

CHAPTER IV

RESULTS AND DISCUSSION

4.1 One-Step Isothermal Process

4.1.1 Water System

4.1.1.1 *Temperature profile*

The MMA syrup, the viscosity of which was measured at 25°C to be 243 cP, was prepared by mixing MMA monomer (containing 10 ppm inhibitor) with either 0.030% or 0.038% by weight of 2,2'-Azobis-(2,4-Dimethyl Valeronitrile) (ADV N) using a mechanical stirrer for 30 minutes. The mixture was poured into a glass mold with the gap thickness of 3 mm. The polymerization temperatures were 60, 62, 65, 68, and 70°C, and the reaction time was fixed at 240 min. Water was used as the heat transfer medium. During polymerization, the temperature of the reaction was detected. Because the polymerization reaction of PMMA is an exothermic reaction (Ramaseshan *et al.*, 1993), the exothermic peak of the reaction can be used to estimate the reaction time.

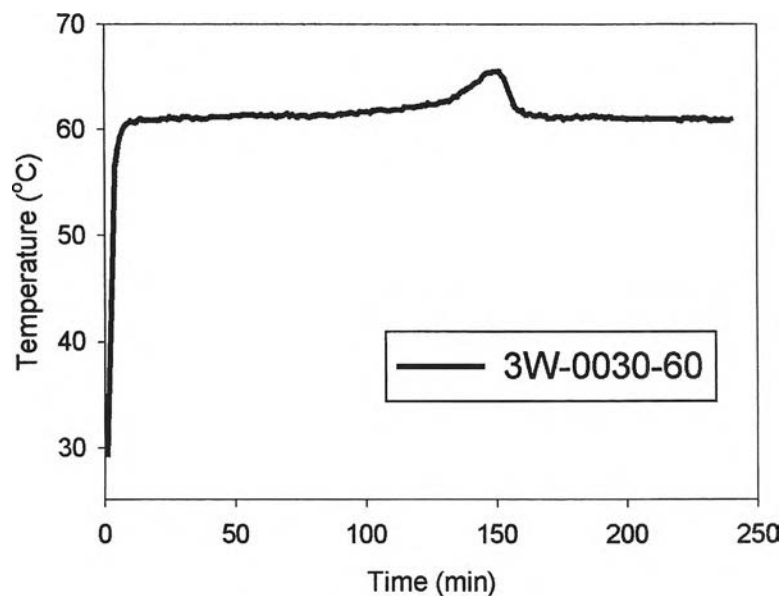


Figure 4.1 Temperature profile of sample polymerized at 60°C with 0.030% ADVN.

In Figure 4.1, the temperature profile of samples polymerized at 60°C with 0.030%ADV N 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 temperatures of the syrup (i.e., ambient temperature) and the water (i.e., the set temperature). In this step, the rate of temperature rise depends strongly on the overall heat transfer coefficient. The second step is the plateau region where the temperature of the syrup is equivalent to that of the medium. The third step is the peak region where the temperature rise occurs, a direct result of the exothermic polymerization heat. In this region, the temperature increases, reaches a maximum and then reverts to the original temperature, which ultimately defines the fourth step. The width and the area of the peak are related to the rate of polymerization, which in turn relates to the polymerization condition studied.

4.1.1.1.1 Effect of reaction temperature on observed reaction time

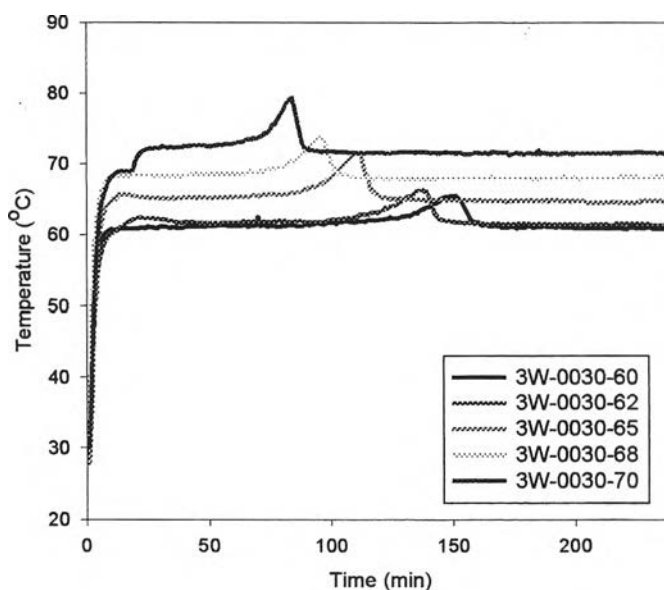


Figure 4.2 Temperature profile of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN.

In order to reduce the total production time of PMMA sheets, the temperature profile of samples polymerized at 60, 62, 65, 68, and 70°C with a fixed initiator concentration of 0.030% ADVN was observed and is

shown in Figure 4.2. Apparently, the reaction time depended strongly on the choice of polymerization temperature. At 60°C, 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) was ca. 150 minutes. For 62, 65, 68, and 70°C, they were ca. 140, 110, 95, and 85 minutes, respectively (see Table 4.1). The maximum peak temperature was also observed for each condition: they are ca. 65, 66, 72, 74, and 79°C at 60, 62, 65, 68, and 70°C, respectively. In conclusion, the maximum peak temperature was found to increase, while the observed reaction time decreased, with increasing reaction temperature.

Table 4.1 Maximum peak temperature and the observed reaction time of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN

Reaction temperature (°C)	Maximum temperature (°C)	Observed reaction time (min)
60	65.5	149
62	66.3	136
65	71.6	110
68	73.8	96
70	79.3	84

4.1.1.1.2 *Effect of initiator concentration on observed reaction time*

The effect of initiator concentration on the observed reaction time was also studied by observation of the temperature profile of samples polymerized at 60°C for the initiator concentration of 0.030 and 0.038% ADVN, respectively. The results are shown in Figure 4.3.

According to Figure 4.3, the observed reaction times for samples polymerized with 0.030% and 0.038% ADVN are ca. 135 and 150 minutes, respectively. The result suggests that the polymerization rate increased with increasing initiator concentration. The observed reaction time was not the only parameter affected by the increase in the initiation concentration. The maximum

peak temperature of the sample polymerized using 0.038% ADVN was ca. 3°C greater than that for 0.030% ADVN. This suggests that the higher the initiator concentration, the higher the polymerization rate and the maximum peak temperature. The latter poses a limitation problem, when one wants to further increase the initiator concentration in order to further reduce the reaction time, in that the reaction may be out of control.

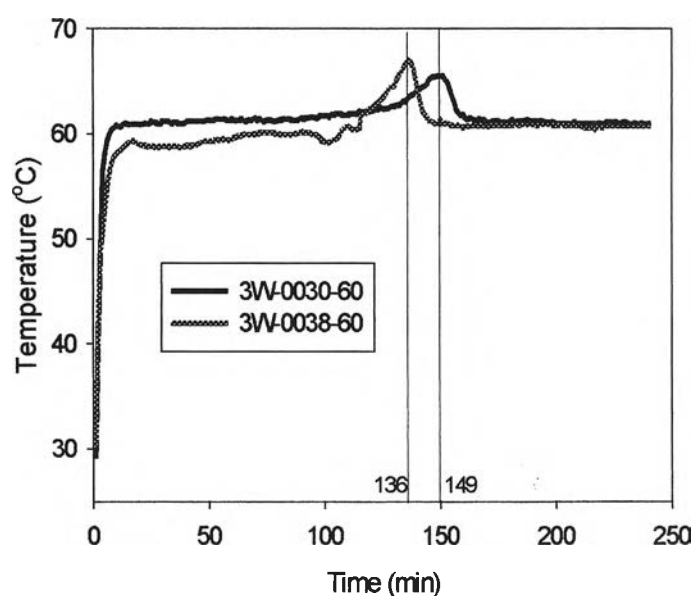


Figure 4.3 Temperature profile of samples polymerized at 60°C with by 0.030 and 0.038% ADVN, respectively.

Figure 4.4 reports the temperature profile of samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN. The observed reaction times for samples polymerized with 0.030% and 0.038% ADVN for reaction temperatures of 60, 62, 65, 68, and 70°C are compared in Table 4.2.

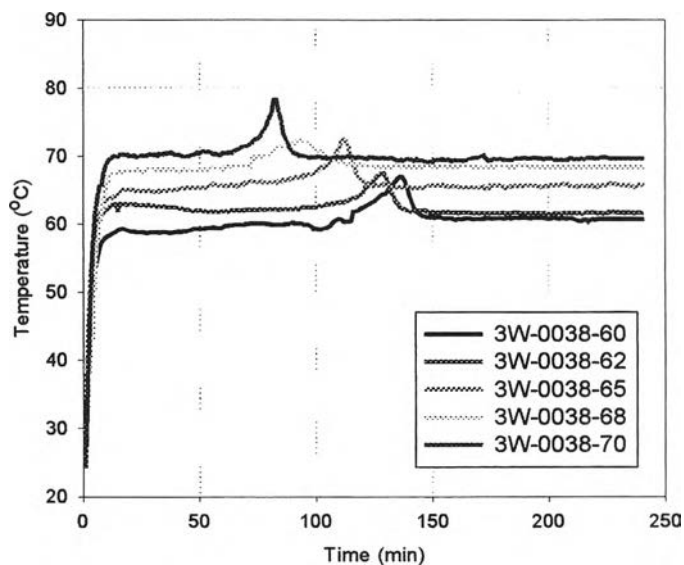


Figure 4.4 Temperature profile of samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN.

Table 4.2 Comparison of the observed reaction times for samples polymerized with 0.030% and 0.038% ADVN for reaction temperatures of 60, 62, 65, 68, and 70°C

Reaction temperature (°C)	Observed reaction time (min)	
	0.030%ADVN	0.038%ADVN
60	149	136
62	136	128
65	110	112
68	96	93
70	84	82

4.1.1.2 Monomer conversion

In an attempt to monitor the conversion of the reaction, samples were taken out from the heating water bath in every 15 minutes for the total reaction time of 240 minutes. The monomer conversion was observed at various reaction temperatures (i.e., 60, 62, 65, 68, and 70°C). The precipitation technique was used to calculate the monomer conversion.

For example, a sample containing 0.030% ADVN was polymerized at 60°C for 15 minutes. In order to determine the percentage of

conversion of this sample, a small portion of the sample was weighed (denoted W_1). The weighed portion was then dissolved in 30 mL of acetone (to dissolve out the unreacted monomer) and was precipitated by 70 mL of methanol. The gel fraction was further purified by methanol and distilled water and dried in an oven at 85°C for 6 hours. The dried solid was again weighed (denoted W_2). The percentage of conversion or the percent yield of PMMA polymerization reaction (% Yield) was calculated according to the following equation:

$$\% \text{ Yield of PMMA} = \frac{W_2 \times 100}{W_1}, \quad (4.1)$$

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 4.8885 g and W_2 was 0.6250 g. As a result, the % Yield was calculated to be:

$$\begin{aligned} \% \text{ Yield of PMMA} &= \frac{0.6250 \times 100}{4.8885} \% \\ &= 12.8\% \end{aligned} \quad (4.2)$$

4.1.1.2.1 Effect of reaction temperature on monomer conversion

Figure 4.5 illustrates the percent conversion as a function of time of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN. Apparently, the percent conversion was found to range from 10 to 15% for samples taken out from the heating water bath at 15 minutes, and continued to increase to 20 to 25%, where the gel or Trommsdoff effect started to play a role. After this point, the percent conversion increased very rapidly. This phenomenon usually occurs for the particular type of free-radical polymerization which the polymer formed is soluble in its own monomer. The reason is that the viscosity of the medium increases as the polymer forms. As a result, the termination rate decreases because of a decrease in the diffusion rate of larger macromolecular species. The reactivity of the radicals is not altered, but the probability for the radicals to find each other is much reduced, so that the termination rate constant (k_t) is reduced (Painter *et al.*, 1997).

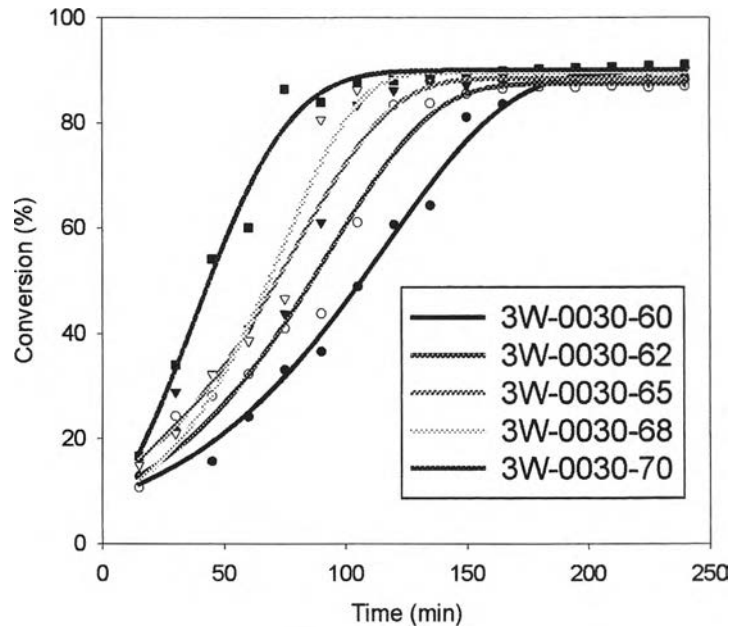


Figure 4.5 Percent conversion as a function of time of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN.

When the percent conversion reached 80%, the reaction progressed very slowly, approaching a constant value of ca. 88% (for sample polymerized at 60°C). The main reason for such a limitation in the attainable percent conversion lies on the fact that when PMMA polymers are formed, the glass transition increased with increasing percent conversion. Since the glass transition of PMMA is much higher than the reaction temperature interested, mobility of PMMA chains becomes diminishes as the percent conversion increases. For samples polymerized at higher temperatures (e.g., 70°C), the attainable percent conversion was greater (e.g., 90%), which, however, may not be significant within experimental error. Moreover, with increasing reaction temperature, the percent conversion curve was shifted to a shorter reaction time, suggesting that the rate of polymerization increased with increasing reaction temperature.

4.1.1.2.2 Effect of initiator concentration on reaction time

Figure 4.6 shows the percent conversion as a function of time of samples polymerized at 62°C with various initiator concentrations of 0.030 and 0.038% ADVN, respectively.

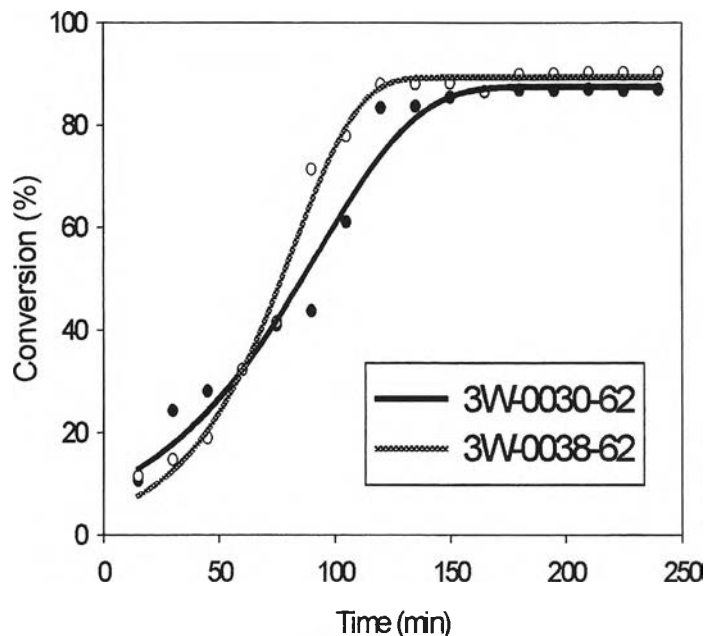


Figure 4.6 Percent conversion as a function of time for samples polymerized at 62°C with varied initiator concentration of 0.030 and 0.038% ADVN, respectively.

In Figure 4.6, it is apparent that when the initiator concentration was increased, the observed reaction time (viz. Measuring from the onset of polymerization to the moment when the percent conversion attains the maximum value) was decreased. This is in an excellent agreement with the earlier result on the temperature profile.

For comparison, Figure 4.7 reports the percent conversion as a function of time of samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN. The result shows that when the reaction temperature was increased, the observed reaction time was decreased. With increasing reaction temperature, the ultimate percent conversion was found to increase, even though very slightly.

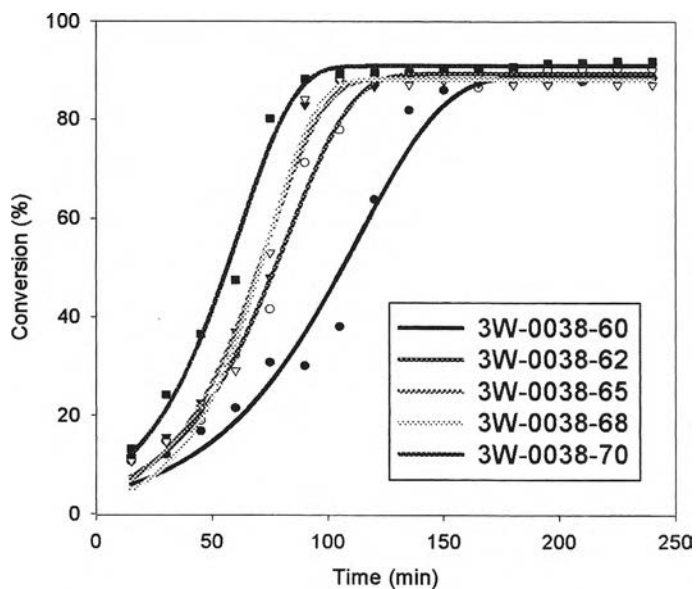


Figure 4.7 Percent conversion as a function of time for samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN.

4.1.1.3 Relationship between temperature profile and percent conversion

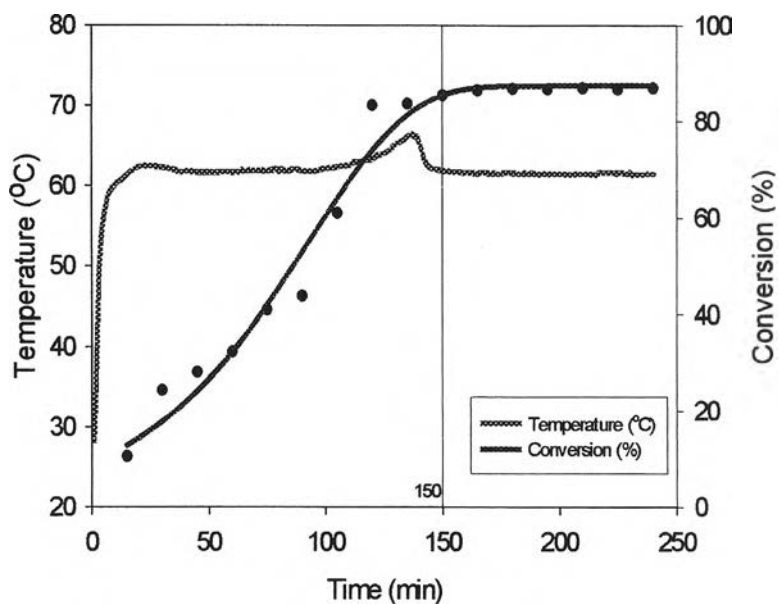


Figure 4.8 Overlay plot of temperature profile and percent conversion for sample polymerized at 62°C with 0.030% ADVN.

The optimal reaction time can be observed more precisely when overlay plot of temperature profile and percent conversion was conducted. It is apparent from Figure 4.8 that the maximum percent conversion was reached after the occurrence of the exothermic polymerization peak. This also holds true for the result obtained for other conditions. Now, instead of going through the cumbersome of getting the percent conversion curve in order to determine the observed reaction time, we can use the much easier obtained temperature profile data to estimate the observed reaction time (as previously shown).

With this technique, the observed reaction time, including the maximum percent conversion, for all of the conditions studied are reported in Table 4.3.

Table 4.3 Observed reaction time and maximum percent conversion for samples polymerized at 60, 62, 65, 68, and 70°C with initiator concentration of 0.030 and 0.038% ADVN

Reaction temperature (°C)	Monomer conversion (%)		Observed reaction time (min)	
	0.030% ADVN	0.038% ADVN	0.030% ADVN	0.038% ADVN
60	89.7±2.8	87.8±0.8	176	151
62	86.6±1.1	89.1±2.6	147	139
65	87.7±1.1	87.9±1.3	124	124
68	89.1±0.8	87.9±2.0	117	113
70	89.7±1.9	90.3±2.1	107	95

4.1.1.4 Effects of reaction temperature and initiator concentration on average molecular weights

Effects of reaction temperature (i.e., 60 to 70°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on average molecular weights are reported in Table 4.4. Obviously, the average molecular weights were not significantly affected by changes in the reaction temperature and the 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 4.5.

The data shown in Table 4.5 was obtained by suspension polymerization of MMA using AIBN as an initiator. It should be noted that the suspension polymerization had a much better control over the homogeneity of the system during polymerization, as compared to the 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):

$$\bar{X}_n = \frac{k_p [M]}{\xi (fk_d k_t [I])^{1/2}} \quad (4.3)$$

When	\bar{X}_n	is the average length of the chain
	[M]	is the monomer concentration
	[I]	is the initiator concentration
	k_p	is rate constant of propagation
	f	is the fraction of initially formed radicals
	ξ	is the average number of dead chains formed per termination
	k_d	is rate constant of determining step
	k_t	is rate constant of termination

Table 4.4 Effects of reaction temperature and initiator concentration on average molecular weights

Synthesis Temperature (°C)	0.030%ADV N					0.038%ADV N				
	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD
60	5.2	1.7	3.8	5.6	3.3	5.9	2.2	4.3	5.9	3.7
62	7.3	2.1	4.2	5.8	2.9	5.2	2.1	4.2	5.9	4.0
65	6.4	1.9	4.0	5.7	3.0	4.6	1.9	3.8	5.5	3.9
68	5.7	1.7	3.7	5.4	3.0	6.7	2.2	4.2	5.8	3.3
70	6.0	1.8	3.8	5.8	3.0	4.6	1.7	3.6	5.3	3.6

Table 4.5 Effects of reaction temperature (T_0) and initiator concentration (M_0/I_0) on average molecular weights (after Scali *et al.*, 1995)

T_0 (K) \ M_0/I_0	164	400	700	1000
333	350000	540000	680000	800000
343	230000	345000	440000	520000
353	150000	210000	275000	335000
363	125000	140000	190000	230000

4.1.1.5 Mechanical properties of PMMA sheets

4.1.1.5.1 Effects of reaction temperature and initiator concentration on surface hardness

Both molecular weight and percent conversion strongly influence the surface hardness of PMMA product. According to Tables 4.3 and 4.4, both percent conversion and average molecular weights were found to be unaffected by changes in the reaction temperature and initiator, surface hardness should be unaffected as well. Indeed, the results shown in Figure 4.9 confirm the hypothesis, and surface hardness of samples studied were found to lie between 91 and 92 shore D.

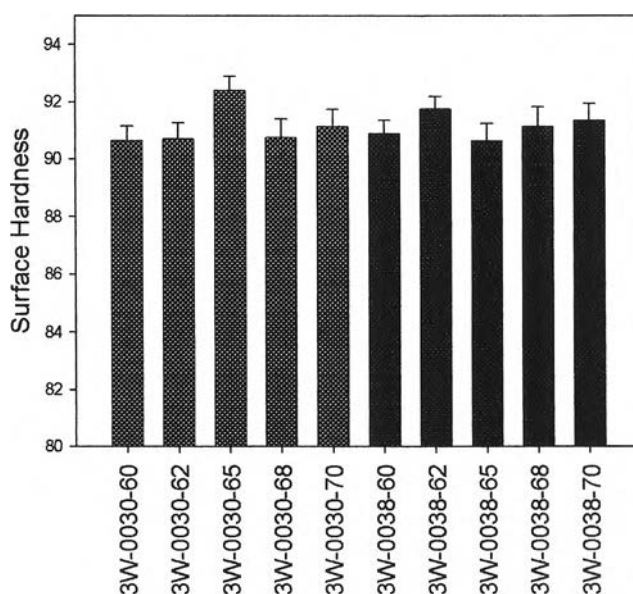


Figure 4.9 Effect of reaction temperature (i.e., 60, 62, 65, 68, and 70°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on surface hardness.

4.1.1.5.2 *Effects of reaction temperature and initiator concentration on impact resistance*

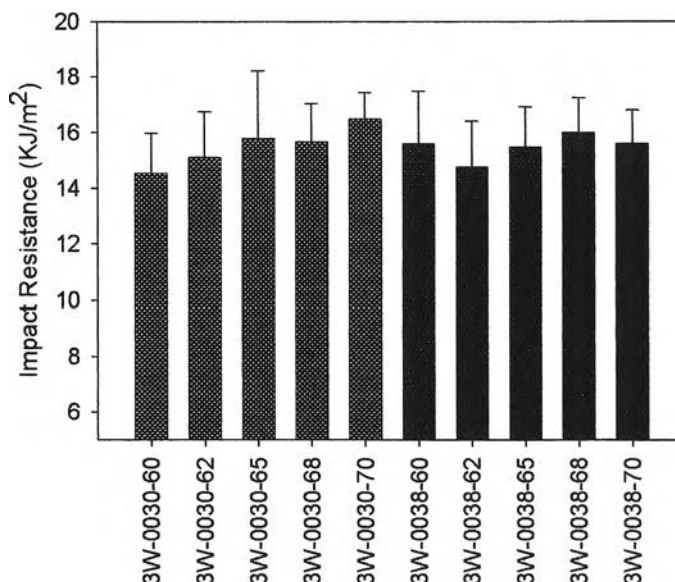


Figure 4.10 Effect of reaction temperature (i.e., 60, 62, 65, 68, and 70°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on impact resistance.

Similar to the case of surface hardness, both molecular weight (rather the number of entanglements) and percent conversion strongly influence the impact resistance of PMMA product. According to Tables 4.3 and 4.4, both percent conversion and average molecular weights were found to be unaffected by changes in the reaction temperature and initiator, impact resistance should be unaffected as well. Indeed, the results shown in Figure 4.10 confirm the hypothesis, and impact resistance of samples studied were found to range from 14 to 17 kJ/m².

4.1.1.6 *Appearance of PMMA sheets*

In this work, not only the temperature profile, percentage of monomer conversion, average molecular weights, and mechanical properties were observed, but the appearance was also observed. This is because, in the industries, good product appearance is also of prime importance to the customers. It is therefore very important to inspect the samples obtained for each polymerization condition

studied. The major type of defects usually found is the formation of bubbles, which may be a result of the evaporation of MMA (due to uncontrollable rise in the temperature of the sample during polymerization) or a result of the inefficient degassing process. Therefore, the products in each condition had to inspect the defect that is generated by processing.

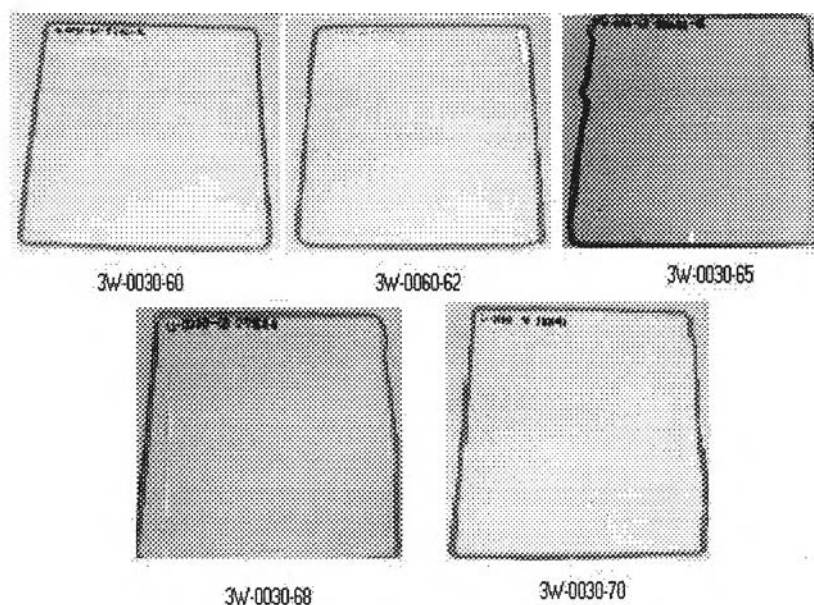


Figure 4.11 Appearance of PMMA sheets polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN.

Appearance of the PMMA sheets polymerized at 60, 62, 65, 68, and 70°C with the initiator concentrations of 0.030 and 0.038% ADVN is illustrated in Figures 4.11 and 4.12, respectively. It is obvious that the sheets polymerized at high temperatures (i.e., 68 and 70°C), despite the short reaction time, were full of bubbles, possibly a result of either MMA evaporation or inefficient degassing process.

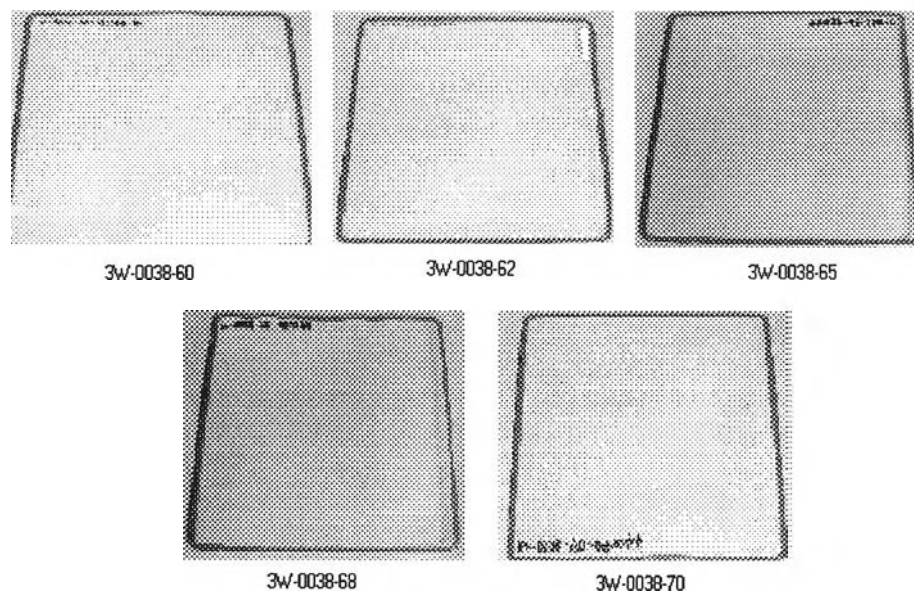


Figure 4.12 Appearance of PMMA sheets polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN.

4.1.2 *Hot-Air System*

4.1.2.1 *Temperature profile*

Methods for sample preparation and data collection were similar to those previously described in the water system, but, in this case, the polymerization was carried out in a hot-air oven, where hot-air was used as the heat transfer medium. Figure 4.13 shows the temperature profile of sample polymerized at 62°C with 0.030% ADVN.

Here, the temperature profile curve can still be divided into four steps, as previously described for the water system, but, in this case, the first step took a longer time for the temperature of the sample to assume that of the medium. This is due to the much lower overall heat transfer coefficient in the hot-air system, as compared with the water system.

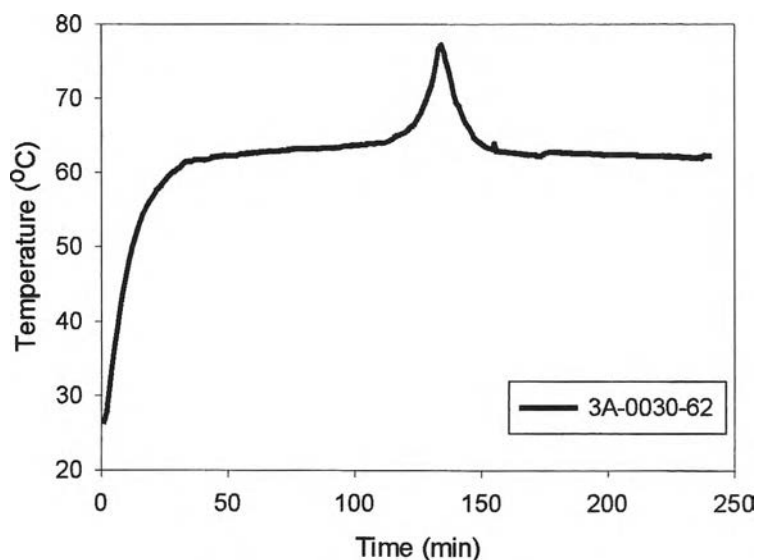


Figure 4.13 Temperature profile of sample polymerized at 62°C with 0.030% ADVN.

4.1.2.1.1 Effect of reaction temperature on reaction time

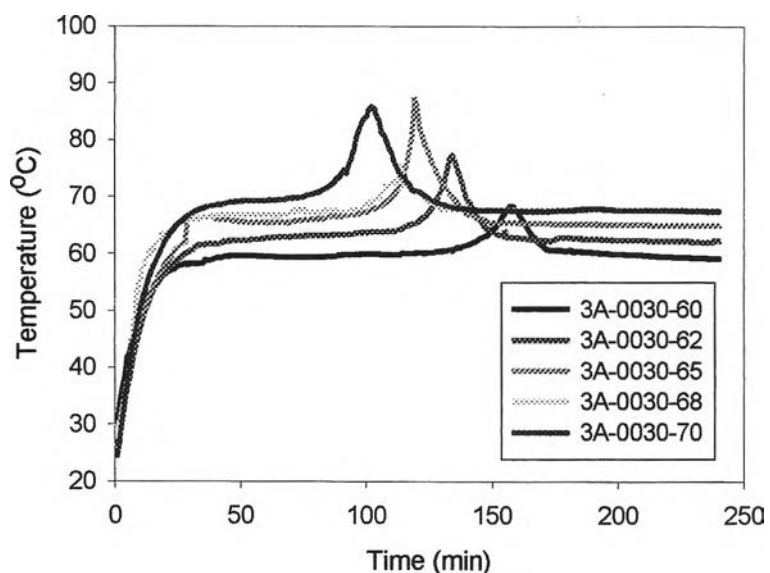


Figure 4.14 Temperature profiles of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN.

Figure 4.14 illustrates temperature profiles of samples polymerized at 60, 62, 65, 68, and 70°C with the initiator concentration of 0.030% ADVN. Clearly, when the reaction temperature increased, the reaction time

was found to decrease, which is similar to that occurring in the water system. Table 4.6 reports the maximum peak temperature and the observed reaction time (i.e., time at maximum peak temperature) for data shown in Figure 4.14.

Table 4.6 Maximum peak temperature and the observed reaction time for samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN

Reaction temperature (°C)	Maximum temperature (°C)	Observed reaction time (Min)
60	68.3	157
62	77.2	134
65	87.2	119
68	72.6	111
70	85.8	102

4.1.2.1.2 *Effect of initiator concentration on observed reaction time*

The effect of initiator concentration on the observed reaction time was investigated by observation of the temperature profile of samples polymerized at 60°C for the initiator concentration of 0.030 and 0.038% ADVN, respectively (see Figure 4.15).

According to Figure 4.15, the observed reaction times for samples polymerized with 0.030% and 0.038% ADVN are 157 and 148 minutes, respectively. The result suggests that the polymerization rate increased with increasing initiator concentration. The observed reaction times for samples polymerized at 60, 62, 65, 68, and 70°C with the initiator concentration of 0.038% ADVN can be determined from the temperature profiles shown in Figure 4.16. Comparison of the observed reaction times for samples polymerized at different temperatures for initiator concentrations of 0.030 and 0.038% ADVN is shown in Table 4.7.

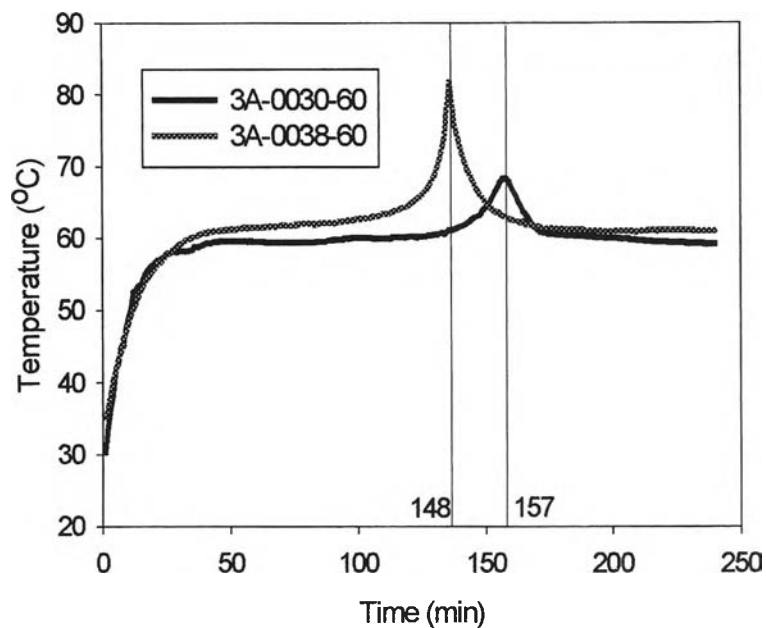


Figure 4.15 Temperature profile of samples polymerized at 60°C with by 0.030 and 0.038% ADVN, respectively.

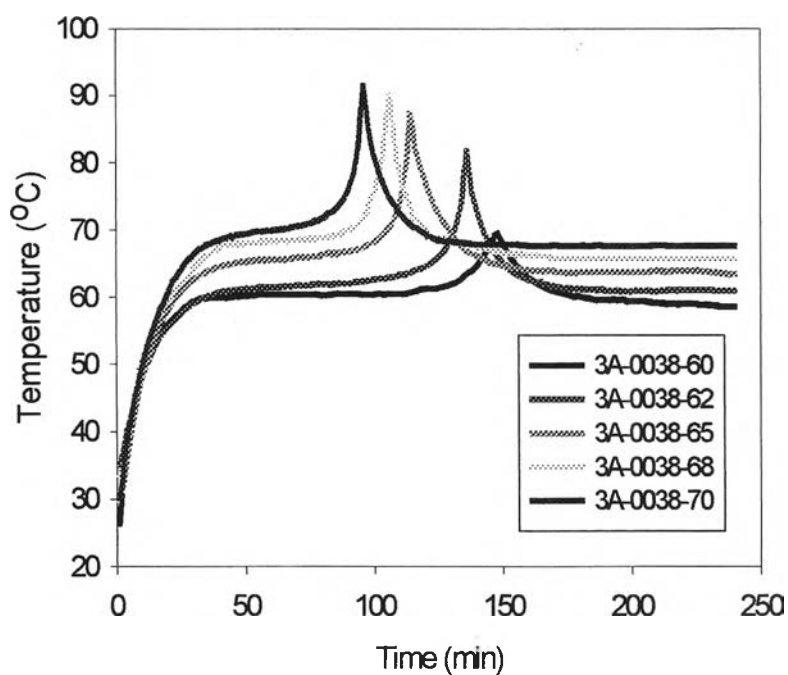


Figure 4.16 Temperature profile of samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN.

Table 4.7 Comparison of the observed reaction times for samples polymerized at 60, 62, 65, 68, and 70°C for initiator concentrations of 0.030 and 0.038% ADVN

Reaction temperature (°C)	Observed reaction time (min)	
	0.030%ADV N	0.038%ADV N
60	157	148
62	134	136
65	119	114
68	111	106
70	102	96

4.1.2.2 Monomer conversion

Similar to the water system, samples were taken out from the heating water bath in every 15 minutes for the total reaction time of 240 minutes. The monomer conversion was observed at various reaction temperatures (i.e., 60, 62, 65, 68, and 70°C). The same precipitation technique was used to calculate the monomer conversion.

4.1.2.2.1 Effect of reaction temperature on monomer conversion

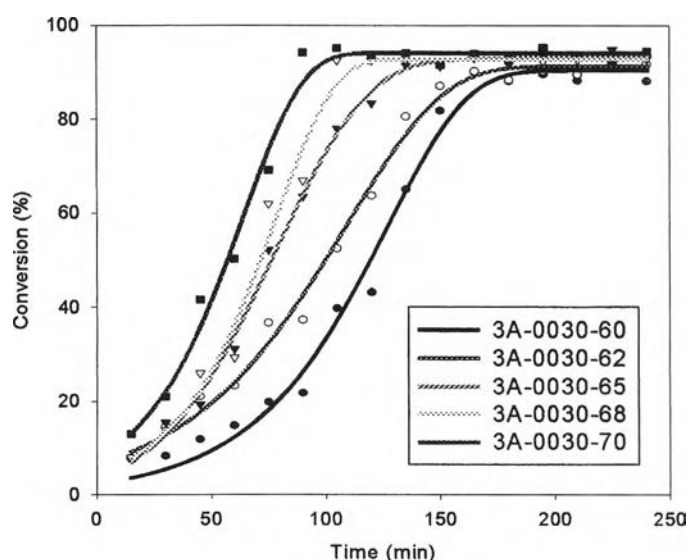


Figure 4.17 Percent conversion as a function of time for samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN.

Figure 4.17 illustrates the percent conversion as a function of time of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN. Apparently, the percent conversion was found to range from 10 to 15% for samples taken out from the heating water bath at 15 minutes, and continued to increase to 20 to 25%, where the gel or Trommsdoff effect started to play a role. After this point, the percent conversion increased very rapidly. The results are, in fact, very similar to those obtained for the water system.

4.1.2.2.2 Effect of initiator concentration on reaction time

Figure 4.18 shows the percent conversion as a function of time of samples polymerized at 60°C with varied initiator concentration of 0.030 and 0.038% ADVN, respectively.

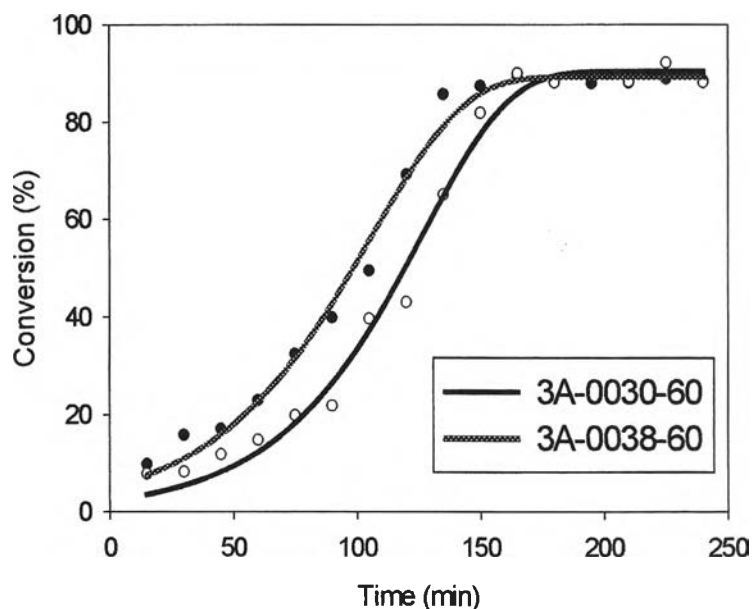


Figure 4.18 Monomer conversion as a function of time for samples polymerized at 60°C with initiator concentration of 0.030 and 0.038% ADVN.

For comparison with the results shown in Figure 4.17, Figure 4.19 reports the percent conversion as a function of time of samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN. The result showed that while the reaction temperature was increased, the observed reaction time was decreased. With increasing reaction temperature, the ultimate percent conversion was found to increase, even though very slightly.

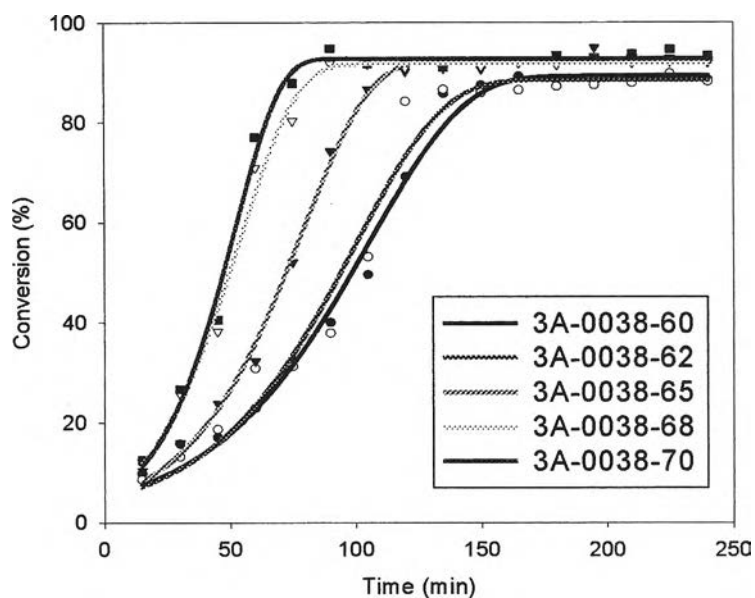


Figure 4.19 Percent conversion as a function of time for samples polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN.

4.1.1.3 Relationship between temperature profile and percent conversion

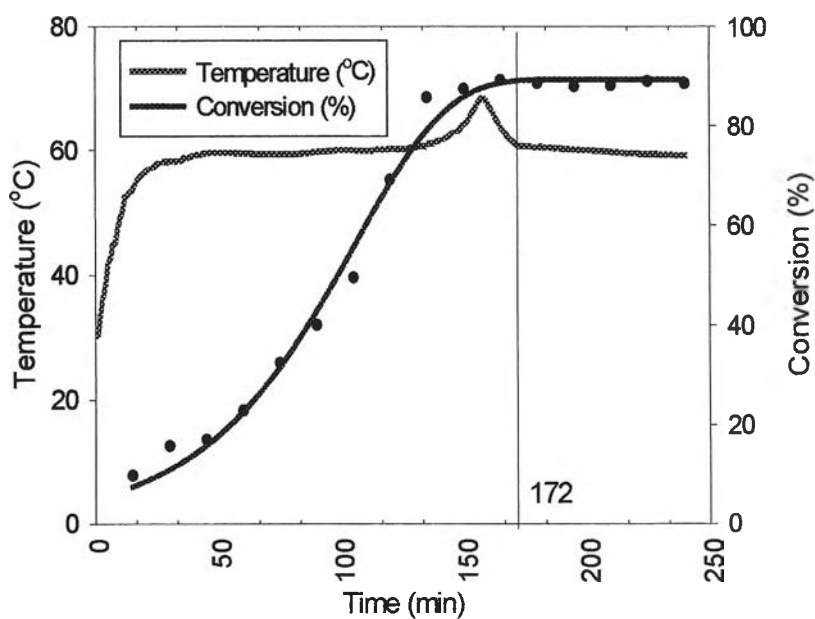


Figure 4.20 Overlay plot of temperature profile and percent conversion for sample polymerized at 60°C with 0.030% ADVN.

Similar to that shown for the water system, the optimal reaction time can be observed more precisely from the overlay plot of temperature profile and percent conversion (see Figure 4.20). According to Figure 4.20, the observed reaction time was observed to be ca. 170 minutes. Similarly, the observed reaction time, including the maximum percent conversion, for all of the conditions studied are reported in Table 4.8.

Table 4.8 Observed reaction time and maximum percent conversion for sample polymerized at 60, 62, 65, 68, and 70°C with initiator concentration of 0.030 and 0.038% ADVN

Reaction temperature (°C)	Monomer conversion (%)		Observed reaction time (min)	
	0.030% ADVN	0.038% ADVN	0.030% ADVN	0.038% ADVN
60	89.4±2.8	88.4±1.0	172	169
62	90.0±3.0	87.4±2.3	156	159
65	92.8±2.1	92.1±2.0	148	142
68	92.3±1.0	91.8±1.3	129	123
70	93.8±2.1	92.8±2.0	122	115

4.1.2.4 Effects of reaction temperature and initiator concentration on average molecular weights

Effects of reaction temperature (i.e., 60 to 70°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on average molecular weights are reported in Table 4.9. Apparently, the average molecular weights were found to slightly decrease with increasing reaction temperature and initiator concentration. This is in an excellent agreement with the results reported by Scali *et al.* (1995).

Table 4.9 Effects of reaction temperature and initiator concentration on average molecular weights

Synthesis Temperature (°C)	0.030%ADV N					0.038%ADV N				
	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD
60	5.5	2.1	4.2	5.8	3.8	4.6	1.8	3.8	5.4	3.9
62	5.3	2.0	4.0	5.6	3.7	4.0	1.6	3.4	5.1	4.1
65	-	-	-	-	-	3.8	1.6	3.4	5.1	4.1
68	3.9	1.4	3.1	4.7	3.7	3.6	1.2	2.6	4.0	3.4
70	4.0	1.7	3.5	5.1	4.2	3.1	1.2	2.8	4.4	3.7

4.1.2.5 Mechanical properties of the PMMA sheets

4.1.2.5.1 Effects of reaction temperature and initiator concentration on surface hardness

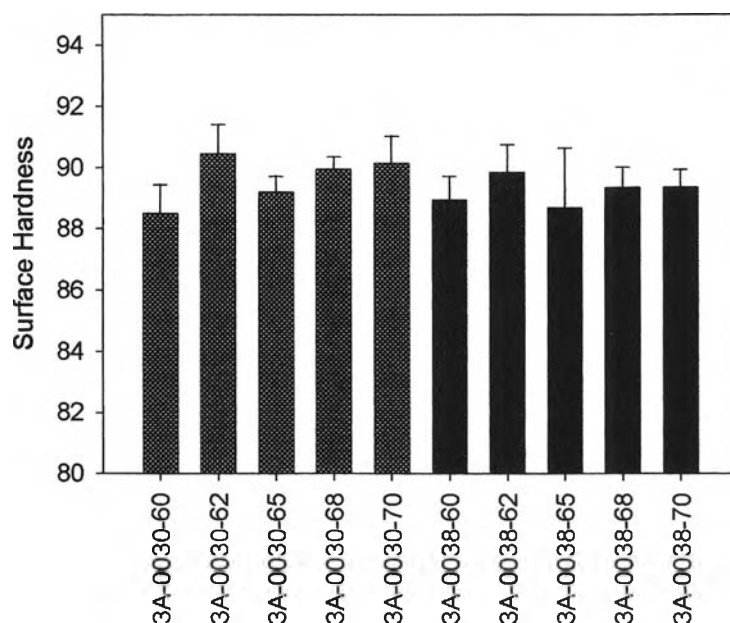


Figure 4.21 Effect of reaction temperature (i.e., 60, 62, 65, 68, and 70°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on surface hardness.

Very similar to the case of water system, the reaction temperature and the initiator concentration did not seem to have a strong effect on the surface hardness of the samples prepared, and surface hardness of samples studied were found to lie between ca. 88 and 91 shore D, which are slightly lower than those observed for samples polymerized in water.

4.1.2.5.2 Effects of reaction temperature and initiator concentration on impact resistance

Similarly, impact resistance did not seem to be affected by changes in the reaction temperature and initiator concentration, and the average values were found to range from 14 to 17 kJ/m².

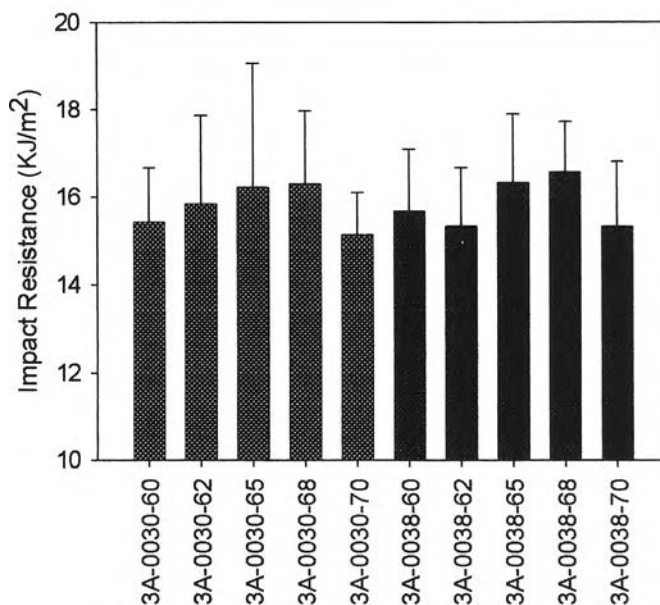


Figure 4.22 Effect of reaction temperature (i.e., 60, 62, 65, 68, and 70°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on impact resistance.

4.1.2.6 Appearance of PMMA sheets

Similar to the water system, the products obtained must be inspected for its appearance.

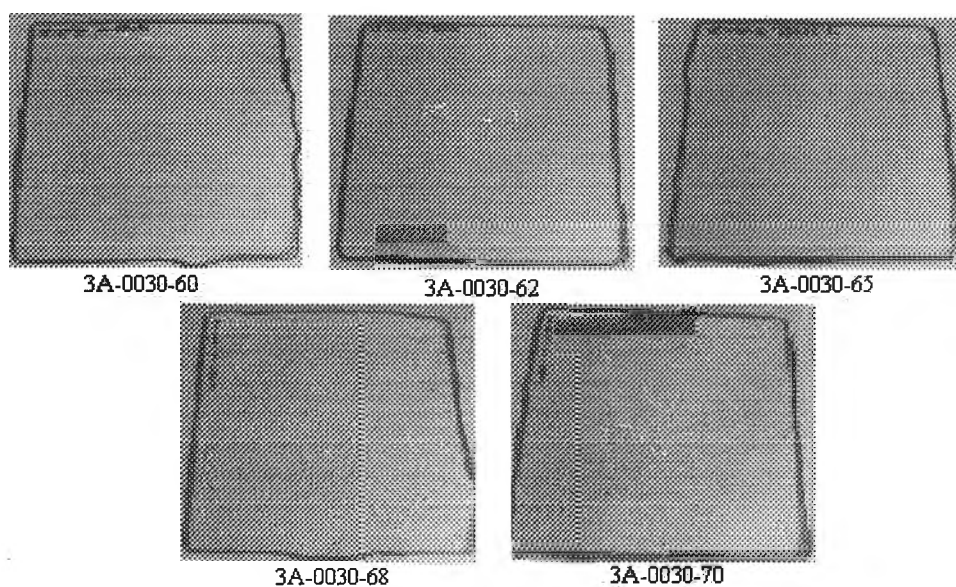


Figure 4.23 Appearance of PMMA sheets polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN.

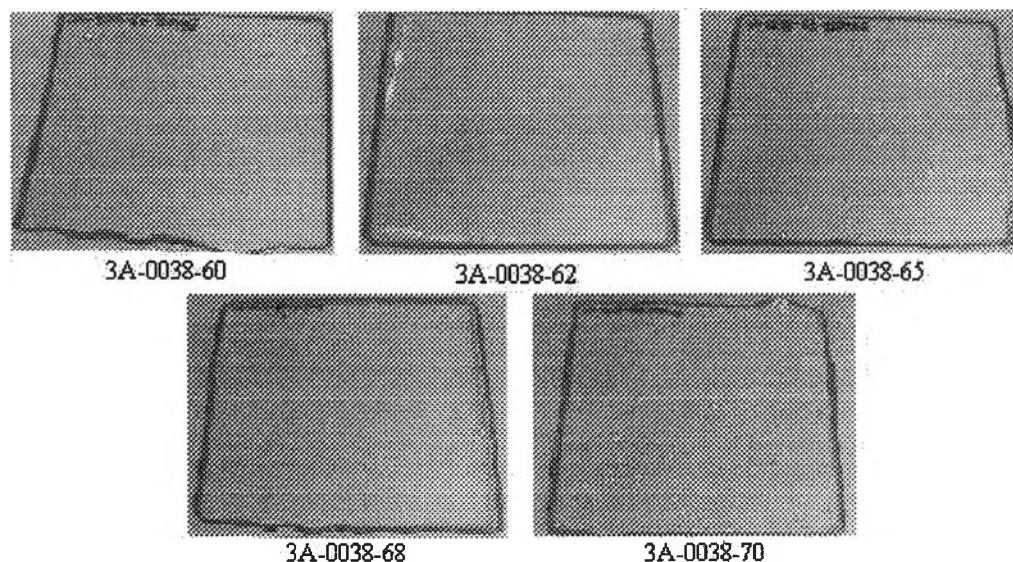


Figure 4.24 Appearance of PMMA sheets polymerized at 60, 62, 65, 68, and 70°C with 0.038% ADVN.

Appearance of the PMMA sheets polymerized at 60, 62, 65, 68, and 70°C with the initiator concentrations of 0.030 and 0.038% ADVN is shown in Figures 4.23 and 4.24, respectively. It is obvious that the sheets polymerized at temperature higher than 62°C, despite the short reaction time, were full of bubbles, possibly a result of either MMA evaporation or inefficient degassing process.

4.1.3 Comparison of One-Step Isothermal Process between Water and Hot-Air Systems

4.1.3.1 *Temperature profile, monomer conversion and observed reaction time*

Figure 4.25 shows comparison of temperature profile of samples polymerized at 65°C with 0.030% ADVN in water and hot-air system. It is obvious that the time required for the sample polymerized in hot-air system to assume that of the medium takes longer than that for the water system. This is due to the much greater overall heat transfer coefficient that the water system has over the hot-air system. As a result of the thermal lag, the observed reaction time for the water system was much shorter than for the hot-air system. Most importantly, the degree of temperature rise in the sample polymerized in the hot-air system was much

greater than in the water system, again a result of the much lower overall heat transfer coefficient. This high temperature rise may be responsible for the formation of bubbles observed in samples polymerized at temperatures greater than 62°C in the hot-air system. Table 4.10 compares the percent conversion and the observed reaction time of samples polymerized in water and hot-air systems.

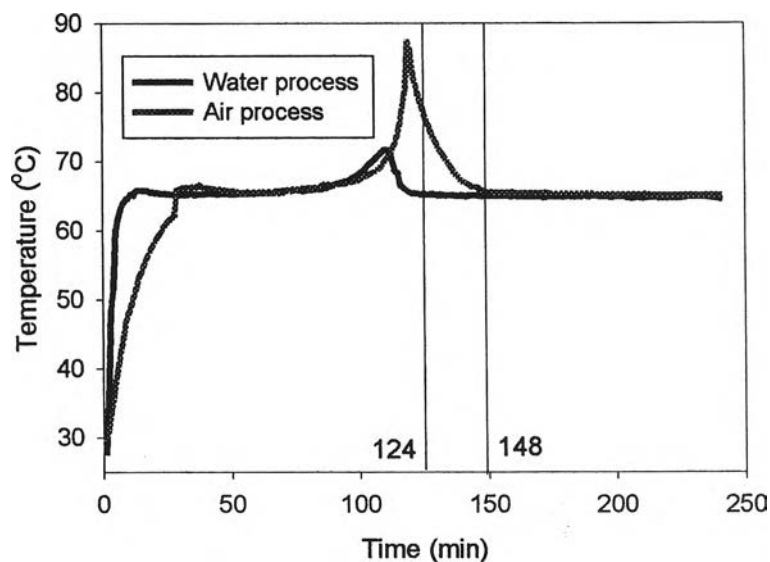


Figure 4.25 Temperature profile of samples polymerized at 65°C with 0.030% ADVN in water and hot-air system.

Table 4.10 Comparison of monomer conversion and observed reaction time for samples polymerized in water and hot-air system at 60, 62, 65, 68, and 70°C with 0.030% ADVN

Reaction temperature (°C)	Monomer conversion (%)		Observed reaction time (min)	
	Water System	Air System	Water System	Air System
60	89.7±2.8	89.4±2.8	176	172
62	86.6±1.1	90.0±3.0	147	156
65	87.7±1.1	92.8±2.1	124	148
68	89.1±0.8	92.3±1.0	117	129
70	89.7±1.9	93.8±2.1	107	122

4.1.3.2. Effect on average molecular weights

Table 4.11 reports average molecular weights of samples polymerized at 60, 62, 65, 68, and 70°C using the initiator concentration of 0.030% ADVN. Apparently, the average molecular weights as well as the molecular weight distribution for sample polymerized in water were systematically greater than those for samples polymerized in hot-air. This could be a direct result of the greater temperature rise in the hot-air system, which may contribute to the much greater extent of chain-transfer reactions.

Table 4.11 Comparison of average molecular weight in water and air system by used 0.030%ADV N at 60, 62, 65, 68, and 70°C

Synthesis Temperature (°C)	Water system					Air system				
	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD
60	5.2	1.7	3.8	5.6	3.3	5.5	2.1	4.2	5.8	3.8
62	7.3	2.1	4.2	5.8	2.9	5.3	2.0	4.0	5.6	3.7
65	6.4	1.9	4.0	5.7	3.0	-	-	-	-	-
68	5.7	1.7	3.7	5.4	3.0	3.9	1.4	3.1	4.7	3.7
70	6.0	1.8	3.8	5.8	3.0	4.0	1.7	3.5	5.1	4.2

4.1.3.3 Effect on mechanical properties

4.1.3.3.1 Effect on surface hardness

Figure 4.26 compares the surface hardness of samples polymerized in both water and hot-air at 60, 62, 65, 68, and 70°C using the initiator concentration of 0.030%. It is evident that the surface hardness of sample polymerized in both systems did not differ significantly, and the average values were in the range of 88 to 93 shore D.

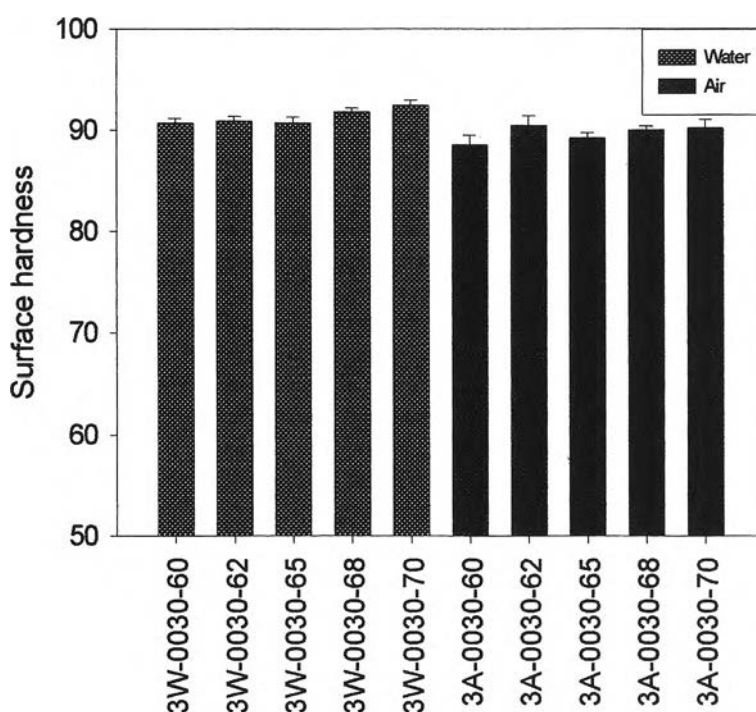


Figure 4.26 Surface hardness of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN in both water and hot-air systems.

4.1.3.3.2 Effect on impact resistance

Figure 4.27 compares the impact resistance of samples polymerized in both water and hot-air at 60, 62, 65, 68, and 70°C using the initiator concentration of 0.030%. It is evident that the impact resistance of sample polymerized in both systems did not differ significantly, and the average values were in the range of 14 to 17 kJ/m².

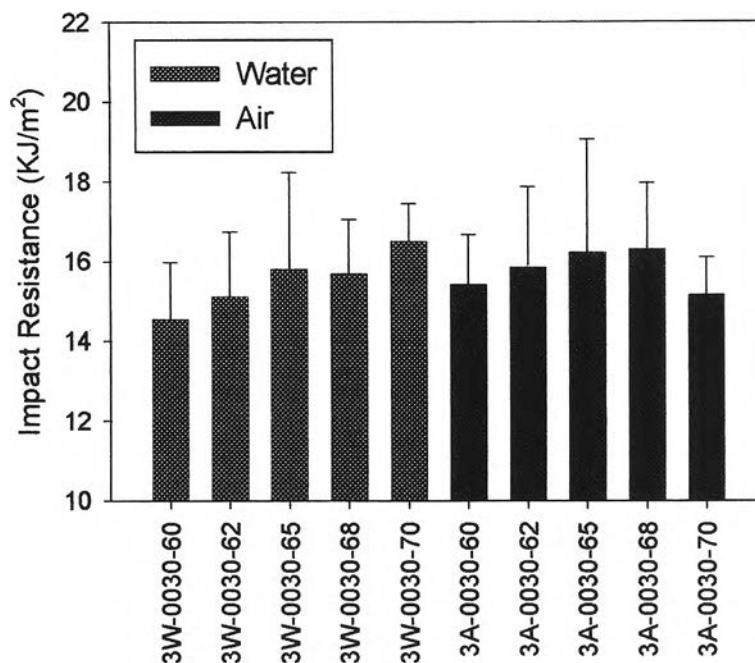


Figure 4.27 Impact resistance of samples polymerized at 60, 62, 65, 68, and 70°C with 0.030% ADVN in both water and hot-air systems.

4.2 Two-Step Isothermal Process

4.2.1 Water-Air System

4.2.1.1 Temperature profile

The MMA syrup, the viscosity of which was measured at 25°C to be 243 cP, was prepared by mixing MMA monomer (containing 10 ppm inhibitor) with either 0.030% or 0.038% by weight of 2,2'-Azobis-(2,4-Dimethyl Valeronitrile) (ADVN) using a mechanical stirrer for 30 minutes. The mixture was poured into a glass mold with the gap thickness of 3 mm. The polymerization temperatures studied were 60, 63, and 65°C, using water as the heat transfer medium. The reaction time for each reaction temperature was measured from the temperature profile, after the drop-off of the exothermic peak. After the specific reaction time was reached, samples were transferred to a hot-air oven, the temperature of which were set at 105, 115, and 125°C, to further the reaction (by increasing the sample temperature above the glass transition of PMMA in order to increase the probability for the reactive species to react). The total observation time was fixed at 240

minutes. During polymerization, the temperature profile of each sample was recorded.

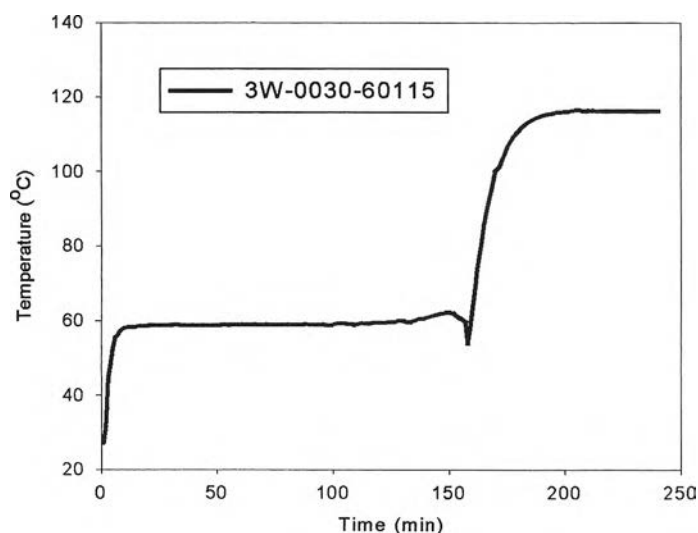


Figure 4.28 Temperature profile for sample polymerized at 60°C (in water) and annealed at 115°C (in hot air) with 0.030% ADVN.

Figure 4.28 illustrates temperature profile of sample polymerized according to two-step isothermal process with polymerization temperature of 60°C and the annealing temperature of 115°C using initiator concentration of 0.030% ADVN. The profile can be divided into five steps, with the first four steps are exactly similar to those described previously for the one-step isothermal process. The first step is the rapid increase in the temperature of syrup as a result of the marked difference in the temperatures of the syrup (i.e., ambient temperature) and the water (i.e., the set temperature). In this step, the rate of temperature rise depends strongly on the overall heat transfer coefficient. The second step is the plateau region where the temperature of the syrup is equivalent to that of the medium. The third step is the peak region where the temperature rise occurs, a direct result of the exothermic polymerization heat. In this region, the temperature increases, reaches a maximum and then reverts to the original temperature, which ultimately defines the fourth step.

According to previous studies in one-step isothermal process, the reaction cannot proceed further at the polymerization temperature as evidenced

by the maximum percent conversion of ca. 90% which coincides with the temperature drop-off after the exothermic peak. In order to drive the reaction further forward, mobility of the PMMA chains need to be increase, by increasing the temperature of the sample. This can be done by annealing the sample at elevated temperature (viz. so chosen so that it is greater than the glass transition of PMMA). As a result, the fifth step refers to the annealing region where the sample was taken out from the water bath to the hot-air oven (the time lag during transfer of the sample from the water bath to the hot-air oven was not included in the temperature profile). Evidently, the sample temperature increases rather rapidly to the annealing temperature and levels off.

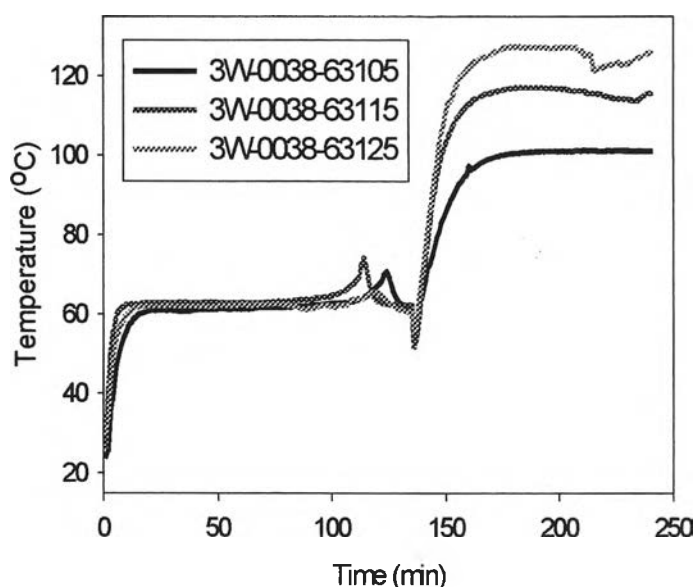


Figure 4.29 Temperature profile of samples polymerized in two-step (water-air) isothermal process for different temperature schemes (e.g., 63-105, 63-115, and 63-125°C) with 0.038% ADVN.

In order to study the effect of annealing temperature on monomer conversion, average molecular weights, and mechanical properties, temperature profile of samples polymerized in two-step (water-air) isothermal process in which the polymerization step was carried out in water at 63°C and the

annealing step was carried out in air at 105, 115, and 125°C, respectively, are shown in Figure 4.29. Further discussion will be given later in appropriate sections.

4.2.1.1.1 Effect of reaction temperature on reaction time

As in the case of one-step isothermal process, the exothermic peak was shifted to the left, suggesting a faster reaction, when the polymerization temperature was increased from 60 to 63°C, as shown in Figure 4.30. As soon as the temperature of the sample assumes that of the medium, the sample was taken out to anneal in a hot-air oven, the temperature of which was set at 115°C. After sample transfer, the temperature of the sample increased rapidly at first due to large temperature difference between the sample and the medium and gradually assumed that of the medium.

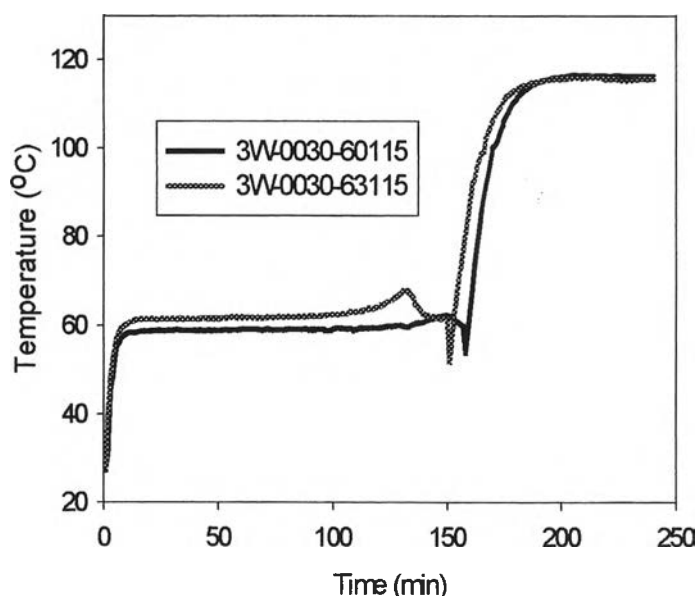


Figure 4.30 Temperature profile of samples polymerized in two-step (water-air) isothermal process for different temperature schemes (e.g., 60-115 and 63-115°C) with 0.030% ADVN.

4.2.1.1.2 Effect of initiator concentration on reaction time

Figure 4.31 illustrates temperature profile of samples polymerized in the two-step (water-air) isothermal process for 63-115°C temperature scheme using initiator concentrations of 0.030 and 0.038% ADVN.

According to Figures 4.30 and 4.31, the temperature profile was not only shifted by change in the reaction temperature, but also by change in the initiator concentration.

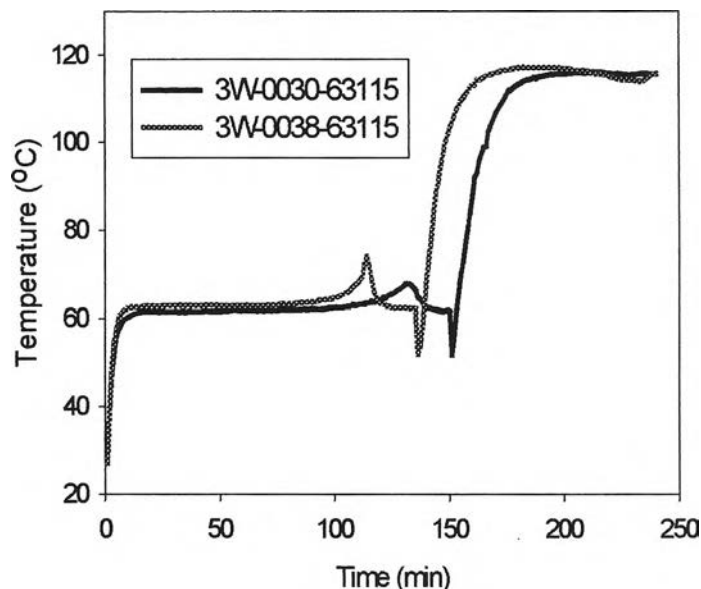


Figure 4.31 Temperature profile of samples polymerized in two-step (water-air) isothermal process for 63-115°C temperature scheme with 0.030 and 0.038% ADVN.

4.2.1.2 Monomer conversion

In an attempt to monitor the conversion of the reaction, samples were taken out from the heating water bath in every 15 minutes for the total reaction time of 240 minutes.

4.2.1.2.1 Effect of polymerization temperature on monomer conversion

Figure 4.32 shows percent conversion as a function of time for samples polymerized in the two-step (water-air) isothermal process for different temperature schemes (e.g., 60-125, 63-125, 65-125, and 68-125°C) using initiator concentration of 0.030% ADVN. Because of the increase in the reaction temperature, the percent conversion was shifted to the left, suggesting the faster reaction rate. Comparing with the maximum percent conversion achieved in the one-step isothermal process, it is evident that samples prepared by the two-step

isothermal process had a much higher maximum percent conversion (i.e., ranging from 97 to 99%).

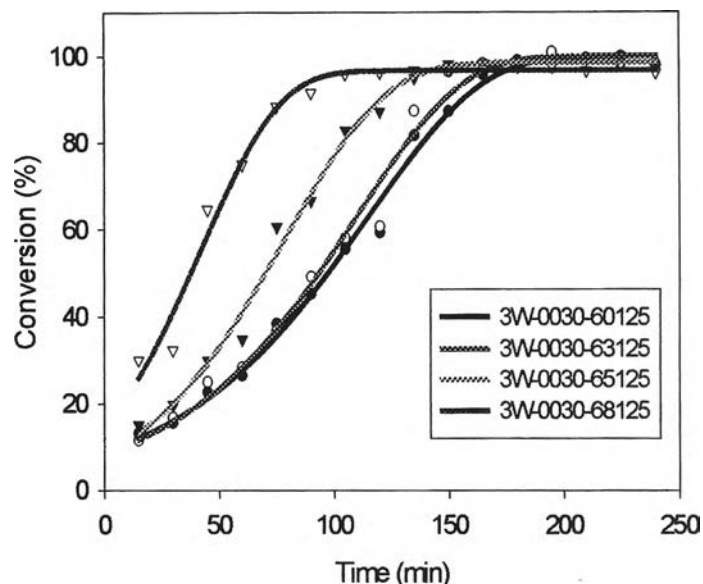


Figure 4.32 Percent conversion as a function of time for samples polymerized in two-step (water-air) isothermal process for different temperature schemes (e.g., 60-125, 63-125, 65-125, and 68-125°C) with 0.030% ADVN.

4.2.1.2.2 *Effect of annealing temperature on monomer conversion*

Figures 4.33 and 4.34 illustrate percent conversion as a function of time for samples polymerized in the two-step (water-air) isothermal process for different temperature schemes (e.g., 65-105 and 65-125°C) using initiator concentration of 0.030 and 0.038% ADVN, respectively. In this case, the polymerization temperature was fixed at 65°C, but the annealing temperature was varied between 105 and 125°C. Obviously, the difference in the annealing conversion at a specific polymerization temperature did not affect the maximum conversion, as long as the annealing temperature chosen was greater than the glass transition temperature of PMMA.

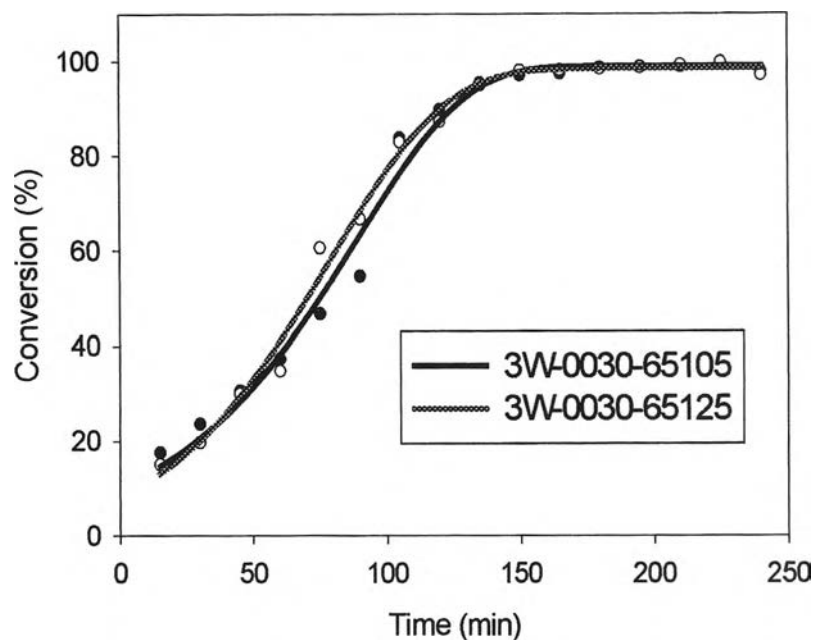


Figure 4.33 Percent conversion as a function of time for samples polymerized in two-step (water-air) isothermal process for different temperature schemes (e.g., 65-105 and 65-125°C) with 0.030% ADVN.

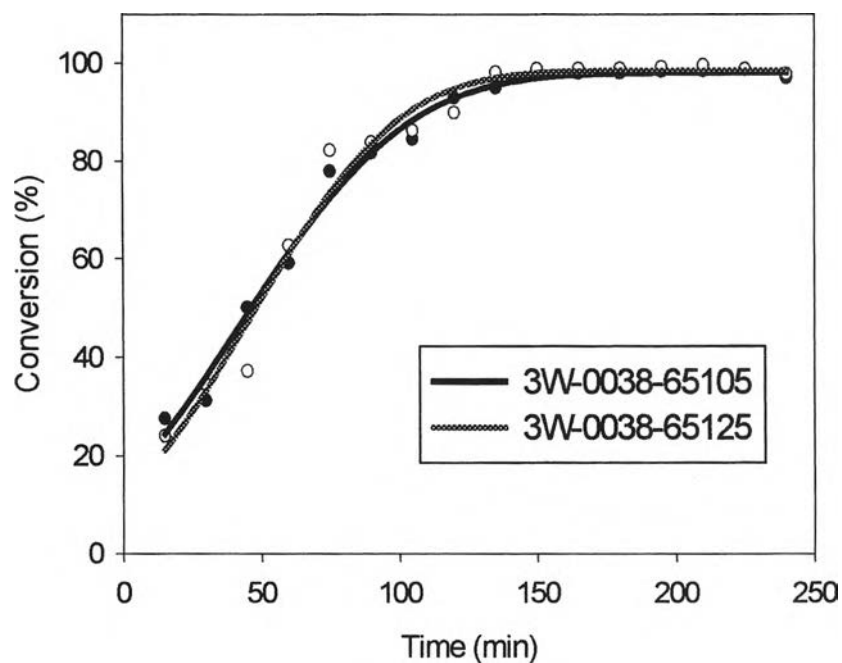


Figure 4.34 Percent conversion as a function of time for samples polymerized in two-step (water-air) isothermal process for different temperature schemes (e.g., 65-105 and 65-125°C) with 0.038% ADVN.

4.2.1.2.3 Effect of initiator concentration on monomer conversion

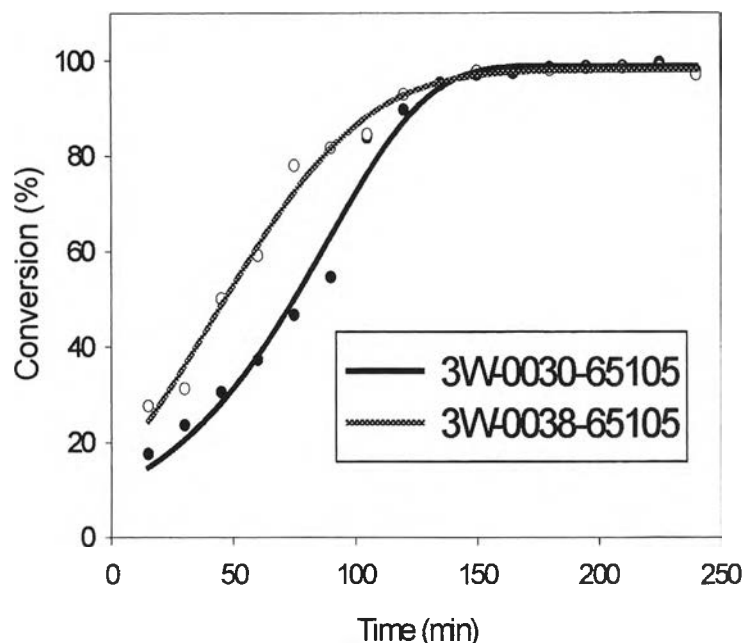


Figure 4.35 Percent conversion as a function of time for samples polymerized in two-step (water-air) isothermal process for 65-105°C temperature scheme with 0.030 and 0.038% ADVN.

Figure 4.35 reports percent conversion as a function of time for samples polymerized in the two-step (water-air) isothermal process for 65-105°C temperature scheme using initiator concentration of 0.030 and 0.038% ADVN. According to Figure 4.35, the percent conversion curve was shifted to the left, suggesting the faster reaction rate. It should be noted that initiator concentration did not affect the maximum conversion.

4.2.1.3 Relationship between temperature profile and percent conversion

The observed reaction times were determined from the overlay plot of temperature profile and percent conversion, such as those shown in Figure 4.36. Table 4.12 summarizes the maximum percent conversion and the

observed reaction time of different samples prepared in the two-step (water-air) isothermal process. According to Table 4.12, it is obvious that both the maximum percent conversion and observed reaction time were not affected by change in the annealing temperature, provided that the polymerization temperature was fixed. The results also suggest that polymerization rate increased with increasing polymerization temperature and increasing initiator concentration.

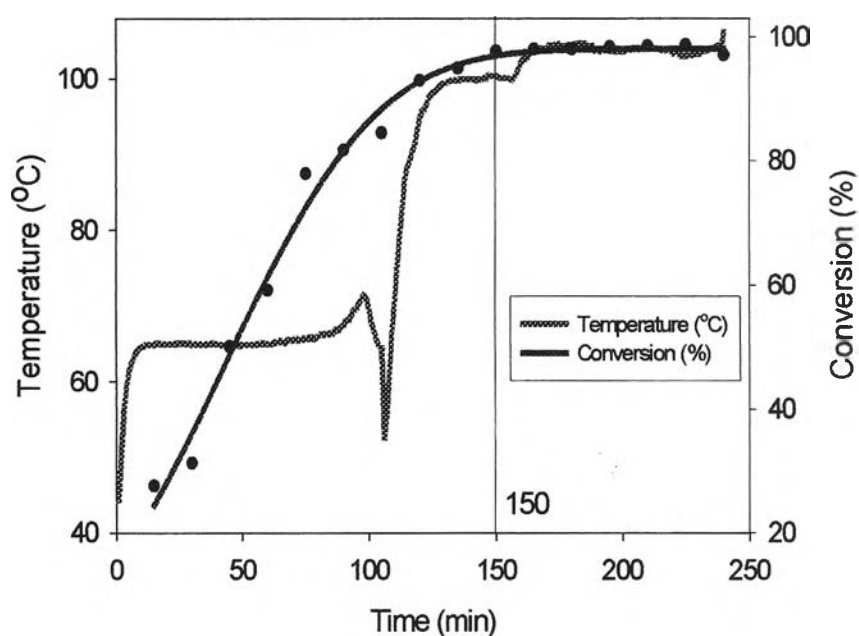


Figure 4.36 Overlay plot of temperature profile and percent conversion for samples polymerized in two-step (water-air) isothermal process for 65-105°C temperature scheme with 0.038% ADVN.

Table 4.12 Observed reaction time and maximum percent conversion for samples polymerized in the two-step (water-air) isothermal process for different temperature schemes (i.e., 60-105-125, 63-105-125, 65-105-125, and 68-125°C) with 0.030 and 0.038%ADV N, respectively

Reaction temperature (°C)	Monomer conversion (%)		Observed reaction time (min)	
	0.030% ADVN	0.038% ADVN	0.030% ADVN	0.038% ADVN
60-105	97.5±0.5	96.9±0.9	200	190
60-115	95.0±0.8	96.2±1.6	200	190
60-125	99.0±0.8	99.7±0.3	200	190
63-105	95.8±2.2	97.3±1.0	180	170
63-115	98.3±1.3	97.2±0.5	180	170
63-125	98.7±0.9	96.8±1.8	180	170
65-105	98.3±1.3	98.1±1.0	170	150
65-125	98.5±1.4	98.8±1.0	170	150
68-125	96.9±1.0	97.5±1.2	130	120

4.2.1.4 Effects of reaction temperature and initiator concentration on average molecular weights

Effects of reaction temperature (i.e., 60 and 63°C), annealing temperature (i.e., 105 to 125°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on average molecular weights are reported in Table 4.13. Obviously, the average molecular weights were not significantly affected by changes in the reaction, the annealing temperature and the initiator concentration. The molecular weight distributions were quite broad, suggesting the occurrence of chain-transfer reaction.

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4.2.1.5 Mechanical properties of the PMMA sheets

4.2.1.5.1 Effects of reaction temperature and initiator concentration on surface hardness

Both molecular weight and percent conversion strongly influence the surface hardness of PMMA product. According to Tables 4.12 and 4.13, both percent conversion and average molecular weights were found to be unaffected by changes in the reaction temperature and initiator, surface hardness should be unaffected as well. Indeed, the results shown in Figure 4.37 confirm the hypothesis, and surface hardness of samples studied were found to lie between 94 and 96 shore D.

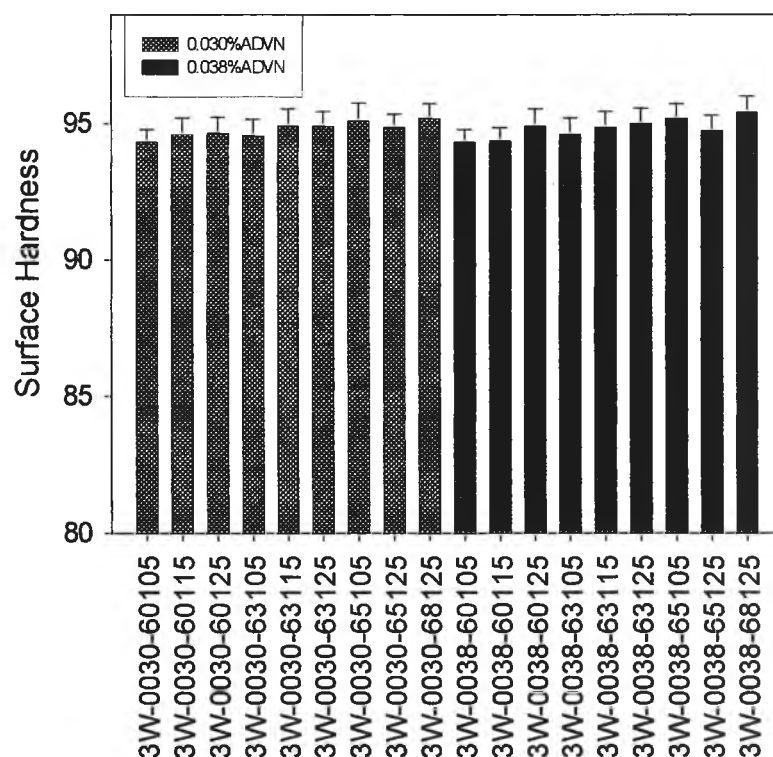


Figure 4.37 Effect of reaction temperature (i.e., 60-105-125 63-105-125, 65-105-125, and 68-125°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on surface hardness.

4.2.1.5.2 Effects of reaction temperature and initiator concentration on impact resistance

Similar to the case of impact resistance, both molecular weight (rather the number of entanglements) and percent conversion strongly influence the impact resistance of PMMA product. According to Tables 4.12 and 4.13, both percent conversion and average molecular weights were found to be unaffected by changes in the reaction temperature and initiator, impact resistance should be unaffected as well. Indeed, the results shown in Figure 4.38 confirm the hypothesis, and impact resistance of samples studied were found to range from 19 to 22 kJ/m².

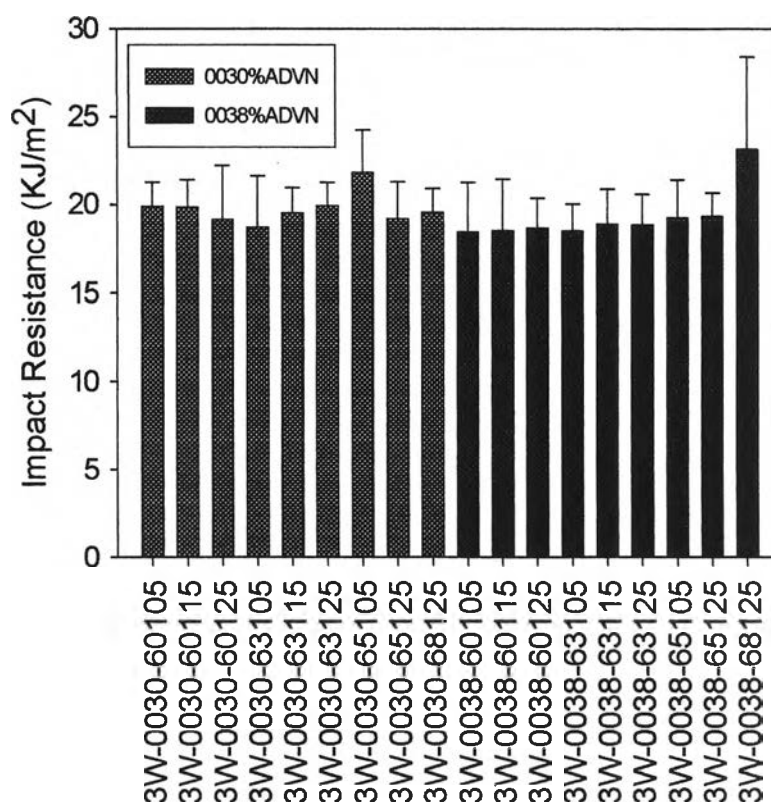


Figure 4.38 Effect of reaction temperature (i.e., 60-105-125, 63-105-125, 65-105-125, and 68-125°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on impact resistance.

4.1.1.6 Appearance of PMMA sheets

In this work, not only the temperature profile, percentage of monomer conversion, average molecular weights, and mechanical properties were observed, but the appearance was also observed. This is because, in the industries, good product appearance is also of prime importance to the customers. It is therefore very important to inspect the samples obtained for each polymerization condition studied. The major type of defects usually found is the formation of bubbles, which may be a result of the evaporation of MMA (due to uncontrollable rise in the temperature of the sample during polymerization) or a result of the inefficient degassing process. Therefore, the products in each condition had to inspect the defect that is generated by processing.

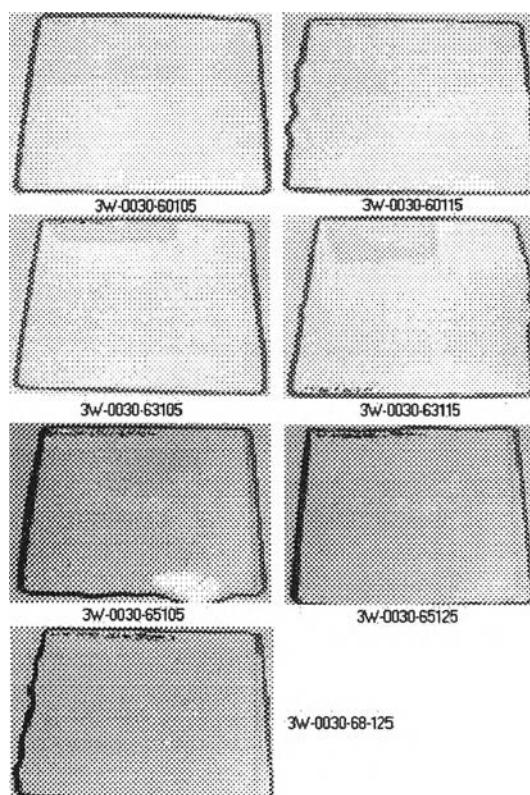


Figure 4.39 Appearance of PMMA sheets polymerized at 60-105-125, 63-105-125, 65-105-125, and 68-125°C with 0.030% ADVN.

Appearance of the PMMA sheets polymerized at 60-105-125, 63-105-125, 65-105-125, and 68-125°C with the initiator concentrations of 0.030 and

0.038% ADVN is illustrated in Figures 4.39 and 4.40, respectively. It is obvious that the sheets polymerized at high temperatures (i.e., 68-125°C), despite the short reaction time, were full of bubbles, possibly a result of either MMA evaporation or inefficient degassing process.

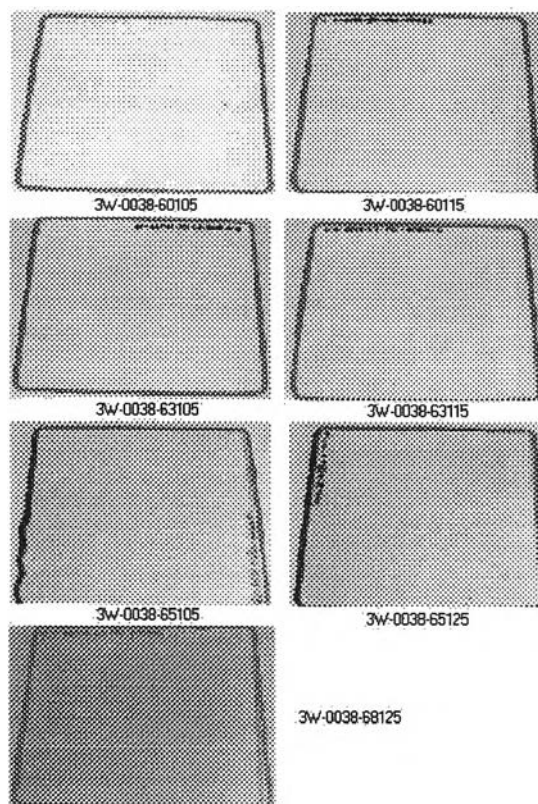


Figure 4.40 Appearance of PMMA sheets polymerized at 60-105-125, 63-105-125, 65-105-125, and 68-125°C with 0.030% ADVN.

4.2.2 Air-Air system

4.2.2.1 *Temperature profile*

Methods for sample preparation and data collection were similar to those previously described in the water-air system, but, in this case, the polymerization was carried out in a hot-air oven, where hot-air was used as the heat transfer medium. Figure 4.41 shows the temperature profile of sample polymerized at 63oC and annealed at 115°C with 0.038% ADVN.

Here, the temperature profile curve can still be divided into five steps, as previously described for the water-air system, but, in this case, the first

step took a longer time for the temperature of the sample to assume that of the medium. This is due to the much lower overall heat transfer coefficient in the air-air system, as compared with the water-air system.

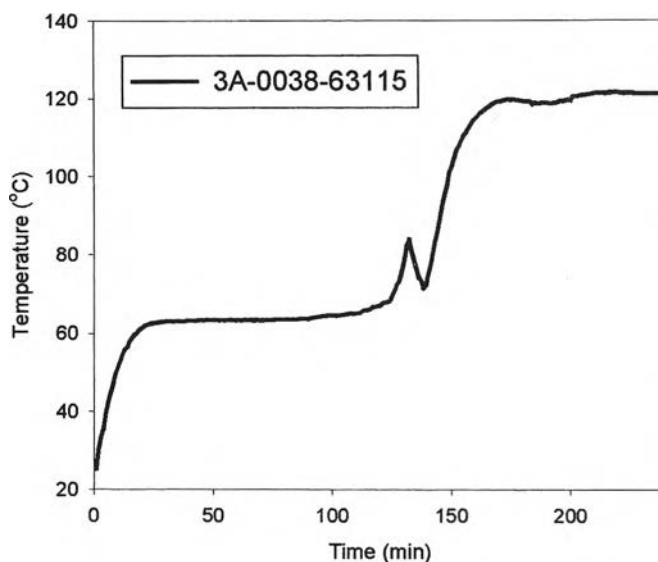


Figure 4.41 Temperature profile for sample polymerized at 63°C (in hot air) and annealed at 115°C (in hot air) with 0.038% ADVN.

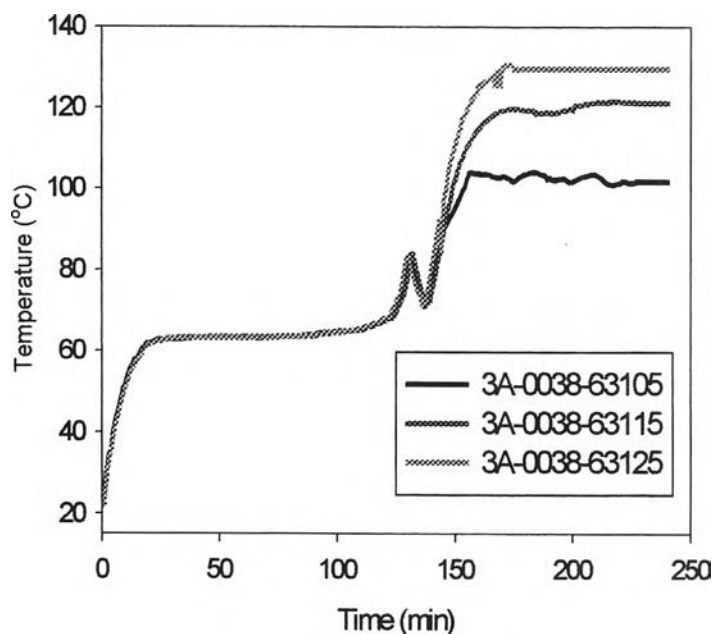


Figure 4.42 Temperature profile of samples polymerized in two-step (air-air) isothermal process for different temperature schemes (e.g., 63-105, 63-115, and 63-125°C) with 0.038% ADVN.

Similarly to the water-air system, the effect of the second step temperature on monomer conversion, molecular weight, and mechanical properties was observed and also the temperature profile of two-step isothermal synthesis process. The polymerization temperature was at 63°C and annealing temperature was at 105, 115, and 125°C shown in Figure 4.42. At the same reaction temperature, the maximum temperature of exothermic peak was appeared nearly and in annealing step temperature, the graph was spited in three lines which depend on its temperature.

4.2.2.1.1 Effect of reaction temperature on reaction time

As in the case of one-step isothermal process, the exothermic peak was shifted to the left, suggesting a faster reaction, when the polymerization temperature was increased from 60 to 63°C, as shown in Figure 4.43. after the polymerization, the sample was continuously annealed in a hot-air oven, the annealing temperature of which was set at 125°C.

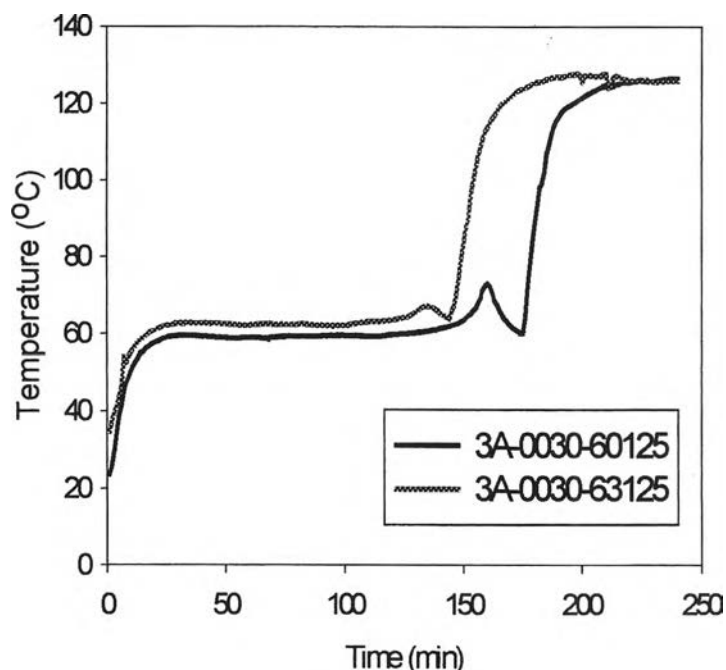


Figure 4.43 Temperature profile of samples polymerized in two-step (air-air) isothermal process for different temperature schemes (e.g., 60-125 and 63-125°C) with 0.030% ADVN.

4.2.2.1.2 Effect of initiator concentration on reaction time

Figure 4.44 illustrates temperature profile of samples polymerized in the two-step (air-air) isothermal process for 63-125°C temperature scheme using initiator concentrations of 0.030 and 0.038% ADVN. According to Figures 4.43 and 4.44, the result of temperature profile similar to the two-step (water-air) that it was not only shifted by change in the reaction temperature, but also by change in the initiator concentration.

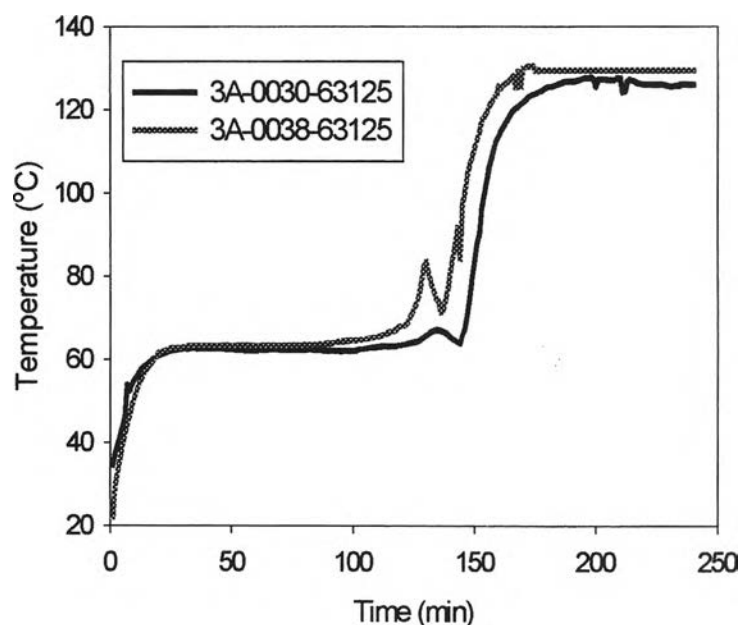


Figure 4.44 Temperature profile of samples polymerized in two-step (air-air) isothermal process for 63-125°C temperature scheme with 0.030 and 0.038% ADVN.

4.2.2.2 Monomer conversion

During the polymerization, sample was taken out every 15 minutes until 240 minutes.

4.2.2.2.1 Effect of polymerization temperature on monomer conversion

Figure 4.45 shows percent conversion as a function of time for samples polymerized in the two-step (air-air) isothermal process for different temperature schemes (e.g., 60-125 and 63-125°C) using initiator



concentration of 0.038% ADVN. Because of the increase in the reaction temperature, the percent conversion was shifted to the left, suggesting the faster reaction rate. Comparing with the maximum percent conversion achieved in the water-air system, it is evident that samples prepared by the air-air system had nearly maximum percent conversion (i.e., ranging from 97 to 99%).

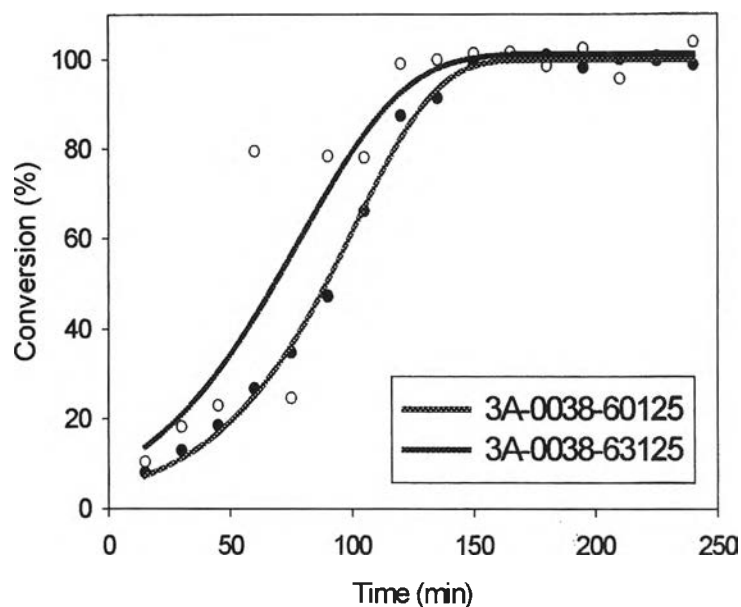


Figure 4.45 Percent conversion as a function of time for samples polymerized in two-step (air-air) isothermal process for different temperature schemes (e.g., 60-125, 63-125°C) with 0.038% ADVN.

4.2.2.2.2 *Effect of annealing temperature on monomer conversion*

Figures 4.46 illustrate percent conversion as a function of time for samples polymerized in the two-step (air-air) isothermal process for different temperature schemes (e.g., 63-105, 63-115 and 63-125°C) using initiator concentration of 0.038% ADVN. In this case, the polymerization temperature was fixed at 63°C, but the annealing temperature was varied at 105 to 125°C. Obviously, the difference in the annealing conversion at a specific polymerization temperature did not affect the maximum conversion, as long as the annealing temperature chosen was greater than the glass transition temperature of PMMA.

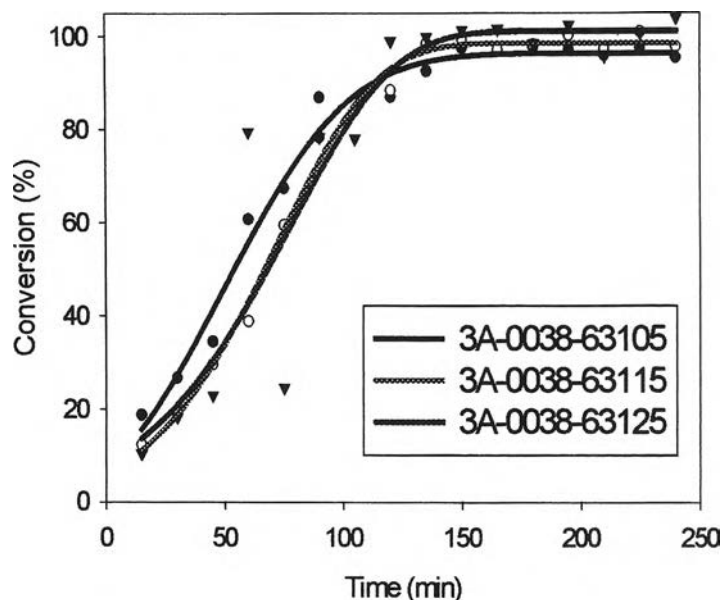


Figure 4.46 Percent conversion as a function of time for samples polymerized in two-step (air-air) isothermal process for different temperature schemes (e.g., 63-105, 63-115 and 63-125°C) with 0.038% ADVN.

4.2.2.2.3 Effect of initiator concentration on monomer conversion

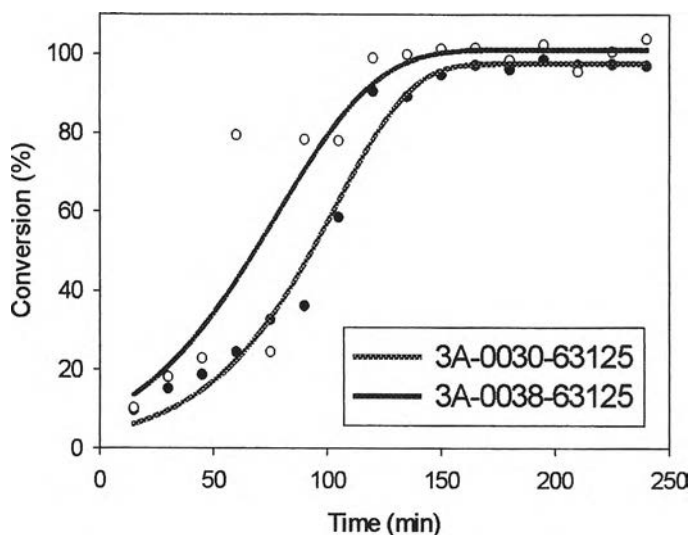


Figure 4.47 Percent conversion as a function of time for samples polymerized in two-step (air-air) isothermal process for 63-125°C temperature scheme with 0.030 and 0.038% ADVN.

Figure 4.47 reports percent conversion as a function of time for samples polymerized in the two-step (air-air) isothermal process for 63-125°C temperature scheme using initiator concentration of 0.030 and 0.038% ADVN. According to Figure 4.47, the percent conversion curve was shifted to the left, suggesting the faster reaction rate. It should be noted that initiator concentration did not affect the maximum conversion.

4.2.2.3 Relationship between temperature profile and percent conversion

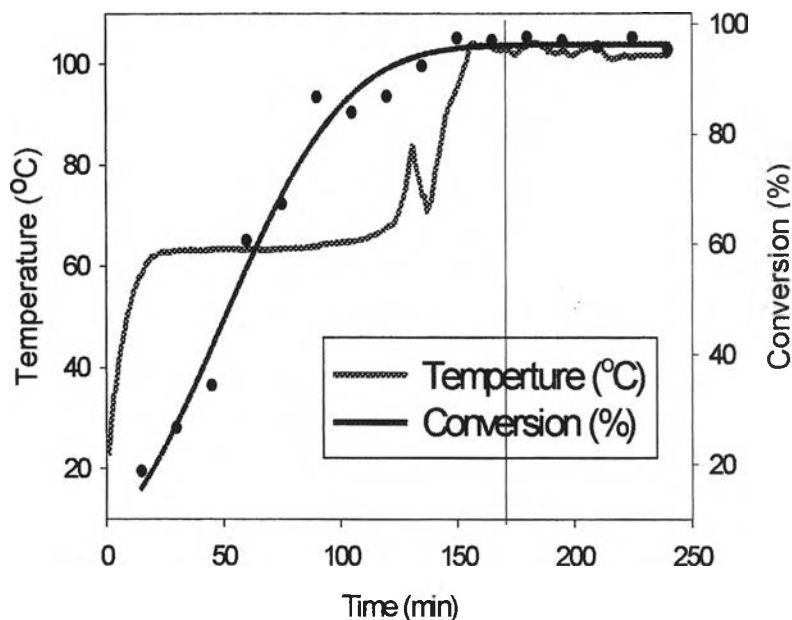


Figure 4.48 Overlay plot of temperature profile and percent conversion for samples polymerized in two-step (air-air) isothermal process for 63-105°C temperature scheme with 0.038% ADVN.

The reaction times were observed from the overlay plot of temperature profile and percent conversion, such as those shown in Figure 4.48. Table 4.14 summarizes the maximum percent conversion and the observed reaction time of different samples prepared in the two-step (air-air) isothermal process. According to Table 4.14, it is obvious that both the maximum percent conversion and observed reaction time were not affected by change in the annealing temperature,

provided that the polymerization temperature was fixed. The results also suggest that polymerization rate increased with increasing polymerization temperature and increasing initiator concentration.

Table 4.14 Observed reaction time and maximum percent conversion for samples polymerized in the two-step (water-air) isothermal process for different temperature schemes (i.e., 60-105-125 and 63-105-125°C) with 0.030 and 0.038% ADVN, respectively

Reaction temperature (°C)	Monomer conversion (%)		Observed reaction time (min)	
	0.030% ADVN	0.038% ADVN	0.030% ADVN	0.038% ADVN
60-105	98.9±1.1	97.9±2.1	220	200
60-115	96.5±1.1	98.8±1.2	220	200
60-125	98.6±1.1	99.5±0.5	220	-
63-105	99.3±0.4	96.9±1.5	190	180
63-115	98.2±0.9	98.6±1.4	190	-
63-125	97.3±1.3	100.0±0.0	190	-

4.2.2.4 *Effects of reaction temperature and initiator concentration on average molecular weights*

Effects of reaction temperature (i.e., 60 and 63°C), annealing temperature (i.e., 105 to 125°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on average molecular weights are reported in Table 4.15. Obviously, the average molecular weights were not significantly affected by changes in the reaction, the annealing temperature and the initiator concentration. The molecular weight distributions were quite broad, suggesting the occurrence of chain-transfer reaction.

Table 4.15 Effects of reaction temperature and initiator concentration on average molecular weights

Synthesis Temperature (°C)	0.030%ADV N					0.038%ADV N				
	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD
60-105	4.5	1.7	3.8	5.9	3.8	-	-	-	-	-
60-115	5.2	2.1	4.1	5.7	3.9	-	-	-	-	-
60-125	5.6	2.1	4.2	5.7	3.7	4.5	1.7	3.8	5.5	3.8
63-105	4.6	1.8	3.9	5.5	3.9	4.3	1.6	3.5	5.3	3.6
63-115	4.8	1.8	3.8	5.5	3.7	4.0	1.6	3.5	5.2	3.9
63-125	4.8	1.7	3.7	5.5	3.6	4.4	1.6	3.6	5.3	3.7

4.2.2.5 Mechanical properties of the PMMA sheets

4.2.3.5.1 Effects of reaction temperature and initiator concentration on surface hardness

Both molecular weight and percent conversion strongly influence the surface hardness of PMMA product. According to Tables 4.14 and 4.15, both percent conversion and average molecular weights were found to be unaffected by changes in the reaction temperature and initiator, surface hardness should be unaffected as well. Indeed, the results shown in Figure 4.49 confirm the hypothesis, and surface hardness of samples studied was found to lie between 94 and 95 shore D.

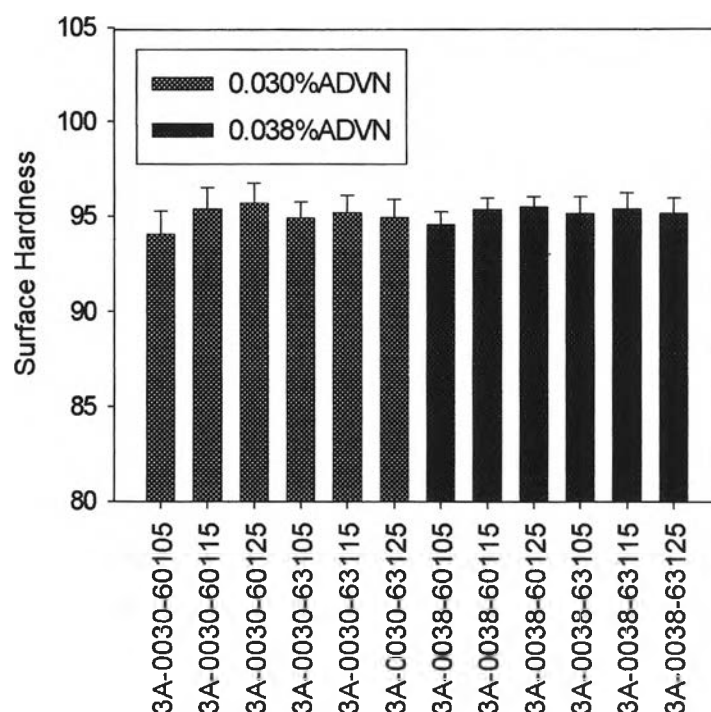


Figure 4.49 Effect of reaction temperature (i.e., 60-105-125 and 63-105-125°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on surface hardness.

4.2.2.5.2 Effects of reaction temperature and initiator concentration on impact resistance

Similar to the case of impact resistance, both molecular weight (rather the number of entanglements) and percent conversion

strongly influence the impact resistance of PMMA product. According to Tables 4.14 and 4.15, both percent conversion and average molecular weights were found to be unaffected by changes in the reaction temperature and initiator, impact resistance should be unaffected as well. Indeed, the results shown in Figure 4.50 confirm the hypothesis, and impact resistance of samples studied were found to range from 15 to 18 kJ/m².

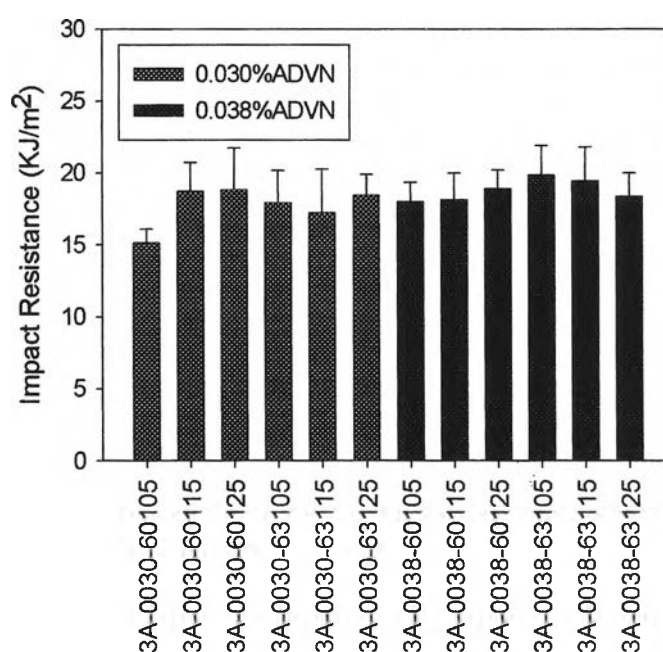


Figure 4.50 Effect of reaction temperature (i.e., 60-105-125 and 63-105-125°C) and initiator concentration (i.e., 0.030 and 0.038% ADVN) on impact resistance.

4.2.2.6 Appearance of PMMA sheets

Similarly to the water-air system, not only the temperature profile, percentage of monomer conversion, average molecular weights, and mechanical properties were observed, but the appearance was also observed. This is because, in the industries, good product appearance is also of prime importance to the customers. It is therefore very important to inspect the samples obtained for each polymerization condition studied. The major type of defects usually found is the formation of bubbles, which may be a result of the evaporation of MMA (due to uncontrollable rise in the temperature of the sample during polymerization) or a

result of the inefficient degassing process. Therefore, the products in each condition had to inspect the defect that is generated by processing.

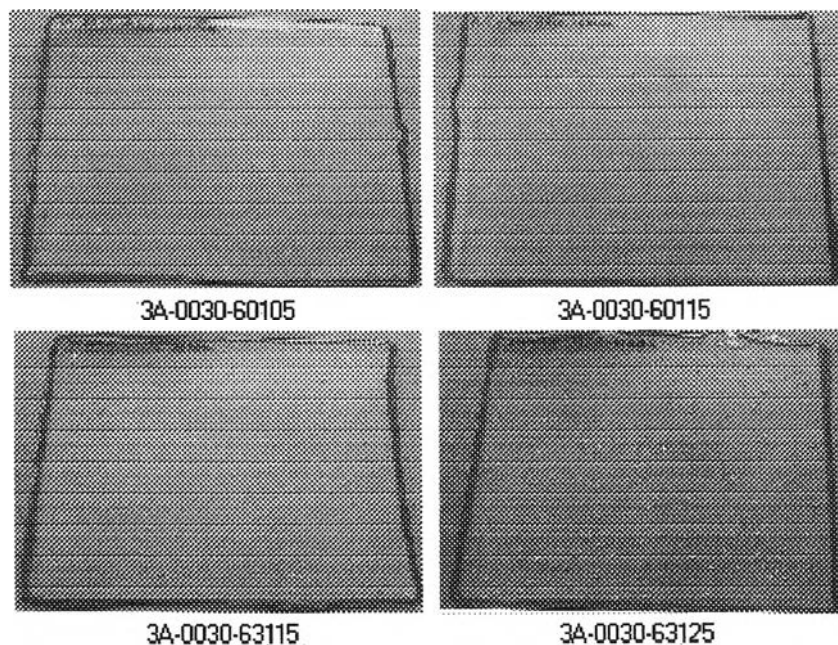


Figure 4.51 Appearance of PMMA sheets polymerized at 60-105-125 and 63-105-125°C with 0.030% ADVN.

Appearance of the PMMA sheets polymerized at 60-105-125 and 63-105-125°C with the initiator concentrations of 0.030 and 0.038% ADVN is illustrated in Figures 4.51 and 4.52, respectively. It is obvious that the sheets polymerized at high temperatures (i.e., 65-105°C), despite the short reaction time, were full of bubbles, possibly a result of either MMA evaporation or inefficient degassing process.

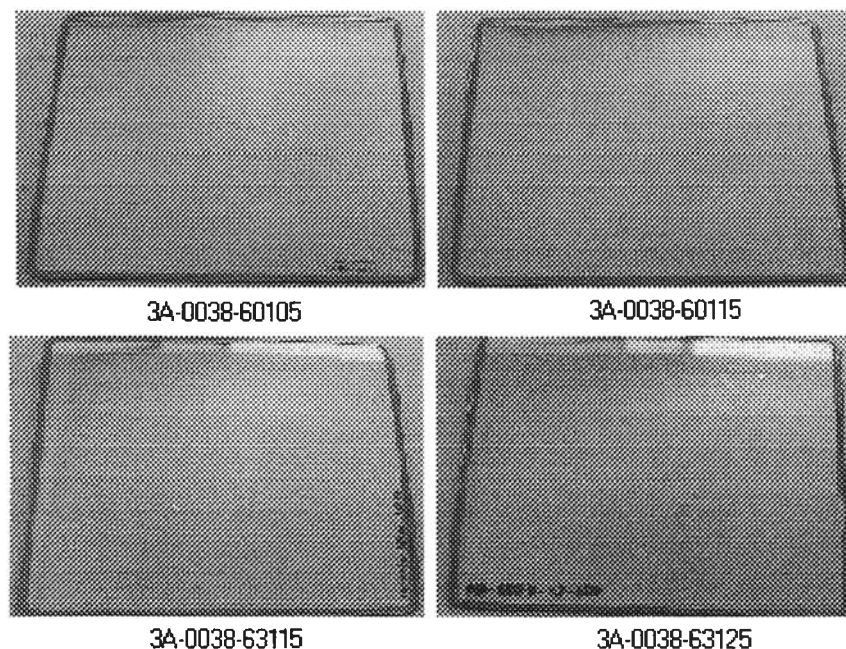


Figure 4.52 Appearance of PMMA sheets polymerized at 60-105-125 and 63-105°C with 0.038% ADVN.

4.2.3 Comparison of Two-Step Isothermal Synthesis between Water-Air and Air-Air System

4.2.3.1 *Temperature profile, monomer conversion and observed reaction time*

Figure 4.53 shows the comparison of temperature profile with time by used 0.038%ADV N at 63-105°C between water-air and air-air system. It is obvious that the time required for the sample polymerized in air-air system to assume that of the medium takes longer than that for the water-air system. This is due to the much greater overall heat transfer coefficient that the water-air system has over the air-air system. As a result of the thermal lag, the observed reaction time for the water system was much shorter than for the hot-air system. Most importantly, the degree of temperature rise in the sample polymerized in the air-air system was much greater than in the water-air system, again a result of the much lower overall heat transfer coefficient. Table 4.16 compares the percent conversion and the observed reaction time of samples polymerized in water-air and air-air systems.

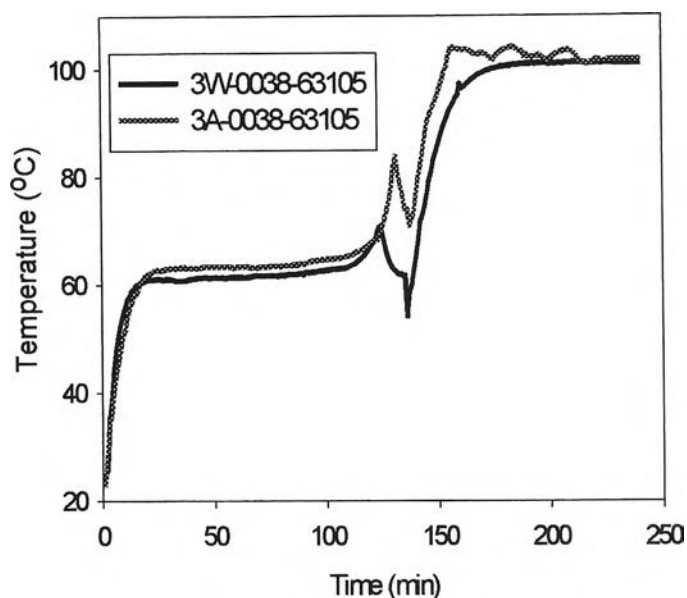


Figure 4.53 Temperature profile of samples polymerized at 63-105°C with 0.038% ADVN in water-air and air-air system.

Table 4.16 Comparison of monomer conversion and observed reaction time for samples polymerized in water-air system (i.e., 60-105-125, 63-105-125, and 65-105-125°C) and air-air system (i.e., 60-105-125, and 63-105-125°C) with 0.038%ADV N

Reaction temperature (°C)	Monomer conversion (%)		Total reaction time (min)	
	Water-air System	Air System	Water-air System	Air System
60-105	96.9±0.9	97.9±2.1	190	200
60-115	96.2±1.6	98.8±1.2	190	200
60-125	99.7±0.3	99.5±0.5	190	-
63-105	97.3±1.0	96.9±1.5	170	180
63-115	97.2±0.5	98.6±1.4	170	-
63-125	96.8±1.8	100.0±0.0	170	-
65-105	98.1±1.0	-	150	-
65-125	98.8±1.0	-	150	-

4.2.3.2 Effect on average molecular weights

Table 4.17 reports average molecular weights of samples polymerized at 60-105-125 and 63-105-125°C using the initiator concentration of 0.038% ADVN. Apparently, the average molecular weights as well as the molecular weight distribution for sample polymerized in water-air were systematically greater than those for samples polymerized in air-air. This could be a direct result of the greater temperature rise in the air-air system, which may contribute to the much greater extent of chain-transfer reactions.

Table 4.17 Comparison of average molecular weight in water-air system and air-air system with 0.038% ADVN

Synthesis Temperature (°C)	Water-air system					Air-Air system				
	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD	M_n ($\times 10^5$)	M_w ($\times 10^6$)	M_z ($\times 10^6$)	M_{z+1} ($\times 10^6$)	MWD
60-105	5.4	2.0	4.1	5.8	3.7	-	-	-	-	-
60-115	5.6	2.1	4.2	5.9	3.7	-	-	-	-	-
60-125	5.2	1.8	3.9	5.6	3.6	4.5	1.7	3.8	5.5	3.8
63-105	5.6	1.9	4.0	5.7	3.3	4.3	1.6	3.5	5.3	3.6
63-115	4.8	1.9	4.0	5.7	4.0	4.0	1.6	3.5	5.2	3.9
63-125	4.9	1.9	4.0	5.6	3.8	4.4	1.6	3.6	5.3	3.7

4.2.3.3 Effect on mechanical properties

4.2.3.3.1 Effect on surface hardness

In order to compare the surface hardness of both systems, the graph in Figure 4.54 was shown the surface hardness in water-air system (i.e., 60-105-125, 63-105-125, 65-105-125, and 68-125°C) and air-air system (i.e., 60-105-125, 63-105-125°C) with 0.038%ADV. It was found that both reaction temperature and initiator conversion had not effect to surface hardness. It is evident that the surface hardness of sample polymerized in both systems did not differ significantly, and the average values were in the range of 94 to 95 shore D. Therefore, the surface hardness could be improved by two-step isothermal process.

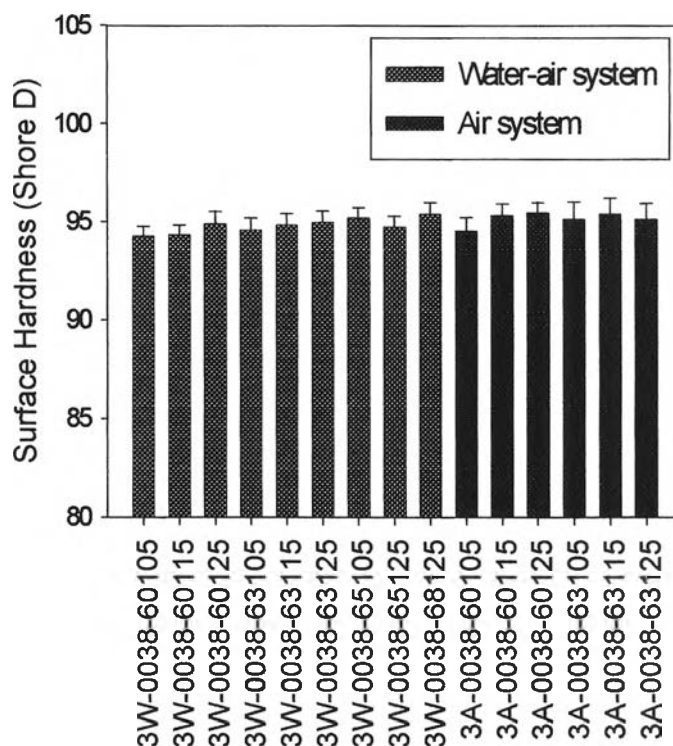


Figure 4.54 Surface hardness of samples polymerized at 60-105-125, 63-105-125, 65-105-125, and 68-125°C in water-air system and at 60-105-125 and 63-105-125°C in air-air system with 0.038%ADV.

4.2.3.3.2 Effect on impact resistance

Figure 4.55 compares the impact resistance of samples polymerized in both water-air and air-air using the initiator concentration of 0.030%. It is evident that the impact resistance of sample polymerized in both systems did not differ significantly, and the average values were in the range of 18 to 20 kJ/m². The result of those showed higher impact resistance compared with one-step isothermal process.

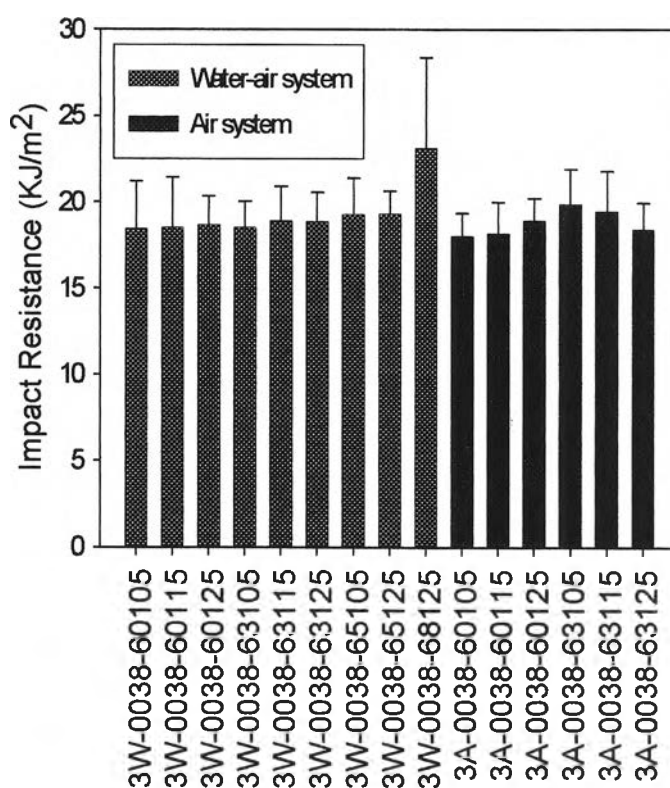


Figure 4.55 Impact resistance of samples polymerized in water-air system (i.e., 60-105-125, 63-105-125, 65-105-125, and 68-125°C) and air-air system (i.e., 60-105-125, and 63-105-125°C) with 0.038%ADVN.