CHAPTER IV
RESULTS AND DISCUSSION

4.1 Isothermal Methyl Methacrylate Polymerization in Casting Process

4.1.1 Monomer Conversion

The polymerization extension of poly(methyl methacrylate) (PMMA) was determined by means of the percent conversion of methyl methacrylate monomer (MMA) to the PMMA. The percent conversion was determined by the ratio of PMMA after precipitating the residue monomer out to the weight of PMMA before precipitation.

The MMA syrup was prepared by mixing MMA monomer, which already mixed with 10 ppm azo-bisbutylonitrile (AIBN) with 0.038% by weight of 2,2'-azobis-(2,4-dimethyl valeronitrile) (ADVN) in mechanical stirrer for 20 minutes. The syrup was poured into glass mold and the polymerization was carried out in a certain condition with 4 hours reaction time.

During the polymerization, sample was taken out every half an hour, the percent conversion was determined as described in 3.3.4.1.

For example, in 0.038 wt% ADVN mixed MMA monomer polymerized at 60 °C for 4.0 hours, the 0.9152 g of crude PMMA was weighed, defined as W_1, then dissolved in 30 ml acetone and then precipitated by 70 ml methanol.

The solid from precipitation was purified by methanol and distilled water and the excess solvent was dried out in oven at 110 °C for 12 hours.

The solid after drying was weighed at 0.7925 g then the percent conversion of MMA to PMMA was calculated by:

$$\%\ \text{yield of PMMA} = \frac{W_2 \times 100}{W_1} \tag{4.1}$$

where W_1 = weight of PMMA before dissolving = 0.9152g,

W_2 = weight of PMMA after precipitation = 0.7925g.

Then,

$$\%\ \text{yield of PMMA} = \frac{0.7925 \times 100}{0.9152}$$

$$= 86.59\%$$

4.1.1.1 Effect of Reaction Temperature

The effect of reaction temperature to the monomer conversion was studied by controlling the initiator concentration (ADVN) at 0.038 wt% and varying the casting temperature, in the isothermal polymerization, from 50, 58, 60, 62, to 70°C. The monomer conversion determined by precipitation method by varying the casting temperature were shown in figure 4.1 and 4.2.

From those results, when the reaction occurred, the monomer conversion was slightly increased at the beginning of the reaction then sharply increased when the conversion reached about 20 percent, and became stable at the conversion around 88 percent. The starting of the increase of the conversion depended on the casting temperature, the higher temperature, the faster reaction occurred.

Figure 4.3 shows the percent monomer conversion of the MMA polymerization in two different casting processes. The PMMA sheet is normally produced, in the factory (especially, the Pan Asia Co., Ltd.), by using the hot water bath as a heat source. The temperature of water bath was set at

60°C the same as the method that was used in this experiment, which used heating oven as a heat source instead. The results of percent monomer conversion of different casting process showed the same trend as the results from figure 4.1 and 4.2.

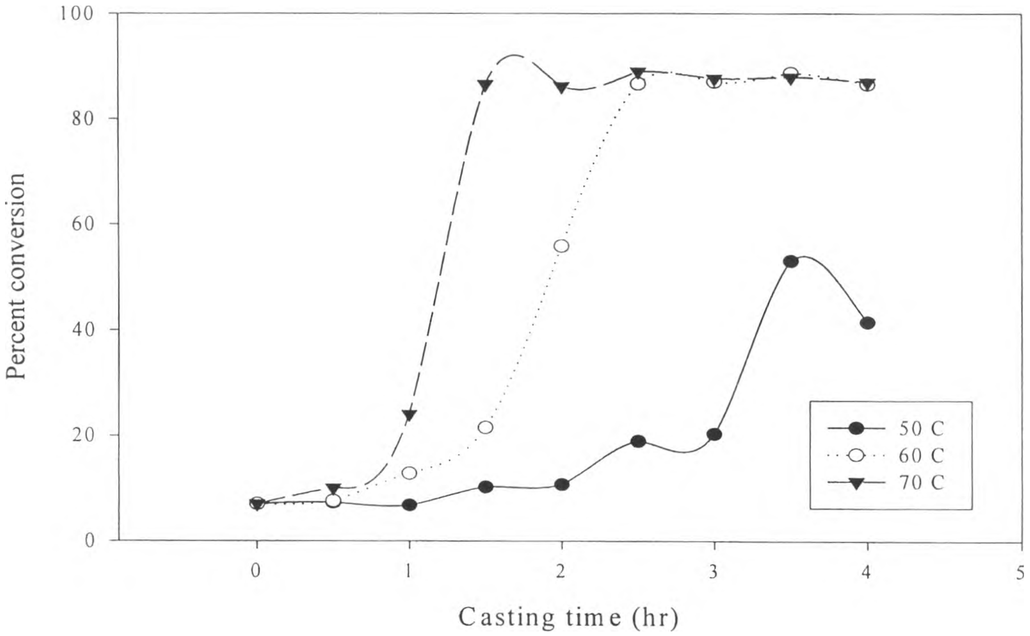


Figure 4.1 Monomer conversion as a function of casting time by varying casting temperatures (50, 60, and 70°C).

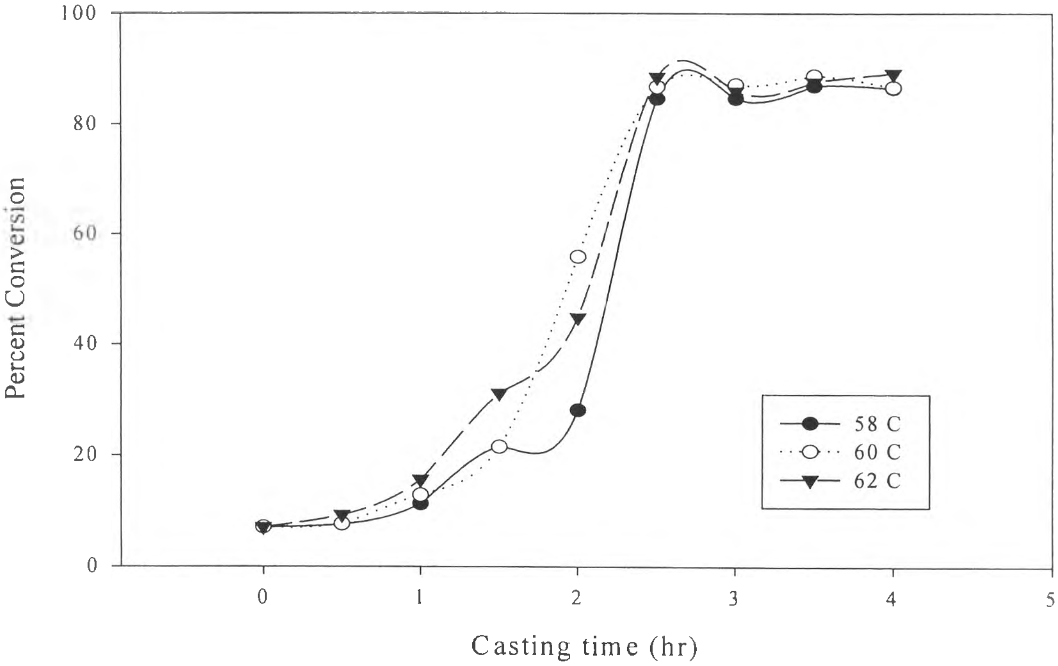


Figure 4.2 Monomer conversion as a function of casting time by varying casting temperature and conditions (58, 60, and 62°C).

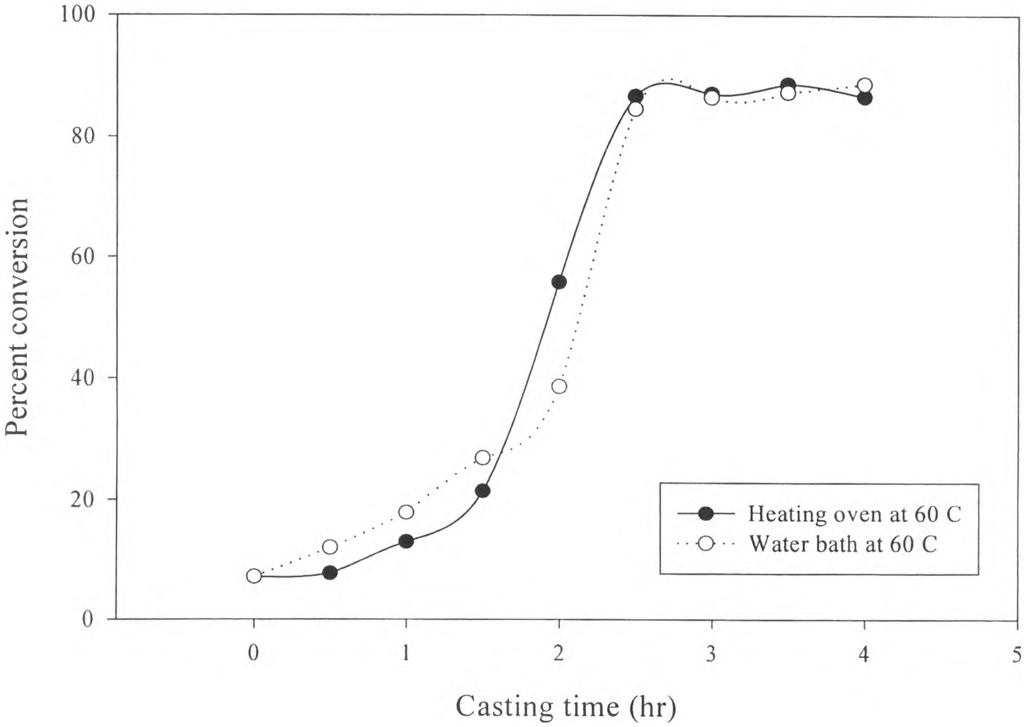


Figure 4.3 Monomer conversion as a function of casting time of different casting processes.

4.1.1.2 Effect of Initiator Concentration

The effect of initiator concentration to the monomer conversion was studied by controlling the casting temperature at 60°C and varying initiator concentration from 0.019, 0.038, to 0.076 wt%. The monomer conversion determined by precipitation method by varying the casting temperature was shown in figure 4.4.

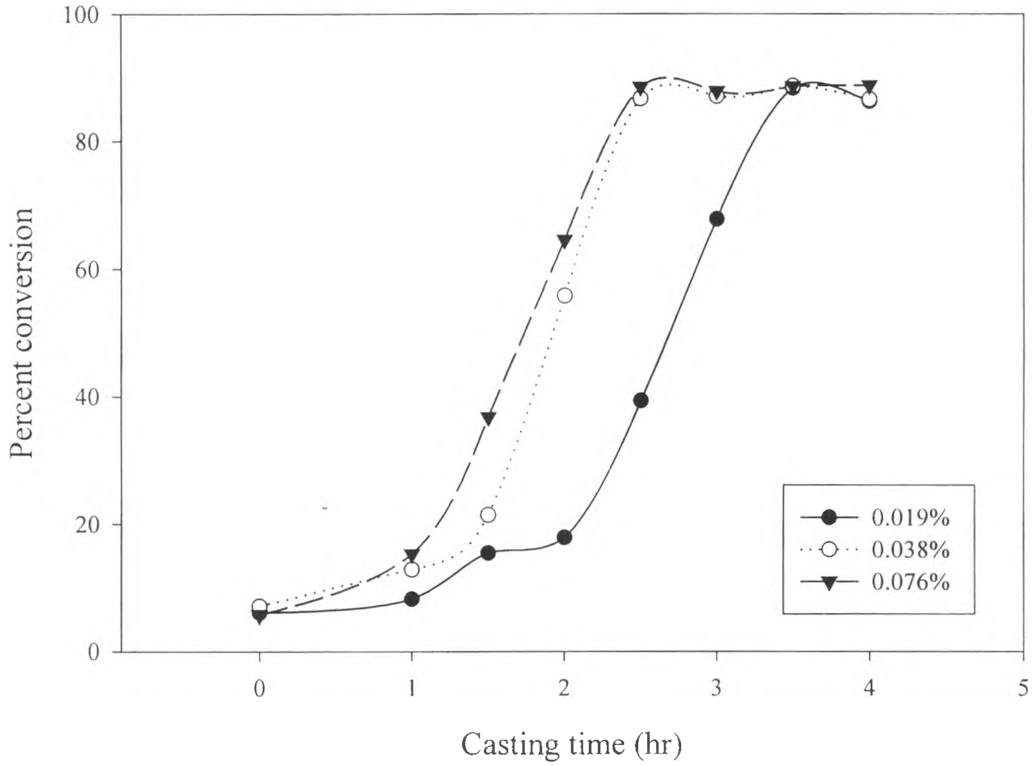


Figure 4.4 Monomer conversion as a function of casting time by varying ADVN concentrations.

From those results, at the starting of the reaction, monomer conversion increased slightly then sharply increased when the conversion reached about 20 percent, then became stable at the conversion around 88 percent. The starting of the increase of the conversion depended on the initiator concentration, the higher the amount of initiator, the faster the reaction occurred.

The sharp increase in the monomer conversion phenomenon is due to the autoacceleration, often called Trommsdoff effect or gel effect. This phenomenon usually occurs in the free-radical polymerization which has a concentrated solution or undiluted monomer as a starting material. The reason for this is that the viscosity of the medium increases as polymer forms, then the termination rate is decreased because of much slower diffusion of larger macromolecular species. The reactivity of the radicals is not altered, but the ability of the radicals to find each other is, so that the value of the termination rate constant (k_t) is reduced (Painter *et al.* 1997).

Soh *et al.* (1982) suggested that vinyl polymerization of monomer soluble in its own polymer consists of four phases of distinctive polymerization behavior. Depending on the monomer used or reaction conditions, one or more of the four phases may be absent. At low conversions the polymerization rate is described by conventional kinetics (phase I). After certain conversion, which appears to be independent of initiator concentration at the same polymerization temperature, the well known gel effect is observed (phase II). At still higher conversions the gel effect appears to stop. The polymerization rate is fast, but the cumulative molecular weight averages (except number-average molecular weight) level off or begin to decrease slightly (phase III). Eventually the deceleration becomes profound and when the polymerization temperature is lower than the glass transition temperature of the polymer formed a limiting conversion is reached beyond which the reaction does not continue (phase IV). A conversion profile and conversion dependence of molecular weight averages describing the phases of vinyl polymerization were shown in figure 4.5 and 4.6.

From these suggestions, the results of monomer conversion by varying, even, casting temperature or initiator concentration, the final conversion was limited to around 88 percent due to the gel effect occurring during the casting.

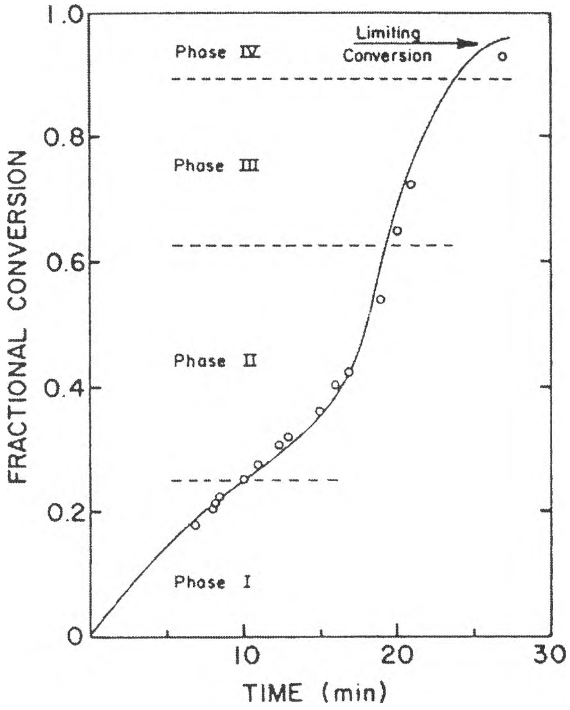


Figure 4.5 Fractional conversion as a function of time for methylacrylate polymerization depicting different phases of reaction. (Soh *et al.* 1982).

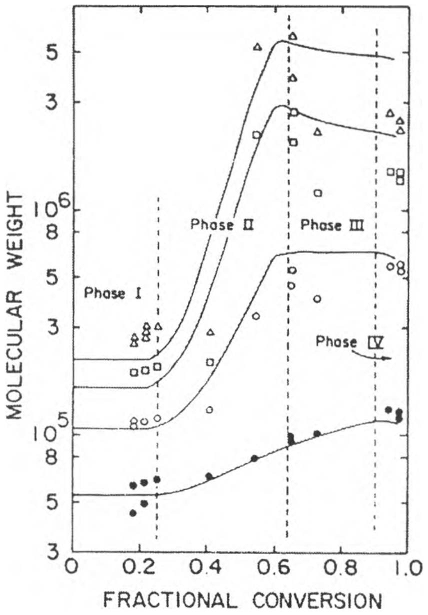


Figure 4.6 Conversion dependence of molecular weight average for methyl methacrylate polymerization. (●) $\overline{M}_n$, (○) $\overline{M}_w$, (□) $\overline{M}_z$, (△) $\overline{M}_{z+1}$ (Soh *et al.* 1982).

The values of the final conversion of PMMA casted sheet produced by heating oven and water bath at 60°C were listed in Table 4.1 and compared to the final conversion of the blank sample, which is the PMMA sheet produced by using the process that is normally used in the factory.

Table 4.1 Final monomer conversion of PMMA sheet in various isothermal casting conditions.

Condition	Conversion (%)
Heating oven at 60°C	86.6
Water bath at 60°C	88.7
Blank	98.6

The results showed that the final conversion of PMMA casted sheet by isothermal casting temperature was less than the blank sample.

The attempt to use the non-isothermal casting temperature will be described in 4.2.

4.1.2 Mechanical Properties of Poly (methyl methacrylate) Casted Sheet

4.1.2.1 Impact Resistance

Impact resistance is one of the important mechanical properties that is very useful for the application of PMMA sheets. It can be used to describe the strength of that material.

The results of impact resistance of PMMA sheets with 0.038 weight percent of ADVN and varying casting temperature were shown in figure 4.7. When the temperature increased, impact resistance of PMMA sheets tended to decrease. This resulted from the lower degree of molecular entanglement due to the decrease in molecular weight as the casting temperature increased. The results of molecular weight of isothermal casted PMMA sheets by varying casting temperature were shown in Table 4.2.

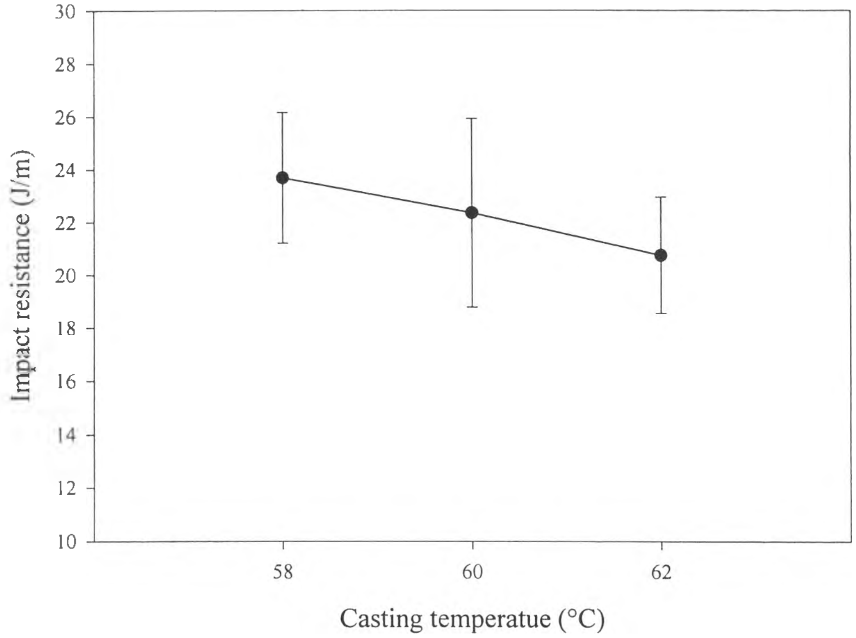


Figure 4.7 Impact resistance of PMMA casted sheet as a function of reaction temperature in isothermal casting process.

A comparison between the impact resistance of 0.038 wt% ADVN PMMA sheets produced to various casting processes was shown in figure 4.8. The impact resistance of PMMA sheets produced by 'water bath' method reached the highest value. This was also because of the high molecular weight as shown in Table 4.2.

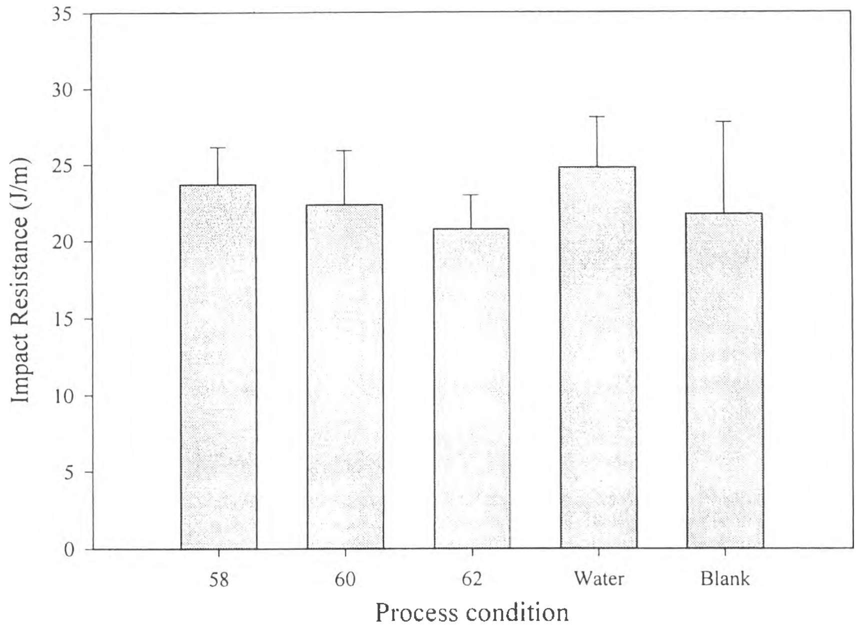
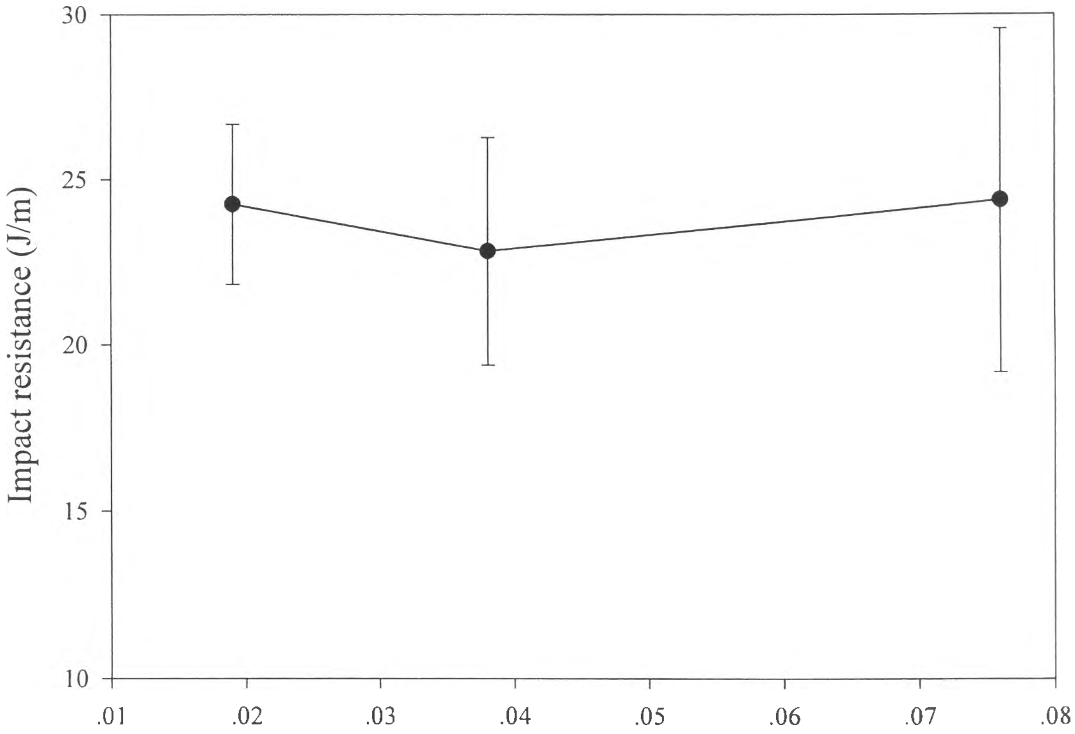


Figure 4.8 Impact resistance of PMMA casted sheet at various isothermal casting condition.

From figure 4.8, is was also shown that the value of impact resistance of PMMA sheets produced by heating oven either at 60 or 62°C was almost equal to the value of the blank sample.

The results of impact resistance of PMMA sheets produced by varying initiator concentration were shown in figure 4.9. The value of impact resistance had a tendency to remain unchanged as the initiator concentration increased and has a average value at 23.8 J/m. From this point, it can be concluded that only the casting temperature will affect the impact resistance of PMMA sheets.



Initiator concentration (wt%)

Figure 4.9 Impact resistance of PMMA casted sheet as a function of initiator concentration.

Another mechanical property that is important to the application of the PMMA sheets is the surface hardness. This property was measured by Shore D hardness durometer following ASTM D2240.

4.1.2.2 Surface Hardness

A relationship between surface hardness and casting temperature of PMMA sheets was shown in figure 4.10. As the casting temperature was increased from 58 to 62°C surface hardness remained unchanged.

The surface hardness as a function of initiator concentration was shown in figure 4.11. The values of surface hardness of PMMA sheets by varying initiator concentration were shown to be approximately equal to the value of PMMA sheets produced by varying casting temperature. However, it was shown that as the initiator concentration increased, surface hardness slightly increased.

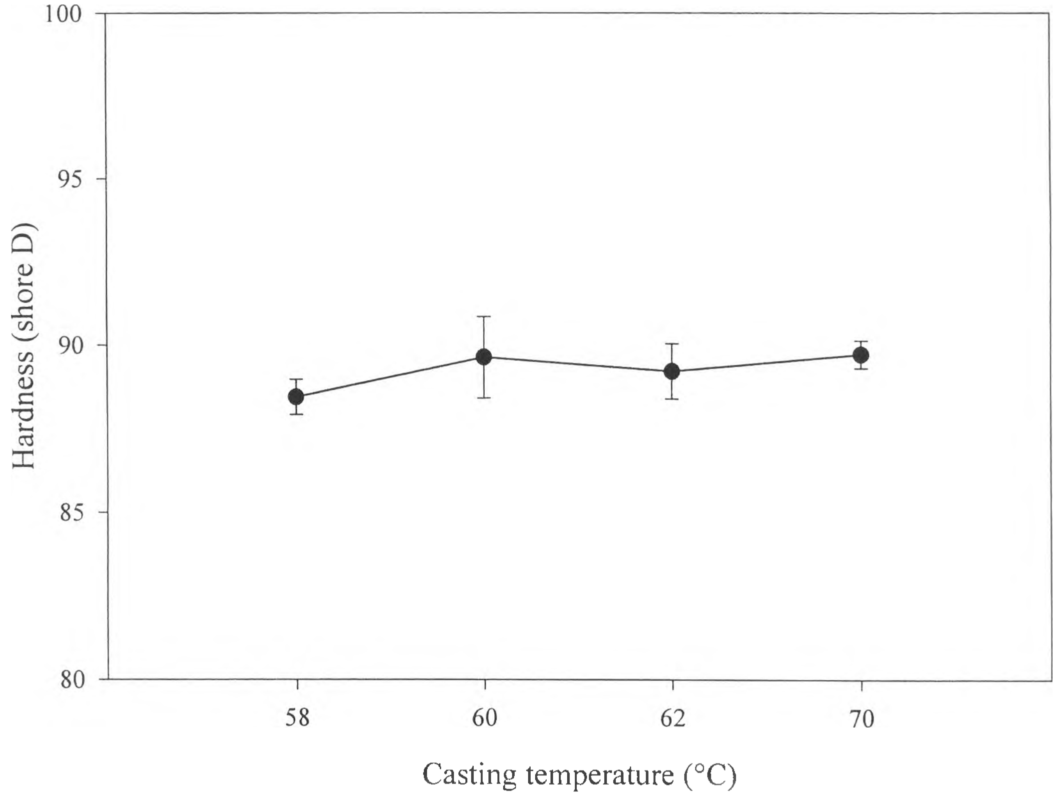


Figure 4.10 Surface hardness as a function of reaction temperature of PMMA casted sheet produced by isothemal casting process.

From both surface hardness results of PMMA sheets produced by varying casting temperature and initiator concentration, it can be concluded that by using the isothermal casting temperature profile, the surface hardness was not affected by those casting temperature or initiator concentrations.

A comparison of surface of PMMA sheets produced by different methods was shown in figure 4.12. The PMMA sheets that were produced by using heating oven and water bath at 60°C has equally the same value of surface hardness. However, when comparing those values to surface hardness of the blank sample, both hardness results of heating oven and water bath were less than the hardness of blank sample by about 5 percent.

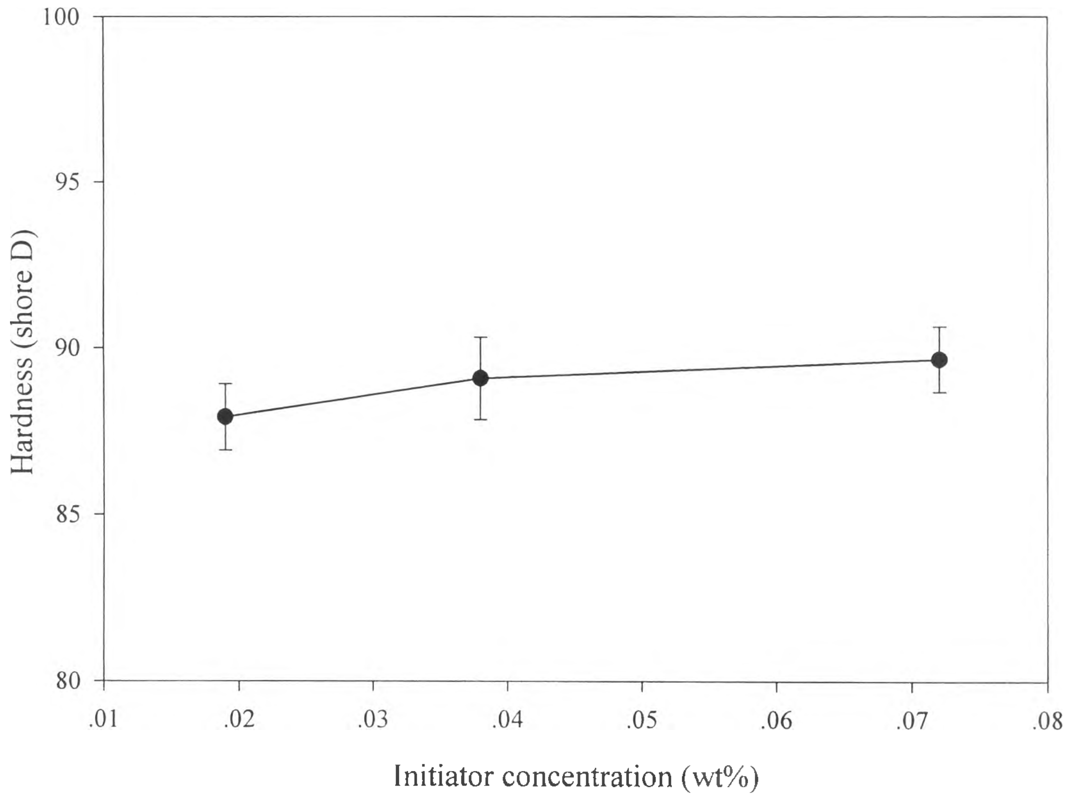


Figure 4.11 Surface hardness as a function of initiator concentration of PMMA casted sheet produced by isothermal casting process.

The comparison from figure 4.12 shows that by using isothermal casting temperature profile, the reaction was not as complete as the commercialized process. In other words, the residue monomer is not able to contribute to improve hardness.

An improvement of the surface hardness by producing PMMA sheets with the non-isothermal casting temperature profile will be discussed in 4.2.

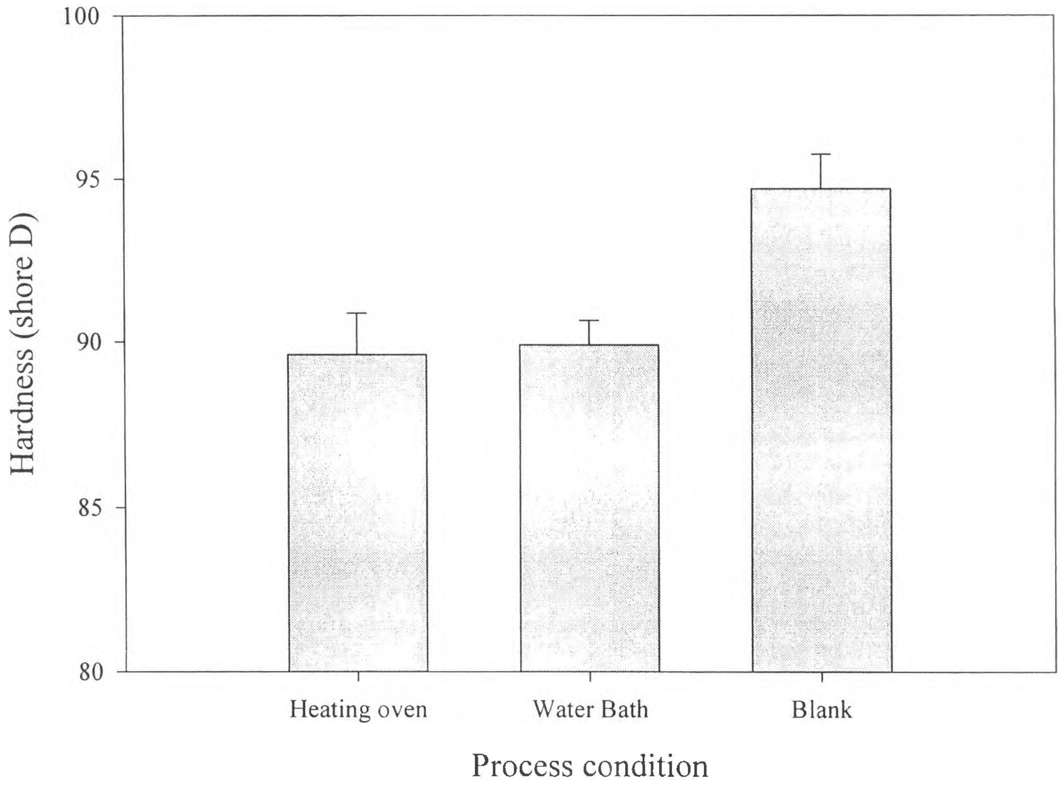


Figure 4.12 Surface hardness of PMMA casted sheet produced by different isothermal casting conditions.

4.1.3 Molecular Weight Average and Molecular Weight Distribution of PMMA Sheets

The number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and molecular weight distribution, $\overline{M}_w/\overline{M}_n$, (MWD), so called polydispersity, were determined by gel permeation chromatography technique. The results of $\overline{M}_n$, $\overline{M}_w$, and MWD of PMMA sheets produced by varying casting temperature were summarized in Table 4.2.

From the results, it is shown that molecular weight of PMMA sheets, often represented by $\overline{M}_w$, is very high ($> 10^6$) and also the MWD is relatively high (> 5).

The plot of casting temperature with $\overline{M}_w$ is shown in figure 4.13. As $\overline{M}_w$ decreased, the casting temperature increased. This can be explained that at higher casting temperature, the faster reaction occurred. Then the gel occurred during the reaction at high conversion will limit the diffusion of active species. As a result, the higher molecular weight PMMA cannot be formed.

Table 4.2 Molecular weight average and molecular weight distribution of PMMA sheets produced by isothermal casting using 0.038 wt% of ADVN with varying reaction temperatures.

Condition	$\overline{M}_n$	$\overline{M}_w$	MWD
58°C	319342	1688237	5.29
60°C	142047	1389213	9.78
62°C	155309	1344844	8.66
70°C	158713	1168176	7.36
Water Bath at 60°C	218287	1686094	7.72
Blank	218394	1496945	6.85

The results of $\overline{M}_n$, $\overline{M}_w$, and MWD of the PMMA sheets produced by varying initiator concentration were summarized in table 4.3. The results also show that, by varying initiator concentration, $\overline{M}_w$ is very high, as high as PMMA sheets produced by varying casting temperature ($> 10^6$). Also, the MWD is very high (> 4)

The relationship between initiator concentration and weight average molecular weight of PMMA sheets produced by varying initiator concentration is shown in figure 4.14. As the initiator concentration increased, $\overline{M}_w$ strongly decreased.

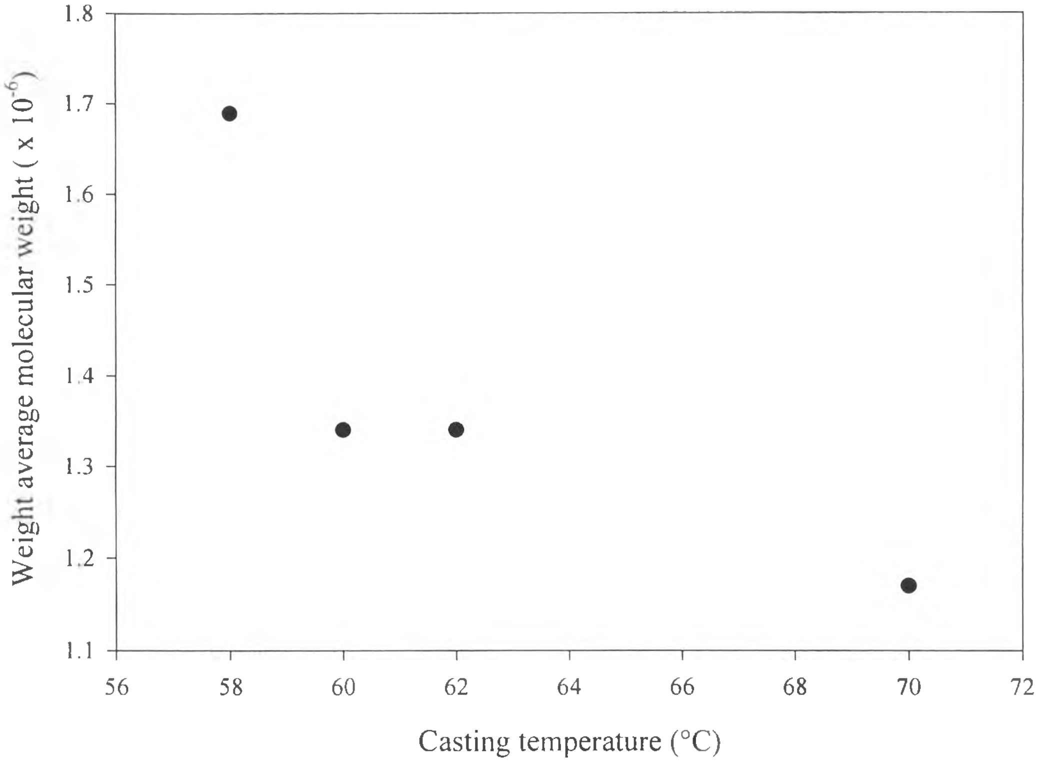


Figure 4.13 Weight average molecular weight ($\overline{M}_w$) of PMMA casted sheet produced by using isothermal temperature profile as a function of reaction temperature.

This phenomenon can be explained that as the amount of initiator increased, the more radical, and also, polymeric radical, will be formed. Since the amount of monomer is equal, the chain length, or molecular weight, of the polymer should be decreased.

Table 4.3 Molecular weight average and molecular weight distribution of PMMA sheets produced by isothermal casting using reaction temperature at 60°C by varying initiator concentrations.

Initiator concentration (wt%)	$\overline{Mn}$	$\overline{Mw}$	MWD
0.019	234571	1889639	8.06
0.038	142047	1389213	9.78
0.076	227627	1096998	4.82

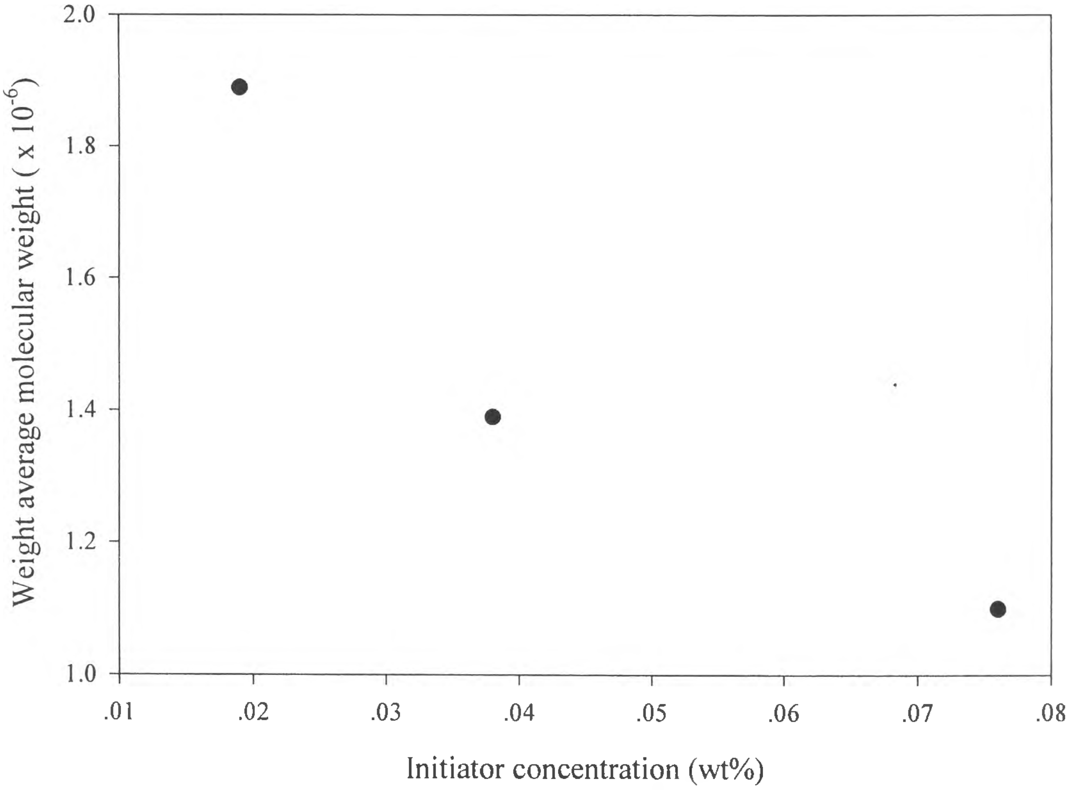


Figure 4.14 Weight average molecular weight ($\overline{M}_w$) of PMMA casted sheet produced by using isothermal temperature profile as a function of initiator concentration.

4.2 Non-Isothermal Methyl Methacrylate Polymerization in Casting Process

As discussed earlier, by using isothermal casting temperature profiles with temperature lower than glass transition temperature of PMMA, maximum conversion of PMMA casted sheets was limited by the gel effect occurring during the reaction.

The needs for high conversion, approximately 100 percent, of the commercial PMMA sheets is very necessary because the residue monomer would contaminate the product.

The calculated curing profiles of PMMA bulk casting initiated by benzoyl peroxide were reported by Ramaseshan *et al.* (1993). An example of that curing profile was shown in figure 4.15.

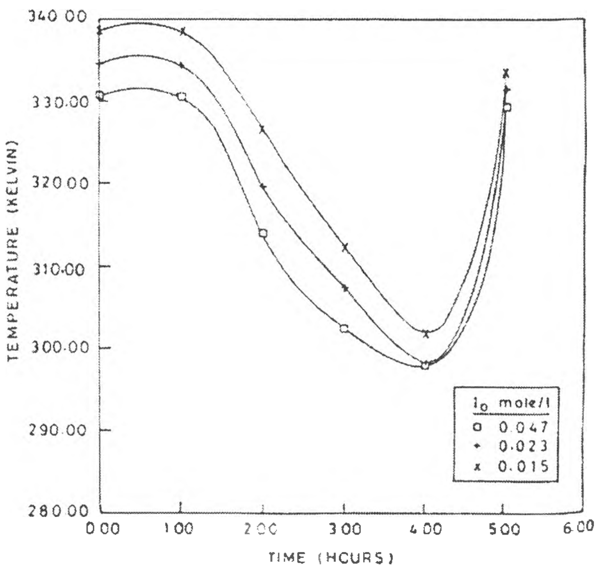


Figure 4.15 Curing profiles for an 8 hr cycle of MMA polymerization with three initiator loadings (Ramaseshan *et al.* (1993)).

The curing profiles, in figure 4.15, showed that at some point of curing process, there was a cooling step in order to reduce large amount of heat dissipated out from the reaction. Then the temperature went up to a higher temperature in order to annealed the PMMA casting.

By this proposed concept, if the temperature profile goes up, at the point that the maximum conversion by isothermal reaction was reached, to a temperature higher than its glass transition temperature, the maximum conversion would be increased.

4.2.1 Monomer Conversion

In this part, the PMMA sheets were casted by two different temperature profiles. Firstly, referred to condition A, the temperature was started at 60°C for 2.5 hours, then the temperature was raised to 120°C for another 1.5 hours. Secondly, condition B, the starting temperature was 62°C for 2.5 hours, then raised to 120°C for another 1.5 hours. So that, the total casting time was 4 hours. A non-isothermal casting temperature profile used in this experiment was shown in figure 4.16.

4.2.1.1 Effect of Temperature Profiles

Monomer conversion of both conditions A and B were determined by the method described in chapter III. The percent conversion as a function of casting temperature was shown in figure 4.17. By increasing the casting temperature after the reaction time of 2.5 hours, the final conversion of both conditions reached almost 100 percent (= 97.6% while blank = 98.6%).

A comparison of monomer conversion of PMMA casted sheets by isothermal condition and condition A was shown in figure 4.18. And also for condition B was shown in figure 4.19.

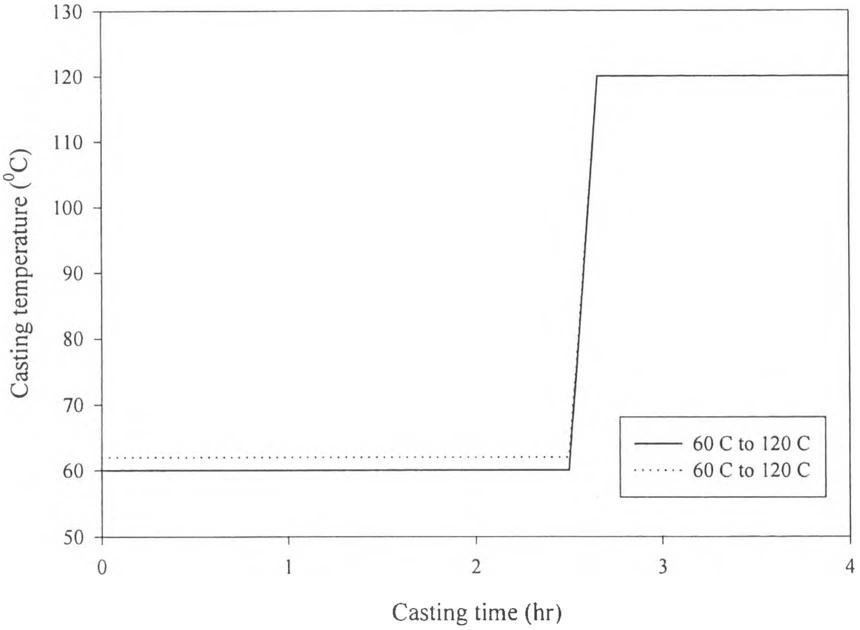


Figure 4.16 Non-isothermal casting temperature profiles.

From figure 4.18 and 4.19, the final conversion of PMMA sheets casted by non-isothermal condition showed higher value when compared to the sheets casted by isothermal condition. It can be concluded that, by increasing temperature in order to anneal the PMMA sheets instantaneously, the monomer conversion of reaction increased.

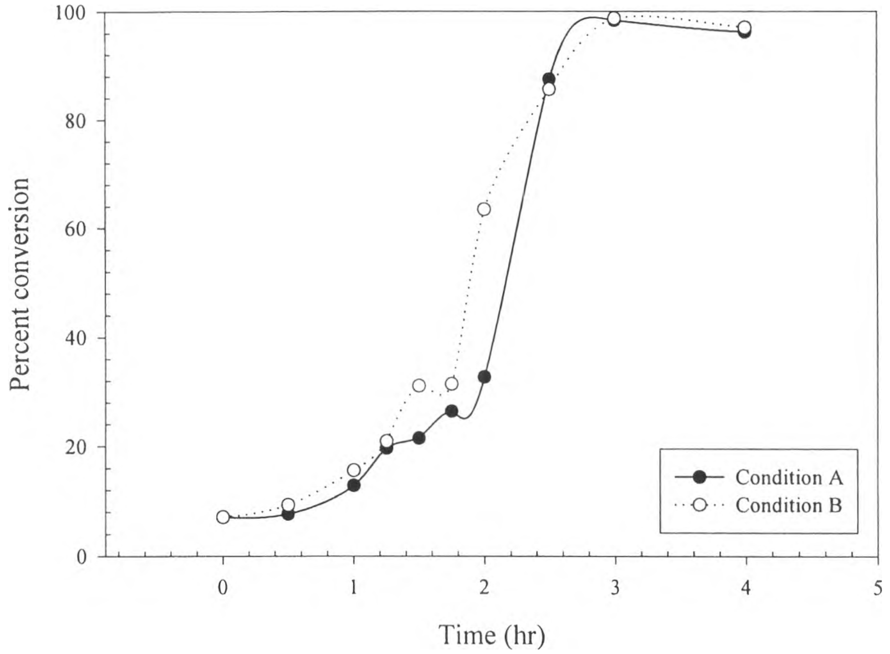


Figure 4.17 Monomer conversion as a function of reaction time of PMMA casted sheet produced by different non-isothermal condition (*A is 60°C for 1.5 hr and 120 °C for 2.5 hr, B is 62°C for 1.5 hr and 120 °C for 2.5 hr).

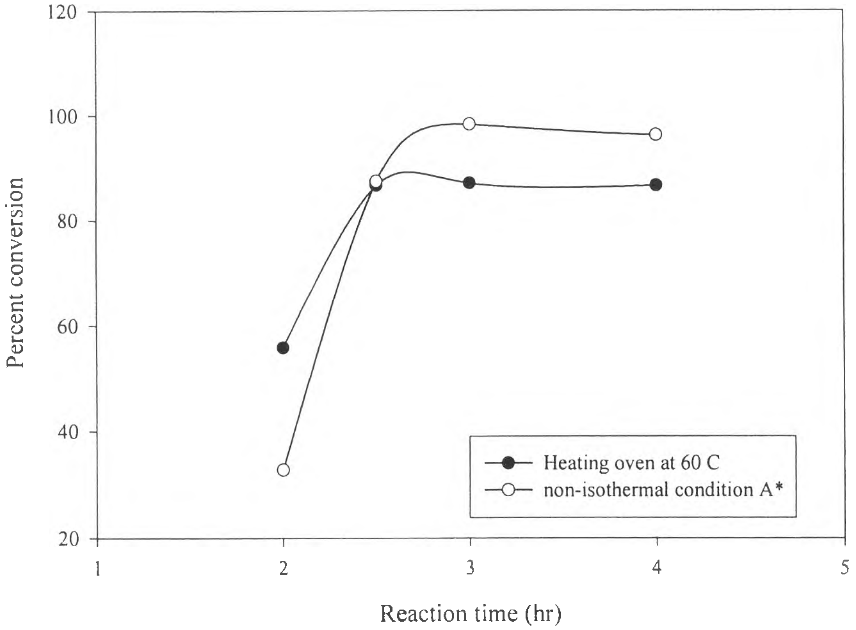


Figure 4.18 Monomer conversion as a function of reaction time of PMMA casted sheet produced by isothermal condition at 60°C and non-isothermal condition A (*A is 60°C for 2.5 hr and 120 °C for 1.5 hr).

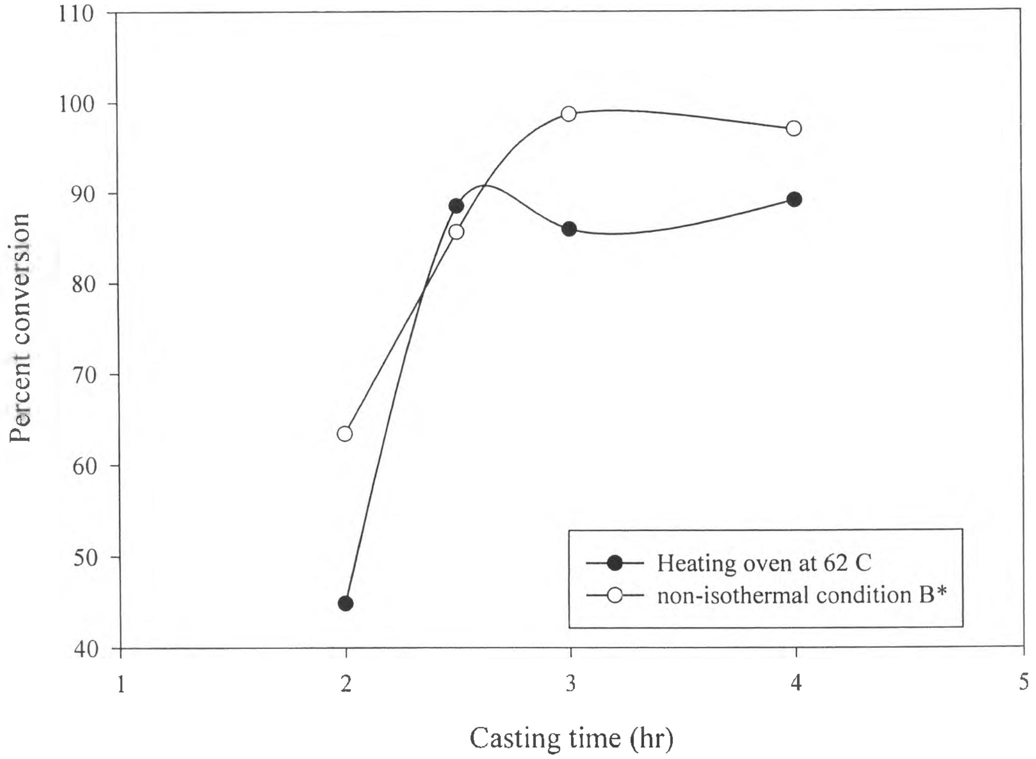


Figure 4.19 Monomer conversion as a function of reaction time of PMMA casted sheet produced by isothermal condition at 60°C and non-isothermal condition B (*B is 62°C for 2.5 hr and 120 °C for 1.5 hr).

4.2.2 Mechanical Properties of Poly(Methyl Methacrylate) Casted Sheet

4.2.2.1 Impact Resistance

It is expecting that if the conversion of PMMA sheets is nearly 100 percent, PMMA sheets should have more brittleness. As a result, impact resistance would be decreased as well.

A relationship between impact resistance to the casting time produced by condition A and B is shown in figure 4.20 and 4.21 respectively. By this relationship, the optimum casting time for the lowest impact resistance (highest conversion) could be determined.

From figure 4.20, impact resistance was decreased at casting time from 2.5 to 3.0 hours, then became steady at 19 J/m. It was the same trend in figure 4.21 and the final impact resistance was 21 J/m.

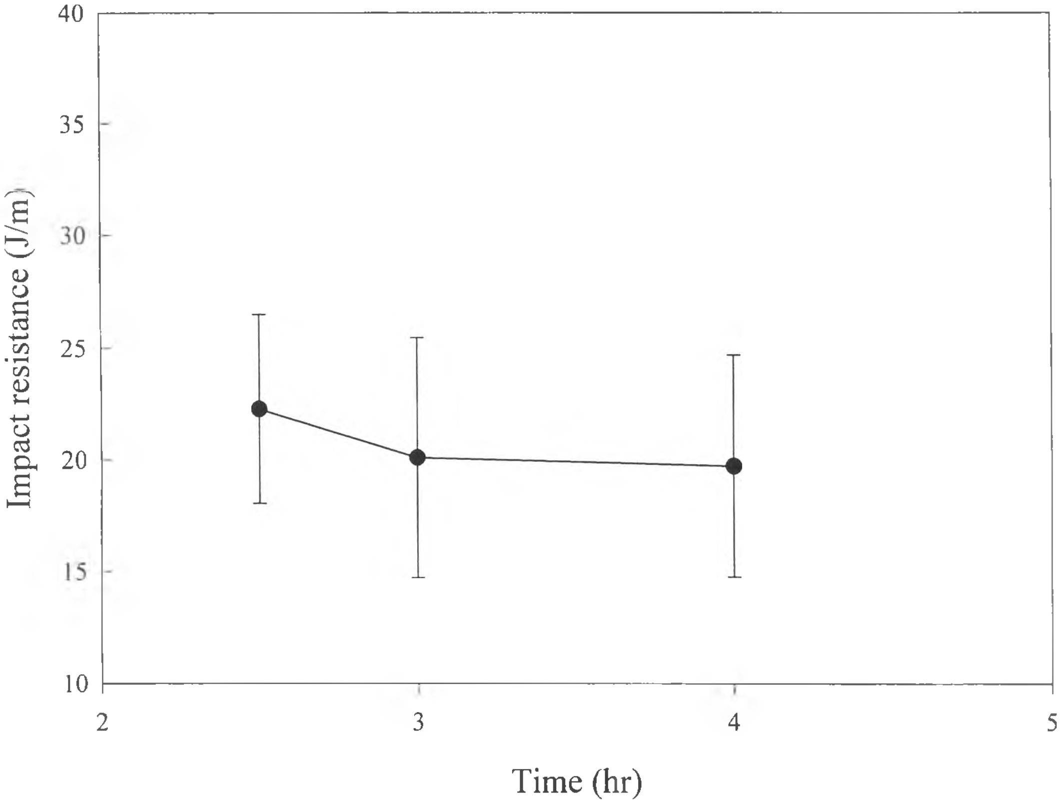


Figure 4.20 Impact resistance of PMMA casted sheet produced by using non-isothermal casting condition A as a function of reaction time(*A is 60°C for 2.5 hr and 120 °C for 1.5 hr).

A comparison of PMMA sheets produced by conditions A, B and blank sample is shown in figure 4.22. Impact resistance of blank sample showed the highest value at 22 J/m. However, the values from all conditions were not significantly different.

Therefore, it can be concluded that, by using non-isothermal casting temperature profiles, impact resistance of PMMA sheets produced by both conditions A and B were shown approximately equal values to blank samples.

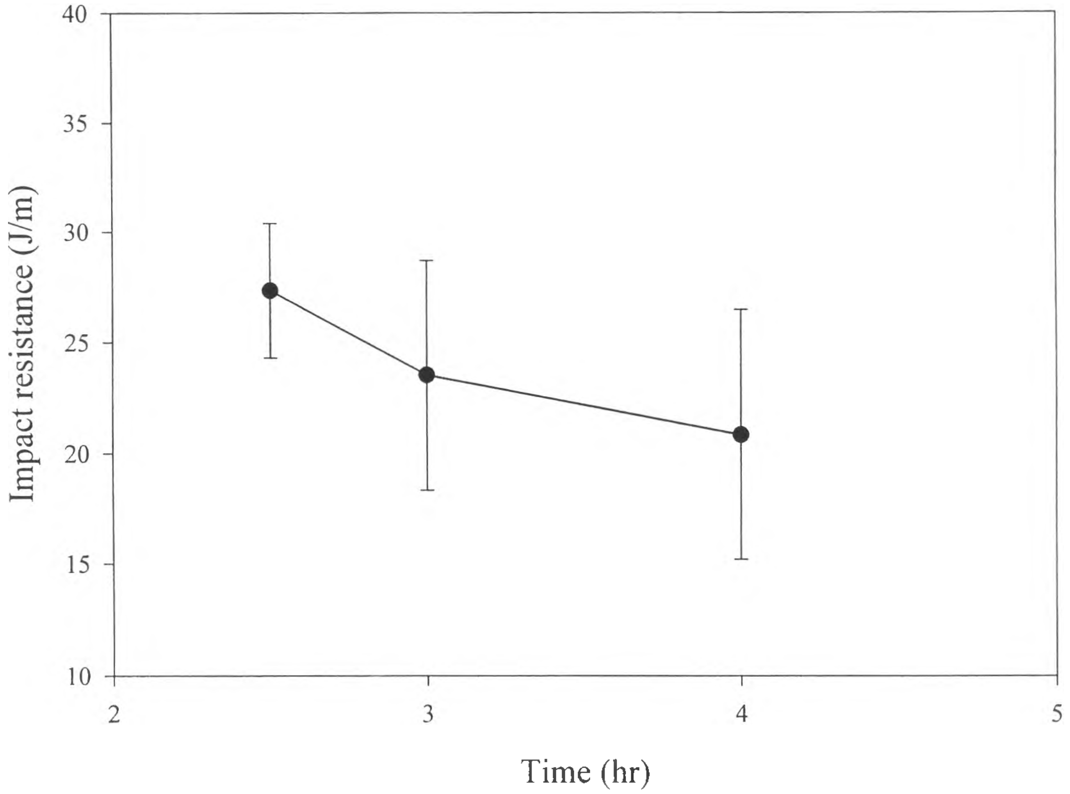


Figure 4.21 Impact resistance of PMMA casted sheet produced by using non-isothermal casting condition B as a function of reaction time(*B is 62°C for 2.5 hr and 120 °C for 1.5 hr).

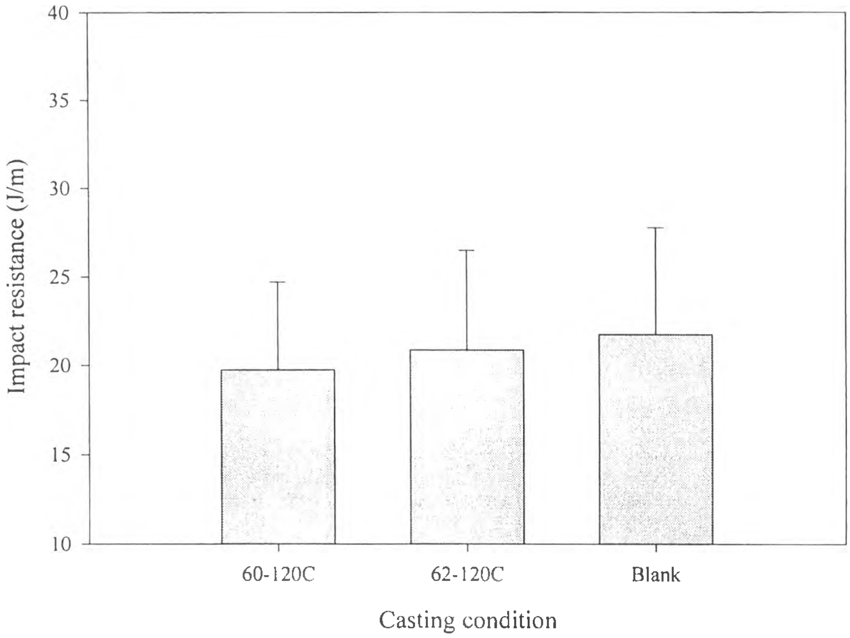


Figure 4.22 Impact resistance of PMMA casted sheet produced by various non-isothermal casting condition.

4.2.2.2 Surface Hardness

A relationship between surface hardness and casting time of PMMA sheets produced by conditions A and B is shown in figure 2.23 and 2.24, respectively.

As discussed earlier, monomer conversion of PMMA casting, by using non-isothermal temperature profile, reached the maximum value when the reaction time was 3 hours. The surface hardness also followed this phenomenon. The surface hardness of PMMA sheets by using non-isothermal casting temperature profiles showed the increasing value from casting time at 2.5 to 3 hours then became stable at the casting time about 3 to 4 hours. The maximum surface hardness of both PMMA sheets produced by condition A and B was 94 shore D unit.

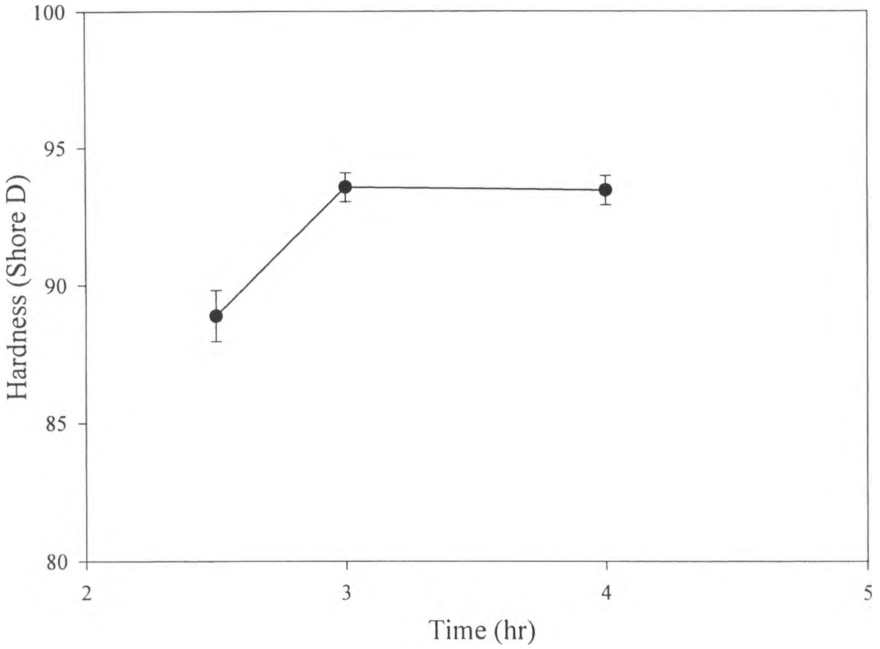


Figure 4.23 Surface hardness of PMMA casted sheet produced by using non-isothermal casting condition A as a function of reaction time (*A is 60°C for 2.5 hr and 120 °C for 1.5 hr).

A comparison between surface hardness of PMMA sheets produced by non-isothermal temperature profiles and of blank sample was shown in figure 4.25. The surface hardness of both sheets produced from condition A and B were slightly lower than blank sample, with a value of 95 shore D unit.

It was shown that, by casting PMMA sheets using non-isothermal temperature profiles, the surface hardness of PMMA sheets was approximately equal to that of the commercial PMMA sheets.

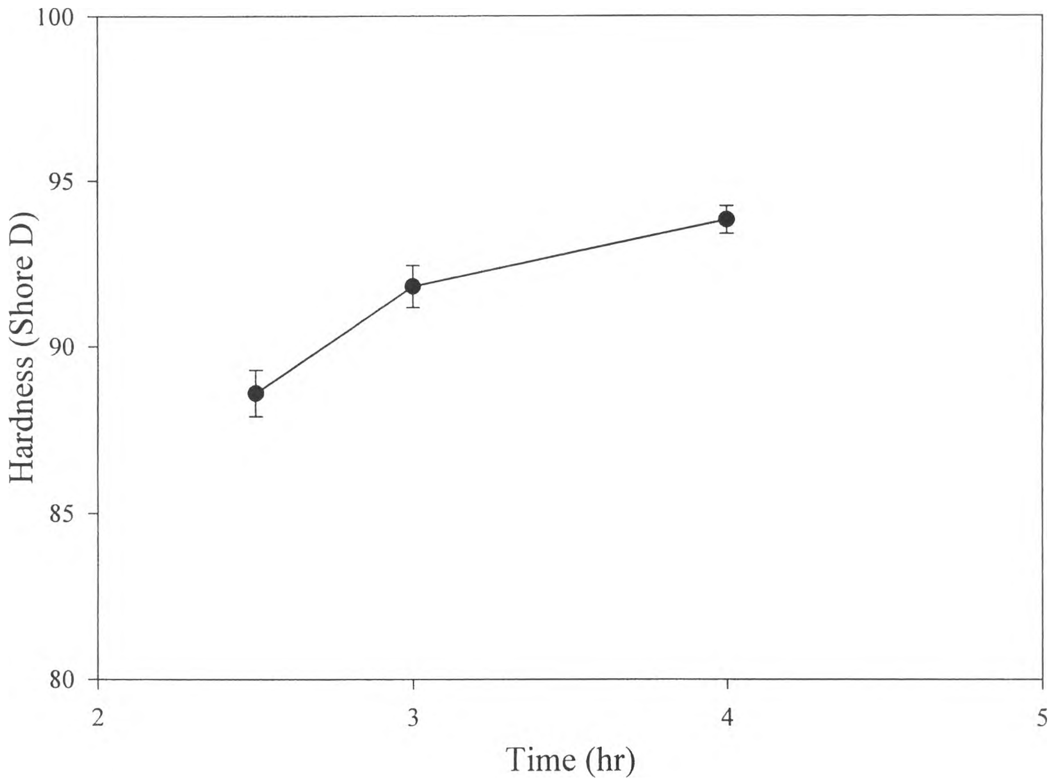


Figure 4.24 Surface hardness of PMMA casted sheet produced by using non-isothermal casting condition B as a function of reaction time (*B is 62°C for 2.5 hr and 120 °C for 1.5 hr).

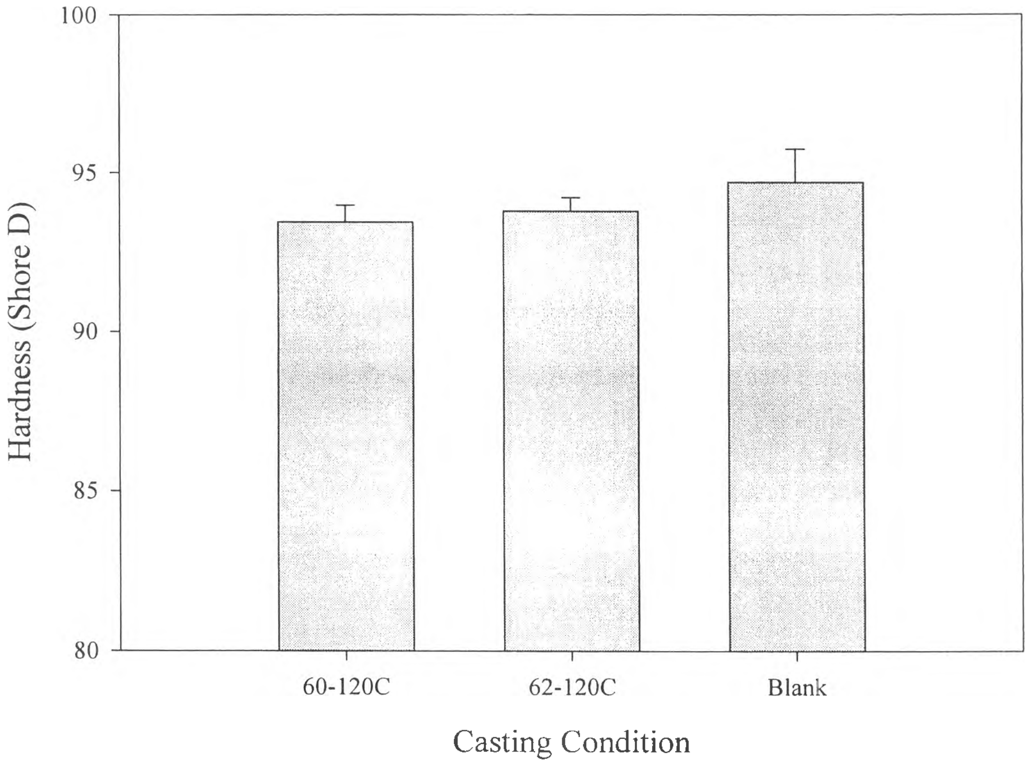


Figure 4.25 Surface hardness of PMMA casted sheet produced by various non-isothermal casting conditions.

4.2.3 Molecular Weight Average and Molecular Weight Distribution of PMMA Sheets

Molecular weight average ($\overline{M}_n$ and $\overline{M}_w$) and MWD of PMMA sheets produced by non-isothermal casting temperature profiles, condition A and B, were listed in Table 4.4 and 4.5, respectively. As the casting time increased, molecular weight of PMMA of both conditions, A and B, were very high ($> 10^6$), equaling the sheets produced from isothermal process, and did not change much. The MWD was also very high for both conditions.

It can be concluded that, by using non-isothermal temperature profiles, molecular weight average and molecular weight distribution of PMMA sheets were independent on the casting time.

Table 4.4 Molecular weight average and molecular weight distribution of PMMA sheets produced by non-isothermal casting using reaction temperature at 60°C for 2.5 hr and 120°C for 1.5 hr.

Reaction time (hr)	$\overline{M}_n$	$\overline{M}_w$	MWD
2.5	397157	1712079	4.31
3.0	231146	1425971	6.17
4.0	210928	1534410	7.27

Table 4.5 Molecular weight average and molecular weight distribution of PMMA sheets produced by non-isothermal casting using reaction temperature at 62°C for 2.5 hr and 120°C for 1.5 hr.

Reaction time (hr)	$\overline{M}_n$	$\overline{M}_w$	MWD
2.5	171939	1567709	9.12
3.0	211655	1325984	6.26
4.0	184841	1445956	7.82

Molecular weight average ($\overline{M}_n$ and $\overline{M}_w$) and MWD of PMMA sheets produced by non-isothermal casting temperature profiles, conditions A and B, and of blank sample were listed in table 4.6. All of the molecular weight average and MWD of PMMA sheets from both conditions A and B were approximately equal to blank sample.

It can be summarized that, the high temperature step in non-isothermal casting temperature profiles did not affect the molecular weight average and MWD of PMMA sheets.

Table 4.6 Molecular weight average and molecular weight distribution of PMMA sheets produced by non-isothermal casting temperature at 4 hr and of blank sample (*A is 60°C for 2.5 hr and 120 °C for 1.5 hr, B is B is 62°C for 2.5 hr and 120 °C for 1.5 hr, and blank sample is the commercial PMMA sheets).

Condition	$\overline{M}_n$	$\overline{M}_w$	MWD
Condition A	210928	1534410	7.27
Condition B	184841	1445956	7.82
Blank sample	218394	1496945	6.85

4.3 Observed Product Defects

During the reaction or casting process, some of the defects in the final PMMA sheet may occur. Some occur by means of physical change of the PMMA sheet in the mold, some occur by means of the strong chemical reaction and unsuitable recipe.

Whether it occurs by physical or chemical means, the defects are completely unwanted. Examples of the defects are discussed below.

4.3.1 Uneven Surface

Sometimes there may be some uneven surface of PMMA sheet even in the commercial product or in this experiment. The reason of uneven surface was the air flow into the mold. There are many points that can cause leakage of the mold, for example, uneven surface and irregular shape of glass mold, unsuitable clamp pressure, and the lost of toughness of the spacer made of poly (vinyl chloride) (PVC) due to degradation of that spacer. A schematic drawing of uneven surface of PMMA sheet is shown in figure 4.26.

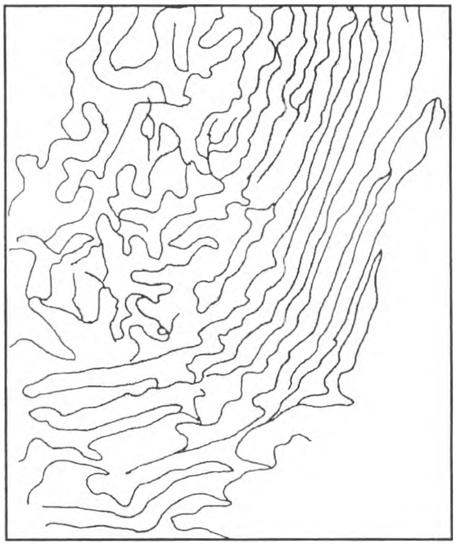
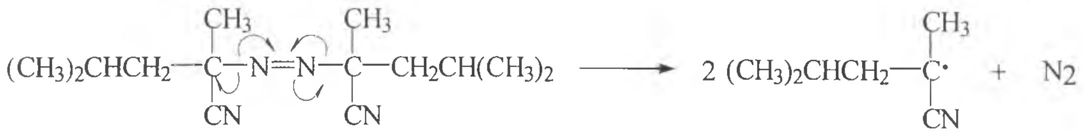


Figure 4.26 Schematic drawing of surface defect of PMMA sheets observed during experiment.

4.3.2 Voids Occurring in PMMA Sheet

There are many causes of voids occurring in PMMA sheet. For example, air trapped inside the mold during mold installation step, when, either a high amount of initiator or temperature is used. By the nature of initiator used in this experiment, which is ADVN, it can release some nitrogen gas (N_2) during reaction. If the suitable initiator loading or temperature is used, N_2 will slowly occur and moved to the edge of the sheet, then the voids will not be formed. In case of high initiator loading, it might increase the amount of N_2 that will be released, then N_2 can not move to the edge and will be stuck inside the sheet due to the gel occurring. By using high temperature, the gel will occur faster, and then N_2 released cannot move to the edge as well. A mechanism of N_2 releasing from the degradation of ADVN is shown in Figure 4.27.



$$(CH_3)_2CHCH_2-\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}-CH_2CH(CH_3)_2 \longrightarrow 2\ (CH_3)_2CHCH_2-\overset{CH_3}{\underset{CN}{C}}\cdot + N_2$$

ADVN

Figure 4.27 The degradation of 2,2'-Azobis-(2,4-dimethyl Valeronitrile) (ADVN).