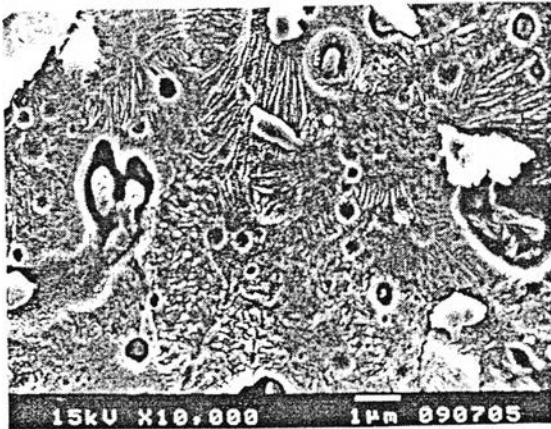
(a) HC0

Rod-like structure of β -spherulite boundaries

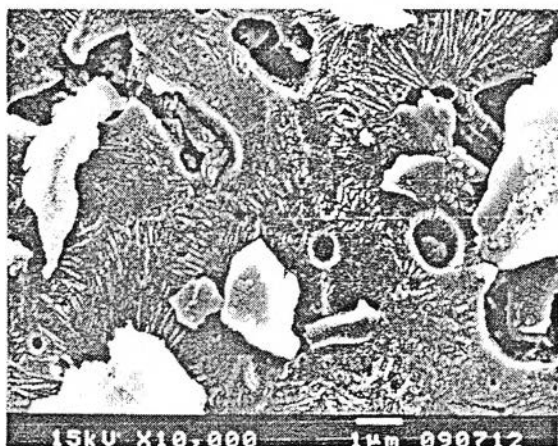


(b) HC1

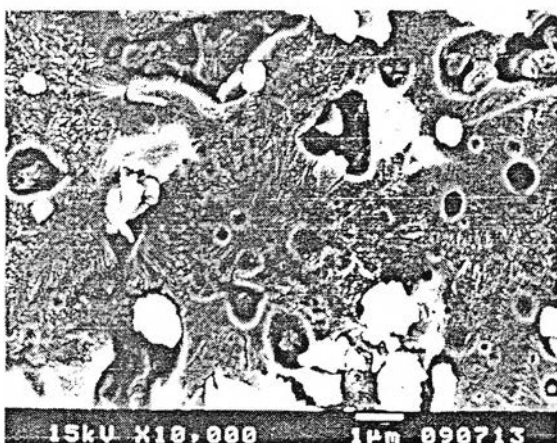
α -spherulite region



(c) HC2



(d) HC3



(e) HC4

Figures 4.3 SEM micrographs of talc-filled β -PP/PER blends:

(a) unfilled, (b) 30%wt of talc, (c) 40%wt of talc, (d) 30%wt of talc and 0.1%wt of Ca-Pim, (e) 40%wt of talc and 0.1%wt of Ca-Pim

4.2.4 Morphological study of talc-filled PP and PP/EPR blend based on WAXD technique

It was obviously seen that from Figures 4.4 (a) and (b) exhibited the typical WAXD diagrams of the β -phase content in homopolymer and PP/EPR blends. The relative amount of the β -phase content (defined as “K-value”) in testing specimens can be calculated by equation in Chapter II. The calculated K-value of homopolymer as well as PP/EPR blends (without talc-loaded) are 0.089 and 0.209, respectively. The results were summarized in Table 4.4. It indicated that β -crystalline phase could occur more rarely than the α -form did under most conditions. Fujiwara *et al.* [56] reported that the β -form is observed only occasionally during crystallization or in melt-crystallized spherulites formed in particular conditions and it appears as a minority constituent of the iPP. Under specific crystallization conditions or when appropriate β -nucleators are used, high levels of β -form can be generated.

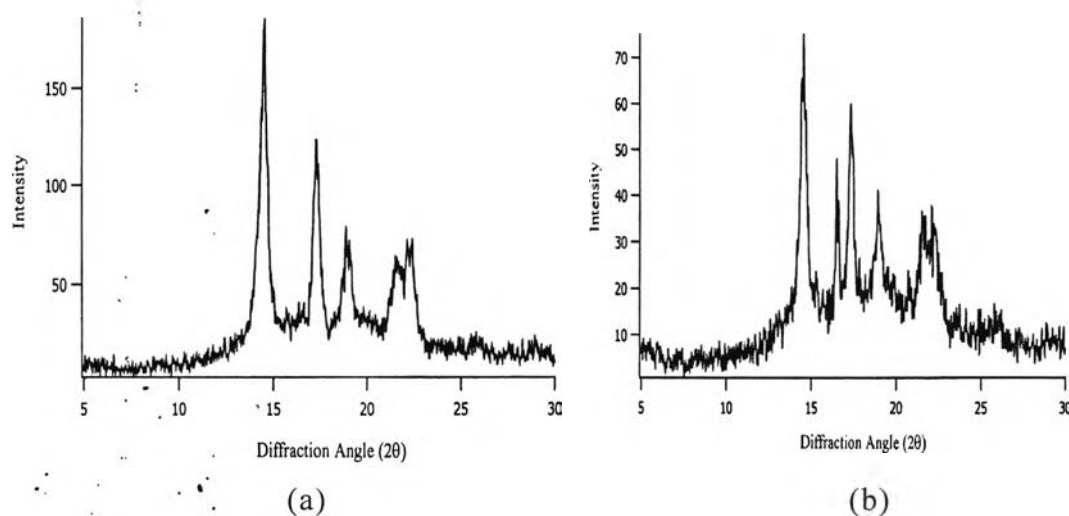


Figure 4.4 WAXD diagrams of : (a) homopolymer PP (HM0) and PP/EPR blends (HC0)

Figures 4.5 (a)-(f) show WAXD patterns for homopolymer and PP/EPR blend with 0.1% β -nucleator plus talc-filled at 30 and 40% wt.

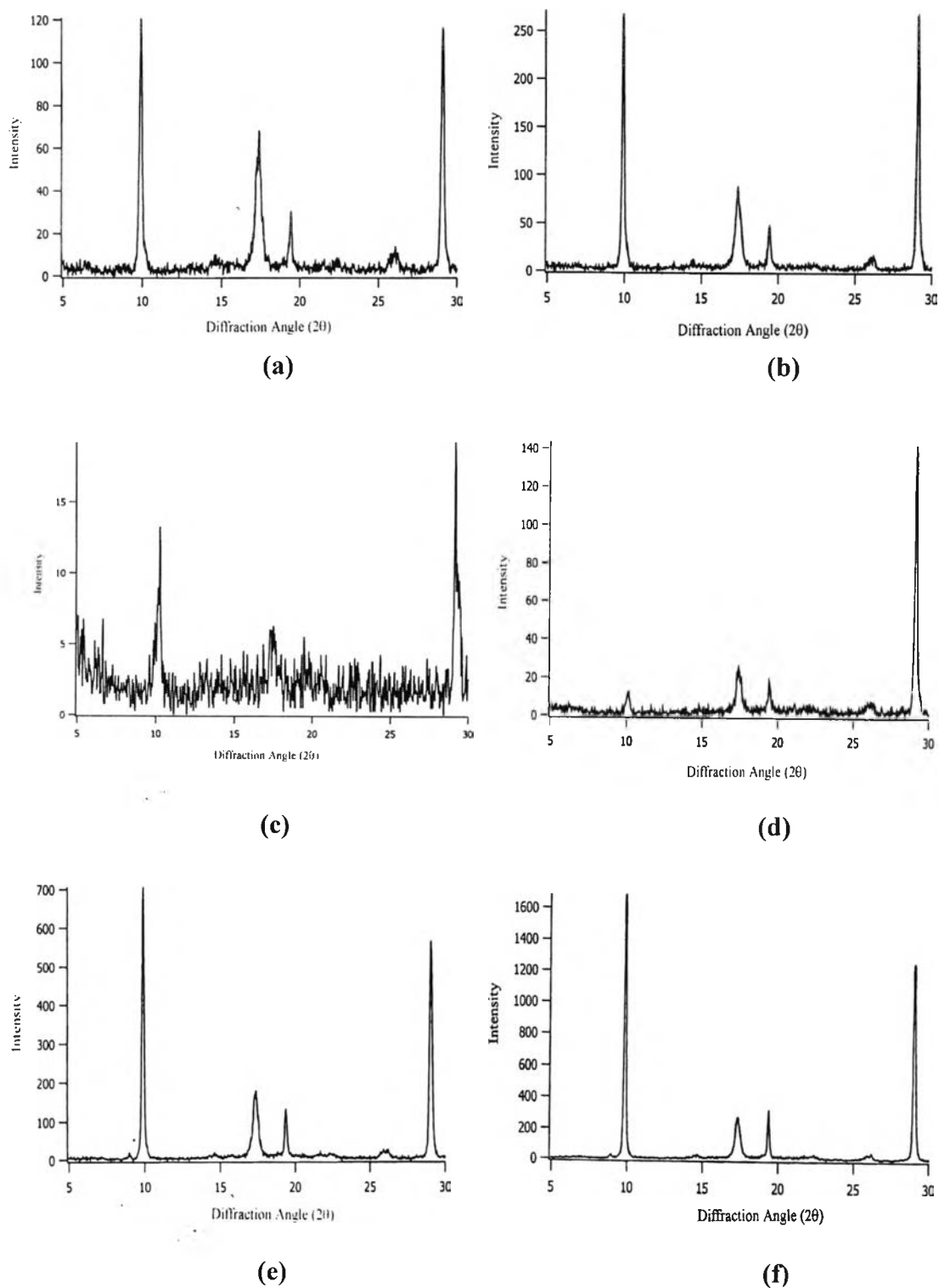


Figure 4.5 WAXD diagrams of : (a) HM1, (b) HM2, (c) HC1, (d) HC2, (e) HC3 and (f) HC4

Table 4.4 β -Phase index (defined as K- value) of the talc-filled PP and PP/EPR blend resins

	Composition (%wt)		$H\beta$	$H\alpha_1$	$H\alpha_2$	$H\alpha_3$	K-value
	Talc	Ca-Pim					
HM0 (homopolymer)	-	-	41	198	129	91	0.089
HM1	30	0.1	0	128	69	112	0
HM2	40	0.1	0	0	88	46	0
HC0 (PP/EPR blends)	-	-	49	79	61	45	0.209
HC1	30	-	0	0	8	6	0
HC2	40	-	0	0	37	18	0
HC3	30	0.1	0	0	198	176	0
HC4	40	0.1	0	0	226	380	0

As expected, PP/EPR blends with talc loading contents at 30 and 40% by weight, HC1 and HC2, respectively were attributed the K-value dropped significantly to zero. Apparently, the WAXD patterns in accordance with Figures 4.5 also clearly confirmed that the (300) diffracting plane of the β -phase diminished as talc content reaches 30 and 40 %wt. In this case, only diffraction peak of the α -crystalline form and talc phases predominate.

Besides, there was no β -peak occurrence in WAXD diagrams of the formular HM1, HM2, HC3 and HC4, that contained 0.1%wt Ca-Pim. Their K-values were also dropped to zero according to Table 4.4. This implies that the small amount of Ca-Pim may not influence the prevalent α -crystalline phase, therefore it could not

4.2.5 Effect of talc-filled to β -PP and PP/EPR blends on melting behavior DSC

In this study, the DSC measurements revealed the melting temperature and the percentage of crystallinity values. Theoretically, homopolymer PP normally provides melting temperature approximately 161-164°C with the percentage of crystallinity at 55. However, PP/EPR blends resin gives melting temperature as well as the percentage of crystallinity somewhat a bit lower than homopolymer. The previous study of Jacoby and Bersted had reported that the melting peak at 148°C was belong to the melting of β -crystalline form PP. On the other hands, the endothermic peak at 160°C is due to the melting of α -form PP.

Table 4.5 exhibits thermal properties data of β -PP and PP/EPR blends with and without talc loading. Moreover, it was seen from the DSC endothermic curve as of Figure 4.6 that the melting temperature of PP/EPR blends resin is 160.4°C. From calculation, the percentage of crystallinity is approximately 46.7. Small amount of ethylene unit in EPR could contribute to the observed T_m at 160°C, lower than homopolymer PP. In addition, the irregular chain structure of EPR could also suppress crystallization efficiency of PP to α - and β -forms. The effects of PP/EPR blends structure is to specially obtain the impact strength enhancement with balancing of better flexural modulus than conventional PP resin.

It is evidently shown from the DCS thermogram (Figure 4.6) that the melting peaks of HC1 and HC2 shifted up to higher values. The increase of T_m is possibly due to the high-temperature raising up the melting of the α -crystalline phase which formed by talc addition. In addition, the percentage of crystallinity of HC1 and HC2 were lower than both conventional PP/EPR blends and homopolymer PP. It is truly remarkable since an increase in flexural modulus or stiffness in a filled PP, is normally associated with a decrease in impact strength. Actually, it is certainly accepted that increasing of percentage of crystallinity value will relate to increasing of flexural modulus of PP [72]. As a result of its lamellae or plate-like structure, it demonstrated that talc platelets are aligned parallel to each other in the composites. Hence, it is undoubtedly to invoke the explanation why talc enhances modulus of

Table 4.5 Crystallization and melting of nucleated homopolymer PP and PP/EPR blend resins

PP compositions	T_m (°C)	T_c (°C)	Percentage of crystallinity
PP (reference)	161.1	92.5	54.5
HM0 (homopolymer)	160.7	92.3	53.8
HM1	162.7	115.3	42.4
HM2	162.4	115.9	33.0
HC0 (PP/EPR blends)	160.4	97.6	46.7
HC1	164.4	112.6	36.2
HC2	164.1	112.9	34.8
HC3	162.7	115.6	32.4
HC4	163.1	116.6	26.8

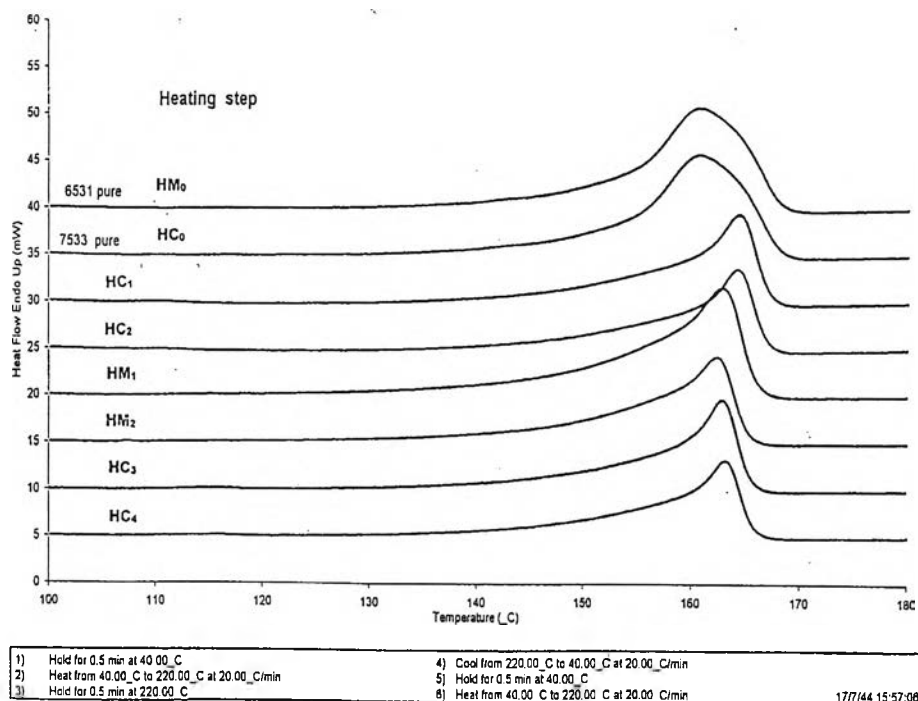


Figure 4.6 DSC thermograms of homopolymer PP and PP/EPR blends with and without additives

elasticity or stiffness but degrades impact properties [63]. The disturbance in percentage of crystallinity reduction instead of increment after talc filled to PP/EPR blends alone, would probably from interference of crystallization of EPR-phase and talc particles alignment or the hindrance from talc agglomeration during crystallization.

Composite blends of 0.1%wt Ca-Pim added to homopolymer PP and/or PP/EPR blends with 30 and 40% wt talc showed higher melting temperatures than those of the unfilled PP, PP/EPR blends and previous talc formulates alone presented. That meant β -crystallization has rarely occurrence but would rather have α -crystalline form instead. From table 4.5 and DSC thermograms in Figures 4.6, it was obviously found that 0.1%wt of Ca-Pim added to the polymers could not induce β -crystal formation. Somehow, this finding is opposite to a recent publication by Shi and coworkers. They found that adding only 0.1%wt of Ca-Pim to homopolymer PP could build up the relative β -phase content as high as 94%. They also pointed out that the β -form PP specimens exhibit a lower yield strength but a higher impact strength than those of the α -form samples. By referring to all WAXD and DSC measurements data relative to mechanical properties value obtained in sections 4.1, 4.2.1, 4.2.2, 4.2.3 and 4.2.4, were all in line with mostly of literature reviews. It is to confirm talc behavior the physical testing results of homo. PP and PP/EPR blends in items 4.2.1 and 4.2.2.

4.3 Formation of β -phase by Ca-Pim in PP/EPR blends

As discussed in previous sections, both PP and PP/EPR blends filled with talc was found that it tended to suppress the formation of β -crystalline form, whereas Ca-Pim enhanced β -crystalline formation. In order to confirm the existence of β -crystalline form in PP/EPR blends, several techniques can be used such as x-ray diffraction, scanning electron microscopy and differential scanning calorimetry. In addition, the measurement of izod impact strength as well as flexural modulus can indicate whether there is β -crystalline creation or not. From a recent paperwork of

Jacoby *et al*, quinacridone dye, one type of high effective β -nucleator filled with homopolymer PP also produced β -crystalline form. The report was presented that homopolymer PP containing high levels of the β -crystalline form, exhibited lower values of the modulus and yield stress but higher impact strength and percentage of elongation. It is very interesting to extend and clarify relationship between β -crystalline formation onto mechanical behavior of PP/EPR blends. As a consequence, this thesis paperwork was scoped for better understanding the relationship among crystallization, thermal properties, morphological characteristics and mechanical properties of β -PP/EPR blend.

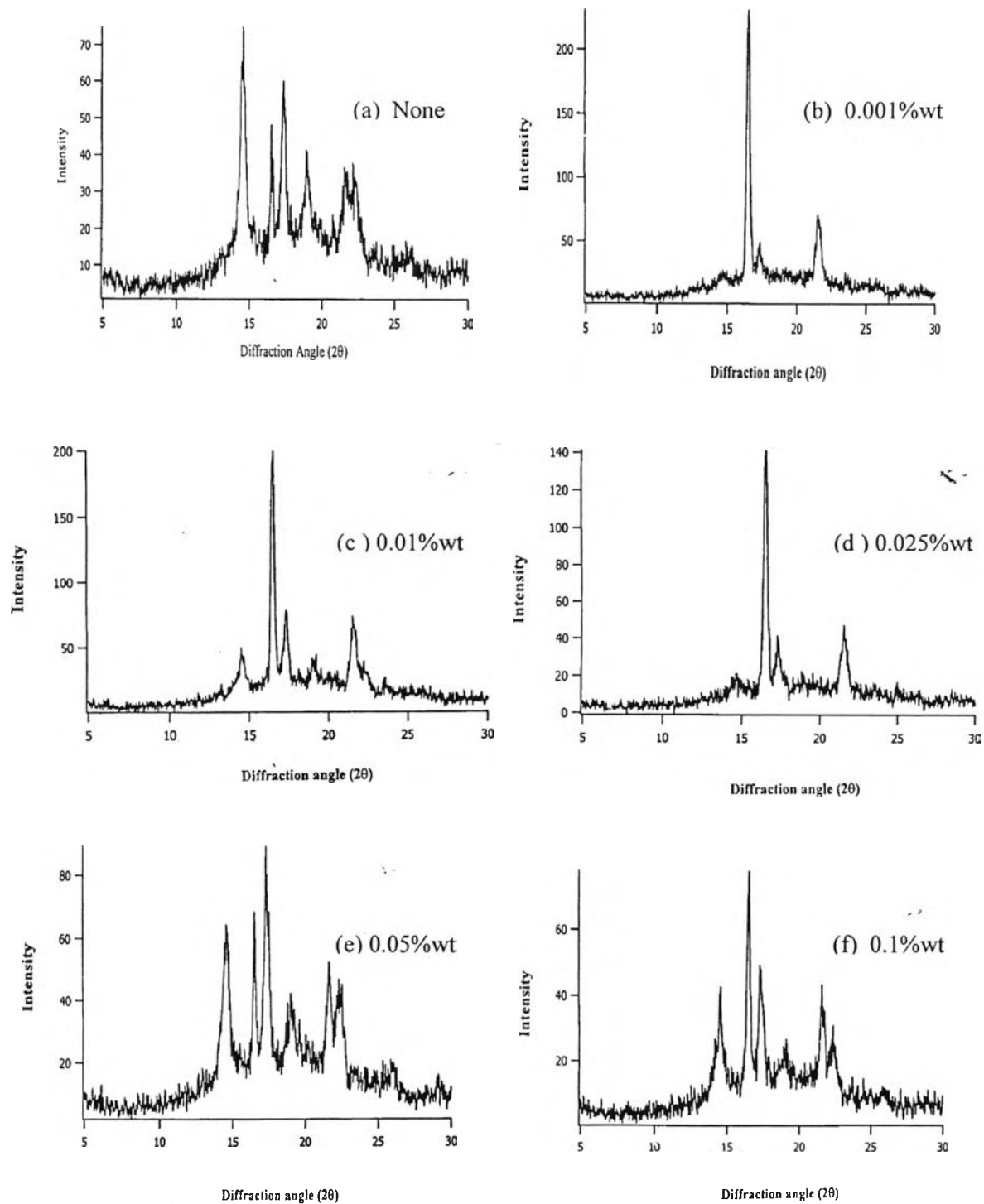
4.3.1 Determination of β -PP/ EPR blends using WAXD

The compression-molded plaque samples of PP/EPR blends with various amount of Ca-Pim, i.e., PP/EPR₀ (no Ca-Pim content), PP/EPR₁ (0.001%wt. Ca-Pim), PP/EPR₂ (0.01%wt. Ca-Pim), PP/EPR₃ (0.025%wt. Ca-Pim), PP/EPR₄ (0.05%wt. Ca-Pim) and PP/EPR₅ (0.1%wt. Ca-Pim), were prepared. They were examined by using wide angle x-ray diffractometry. The WAXD diagrams of these samples were shown in figures 4.7(a) – (f). The relative proportions of both α and β -forms could be obtained by calculating the height of the designated peaks according to equation in chapter II. The relative amounts of the β -form expressed in terms of the K-value were all summarized in Table 4.6

For unfilled PP/EPR blend, the amount of β -crystalline form is low, 20.9% which is indicated as K-value of 0.209. The amount of β -crystalline form increased when Ca-Pim was added, to a maximum % CaSt form of 74.5% for 0.001%wt Ca-Pim. At 0.1%wt. of Ca-Pim, the β -crystalline form was nearly the same as unfilled PP/EPR blends.

Table 4.6 K- value of β -PP/EPR blends at various Ca-Pim contents

Samples	Ca-Pim contents (% wt.)	H β	H α_1	H α_2	H α_3	K- value
PP/EPR ₀	0.000	49	79	61	45	0.209
PP/EPR ₁	0.001	234	30	50	0	0.745
PP/EPR ₂	0.010	147	24	46	0	0.68
PP/EPR ₃	0.025	209	48	75	40	0.54
PP/EPR ₄	0.050	68.5	63.75	89.5	42.5	0.395
PP/EPR ₅	0.100	61	47	68	37	0.26



Figures 4.7 WAXD diagrams of β -crystalline form PP/EPR blends with and without Ca-Pim

4.3.2 Thermal analysis of β -PP/EPR blend using DSC

In this study, DSC is also used to identify the existence of β -crystalline form in PP/PER blends. It has been known that β - and α - crystalline forms in both homopolymer PP and copolymer PP exhibited endothermic melting peaks in the range of 146-149°C and 160-161°C, respectively. Figures 4.8 shows the DSC traces of PP/EPR blend with various amount of Ca-Pim. Only one melting peak at 160.4°C is observed for unfilled PP/EPR blend, PP/EPR₀. For PP/EPR blends with Ca-Pim, i.e., PP/EPR₁, PP/EPR₂, PP/EPR₃, PP/EPR₄ and PP/EPR₅ at least two melting peaks can be found at 140-150°C and 155-165°C. This observation clearly confirmed that the transformation of α to β -crystalline forms when Ca-Pim is added into PP/EPR blends. It can be seen easily that the relative areas of both peaks change with the amount of Ca-Pim in PP/EPR blends. The high amount of Ca-Pim is used, the melting peak of α -crystalline form is more dominant.

Besides, sample PP/EPR₂ presented the double melting of the β -crystalline form. Fujiwara and Shi *et al.* [56, 46] explained that the double melting peak were caused by melting of the original β -crystalline form and subsequent recrystallization to a stabler structure (β') and its melting during scanning. Moreover, the PP/EPR₂ and PP/EPR₃ also exhibit two melting peaks of the α -crystalline form at 166 and 171°C. The presence of two α -form peaks could be induced by conditioning at higher temperature than 155°C or DSC performed at low scanning rate, less than 5°C/ min [57-58].

From Table 4.7 and Figures 4.8, it was found that PP/EPR₁ containing 0.001%wt. of Ca-Pim, has the highest β -crystalline form comparing to the other blends.

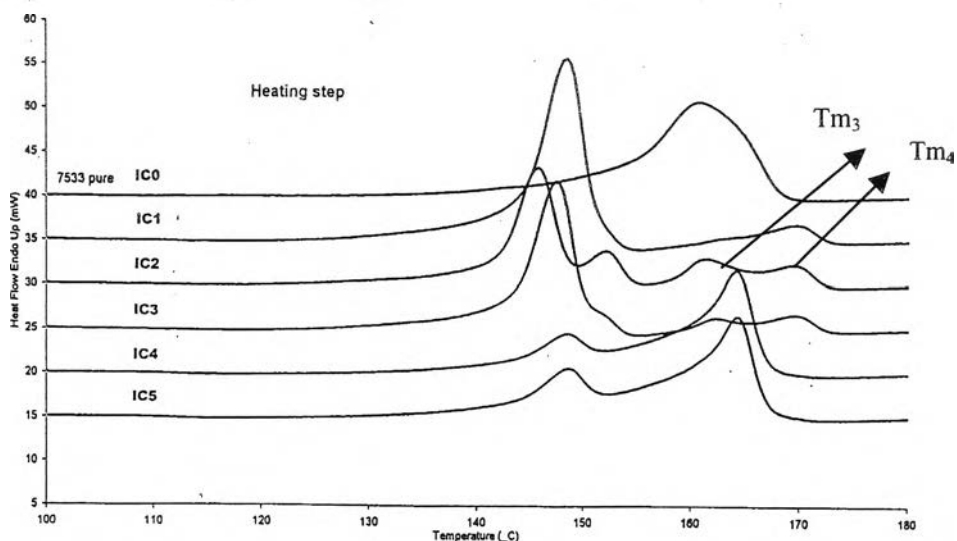


Figure 4.8 DSC traces of PP/EPR blend at various Ca-Pim content (%wt.)

Table 4.7 Crystallization and melting characteristics of Ca-Pim filled PP/EPR blends

Samples	Ca-Pim loading Content (%wt.)	Tm (α) (°C)	Tm (β) (°C)	Percentage of crystallinity	K value
PP/EPR ₀ (IC0)	0	160.4	-	46.7	0.209
PP/EPR ₁ (IC1)	0.001	162.5	148.4	40.98	0.745
PP/EPR ₂ (IC2)	0.01	166.3	147.2	41.24	0.68
PP/EPR ₃ (IC3)	0.025	167.8	150.1	41.32	0.54
PP/EPR ₄ (IC4)	0.05	164.4	151.4	43.90	0.395
PP/EPR ₅ (IC5)	0.1	164.8	152.5	49.5	0.26

Accordingly, the position of endothermic melting peak dominantly exhibited at 148.4°C. The analogous samples containing 0.01%wt of Ca-Pim, PP/EPR₂ also offered the β -form at melting peak of 147°C, which was closely to the PP/EPR₁ sample showed. However, the other analogous samples with concentration of Ca-Pim at 0.025, 0.05 and 0.1%, respectively were seen to have less of the β -form but gradually exhibited the position of α -form instead. The respective melting

temperature (T_m) for PP/EPR₃, PP/EPR₄ and PP/EPR₅ were 150.1, 151.4 and 152.5°C, respectively. It was obviously seen from endothermic peak positioning that shifted to the right-hand side value step by step. In fact, the presence of β -form should be increasing in accordance with increasing of Ca-Pim concentration in PP/EPR blend samples. Nevertheless, these observations indicated that Ca-Pim at higher concentrations effectively induced the α -form, since the reduction of β -peak had become less and less and detected the melting peak of α -form instead.

4.3.3 Morphology study of β -PP/ EPR blends using SEM

In order to examine the crystalline structure of PP/EPR blend filled with Ca-Pim, the compression-molded plaque of PP/EPR₁-PP/EPR₅ samples were etched in an aqueous solution of $\text{KMnO}_4/\text{H}_2\text{SO}_4.\text{H}_3\text{PO}_4.\text{H}_2\text{O}$ for at least 5 hours and then dried at room temperature. A thin layer of gold was evaporated on each plaque specimen before having the SEM investigations. Figure 4.9 – 4.15 exhibit the scanning electron micrographs of PP/EPR blends. These micrographs reveal that the addition of Ca-Pim 0.001%wt can induce the parallel stacked lamellae to cluster into bundles as shown in Figure 4.10. This phenomenon leads to the high packing rating and corresponds to the highest K-value and impact strength. When more Ca-Pim are added to PP/EPR blends, it may cause the separation of PP and EPR during processing. The agglomeration of EPR is thus possible which will prevent the formation of β -PP in the annealing stages. Moreover, Figures 4.11 and 4.14 presented the voids at the surface of specimens and it could possible a part of β -PP obstacle.

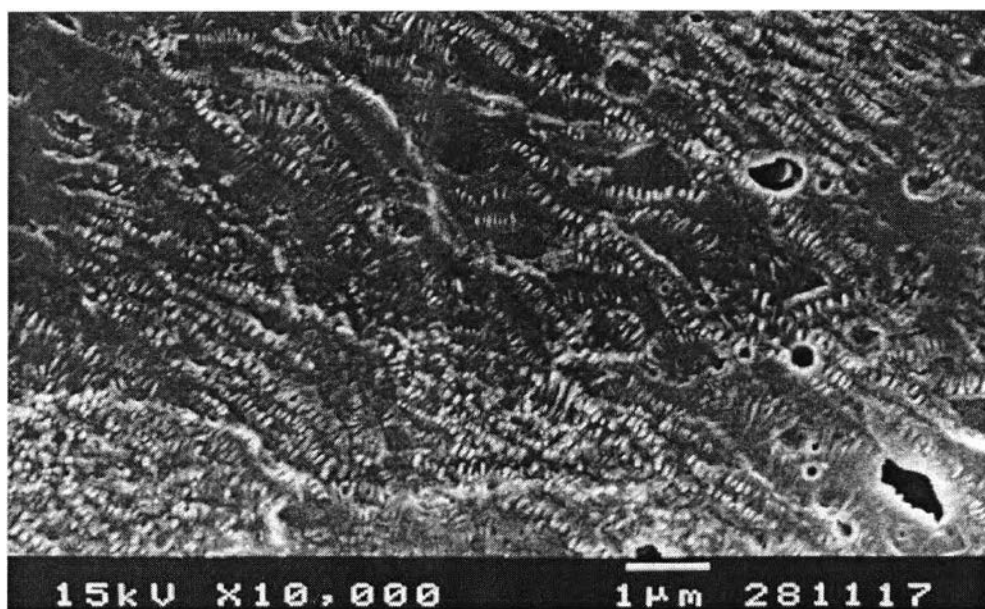


Figure 4.9 SEM micrograph of PP/EPR blend without addition of Ca-Pim

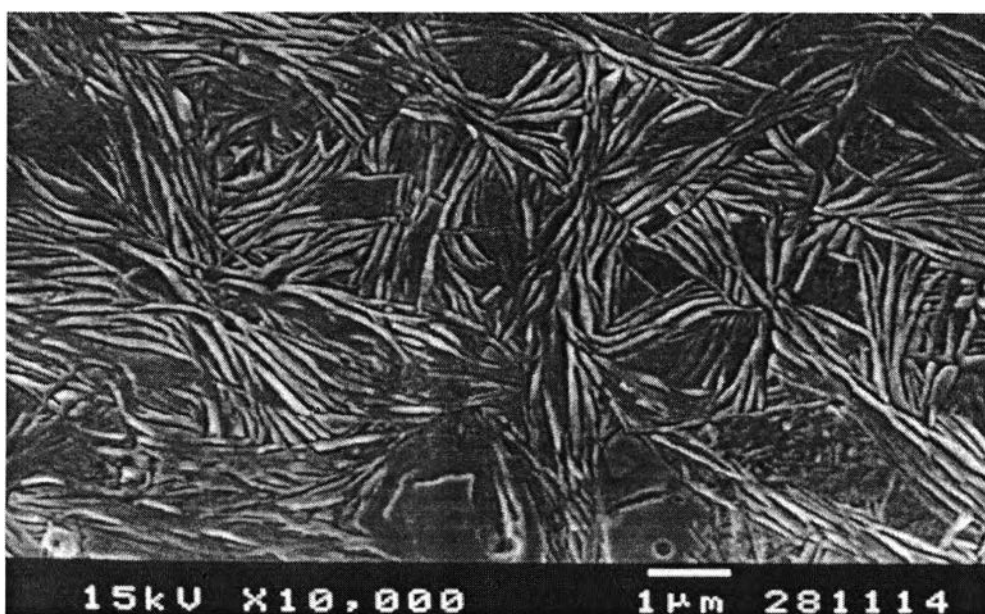
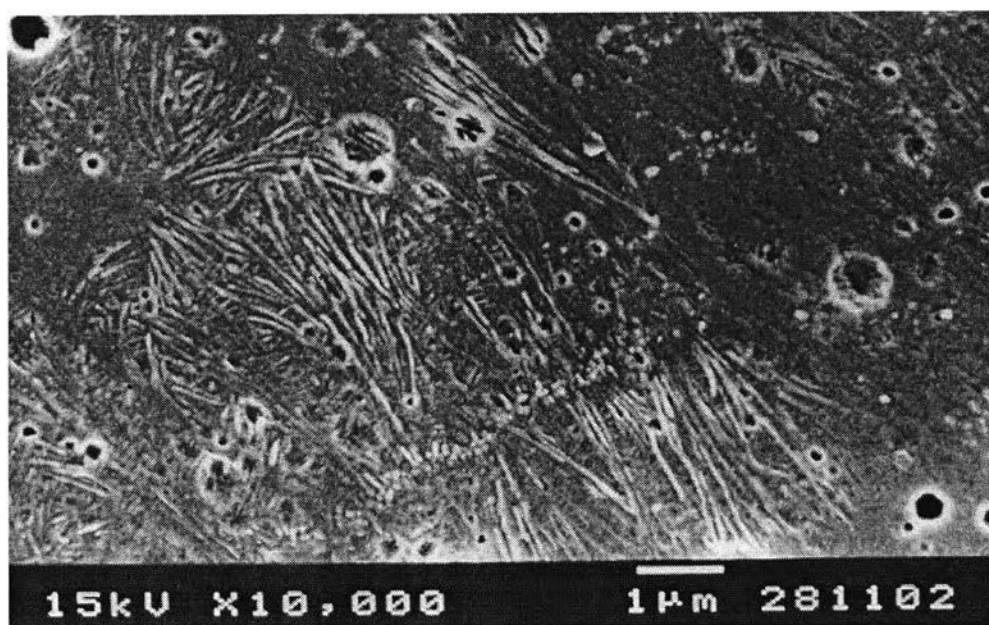
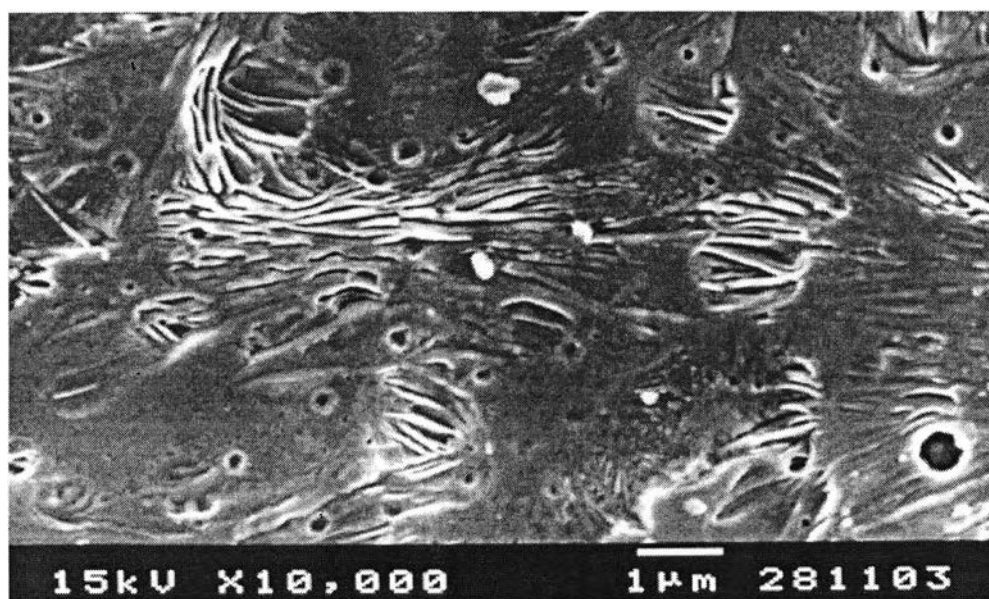


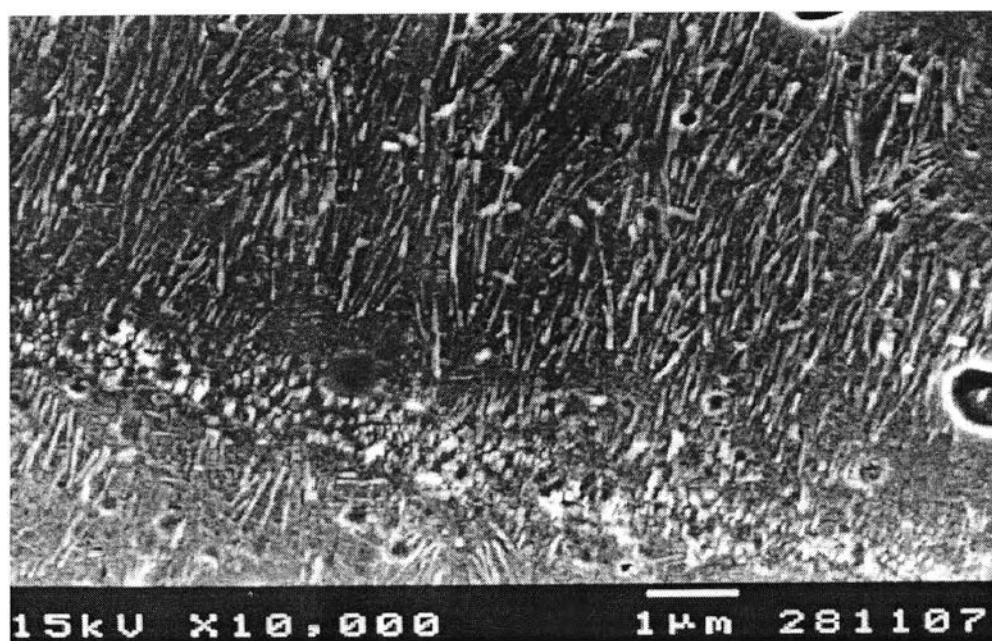
Figure 4.10 SEM micrograph of β -PP/EPR blend with concentration of Ca-Pim 0.001%wt.



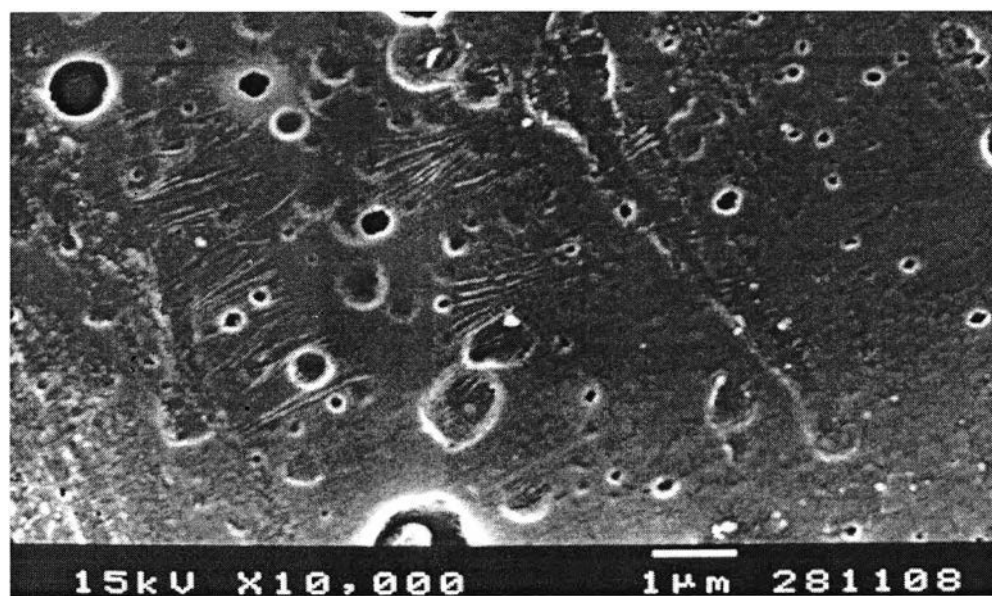
Figures 4.11 SEM micrograph of β -PP/EPR blend with concentration of Ca-Pim 0.01%wt.



Figures 4.12 SEM micrograph of β -PP/EPR blend with concentration of Ca-Pim 0.025%wt.



Figures 4.13 SEM micrograph of β -PP/EPR blend with concentration of Ca-Pim 0.05%wt.



Figures 4.14 SEM micrograph of β -PP/EPR blend with concentration of Ca-Pim 0.1%wt.

4.3.4 Mechanical properties of β -PP/EPR blends

In order to understand the parameter affecting mechanical properties of β -nucleated PP/EPR blend, it is worthwhile to looking closely at the relationship between the β -crystalline phase index, simply known as the K-value, and the mechanical testing results of each sample. Such data are summarized in Table 4.8

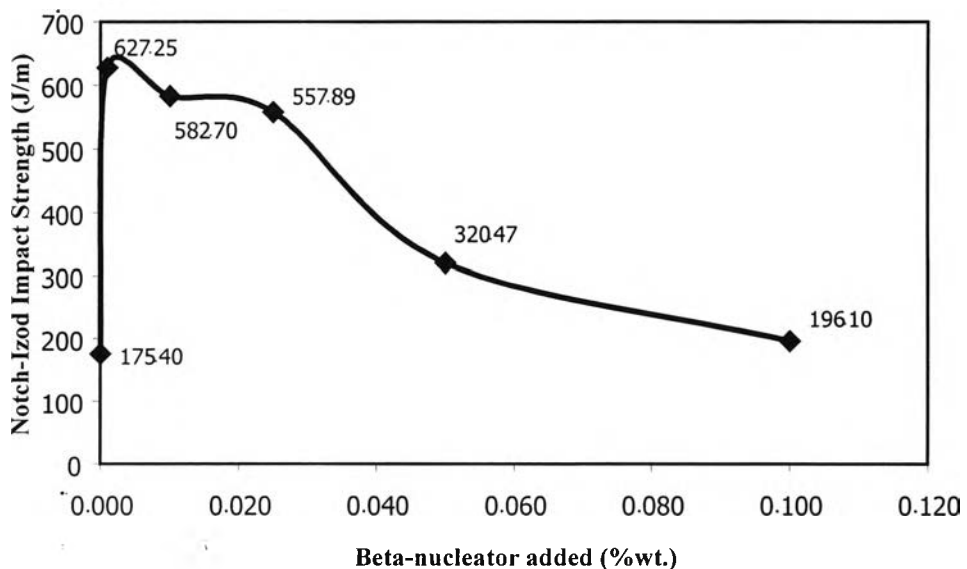
Table 4.8 Tensile strength, notch Izod impact strength, flexural modulus and % elongation at yield of β -PP/EPR blend at various contents of Ca-Pim and K-value.

	Ca-Pim concentration (%wt.)	K value	Tensile strength @ yield (MPa)	Notch Izod impact strength (J/m)	Flexural modulus (MPa)	% Elongation at yield
PP/EPR ₀	0	0.209	25.50 \pm 0.03	175.4 \pm 0.02	1,080 \pm 1.17	9.07
PP/EPR ₁	0.001	0.745	21.25 \pm 0.02	627.25 \pm 0.07	896.75 \pm 3.56	10.05
PP/EPR ₂	0.01	0.62	21.10 \pm 0.03	582.70 \pm 0.20	972.90 \pm 2.15	9.70
PP/EPR ₃	0.025	0.54	21.39 \pm 0.04	557.89 \pm 0.08	994.35 \pm 1.85	9.29
PP/EPR ₄	0.05	0.395	22.95 \pm 0.02	320.47 \pm 0.04	1,116.42 \pm 1.94	8.99
PP/EPR ₅	0.1	0.26	26.42 \pm 0.04	196.1 \pm 0.11	1,220 \pm 3.14	7.69

From Table 4.8, it is apparent that 0.001%wt-Ca-Pim-filled PP/EPR sample exhibited the highest Izod impact strength, which corresponding very well with the highest observed K-value of 0.745 as compared with other formulations. The fact that

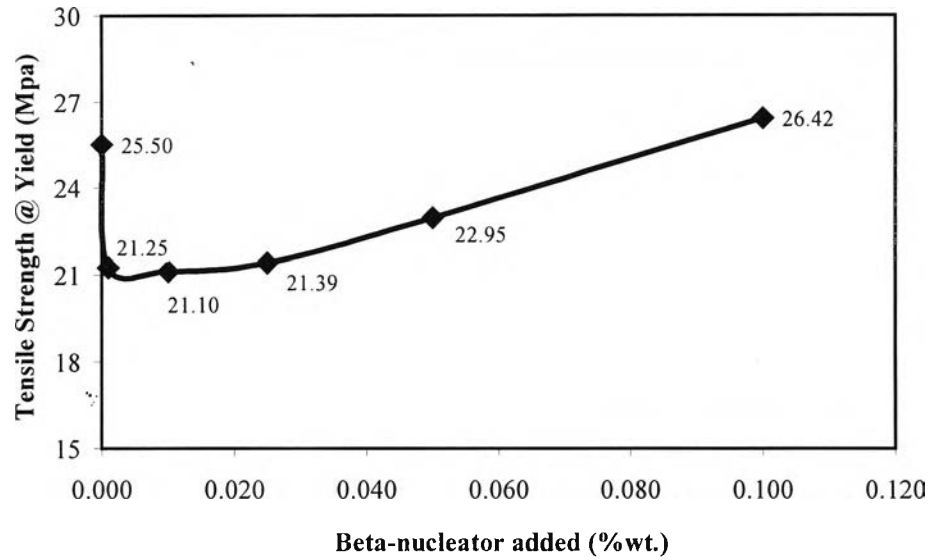
Ca-Pim is a melt-sensitive nucleating agent which melts at the processing temperatures could help maximize its dispersion in the matrix. Upon subsequent cooling, Ca-Pim crystallites which disperse homogeneously in the matrix can induce the β -form to occur.

Further increase in the percent loading of Ca-Pim resulted in the reduction of the Izod impact strength (see Figure 4.15), possibly as a result of the reduction in the amount of β -phase present (as indicated by the K-values listed in Table 4.8) in these samples. The explanation to this observation may lie on the notion that as the concentration of the β -nucleator increased the concentration of morphological aggregates of the β -form also increased, leading to the larger number of defects (e.g. grain boundaries) formed. It is a known fact that formation of boundary defects usually leads to the reduction in the impact strength.

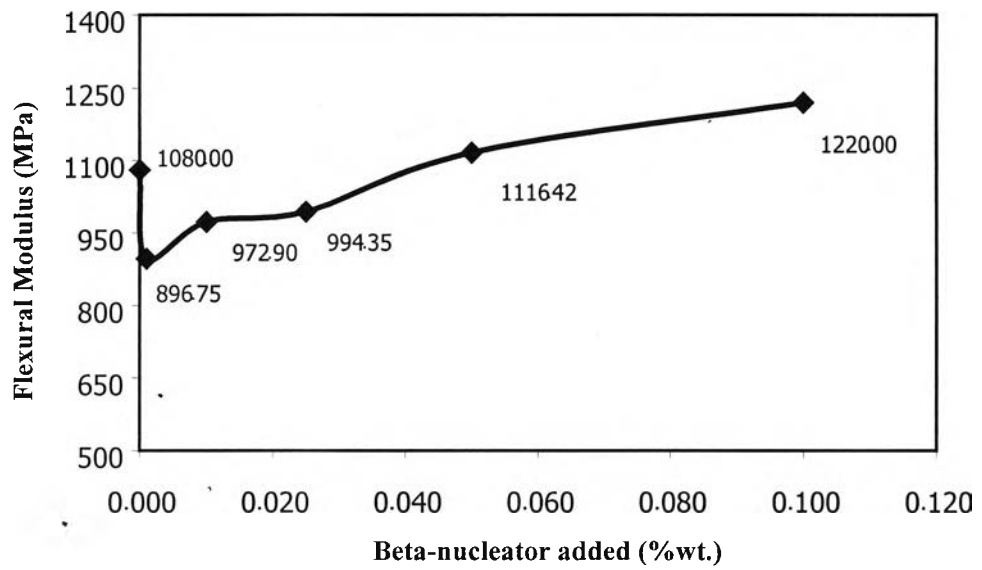


Figures 4.15 Notch Izod impact strength of β -PP/EPR blends

On the contrary to the Izod impact strength, tensile strength (at yield) and flexural modulus were found to increase with increasing percent loading of Ca-Pim (see Figures 4.16 and 4.17). The most likely explanation to this observation could be the increase in the apparent percent of crystallinity with increasing percent loading of the nucleator.



Figures 4.16 Tensile strength value of β -PP/EPR blends



Figures 4.17 Flexural modulus value of β -PP/EPR blends