Chapter V

Results and Discussion

5.1 Effects of kneading conditions on the dispersion of pigments in HDPE.

As mentioned earlier, Scanning Electron Microscope (SEM) photographs had to be used to obtain the fractal dimension of the dispersion states. A sufficient magnifying power is necessary to distinguish the differences between pigment particles and air bubbles or even polymer matrix. In the present work, it was found that the appropriate magnifying power of SEM should be 15000 X for the carbon black pigment and 7500 X for the quinacridone violet pigment. **Figure 5.1** shows some examples of the microphotographs of both pigments thus obtained.

The present experiments were carried out to study the effects of kneading conditions on the dispersibility of pigments in HDPE using a continuous kneader. The resulting dispersibility of pigment in HDPE was evaluated using the observed fractal dimension defined by equation (2.2). Since the observed fractal dimension depends considerably on the sample population size and the actual number of pigment particles varies somewhat in each sample, the experimental result has to be normalized using the corresponding ideal-case value obtained via computer simulation. In this way, a comparison between the corresponding cases of the

carbon black and quinacridone violet pigments and among the same case at the same kneading conditions can be carried out correctly.

$$D^* = \frac{D}{D_{uniform}}$$ (5.1)

where D^* = normalized fractal dimension with respect to the corresponding uniform random dispersion.

D = experimental fractal dimension.

$D_{uniform}$ = fractal dimension for the ideal uniform random dispersion with the same sample population size.
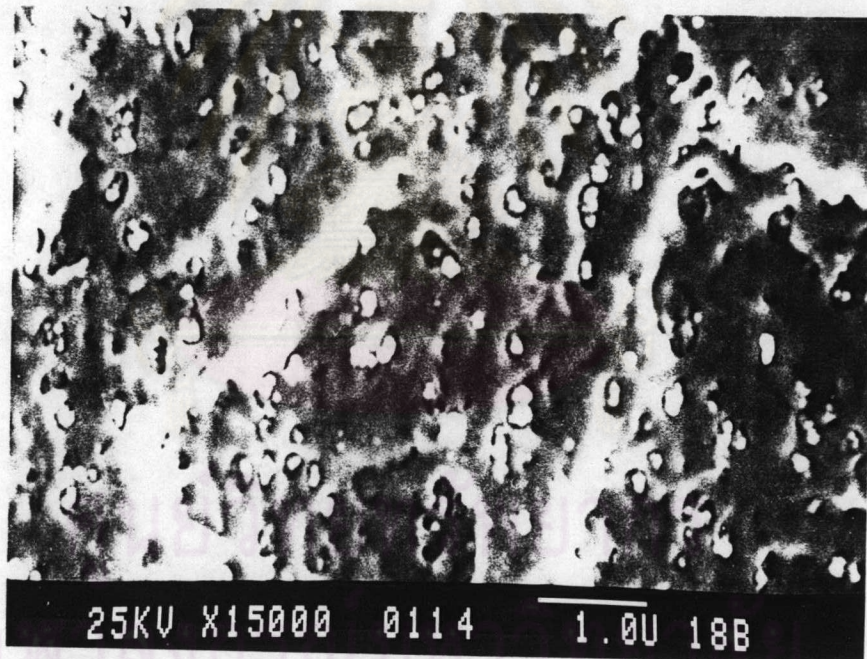

Figure 5.1 a) An example of SEM microphotographs in the case of carbon black
pigment at kneading temperature 200 °C, speed of screw 162 rpm,
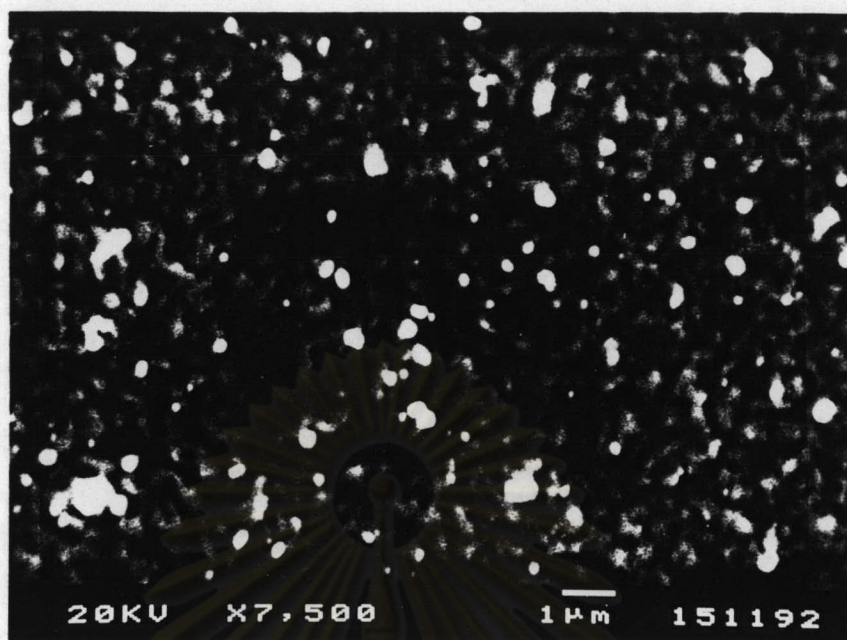feed rate 51.2 g/min, premixed time 30 minutes

Figure 5.1 b) An example of SEM microphotographs in the case of quinacridone

violet pigment at kneading temperature 200 ^{o}C, speed of screw

162 rpm, feed rate 51.2 g/min, premixed time 30 minutes

5.1.1 Kneading temperature

The dispersion state of each pigment was examined at 200, 220 and 240 ^{o}C in the case of carbon black and at 180, 200, 220 ane 240 ^{o}C in the case of quinacridone violet. The results at these temperatures for both pigments are summarized respectively in **tables 5.1** and **5.2 Figure 5.2** shows the relationship between the normalized fractal dimension and the kneading temperature for the case of carbon black pigment whereas the case of quinacridone violet pigment is shown in **figure 5.3**

Table 5.1 Effect of the kneading conditions on the dispersion of carbon black

pigment in HPDE.

Kneading Temp. T (°C)	Speed of screw R (rpm)	Flow rate F (g/min.)	Pre-mixed time t_p (min)	D	D*
200	162	51.2	10	1.741	0.931
			20	1.761	0.932
			30	1.746	0.934
		71.9	10	1.745	0.928
			30	1.748	0.930
		92.5	10	1.747	0.929
			20	1.755	0.929
			30	1.758	0.930
	243	51.2	10	1.810	0.968
			30	1.798	0.962
		92.5	10	1.789	0.952
			30	1.834	0.970
	324	51.2	10	1.834	0.981
			20	1.834	0.981
			30	1.831	0.979
		71.9	10	1.821	0.969
			30	1.855	0.969
		92.5	10	1.827	0.977
			20	1.840	0.979
			30	1.835	0.971
220	162	51.2	10	1.762	0.942
			30	1.776	0.950
		92.5	10	1.763	0.933
			30	1.765	0.934
	324	51.2	10	1.856	0.993
			30	1.860	0.989
		92.5	10	1.839	0.978
			30	1.873	0.981

Table 5.1   Effect of the kneading conditions on the dispersion of carbon black

pigment in HPDE. (continued)

Kneading Temp. T (°C)	Speed of screw R (rpm)	Flow rate F (g/min.)	Pre-mixed time t_p (min)	D	D*
240	162	51.2	10	1.785	0.955
			20	1.783	0.953
			30	1.799	0.957
		71.9	10	1.820	0.953
			30	1.794	0.949
		92.5	10	1.789	0.952
			20	1.783	0.953
			30	1.790	0.957
	243	51.2	10	1.831	0.979
			30	1.835	0.976
		92.5	10	1.821	0.963
			30	1.861	0.974
	324	51.2	10	1.883	0.996
			20	1.859	0.994
			30	1.885	0.997
		71.9	10	1.889	0.989
			30	1.885	0.997
		92.5	10	1.875	0.982
			20	1.876	0.982
			30	1.864	0.986

Table 5.2 Effect of the kneading conditions on the dispersion of quinacridone violet pigment in HDPE. (Premixed time = 30 minutes)

Kneading Temp. T (°C)	Speed of screw R (rpm)	Flow rate F (g/min.)	D	D*
180	162	51.2	1.559	0.829
		92.5	1.510	0.812
	324	51.2	1.625	0.855
		92.5	1.590	0.846
200	81	51.2	1.684	0.915
		92.5	1.641	0.873
	162	30.0	1.814	0.955
		51.2	1.703	0.931
		71.9	1.736	0.923
		92.5	1.644	0.893
	243	51.2	1.748	0.935
		92.5	1.737	0.919
	324	30.0	1.818	0.960
		51.2	1.782	0.948
		71.9	1.774	0.934
		92.5	1.731	0.921
220	162	51.2	1.741	0.936
		92.5	1.667	0.896
	324	51.2	1.818	0.957
		92.5	1.736	0.933
240	81	51.2	1.786	0.945
		92.5	1.713	0.911
	162	30.0	1.810	0.959
		51.2	1.794	0.949
		71.9	1.801	0.948
		92.5	1.651	0.917
	243	51.2	1.829	0.949
		92.5	1.748	0.930
	324	30.0	1.856	0.982
		51.2	1.861	0.979
		71.9	1.848	0.973
		92.5	1.778	0.946
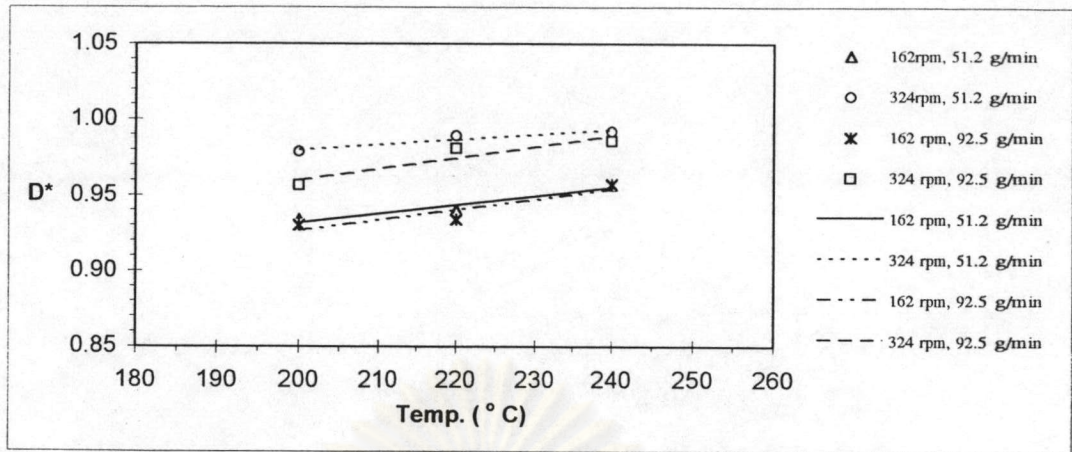
(a) Effect of rotational speed and feed rate (constant premixed time at 30 minutes)
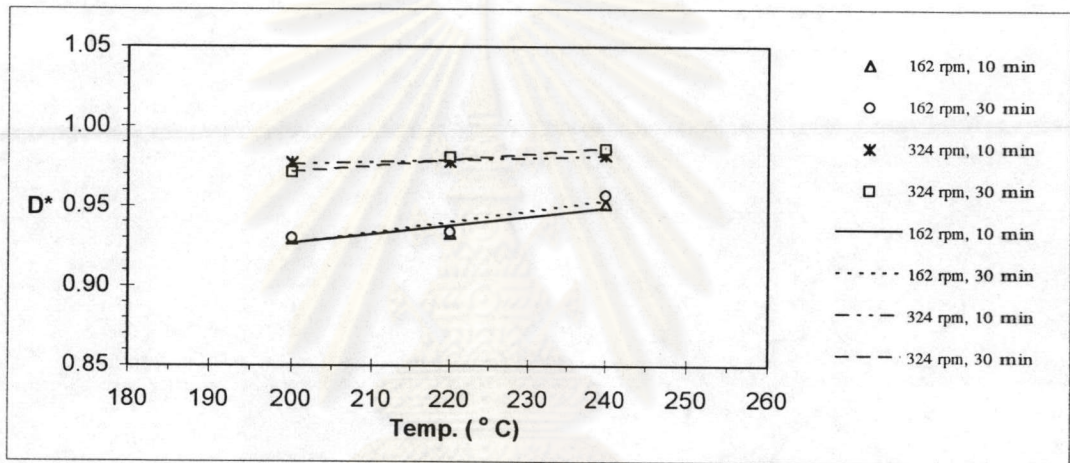
(b) Effect of rotational speed and premixed time (constant feed rate at 92.5 g/min)
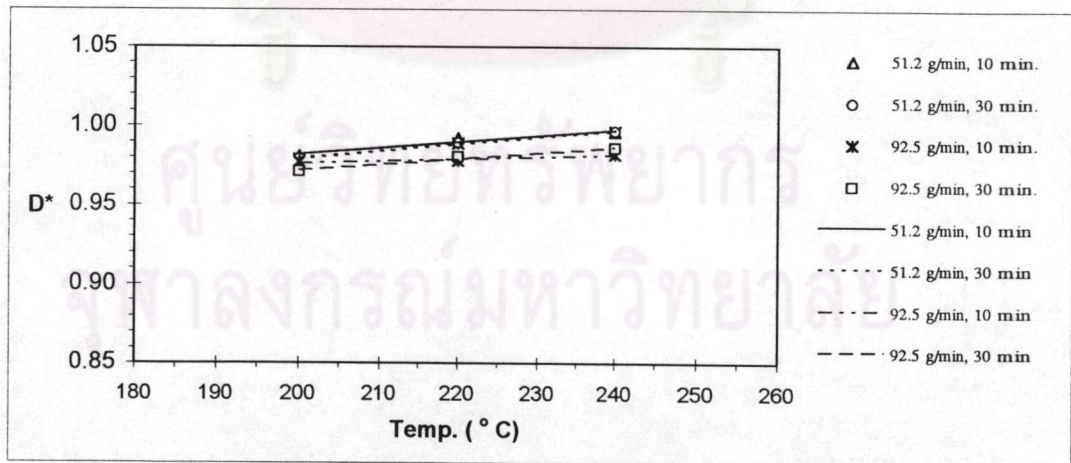
(c) Effect of feed rate and premixed time (constant rotational speed at 324 rpm)

Figure 5.2 Relationship between the kneading temperature (Temp) and the fractal

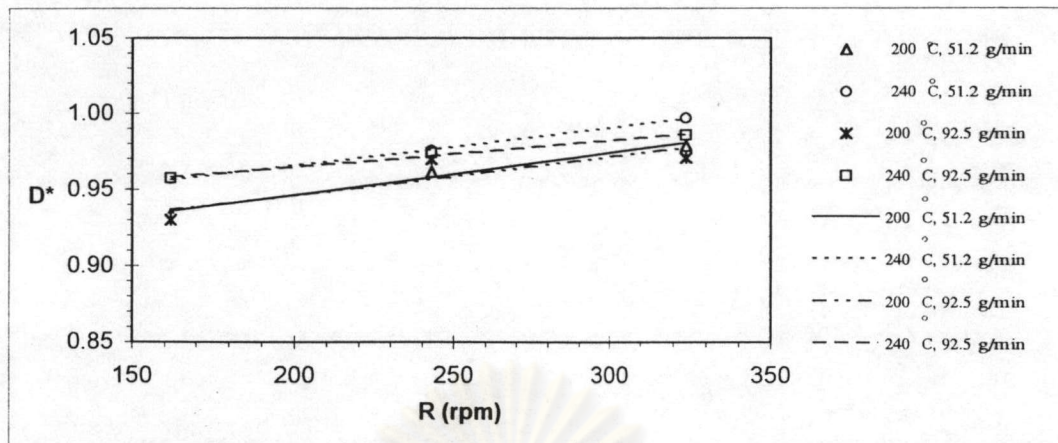dimension (D) in the case of the carbon black pigment
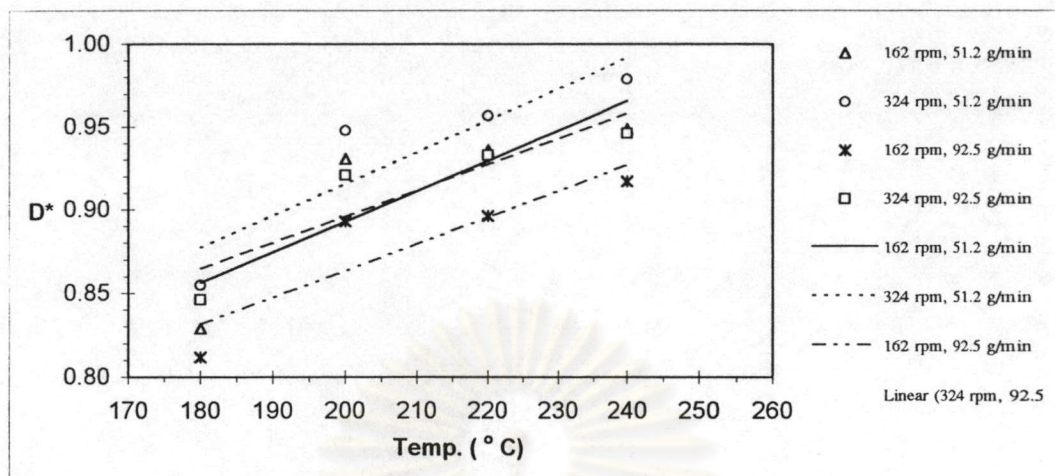
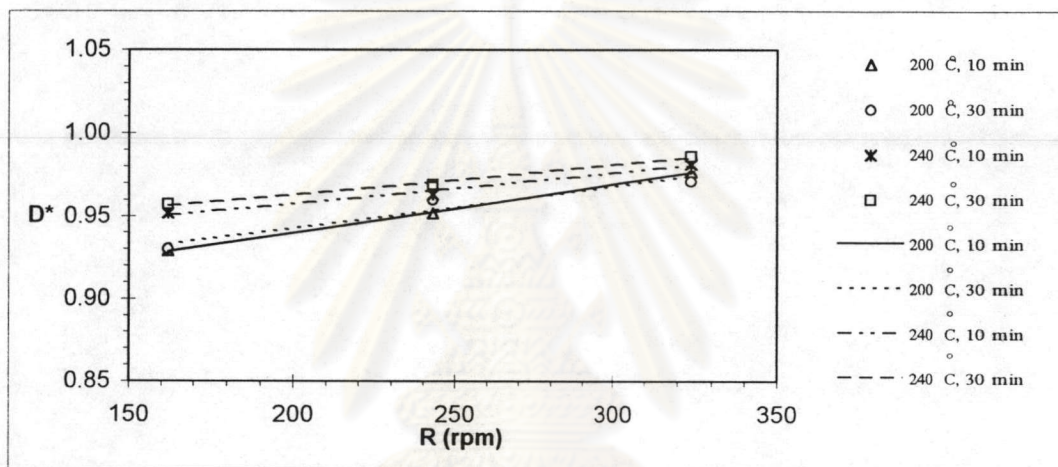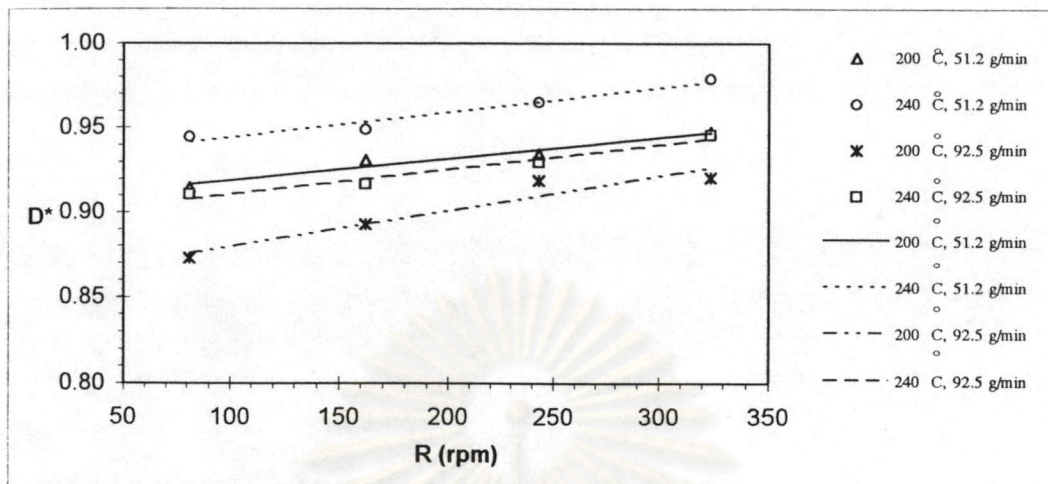Effect of rotational speed and feed rate (constant premixed time at 30 minutes)

Figure 5.3 Relationship between the kneading temperature (Temp) and the fractal

dimension (D) in the case of the quinacridone violet pigment

From these figures, it is seen that the normalized fractal dimension increased as the kneading temperature increased for both pigments, especially around 180-200 ^{o}C for quinacridone violet. In other words, the degree of dispersion tended to increase as the kneading temperature increased. This is probably because the decrease in melt viscosity caused by the increased kneading temperature made the pigment disperse into the matrix more easily. Moreover, the distribution of pigment in melt polymer was better because the flow of melt polymer increased. In this study, the highest kneading temperature (T = 240 ^{o}C) gives the best dispersibility. It should be cautioned, however, that an excessively high kneading temperature could and did cause thermal degradation that impaired the tensile properties of the kneaded polymer. The evidence for thermal degradation will be presented in the later section.

(a) Effect of kneading temperature and feed rate (constant premixed time at 30 minutes)

(b) Effect of kneading temperature and premixed time (constant feed rate at 92.5 g/min)
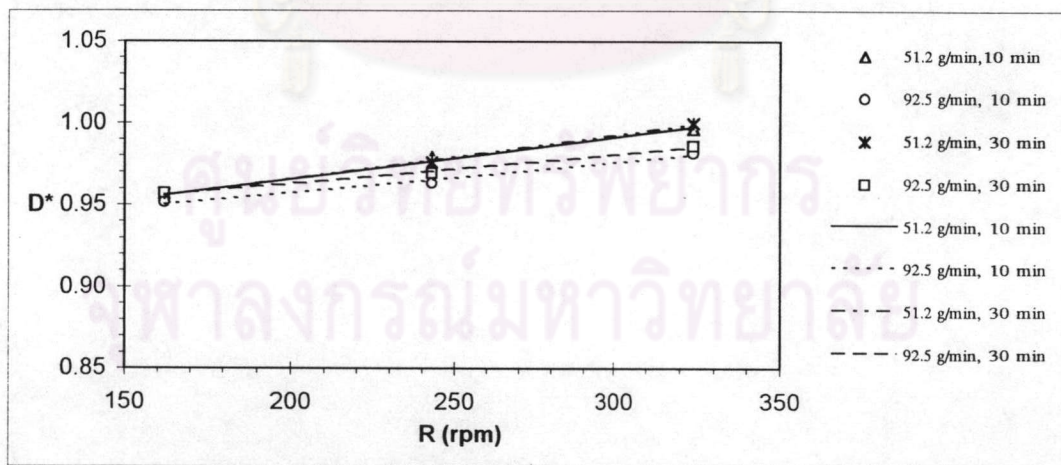
(c) Effect of feed rate and premixed time (constant kneading temperature at 240 ° C)

Figure 5.4 Relationship between the rotational speed of screw (R) and the fractal
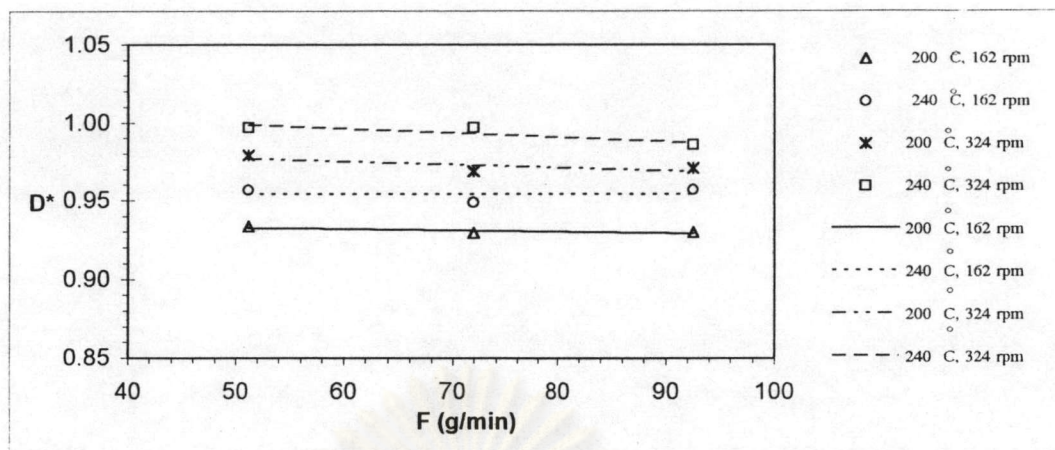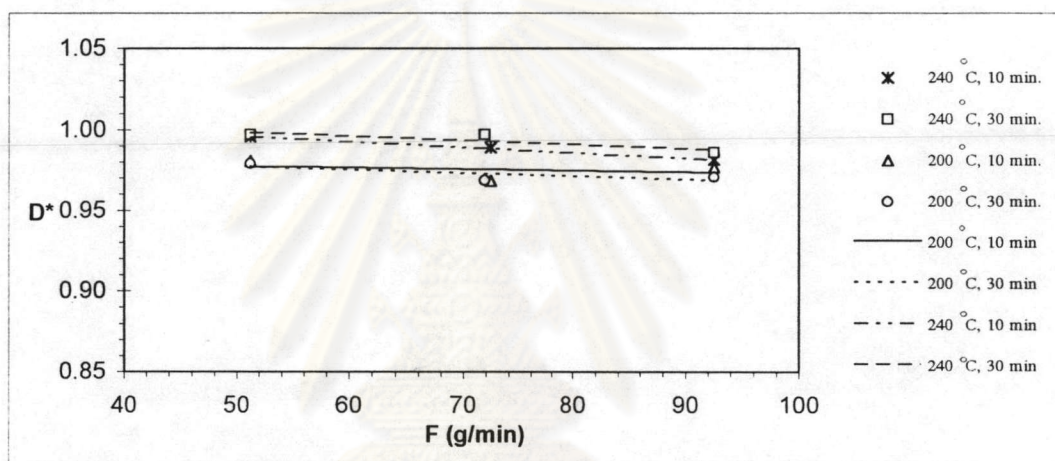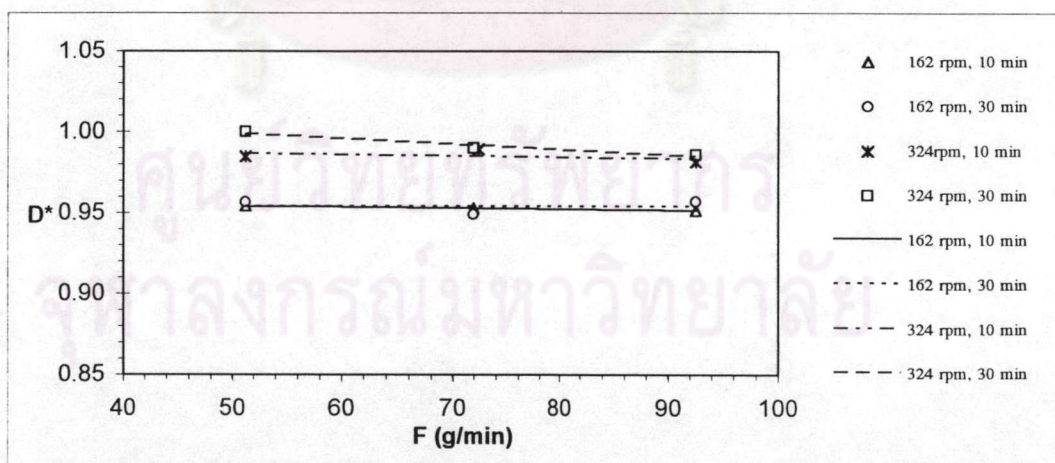
dimension (D) in the case of the carbon black pigment

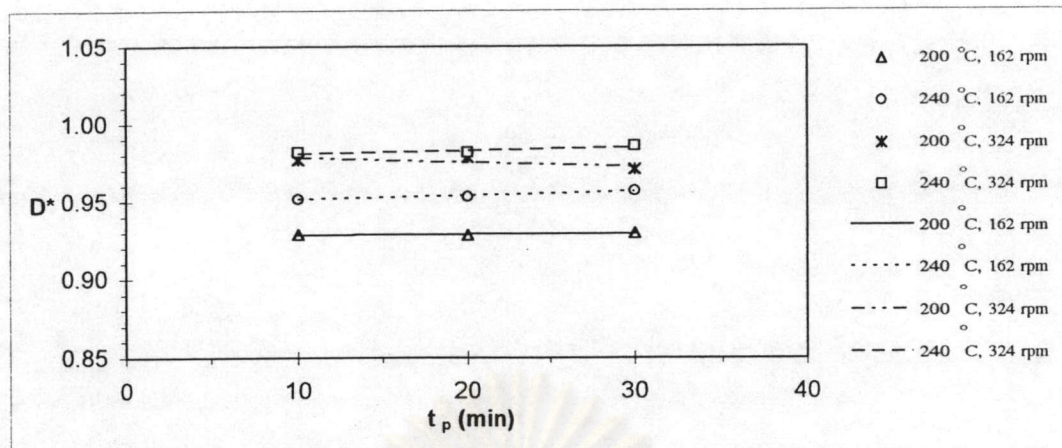Effect of kneading temperature and feed rate (constant premixed time at 30 minutes)

Figure 5.5 Relationship between the rotational speed of screw (R) and the fractal

dimension (D) in the case of the quinacridone violet pigment
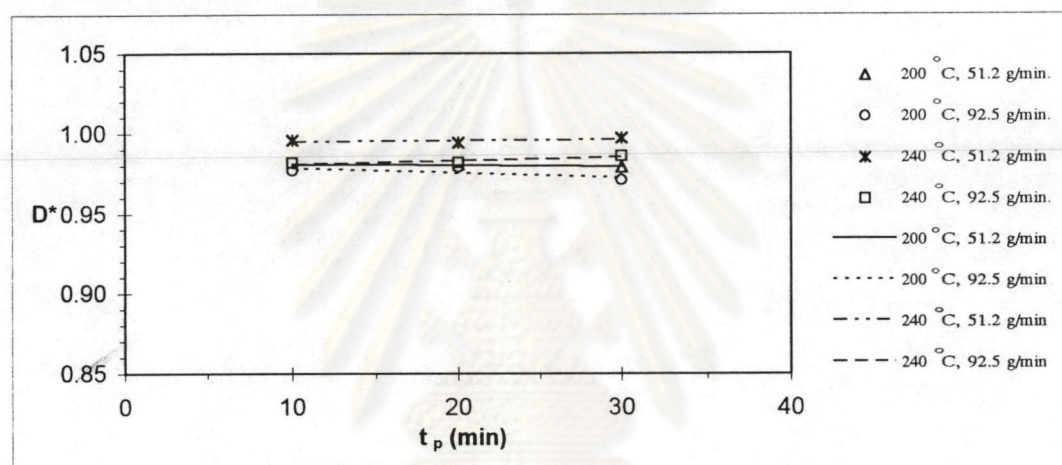
5.1.2 Rotational speed of screw

The effect the rotational speed of the twin screws on the dispersibility of both pigments, carbon black and quinacridone violet, was investigated at 162, 243, and 324 rpm. The effect of the rotational speed on the dispersion state was shown in **figure 5.4** for carbon black and in **figure 5.5** for quinacridone violet pigment. As seen from the figures, it was found that the normalized fractal dimension tended to increase as the rotational speed increased. In other words, this means that the higher the rotational speed at which the sample was kneaded, the higher the degree of dispersion. It is surmised that the increase in the intensity of shear stresses resulting from increasing the rotational speed led to more destruction of the particle network structure as well as more breakdown of the agglomerates.
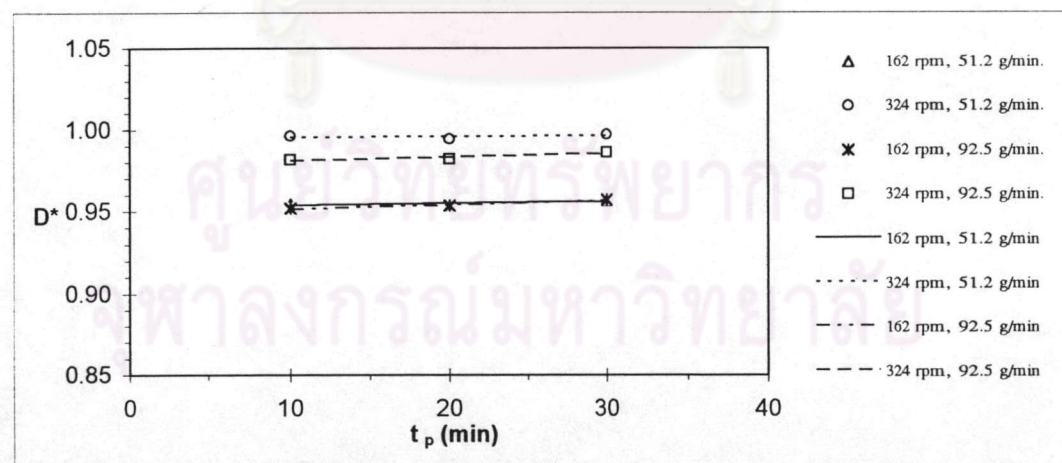
(a) Effect kneading temperature and rotational speed (constant premixed time at 30 minutes)

(b) Effect of kneading temperature and premixed time (constant rotational speed at 324 rpm)

(c) Effect of rotational speed and rotational speed (constant kneading temperature at 240 °C)

Figure 5.6   Relationship between the feed rate (F) and the fractal dimension

(D) in the case of the carbon black pigment
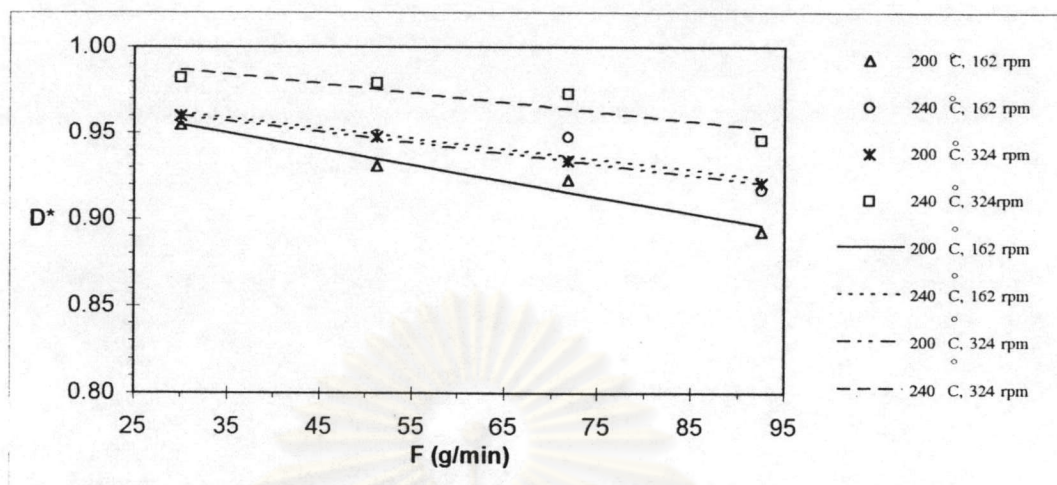
Effect of kneading temperature and rotational speed (constant premixed time at 30 minutes)

Figure 5.7   Relationship between the feed rate (F) and the fractal dimension

(D) in the case if the quinacridone violet pigment

5.1.3   Feed rate

The feed rate of the premixed mixture between HDPE and either pigment was varied from 30.0 to 92.5 g/min to examine the effect of the feed rate on the dispersion. **Figure 5.6 and 5.7** show the effect of the feed rate on the dispersion for the carbon black and quinacridone violet pigments, respectively.

From the figures, it was seen that the normalized fractal dimension tended to decrease shightly as the feed rate increased. In short, the dispersibility of either pugment increased as the feed rate decreased. It is speculated that at the same rotational speed of the twin screws, a lower feed rate prolonged the resitence time of the mixture, thus resulting in better dispersion.

(a) Effect of kneading temperatureand rotational speed (constant feed rate at 92.5 g/min)

(b) Effect of kneading temperature and feed rate (constant rotational speed at 324 rpm)

(c) Effect rotational speed of screw and feed rate (constant kneading temoerature at 240 °C)

Figure 5.8   Relationship between the premixed time (t_p) and the fractal dimension
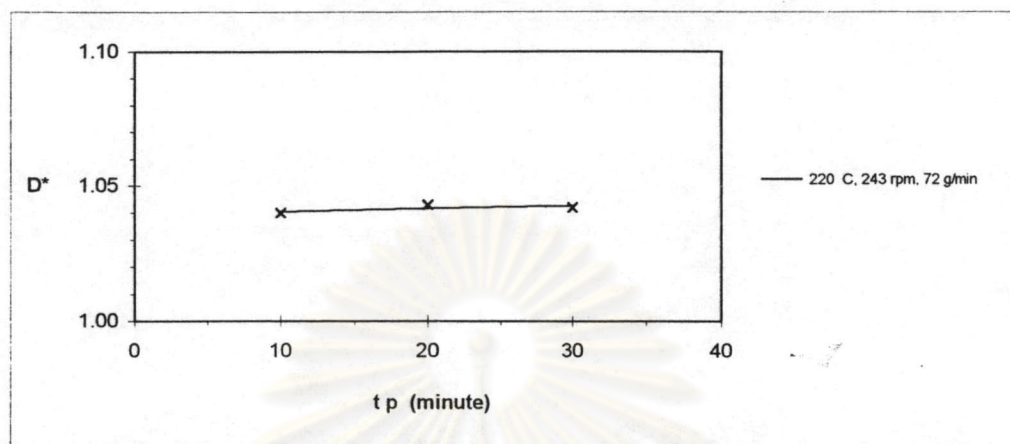
(D) in the case of the carbon black pigment

Figure 5.9   Relationship between the premixed time (tp) and the dimension in the
case of quinacridone violet pigment

5.1.4   Premixed time

Effect of the premixed time on the dispersibility of either of the pigments, carbon black and quinacridone violet, was investigated at 10, 20 and 30 minutes. **Figure 5.8** shows the effect of the premixed time on the dispersion state of the carbon black pigment. This figure shows that, the normalized fractal dimension as well as the degree of dispersion remained rather constant as the premixed time was varied. It may be explained that the shortest premixed time of 10 minutes used in this study could already provide sufficient premixing between either pigment and the polymer. Therefore, any further increase in the premixed time had insignificant effect on the dispersion of the pigments.

As shown in **Figure 5.9**, a subsequent set of experiments in the case of the quinacridone violet pigment also supported the above conclusion, so no

further experiments were not carried out in the case of the quinacridone violet pigment.

5.2 Effects of kneading conditions and the dispersibility of pigments on tensile properties

In this study, the effects of kneading conditions on tensile properties were also investigated. The tensile properties were measured according to ASTM D882-91. An example of the measured stress-strain curve is shown in **figure 5.10**. From each of the stress-strain curves, four tensile properties, namely, the strain at break, 0.2% offset yield stress, work done and modulus of elasticity were obtained and shown graphically in **figure 5.11** to **figure 5.38**.

The strain at break is the maximum strain exhibited by the test sample at the point of breakage. The 0.2 % offset yield stress is the value of the yield stress on the stress-strain curve where the curve departs from linearity by 0.2% of the strain. The work done is the total work (energy) experienced by the test sample from the start up to the time of breakage. The modulus of elasticity is defined as the slope of the tangent to the stress-strain curve at low strain.

It should be noted that generally the tensile stress-strain relationship of a polymer depends on both the test temperature and the strain rate. Here the temperature was room temperature and was the strain rate 50 mm/min, which corresponds to the medium rate specified in ASTM D-638.
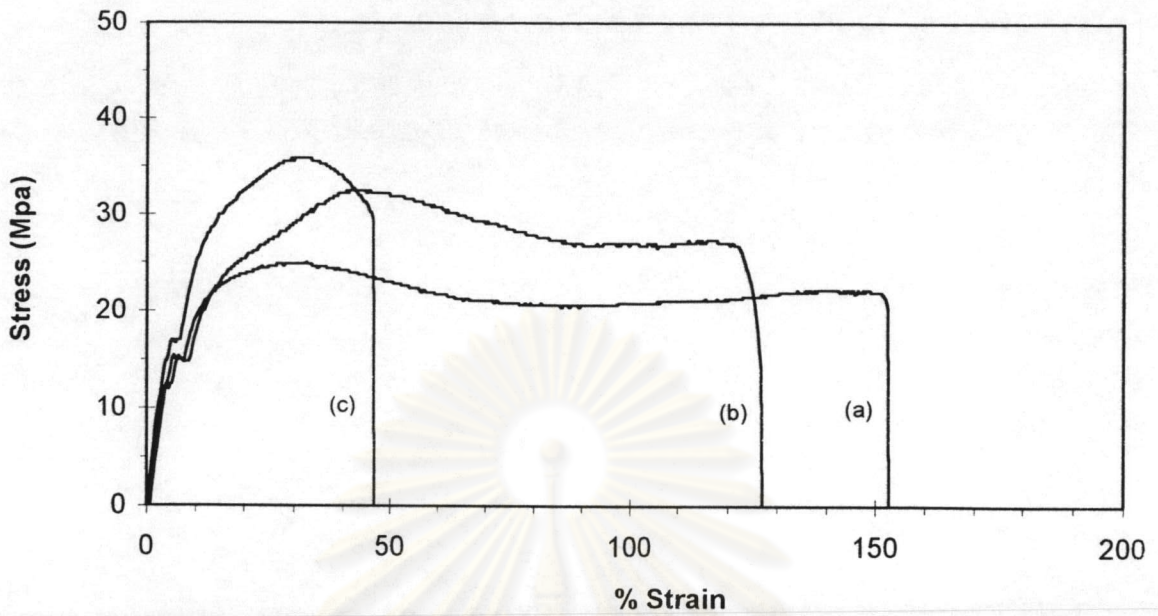
Figure 5.10   An example of the stress-strain curve

: Constant speed of screw at 162 rpm, feed rate at 92.5 g/min and premixed time at 30 min.

(a) at kneading temp. 200 °C, (b) at kneading temp. 220 °C, (c) at kneading temp. 240 °C
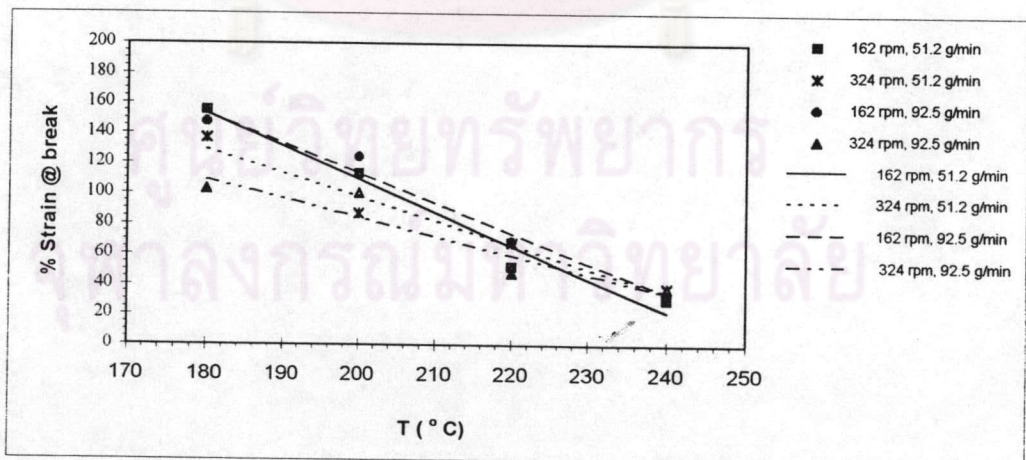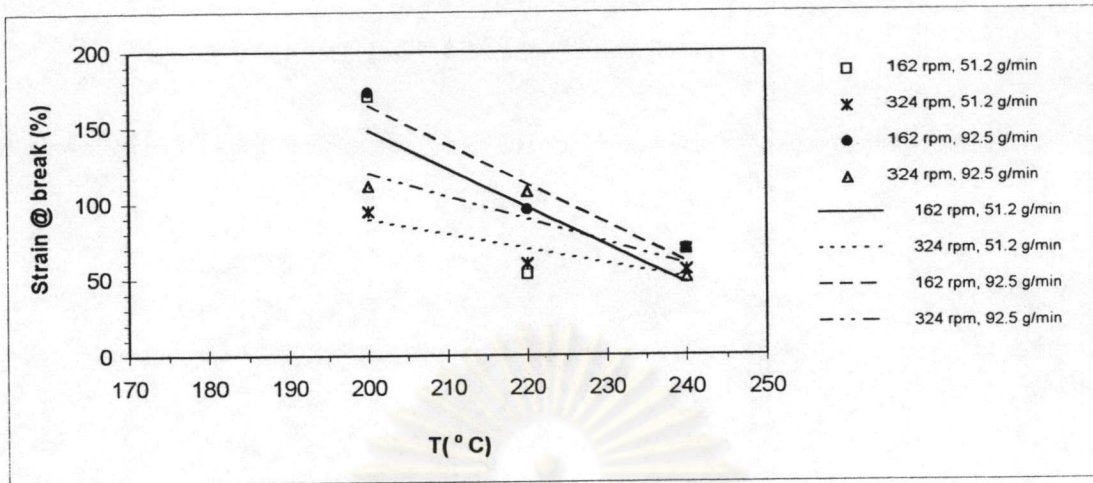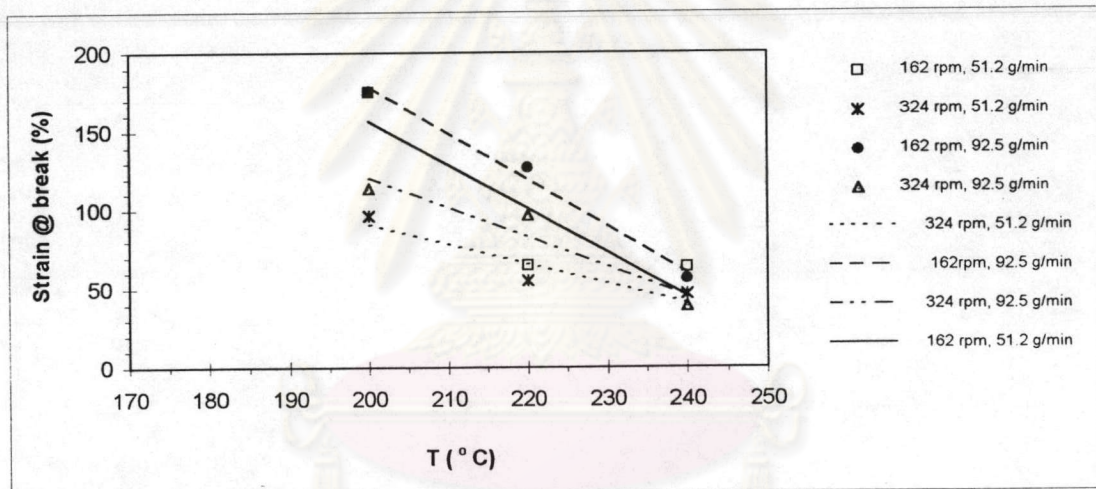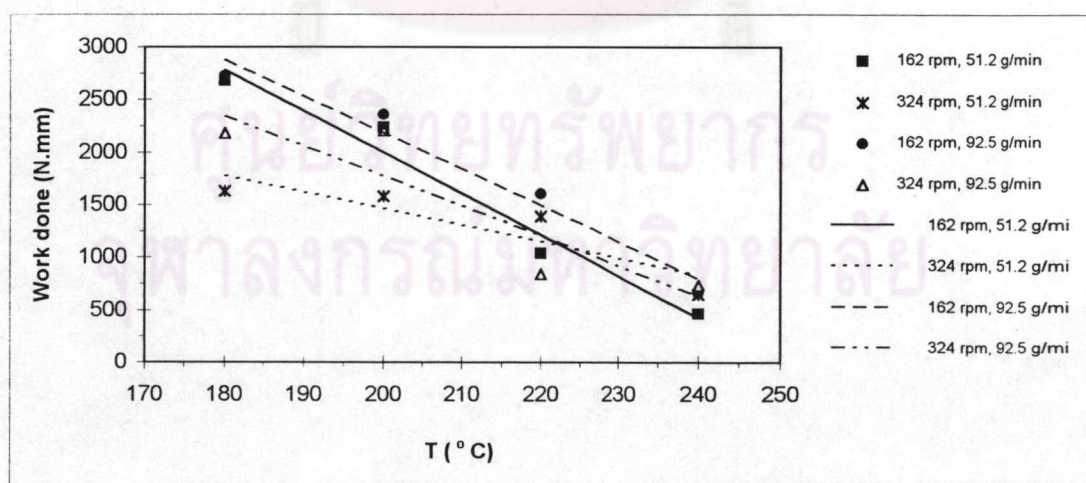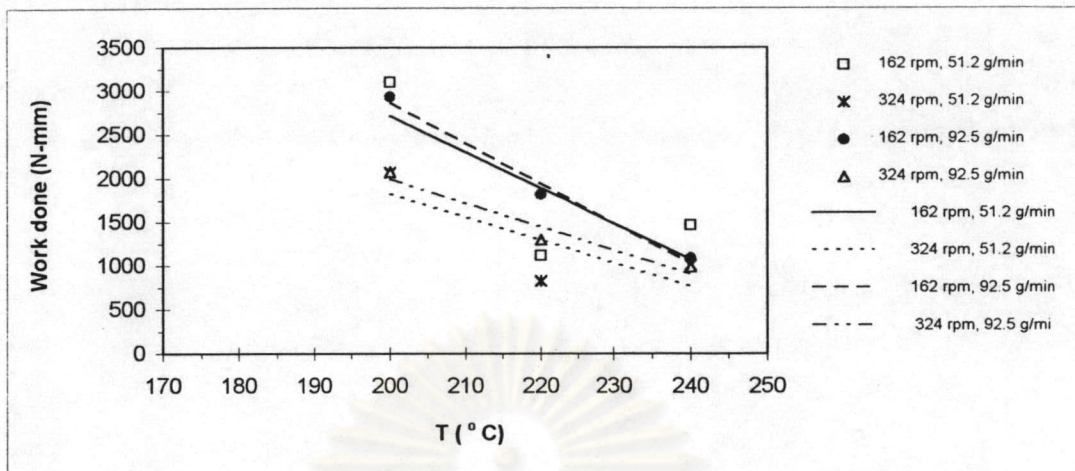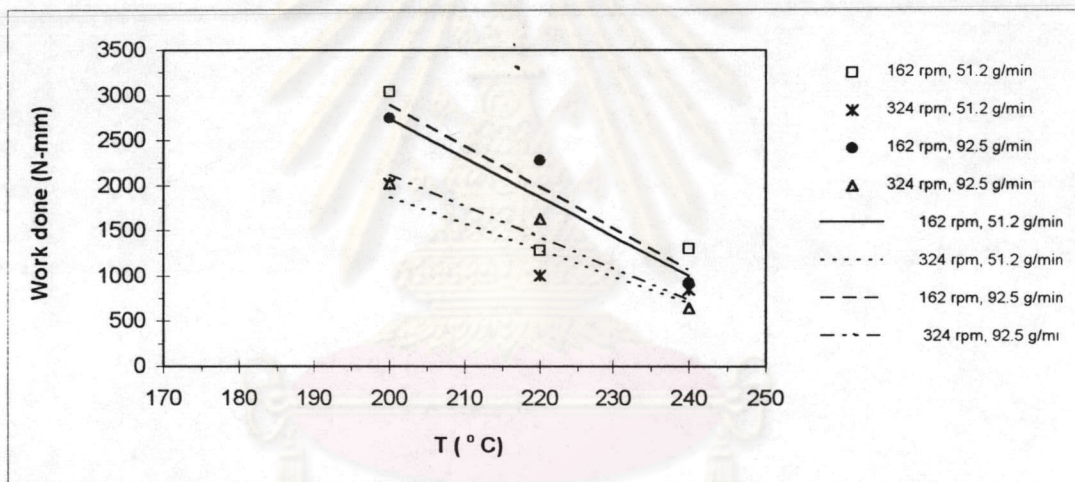

Figure 5.11 Relationship between the strain at break and the kneading temperature

(T) in the case of quinacridone violet pigment

(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.12 Relationship between the strain at break and the kneading temperature

(T) in the case of carbon black pigment

5.2.1 Effect of the kneading temperature on tensile properties

The effect of the kneading temperature on the strain at break is shown in **figure 5.11** for the quinacridone violet pigment and in **figure 5.12** for the carbon black. The strain at break for both pigments tended to decrease substantially as the kneading temperature increased, regardless of the other kneading conditions. This can be attributed to the fact that the heat history of a polymer considerably influences its properties. Moreover, an excessively high kneading temperature led to oxidative degradation of HDPE, especially in the absence of antioxidant additives. In fact, thermal degradation of pure HDPE was evident at the higher kneading temperatures as the HDPE extrudate turned yellow and brittle. As a consequence, the corresponding work required to stretch and break the specimens decreased significantly as shown in **figure 5.13** for the quinacridone violet pigment and in **figure 5.14** for the carbon black, regardless of the other kneading conditions.
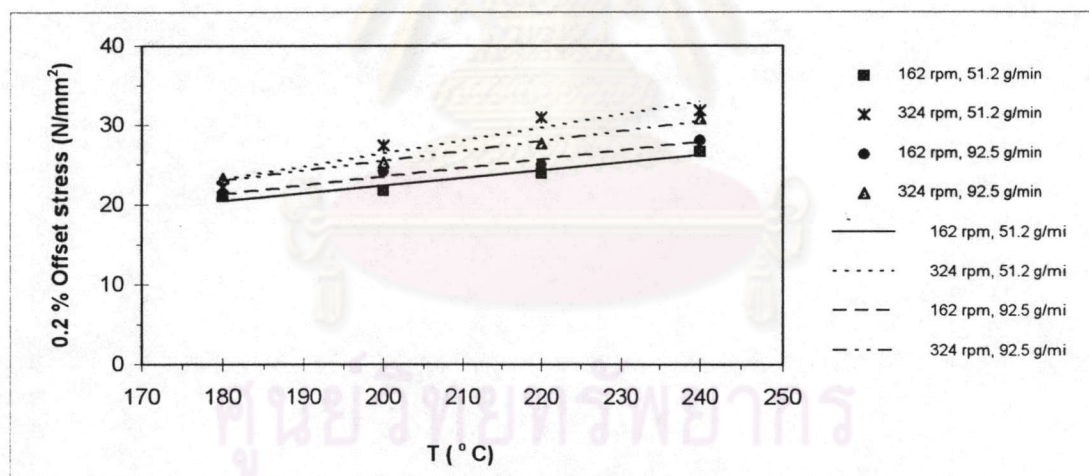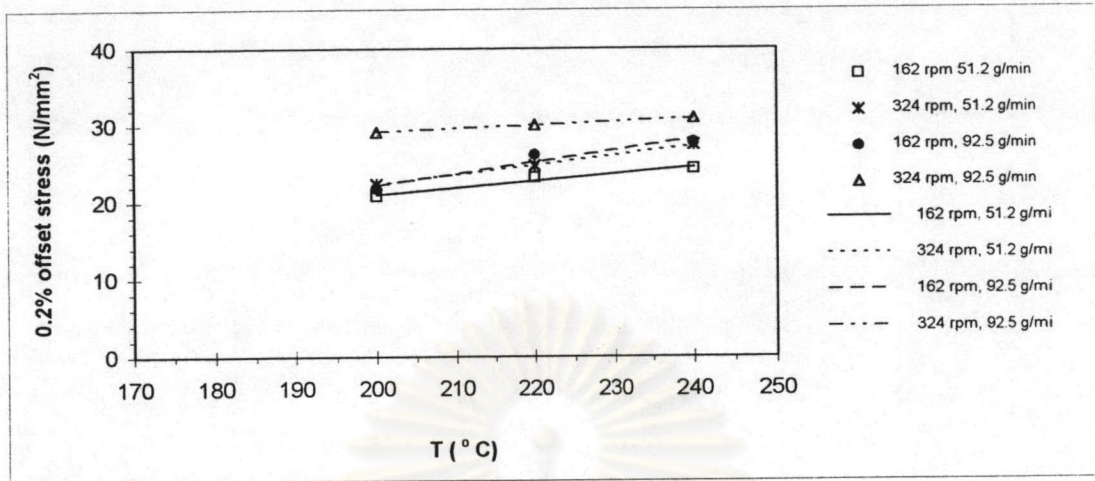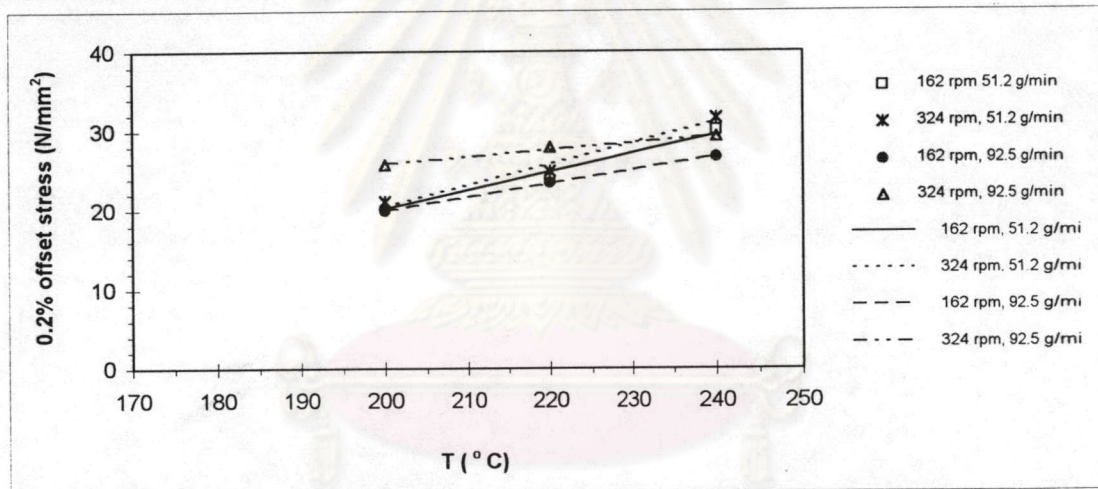

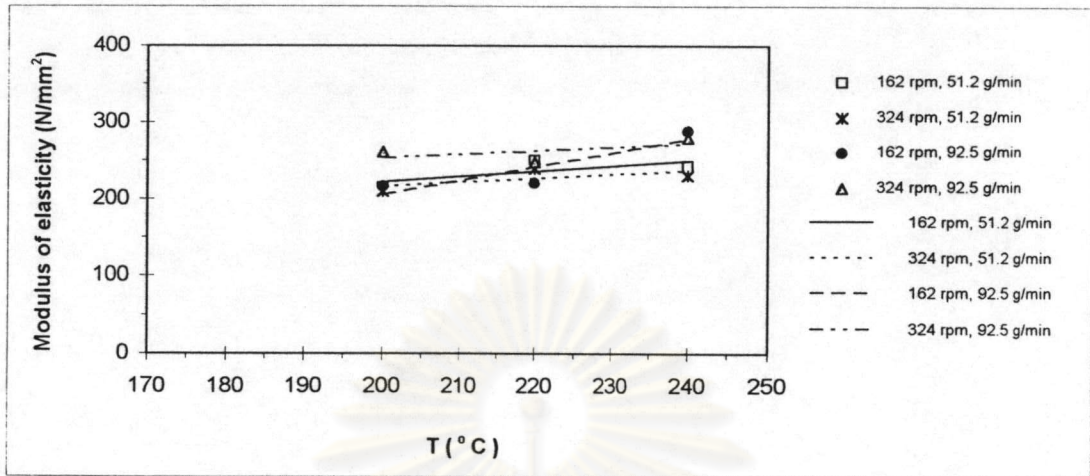Figure 5.13 Relationship between the work done and the kneading temperature (T) in the case of quinacridone violet pigment
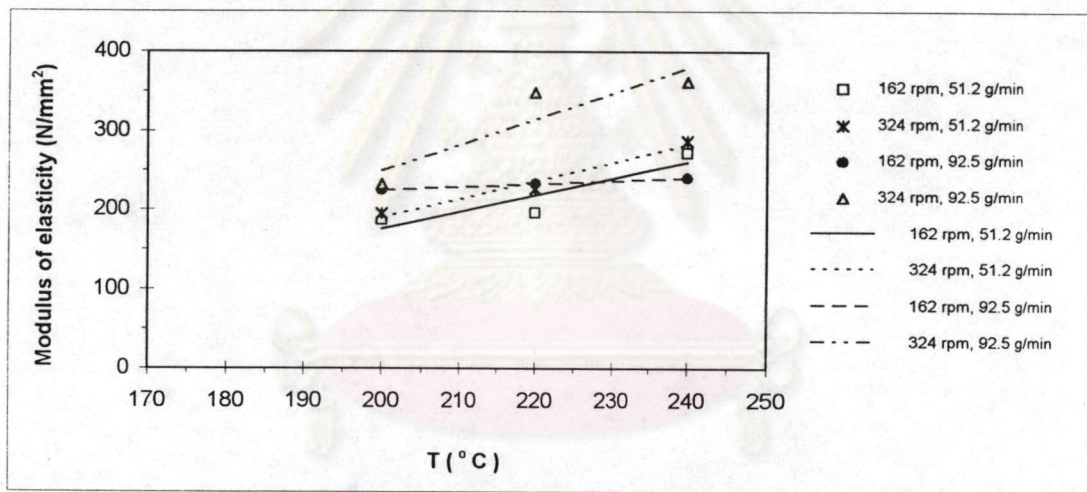
(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.14 Relationship between the work done and the kneading temperature (T)

in the case of carbon black pigment

The HDPE containing either pigment, carbon black or quinacridone violet, did not exhibit a clear yield point. Hence, the 0.2 % offset yield stress is reported instead in this study. **Figure 5.15** and **figure 5.16** show the effect of kneading temperature on the 0.2 % offset yield stress for the quinacridone violet and carbon black pigments, respectively. As seen from these figures, the higher the kneading temperature, the higher the 0.2 % offset yield stress. It may be attributed to the fact that the fine pigment particles with much higher hardness than the polymer matrix were quite uniformly distributed in it, thus enhancing the hardness and the load tolerance of the HDPE extrudate.

Figure 5.15 Relationship between the 0.2% offset yield stress and the kneading

temperature (T) in the case of quinacridone violet pigment

(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.16 Relationship between the 0.2% offset yield stress and the kneading

temperature in the case of carbon black pigment

(a) constant fixed premixed time at 10 minutes.

(b) constant fixed premixed time at 30 minutes.

Figure 5.17 Relationship between the modulus of elasticity and the kneading
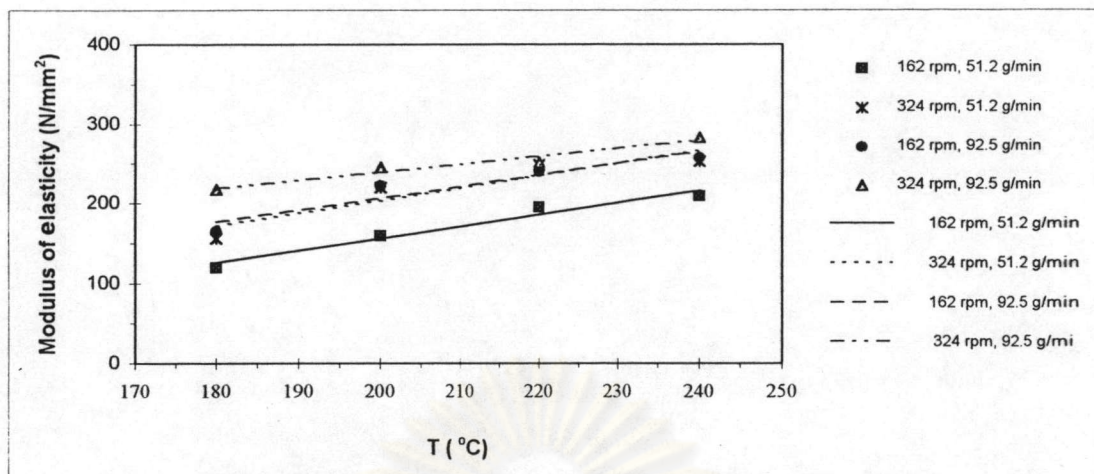
temperature (T) in the case of carbon black pigment

Figure 5.18 Relationship between the modulus of elasticity and the kneading

temperature (T) in the case of quinacridone violet pigment

From **figure 5.17** and **figure 5.18** , it is evident that the modulus of elasticity

increased with the kneading temperature for both pigments. This may again be

attributed to the brittleness imparted by the dispersion of pigment particles in the

kneaded polymer, which was accompanied by a decrease of the work done.
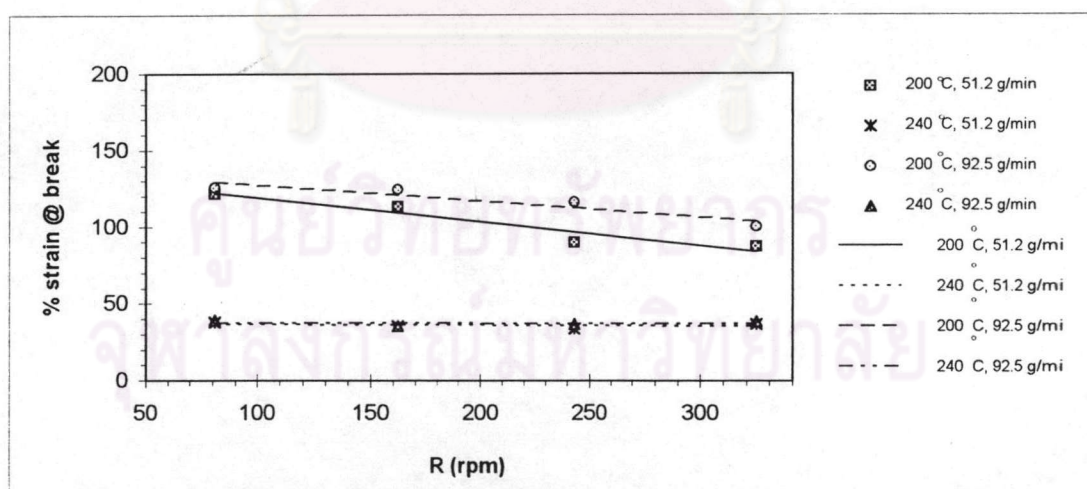
Figure 5.19   Relationship between the strain at break and the rotational speed of

screw (R) in the case of quinacridone violet pigment
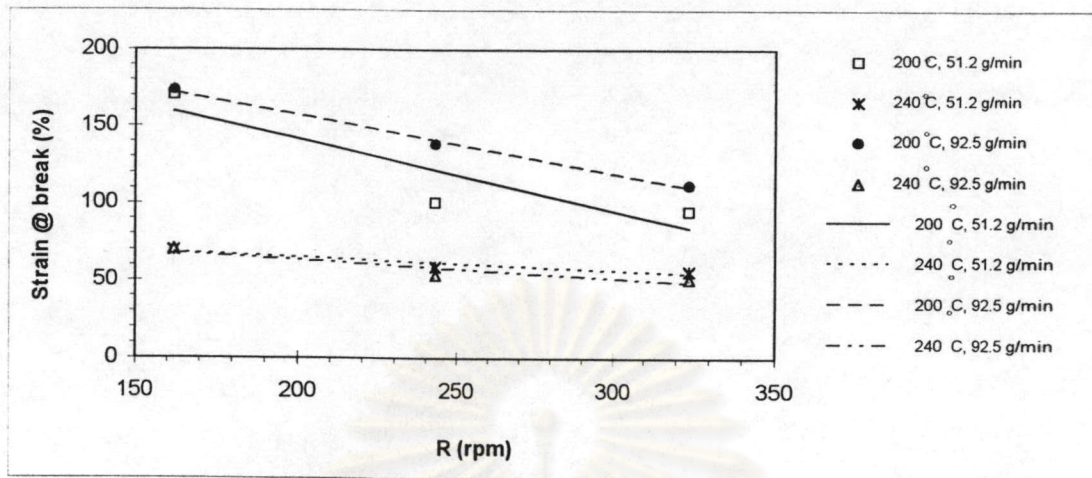
(a)   constant premixed time at 10 minutes.
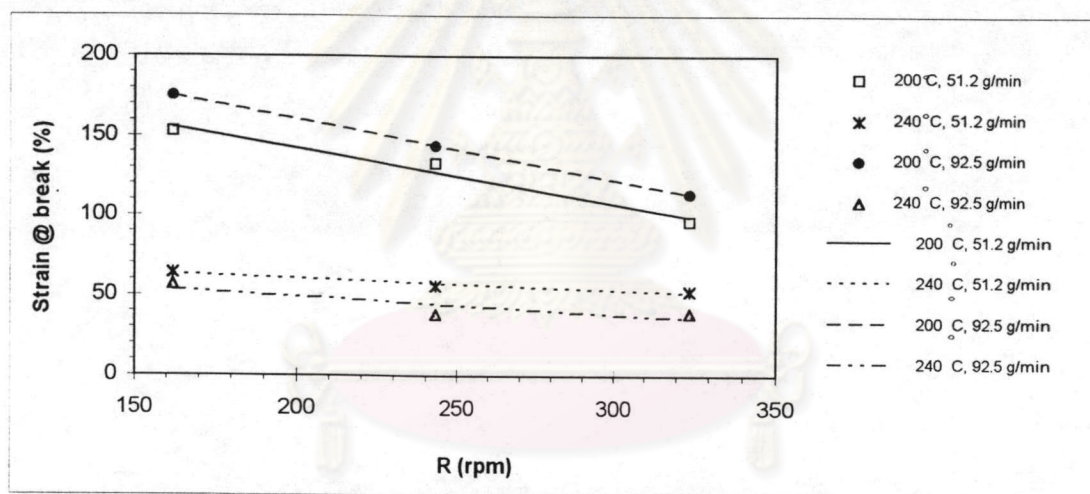
(b)   constant premixed time at 30 minutes.

Figure 5.20 Relationship between the strain at break and the rotational speed of
screw (R) in the case of carbon black pigment

5.2.2 Effect of screw rotational speed on tensile properties

The effect of the rotational speed of the twin screws on the strain at break is shown in **figure 5.19** for the quinacridone violet and in **figure 5.20** for the carbon black pigment. The strain at break clearly decreased as the rotational speed increased. This effect may be attributed to more frequent polymer chain scission at higher shear rates. The presence of shorter chains in the kneaded polymer resulted in more brittleness.

Similarly, **figure 5.21** and **figure 5.22** reveal that the required work done decreased as the rotational speed increased. On the other hand, the modulus of elasticity increased as seen from **figure 5.23** for the carbon black and **figure 5.24** for the quinacridone violet pigment.
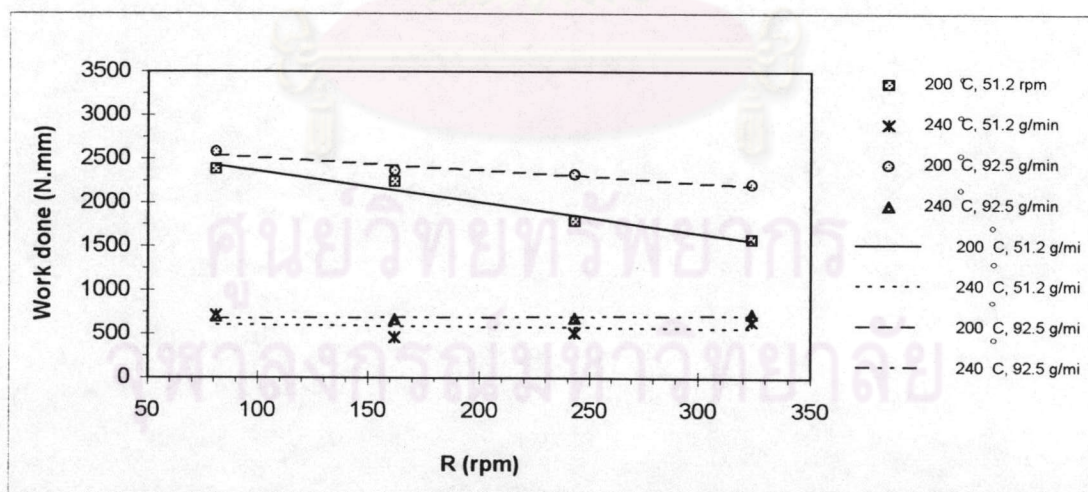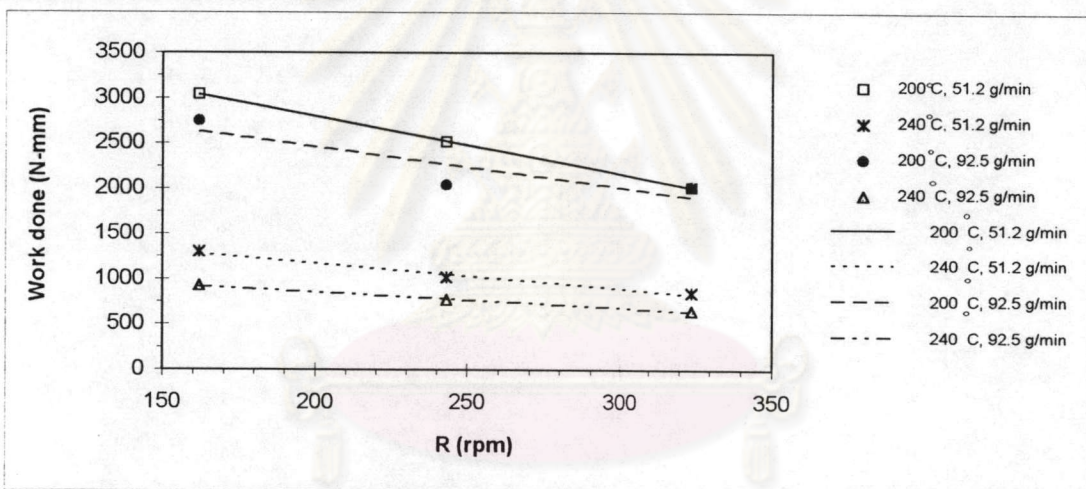

Figure 5.21 Relationship between the work done and the rotational speed of

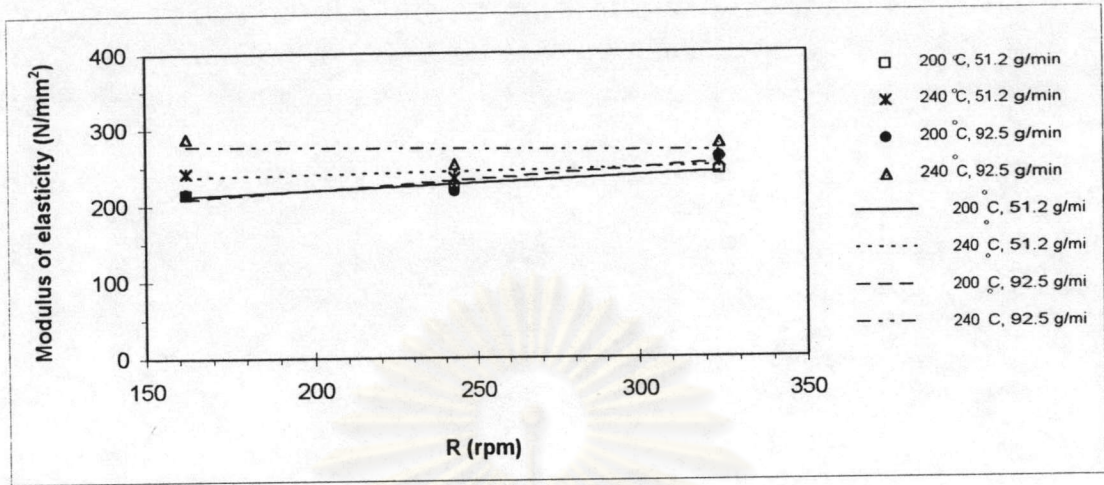screw (R) in the case of quinacridone violet pigment
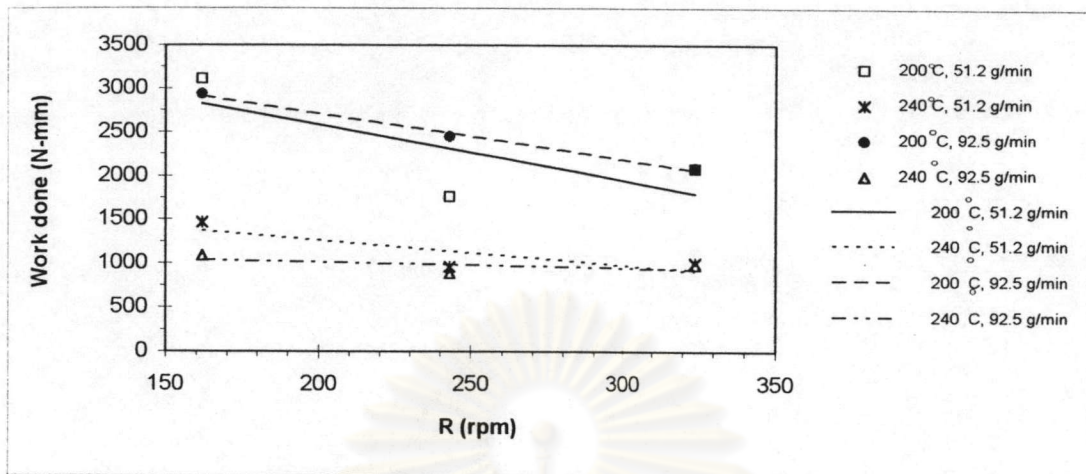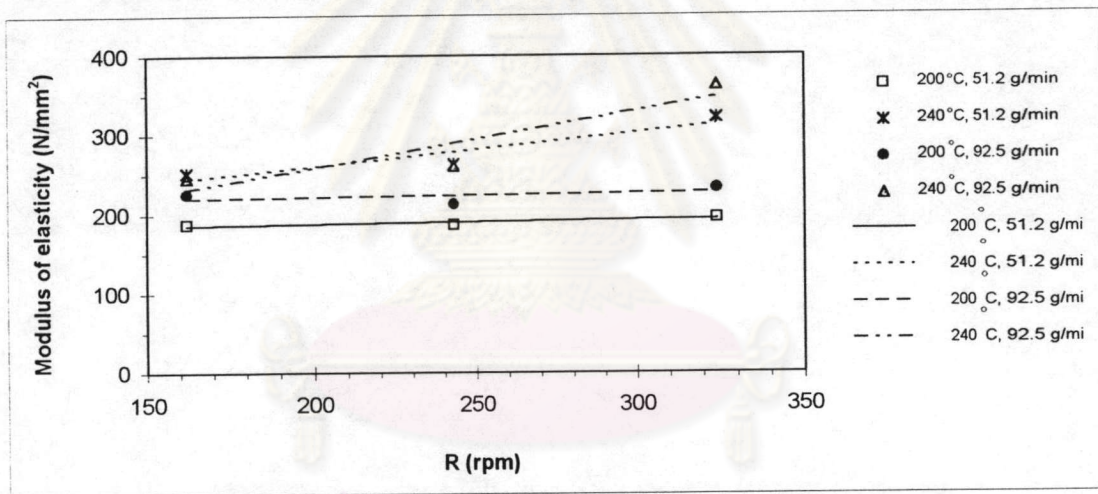
(a)   constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.22 Relationship between the work done and the rotational speed of screw

(R) in the case of carbon black pigment

(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.23 Relationship between the modulus of elasticity and the rotational speed
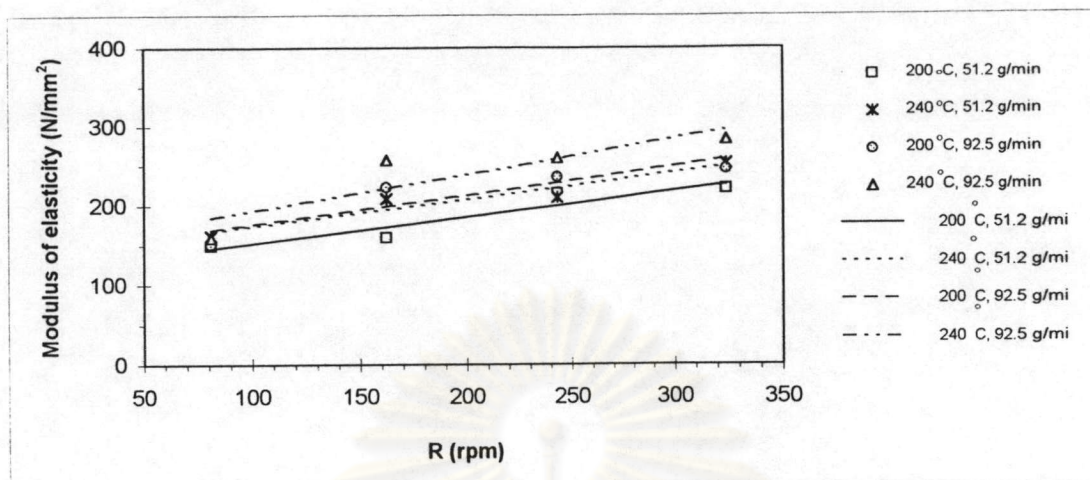
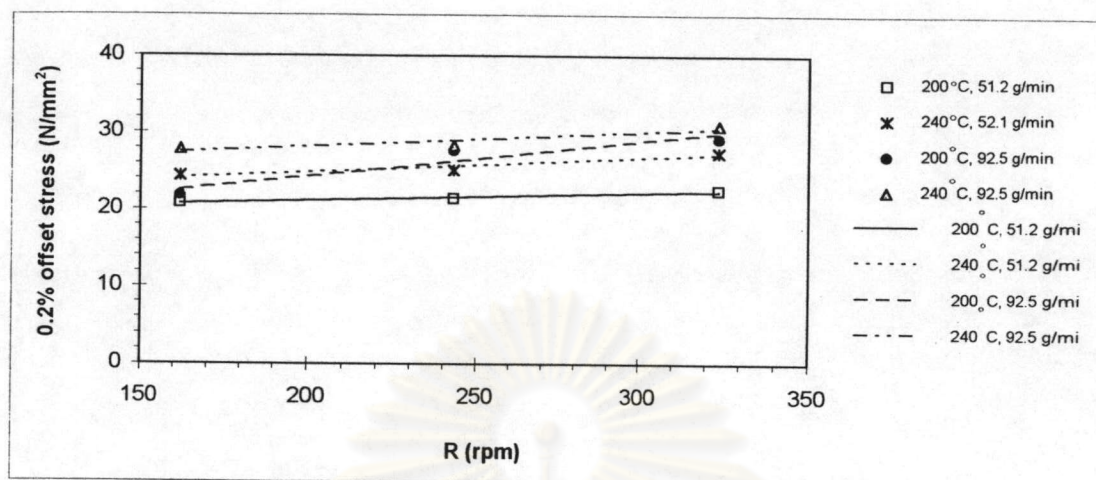of screw (R) in the case of carbon black pigment

Figure 5.24 Relationship between the modulus of elasticity and the rotational

speed of screw (R) in the case of quinacridone violet pigment

As in section 5.2.1, the fact that the hardness rose with the rotational

speed of screw could be supported by the increase in the 0.2 % offset yield stress,

as shown in **figures 5.25** and **5.26** in the case of carbon black and quinacridone

violet pigments, respectively.

Obviously, thermal degradation at an excessive kneading temperature

(240°C) had a more dominant effect on all four tensile properties than the rotational

speed had.

(a) constant premixed time at 10 minutes.
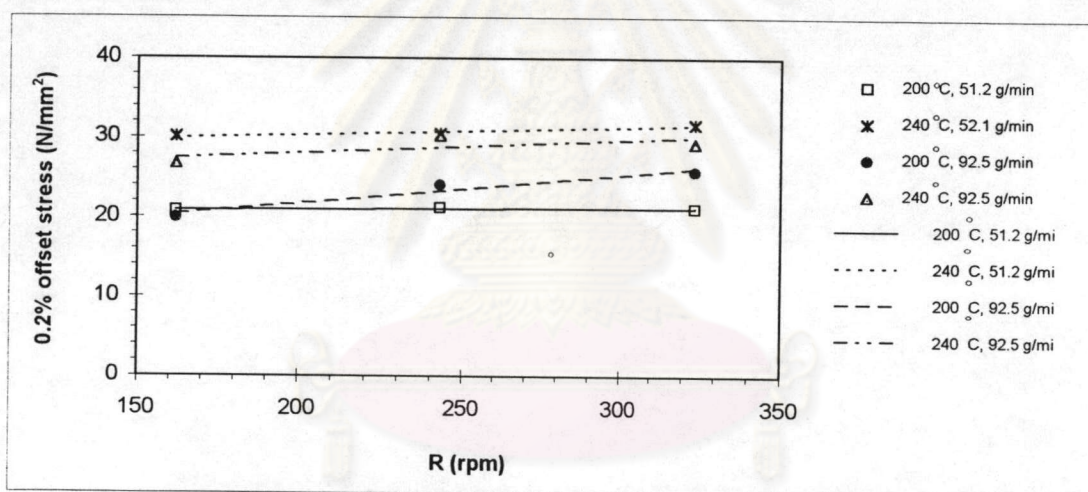
(b) constant premixed time at 30 minutes.

Figure 5.25 Relationship between the 0.2% offset yield stress and the rotational

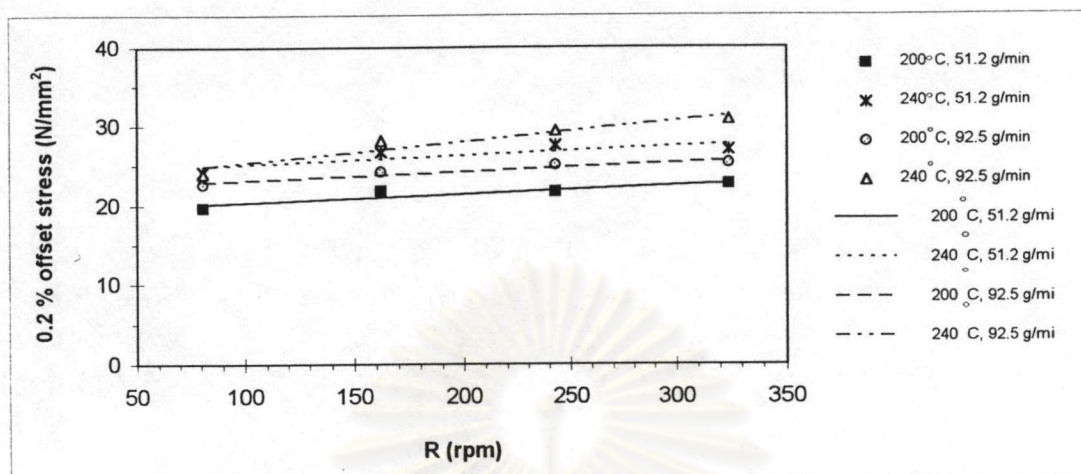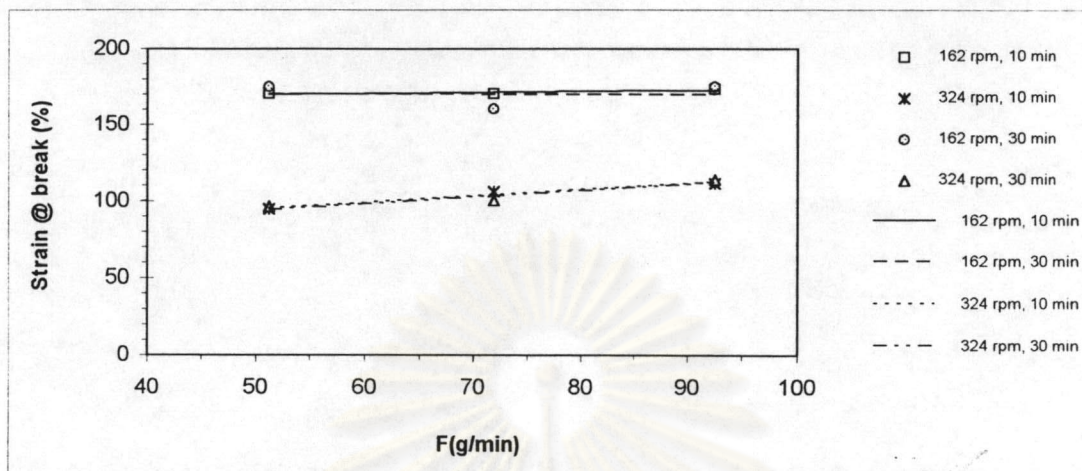speed of screw (R) in the case of carbon black pigment

Figure 5.26 Relationship between the 0.2% offset yield stress and the rotational

speed of screw (R) in the case of quinacridone violet pigment

5.2.3 Effect of feed rate on tensile properties.

Figure 5.27 to figure 5.30 show the effect of feed rate on all four tensile properties for the case of the carbon black and figure 5.31 to figure 5.34 for the case of the quinacridone violet pigment. Two conclusions may be reached. First, in contrast to the kneading temperature and the screw rotational speed, the feed rate had much less effect on the four tensile properties. Second, the feed rate had only a secondary effect. This is the reason that the trend of its effect could become reverse when one of the key (primary) factors was different.
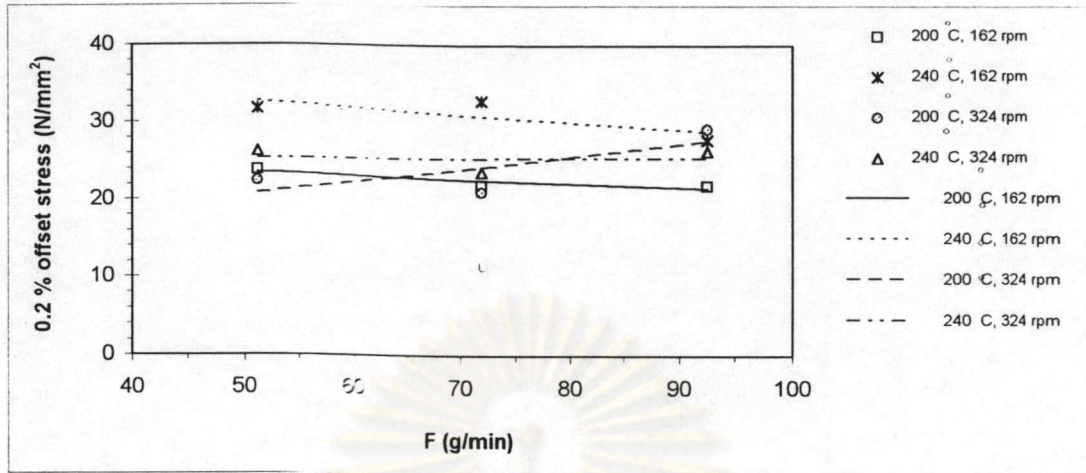
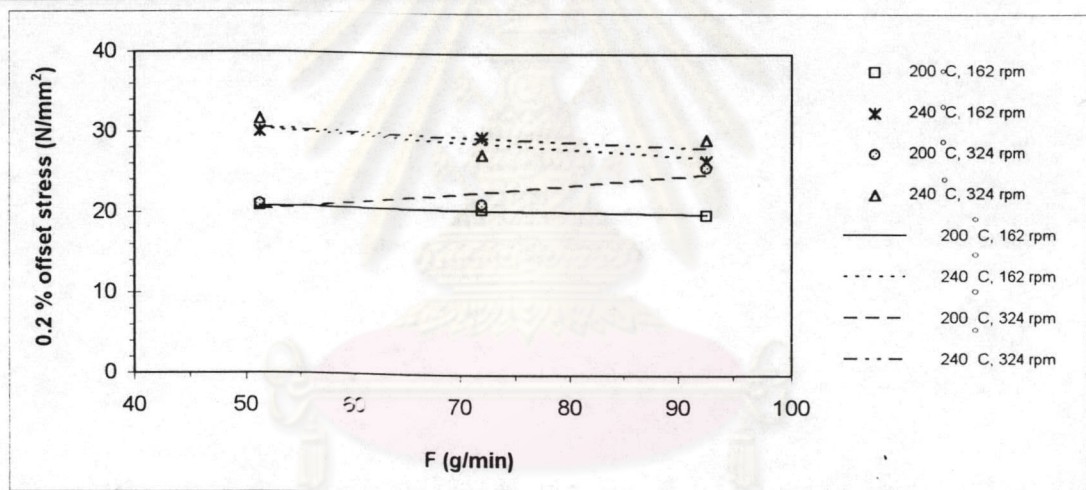(a) constant kneading temperature at 200 °C
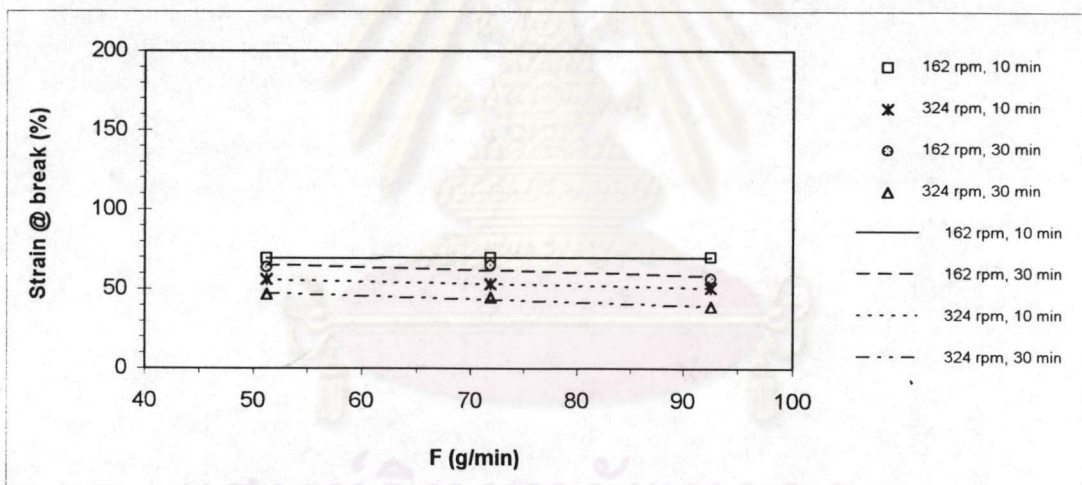
(b) constant kneading temperature at 240 °C

Figure 5.27 Relationship between the strain at break and the feed rate (F) in the
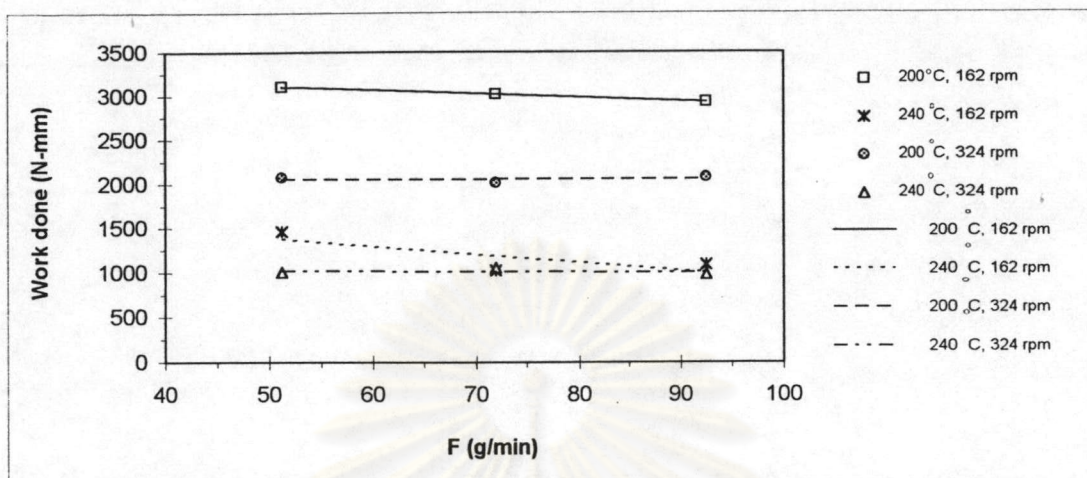
case of carbon black pigment

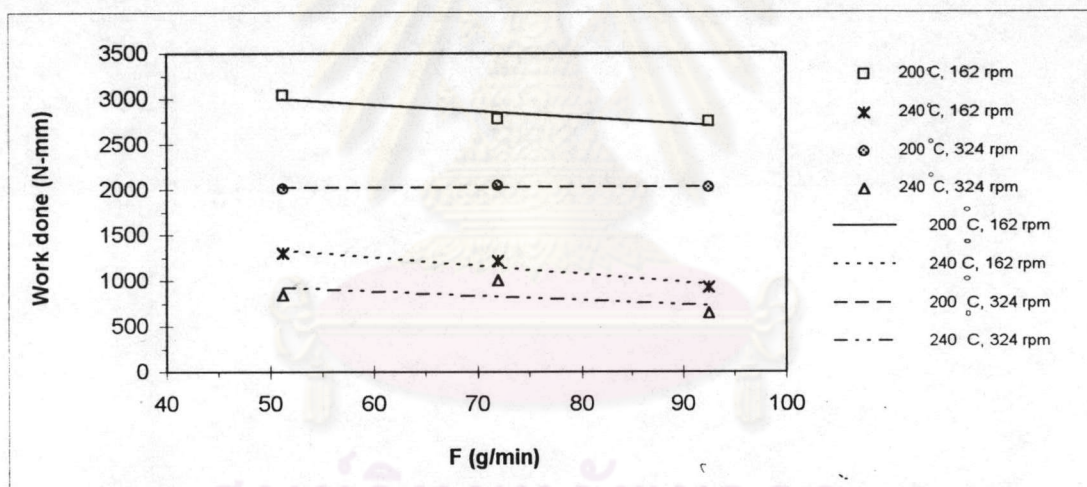(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.28 Relationship between the 0.2% offset yield stress and the feed rate (F)
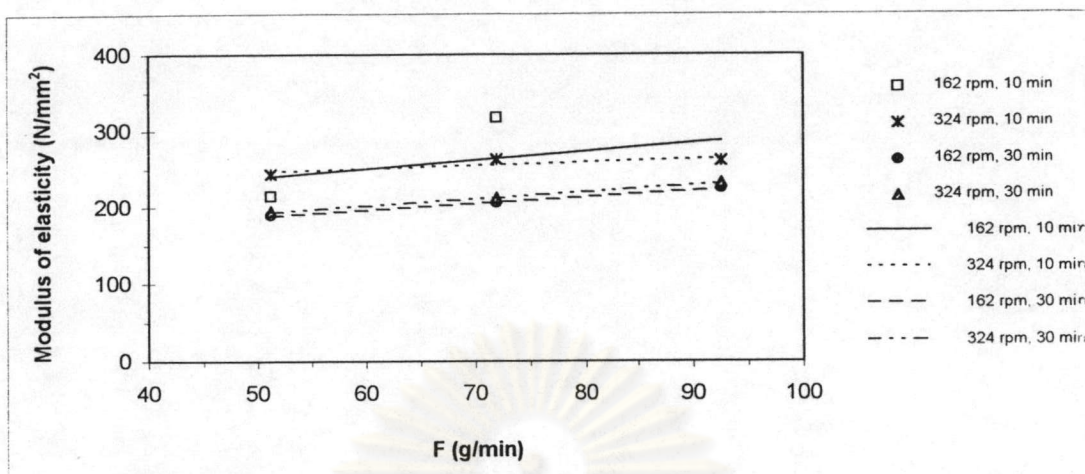
in the case of carbon black pigment

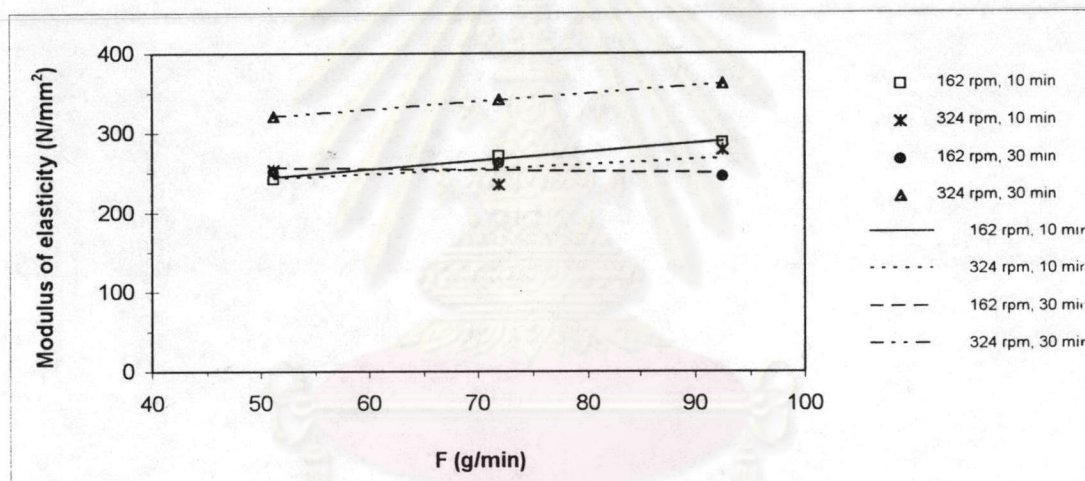(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.29 Relationship between the work done and the feed rate (F) in the case

of carbon black pigment

(a) constant kneading temperature at 200 °C

(b) constant kneading temperature at 240 °C

Figure 5.30 Relationship between the modulus of elasticity and the feed rate (F)

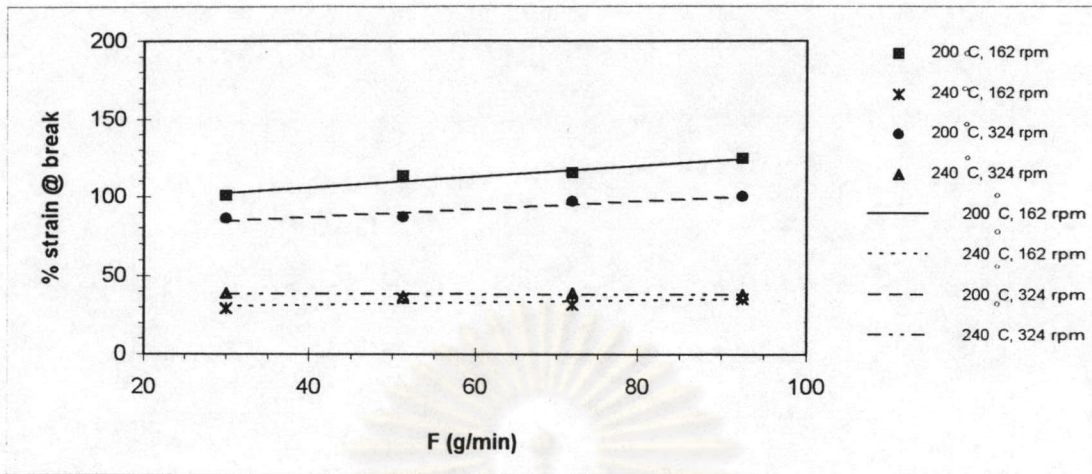in the case of carbon black pigment

Figure 5.31 Relationship between the strain at break and the feed rate (F) in the

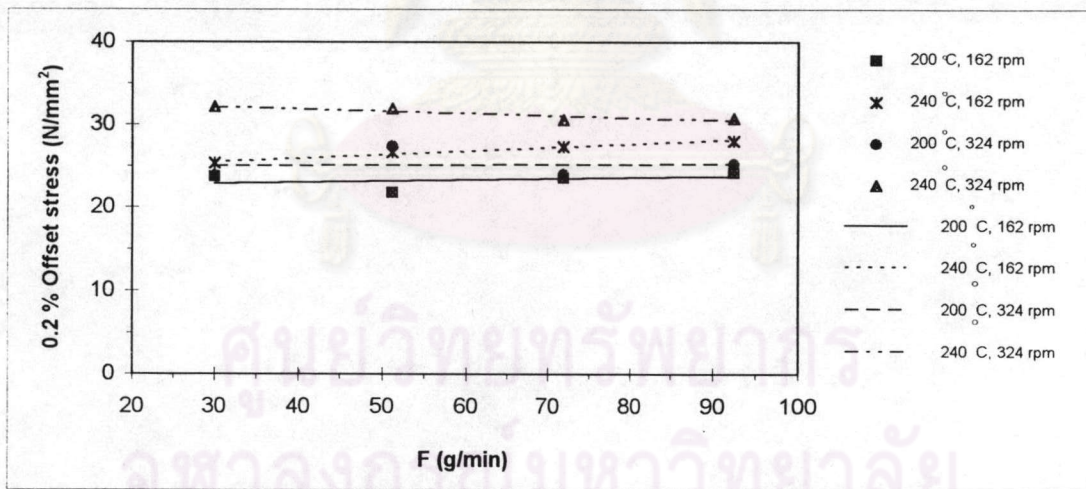case of quinacridone violet pigment

Figure 5.32 Relationship between the 0.2% offset yield stress and the feed rate (F)

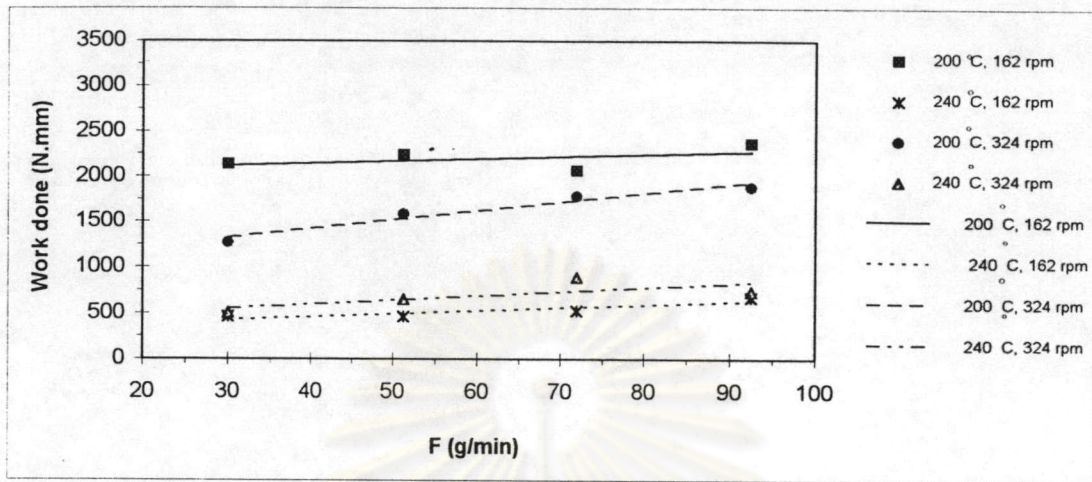in the case of quinacridone violet pigment

Figure 5.33 Relationship between the work done and the feed rate (F) in the case

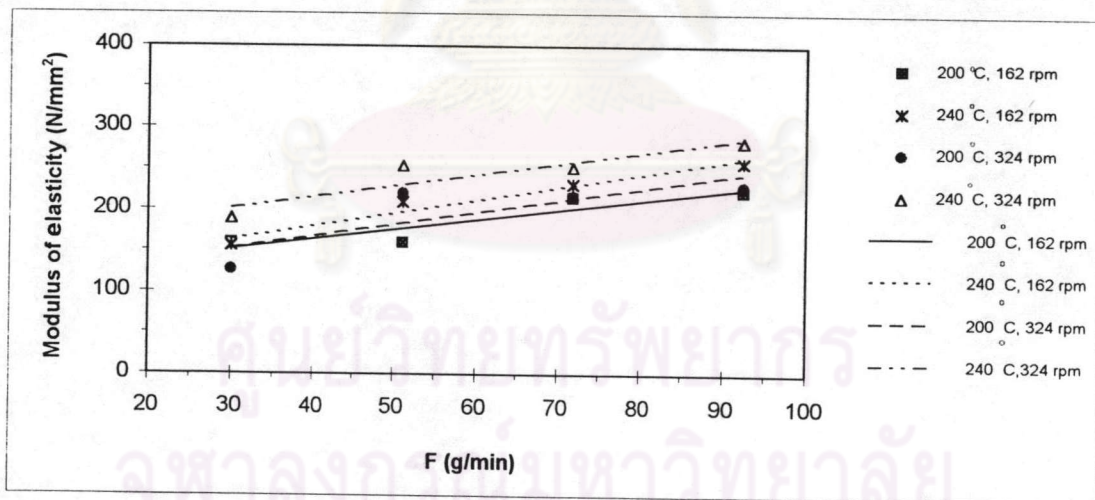of quinacridone violet pigment

Figure 5.34 Relationship between the modulus of elasticity and the feed rate (F) in

the case of quinacridone violet pigment

5.2.4 Effect of premixed time on tensile properties

From **figure 5.35** to **figure 5.38**, it is seen that, as in the case of the feed rate, the premixed time had only minor secondary effect on the tensile properties. It may be attributed to the fact that the lowest premixed time in this work (10 minutes) was sufficient for premixing.
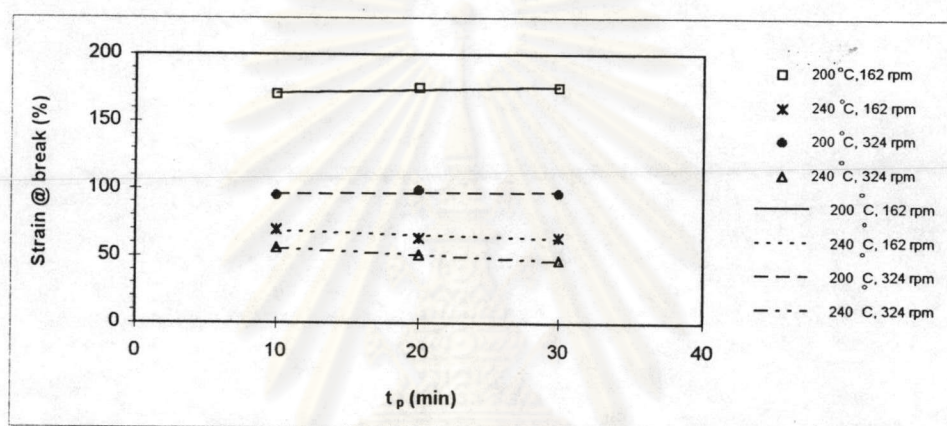
(a) constant feed rate at 51.2 g/min
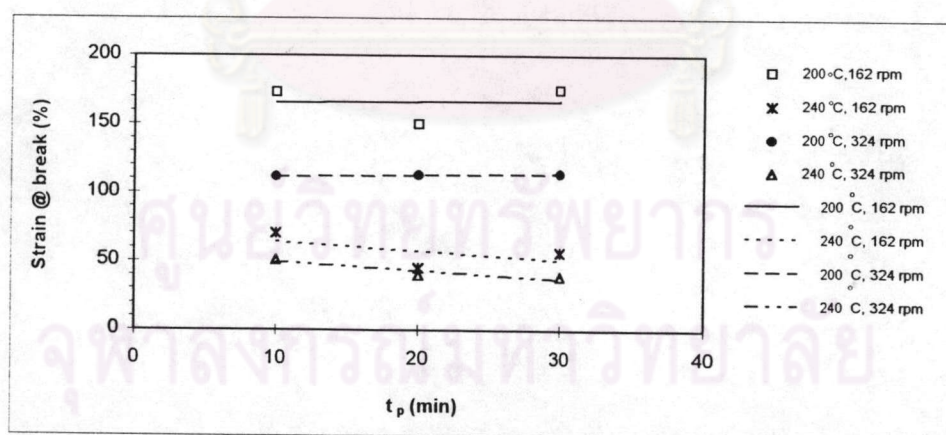
(b) constant feed rate at 92.5 g/min

Figure 5.35 Relationship between the strain at break and the premixed time (t_p) in

the case of carbon black pigment

(a) constant feed rate at 51.2 g/min.

(b) constant feed rate at 92.5 g/min.

Figure 5.36 Relationship between the 0.2% offset yield stress and the premixed

time (t_p) in the case of carbon black pigment

(a) constant feed rate at 51.2 g/min.

(b) constant feed rate at 92.5 g/min.

Figure 5.37 Relationship between the work done and the premixed time (t_p) in the

case of carbon black pigment

(a) constant premixed time at 10 minutes.

(b) constant premixed time at 30 minutes.

Figure 5.38 Relationship between the modulus of elasticity and the premixed time
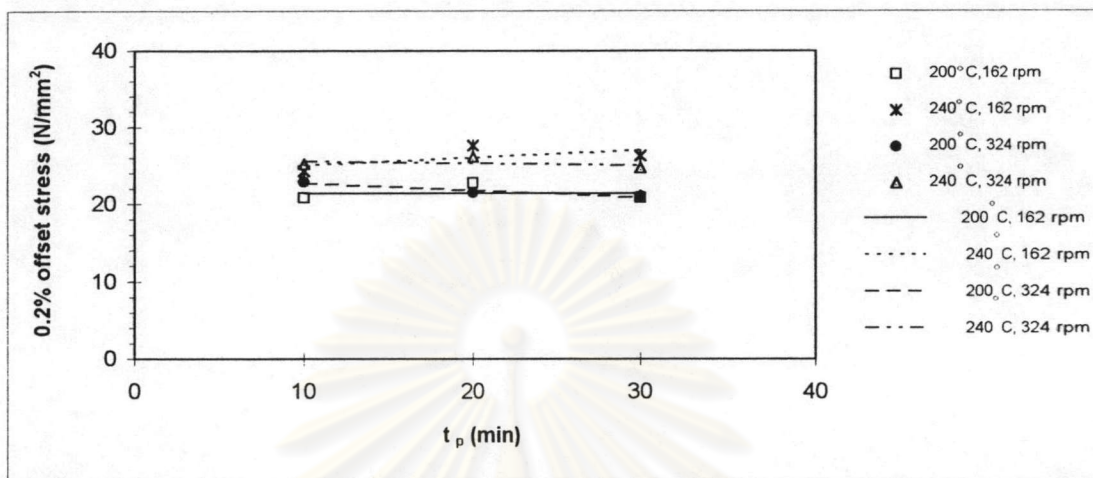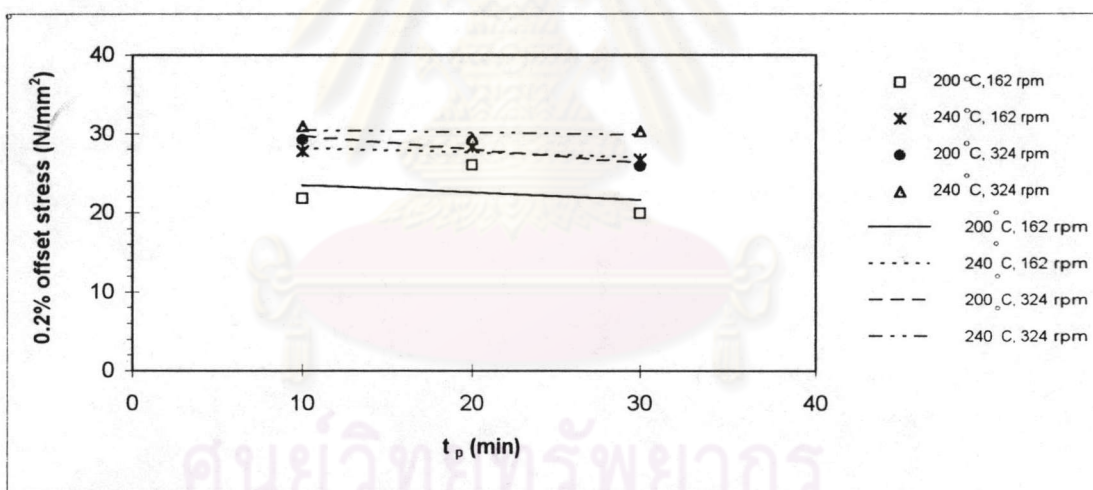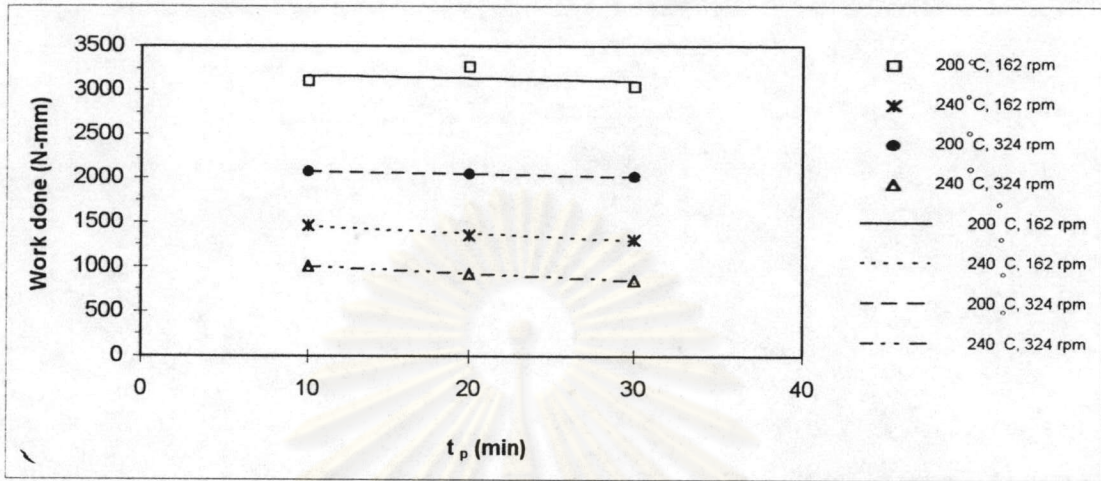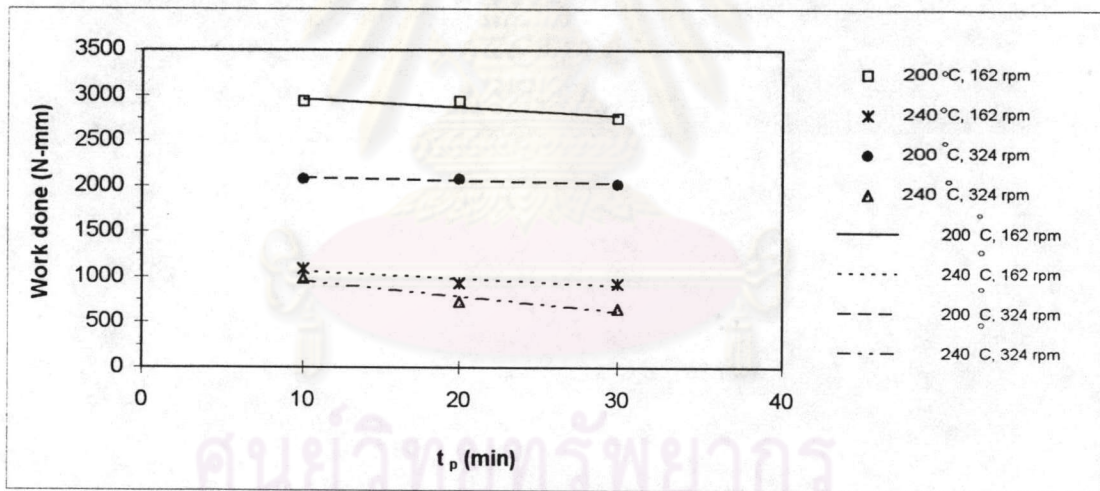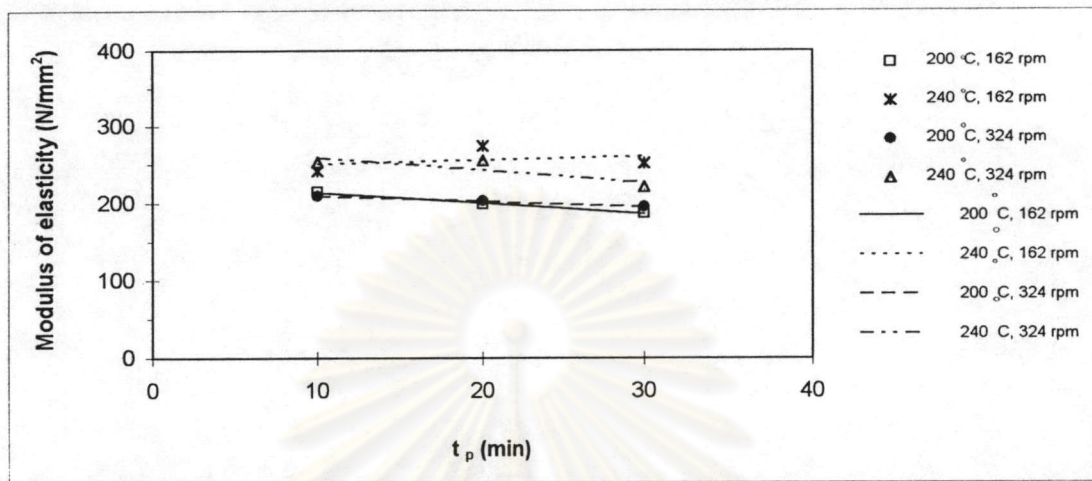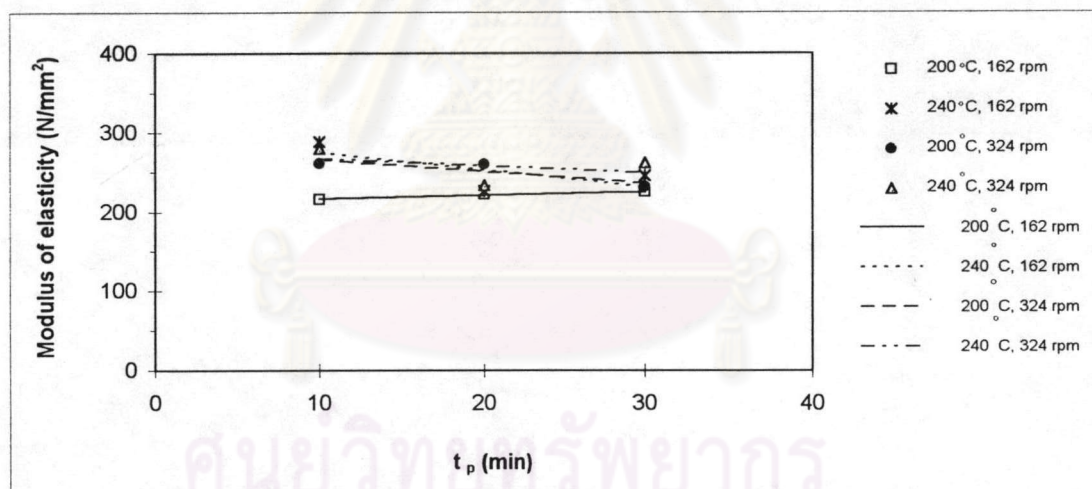
(t_p) in the case of carbon black pigment

5.3   Relationship between pigment dispersion state and tensile properties

Other key experimental factors being the same, the tensile behavior is expected to be influenced by the dispersion state of pigment particles in the polymer matrix. HDPE is a highly crystalline polymer whose structure consists of spherulites, spherical aggregates ranging from submicroscopic in size to millimeters in diameter. If the pigment particles are dispersed uniformly in the melt during kneading, the growth of the spherulites in the polymer is expected to occur uniformly throughout the melt and the sizes of the spherulites will not only be smaller but also more uniform. It may be because the pigment particles play the role of nuclei for initiating the spherulite growth. For this reason, the pigment dispersion state is expected to affect the tensile behavior, leading to an increase in the modulus of elasticity and to brittle failure at lower strains.

Table 5.3 Effect of the key kneading conditions on the averaged tensile properties
and normalized fractal dimension in the case of carbon black pigment

T ($^\circ$C)	R (rpm)	Strain @ break (%)	Work done (N-mm)	0.2% offset stress (N/mm^2)	E (N/mm^2)	D*
200	162	168.8	2978	21.3	223.4	0.931
	243	128.9	2192	23.6	209.8	0.963
	324	104.3	2117	24.0	233.9	0.976
220	162	85.3	1663	24.2	224.8	0.940
	324	80.0	1191	26.9	265.4	0.985
240	162	62.9	1164	29.3	256.6	0.954
	243	51.5	906	28.6	252.3	0.973
	324	47.7	899	28.5	285.3	0.991

Table 5.4 Effect of the key kneading conditions on the averaged values of tensile properties and normalized fractal dimension in the case of quinacridone violet pigment

T (°C)	R (rpm)	Strain @ break (%)	Work done (N-mm)	0.2% offset stress (N/mm^2)	E (N/mm^2)	D*
180	162	151.6	2705	21.0	142.4	0.821
	324	119.9	1904	22.7	186.9	0.851
200	81	123.8	2479	21.9	150.0	0.894
	162	113.5	2199	23.3	188.8	0.926
	243	102.9	2056	25.1	225.0	0.927
	324	92.7	1711	25.2	202.3	0.941
220	162	60.7	1323	24.5	217.5	0.916
	324	58.2	1116	29.3	250.1	0.945
240	81	38.5	705	24.1	160.8	0.928
	162	32.9	533	26.9	213.1	0.943
	243	35.2	601	28.4	235.1	0.940
	324	38.2	696	31.4	243.9	0.970

Table 5.3 and **5.4** summarize the interrelations between the key kneading conditions, the averaged values of the tensile properties and normalized fractal dimension (an index of the dispersion state) in the case of the carbon black and quinacridone violet pigments, respectively.

As seen from **table 5.3**, the average value of D* (normalized fractal dimensions) at each temperature clearly higher as the rotational speed of the kneader increased from 162 to 324 rpm. A similar effect on D* was observed as the kneading temperature rose from 200 to 240 °C at each fixed rotational speed. These observations undisputedly confirmed the earlier conclusions that both the kneading temperature (T) and rotational speed (R) greatly enhanced the degree of dispersion of the carbon black pigment.

Clear-cut trends of the tensile properties with respect to T and R were also effect. In brief, T and R clearly exerted a negative effect on the strain at break and

the work done, whereas they exerted a slightly positive effect on the 0.2 % offset stress. The only exception appeared at T = 240 ^{o}C, in which case the effect of R was slightly negative. As for the modulus of elasticity (E), T clearly exerted a positive effect but an intermediate rotational speed (R) appeared to yield a minimum value of E.

The strongly negative trend of the strain at break as well as the work done versus T, when contrasted to the positive effect of T on D*, clearly indicated thermal degradation was a serious cause of the deterioration of the tensile properties. Though the negative trend of the strain at break versus R was less strong at 220 and 240 ^{o}C because the unfavorable effect of scission of polymer chains was less severe than that of thermal degradation, it may be concluded that these two tensile properties deteriorated when the rotational speed increased.

Next it can be seen from **table 5.4** that again in the case of quinacridone violet pigment, the same conclusions and comments as those in the case of carbon black were also applicable.
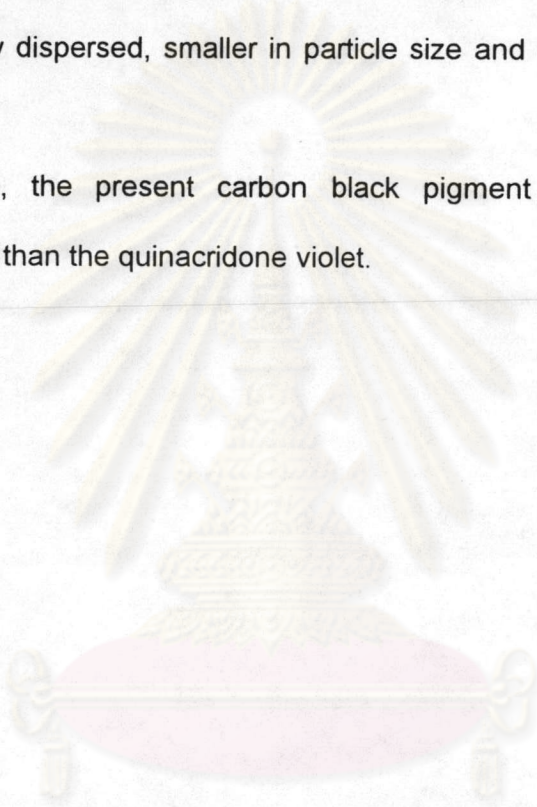
5.4 Comparison between the two pigments

When the values of D* in **tables 5.3** and **5.4** were compared under the same kneading conditions (T and R), it was obvious that carbon black was more uniformly dispersed in the polymer matrix than quinacridone violet was. One reason is that the average size of carbon black particles is only 0.02 μm, about one-sixth of that of quinacridone violet (0.12 μm). Another reason is that carbon black molecules have

less polarity (are less polar) than quinacridone violet molecules. Thus the former is more compatible to the non-polar HDPE matrix. So it was more easily dispersed.

When the values of the strain at break (and the work done) in **tables 5.3** and **5.4** were compared under the same kneading conditions, it was again obvious that carbon black yielded better properties than quinacridone violet because the former was more uniformly dispersed, smaller in particle size and more compatible to the matrix.

In conclusion, the present carbon black pigment was a better (more preferable) additive than the quinacridone violet.