CHAPTER IV
RESULTS AND DISCUSSION

4.1 Effect of the Thickness on the Observed Reaction Time

4.1.1 Fixed Initiator Concentration (various thickness)

The MMA syrup was prepared by mixing MMA monomer (containing 10 ppm inhibitor) with 18 ppm 2,2'-azobisisobutylonitrile (AIBN) at 80°C using a mechanical stirrer for 45 minutes. After the MMA syrup was cooled down, it was mixed with 0.010% or 0.015% by weight of 2,2'-azobis-(2,4-dimethyl valeronitrile) (ADVN) using a mechanical stirrer for 20 minutes. The mixture was filled into a glass mold with the gap thickness 5, 8, and 10 mm. The polymerization temperature was 60°C and the annealing temperature was 120°C. During polymerization, the temperature of the exothermic reaction occurs (Ramaseshan *et al.*, 1993), the exothermic peak of the reaction can be used to estimate the reaction time.

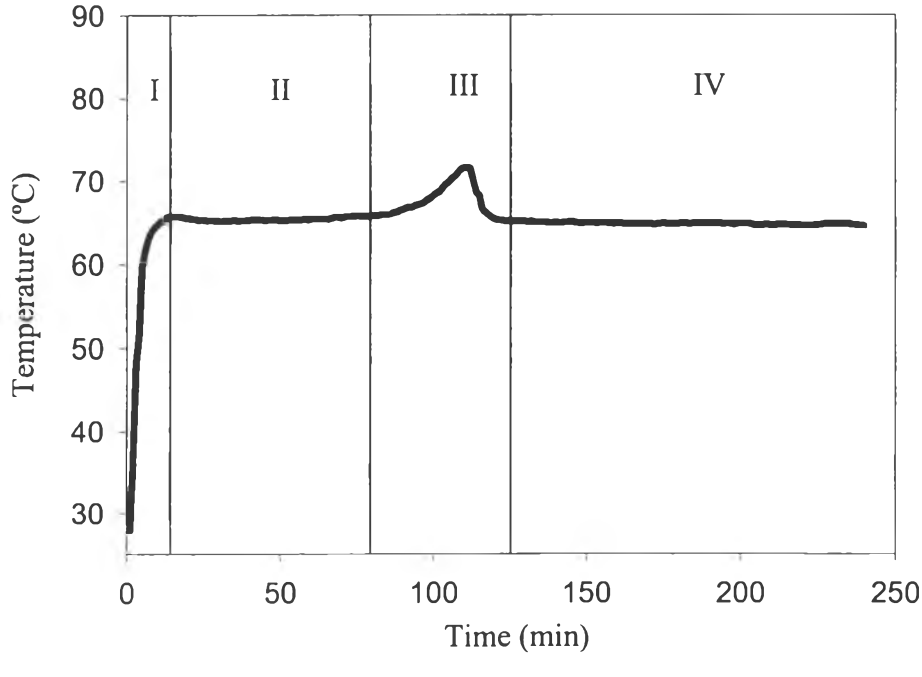

Figure 4.1 Temperature profile of the sample polymerized at 60°C with 0.030% ADVN (3 mm).

In Figure 4.1, the temperature profile of sample polymerized at 60°C with 0.030% ADVN is shown. The profile can be schematically divided into four steps. The first step is the rapid increase in the temperature of syrup as a result of the marked difference in the temperature syrup (room temperature) and the water (the set temperature). In this step, the rate of temperature rise depends strongly on the heat transfer coefficient (conductivity coefficient). The second step is the plateau region where the temperature of the syrup is equivalent to the water temperature. The third step is the peak region where the temperature rise occurs, a direct result of the exothermic polymerization heat. In the forth step, the temperature drop to the water temperature. The width and the area of the peak are related to the rate of polymerization, which in turn relates to the polymerization condition studied.

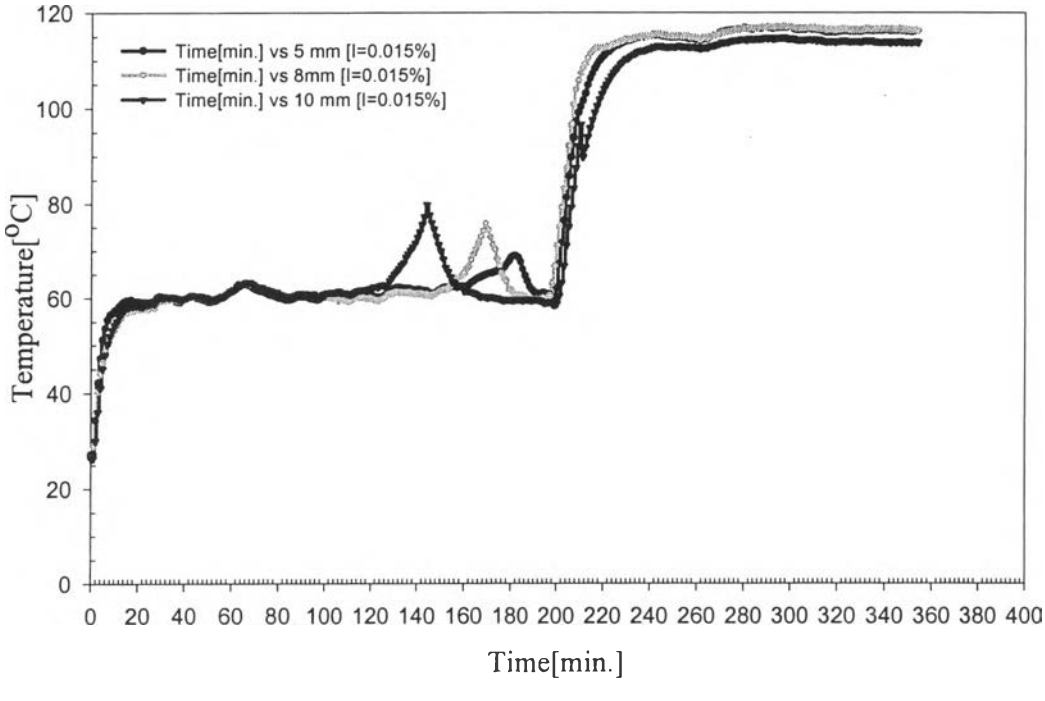

Figure 4.2 Temperature profiles of samples polymerized at 60°C with 0.015% ADVN, the thickness is varied from 5, 8, and 10 mm.

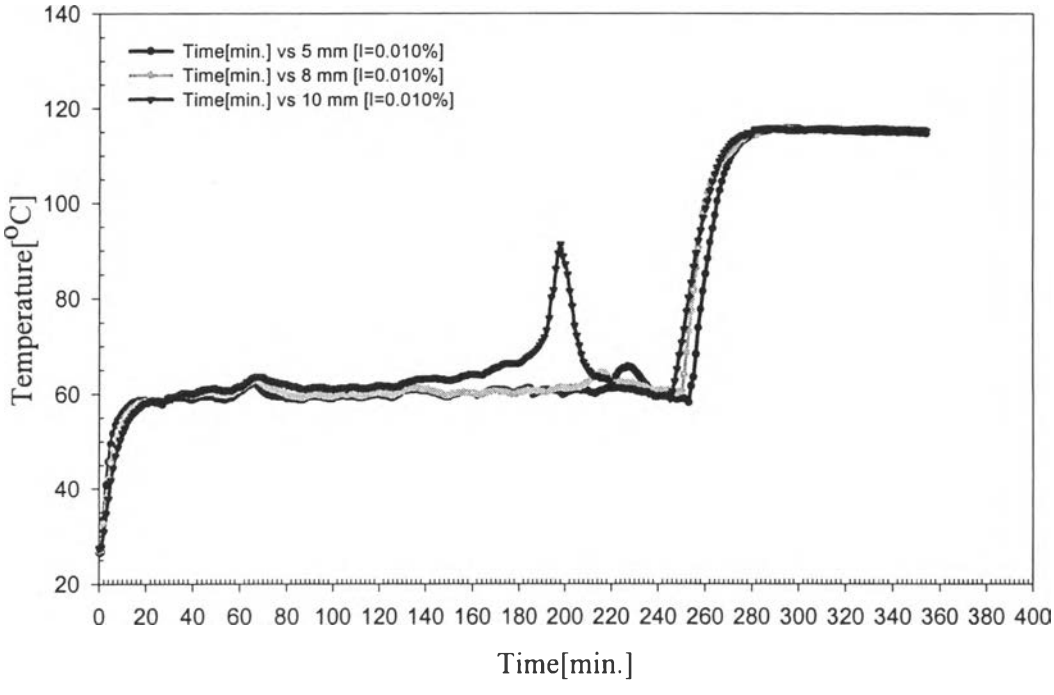

Figure 4.3 Temperature profiles of samples polymerized at 60°C with 0.010% ADVN, the thickness is varied from 5, 8, and 10 mm.

In Figures 4.2 and 4.3, the temperature profiles of the difference thickness (5, 8, and 10 mm) samples polymerized at 60°C with 0.010% and 0.015% by weight are shown, respectively. Apparently, the reaction time depended strongly on the thickness of the sample. The reaction time (viz. defined by the time interval from the beginning of the polymerization process to the time at which the maximum in the temperature profile was observed) of 5, 8, and 10 mm thickness with 0.010% were ca. 241, 223, and 216 minutes, respectively. The maximum temperature was also observed for each thickness: they are ca. 65.7°, 64.5°, and 91.3 °C at thickness 5, 8, and 10 mm with 0.010% ADVN by weight, respectively. In conclusion, the maximum peak temperature was found to increase, while the observed reaction time decreased, with increasing the sample thickness. However, the maximum peak temperature is a major parameter that concerns with the defect of the samples, therefore the reduction of the reaction time are limited by the maximum temperature (not greater than 90°C due to the boiling point of MMA monomer).

Table 4.1 Maximum peak temperature and the observed reaction time of samples, thickness 5, 8, and 10 mm, with 0.010% and 0.015% ADVN polymerized at 60°C

ADVN concentration (% wt)	Thickness (mm)	Maximum temperature (°C)	Observed reaction time (minute)
0.010	5	65.7	241
0.010	8	64.5	223
0.010	10	91.3	216
0.015	5	68.9	192
0.015	8	75.8	180
0.015	10	79.8	158

4.2 Effect of the Initiator Concentration at Each Thickness

4.2.1 The 5 mm Thickness Samples

Temperature Profile

In order to reduce the production time of PMMA sheets, the temperature profile of samples polymerized at 60°C with 0.015%, 0.018%, and 0.022% ADVN by weight was determined and shown in Figure 4.4 for one-step process and two-step process is shown in Figure 4.5. The reaction time depended strongly on the ADVN concentration (initiator concentration). The reaction time of the 5 mm thickness with 0.015% ADVN that polymerized at 60°C was ca. 214 minutes. For 0.018% and 0.022% ADVN, they were 196 and 175 minutes, respectively (see Table 4.2). The maximum temperature for one-step process was also observed for each condition from the temperature profile. As a result, the maximum peak temperature was found to increase, while the observed reaction time decreased, with increasing reaction temperature.

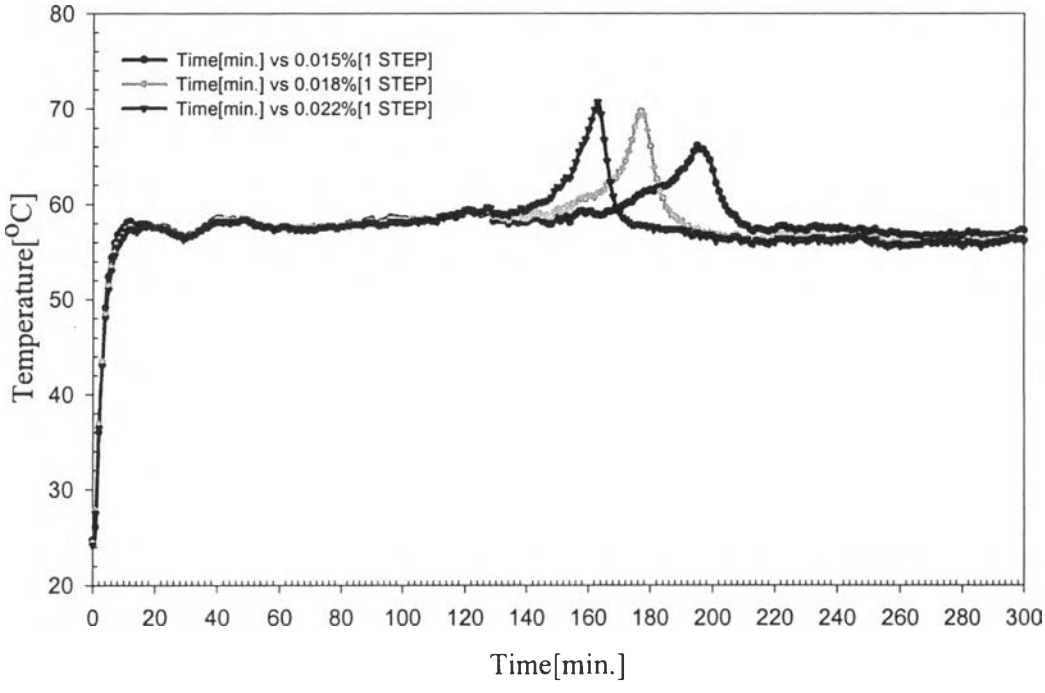

Figure 4.4 Temperature profiles of 5 mm thickness samples polymerized at 60°C with 0.015%, 0.018%, and 0.022% ADVN for 1-step process.

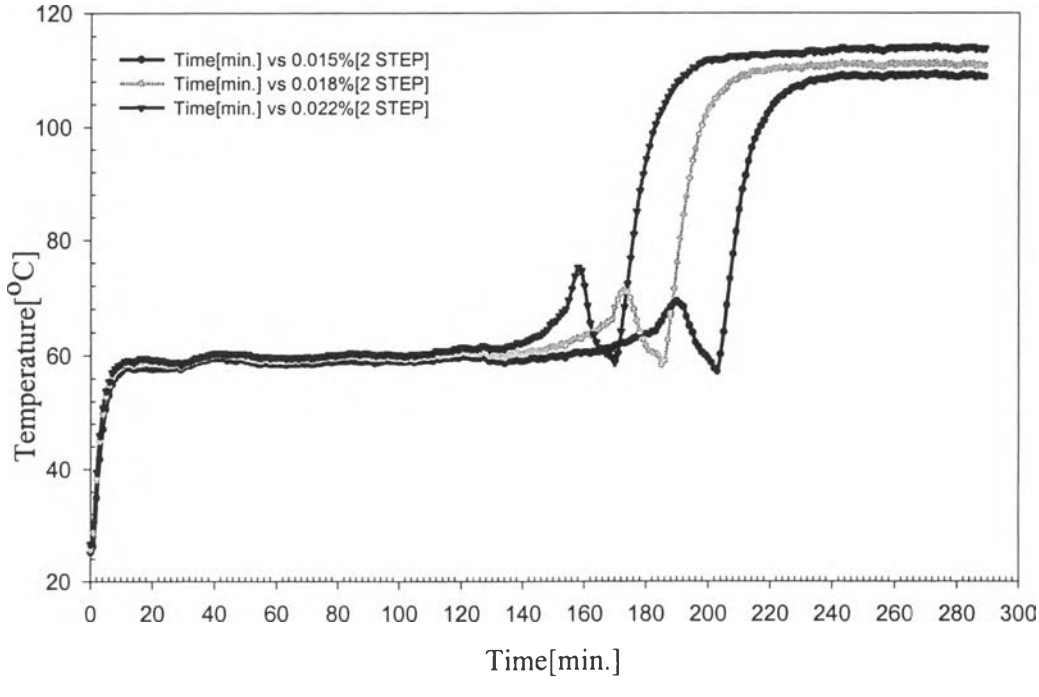

Figure 4.5 Temperature profiles of 5 mm thickness samples polymerized at 60°C and annealed at 120 °C with 0.015%, 0.018%, and 0.022% ADVN for 2-step process.

Table 4.2 Maximum peak temperature and the observed reaction time of 5 mm thickness samples with 0.015%, 0.018% and 0.022% ADVN polymerized at 60°C and annealed at 120°C

ADVN concentration (% wt)	Process	Maximum peak temperature (°C)	Observed reaction time (minute)
0.015	One-step process	66.1	214
0.018		69.7	196
0.022		70.7	175
0.015	Two-step process	69.3	202
0.018		71.3	186
0.022		75.2	170

Monomer Conversion and Hardness

In an attempt to monitor the monomer conversion of the reaction, samples were cut from the final product that already annealed. The monomer conversion was observed at various conditions by the precipitation technique. For example, a 5 mm thickness sample with 0.015% ADVN was polymerized at 60°C and annealed at 120°C. In order to determine the monomer conversion of this sample, a small piece of the sample was weighted (denoted W_1). Then the weighted piece was dissolved in 30 mL of acetone and was precipitated by 70 mL of methanol (to extract the reacted monomer). The solid fraction was further purified by methanol and dried in an oven at 85°C for overnight. The dried solid was again weighted (denoted W_2). The percentage of conversion or monomer conversion of PMMA polymerization reaction (% yield) was calculated according to the following equation:

$$\%\text{Yield of PMMA} = \frac{W_2 \times 100}{W_1}, \qquad \text{<4.1>}$$

where W_1 = weight of sample prior to dissolution, and

W_2 = weight of sample after precipitation.

Then, according to the example, W_1 was 0.3411 g and W_2 was 0.2906 g. As a result, the % yield or monomer conversion was calculated to be:

$$\%\text{Yield of PMMA} = \frac{0.2906 \times 100}{0.3411} = 85.19\% \qquad <4.2>$$

In order to observe the surface hardness of the samples, the Rockwell hardness tester was used using 0.25 inch indenter and load 100 kg (scale-M). Typically, the mechanical properties are a function of molecular weight and monomer conversion so Figure 4.6 show the relationship between monomer conversion and surface hardness of the 5 mm thickness with 0.015%, 0.018%, and 0.022% ADVN for one-step and two-step process. In conclusion, the surface hardness was found to increase as a function of the monomer conversion, with increasing ADVN concentration.

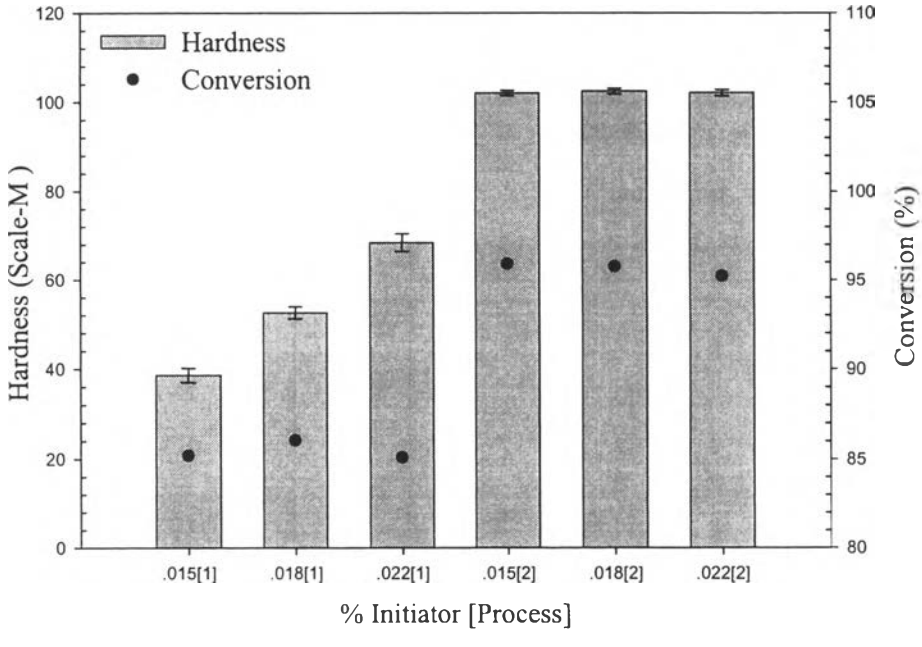

Figure 4.6 The relationship between the surface hardness and monomer conversion of the 5 mm thickness with 0.015%, 0.018%, and 0.022% ADVN polymerized and annealed at 60°C and 120°C, respectively.

Molecular Weight Average

An effect of the initiator concentration on the average molecular weight is reported in Table 4.3. Evidently, the average molecular weights were not significantly affected by changes in the reaction temperature (from previous work) and initiator concentration. The molecular weight distributions were quite broad, suggesting the occurrence of chain-transfer reaction. In order to elucidate the effect of reaction temperature and initiator concentration on the average molecular weights, the data reported by Scali *et al.*(1995) are listed in Table 4.4.

The data shown in Table 4.4 were obtained by suspension polymerization of MMA using AIBN as an initiator. It should be noted that the suspension polymerization had much better control over the homogeneity of the system during polymerization, as compared to bulk polymerization used in this study. At a constant initiator concentration, average molecular weights decreased with increasing reaction temperature, while, at a constant reaction temperature, average molecular weights decreased. The proper explanation may lie on the use of a kinetic equation to explain such behavior (Painter *et al.*, 1997):

$$\overline{Xn} = \frac{k_p[M]}{\xi(fk_dk_t[I])^{1/2}} \qquad <4.3>$$

when $\overline{Xn}$ is the average length of the chain

[M] is the monomer concentration

[I] is the initiator concentration

k_p is rate constant of propagation step

k_d is rate constant of determination step

k_t is rate constant of termination step

f is the fraction of initially formed radicals

ξ is the average number of dead chains formed per termination

Table 4.3 Effects of initiator concentration on average molecular weights

Sample	Process	Mn x 10^{-5}	Mw x 10^{-6}	MP x 10^{-6}	Polydispersity
0.015%	One-step process	6.4	2.3	0.15	3.6
0.018%		7.7	2.2	1.30	2.9
0.022%		6.7	2.1	1.10	3.1
0.015%	Two-step process	5.8	2.0	1.10	3.4
0.018%		4.7	1.7	0.94	3.7
0.022%		4.8	1.8	1.10	3.7

Table 4.4 Effects of reaction temperature (T_o) and initiator concentration (M_o / I_o) on average molecular weights (Scali *et al.*, 1995)

T_o(K) \ (M_o / I_o)	164	400	700	1000
333	350000	540000	680000	800000
343	230000	345000	440000	520000
353	150000	210000	275000	335000
363	125000	140000	190000	230000

Due to the previous work and this result, the average molecular weight is not a function of reaction temperature and initiator concentration therefore the average molecular weight is not a significant variable for next study (other thickness). However, the molecular weight and monomer conversion strongly influence the surface hardness of PMMA product. Consequently, the surface hardness should be measured and considered to replace the average molecular weight.

4.2.2 The 8 mm Thickness Samples

Temperature Profile

In order to reduce the production time of PMMA sheets, the temperature profiles of samples polymerized at 60°C with 0.008%, 0.011%, and 0.013% ADVN by weight were determined and shown in Figure 4.7 for one-step process and two-step process in Figure 4.8. The reaction time depended strongly on the ADVN concentration (initiator concentration). The reaction time of the 8 mm thickness with 0.008% ADVN that polymerized at 60°C was ca. 263 minutes. For 0.011% and 0.013% ADVN, they were 222 and 208 minutes, respectively (see Table 4.5). The maximum temperature for one-step process was also observed for each condition from the temperature profile. Similarly to the result from 5 mm thickness, the maximum peak temperature was found to increase, while the observed reaction time decreased, with increasing reaction temperature.

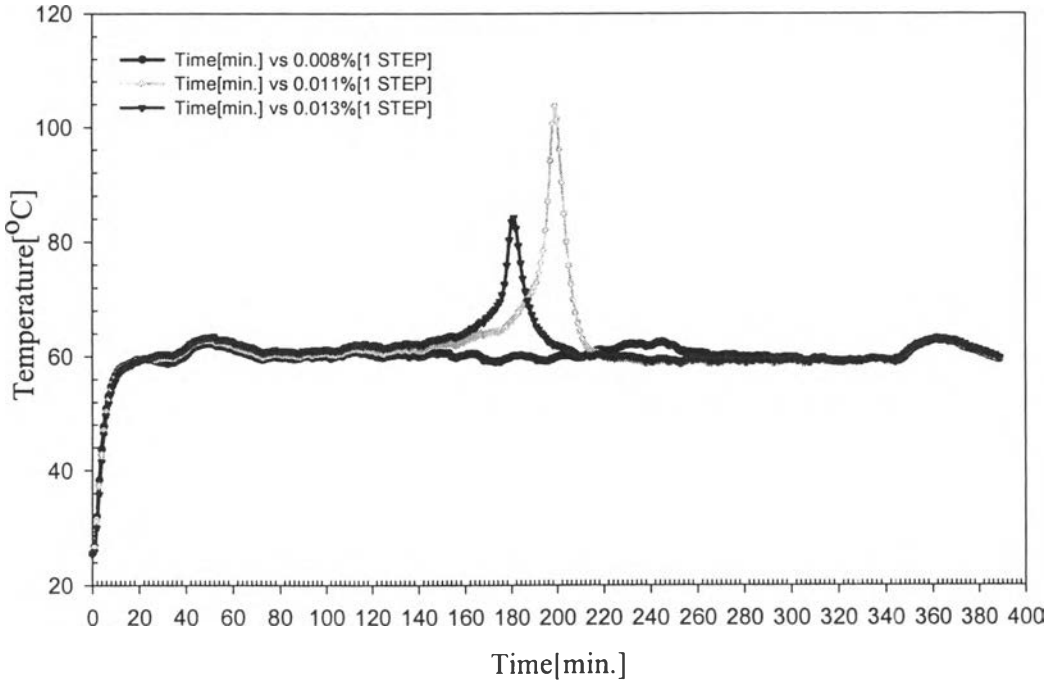

Figure 4.7 Temperature profiles of 8 mm thickness samples polymerized at 60°C with 0.008%, 0.011%, and 0.013% ADVN for 1-step process.

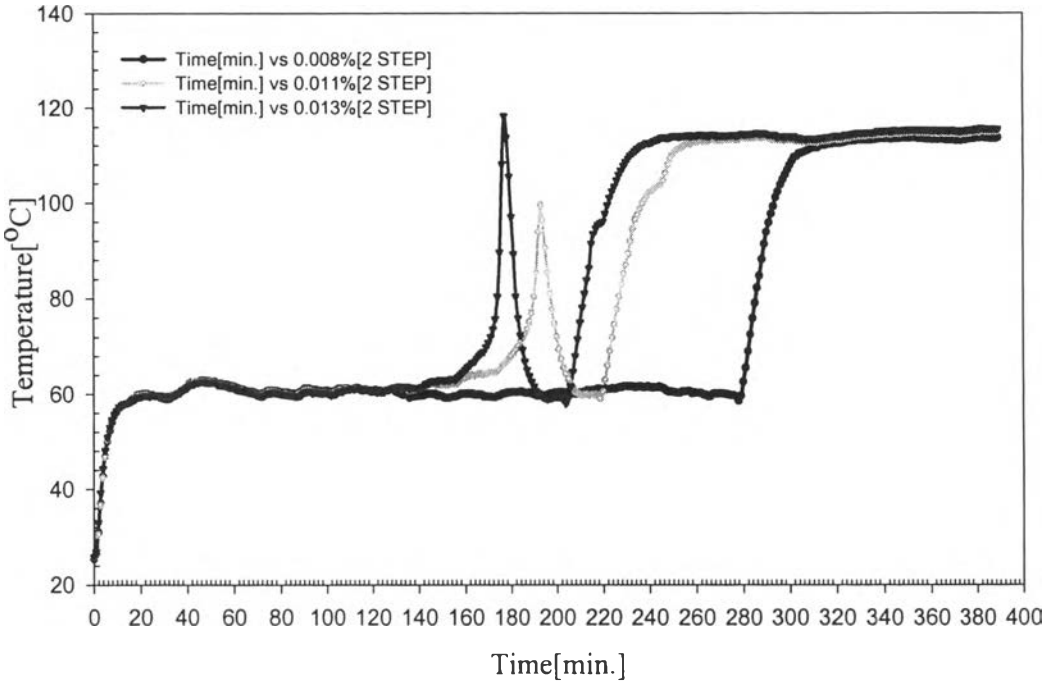

Figure 4.8 Temperature profiles of 8 mm thickness samples polymerized at 60°C and annealed at 120 °C with 0.008%, 0.011%, and 0.013% ADVN for 2-step process.

Table 4.5 Maximum peak temperature and the observed reaction time of 8 mm thickness samples with 0.008%, 0.011% and 0.013% ADVN polymerized at 60°C and annealed at 120°C

ADVN concentration (% wt)	Process	Maximum peak temperature (°C)	Observed reaction time (minute)
0.008	One-step process	63.0	263
0.011		103.	222
0.013		84.2	208
0.008	Two-step process	62.9	254
0.011		99.6	209
0.013		118.3	196

Monomer Conversion and Hardness

Monomer conversion and surface hardness were determined same as the previous studied. Figure 4.9 show the relationship between monomer conversion and surface hardness of the 8 mm thickness with 0.008%, 0.011%, and 0.013% ADVN for one-step and two-step process. Similarly to the 5 mm thickness result, the surface hardness was found to increase as a function of the monomer conversion, with increasing ADVN concentration.

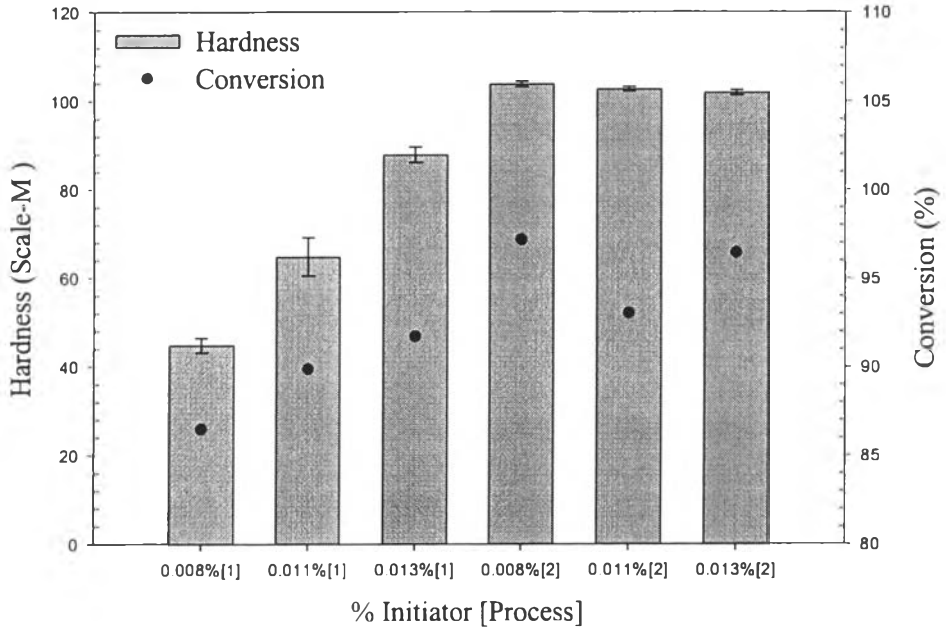

Figure 4.9 The relationship between the surface hardness and monomer conversion of the 5 mm thickness with 0.015%, 0.018%, and 0.022% ADVN polymerized and annealed at 60°C and 120°C, respectively.

4.2.3 The 10 mm Thickness Samples

Temperature Profile

In order to reduce the production time of PMMA sheets, the temperature profiles of samples polymerized at 60°C with 0.004%, 0.006%, and 0.008% ADVN by weight were determined and shown in Figure 4.10 for one-step process and two-step process in Figure 4.11. The reaction time depended strongly on the ADVN concentration (initiator concentration). The reaction time of the 10 mm thickness with 0.004% ADVN that polymerized at 60°C was ca. 440 minutes. For 0.006% and 0.008% ADVN, they were 302 and 248 minutes, respectively (see Table 4.6). The maximum temperature for one-step process was also observed for each condition from the temperature profile. Similarly to the result from 8 mm thickness, the maximum peak temperature was found to increase, while the observed reaction time decreased, with increasing reaction temperature.

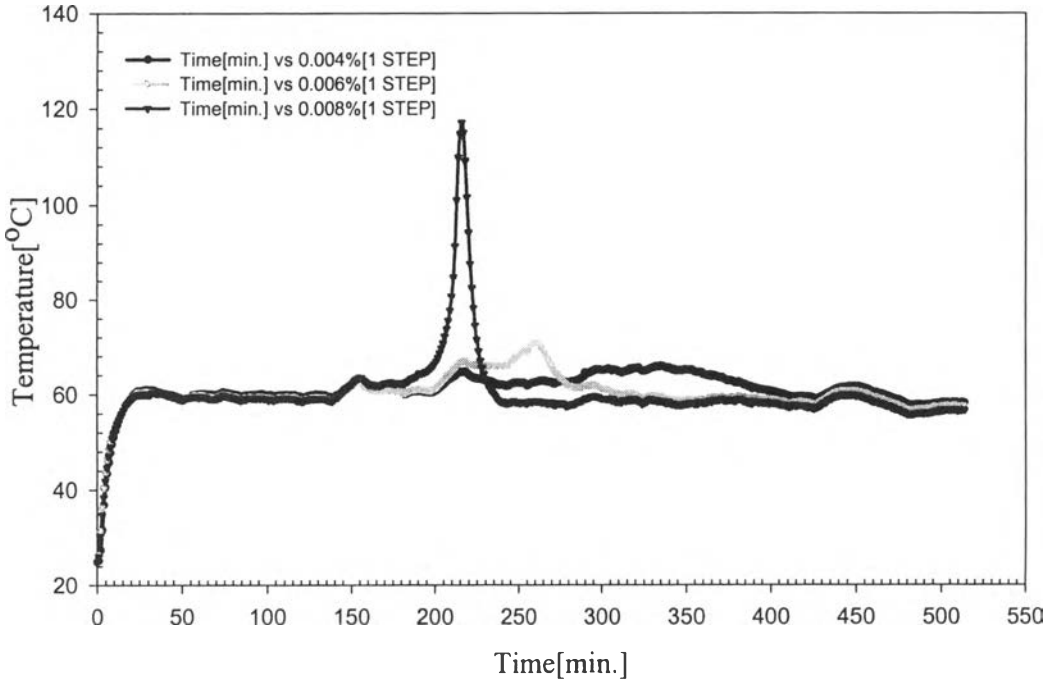

Figure 4.10 Temperature profiles of 10 mm thickness samples polymerized at 60°C with 0.004%, 0.006%, and 0.008% ADVN for 1-step process.

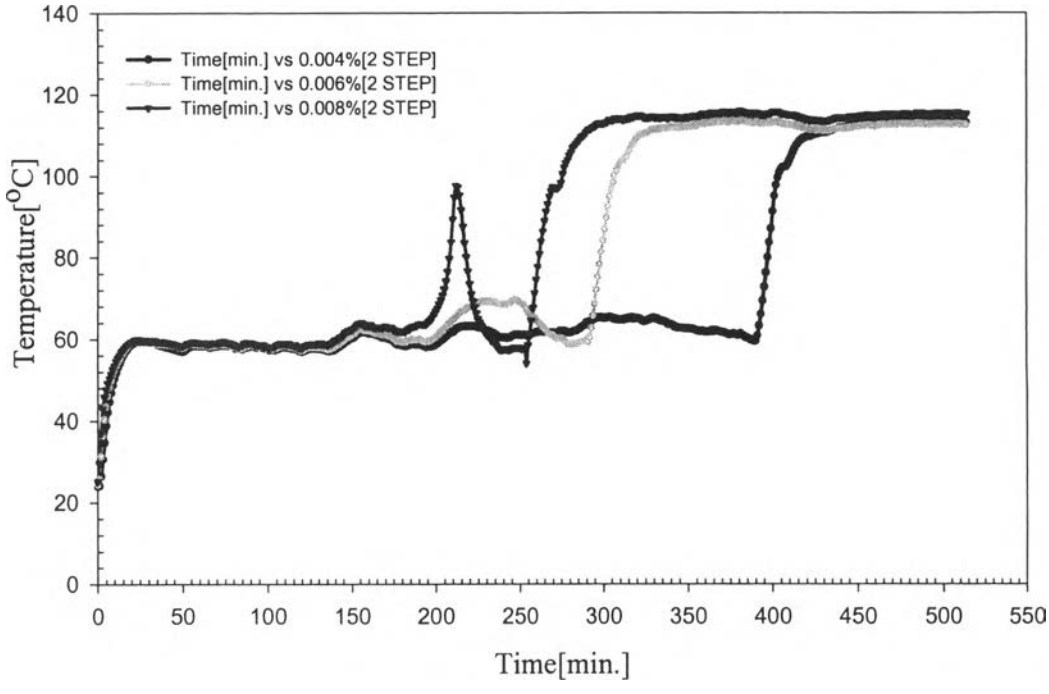

Figure 4.11 Temperature profiles of 10 mm thickness samples polymerized at 60°C and annealed at 120 °C with 0.004%, 0.006%, and 0.008% ADVN for 2-step process.

Table 4.6 Maximum peak temperature and the observed reaction time of 10 mm thickness samples with 0.004%, 0.006% and 0.008% ADVN polymerized at 60°C and annealed at 120°C

ADVN concentration (% wt)	Process	Maximum peak temperature (°C)	Observed reaction time (minute)
0.004	One-step process	65.9	440
0.006		70.8	302
0.008		117.1	248
0.004	Two-step process	65.4	364
0.006		69.6	263
0.008		97.6	242

Monomer Conversion and Hardness

Monomer conversion and surface hardness were determined same as the previous studied. Figure 4.12 shows the relationship between monomer conversion and surface hardness of the 10 mm thickness with 0.004%, 0.006%, and 0.008% ADVN for one-step and two-step process. Similarly to the 8 mm thickness result, the surface hardness was found to increase as a function of the monomer conversion, with increasing ADVN concentration.

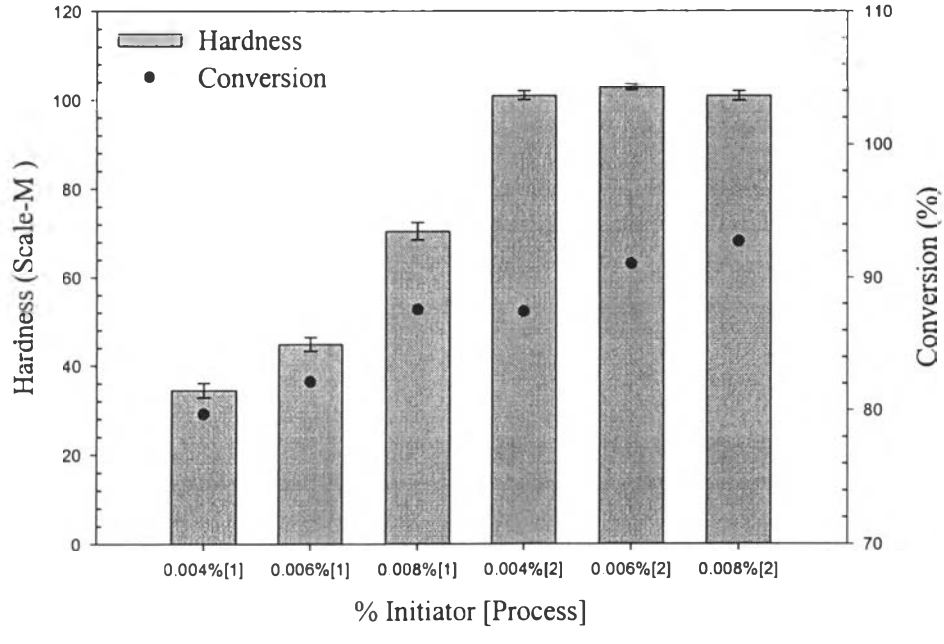

Figure 4.12 The relationship between the surface hardness and monomer conversion of the 10 mm thickness with 0.004%, 0.006%, and 0.008% ADVN polymerized and annealed at 60°C and 120°C, respectively.

4.3 Effect of the Pigment on the Observed Reaction Time

In this section, some colored PMMA sheets were studied because they were the important products in the industries. The reaction time is a significant factor that should be observed to reduce the cycle time. Furthermore, the defect and mechanical properties are the interesting factors that have to study. The selected colored sheets were choosing for this study due to the their cycle time. Normally, the popular

initiators, which are used for polymerized PMMA, are AIBN and ADVN. The ADVN gave the efficiency greater than AIBN about 4 times that was shown in Figure 4.13.

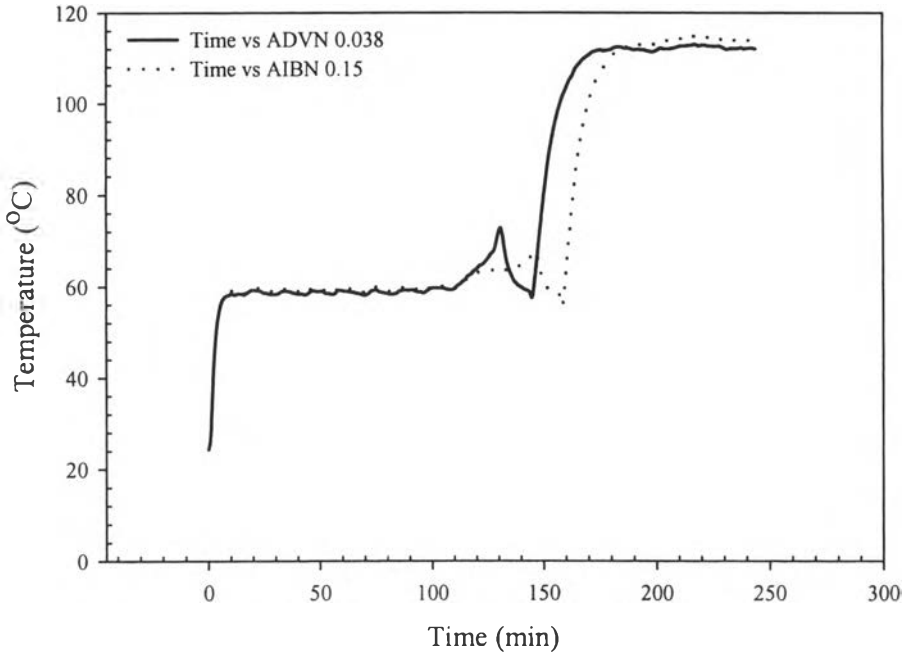

Figure 4.13 Temperature profiles of transparent 3 mm thickness with the different type and concentration of initiator polymerized and annealed at 60°C and 120°C, respectively.

4.3.1 Fixed AIBN at 0.15% by weight

Pigment Ingredient

Typically, almost all colored sheets have to add some several ingredients such as UV protection (use for prevent color paling), 7001 (copolymer that use for the opaque color), pigment particle, and others. The quantity of each ingredient for all selected color sheets is shown in Table 4.7.

Table 4.7 Pigment ingredients of each colored PMMA sheet

Sample	AIBN [%]	UV [%]	7001 [%]	Pigment [%]	Name of Pigment
P-000	0.15	0.03	-	-	-
P-018	0.15	0.03	1.000	-	-
P-102	0.15	0.03	-	0.150	364
P-115	0.15	0.03	1.100	1.000	115
P-136	0.15	0.03	0.600	1.000	136
P-137	0.15	0.03	1.100	1.160	137
P-235	0.15	0.03	0.600	1.000	235
P-302	0.15	0.03	-	1.100	302
P-327	0.15	0.03	0.600	1.000	327
P-348	0.15	0.03	0.600	1.000	348
P-373	0.15	0.03	-	1.000	373
P-422 K	0.15	0.03	1.100	-	-
P-433 S	0.15	0.03	0.625	0.687	9115

Temperature Profile

In this section, only 3 mm thickness sheet was studied the effect on the reaction time. The observed reaction time of each pigment may increase or decrease depends on the thermal properties of the pigment particles. For example, the observed reaction time of P-018, P-102, and P-115 are 144, 202, and 150, respectively. Table 4.8 shows the data of the observed reaction time, delay time (compare with the reaction time of transparent sheet), and maximum temperature of the selected colored PMMA sheets. In conclusion, the reaction time tended to decrease, while the maximum temperature increased.

Table 4.8 The observed reaction time and maximum temperature of each selected colored sheet with 0.15% AIBN polymerized and annealed at 60°C and 120°C, respectively

Sample	Observed reaction time (min)				Maximum Temperature (°C)				Delay time (min)
	EX 1	EX 2	EX 3	AVG	EX 1	EX 2	EX 3	AVG	
000	144	144	146	145	66.3	65.8	67.9	66.7	0
018	145	148	140	144	68.8	69.4	68.4	68.9	-1
102	195	197	215	202	63.4	64.0	63.4	63.6	58
115	150	153	148	150	78.1	67.5	67.8	71.1	6
136	151	164	158	158	67.0	67.7	68.9	67.9	13
137	153	150	149	151	72.1	70.6	70.8	71.2	6
235	140	146	140	142	70.0	67.8	71.4	69.7	-3
302	161	155	167	161	66.4	64.5	67.2	66.0	16
327	142	145	143	143	72.2	74.5	69.0	71.9	-1
348	145	153	147	148	69.2	73.1	64.2	68.8	4
373	164	156	167	162	70.7	68.6	70.7	70.0	18
422 K	150	148	140	146	71.6	67.8	72.3	70.6	1
433 S	146	152	146	148	69.6	70.3	74.1	71.3	3

Mechanical Properties

The effect of the pigment on the mechanical properties for the selected colored PMMA sheet was investigated by observation of the surface hardness and impact resistant of samples with the initiator concentration of 0.15% AIBN polymerized and annealed at 60°C and 120°C, respectively.

Surface Hardness

Surface hardness of the samples was measured using the Rockwell hardness tester in scale-M unit (ball indenter with 0.25 inch diameter and load at 100 kg), which the normal commercial grade of PMMA sheet gives the value between 80-100 in scale-M.

According to the Figure 4.14, the observed surface hardness for samples with 0.15% AIBN was ranged from 93 to 100 in scale-M. The result suggested that the pigment particles have a slightly effect on the surface hardness of the colored PMMA sheets.

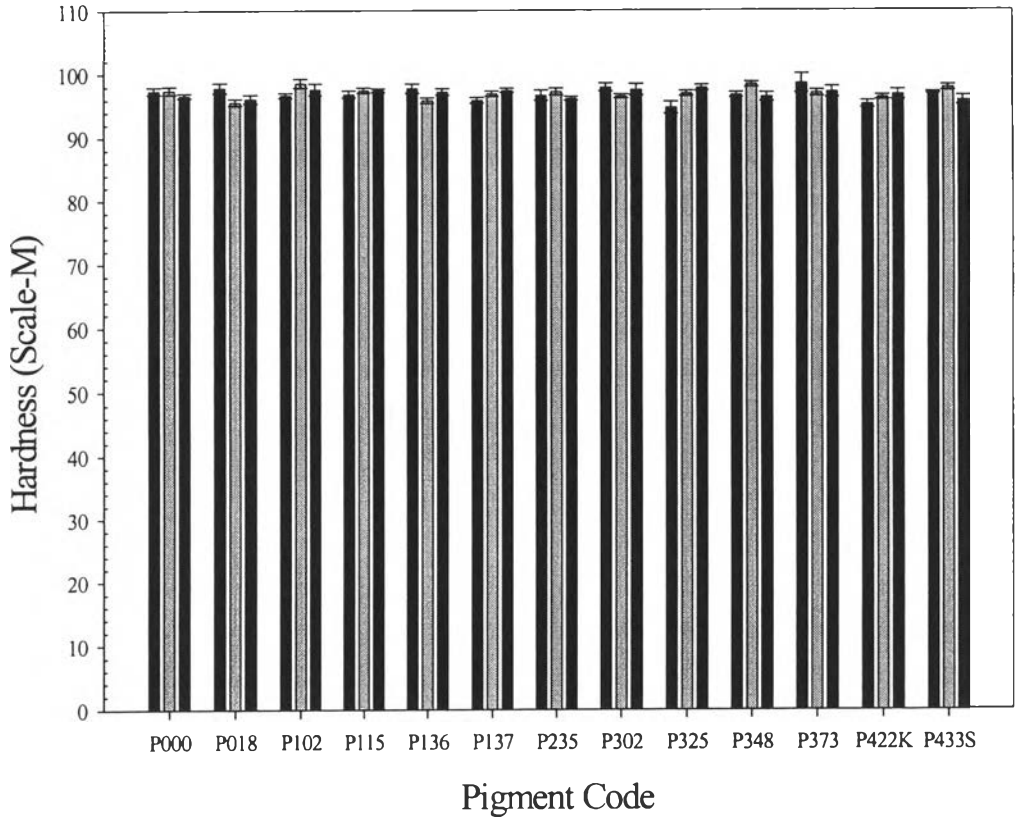

Figure 4.14 The surface hardness of the 3 mm thickness selected colored PMMA sheets with 0.15% AIBN polymerized and annealed at 60°C and 120°C, respectively.

Impact Resistance

Impact resistance of the samples was measured using Zwick pendulum impact tester followed the ASTM D256. Similarly, with the surface hardness, impact resistance did not seem to be affected by the pigment particles, and the average values were found in a range from 11 to 25 kJ/m^2 (see figure 4.15).

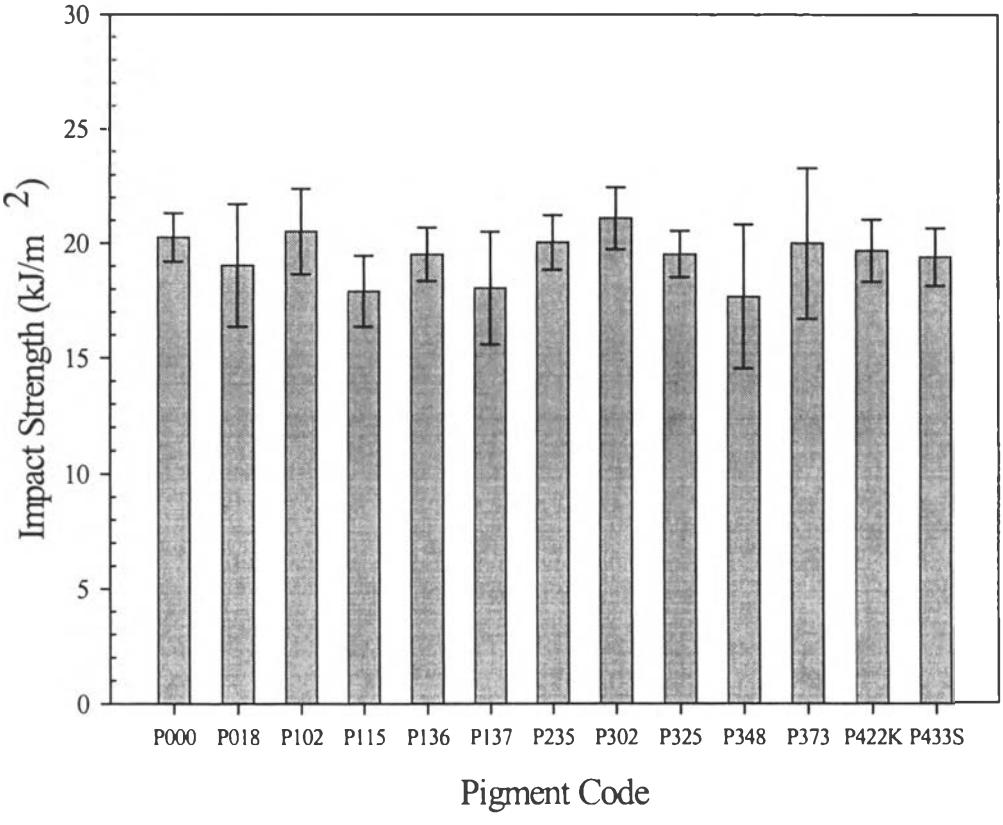

Figure 4.15 The impact resistance of the 3 mm thickness selected colored PMMA sheets with 0.15% AIBN polymerized and annealed at 60°C and 120°C, respectively.

4.3.2 Fixed ADVN at 0.038% by weight

Pigment Ingredient

In this section, 20 colored PMMA sheets were selected, because this condition was the same condition in the real process. The quantity of each ingredient for all selected color sheet was shown in Table 4.9.

Table 4.9 Pigment ingredients of each colored PMMA sheet

Sample	ADVN [%]	UV [%]	7001 [%]	OB [%]	Pigment [%]
P-000	0.038	0.03	-	-	-
P-018	0.038	0.03	1.000	-	-
P-102	0.038	0.03	-	-	0.150
P-115	0.038	0.03	1.100	-	1.000
P-136	0.038	0.03	0.600	-	1.000
P-137	0.038	0.03	1.100	-	1.160
P-202	0.038	0.03		-	1.250
P-212	0.038	0.03		-	0.010
P-235	0.038	0.03	0.600	-	1.000
P-302	0.038	0.03	-	-	1.100
P-327	0.038	0.03	0.600	-	1.000
P-348	0.038	0.03	0.600	-	1.000
P-373	0.038	0.03	-	-	1.000
P-402	0.038	0.03	0.300	0.005	1.200
P-422 K	0.038	0.03	1.100	-	-
P-433 S	0.038	0.03	0.625	-	0.687
P-502	0.038	0.03	0.500	-	1.100
P-522	0.038	0.03	-	-	0.074
P-531	0.038	0.03	-	-	1.100
P-814	0.038	0.03	0.600	-	1.200
P-993	0.038	0.03	-	-	0.013

Temperature Profile

In this section, only 3 mm thickness sheet was studied the effect on the reaction time. The observed reaction time of each pigment may increase or decrease depending on the thermal properties of the pigment particles. For example, the observed reaction time of P-018, P-102, and P-115 are 144, 202, and 150,

respectively. Table 4.10 shows the data of the observed reaction time, delay time (compared with the reaction time of transparent sheet), and maximum temperature of the selected colored PMMA sheets. In conclusion, the reaction time depended on the pigment due to their thermal property.

Table 4.10 The observed reaction time and maximum temperature of each selected colored sheet with 0.038% ADVN polymerized and annealed at 60°C and 120°C, respectively

Sample	Reaction time (min)	Maximum temperature (°C)	Delay time (min)
P-000	133	64.9	0
P-018	134	65.2	1
P-102	160	64.0	27
P-115	139	65.9	6
P-136	150	63.5	17
P-137	136	65.7	3
P-202	146	63.0	13
P-212	149	64.4	16
P-235	131	64.4	-2
P-302	155	63.2	22
P-327	146	63.7	13
P-348	132	64.5	-1
P-373	142	64.4	9
P-402	145	62.6	12
P-422 K	132	63.7	-1
P-433 S	137	66.7	4
P-502	150	62.6	17
P-522	145	64.3	12
P-531	146	66.6	13
P-814	152	62.3	19
P-993	143	65.5	10

Mechanical Properties

The effect of the pigment on the mechanical properties for the selected colored PMMA sheet was investigated by observation of the surface hardness and impact resistant of samples with the initiator concentration of 0.038% ADVN polymerized and annealed at 60°C and 120°C, respectively.

Surface Hardness

Surface hardness of the samples was measured using the Rockwell hardness tester in scale-M unit (ball indenter with 0.25 inch diameter and load at 100 kg), which the normal commercial grade of PMMA sheet give the value between 80-100 in scale-M.

According to the Figure 4.16, the observed surface hardness for samples with 0.038% ADVN is ranged from 97 to 101 in scale-M. The result suggested that the pigment particles have a very weak effect on the surface hardness of the colored PMMA sheets.

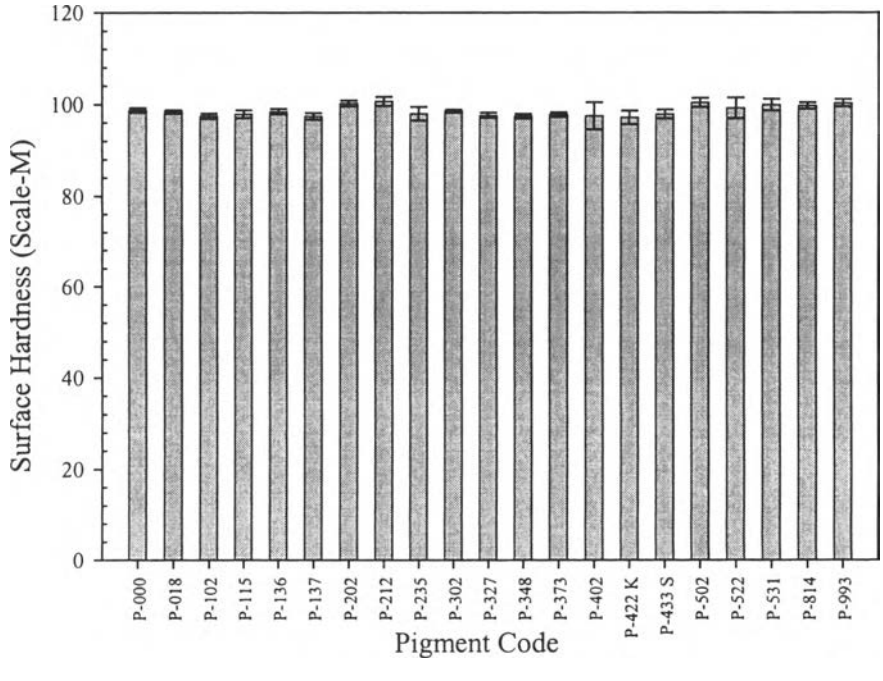

Figure 4.16 The surface hardness of the 3 mm thickness selected colored PMMA sheets with 0.038% ADVN polymerized and annealed at 60°C and 120°C, respectively.

Impact Resistance

Impact resistance of the samples was measured using Zwick pendulum impact tester followed the ASTM D256. Similarly with the surface hardness, impact resistance did not seem to be affected by the pigment particles, and the average values were found in a range from 17 to 21 kJ/m^2 (see Figure 4.17).

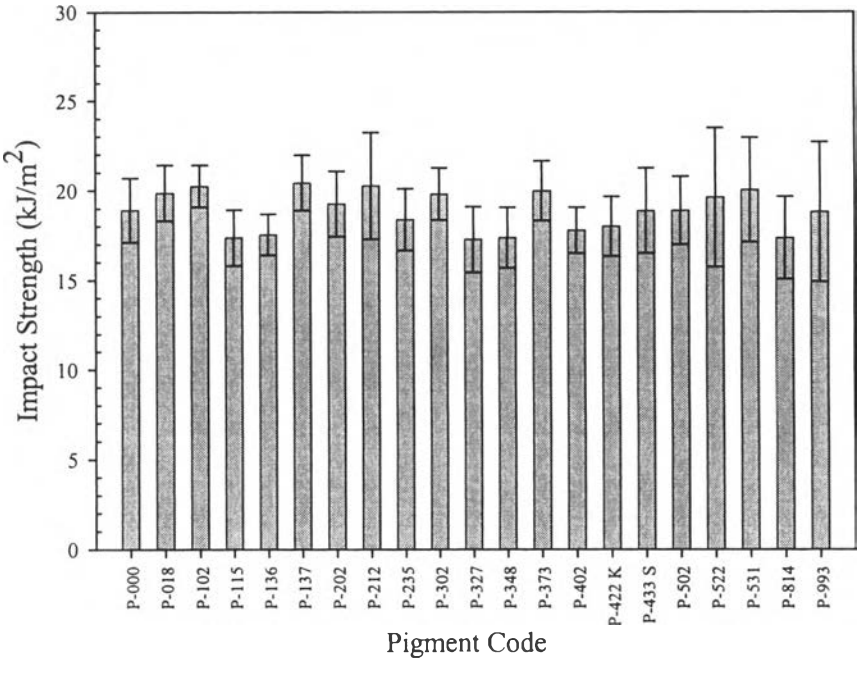

Figure 4.17 The impact resistance of the 3 mm thickness selected colored PMMA sheets with 0.038% ADVN polymerized and annealed at 60°C and 120°C, respectively.