Chapter IV

Results and Discussion

4.1 Blending Condition Characterization

Because of the requirement for the optimum process condition to disperse the organic pigment powder in medium density polyethylene, various experimental conditions regarding screw speed and processing temperature of twin screw extruder were tested. This experimental procedure is needed in order to select the optimum process condition for melt blending technique.

Table 4.1 summarizes the average particle size of three different kinds of pigment powder measured from the laser particle size analysis. Among them, PB15 has the largest particle size of 17.53 μm, whereas PR122 has the smallest particle size.

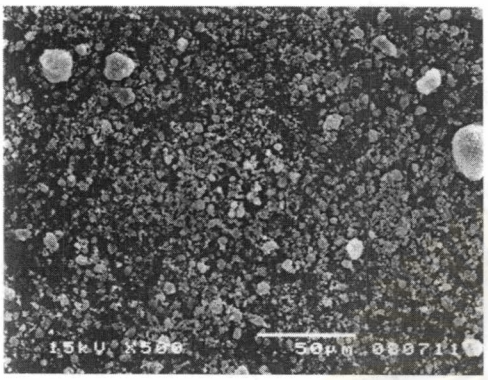
In addition, as shown in Figure 4.1, many agglomeration of pigment particles can be observed, in particular with the case of PB15, numbers of pigment agglomeration are more obvious and greater than the other two pigments.

Table 4.1 Particle size of pigment powder from laser particle size analysis

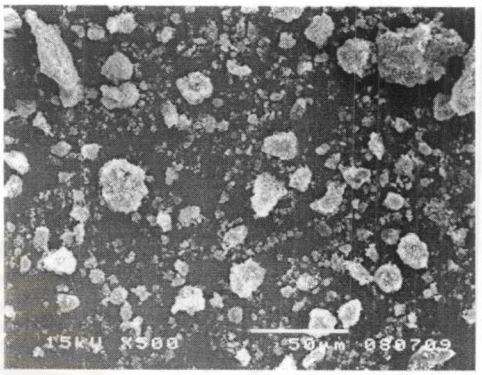
Pigment Type	Mean Diameter of each Trial (μm)			Mean (μm)	SD
	1	2	3		
Diarylide (PY 83)	1.37	1.43	1.30	1.37	0.05
Phthalocyanine (PB 15)	16.66	17.86	18.08	17.53	0.62
Quinacridone (PR 122)	0.48	0.49	0.51	0.49	0.01

Comparing between PR122 and PY83 powder, although the size of PY83 powder which analyzed by laser particle size analysis is larger, the SEM micrographs reveal that the dispersion of PY83 powder is better (and its size is smaller than that of PR122 powder). It can be defined that in the air PR122 powder has aggregates and agglomerates forms more than PY83 powder. In contrast, when PR122 powder was analyzed by laser particle size analyzer which used water as a medium, the

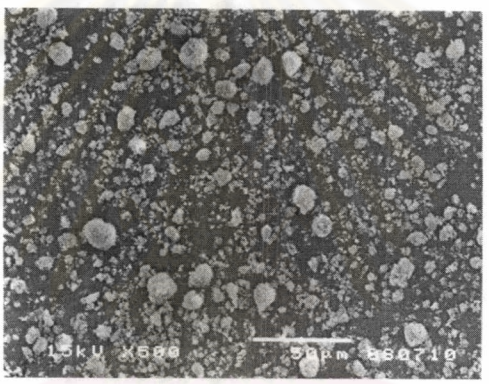
coalescence in PR122 powder might separate to the actual particle size. Thus, based on this technique PR122 powder has a smaller size than PY83 powder.



(a) Diarylide pigment (PY83)



(b) Phthalocyanine pigment (PB15)



(c) Quinacridone pigment (PR122)

Figure 4.1 SEM micrographs of pigment powder

Since 2 out of 3 organic pigment used were classified as polycyclic pigment (phthalocyanine (PB15) and quinacridone (PR122) pigment), whereas diarylide (PY83) pigment was classified in disazo pigment. And because of the greater dispersibility and smaller particle size of PR122 powder, compared to PB15 powder, PR122 powder was chosen as a representative pigment to use in this section.

All conditions of the actual practice by twin screw extruder are exhibited in Table 3.5. 0.4 phr of PR122 powder was mixed with MDPE powder to produce colored MDPE for every conditions. The colored MDPE extrudated from condition no. 1 (10 rpm and 160 °C) has an irregular size through the strand, i.e., the diameter of strand was not

consistency. This is probably due to the inconsistent viscosity of the melt MDPE. Thus, if solely based on this result, condition no.1 is not suitable to be used in the extrusion process. When considering screw speed and approximate processing time (from feed hopper to chopper), as listed below, the slower the screw speed, the longer the processing time.

Screw Speed (rpm)	Processing Time (hour per 1 kg of dry mixture)
10	4
20	2
30	1

As seen, at 10 rpm, the mixture has spent approximately 4 times longer than that at 30 rpm. There, economically, the condition no.1,2,3 (10 rpm) should not be used. These results suggest that the output rate seems to be dependent on the melt viscosity of MDPE. As screw speed increases, the shear rate increases resulting in the decreasing in melt viscosity of MDPE. In other words, the material demonstrates shear thinning as shear rate from twin screw extruder increases and hence, the viscosity decreases [58].

As a result, it took only 1 hour for mixture to be processed at 30 rpm. The dispersibility of pigment powder in MDPE via twin screw extruder has been shown in Figure 4.2. Good dispersion of pigment powder in MDPE can be observed in every conditions.

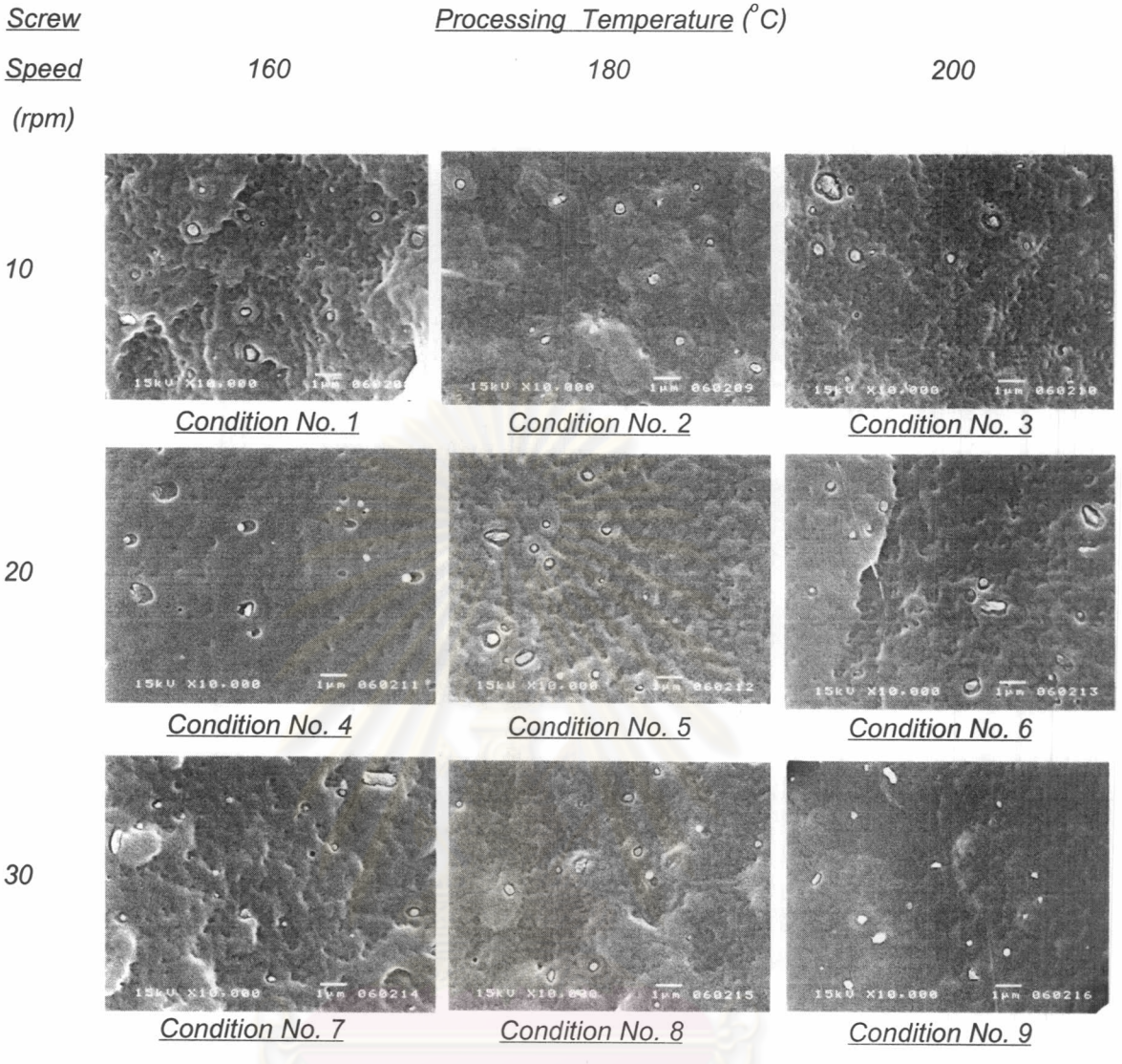
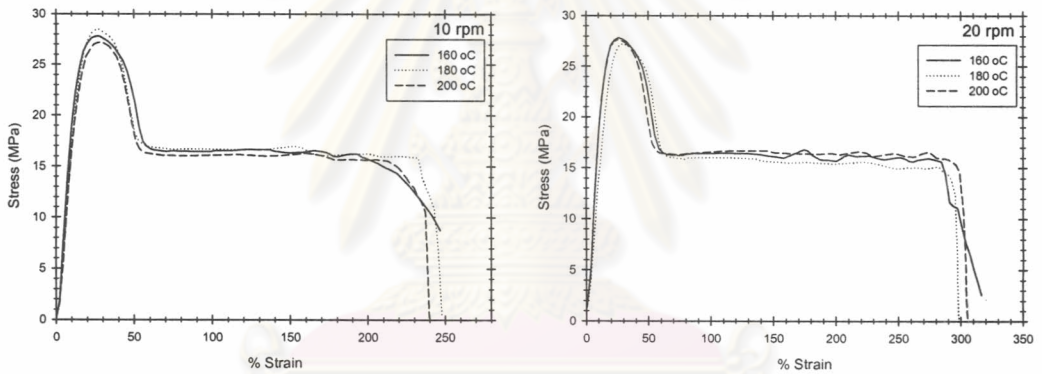


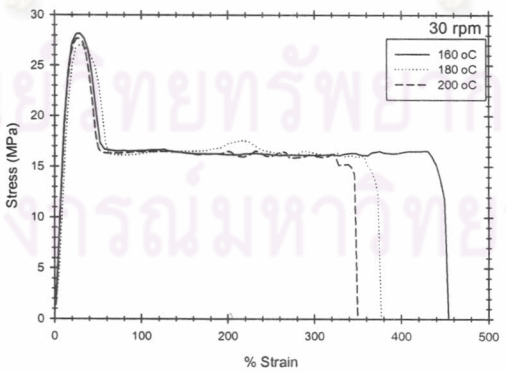
Figure 4.2 SEM micrographs of the fractured surfaces of colored MDPE extrudate with PR122 on different conditions

4.1.1 Effects of Processing Temperature

Figure 4.3 (a) – (c) presents the effect of processing temperature on the stress-strain behavior of the colored MDPEs with PR122 processed at three different screw speeds, i.e., 10 rpm, 20 rpm, and 30 rpm. As shown, at each screw speed the tensile properties are not influenced by the processing temperature except at 30 rpm, there seems to have slight effect on %strain. Unlike Figure 4.3 (a) and (b), the stress-strain curves of colored MDPE with PR122 mixed at screw speed of 30 rpm (Figure 4.3 (c)) are not superimposed to each other. Increasing processing temperature shows adverse effect on %strain at break upon varying the processing temperature. In addition, comparing between these 3 graphs, %strain at break increases with increasing screw speed. This result will be detailed in the next section.



(a) 10 rpm (condition no.1, 2, 3) (b) 20 rpm (condition no.4, 5, 6)

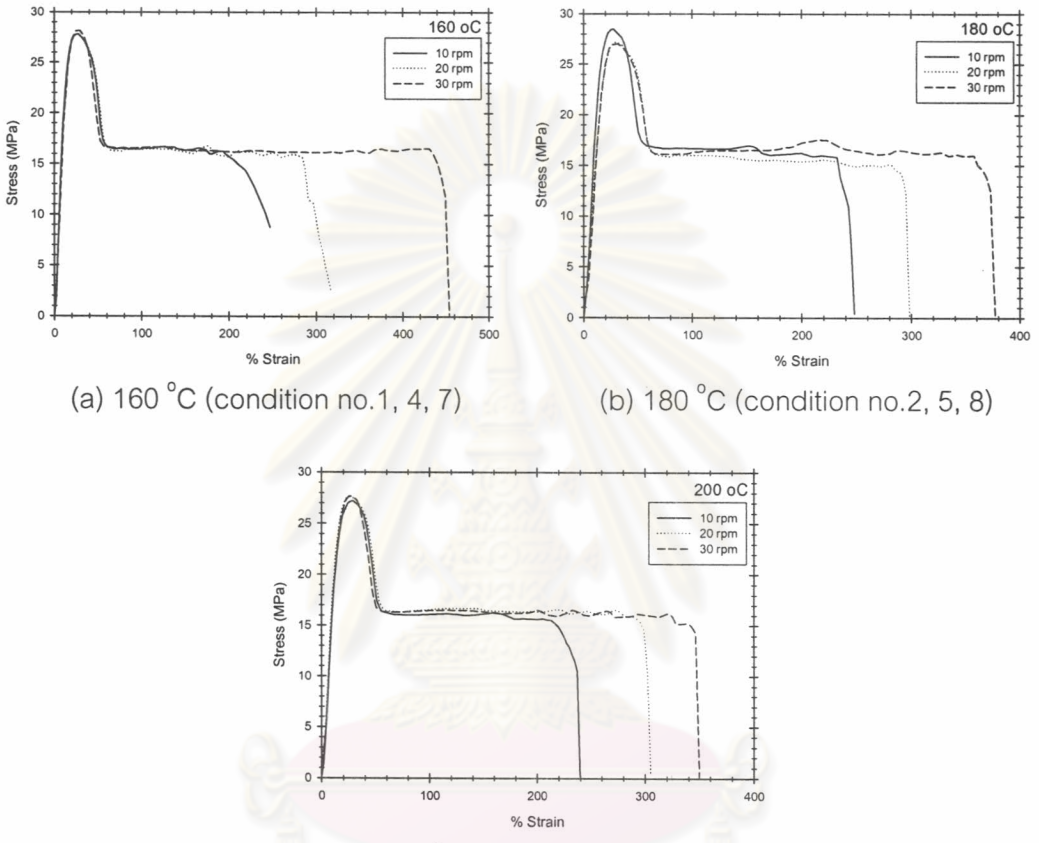


(c) 30 rpm (condition no.7, 8, 9)

Figure 4.3 Effect of the processing temperature on the tensile properties of colored MDPEs with PR122

4.1.2 Effects of Screw Speed

Similar to Figure 4.3, Figure 4.4 (a) – (c) exhibits the effect of screw speed on the stress-strain curve of colored MDPE with PR122 at three different processing temperatures.



(a) 160 °C (condition no.1, 4, 7)

(b) 180 °C (condition no.2, 5, 8)

(c) 200 °C (condition no.3, 6, 9)

Figure 4.4 Effect of screw speed on the tensile properties of colored MDPE containing PR122

As mentioned earlier, the same trend of tensile properties, including tensile modulus, tensile stress at maximum load, and tensile stress at break, are found in both effects. Screw speed and processing temperature have no effect on these tensile properties, except their %strain at break. As shown, % strain of the samples seems to be affected by varying screw speed. Obviously, % strain at break increases with an increase in screw speed of twin screw extruder. This result can be explained that the pigment powder has better dispersion in MDPE when increasing the screw speed or

shear rate. Also, the higher screw speed helps facilitating the compatibility of mixture between MDPE and pigment powder and hence promotes % strain at break. Oliveira, M.J. and Cramez, M.C. have also addressed that the more effective compounding as using extrusion allows the pigment to disperse and distribute better [45].

In addition, In-eure, P. [9] studied the effects of kneading conditions on the dispersion of pigments in PE using a continuous kneader. The results showed that the dispersibility of the pigment increased as the rotational speed of the screw increased and a higher speed provided higher intensity of shear stress to break agglomerates of the pigment. Furthermore, Phingchin, N. [9] reported that the dispersion state of pigment in PS increased when increasing the kneading temperature and the rotational speed of the screw. As previously discussed, the increasing of processing temperature can not improve % strain at break, but can reduce the melt viscosity of MDPE. The melt MDPE containing pigment powder can flow easily during processing.

Figure 4.5 displays the effects of processing conditions (no.1 - 9) on the tensile properties of the colored MDPE with PR122. Obviously, conditions no.7 – 9 give higher %strain at break than the others, while they have no effect on other tensile properties (Figure 4.5 (a) - (c)). Considering other processing conditions (no.1 - 6), it can be concluded that processing conditions have no effect on the tensile properties. Therefore, based on the processing time and %strain at break, condition no.7 – 9 are more suitable to be further used in the melt blending process than the other 6 conditions.

Comparing among three conditions (no.7 - 9), although their process time and %strain at break are quite similar and, as seen in Figure 4.2, good dispersibility of quinacridone pigment powder in MDPE can be observed. Some agglomeration of pigment powder can be noticed in both conditions no.7 and 9. In addition, as listed below, the output rate (g min^{-1}) or the processing time (min kg^{-1}) of condition no.7 is lower than the other two conditions; therefore, condition no.7 is not suitable to be used due to the above reasons. Similar in output rate, the efficiency in dispersion and tensile properties were observed in both conditions no.8 and 9. However, condition no.9 (200°C) consumed higher in electrical energy than condition no.8 (180°C).

Consequently, condition no.8 (30 rpm and 180 °C) is the most suitable method for the process optimization in melt blending technique via twin screw extruder.

Condition No.	Output Rate (g min^{-1})	Process Time (min kg^{-1})
7	12.20	82
8	15.38	65
9	16.39	61

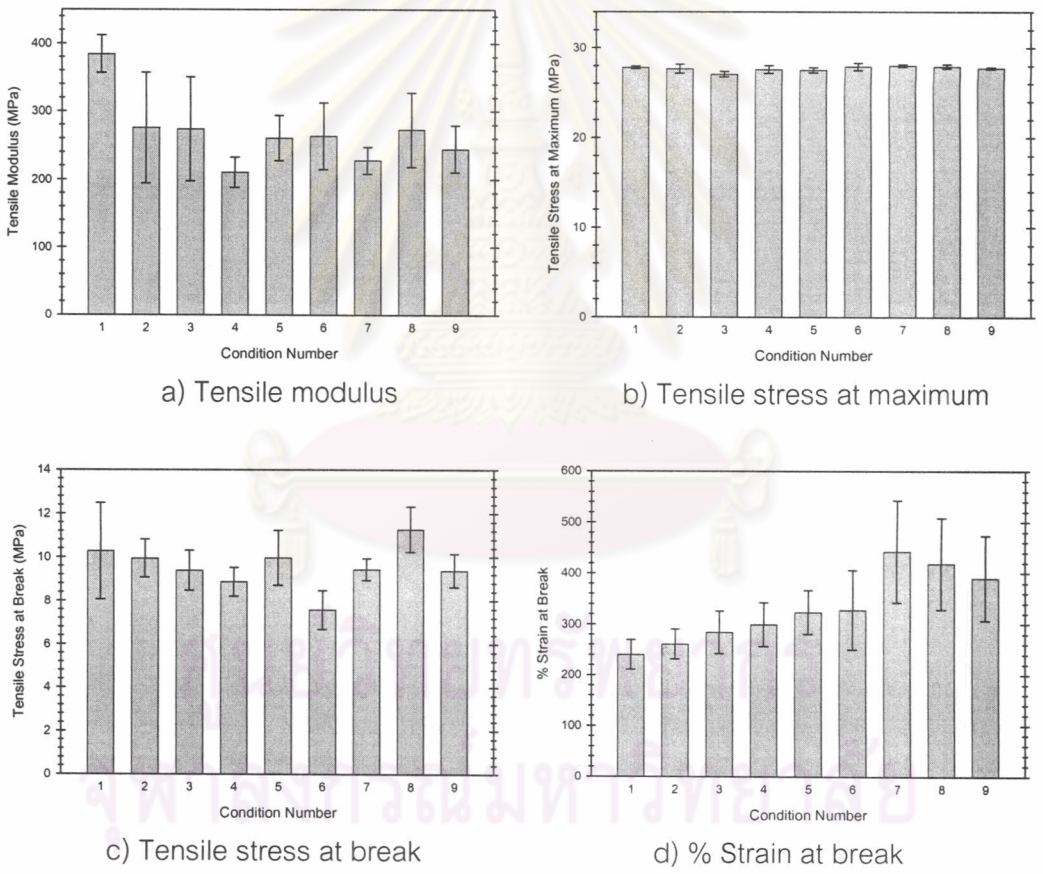


Figure 4.5 Effect of extrusion conditions on the tensile properties of pigments (PR122) in medium density polyethylene

4.2 Mechanical Properties Characterization

4.2.1 Tensile Properties

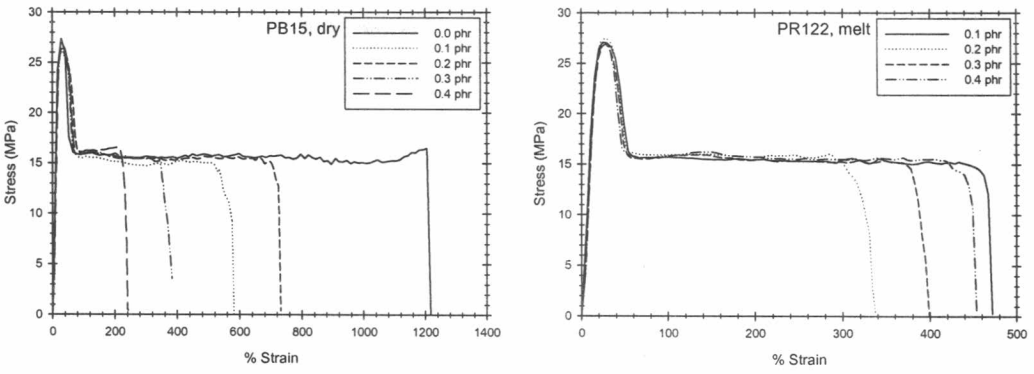
In this study, the effects of pigment content, pigment type, blending technique, and manufacturing process were also investigated. The tensile properties were measured according to ASTM D 638. From each of the stress-strain curves, four tensile properties, namely, tensile modulus, tensile stress at maximum load, tensile stress at break, and % strain at break were obtained and graphically shown in Figure 4.6 through 4.17.

The tensile modulus is defined as the slope of the tangent to the stress-strain curve at low strain. The tensile stress at maximum load and tensile stress at break are the values of the stress on the stress-strain curve where the curve occurred at the maximum and the point of breakage, respectively. The % strain at break is the maximum strain exhibited by the test sample at the point of breakage.

It should be noted that generally the tensile stress-strain relationship of a polymer depends on both the test temperature and the crosshead speed. Here, the temperature was ambient temperature and the crosshead speed was 50 mm min^{-1}, which corresponds to the medium speed specified in ASTM D 638.

4.2.1.1 Effect of Pigment Contents

Figure 4.6 presents the effect of pigment content on the stress-strain curves of the colored MDPE. For both blending techniques, similar trend can be observed. Obviously, the initial portion of the stress-strain curve of each plot seems to be coincidently identical, however, their %strain at break are different. As varying the amount of pigment, %strain at break of the composite is decreased, in particular, for dry blending technique. Effects of pigment content on the tensile properties of the composites are graphically displayed and tabulated in Figure 4.7 through 4.10 and Table 4.2 through 4.5, respectively.



(a) PB 15, dry blending (b) PR 122, melt blending

Figure 4.6 Effect of pigment contents on the stress-strain curves of (a) Colored MDPE with PB15 from dry blending technique and (b) Colored MDPE with PR122 from melt blending technique

The tensile properties of colorless MDPE and colored MDPE fabricated from rotational molding are also presented, for comparison, in Table 4.2 through 4.5. From the results, it can be concluded that there is no significant change on the tensile modulus, tensile stress at maximum load, and tensile stress at break of the samples upon increasing the amount of pigment.

However, as stated earlier, %strain at break of the colored MDPEs explicitly decreases with an increase of pigment content. For example, at 0.4 phr, %strain at break of MDPE/PY83, MDPE/PB15, and MDPE/PR122 mixed from dry blending technique decrease about 76.8%, 80.8%, and 96.2% compared to colorless MDPE, respectively (Table 4.5). The greatest decrease is of colored MDPE with PR122. This result is consistent with that of rotational molding, i.e., %strain at break of colored MDPE with PR122 decreased from 261.8% to 33.4% when 0.4 phr of the PR122 pigment was added into the MDPE. It should be noted that, however, there is no effect on %strain at break upon increasing pigment content for colored MDPE from melt blending technique. The effect of pigment type and blending techniques will be separately discussed in the next section.

Based on the composite theories, the modulus of the composite is dependent upon both volume fraction and the modulus of each component. However, from the results, increasing pigment content has no influence on the tensile modulus of the

colored MDPEs. This implies that the volume fraction or the pigment loading is too small to cause any pronounced effect on the tensile modulus values. This is because the highest amount of pigment used, 0.4 phr, is accounted for less than 0.4%, which is apparently too small for effective reinforcement to occur.

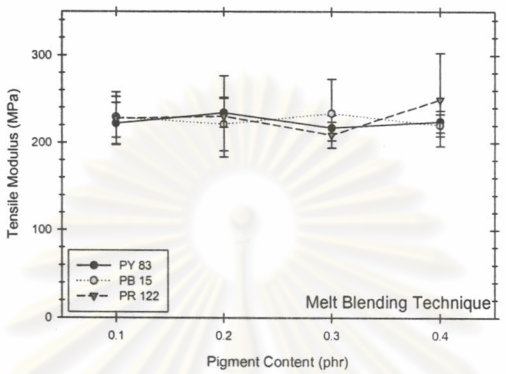
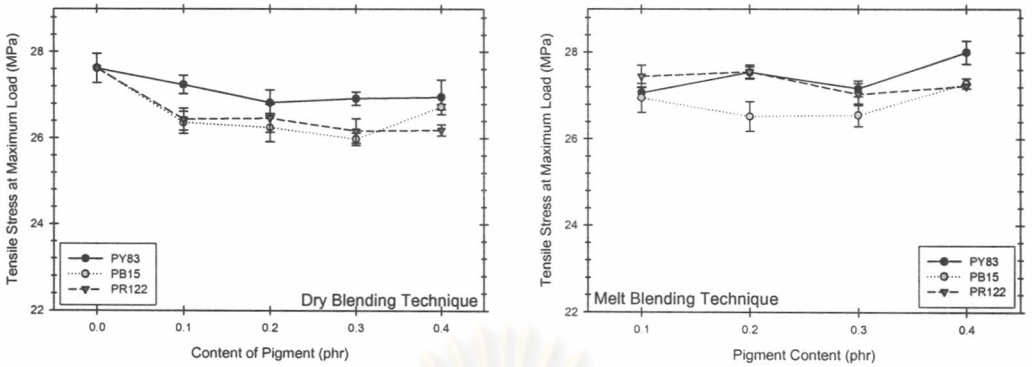


Figure 4.7 Effect of pigment contents on the tensile modulus of colored MDPEs via melt blending technique

Table 4.2 Tensile modulus of colored MDPEs

Pigment Type	Pigment Content (phr)	Tensile modulus of colored MDPEs (MPa)		
		Dry blending technique*	Melt blending technique*	Rotational molding
MDPE**	0.0	216.9 ± 23.4	-	160.3 ± 1.6
PY 83	0.1	228.6 ± 5.8	221.9 ± 23.7	-
	0.2	206.1 ± 15.8	234.3 ± 16.7	-
	0.3	238.9 ± 31.1	217.1 ± 14.7	-
	0.4	242.9 ± 23.7	224.3 ± 12.3	171.4 ± 21.7
PB 15	0.1	193.1 ± 16.9	229.1 ± 23.4	-
	0.2	203.8 ± 19.5	221.2 ± 30.6	-
	0.3	213.6 ± 25.0	233.6 ± 39.4	-
	0.4	174.4 ± 16.6	220.1 ± 12.5	160.1 ± 10.7
PR 122	0.1	201.0 ± 13.1	227.6 ± 30.1	-
	0.2	200.9 ± 10.7	230.2 ± 46.3	-
	0.3	193.1 ± 9.8	208.9 ± 15.0	-
	0.4	261.7 ± 55.6	249.5 ± 53.4	169.2 ± 7.7

* Compression molding process, ** Colorless MDPE



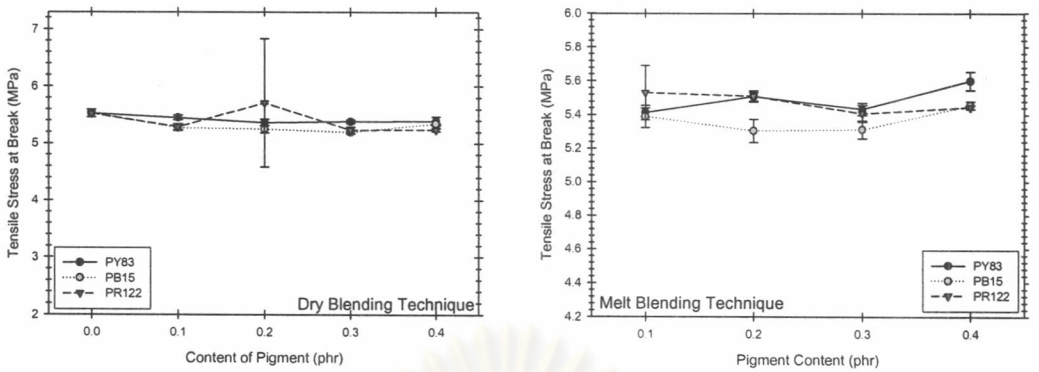
(a) Dry blending technique (b) Melt blending technique

Figure 4.8 Effect of pigment contents on tensile stress at maximum load of colored MDPEs

Table 4.3 Tensile stress at maximum load of colored MDPEs

Pigment Type	Pigment Content (phr)	Tensile stress at maximum of colored MDPEs (MPa)		
		Dry blending technique*	Melt blending technique*	Rotational molding
MDPE**	0.0	27.6 ± 0.3	-	27.2 ± 0.2
PY 83	0.1	27.2 ± 0.2	27.1 ± 0.1	-
	0.2	26.8 ± 0.3	27.5 ± 0.1	-
	0.3	26.9 ± 0.2	27.2 ± 0.2	-
	0.4	27.0 ± 0.4	28.0 ± 0.3	27.2 ± 0.1
PB 15	0.1	26.4 ± 0.3	26.9 ± 0.3	-
	0.2	26.2 ± 0.3	26.5 ± 0.3	-
	0.3	26.0 ± 0.1	26.6 ± 0.3	-
	0.4	26.7 ± 0.1	27.3 ± 0.1	27.3 ± 0.7
PR 122	0.1	26.4 ± 0.3	27.4 ± 0.3	-
	0.2	26.5 ± 0.3	27.5 ± 0.2	-
	0.3	26.2 ± 0.3	27.0 ± 0.3	-
	0.4	26.2 ± 0.1	27.2 ± 0.1	25.3 ± 0.5

* Compression molding process, ** Colorless MDPE



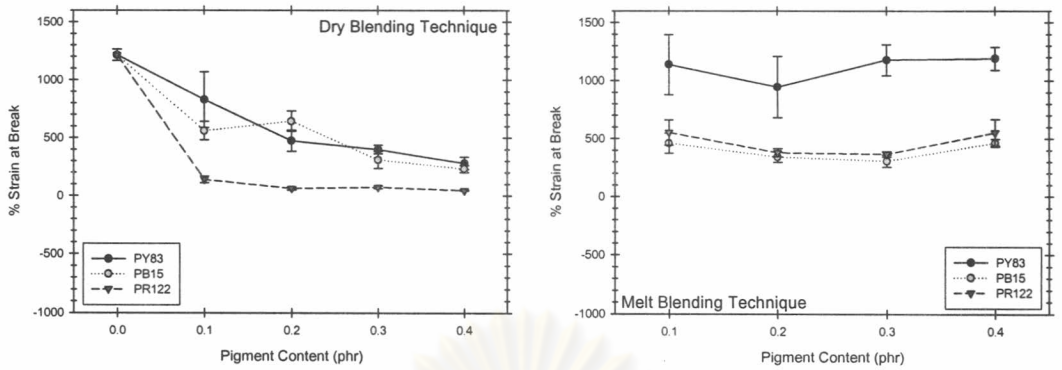
(a) Dry blending technique (b) Melt blending technique

Figure 4.9 Effect of pigment contents on tensile stress at break of colored MDPEs

Table 4.4 Tensile stress at break of colored MDPEs

Pigment Type	Pigment Content (phr)	Tensile stress at break of colored MDPEs (MPa)		
		Dry blending technique*	Melt blending technique*	Rotational molding
MDPE**	0.0	5.5 ± 0.07	-	5.4 ± 0.03
PY 83	0.1	5.4 ± 0.04	5.4 ± 0.03	-
	0.2	5.4 ± 0.06	5.5 ± 0.03	-
	0.3	5.4 ± 0.03	5.4 ± 0.04	-
	0.4	5.4 ± 0.08	5.6 ± 0.05	5.4 ± 0.02
PB 15	0.1	5.3 ± 0.05	5.4 ± 0.07	-
	0.2	5.2 ± 0.07	5.3 ± 0.07	-
	0.3	5.2 ± 0.03	5.3 ± 0.05	-
	0.4	5.3 ± 0.01	5.5 ± 0.02	5.5 ± 0.14
PR 122	0.1	5.3 ± 0.05	5.5 ± 0.16	-
	0.2	5.7 ± 1.12	5.5 ± 0.03	-
	0.3	5.2 ± 0.06	5.4 ± 0.05	-
	0.4	5.2 ± 0.02	5.4 ± 0.01	5.1 ± 0.09

* Compression molding process, ** Colorless MDPE



(a) Dry blending technique (b) Melt blending technique

Figure 4.10 Effect of pigment contents on percentage strain at break (%) of colored MDPEs

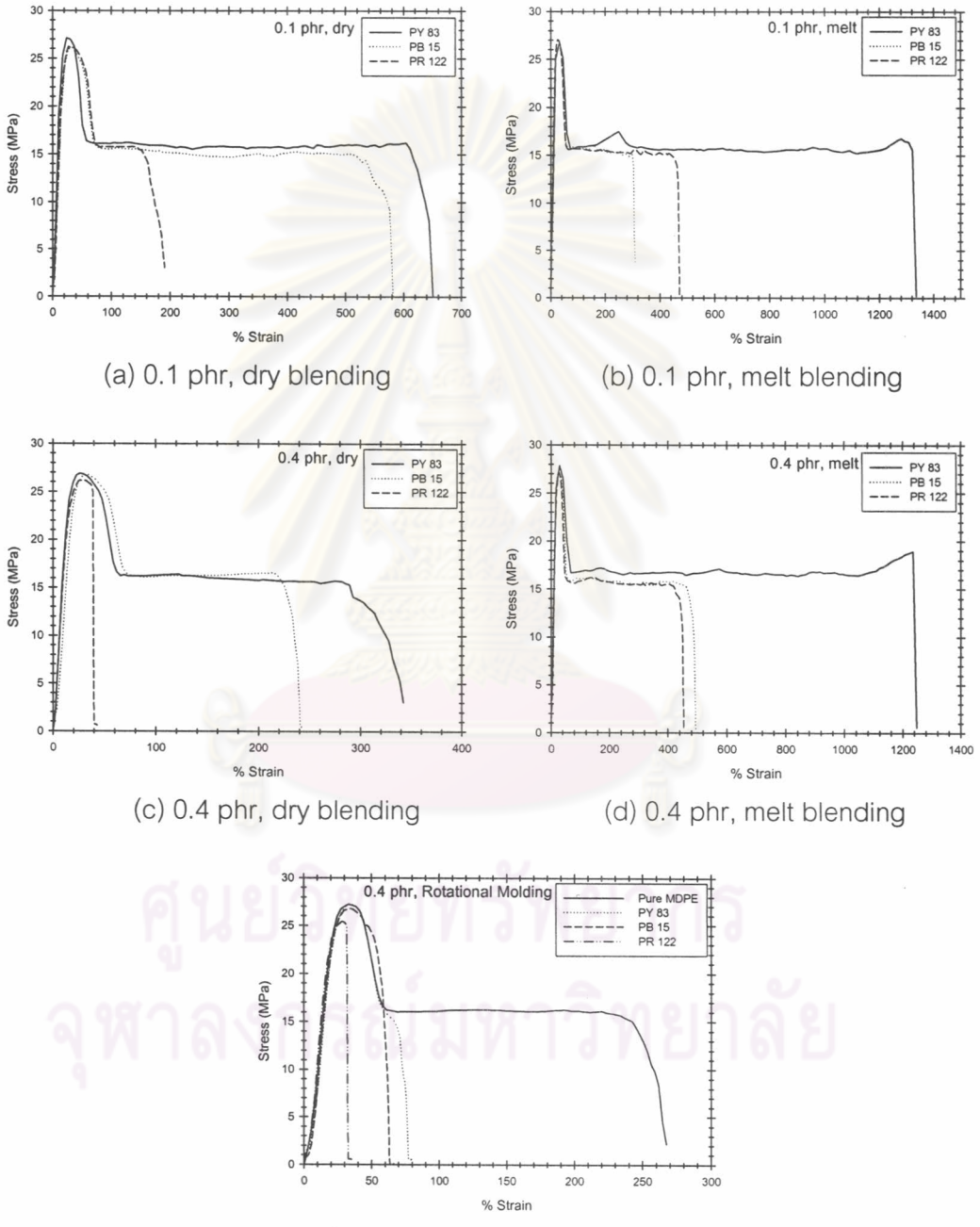
Table 4.5 Percentage strain at break of colored MDPEs

Pigment Type	Pigment Content (phr)	Percentage strain at break of colored MDPEs (%)		
		Dry blending technique*	Melt blending technique*	Rotational molding
MDPE**	0.0	1213.6 ± 49.5	-	261.8 ± 12.0
PY 83	0.1	829.4 ± 240.0	1137.7 ± 258.3	-
	0.2	474.3 ± 91.8	945.4 ± 263.8	-
	0.3	399.4 ± 37.4	1177.3 ± 132.6	-
	0.4	281.6 ± 54.2	1190.6 ± 99.2	67.8 ± 6.8
PB 15	0.1	560.3 ± 79.4	461.6 ± 86.9	-
	0.2	642.9 ± 87.6	342.2 ± 44.2	-
	0.3	309.8 ± 71.6	308.0 ± 52.3	-
	0.4	232.7 ± 30.1	463.8 ± 34.0	60.7 ± 3.1
PR 122	0.1	139.5 ± 28.5	553.7 ± 110.1	-
	0.2	61.7 ± 12.8	379.2 ± 35.8	-
	0.3	73.2 ± 12.7	367.5 ± 22.8	-
	0.4	45.9 ± 5.2	553.9 ± 113.7	33.4 ± 0.8

* Compression molding process, ** Colorless MDPE

4.2.1.2 Effect of Pigment Types

The effect of pigment type on the stress-strain curves of colored MDPEs is illustrated in Figure 4.11. Their tensile properties are presented in Figure 4.7 through 4.10 and Figure 4.12.



(a) 0.1 phr, dry blending

(b) 0.1 phr, melt blending

(c) 0.4 phr, dry blending

(d) 0.4 phr, melt blending

(e) 0.4 phr, rotational molding

Figure 4.11 Effect of pigment types on the stress-strain curves of colored MDPEs

Comparing among three types of pigment, similar to the effect of pigment concentration, there is no differences in the tensile properties, except the %strain at break of the colored MDPEs. These results are true for both melt blending and dry blending techniques. For instance, the tensile stress at maximum load, as tabulated in Table 4.3, are approximately 26 – 27 MPa, whereas their tensile stress at break are in the range of 5.2 – 5.5 MPa, as shown in Table 4.4.

However, for rotational molding technique, the tensile stress at maximum load and tensile stress at break of the colored MDPE with PR122 are slightly lower than colorless MDPE and the other two types of pigments in colored MDPEs.

As mentioned above, pigment type plays an important role on the %strain at break. Clearly, the %strain at break of colored MDPE with PY83 (diarylide pigment) is greater than that of the other two types of colored MDPEs. In fact, the colored MDPEs containing PY83 give highest values of %strain at break, whereas the colored MDPE with PR122 (quinacridone pigment) show lowest %strain at break. This trend can be obviously seen in both dry blending technique and rotational molding. When comparing to colorless MDPE, it is found that the addition of various types pigment leads to a remarkably reduction in %strain at break, especially in colored MDPEs with PR122. In other words, the MDPE containing quinacridone pigment has inferior %strain at break compared to the other two organic pigments used.

Conclusively, colored MDPEs with PR122 have inferior tensile properties, especially from the rotational molding point of view, compared to the other colored MDPEs. This result can be explained as follows.

In general, there are a few important parameters known to affect the properties of composites in general : average particle size of the filler and the distribution thereof, adhesion of the binder to the filler or interfacial adhesion, the wettability of the filler, and the amount of binder used. It is also important to note that with small particles, the interface between the filler and the binder plays a significant role. Smaller particles are not desirable, for they require more polymer for effective binding, resulting in a lower tensile strength. Too large particles, on the other hand, act as discontinuities, again lowering the tensile strength [59]. Because quinacridone pigment (PR122) has smaller particle size (0.49 μm) compared to the other two pigments as previously reported in

section 4.1, the tensile stress at maximum load, tensile stress at break, and %strain of the colored MDPEs with PR122 are greatly affected. In the same fashion, the larger particle size of phthalocyanine pigment (PB15) (17.53 μm) might be accounted for the decrease in %strain at break of the colored MDPEs containing PB15 compared with colorless MDPE. As discussed earlier, PB15 powder tends to coalesce more than the other two pigments, so colored MDPE with PB15 showed poor dispersibility as seen in Figure 4.1.

However, besides the above parameters mentioned, Verbeek, C.J.R. [59] has shown in his model that the porosity of the composite and the aspect ratio of the reinforcement are key factors influencing both young's modulus and tensile strength. Factors such as particle irregularities and particle size distribution are accounted for by the maximum packing fraction of the reinforcement. This in turn influences the final porosity of the composite.

In addition, the results showed that the aspect ratio is far a more important parameter than particle size and distribution and optimal composite behavior can only be obtained by maximizing this property of the reinforcement. The variance in the data can most likely be attributed to the variation in aspect ratio and final composite porosity. Denser packing, i.e., a smaller composite porosity will result in a highest tensile strength. However, since these parameters are beyond the scope of this research, the results are solely explained based on the average particle size of each pigment used. Further investigation regarding the aspect ratio, in particular, should be carried out to ensure the results. Figure 4.12 shows tensile properties of rotationally molded part of colored MDPEs.

As described earlier, all tensile properties of pigment type in colored MDPE could be organized into order as PY83, PB15, PR122, respectively. That means the tensile properties, including the tensile stress at maximum load, the tensile stress at break, and the % strain at break of colored MDPEs with PY83 has superior value. And vice versa, colored MDPEs with PR122 show inferior tensile properties compared to the two organic pigment type using in colored MDPE, especially in the % strain at break.

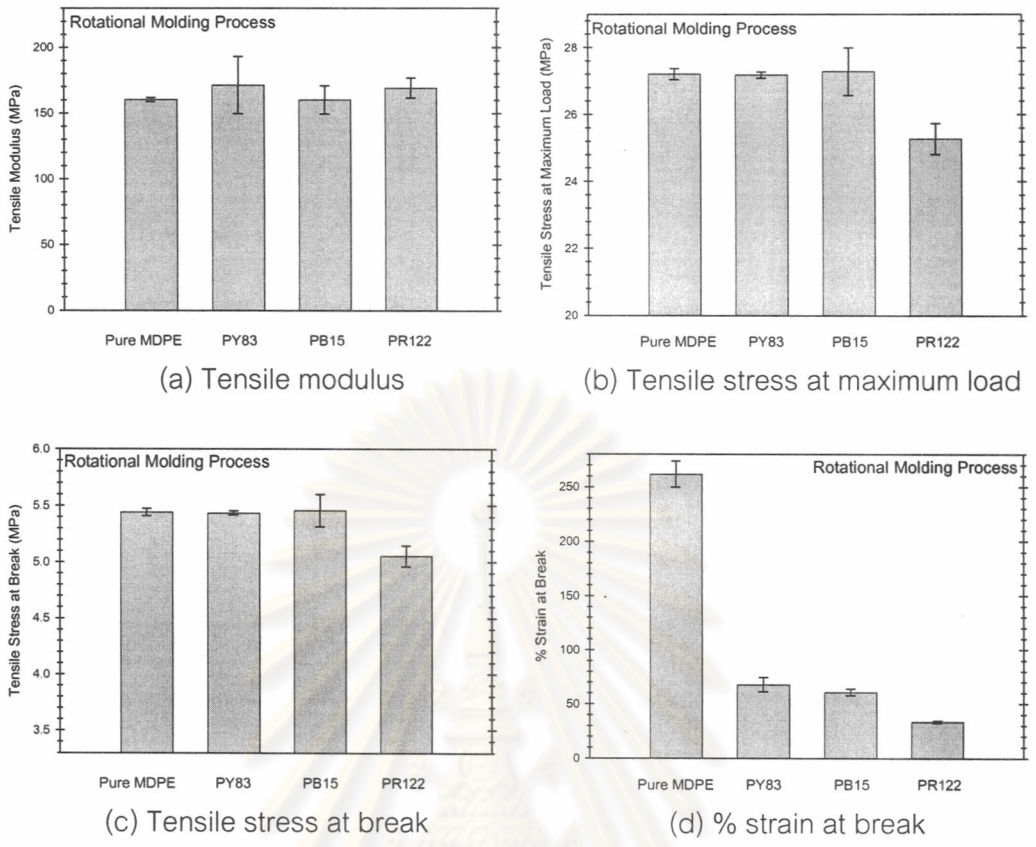


Figure 4.12 Tensile properties of colored MDPEs via rotational molding process

4.2.1.3 Effect of Blending Techniques and Manufacturing Processes

Figure 4.13 through 4.17 show the effect of blending techniques and manufacturing processes on the stress-strain curves and the tensile properties of the samples. Obviously, the results from melt blending technique are superior than those of dry blending technique and rotational molding process. The tensile properties of the dry blending technique appear in the almost same value as their rotational molding process, since both also used the dry blending method.

However, the tensile properties of the samples obtained from rotational molding process are lower than those of dry blending technique via compression molding process, especially in tensile modulus and %strain at break values. This is because compression molding process may pack the molecules between plastic and pigment better than rotational molding process, owing to compression force during processing. From machine window, this force was received from pressure setting about 5 MPa which

may be actually higher. As discussed in tensile testing on the effect of pigment type, the difference in packing density concerns to the mechanical properties. Again here, denser packing has a smaller composite porosity that will result in a higher the mechanical properties [59].

On the other hand, rotational molding process has only the compression forces from the rotational motion in the mold to pack the component, which is almost zero MPa. More precisely, the warpage and global shrinkage are associated with the level of residual stresses in the rotationally molded parts. There are compressive on the outer surface and zero on the inner surface. This profile is obviously associated with the anisotropic quench of the parts [6]. Therefore, tensile properties of the samples from compression molding process are slightly better than those from rotational molding process.

For melt blending technique, because of the packing from the compression molding process and the compatibility and dispersibility of the pigment powder in MDPE obtained from the twin screw extruder, tensile properties of the samples from melt blending technique are the best. Shear forces applied to the MDPE/pigment mixture during mixing via twin screw extruder help enhancing the compatibility, dispersibility, and molecular orientation, resulting in greatest tensile properties comparing to the other two techniques. Similarly, Kalay, G. et al [60] have found that an increase of molecular orientation occurs with the consequent enhancement of stiffness. The molecular alignment which developed during shear flow, seems to be promoted by the application of high holding pressures, high shear stresses, and longer duration of shear.

In addition, the poor dispersibility of pigment powder has been more obviously displayed in the dry blending technique than the melt blending technique. Because of the mix of dry mixture via twin screw extruder, the compatibility between components between MDPE and pigment, for instance, dispersion and distribution, has been improved. Therefore, the % strain at break in the melt blending technique is not significantly influenced by the pigment content.

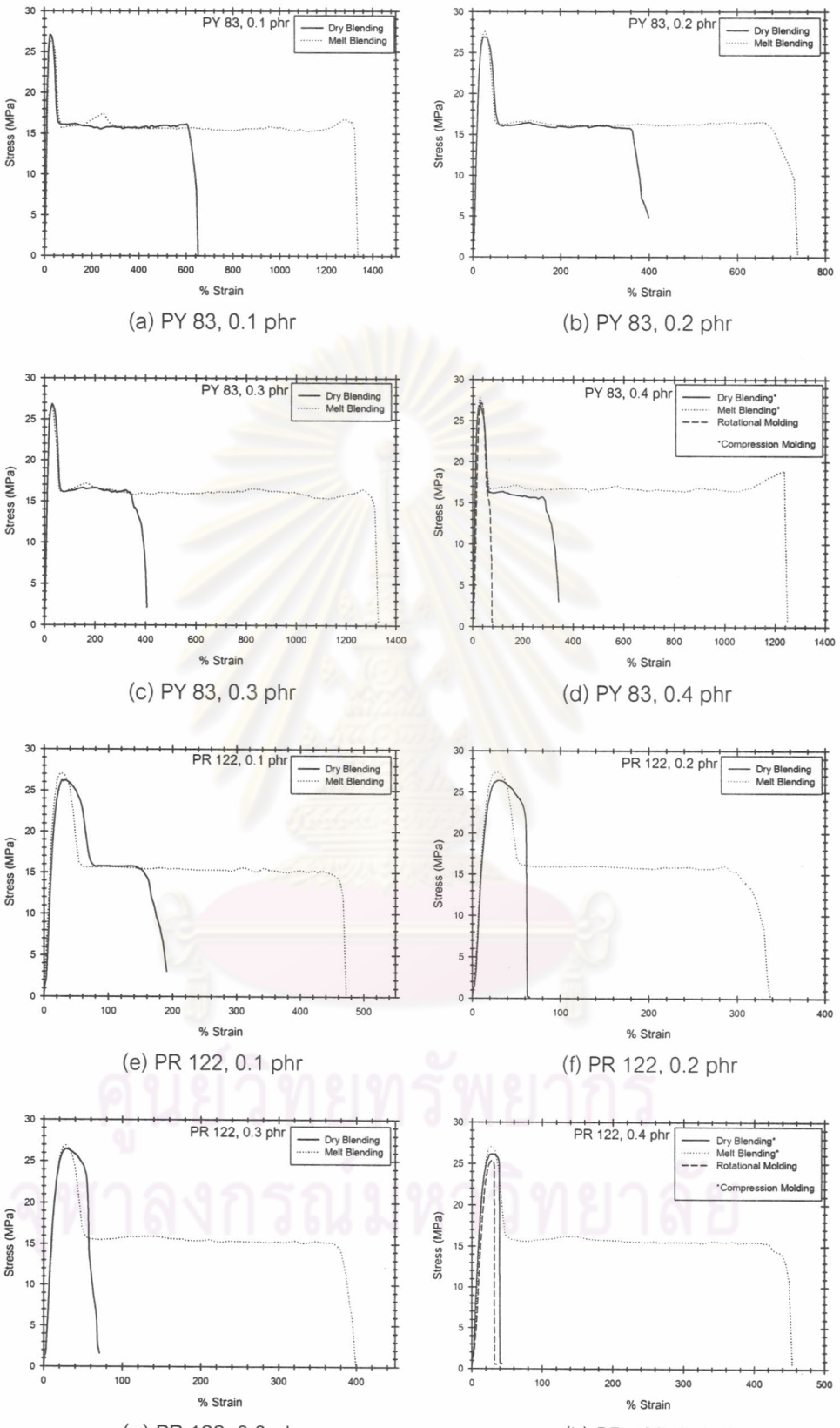


Figure 4.13 Effect of blending techniques and manufacturing processes on the stress-strain curves of colored MDPEs

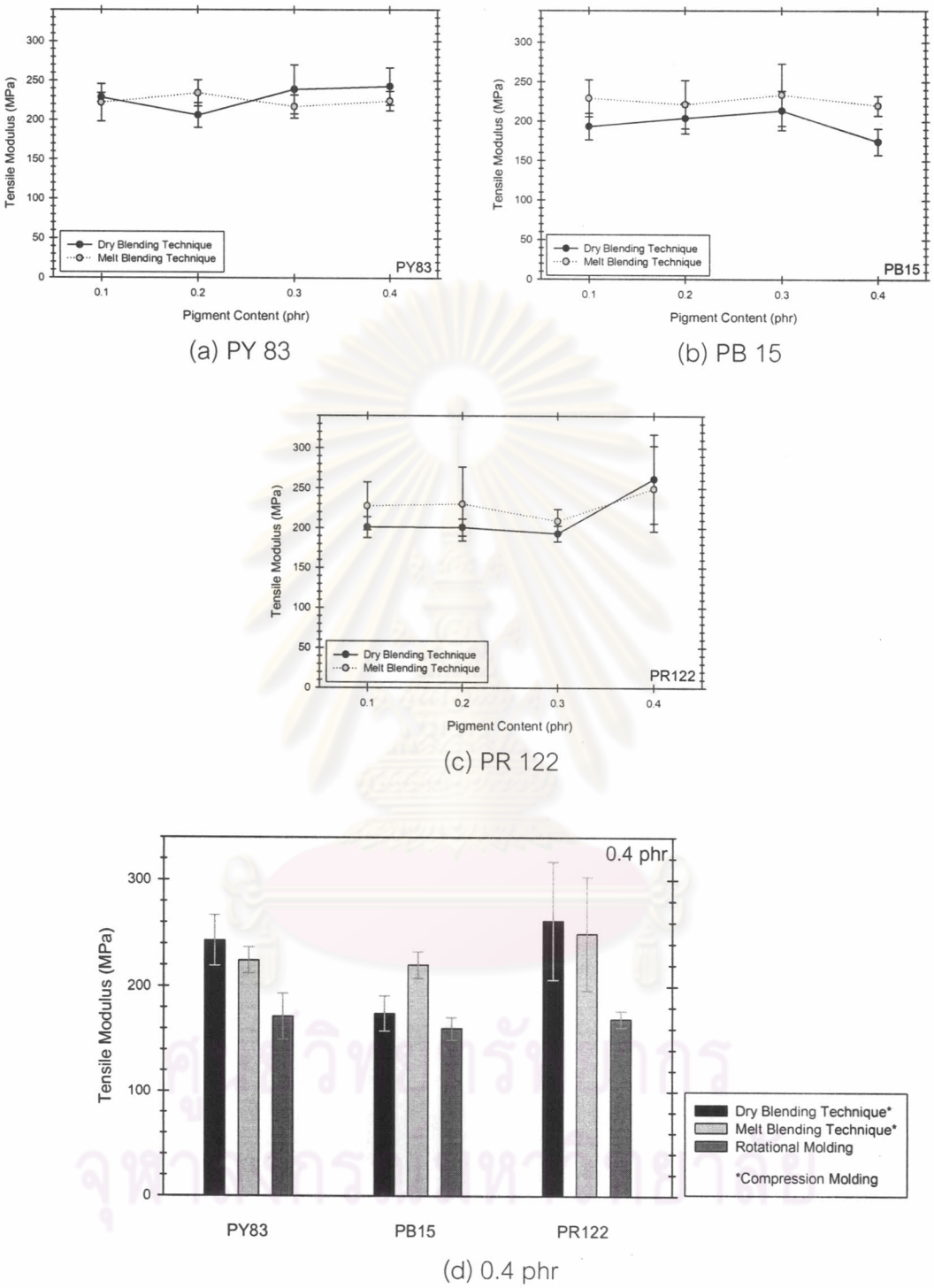


Figure 4.14 Effect of blending techniques and manufacturing processes on the tensile modulus of colored MDPEs

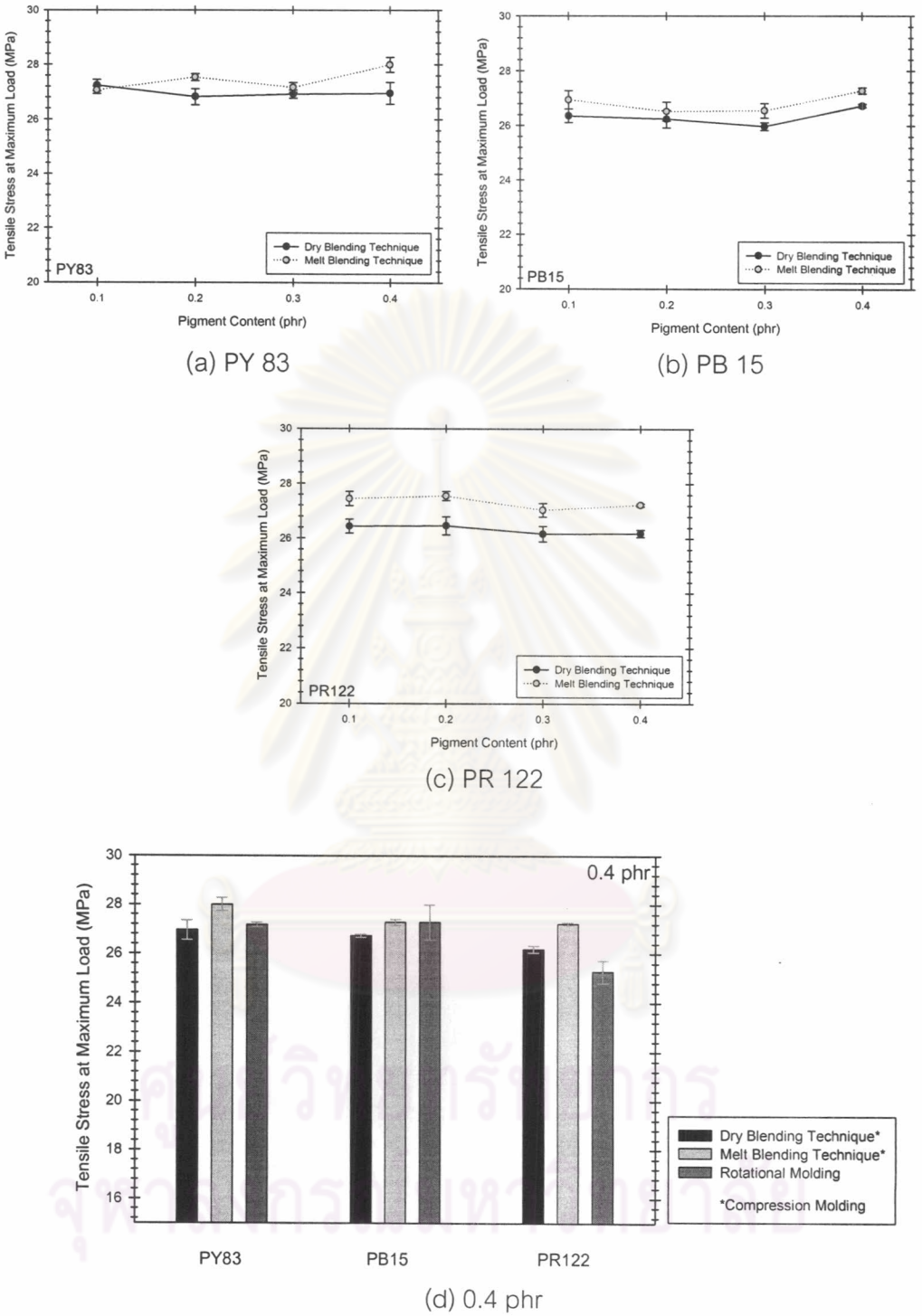
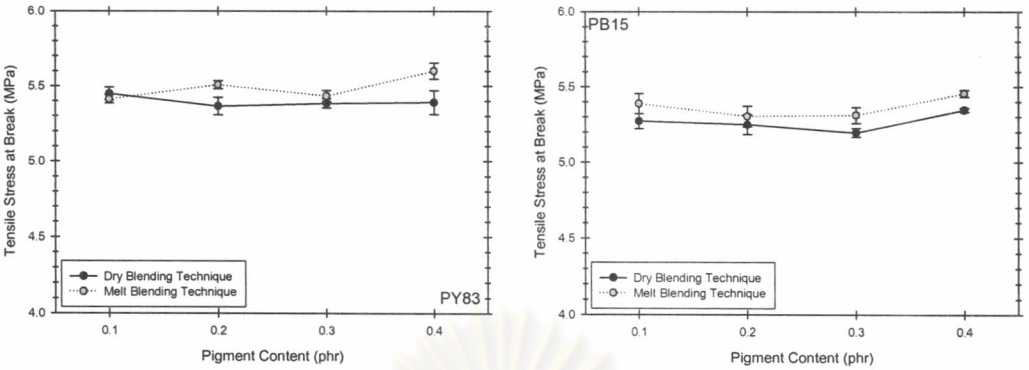
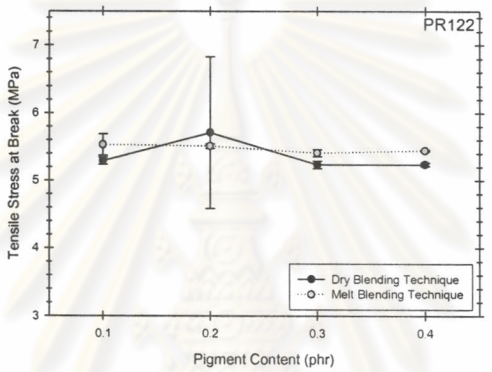


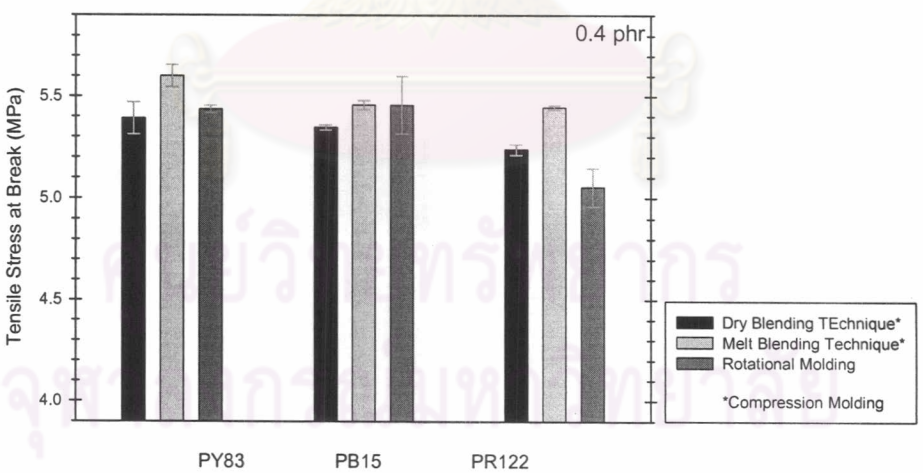
Figure 4.15 Effect of blending techniques and manufacturing processes on the tensile stress at maximum load of colored MDPEs



(a) PY 83 (b) PB 15



(c) PR 122



(d) 0.4 phr

Figure 4.16 Effect of blending techniques and manufacturing processes on the tensile stress at break of colored MDPEs

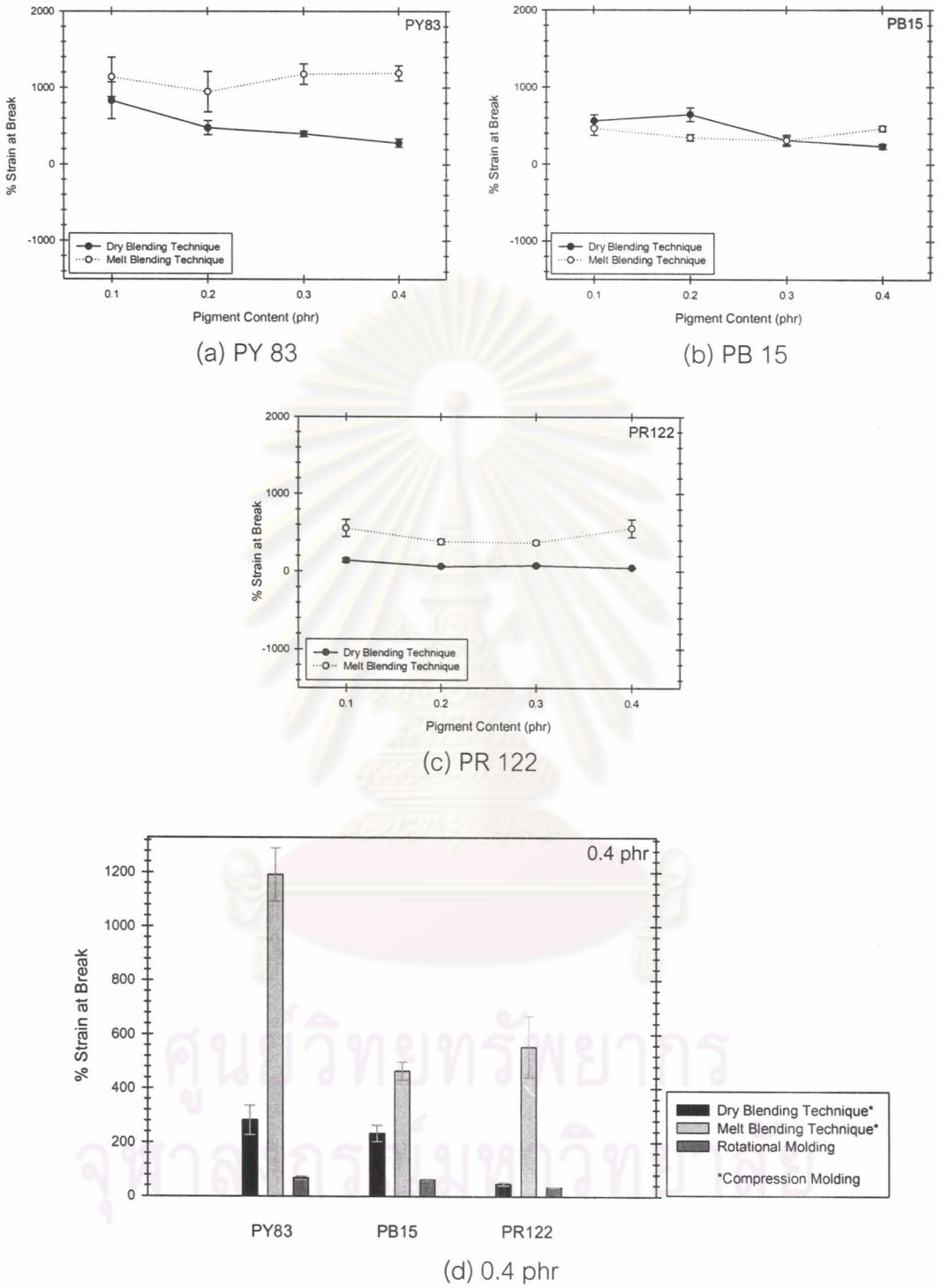
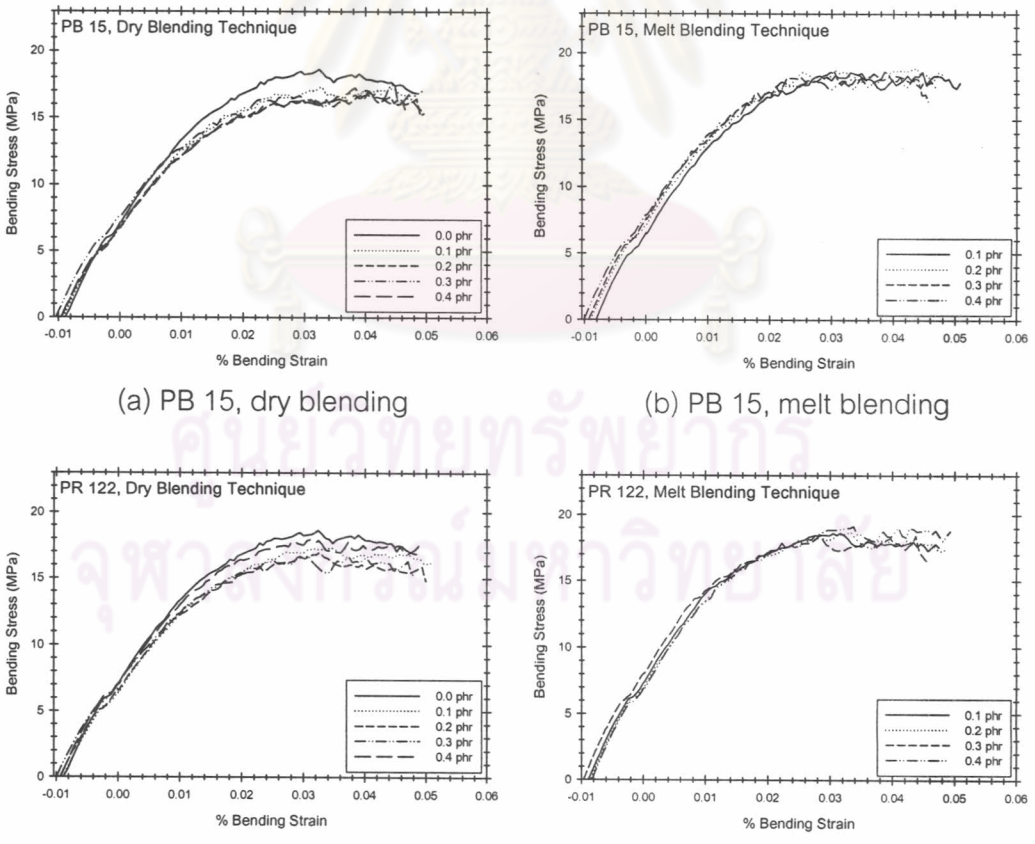


Figure 4.17 Effect of blending techniques and manufacturing processes on the percentage strain at break of colored MDPEs

4.2.2 Flexural Properties

4.2.2.1 Effect of Pigment Contents

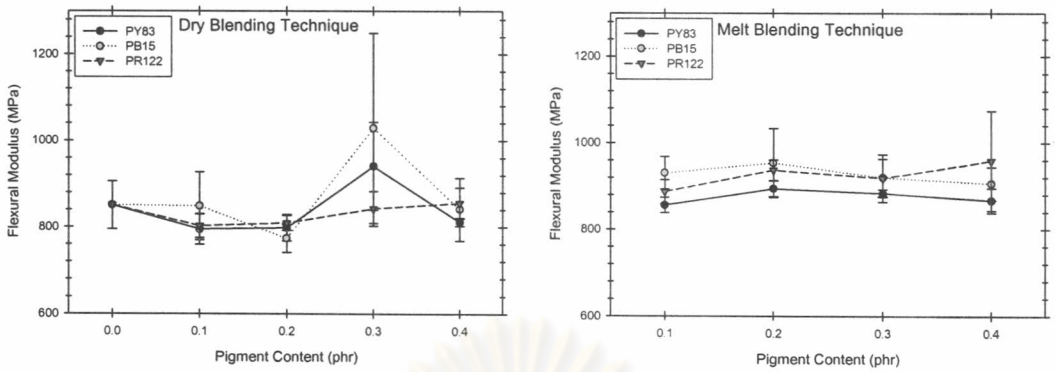
Figure 4.18 through 4.20 demonstrate the effect of pigment content on the flexural properties of the colored MDPEs. As shown and also summarized in Table 4.6 and 4.7, little effect on the flexural properties can be observed. For dry blending technique, the flexural strength of colorless MDPE listed in Table 4.7, however, is slightly superior than that of the colored MDPE. The reason for these results will be further discussed in the next section along with the effect of pigment type. In other words, comparing to colorless MDPE, the addition of pigment caused a reduction about 7 – 9%, depending on the pigment type, in the flexural strength of the colored MDPEs, whereas, similar to tensile modulus, the amount of pigment might be too small to cause any significant changes in those mechanical properties.



(a) PB 15, dry blending (b) PB 15, melt blending

(c) PR 122, dry blending (d) PR 122, melt blending

Figure 4.18 Effect of pigment contents on the flexural properties of colored MDPEs



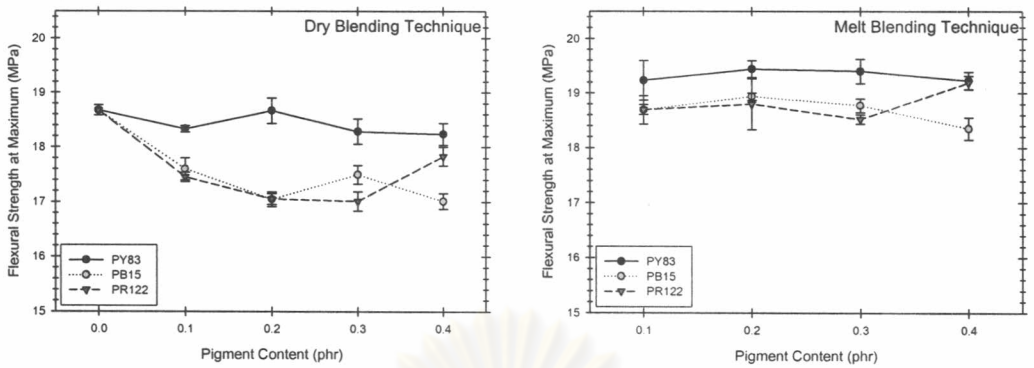
(a) Dry blending technique (b) Melt blending technique

Figure 4.19 Effect of pigment contents on flexural modulus of colored MDPEs

Table 4.6 Flexural modulus of colored MDPEs

Pigment Type	Pigment Content (phr)	Flexural modulus of colored MDPEs (MPa)			
		Dry blending technique*	Melt blending technique*	Rotational molding (outer surface)	Rotational molding (inner surface)
MDPE**	0.0	850.4 ± 55.5	-	-	-
PY 83	0.1	794.7 ± 35.6	855.9 ± 17.8	-	-
	0.2	798.1 ± 30.5	894.2 ± 18.0	-	-
	0.3	940.8 ± 101.6	883.1 ± 8.9	-	-
	0.4	811.7 ± 9.3	866.9 ± 28.3	690.1 ± 38.1	699.1 ± 32.6
PB 15	0.1	848.2 ± 78.7	930.2 ± 37.4	-	-
	0.2	773.3 ± 32.1	953.5 ± 79.5	-	-
	0.3	1028.8 ± 220.0	919.8 ± 42.6	-	-
	0.4	841.2 ± 73.0	906.0 ± 38.1	699.0 ± 16.4	629.0 ± 37.7
PR 122	0.1	802.4 ± 27.3	886.9 ± 27.7	-	-
	0.2	809.0 ± 17.2	936.7 ± 23.4	-	-
	0.3	842.4 ± 40.1	918.4 ± 54.7	-	-
	0.4	855.6 ± 36.2	958.5 ± 115.1	606.7 ± 24.7	559.2 ± 12.3

* Compression molding process, ** Colorless MDPE



(a) Dry blending technique (b) Melt blending technique

Figure 4.20 Effect of pigment contents on the flexural strength at maximum of colored MDPEs

Table 4.7 Flexural strength at maximum of colored MDPEs

Pigment Type	Pigment Content (phr)	Flexural strength at maximum of colored MDPEs (MPa)			
		Dry blending technique*	Melt blending technique*	Rotational molding (outer surface)	Rotational molding (inner surface)
MDPE**	0.0	18.7 ± 0.1	-	-	-
PY 83	0.1	18.3 ± 0.1	19.2 ± 0.4	-	-
	0.2	18.7 ± 0.2	19.4 ± 0.2	-	-
	0.3	18.3 ± 0.2	19.4 ± 0.2	-	-
	0.4	18.2 ± 0.2	19.2 ± 0.2	17.2 ± 0.2	16.9 ± 0.3
PB 15	0.1	17.6 ± 0.2	18.7 ± 0.3	-	-
	0.2	17.0 ± 0.1	18.9 ± 0.1	-	-
	0.3	17.5 ± 0.2	18.8 ± 0.1	-	-
	0.4	17.0 ± 0.1	18.4 ± 0.2	19.3 ± 0.2	16.5 ± 1.2
PR 122	0.1	17.4 ± 0.1	18.7 ± 0.1	-	-
	0.2	17.1 ± 0.1	18.8 ± 0.5	-	-
	0.3	17.0 ± 0.2	18.5 ± 0.1	-	-
	0.4	17.8 ± 0.2	19.2 ± 0.1	15.4 ± 0.2	14.7 ± 0.2

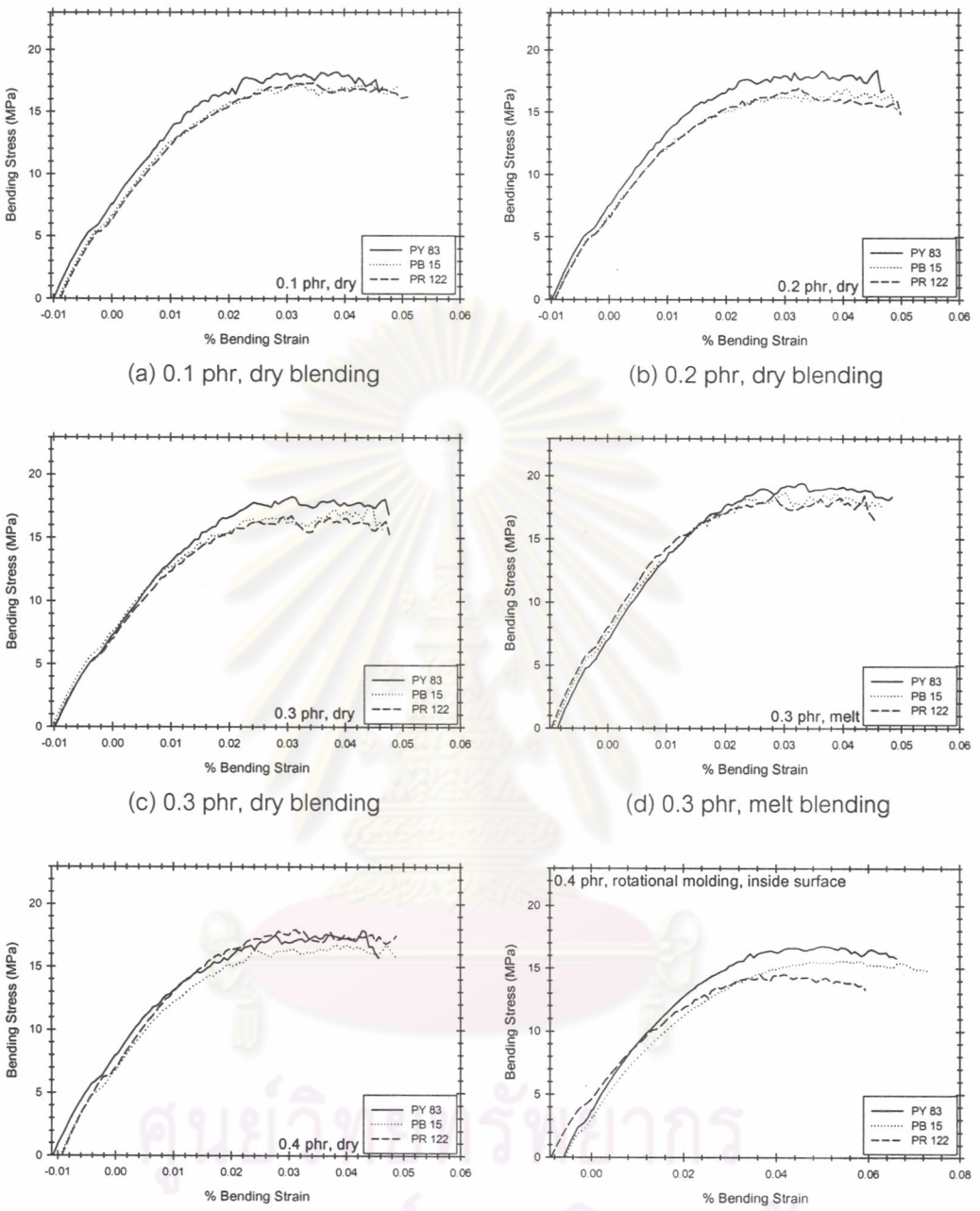
* Compression molding process, ** Colorless MDPE

4.2.2.2 Effect of Pigment Types

Figure 4.19 through 4.21 show the effect of pigment type on the flexural properties of the colored MDPEs. As shown in Figure 4.19, there is no apparent difference on the flexural modulus of the three types of colored MDPEs from dry blending technique. However, the pigment type affects the flexural modulus of the colored MDPEs prepared from melt blending technique, i.e., as seen in Figure 4.19 (b), the colored MDPEs with PY83 show lowest in flexural modulus compared to the others.

For flexural strength, Figure 4.20 and 4.21 show that the flexural strength of colored MDPEs with PY83 is actually better than the other colored MDPEs. The result from dry blending technique displays more clearly compared to the melt blending technique. This result might be due to the more suitability of the interfacial adhesion between MDPE and diarylide pigment (PY83).

Because the stiffness or modulus of the composite is mainly due to the filler, while the flexural strength improvement is also caused by the interfacial adhesion between the two phases which should be enough during being stretched [61]. Consequently, these results suggest that the interfacial adhesion between MDPE and PY83 might be greater than that of MDPE with the other two types of pigments. As described earlier, the suitable particle size of pigment is needed to acquire the effective interfacial adhesion. Too large or very small particles result in lower tensile strength. As a result, PY83 which has particle size of approximately 1.37 μm is more appropriate to be used in the composites since it yields the colored MDPEs with the highest flexural strength.



(a) 0.1 phr, dry blending

(b) 0.2 phr, dry blending

(c) 0.3 phr, dry blending

(d) 0.3 phr, melt blending

(e) 0.4 phr, dry blending

(f) 0.4 phr, rotational molding, inner surface

Figure 4.21 Effect of pigment types on the flexural properties of colored MDPEs

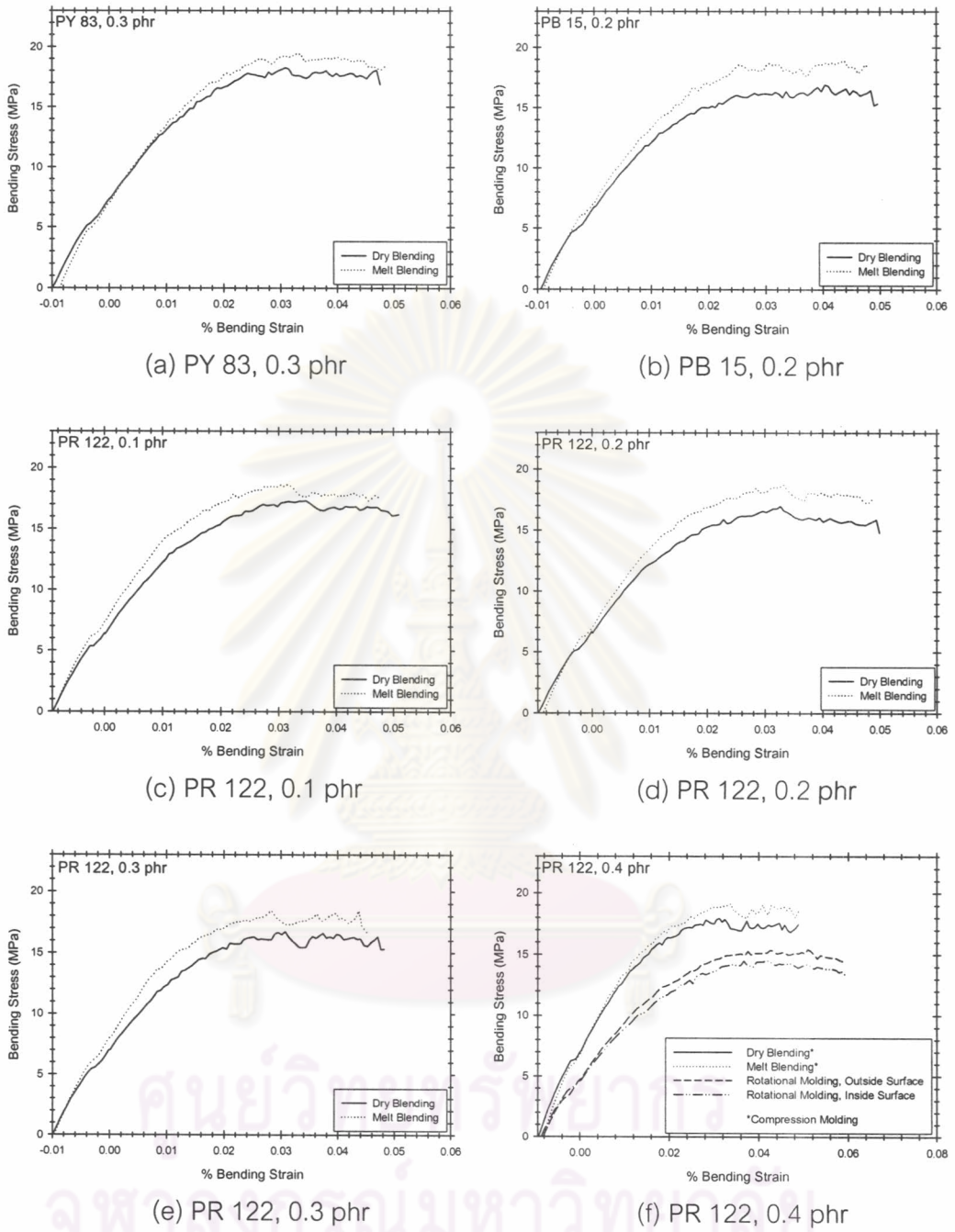
4.2.2.3 Effect of Blending Techniques and Manufacturing Processes

Figure 4.22 through 4.24 present the effect of blending techniques and manufacturing processes on the flexural properties of the colored MDPEs. The flexural properties of the MDPE containing 0.4 phr of pigment powder fabricated from the rotational molding are much lower than those of the samples obtained from compression molding process in both dry and melt blending techniques. In addition, as shown in Figure 4.22 (f), the outer surface of the specimen can withstand the bending force more than the inside.

This result may be explained that since the outer surface of the test specimen was in the pre-tension state due to its processing, the applied force from bending or flexural test can be considered as compressive force which will then counteract with the pre-stress in the specimen. In contrast, when applying compressive force onto the inner side of the specimen, this side is already, in fact, in the compressive mode. Therefore, the applied load acts as a promoter or enhances the failure of the specimen. As a result, the results reveal that the inner surface can tolerate bending force less than the outer surface.

This result appears in the same trend as the utilization of a hollow product and can be explained that the outer surface of hollow product from rotational molding process should be stronger than the inside. The outside has to absorb many forces, especially bending force for maintaining the lifetime of the products.

As defined in the tensile properties earlier, the packing of the component particles of the compression molding process is better than the rotational molding. Again here, the denser packing provides the specimen with small porosity that will result in a greater the mechanical properties. Moreover, the melt blending technique has more compatibility and better dispersibility of pigment powder in MDPE than the dry blending technique. Thus, the colored MDPEs produced from the melt blending technique are able to absorb and endure the bending force higher than the other two techniques.



(a) PY 83, 0.3 phr (b) PB 15, 0.2 phr

(c) PR 122, 0.1 phr (d) PR 122, 0.2 phr

(e) PR 122, 0.3 phr (f) PR 122, 0.4 phr

Figure 4.22 Effect of blending techniques and manufacturing processes on the flexural properties of colored MDPEs

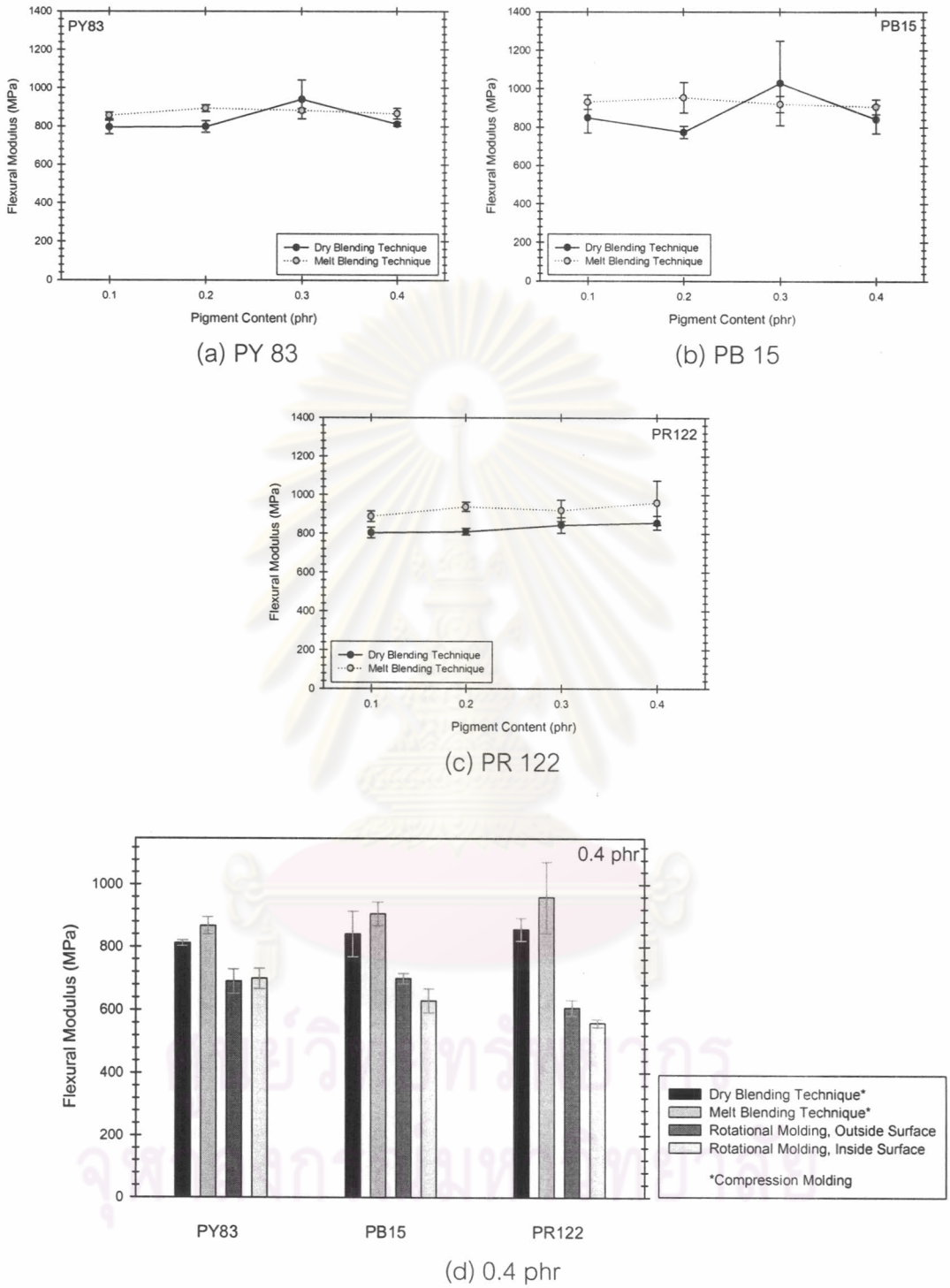


Figure 4.23 Effect of blending techniques and manufacturing processes on the flexural modulus of colored MDPEs

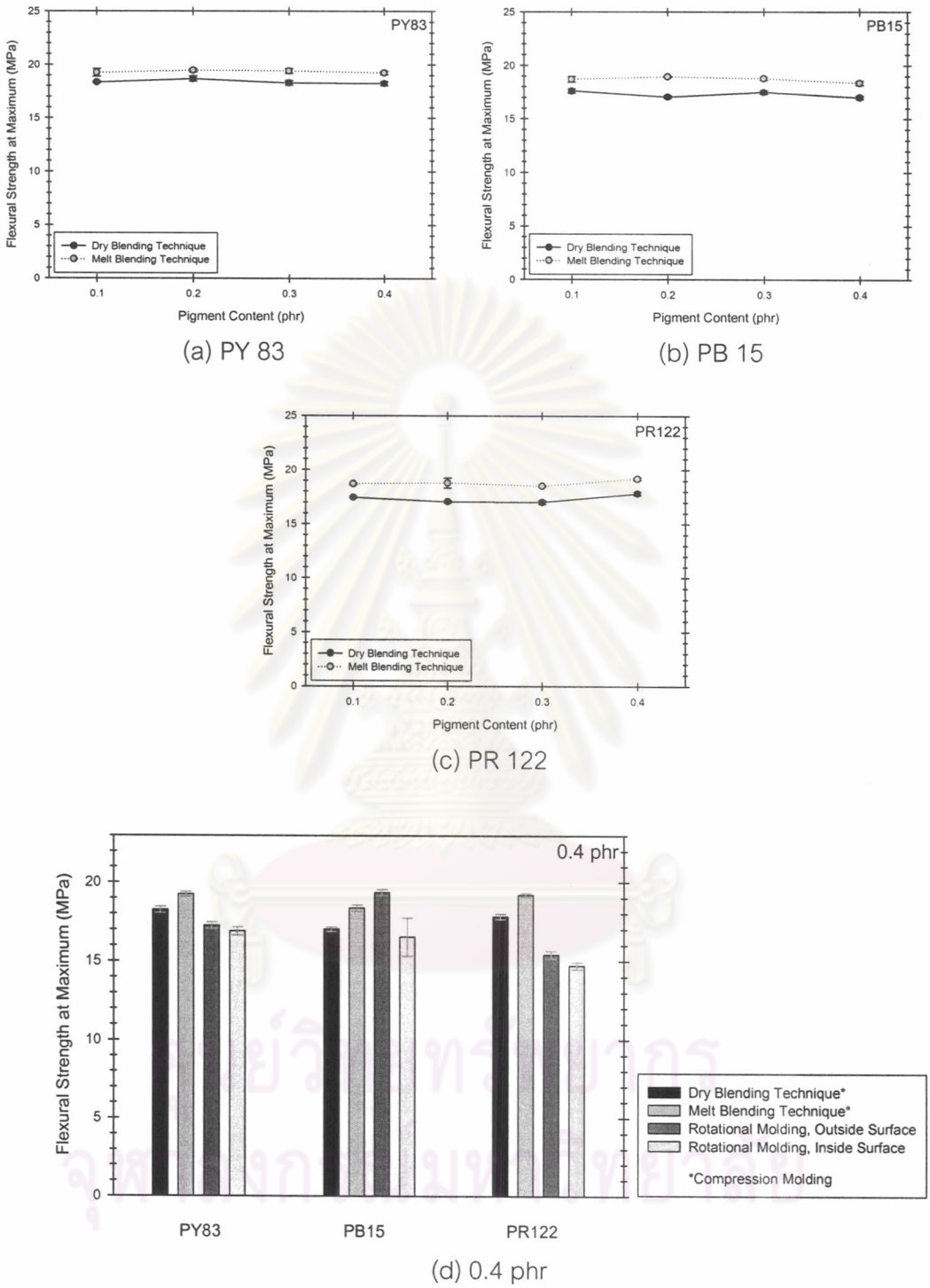
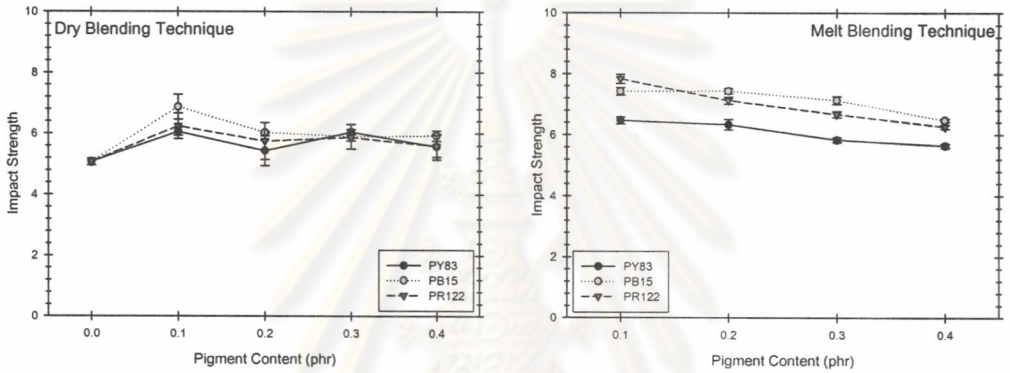


Figure 4.24 Effect of blending techniques and manufacturing processes on the flexural strength at maximum of colored MDPEs

4.2.3 Impact Properties

4.2.3.1 Effect of Pigment Contents

The impact strength of the colored MDPEs shows slightly reduction upon increasing pigment content. This result can be observed in Figure 4.25 and Table 4.8. However, comparing to colorless MDPE (0.0 phr), the addition of all pigments leads to an increase in impact strength and then upon increasing the amount of pigment, the impact values start decreasing, as seen in Figure 4.25 (a).



(a) Dry blending technique (b) Melt blending technique

Figure 4.25 Effect of pigment contents and pigment types on the impact strength (kJ m^{-2}) of colored MDPEs

Generally, the addition of the solid particle, which is brittle, into a tough material such as a thermoplastic can reduce toughness of the thermoplastics. Since, impact properties of polymer directly relate to the toughness [62]. Therefore, the gradual decrease in the impact strength of the colored MDPEs was varied from 0.1 to 0.4 phr of the pigment content.

From the flexural testing of colored MDPEs with PR122 shown earlier in Figure 4.23 (c), flexural modulus improves with increasing pigment content while impact strength decreases. A similar fashion was also observed in the study of Harkin, J.E. and Crawford, R.J. [63].

4.2.3.2 Effect of Pigment Types

From Table 4.8 and Figure 4.25, the effect of pigment type can be clearly seen from the colored MDPEs from melt blending technique. As shown, each pigment responds to the impact strength differently. The colored MDPEs containing phthalocyanine pigment (PB15) have higher impact strength in almost every ratio. Whereas, the lowest impact strength belongs to the colored MDPEs with PY83. For rotational molding process, the impact strength of colored MDPEs with PR122 is however greater among the three colored MDPEs.

Table 4.8 Impact strength of colored MDPEs

Pigment Type	Pigment Content (phr)	Impact strength of colored MDPEs (kJ/m^2)		
		Dry blending technique*	Melt blending technique*	Rotational molding
MDPE**	0.0	5.07 ± 0.11	-	3.91 ± 0.05
PY 83	0.1	6.06 ± 0.13	6.47 ± 0.11	-
	0.2	5.43 ± 0.49	6.33 ± 0.17	-
	0.3	6.05 ± 0.08	5.83 ± 0.08	-
	0.4	5.57 ± 0.42	5.64 ± 0.07	3.61 ± 0.09
PB 15	0.1	6.87 ± 0.41	7.42 ± 0.12	-
	0.2	6.03 ± 0.04	7.43 ± 0.09	-
	0.3	5.90 ± 0.40	7.13 ± 0.13	-
	0.4	5.92 ± 0.16	6.47 ± 0.05	3.88 ± 0.17
PR 122	0.1	6.24 ± 0.42	7.83 ± 0.15	-
	0.2	5.75 ± 0.60	7.12 ± 0.12	-
	0.3	5.87 ± 0.11	6.67 ± 0.10	-
	0.4	5.59 ± 0.36	6.26 ± 0.06	3.99 ± 0.13

* Compression molding process, ** Colorless MDPE

This result is in good agreement with the result from the SEM micrographs of the colored MDPE with PY83, as will be presented in the next section in Figure 4.27. However, short explanation shall be addressed here. The three figures have illustrated the fractured surfaces of the colored MDPEs containing (a) PY83, (b) PB15, and (c) PR122. The fractured surface of (a) is smoother than that of both (b) and (c), implying the brittle characteristic of colored MDPE with PY83. The results from both experiments

confirm that colored MDPE with PY83 is somewhat more brittle owing to its smooth fractured surface. On the contrary, the tougher materials as colored MDPEs containing PB15 and PR122, are proven by the roughness of their fractured surfaces.

4.2.3.3 Effect of Blending Techniques and Manufacturing Processes

The effect of the blending technique and manufacturing process can be determined from Figure 4.26 and Table 4.8. Because the melt blending technique can improve the compatibility and interfacial adhesion between MDPE and pigment powder, hence, the impact strength is better than the dry blending technique.

Conventionally, the shear stress and interfacial interaction between component particles have a great effect on phase morphology (size and shape) and thus mechanical properties. The enhancement of tensile strength and modulus originates from the formation of oriented layer, while the high impact strength is related to shear induced phase morphology [57]. Therefore, shear forces occurring in twin screw extruder assist in improving the interfacial interaction between MDPE and pigments particles, resulting in the greater impact strength.

At 0.4 phr, the impact strength of the samples from rotational molding process is much less than that of both dry and melt blending techniques. It may be explained in terms of the packing of the molecules in the MDPE/pigment component. The packing of the molecules from the compression molding process in both dry and melt blending technique was superior than the rotational molding process.

Furthermore, it was easily recognized by simple visual inspection that the external and internal surface of the rotational products are different. The external surface was directly contacted to the mold which makes it becomes smoother compared to the internal surface. Unlike the external surface, the internal surface was not contacted to the mold. When processing, the internal surface was produced from the rotational force and also received the heat transfer from mold via its outer surface.

In addition, the lowering in the impact strength of the rotational sample is due to the rough surface which may be the crack initiation or the defect of a product. The total energy which is absorbed into a crack by a material can be disintegrated into the energy of crack initiation and crack propagation [62]. More precisely, the warpage and

global shrinkage in the rotationally molded parts are associated with the level of residual stresses. They are compressive on the outer surface and zero on the inner surface. This profile is obviously associated with the anisotropic quench of the parts [6].

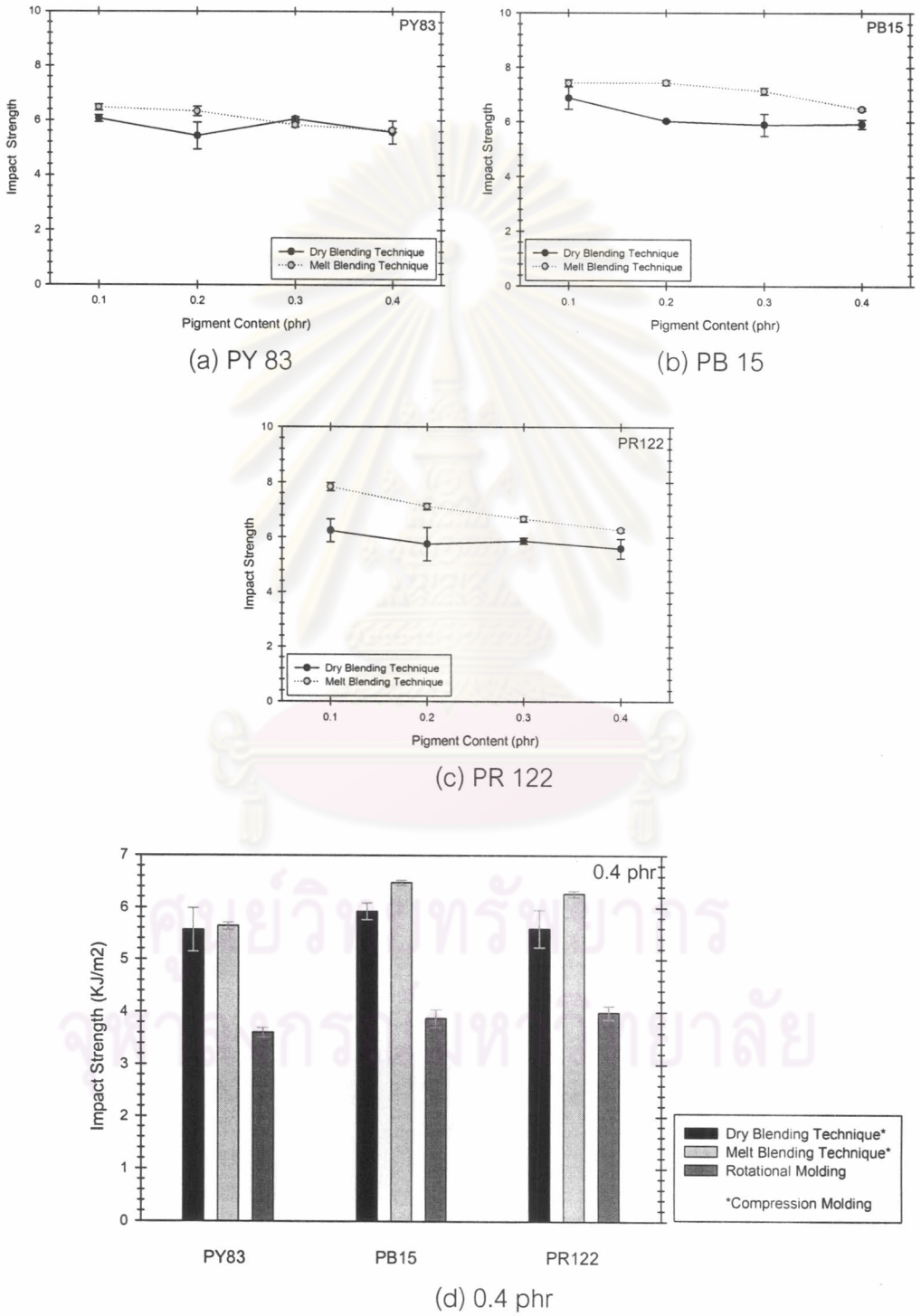


Figure 4.26 Effect of blending techniques and manufacturing processes on the impact strength (kJ m^{-2}) of colored MDPEs

4.3 Physical Properties Characterization

4.3.1 Scanning Electron Microscopy (SEM)

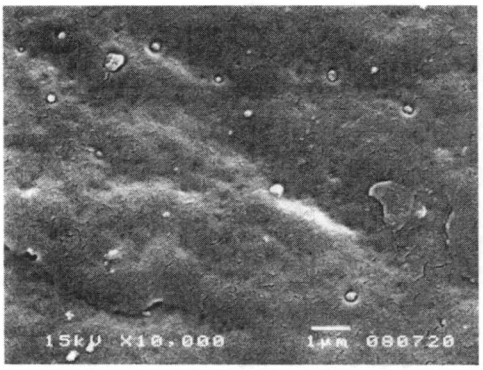
The SEM micrographs have been used to compare the dispersibility of pigment in MDPE from dry and melt blending techniques. Sample sheets from compression molding process were produced from both blending techniques while sample sheets from rotational molding process were produced from dry blending technique.

For ease of observation, because of low pigment powder content, samples at 0.4 phr composition were selected. PE is tough in its nature, therefore it is difficult to prepare the fractured surface of the sample sheets. This tough nature is more significantly influenced to the sample sheets than the extrudate, as the SEM micrographs of sample sheets were exhibited in Figure 4.28 through 4.30.

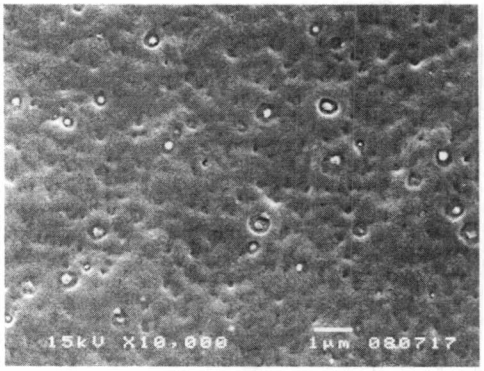
For the colored MDPEs extrudated from twin screw extruder, the SEM micrographs of the fractured surface in Figure 4.27 show good dispersion of pigment powder in MDPE. In contrast, the SEM micrographs of MDPE/pigments sheets show undistinguished appearance on the fractured surface (Figure 4.28 through 4.30).

From the SEM micrographs of extrudate, it can be concluded that the dispersion of pigment powder in MDPE is almost consistent for every pigment types (PY83, PB15, PR122). In addition, the fractured surfaces reveal that the fractured surface of colored MDPE with PY83 is smoother than that of PB15 and PR122, implying the brittle characteristic of colored MDPE with PY83. As mentioned in section 4.2.3.2, the results from both experiments confirm that colored MDPE with PY83 is somewhat more brittle owing to its smooth fractured surface. In contrast, the tougher materials as colored MDPEs containing PB15 and PR122, are proven by the roughness of their fractured surfaces.

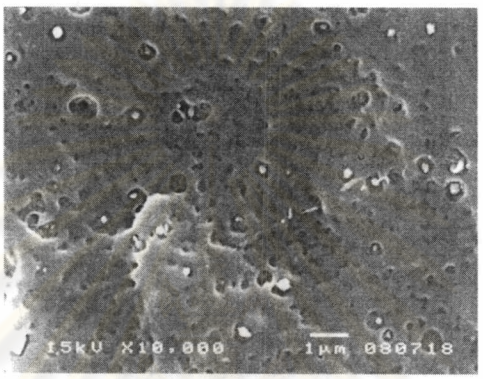
As explained earlier, the observation of SEM micrographs on dispersibility from fractured surface of colored MDPEs sheet is rather difficult. Nevertheless, Figure 4.28 through 4.30 displayed quite good dispersibility of pigment powder in MDPE for every pigment types. Consequently, this result confirms that the process optimization chosen in section 4.1 is suitable to prepare the colored MDPE. More investigation is needed to be able to explain the dispersibility of pigment powder in MDPE.



(a) Diarylide pigment (PY83)

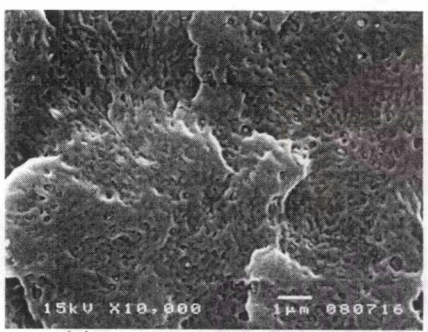


(b) Phthalocyanine pigment (PB15)

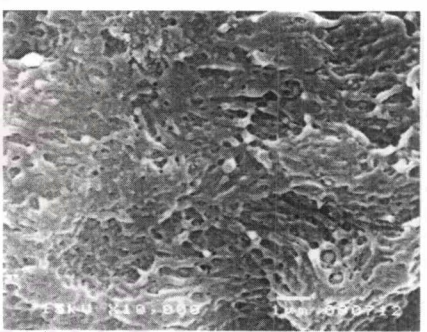


(c) Quinacridone pigment (PR122)

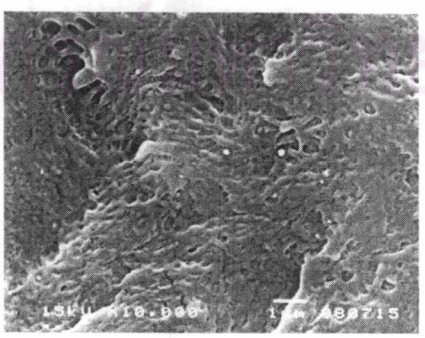
Figure 4.27 SEM micrographs of the fractured surfaces of the colored extrudates from melt blending technique



(a) Diarylide pigment (PY83)

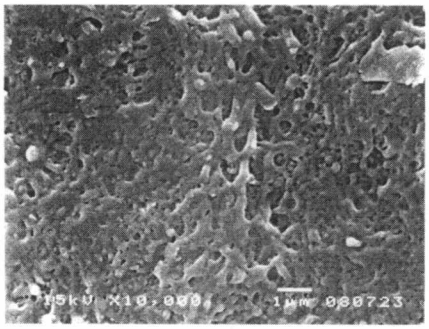


(b) Phthalocyanine pigment (PB15)

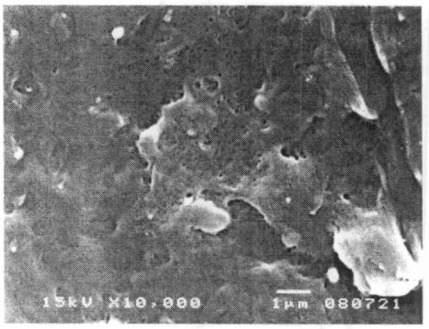


(c) Quinacridone pigment (PR122)

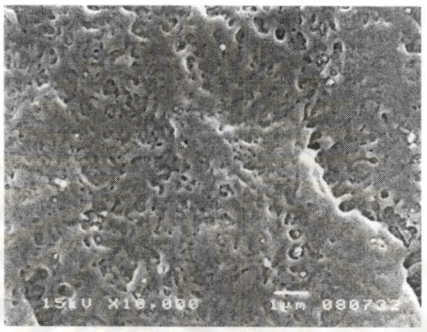
Figure 4.28 SEM micrographs of the fractured surfaces of the compressionally molded colored MDPE sheets via dry blending technique



(a) Diarylide pigment (PY83)

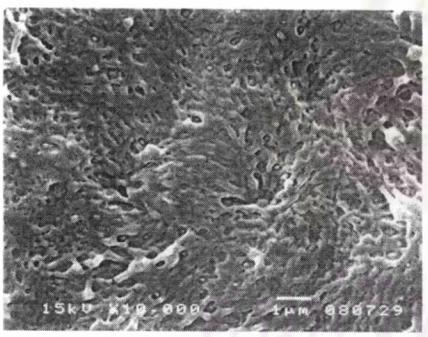


(b) Phthalocyanine pigment (PB15)

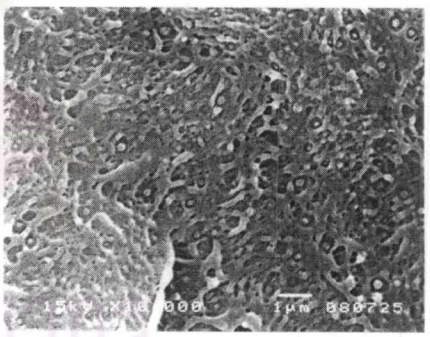


(c) Quinacridone pigment (PR122)

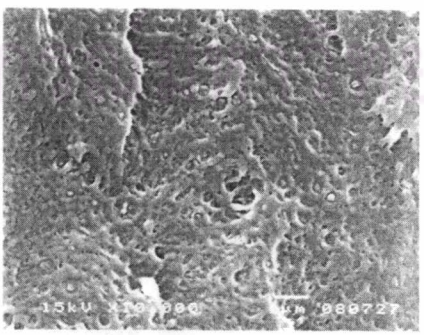
Figure 4.29 SEM micrographs of the fractured surfaces of the compressionally molded colored MDPE sheets via melt blending technique



(a) Diarylide pigment (PY83)



(b) Phthalocyanine pigment (PB15)



(c) Quinacridone pigment (PR122)

Figure 4.30 SEM micrographs of the fractured surfaces of the rotationally molded colored MDPE sheets via dry blending technique

However, there is a summary of guideline to obtain better dispersion from different blending techniques [15]. The foregoing discussion of dispersion principles can be summarized by offering some guidelines for achieving improved quality or more rapid dispersion by the three basic dispersion processes used in the plastics industry. These are listed in the following Tables.

Table 4.9 Guide to quality dispersion by dry blending

Resin Selection • Small particle size • Hard surface in preference to soft, when option exists Chemically compatible with pigment under processing conditions • Rheologically compatible with base resin (especially in concentrate preparation) to minimize letdown difficulties due to differences in melt flow
Select pigment and additive loadings to provide proper flow under operating conditions
Use short, intensive mix cycle (should be adequate for most pigments)
Encourage subsequent melt pressing of these dispersions at high shear

Table 4.10 Guide to quality dispersion by melt shear processing

Resin Selection • Good wetting of both pigment and grind surface • High cohesive strength • Small viscosity change with temperature • Chemically compatible with pigment under processing conditions • Rheologically compatible with base resin (especially in concentrate preparation) to minimize letdown difficulties due to differences in melt flow
Select pigment loading to develop high shear during operation
Pre-blend dry ingredients (see Table 4.9)
Flux resin by shear rather than by application of external heat where possible (e.g., Banbury)

Table 4.11 Guide to quality dispersion in liquid systems

Vehicle selection • Good wetting of both pigment and grind surfaces • "Tack" to suit method, i.e., low tack in processes dependent on impact between particles, high tack in those dependent on shear through liquid layer • Chemically compatible with pigment under processing conditions
Select pigment and additive loadings to provide proper flow for equipment used
Select letdown procedure to avoid seeding, gelling, or poor mix-in (e.g., viscosity adjustment with thinner, high shear mixing, stepwise reduction)

4.3.2 Melt Flow Index

4.3.2.1 Effect of Pigment Contents and Pigment Types

Table 4.12 and Figure 4.31 show the melt flow index of colored MDPEs. From the results it can be concluded that the MFI of the colored MDPEs with PB15 is quite higher than colored MDPEs containing PY83 and PR122. These results maybe attributed to the effect of the density of pigment. As shown in Chapter III in Table 3.2, the density of PB15, PY83, and PR122 are 1.63, 1.49, and 1.47 g cm^{-3}, respectively. Since PB15 has highest density among the three pigments, therefore, the MDPE containing PB15 gives highest MFI value. This result appears in the same trend as those previously reported by Liu, S.J. et al that the increment of the density has an effect on the increasing the MFI [64]. Nevertheless, upon increasing the amount of pigment the MFI values of colored MDPEs remain unchanged. This is due to the small amount of pigments used compared with the MDPE.

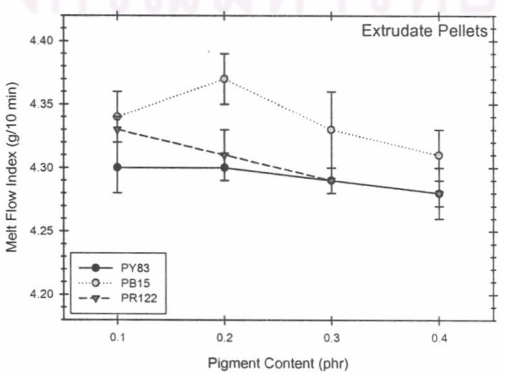


Figure 4.31 Melt flow index of pelletized extrudate of colored MDPE

Table 4.12 Melt flow index of colored MDPEs

Pigment Type	Pigment Content (phr)	Melt Flow Index of colored MDPEs (g / 10 min)	
		Dry Mixture	Extrudate Pellets
MDPE*	0.0	4.26 ± 0.03	-
PY 83	0.1	4.23 ± 0.02	4.30 ± 0.02
	0.2	4.26 ± 0.02	4.30 ± 0.01
	0.3	4.29 ± 0.01	4.29 ± 0.01
	0.4	4.32 ± 0.01	4.28 ± 0.01
PB 15	0.1	4.30 ± 0.02	4.34 ± 0.02
	0.2	4.32 ± 0.03	4.37 ± 0.02
	0.3	4.35 ± 0.02	4.33 ± 0.03
	0.4	4.37 ± 0.01	4.31 ± 0.02
PR 122	0.1	4.35 ± 0.01	4.33 ± 0.00
	0.2	4.28 ± 0.02	4.31 ± 0.02
	0.3	4.23 ± 0.02	4.29 ± 0.01
	0.4	4.16 ± 0.04	4.28 ± 0.02

* Colorless MDPE

4.3.2.2 Effect of Colored MDPE Forms

Table 4.12 and Figure 4.32 display the relationship of the colored MDPE forms with MFI.

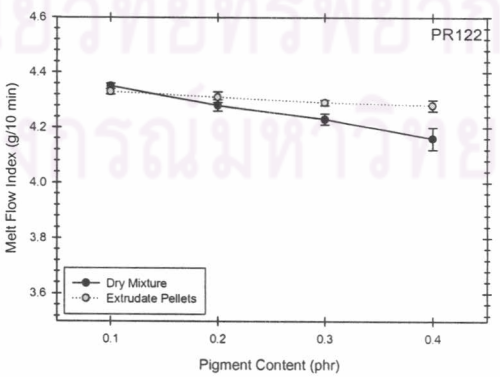


Figure 4.32 Melt flow index of colored MDPEs with PR122

For different forms of both dry mixture and palletized extrudate, it can be addressed that the pellets have slightly higher in MFI values. Conventionally, the results were correlated with rheological properties via melt flow index measurement [65] and might be attributed to the compatibility between components of MDPE and pigment powder. Liang, J.Z. and Ness, J.N. reported that the flow properties of melted polyblend mainly depend on the compatibility between components [66]. These properties are closely related to mixing conditions and blending ratios, which affect the effect of dispersion and distribution of the component particles.

As described in section 4.1 (Blending Condition Characterization), the dry mixture which was obtained from the dry blending technique has poorer dispersibility of pigment powder in MDPE, compared with the pelletized extrudate which was received from the melt blending technique.

More precisely, the melt blending technique in extruder which has a shearing force during processing contributes to the decreasing in melt viscosity. This is owing to the reduction of polymer chain length or weight-average molecular weight (Mw) that then make the MFI increases [35, 67 - 69]. Similarly, Xiang, Q. et al reported that the data showed a decrease in viscosity of polypropylene with the several processing cycle numbers [65]. The greater the processing cycles, the lower the viscosity of colored MDPE; therefore, the compatibility between the components increased, as a result, the MFI value increased.

4.4 Thermal Characterization : Differential Scanning Calorimetry (DSC)

Figure 4.33 presents the DSC thermograms of the colorless and colored MDPEs. The results of the thermal properties including the melting temperature, enthalpy of fusion, and percent of crystallinity are summarized in Table 4.13.

4.4.1 Melting Temperature

The effect of pigment type and pigment concentration on the melting temperature of the colored MDPEs prepared from dry and melt blending techniques are presented in Figure 4.34 and 4.35, respectively.

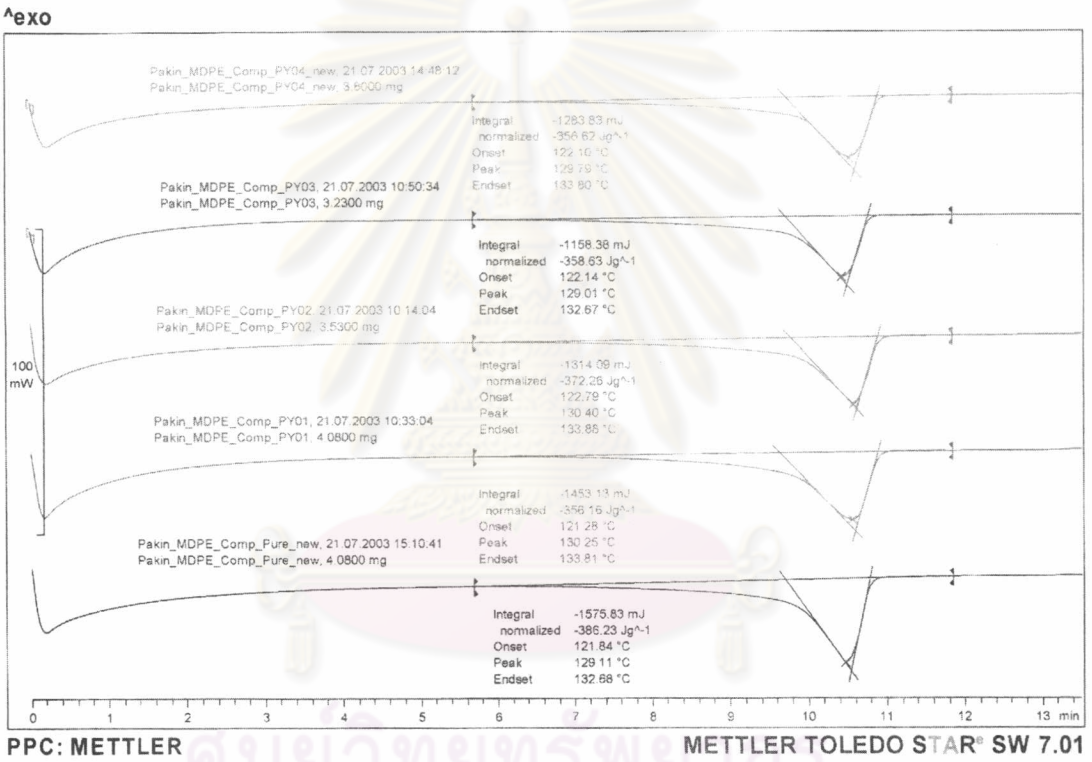


Figure 4.33 The DSC thermograms of colorless and colored MDPEs

Comparing to colorless MDPE, the addition of all pigments has no effect on the DSC thermograms. Melting temperature remains unchanged at approximately 130°C. There is no sign of the melting endotherm of the pigment used due to its small quantity. In addition, an increase in the pigment content does not affect the melting temperature. There is also no effect from blending techniques on the melting temperature of the colored MDPEs as well.

Table 4.13 Thermal properties of colored MDPEs

Pigment Type	Blending Technique	Pigment Content (phr)	Thermal Properties of colored MDPEs				
			Melting Temperature (°C)			Enthalpy of Fusion (J/g)	%Crytallinity
			Onset	Peak	Endset		
MDPE*	dry	0.0	121.84	129.11	132.68	386.23	131.55
PY 83	dry	0.1	121.28	130.25	133.81	356.16	121.31
		0.2	122.79	130.40	133.88	372.26	126.79
		0.3	122.14	129.01	132.67	358.63	122.15
		0.4	122.10	129.79	133.80	356.62	121.46
	melt	0.1	122.64	130.47	133.27	363.91	123.95
		0.2	121.89	130.13	134.20	371.33	126.47
		0.3	122.17	130.28	134.12	364.33	124.09
		0.4	123.34	130.59	134.94	366.89	124.96
PB 15	dry	0.1	121.20	128.77	134.39	376.66	128.29
		0.2	120.59	131.10	135.84	360.93	122.93
		0.3	121.11	129.89	135.00	379.46	129.24
		0.4	124.13	130.45	134.17	384.80	131.06
	melt	0.1	121.27	130.61	135.29	359.87	122.57
		0.2	120.62	131.12	135.89	375.81	128.00
		0.3	126.79	131.17	134.98	350.62	119.42
		0.4	119.52	129.85	134.12	350.11	119.25
PR 122	dry	0.1	120.92	130.52	134.53	367.07	125.02
		0.2	122.63	129.06	134.37	377.52	128.58
		0.3	122.00	130.72	134.67	370.76	126.28
		0.4	123.81	128.89	132.79	354.89	120.88
	melt	0.1	124.15	130.14	133.58	381.92	130.08
		0.2	125.14	130.62	134.00	370.20	126.09
		0.3	121.95	129.49	134.22	357.35	121.71
		0.4	120.32	130.36	134.49	360.94	122.94

* Colorless MDPE

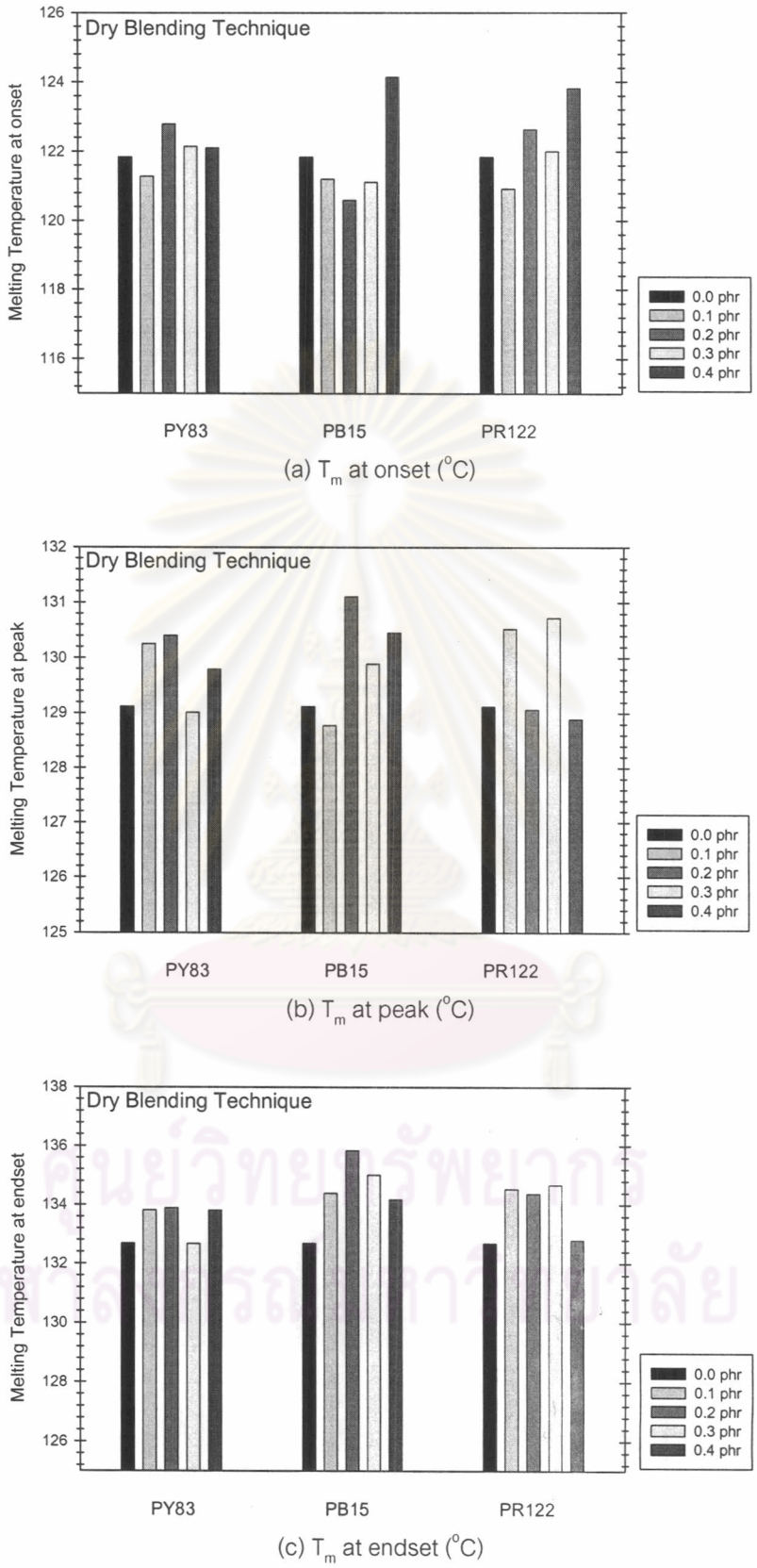


Figure 4.34 Melting temperature of colored MDPEs from dry blending technique

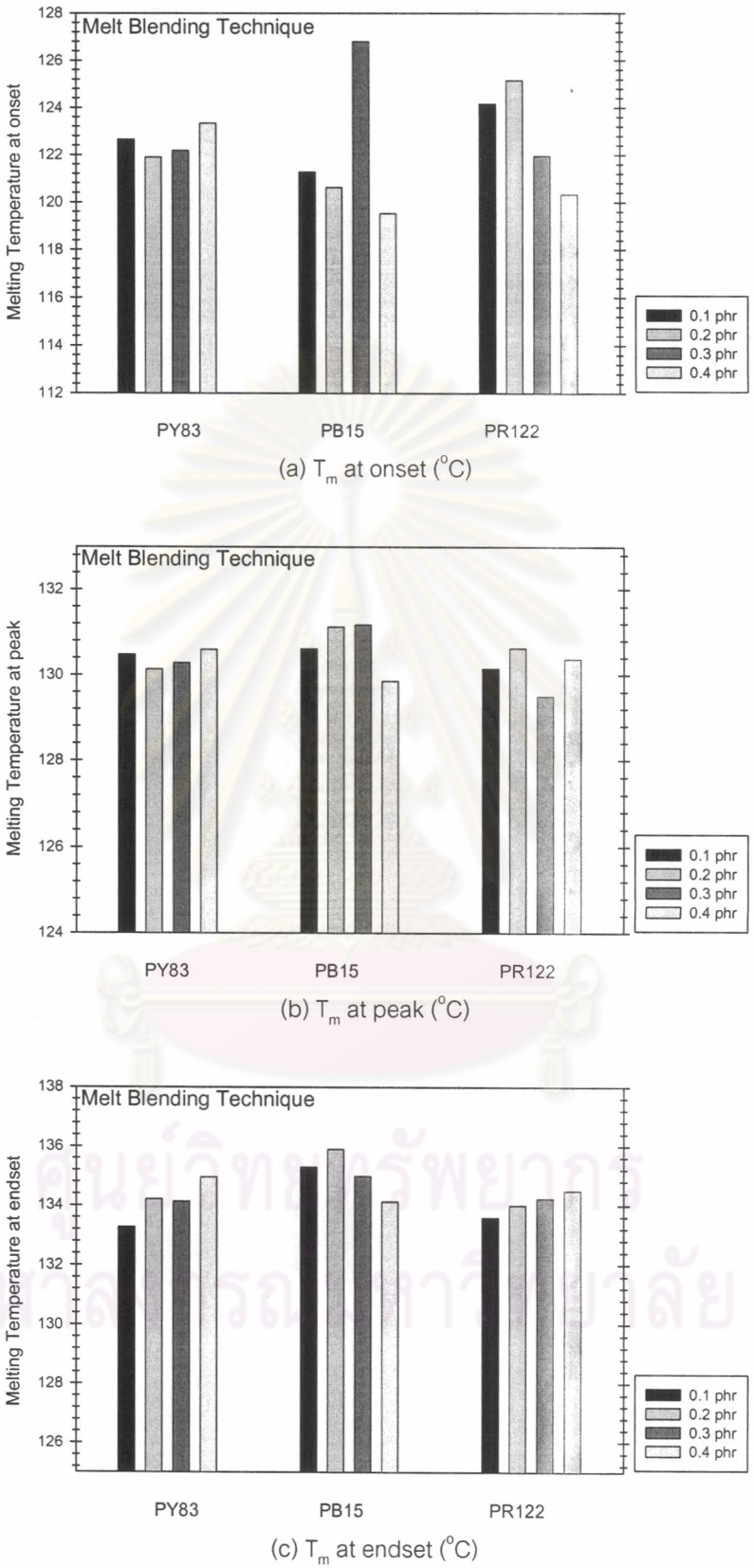


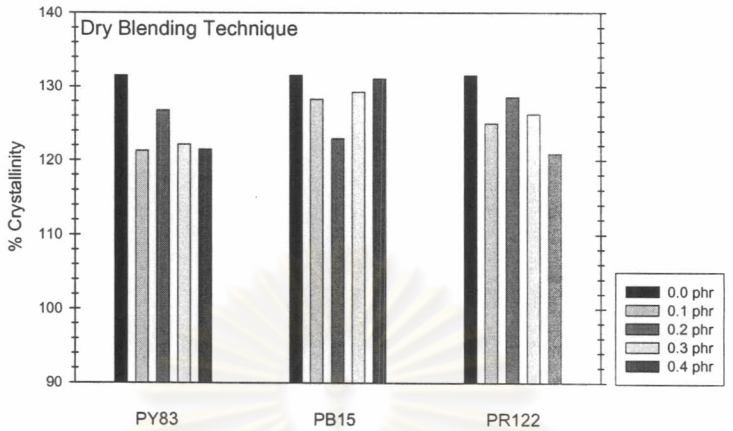
Figure 4.35 Melting temperature of colored MDPEs from melt blending technique

4.4.2 Percent Crystallinity

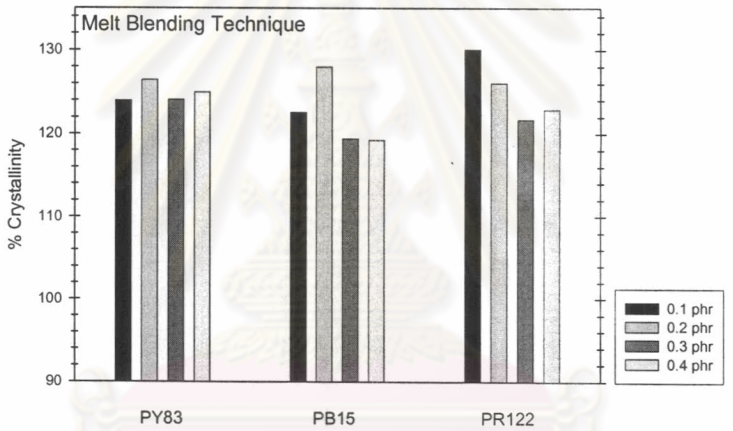
One of the most important properties of semi-crystalline thermoplastics is the percent crystallinity of polymer. This refers to the overall level of crystalline component in relationship to its amorphous component. The percent crystallinity is directly related to many of the key properties exhibited by a semi-crystalline polymer, i.e., brittleness, toughness, stiffness or modulus, optical clarity, creep or cold flow, barrier resistance (ability to prevent gas transfer in or out), and long term stability [56]. The effects of pigment content, pigment type, and blending techniques on the degree of crystallinity of colored MDPEs are also listed in Table 4.13.

The use of pigment produced the lower in percent crystallinity of colored MDPE compared with the colorless MDPE. In addition, an increase of pigment content (0.1 to 0.4 phr) seems to have no effect on the %crystallinity. The %crystallinity of all colored MDPEs was approximately 7% lower than colorless MDPE. From these results, it can be concluded that these pigments act as the interfering on the crystalline formation in medium density polyethylene. Comparing to the tensile properties of colored MDPE containing PR122 (quinacridone pigment) (section 4.2.1), these results appear in the same trend as the values of the tensile stress at maximum load that the tensile stress at maximum load decreases with the reduction of %crystallinity compared to colorless MDPE. As illustrated in Figure 4.33, 4.36 and Table 4.13, %crystallinity of colored MDPE with PB15 is slightly quite higher (in the dry blending technique), while quite less (in the melt blending technique) compared to both PY83 and PR122. These results suggest that the three organic pigments in this work, diarylide yellow (PY83), phthalocyanine blue (PB15), and quinacridone red pigment (PR122), have no significant influence on the %crystallinity of colored MDPEs. However, the phthalocyanine pigment is known as a good nucleator of the α–form, whereas the quinacridone pigment as one of the best nucleators of the β–form in polypropylene (PP) [59 - 60]. While the efficiency of β–crystal nucleator decreases if the γ–Quinacridone level is increased above an optimum level of 10^{-6} wt-%. Also, increasing the concentration of red pigment then appears to inhibit the formation of β–crystals. Likewise in quinacridone pigment, young's modulus and yield stress increased with increasing crystallinity and increasing α–crystal

content, in contrast, elongation at break increased with increasing β content. These results have been observed by previous research [70].



(a) Dry blending technique



(b) Melt blending technique

Figure 4.36 %Crystallinity of colored MDPEs from dry and melt blending techniques

The %crystallinity of colored MDPEs performed via dry and melt blending techniques was exhibited in Table 4.13 and Figure 4.33 and 4.36. The results show that there is no significant difference between both blending techniques.

Compression forces among compression molding process in sample sheets may induce the packing enhancement of the molecules between plastic and pigment, better than the pellets. As prior discussed in tensile testing (the effect of blending technique and manufacturing process) [59], the denser packing has a small porosity that might be resulted in the reduction of the spherulite size. It can be influenced to improve the %crystallinity of colored MDPEs. However, further investigation is necessary to explain the result obtained in this area.