



## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Morphology of the PP/PLA blends

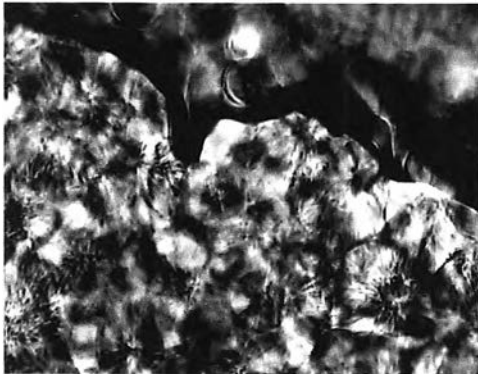
##### 4.1.1 Optical micrographs of the blends

The optical morphologies of PP/PLA blends at the ratio of 80/20 and 80/20/PP-g-MA were investigated by optical microscopy. The blend at 80/20 was chosen to be the representative of the blends for this experiment. The crystallization of PP film shown in Figure 4.1 (A) was evidenced by an abundance of spherulite viewed under an optical zoom lens and a polarized filter. When PP was blended with PLA without a compatibilizer (PP-g-MA), the blend still gave some spherulites with a phase separation between PP and PLA as shown in Figure 4.1 (B). The incompatibilized phases segregated into two discrete phases in which PP still remained spherulite while PLA became non-spherulite globular spheres. The contrast of Figure 4.1 (C) became better when PP-g-MA was incorporated. The segregate and discrete phases became one phase with some amount of PP spherulites.

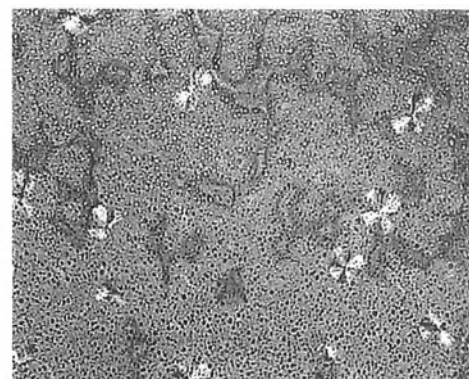
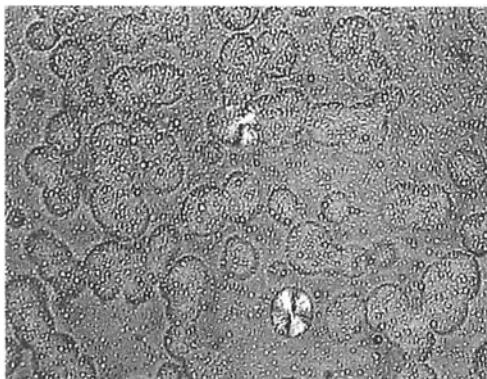
Comparing the spherulitic size of the neat PP, PP/PLA (80/20), and PP/PLA/PP-g-MA/DMDBS (80/20) blends heated at 200 °C for 1 min, PP has a larger crystal size than the PP/PLA blends. It was found that when PP was the major component in the blend, its crystallization behavior was affected by the blending using PLA/PP-g-MA/DMDBS in which the decrease of spherulite size had occurred. In addition, it has been reported that PP spherulites can grow around the PLA droplets and trap the elastomer phase in crystalline domains [17].

PLA is the minor component and dispersed in the immiscible PP matrix. Hence the compatibilization changes predominantly with PP-g-MA from a heterogeneous phase to a homogeneous phase as long as the size of the dispersed PLA phase is smaller than neat PP.

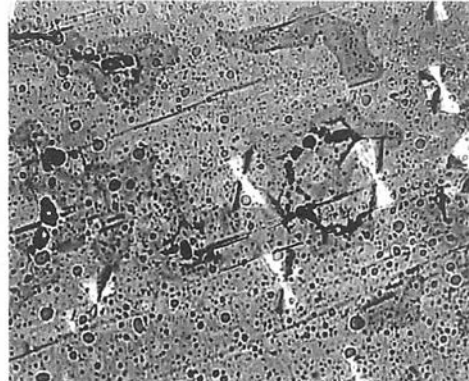
So, it is reasonable to imagine that the incorporation of PLA component in PP blend may increase the ductility and hence change the mechanical properties of the blend films [17].



(A) Spherulite of PP



(B) PP/PLA blend (80/20)



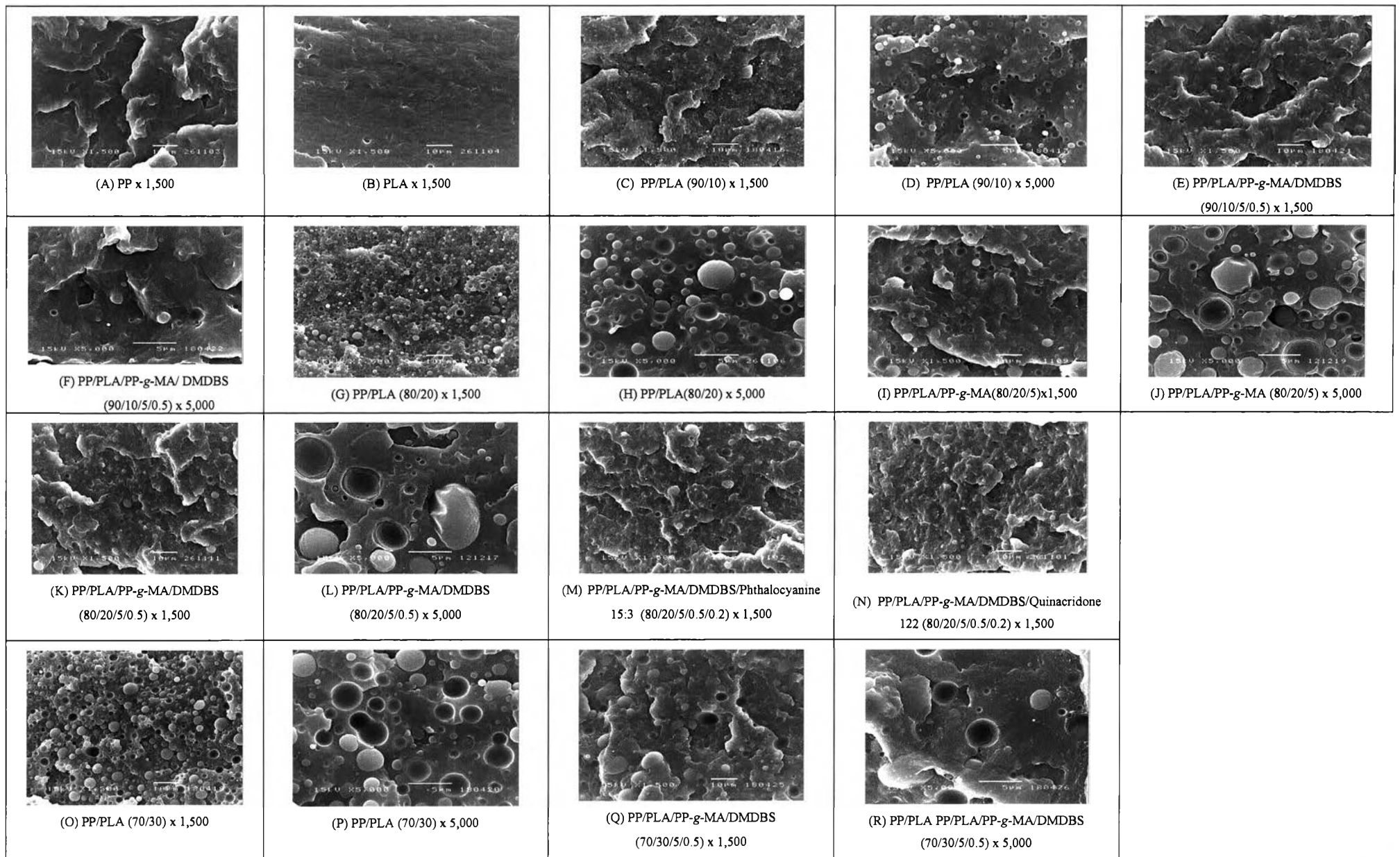
(C) PP/PLA/PP-g-MA blend (80/20/5)

**Figure 4.1** : Optical microscopic viewed under polarized filter : (A) Spherulite of PP (B) PP/PLA blend (80/20), and (C) PP/PLA/PP-g-MA blend (80/20/5).

#### 4.1.2 Phase morphology via scanning electron microscopy (SEM)

Cryofractured surfaces of PP and PLA (Figure 4.2 (A)-(B)), and PP and PLA blends are shown in Figure 4.2 (C)-(R) in which the noncompatibilized PP/PLA blends without PP-g-MA are illustrated in Figure 4.2 (C)-(D), (J)-(H), and (O)-(P). The compatibilized ones with PP-g-MA are given in Figure 4.2 (I),(J) compatibilized with PP-g-MA and DMDBS are depicted in Figure 4.2 (E), (F), (K), (L), (Q), and (R). One can observe that the PP and PLA homopolymer did not have globular particles. When PP/PLA was blended in the absence of compatibilizer, globular spherical particles were observed as an evidence of phase separation as shown in Figure 4.2 ( C), (D ), (J), (H), (O), and (P). This is the cause of difference in polarity since PP is a member of  $\alpha$ -olefin, a hydrophobic type while PLA is a polyester type polymer with a relatively polar group of ester. This can be summarized as that they are different because of polarity.

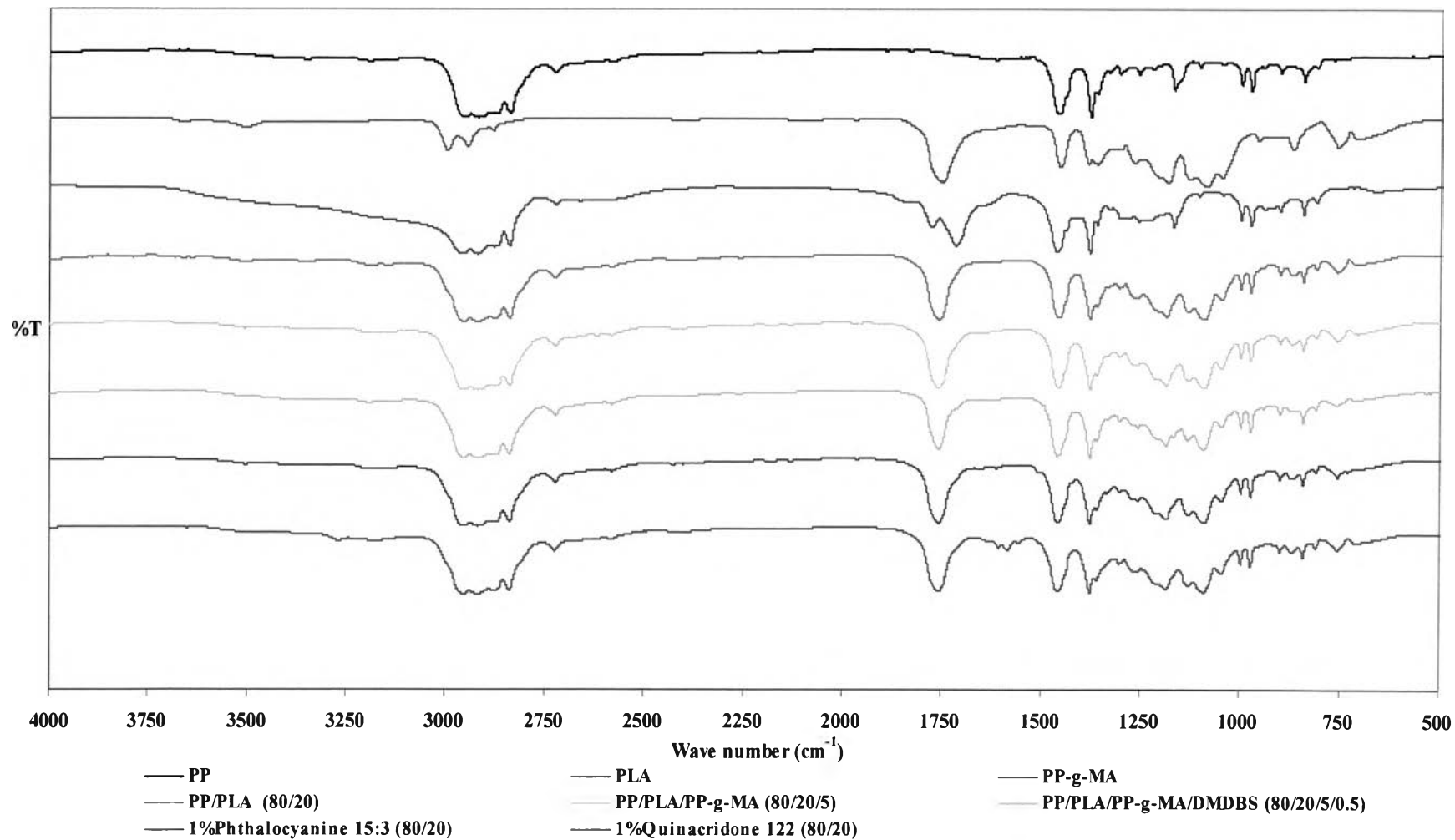
When PP-g-MA, a compatibilizer, was added as an interface promoter, the extent of globular spheres still existed. Then, three types of nucleating agents were added in a small amount of 0.5 and 0.2%, the globular spheres could not be eliminated by the DMDBS but they are dissolved in the presence of pigment blue 15:3 and pigment red 122. (Figure 4.2 (M),(N)) The pigment red 122 gave a finer phase texture. When the amount of PLA was reduced to 10% (PP/PLA = 90/10), the globular spheres were less than those of 20% PLA as shown in Figure 4.2 (F) and (L). This is caused by the decrease in polarity of PLA when its presence is less. The globular spherical particles can be now concluded as the presence of PLA. The smaller the amount of PLA, the less the globular spheres. The globular spheres can be further reduced by the compatibilizer and nucleating agent such as PP-g-MA and DMDBS, respectively, as shown in Figure 4.2 (G), (H), (M), (N), (Q), and (R). In Figure 4.2 (E) the globular spheres disappeared and the polymer blend appears as a compatible blend.



**Figure 4.2 :** Phase behavior of PP/PLA blends at various blend ratios and PP-g-MA and three nucleating agents.

#### 4.2 Characterization and identification of functional groups by FT-IR spectroscopy

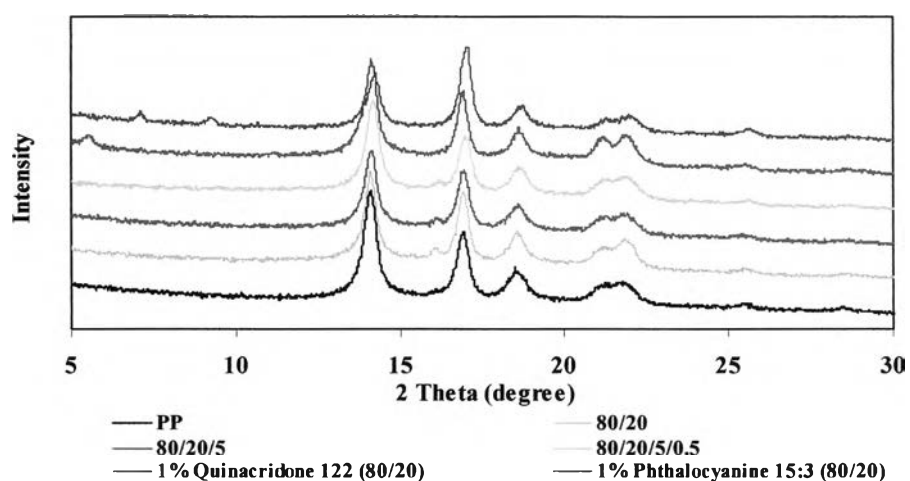
Figure 4.3 shows infrared spectra of the neat PLA and PP, PP-g-MA, and the polymeric blend at 80/20 with compatibilizer and nucleating agent. The blend at 80/20 was chosen to be the representative of the blends for this experiment. The results show that the spectra between 3000 and 4000  $\text{cm}^{-1}$  belonged to the symmetric and asymmetric O–H stretching modes of PLA molecules. A peak appeared at 1750  $\text{cm}^{-1}$  in the PLA and PP/PLA blends, which was not observed in the PP spectrum can be assigned to the C=O stretching band of the ester functional group of the PLA containing moiety. While a peak at 1768  $\text{cm}^{-1}$  is a characteristic of C=O group in cyclic anhydride. General characteristic absorption peaks of PP as observed at 2950 and 2868  $\text{cm}^{-1}$ , are attributed to  $\text{CH}_3$  symmetrical and nonsymmetrical of C-H stretching vibrations, respectively. The peaks at 2914 and 2835  $\text{cm}^{-1}$  are attributed to the  $\text{CH}_2$  nonsymmetrical and symmetrical C-H stretching vibrations, respectively. The peaks at 1458 and 1370  $\text{cm}^{-1}$  are attributed to the  $\text{CH}_2$  bending of straight chains. The spectra of the blends with pigment addition exhibit similar peaks obtained from PP/PLA blend.



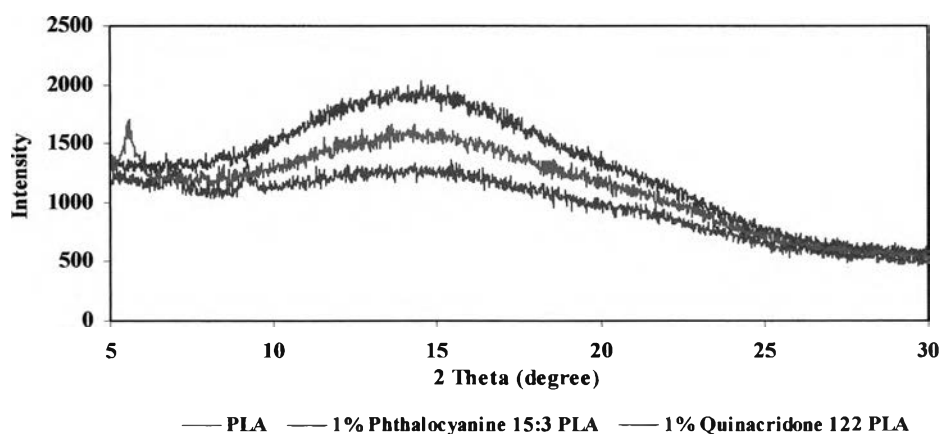
**Figure 4.3** : FT-IR spectrum of PP, PLA, PP-g-MA, 80/20 PP/PLA, 80/20/5 PP/PLA/PP-g-MA, 80/20/5/0.5 PP/PLA/PP-g-MA/DMDBS, 80/20/5/0.5 with 1% Phthalocyanine 15:3, and PP/PLA/PP-g-MA/DMDBS, 80/20/5/0.5 with 1% Quinacridone 122.

### 4.3 Characterization of crystallinity by X-ray diffractometer (XRD)

The blends were characterized by the XRD spectroscopy for their crystallinity. Figure 4.4 displays the  $\alpha$ -form of both pigmented blends found in PP/PLA/PP-g-MA/DMDBS, which is similar to  $\alpha$ -form of polypropylene. The diffraction peaks of 2 Theta (degree) =  $14.0^\circ$ ,  $16.8^\circ$ ,  $18.6^\circ$ ,  $21.2^\circ$ ,  $21.9^\circ$  are assigned to the crystal planes (110), (040), (130), (111), (131) of PP  $\alpha$ -modification, respectively [16].



(A)



(B)

**Figure 4.4 :** XRD diffractograms of (A) PP and the blends at 80/20 with 1%wt pigment and (B) PLA and 1%wt pigmented PLA.

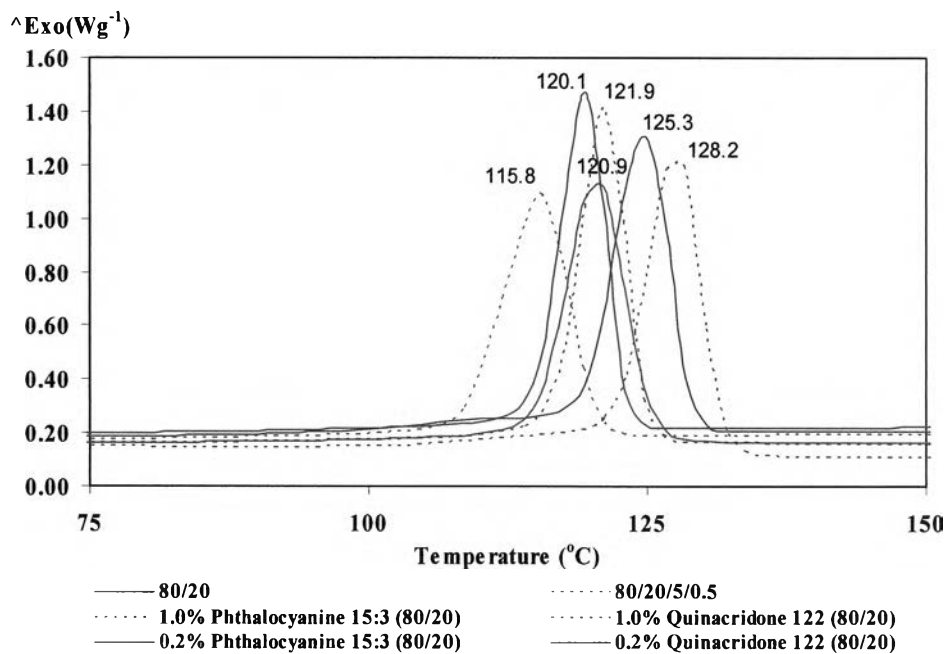
## 4.4 Thermal properties

### 4.4.1 Differential scanning calorimetry characterization of the blends

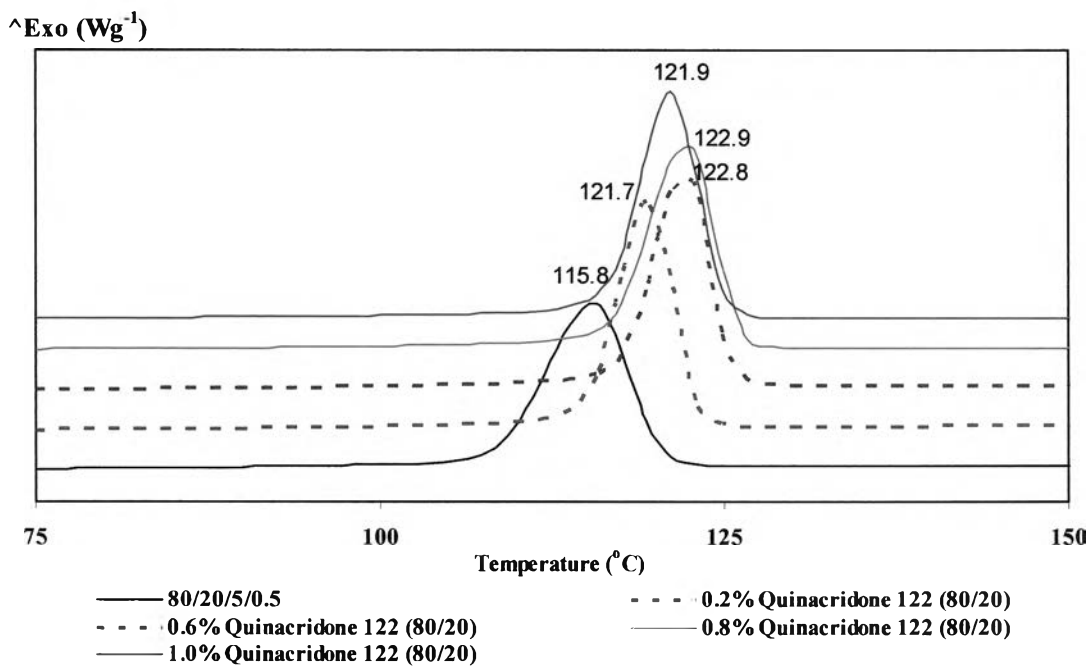
#### 4.4.1.1 Crystallization of PP/PLA and pigmented blends

The crystallization temperature ( $T_c$ ) of the blends in the form of casting films at 80/20 ratio as measured by differential scanning calorimetry (DSC) is displayed in Figures 4.5-4.6. The shift of  $T_c$  towards higher temperature observed in 0.2% to 1%wt of both pigments was compared with the unpigmented blend. The results of  $T_c$  of the neat, blend incorporation of graft copolymer and pigment nucleation in 80/20 blends are demonstrated in Figure 4.5. Decreasing  $T_c$  by grafting, and the effect of adding grafting compatibilizer, and nucleating are presented in Table 4.1. The blends with phthalocyanine C.I. Pigment Blue 15:3 gave a slightly higher value of  $T_c$  than the ones with quinacridone C.I. Pigment Red 122 at the maximum load of 1%wt compared to the minimum load of 0.2% pigment as seen in Figure 4.5. In contrast to the concentration at 0.2% pigment, 1% pigment produced a higher value of  $T_c$  as shown in Figure 4.6. The  $T_c$  peaks presented in Figure 4.6 (A) and (B) increase as a function of pigment concentration. It is known that the nucleating agents are added to the polymer systems to increase the rate of crystallization and temperature of crystallization [25]. The additives function by providing a large number of stable nuclei on which crystallization of the polymer may take place. At the same time, the decrease in spherulite size is obtained through the modified crystallization process due to the productivity increase. A similar shift of  $T_c$  is also observed in 90/10 and 70/30 blends when the pigment concentration is increased (Table 4.1). It is obvious that the blend at 70/30 with phthalocyanine shows a higher  $T_c$  than the blend with quinacridone, suggesting a higher efficiency in nucleation.

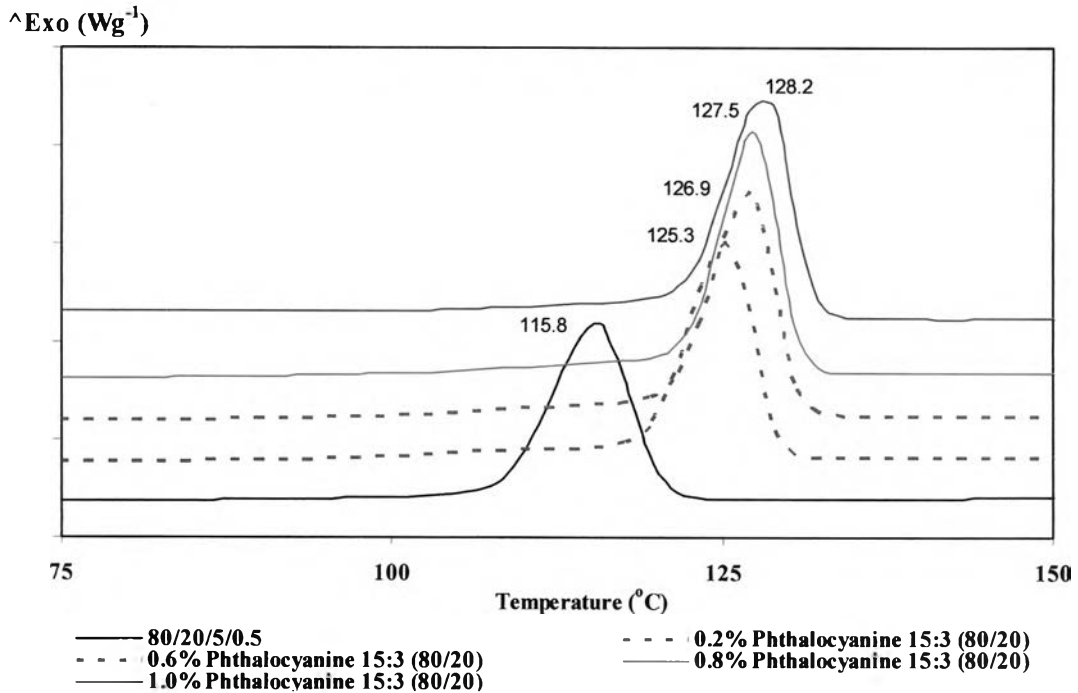




**Figure 4.5 :** Effect of pigment loading, compatibilizer, and nucleating agent on  $T_c$  of the blends (80/20 ratio).



(A)

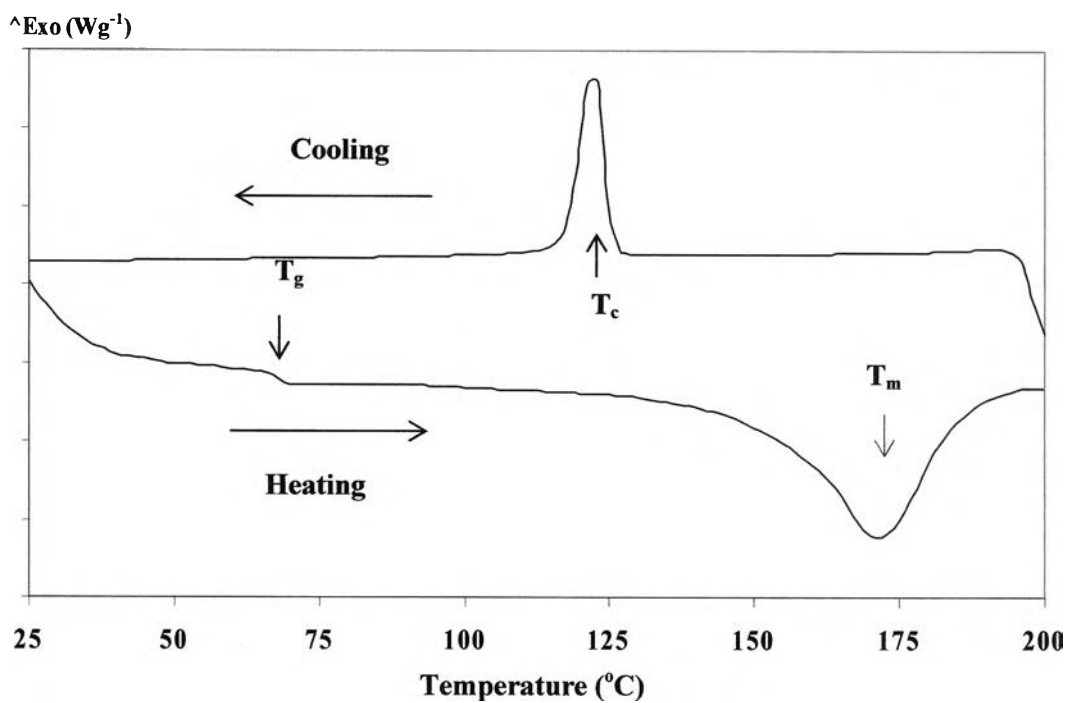


**Figure 4.6 :** Effect of pigment loading on  $T_c$  of the blends (80/20 ratio) (A) Quinacridone 122 (B) Phthalocyanine 15:3.

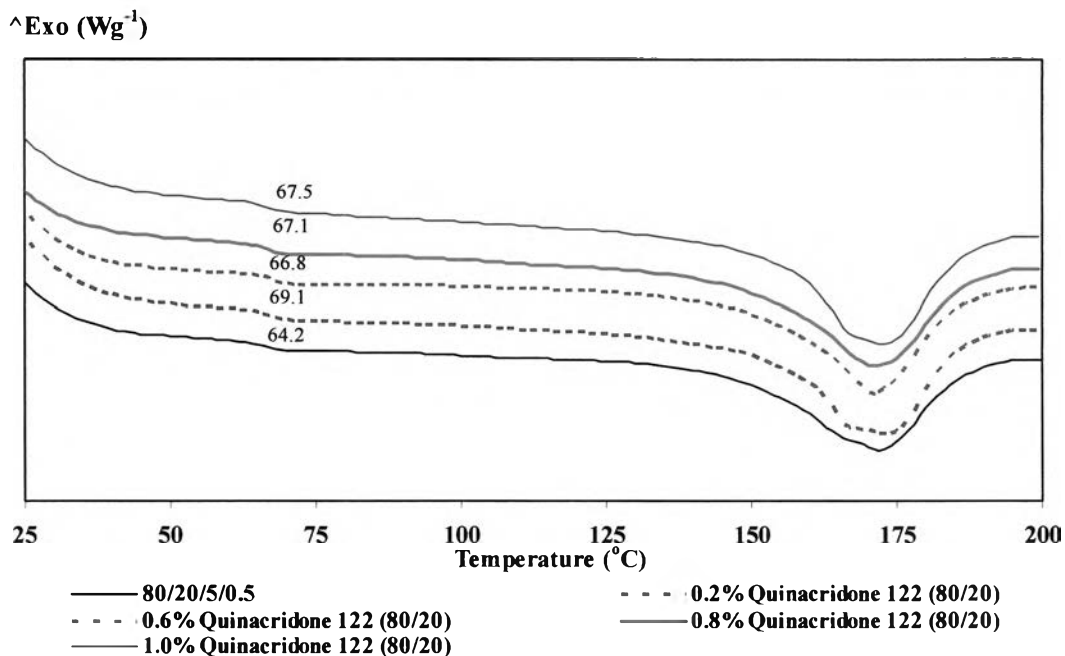
#### 4.4.1.2 Glass transition temperature and melting temperature of the pigmented blends

The glass transition temperature ( $T_g$ ) of PP/PLA/PP-g-MA blends is shown in Figure 4.7. One can observe the  $T_g$  peak at the heating up scanning, and the  $T_m$  indicating the amorphous and crystalline region, respectively. On the cooling scan, one obtains the crystallization at  $T_c$  peak for crystalline region but no  $T_g$  was observed. It can be summarized that upon heating, the amorphous region responded relatively well at increasing temperature. At the cooling down scan, the amorphous regions are still at the relaxation stage and cannot release the retained heat to return to its glassy state. For the crystalline region, the role of the nucleating pigment quinacridone assists in the crystallization process to give a strong  $T_c$  peak which indirectly indicates the formation of crystalline region. The  $T_g$  was observed at 60-70 °C, and it can only be seen in the first cycle of heating. The melting temperature ( $T_m$ ) of the

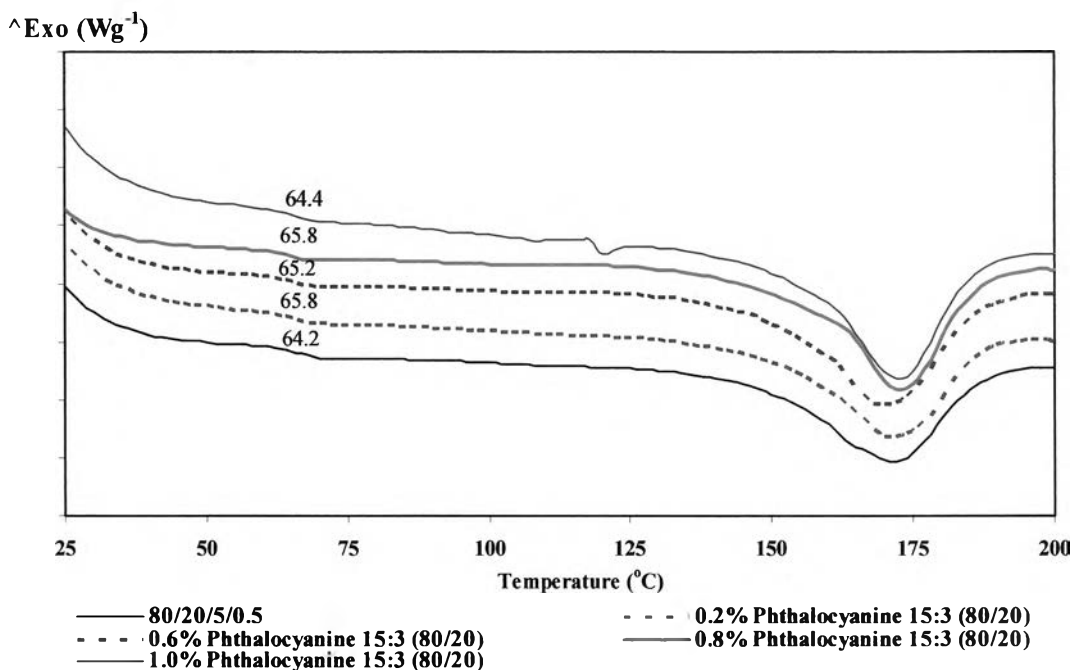
80/20 blend at various pigment concentrations are exhibited a slight change of  $T_m$  in Figure 4.8 (A) and (B). Similar results are seen in other ratios (90/10 and 70/30) as included in Table 4.1.



**Figure 4.7 :** Cyclic scans of PP/PLA/PP-g-MA blends in the presence of 0.6% C.I. Pigment Red 122.



(A)



(B)

**Figure 4.8 :** Thermograms ( $T_g$ ,  $T_m$ ) of the unpigmented and pigmented blends of PP/PLA (80/20) at various pigment concentrations: (A) Quinacridone 122 (B) Phthalocyanine 15:3.

#### 4.4.1.3 %crystallinity of the blend

The amount of crystallinity of the blend is calculated from  $\Delta H_m$  which is the area of the melting temperature. It was found that the crystallinity of the pigmented blends was increased as a function of pigment concentration (Table 4.1). The %crystallinity is affected by the ratios of blending (90/10, 80/20, and 70/30) depending on the loading PLA contents. The %crystallinity was calculated using the equation in Appendix A. PLA could be considered to be an impurity in the blend which affects the growth of nucleation size of PP. However, the addition of pigment affects the %crystallinity in the PLA, whereas it simultaneously decreases the %crystallinity of PP phase (Figure 4.9). The loading of the pigments influences significantly on the percentage of crystallinity in the blends as seen in Table 4.1 [25].

**TABLE 4.1** Thermal properties and calculated percentage crystallinity of PP/PLA blends

Compound ratio	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$\Delta H_c$ (J g <sup>-1</sup> )	%crystallinity
PP	-	110.4	170.0	71.3	88.1	34.1
PLA	64.0	-	156.5	34.7	-	34.3
90/10	64.8	121.4	164.6	87.0	87.8	55.6
90/10/PP-g-MA	64.4	116.5	162.8	90.3	84.1	53.7
90/10/PP-g-MA/DMDBS	62.5	115.3	163.6	94.4	88.4	56.2
0.2% Quinacridone 122 (90/10)	62.2	121.6	162.7	87.8	90.5	56.1
0.6% Quinacridone 122 (90/10)	63.8	122.2	162.8	85.2	92.9	54.4
0.8% Quinacridone 122 (90/10)	65.0	123.9	164.1	64.9	90.0	54.3
1.0% Quinacridone 122 (90/10)	63.5	124.3	162.2	86.0	92.9	55.0
0.2% Phthalocyanine 15:3 (90/10)	63.5	124.9	164.0	91.3	92.2	58.4
0.6% Phthalocyanine 15:3 (90/10)	65.5	125.9	164.8	90.3	92.8	57.7
0.8% Phthalocyanine 15:3 (90/10)	64.5	127.5	163.2	86.1	88.6	55.0
1.0% Phthalocyanine 15:3 (90/10)	64.9	126.6	162.9	89.4	88.0	57.1

Compound ratio	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J g <sup>-1</sup> )	ΔH <sub>c</sub> (J g <sup>-1</sup> )	%crystallinity
80/20	65.8	120.9	164.4	84.7	76.6	50.6
80/20/PP-g-MA	64.8	113.5	162.9	83.6	77.7	50.0
80/20/PP-g-MA/DMDBS	64.2	115.8	163.7	81.0	77.2	48.4
0.2% Quinacridone 122 (80/20)	69.1	120.1	161.2	86.4	78.9	51.6
0.6% Quinacridone 122 (80/20)	66.8	122.8	162.5	83.1	76.1	49.7
0.8% Quinacridone 122 (80/20)	67.1	122.9	162.7	92.8	83.2	55.5
1.0% Quinacridone 122 (80/20)	67.5	121.9	162.2	96.0	82.6	57.4
0.2% Phthalocyanine 15:3 (80/20)	65.8	125.3	163.4	85.8	76.6	51.3
0.6% Phthalocyanine 15:3 (80/20)	65.2	126.9	162.7	87.3	79.9	52.2
0.8% Phthalocyanine 15:3 (80/20)	65.8	127.5	163.0	84.7	76.0	50.6
1.0% Phthalocyanine 15:3 (80/20)	64.4	128.2	163.5	85.1	79.4	50.8
70/30	66.5	119.8	163.3	85.2	65.6	56.0
70/30/PP-g-MA	65.1	117.3	161.9	84.7	68.7	55.7
70/30/PP-g-MA/DMDBS	65.8	116.9	161.4	85.9	70.7	56.5
0.2% Quinacridone 122 (70/30)	63.8	121.6	163.1	87.4	71.7	57.5
0.6% Quinacridone 122 (70/30)	65.3	122.9	162.9	93.8	91.5	61.6
0.8% Quinacridone 122 (70/30)	64.5	125.3	163.2	88.3	73.8	58.1
1.0% Quinacridone 122 (70/30)	64.8	124.6	162.9	87.7	68.2	57.7
0.2% Phthalocyanine 15:3 (70/30)	65.0	127.0	163.3	78.9	64.6	51.0
0.6% Phthalocyanine 15:3 (70/30)	65.2	127.3	163.3	79.7	68.2	52.4
0.8% Phthalocyanine 15:3 (70/30)	65.2	127.9	163.1	75.3	63.4	49.5
1.0% Phthalocyanine 15:3 (70/30)	64.7	128.3	162.4	83.3	69.9	54.8

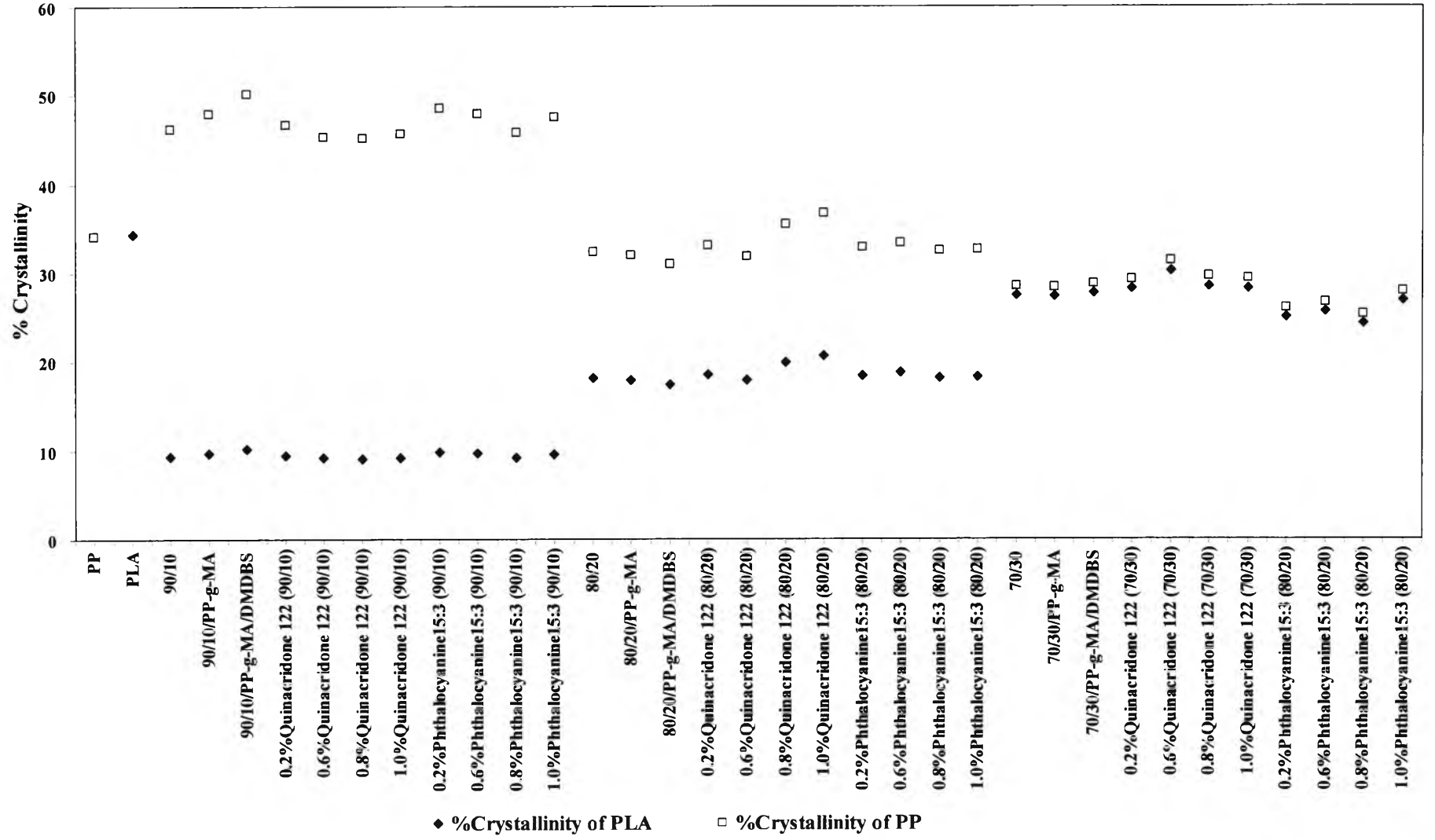
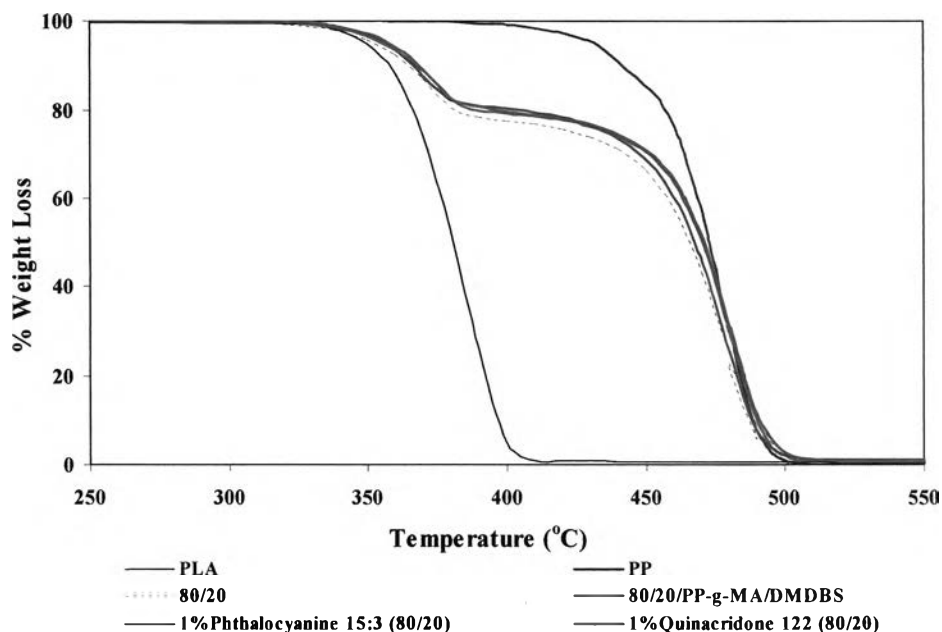


Figure 4.9: % crystallinity of PLA and PP portions in the blends as a function of pigment concentration and blending ratio.

#### 4.4.2 Thermal gravimetric analysis (TGA) of PP/PLA blends

Figure 4.10 displays the TGA thermograms of PLA, PP, PP/PLA blend at 80/20, PP/PLA blend with PP-g-MA, 1% phthalocyanine 15:3 in PP/PLA blend with PP-g-MA, and 1% quinacridone 122 in PP/PLA blend with PP-g-MA. The PP/PLA blend at 80/20 was chosen to be the representative of the blends for this experiment. The  $T_d$  of the blend was obtained between PLA and PP; the blends containing 1% quinacridone 122 had a slightly higher  $T_d$  than those containing 1% phthalocyanine 15:3. Broda [25] observed the similar result in which the quinacridone containing polypropylene showed a higher thermal degradation temperature since polypropylene consists of a  $\beta$ -form structure, which is known to be more heat and impact resistance. The PP/PLA blends have lower thermal stability than PP due to PLA addition, since PLA possesses lower thermal stability which degrades completely at 400 °C. After a pigment addition, the thermal stability of the blend is improved.



**Figure 4.10 :** TGA thermograms of the PP/PLA blends (80/20), the blends with 1%wt pigment addition and the homopolymers.



## 4.5 Physical and Mechanical Properties of the Blends

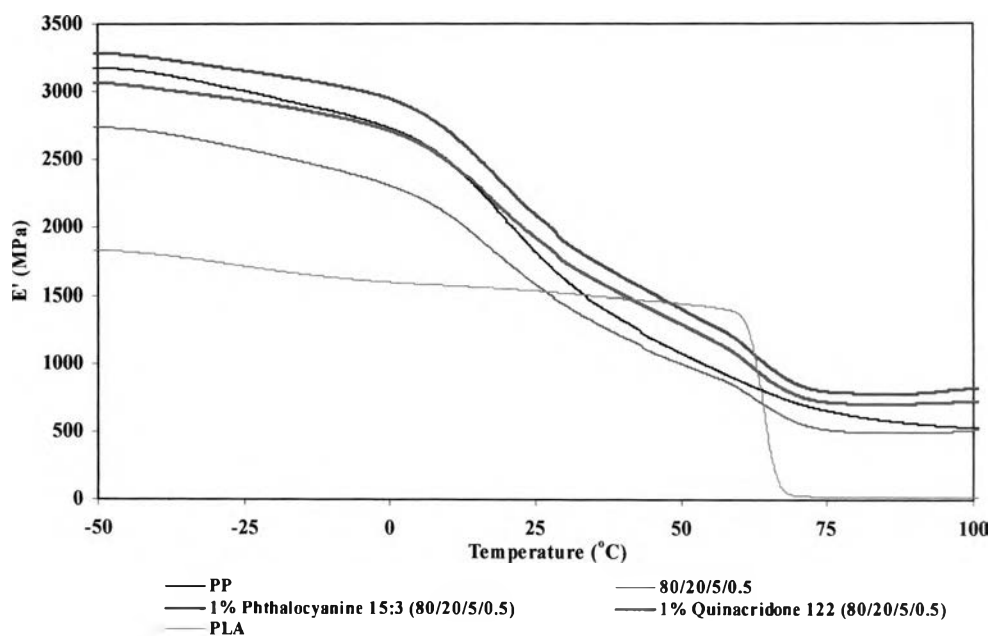
### 4.5.1 Dynamic mechanical analysis of the pigmented PP/PLA blends

The modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of the blends with and without pigment addition as a function of temperature are shown in Figures 4.11–4.13. The PP/PLA blend at 80/20 was chosen to be the representative of the blends for this experiment. It can be seen that increase in 0.2% to 1.0% of pigment content tends to increase the moduli of the cast films. Dynamic mechanical analysis of the blend confirms the glass transition temperature ( $T_g$ ) at around 60-70 °C which is a  $T_g$  of PLA [28]. The result is in agreement with the DSC result (Figure 4.7).

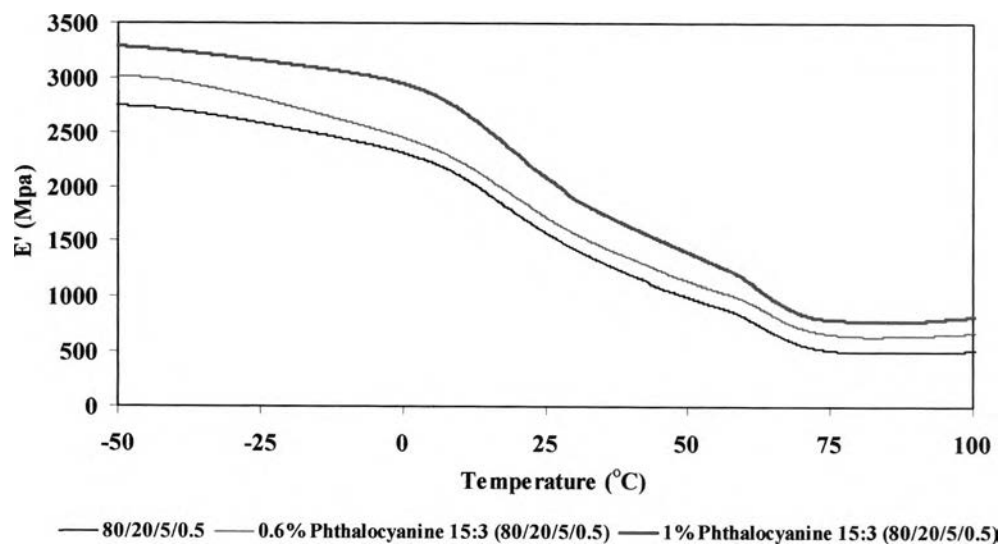
The storage modulus ( $E'$ ) of the blend is characterized as a function of temperature with vibration frequency of 1 Hz. The modulus of mold pressed sample was measured by DMA with increasing pigment content. The modulus of blends is significant increased comparable with the unpigmented blend. The blend with phthalocyanine 15:3 has a higher value of modulus than the one with quinacridone 122 as shown in Figure 4.11 (A). The pigment addition also improved the modulus (Figure 4.11 (B) and (C)). The loss modulus ( $E''$ ) of the blends was similarly found to increase as a function of pigment addition. Phthalocyanine 15:3 blend shows a higher value of modulus than that of quinacridone 122 as shown in Figure 4.12.

The height of loss tangent ( $\tan \delta$ ) of the blends is related to the crystallinity of the blends [28]. This implies that increasing the pigment loading increases the crystallinity of PP/PLA blend. The peak position of  $\tan \delta$  in the blue pigmented blend is observed to slightly shift toward to lower temperature suggests that such a blend contains a bit higher crystallinity than that of the red pigment. The sharp peak of loss tangent ( $\tan \delta$ ) observed in Figure 4.13

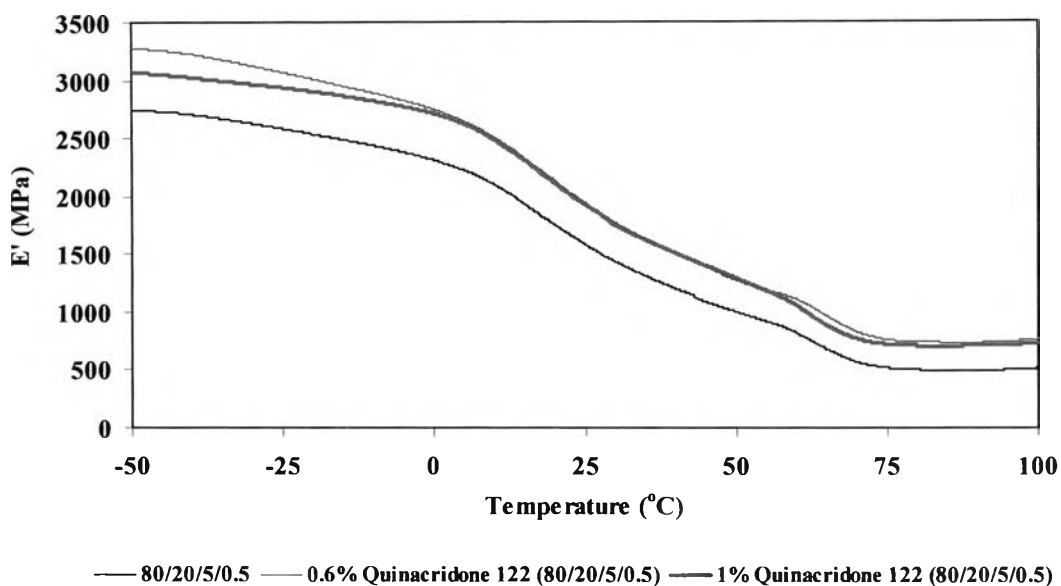
corresponds to the glass transition temperature ( $T_g$ ) at around 60 to 70 °C which is close to the glass transition temperature obtained from the DSC technique (Figure 4.7).



(A)

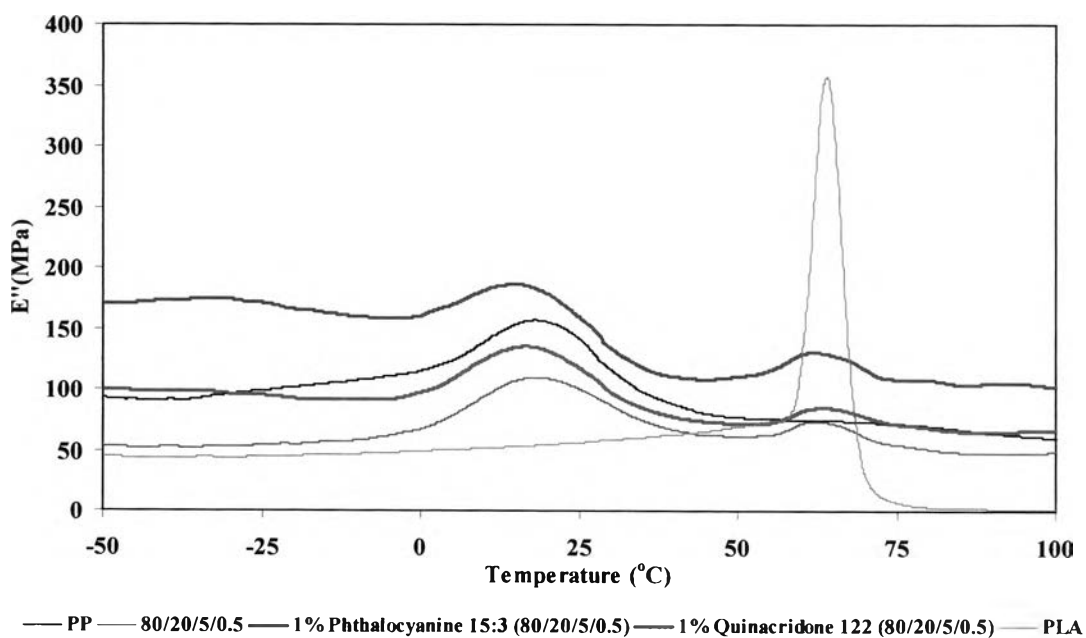


(B)

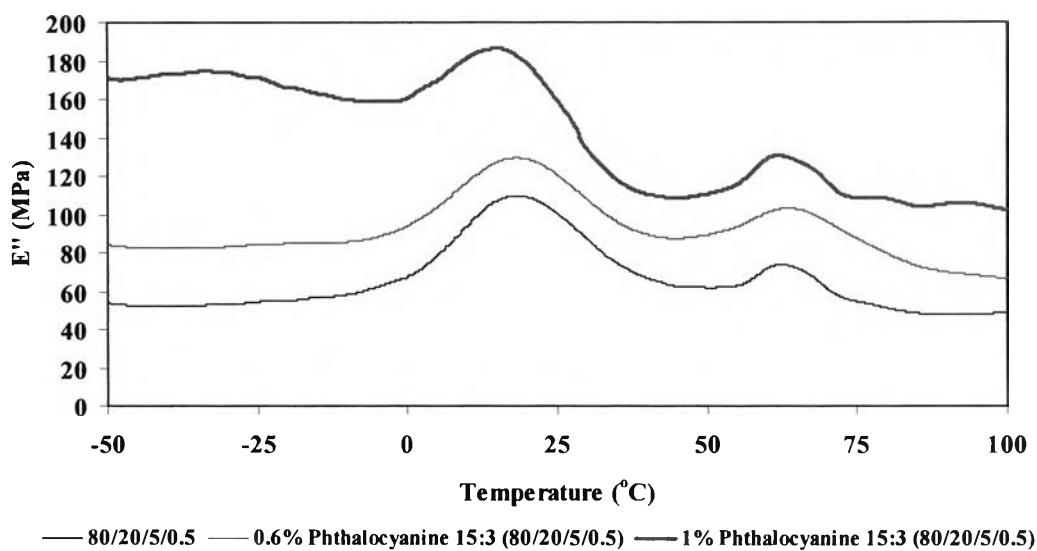


(C)

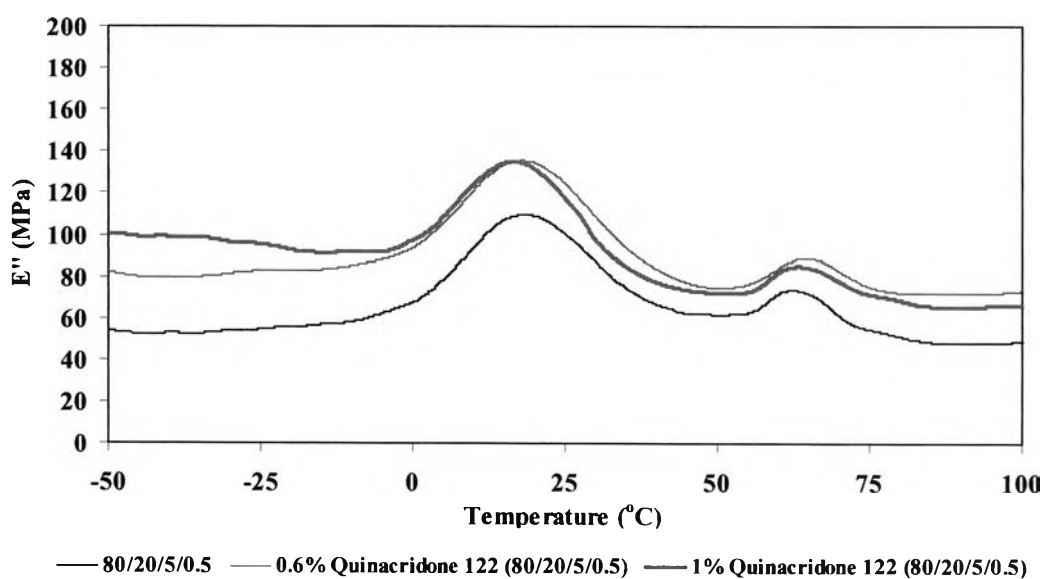
Figure 4.11 : Moduli of the 80/20 blends (A) with 1%wt pigment (B) Phthalocyanine at various concentrations, and (C) Quinacridone at various concentrations.



(A)

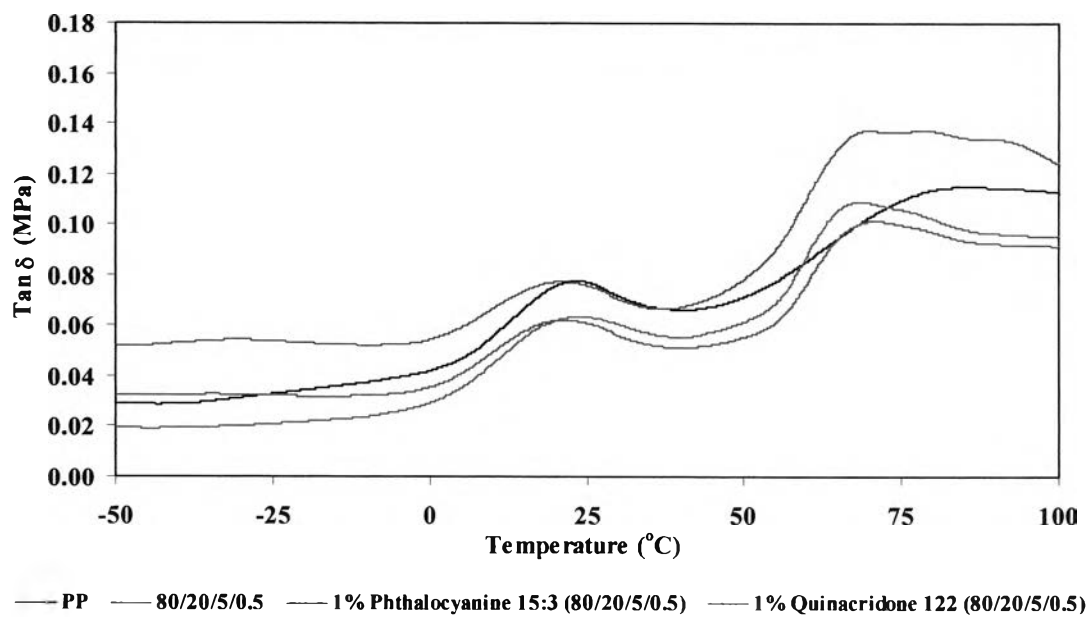


(B)

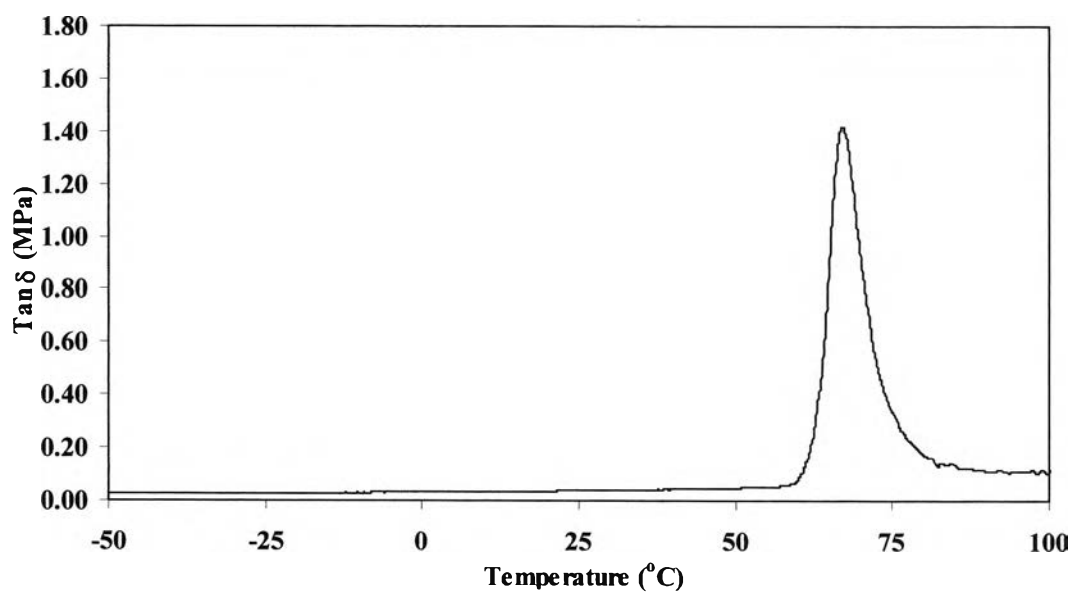


(C)

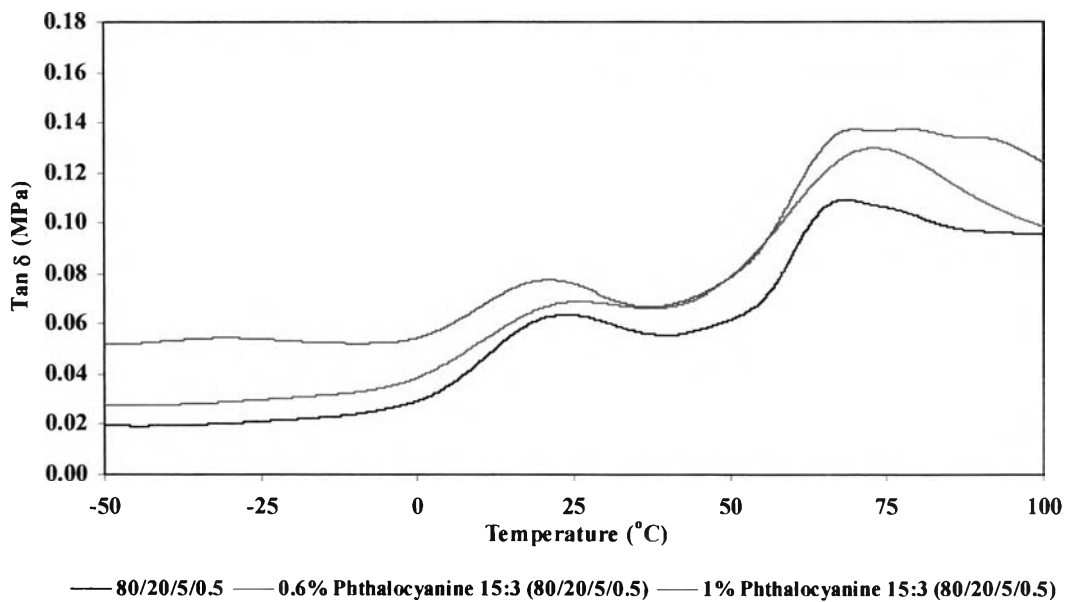
**Figure 4.12** : Loss modulus of the 80/20 blends (A) with 1%wt pigment (B) Phthalocyanine at various concentrations, and (C) Quinacridone at various concentrations.



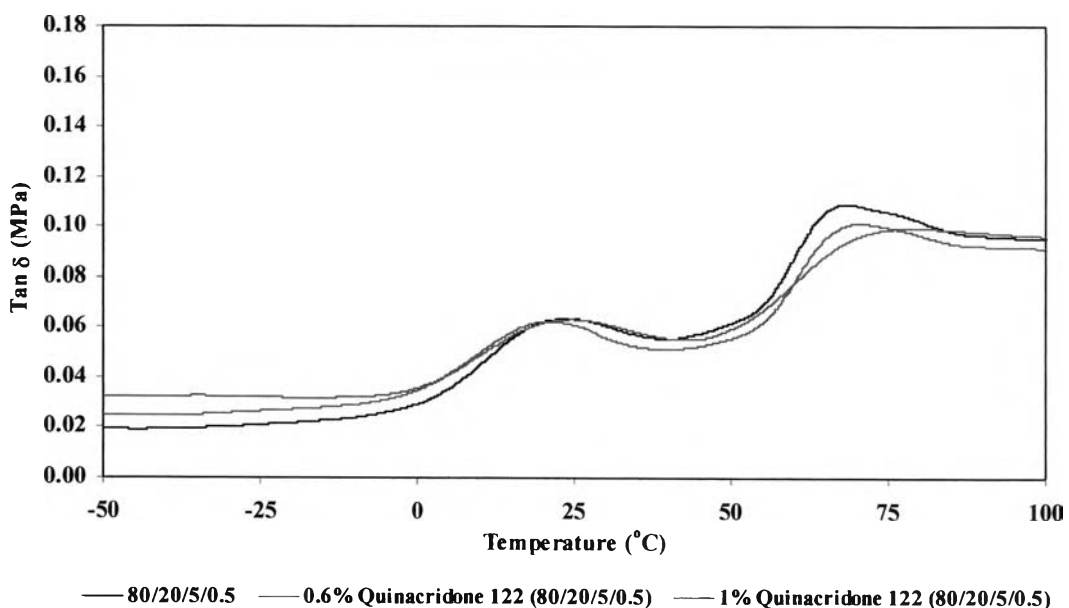
(A)



(B)



(C)



(D)

**Figure 4.13 :** Tan  $\delta$  of PLA and the 80/20 blends (A), with 1%wt pigments (B), neat PLA (C) Phthalocyanine at various concentrations, and (D) Quinacridone at various concentrations.

## **4.5.2 Universal Tensile Testing of PP/PLA blends**

Tensile strength, elongation, and modulus in the machine direction of the blends increased with increasing contents of both nucleating pigments from 0.2%wt to 1.0%wt.

### **4.5.2.1 Effect of pigmented PP/PLA blends on tensile strength**

The tensile strength of PP/PLA blends is shown in Figure 4.14. The films contained both pigments. It can be seen that increased pigment contents from 0.2% to 1.0% enhance the tensile strength of the cast films. Pigments are long known as nucleating agents and have ability to increase crystallinity of the blends. Tensile values of the 90/10 of PP/PLA blend were found higher than those of the 80/20, and 70/30 blends. Compatibility in the lower PLA content with PP is higher because PP-g-MA compatibilizer (5%) can be effective at this level of PLA. At the higher PLA contents, more compatibilizer may be needed. When increasing the pigment loading, the pigment behaves as a nucleating agent to promote crystallinity. Therefore, the polymer becomes more restricted to move due to compact configuration. Since the compatibility in the lower ratio at 90/10 is easier to achieve due to a sufficient concentration of PP-g-MA at 5% wt with increasing pigment, the mobility of matrix molecules became more restricted due to the increase in the crystallinity of matrix.

### **4.5.2.2 Effect of pigmented PP/PLA blends on elongation and modulus**

The elongation at break of PP/PLA/PP-g-MA/DMDBS pigmented cast films was measured by a universal tensile testing machine. The elongation at break in the machine direction of the cast films increased with increasing pigment loading.

The % elongation at break depends on the amount of crystallinity phase present in the cast films. With increasing pigment content, the %crystallinity in blend cast films was found

to increase. The blends containing phthalocyanine blue has a higher value of elongation than those containing quinacridone as illustrated in Figure 4.15.

The moduli of PP/PLA blends by cast film extrusion in comparison with those containing both pigments are shown in Figure 4.16. It can be seen that the increase in the pigment concentration of both pigments tends to increase the moduli of the cast films as well.



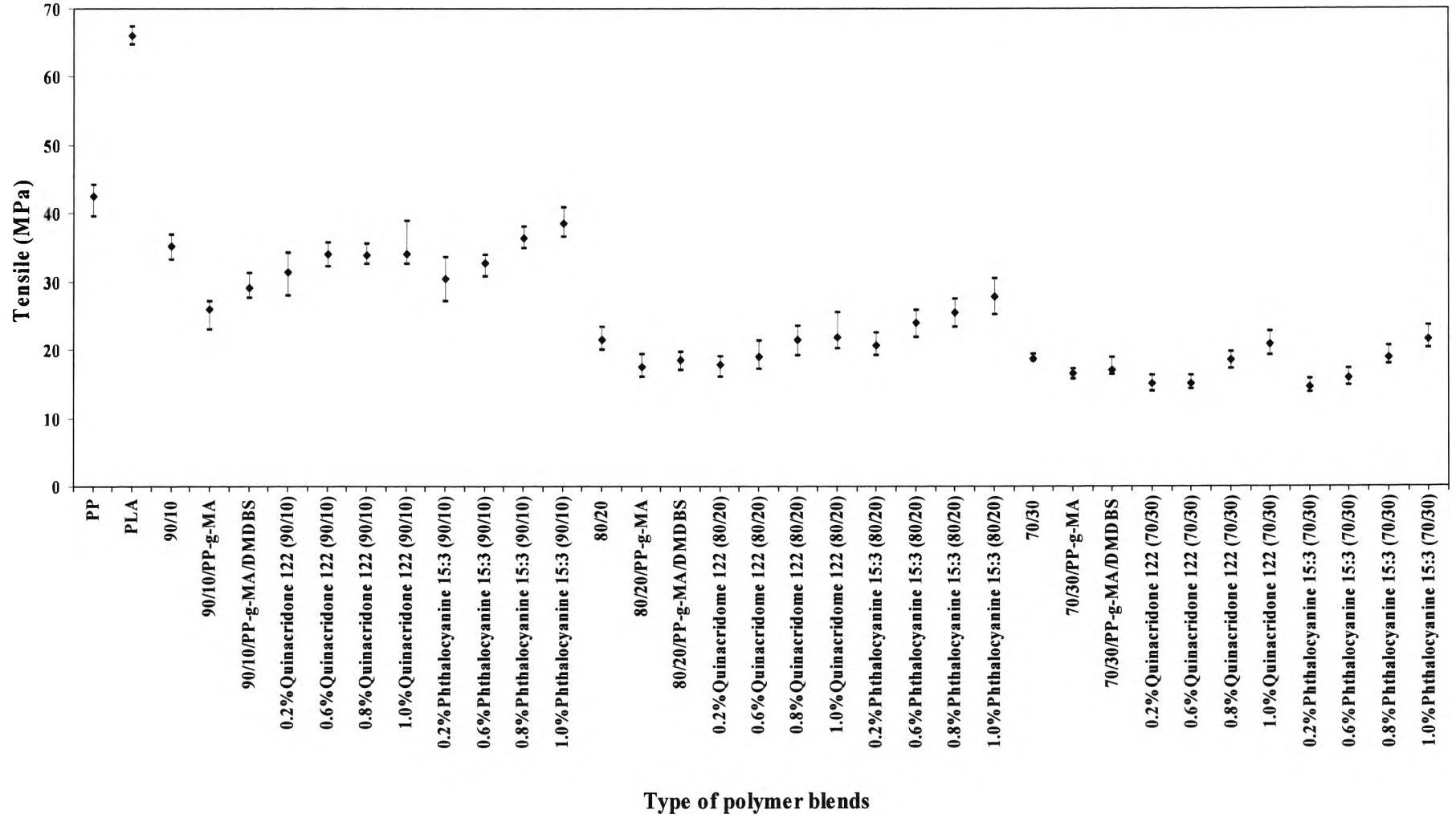


Figure 4.14 : Tensile strength in the machine direction of the PP/PLA blends with two types of pigment.

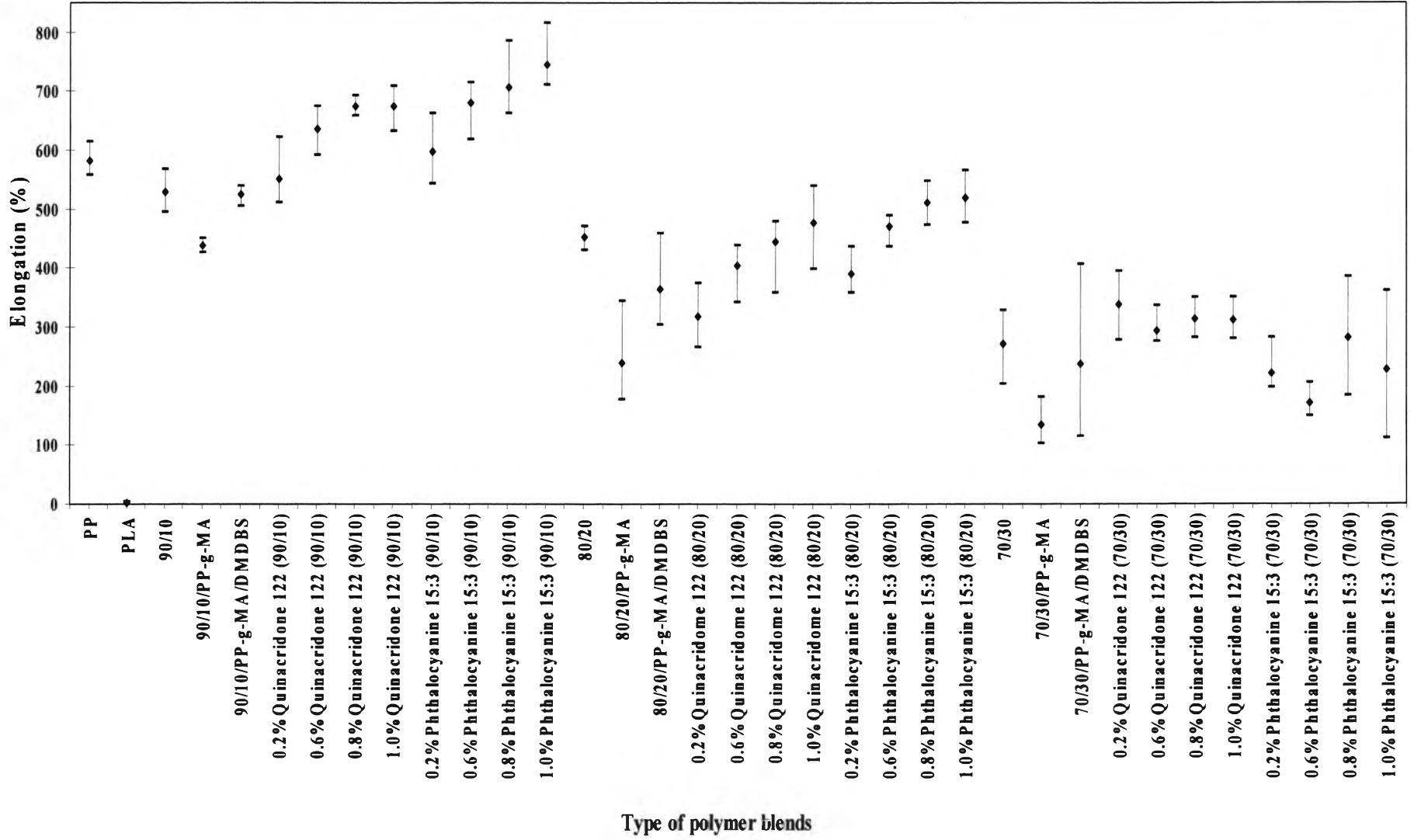


Figure 4.15 : % Elongation in the machine direction of the polymer blends with two types of pigment.

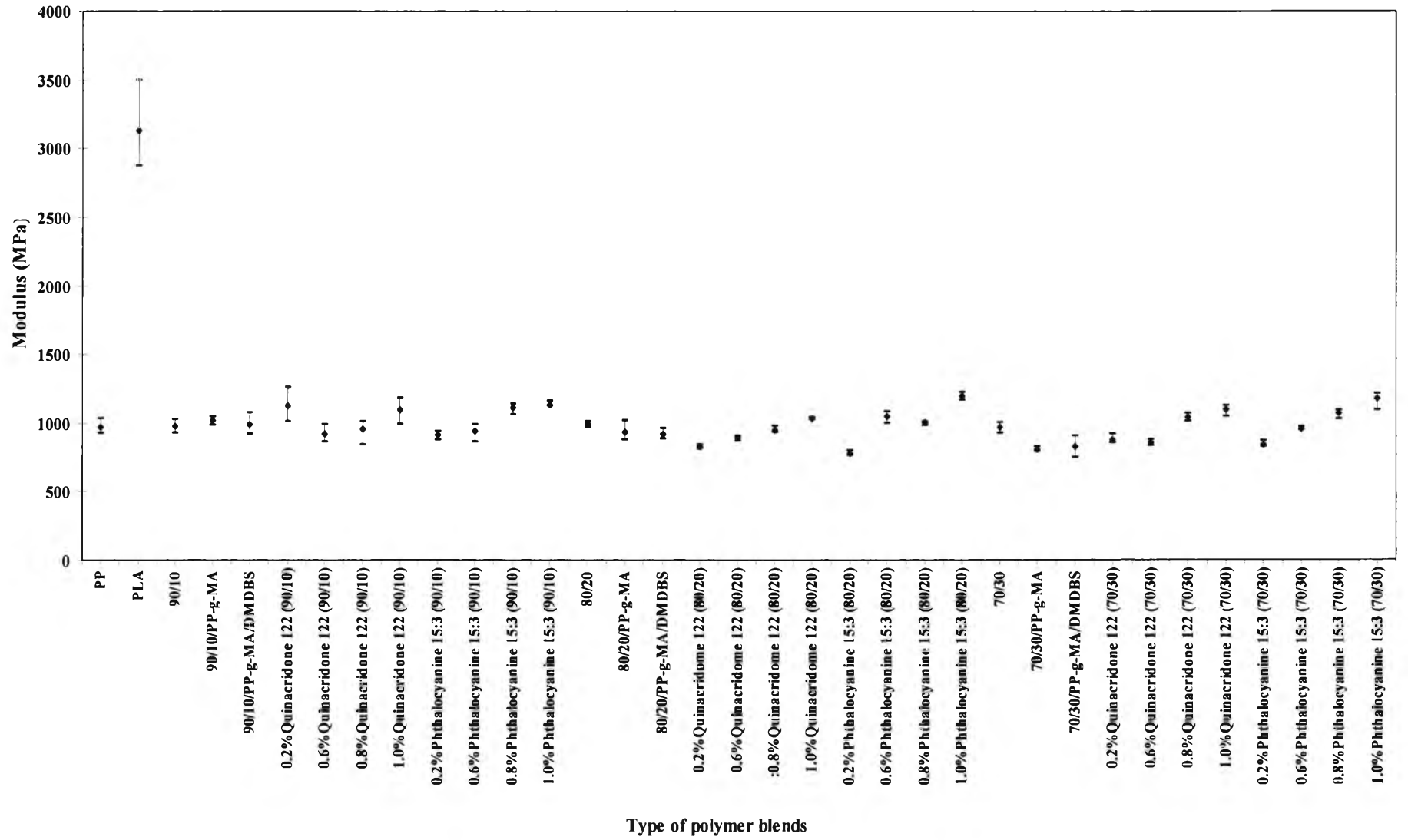


Figure 4.16 : Modulus in the machine direction of the polymer blends with two types of pigment.

## **4.6 Haze appearance and opacity of the polymer blends**

### **4.6.1 Haze measurement by hazemeter**

PP/PLA/PP-g-MA blends characterized by a hazemeter is shown in Figure 4.17. The haze values of the blends gradually increase as the ratios of PLA in PP/PLA increase at 90/10, 80/20, and 70/30. The compatibility of PP/PLA at the ratio of 90/10 is better than other ratios in terms of haze value at a constant content of PP-g-MA added in all polymer blends. At 80/20, the haze value significantly increased while the pigment blue was added at the ratio 0.2 to 1%wt in comparison with the blendings adding the pigment red which exhibited less haze value. At the blend ratio of 70/30, It is observed that haze values increased significantly while both pigments were added to the polymer at a ratio of 0.2-1%wt. It is observed that the haze value of the unpigmented blends is decreased by incorporating PP-g-MA which is the compatibilizer that affects PP/PLA blends. Optional technique is SEM which describes interface adhesion between PP/PLA blends when grafting with PP-g-MA. Traditionally, the effect of adding nucleating agents to PP results in a decreasing haze value because the spherulite size is reduced. On the contrary, haze value of the blends increased regarding incompatibility of PP/PLA blends because nucleating agents influence particularly the PP, but not the PLA phase since it is an amorphous polymer.

### **4.6.2 Opacity measurement by densitometer**

PP/PLA/PP-g-MA blends are characterized by densitometer and shown in Figure 4.17. The results of % dot value of blends are in similarity with the haze results. A jump on haze and opacity results at 70/30 is observed which is probably due to much less compatibility between PP and PLA phases compared to those of 90/10 and 80/20.

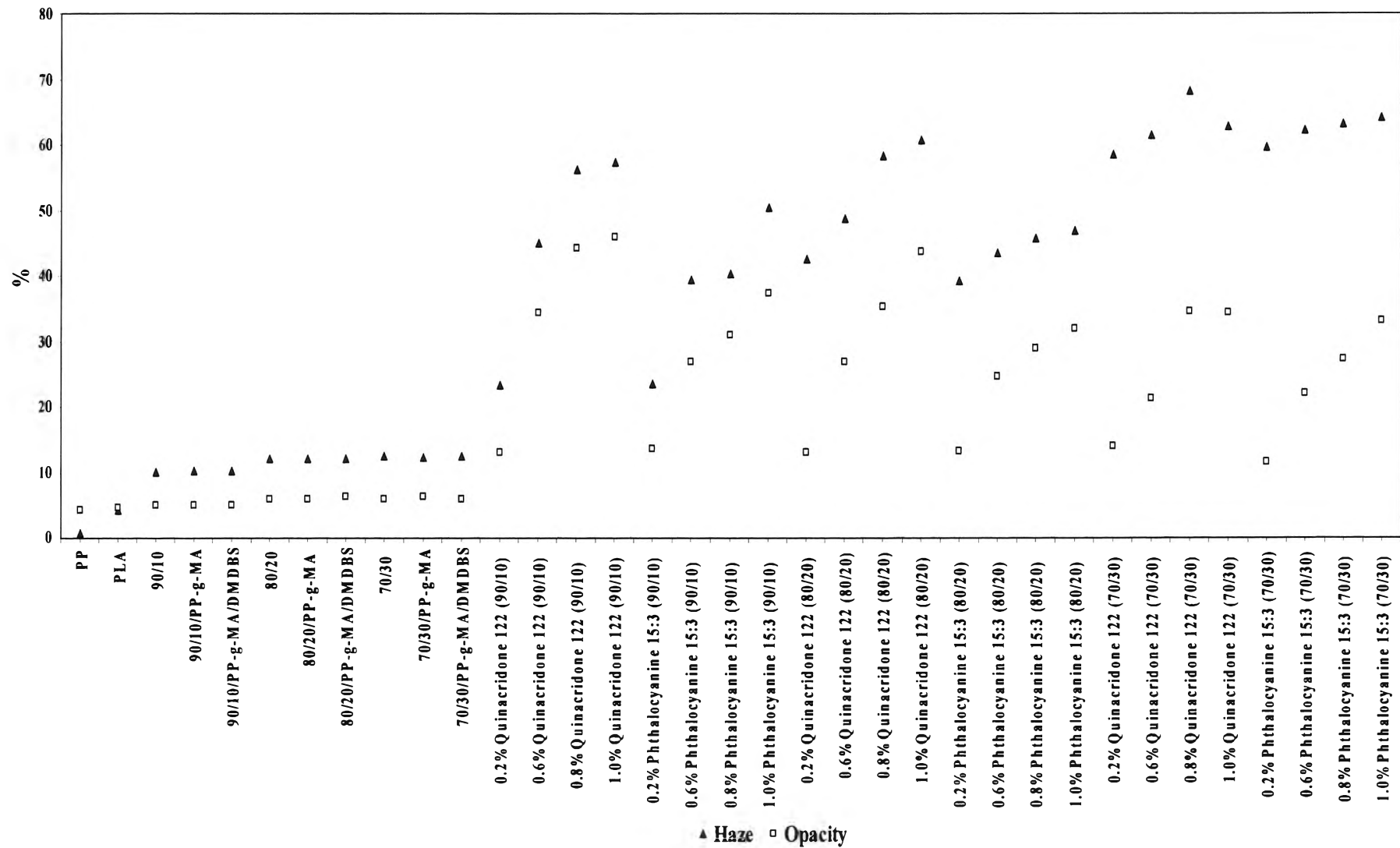


Figure 4.17 : Haze and opacity of the blends at various ratios and pigment concentrations.