

Sheet-cast Poly(methyl methacrylate): One-step (Water) versus Two-step (Water-Air) Isothermal Processes

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Received 11 January 2004; accepted 12 July 2004

ABSTRACT

One-step and two-step isothermal sheet-casting processes for producing poly(methyl methacrylate) (PMMA) sheets, based primarily on water and water-air systems, were studied and compared. The main objectives were: (1) to assess the optimal production time for each system in producing 3-mm thick PMMA sheets at various process conditions and (2) to assess and compare the quality of the PMMA sheets obtained in terms of their mechanical integrity. It was found that the mechanical integrity of the PMMA sheets prepared by the two-step (water-air) isothermal process was much better than those prepared by the one-step (water) isothermal process, a direct result of the much higher ultimate percentage of monomer conversion.

Key Words:

poly(methyl methacrylate);
sheet-casting process;
isothermal process;
mechanical properties.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) in the sheet form is usually manufactured in a wide variety of types i.e., transparent, translucent, coloured, semi-opaque, and opaque. Applications for these products are, for examples, toys, rulers, commercial

billboards and displays, and safety glasses. Commercial production of PMMA sheets can be carried out by one of the three processes: (1) sheet- or cell-casting, either a batch or continuous bulk polymerization process, (2) melt-calendering, and (3) melt-

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extrusion. Among these, sheet-casting is the most popular process due to its flexibility in producing PMMA sheets with diverse physical characteristics. Generally, a batch, sheet-casting process can be divided into three steps [1]: (1) pre-polymerization, (2) polymerization, and (3) annealing.

After the pre-polymerization step, pre-polymer or syrup is filled in a glass mould, assembled from two-tempered glass sheets using a poly(vinyl alcohol) (PVA) or poly(vinyl chloride) (PVC) cord as a spacing gasket. In the polymerization step, the filled glass mould is then heated in order for the syrup to continue to polymerize. Once the polymerization reaction reaches a point where the average molecular weights are high enough such that the glass transition temperature, T_g , of the PMMA molecules is greater than the reaction temperature, the rate of chain propagation reduces appreciably. In order to further the reaction or to achieve higher monomer conversion, the moulding needs to be annealed further at a temperature greater than the T_g of PMMA molecules.

The sheet-casting process used to produce PMMA sheets at the Pan Asia Industrial factory (hereafter called Pan Asia) was essentially similar to the traditional process mentioned above. However, only the polymerization and the annealing steps were of our prime concern in this contribution, simply because these two steps take up most of the total production time. Even though the heating source used in both steps was boiler-generated steam, the heat transferring medium used in each step is totally different (i.e., water in the polymerization step and air in the annealing step). In order to optimize the total production time, it is necessary to investigate each of these two steps in detail. From this point forward, one-step (water) isothermal and two-step (water-air) isothermal processes are referred to polymerization step and polymerization-annealing steps, respectively.

Studies related to bulk polymerization of methyl methacrylate (MMA) are not at all new. Effects of 2,2'-azobis-isobutyronitrile (AIBN) and reaction temperature on conversion and molecular weight averages of bulk-polymerized PMMA were investigated by Balke and Hamielec [2]. Irrespective of the amount of AIBN used, the limiting conversion was found to depend on the reaction temperature (i.e., it was ca. 85% at 50°C, ca. 91% at 70°C, and ca. 95% at 90°C, respectively [2]). Gupta and his co-workers [3] developed a theory accounting the cage, gel, and glass effects during

isothermal bulk and solution polymerization of MMA in a batch reactor and later [4] theory was applied to predict the evolution of the conversion during bulk and solution polymerization of MMA using benzoyl peroxide (BPO) as the initiator in response to step changes in the reaction temperature. Rhee and his co-workers [5] derived a mathematical model describing the polymerization of MMA in a batch reactor. The model included chain transfer effect of both the monomer and the solvent and the termination by both the combination and disproportionation reactions as well as changes in the density of the contents in the reactor and the gel effect.

To our knowledge, Raghunathan and his co-workers [6] were the first to describe the commercial casting process of MMA using BPO as the initiator, which involves an isothermal batch reactor followed by further polymerization in a sheet reactor (i.e., a mould). They concluded that casting of thin sheets had to be carried out at relatively low temperatures and over extended periods of time at a constant rate and that no advantage was gained through the use of the two-stage initiator loading. A more thorough modelling of the sheet-moulding process of PMMA using AIBN as the initiator was recently published by Ray and his co-workers [7]. In addition to the cage, gel, and glass effects, the model also dealt with the effect of heat transfer occurring at the outer boundaries of the sheet reactor. With the use of the model, the effects of wall temperature, initiator loading, and thickness of the sheet reactor (i.e., the mould thickness) on the evolution of the temperature, monomer conversion, number-average molecular weight, and the degree of polydispersity as a function of time and mould thickness were demonstrated.

Despite these many significant contributions, there have not been prior studies on the effects of initiator concentration and polymerization temperature on temperature-time profile, dynamic and ultimate percentage of monomer conversion, ultimate average molecular weights, optimal production time and mechanical properties of PMMA sheets prepared by the one-step and the two-step isothermal sheet-casting processes that have been thoroughly investigated in this contribution.

EXPERIMENTAL

Methyl methacrylate (MMA, boiling point $\approx 100^\circ\text{C}$

[28]) was first pre-polymerized using 2,2'-azobisisobutyronitrile (AIBN) as initiator in a hot reactor to obtain syrup having the percentage of monomer conversion of ca. 7 to 10%. The amount of AIBN used was ca. 18 ppm. The syrup was later cooled down to room temperature and transferred to a mixing container, where it was mixed with another type of initiator, 2,2'-azobis-(2,4-dimethyl valeronitrile) (ADV N). The amount of ADV N used was either 0.030 or 0.038 wt.%. The well-mixed syrup was then filtered, degassed, and poured into a glass mould (i.e., assembled from two-tempered glasses using a PVC cord as the spacing gasket). In one-step (water) isothermal process, the moulding was polymerized in water at 60, 62, 65, 68, or 70°C. In two-step (water-air) isothermal process, the moulding was first polymerized in water at 60, 63, or 65°C, and then annealed in air at 105, 115, or 125°C. The total observation time for both processes was fixed at 4h.

Evolution of the temperature-time curve for each sample was monitored by thermocouples embedded within the sample. Gravimetric method was used to determine both dynamic and ultimate percentage of monomer conversion for each sample. Specifically, 5 g of liquid sample or a 3 10 15 mm³ solid sample was first dissolved in 30 mL of acetone (99.5% purity, Labscan Asia Co., Ltd., Thailand) at room temperature for at least 24 h. A volume of 70 mL of methanol (99.8% purity, Labscan Asia Co., Ltd., Thailand) was then added to precipitate out PMMA while leaving unreacted MMA (including, perhaps, oligo-MMA) in the clear solution. The precipitated PMMA was then put in a vacuum oven for 6 h to remove both acetone and methanol. The percentage of monomer conversion of each sample can then be calculated according to eqn (1):

$$\text{Monomer conversion (\%)} = \frac{W_2 \times 100}{W_1} \quad (1)$$

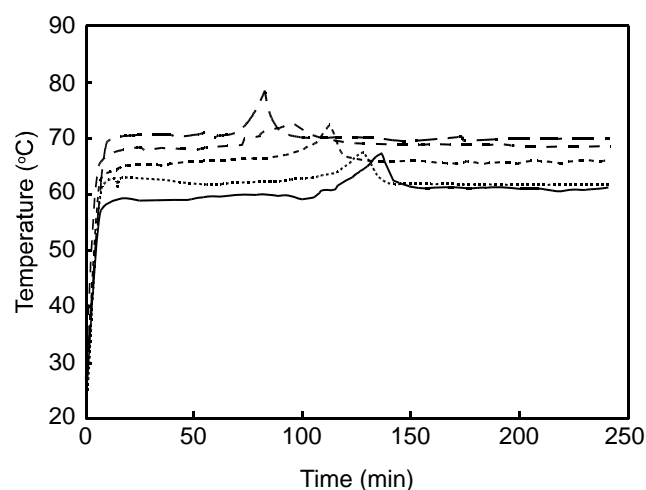
where W_1 and W_2 are, respectively, the dry weights of sample before and after the precipitation procedure. The average molecular weights of some selected samples were determined by gel permeation chromatography (GPC) technique (Waters 150-CV GPC, with the molecular weight resolving range of 500 to 10⁷ Da). Surface hardness (shore D) and unnotched impact resistance of some selected samples were measured by a Zwick 3100 durometer and a Zwick 5113 pendulum impact tester, respectively.

RESULTS AND DISCUSSION

One-Step (Water) Isothermal Process

The MMA syrup was prepared by mixing MMA monomer (containing 10 ppm of an inhibitor) with 18ppm of AIBN in a batch reactor. The mixture was polymerized with vigorous stirring at a reaction temperature of ca. 80°C for 30 min. The obtained MMA syrup had the percentage of monomer conversion in the range of 7 to 10% and the measured viscosity of ca. 245cP at 25°C. The syrup, after it was cooled down to room temperature, was mixed again with ADVN at a composition ratio of either 0.030 or 0.038 wt.% in a mixing tank. After the syrup was well-mixed, it was degassed and was later poured into a glass mould (with the cavity thickness of 3 mm). The polymerization temperatures were 60, 62, 65, 68, and 70°C, respectively, and the total observation time was fixed at 4 h. Water was used as the heat transfer medium. Thermocouples were embedded at the half-thickness position in each sample to monitor the temperature-time profile of the sample.

Figure 1 shows temperature-time profiles for samples polymerized at the polymerization temperatures of 60, 62, 65, 68, and 70°C, respectively, using 0.038 wt.% ADVN. Monitoring of the sample temperature was started as soon as the samples were submerged in water, of which temperature varied in the range between 60 and 70°C. Obviously, as soon as the sam-



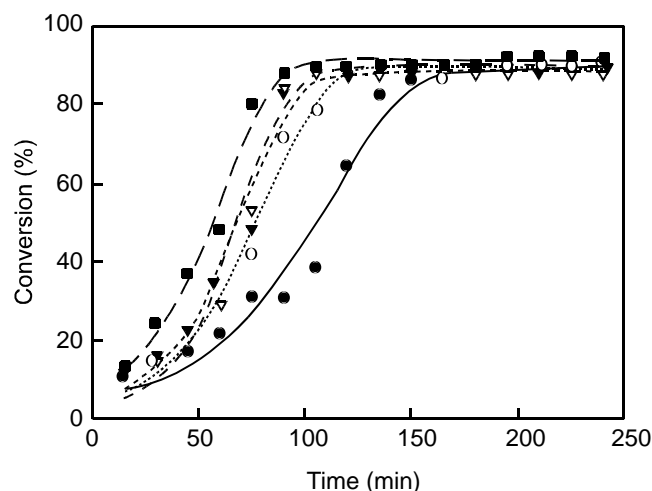
(—) 3W-0038-60; (---) 3W-0038-62; (---) 3W-0038-62; (—) 3W-0038-68; (—) 3W-0038-70.

Figure 1. Temperature-time profile for samples polymerized at 60, 62, 65, 68, and 70°C using 0.038 wt.% ADVN.

ples were submerged in warm water, it took around 15 min for the temperature of the samples to increase from the ambient temperature (i.e., ca. 25°C) to reach the preset polymerization temperature. The temperature of the samples remained pretty much constant for a certain period of time (depending on the reaction temperature considered), before it began to increase, reached a maximum, and then decreased to and remained at the polymerization temperature for the rest of the observation period. It is observed that the difference between the peak and the polymerization temperatures was as much as ca. 8°C and that the higher the reaction temperature is, the earlier the exothermic peak occurs. The increase in the sample temperature from the polymerization temperature is a direct result of the exothermic nature of the polymerization reaction of MMA and, because of this rising in the sample temperature during processing, careful monitoring of the sample temperature is necessary to prevent the unreacted MMA to boil (which is the main cause for the bubbling defects observed in the finished product).

Though not shown, the data obtained for samples polymerized using 0.030 wt.% ADVN also exhibited a behaviour similar to what has been described here. Comparison between the results obtained for samples polymerized using 0.030 and 0.038 wt.% ADVN suggests, as so expected, that the position of the exothermic peak for samples polymerized using 0.038 wt.% ADVN occurred earlier than that for samples polymerized using 0.030 wt.% ADVN (for a given polymerization temperature). According to this observation, it is logical to postulate that the polymerization rate increases with increasing amount of ADVN used.

Plots of the percentage of monomer conversion as a function of observation time for samples polymerized



(—) 3W-0038-60; (---) 3W-0038-62; (- - -) 3W-0038-62; (—) 3W-0038-68; (—) 3W-0038-70.

Figure 2. Percentage of monomer conversion as a function of time for samples polymerized at 60, 62, 65, 68, and 70°C using 0.038 wt.% ADVN.

at 60, 62, 65, 68, and 70°C, respectively, using 0.038 wt.% ADVN are illustrated in Figure 2. It is apparent that, as soon as the samples were submerged in warm water, the percentage of monomer conversion increased steadily with time from the initial value of ca. 7 to 10% to the ultimate percentage of monomer conversion of ca. 87 to 90% (Table 1) and that the observed reaction time decreased with an increase in the polymerization temperature used. Though not shown, the data obtained for samples polymerized with 0.030 wt.% ADVN also exhibited a similar trend. The ultimate percentage of monomer conversion of ca. 87 to 90% was in general accord with the results observed by Balke and Hamielec [2], who found that at 70°C the ultimate percentage of monomer conversion was found to be ca. 91%. The main reason for the ultimate percentage of

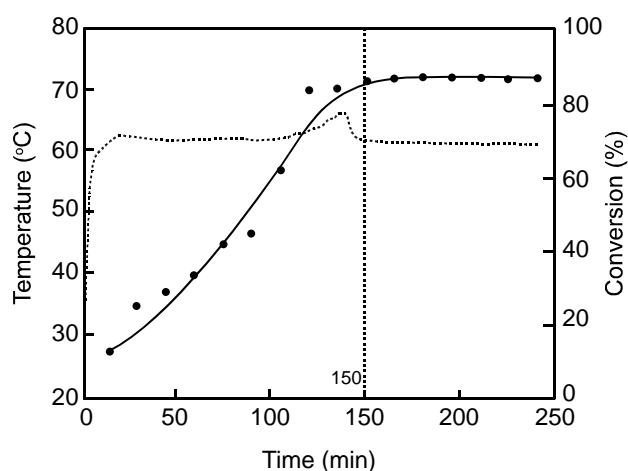
Table 1. Ultimate percentage of monomer conversion and optimal production time for PMMA sheet samples polymerized in the one-step (water) process at 60, 62, 65, 68, and 70°C, respectively, using either 0.030 or 0.038 wt.% ADVN.

Temperature scheme	Monomer conversion (%)		Production time (min)	
	ADVN, 0.030 (wt %)	ADVN, 0.038 (wt %)	ADVN, 0.030 (wt %)	ADVN, 0.038 (wt %)
60	89.7 ± 2.8	87.8 ± 0.8	176 ± 6	150 ± 5
62	86.6 ± 1.1	89.1 ± 2.6	147 ± 7	139 ± 6
65	87.7 ± 1.1	87.9 ± 1.3	124 ± 5	124 ± 6
68	89.1 ± 0.8	87.9 ± 2.0	117 ± 8	113 ± 8
70	89.7 ± 1.9	90.3 ± 2.1	107 ± 6	95 ± 7

monomer conversion for samples prepared in the one-step process being only in the range of 87 to 90% is because the glass transition temperature, T_g , of PMMA (i.e., ca. 105°C [9]) is much higher than the polymerization temperature used. Further annealing at a higher temperature is necessary to achieve higher ultimate percentages of monomer conversion.

Raghunathan and his co-workers [6] suggested that the optimal production time could be estimated from a temperature-time profile recorded during the course of polymerization by taking it to be the time interval to reach the maximum of the exothermic peak. Even though this approach may be reasonable, but, without a direct comparison with the percentage of monomer conversion data, it is unrealistic to conclude as such. Figure 3 shows the overlay plots of the temperature-time profile and the percentage of monomer conversion for samples polymerized at 62°C using 0.030 wt.% ADVN. According to the data shown, the ultimate percentage of monomer conversion was reached after a drop-off in the temperature of the sample from the exothermic peak. This experimental fact helps the determination of the optimal production time for the one-step process to be as convenient as a reading from the temperature-time profile data, instead of going through the cumbersome of obtaining the percentage of monomer conversion data, which has been proven to be very time-consuming (Figure 3).

Table 1 summarizes the ultimate percentage of



(---) Temperature (°C); (—) Conversion (%).

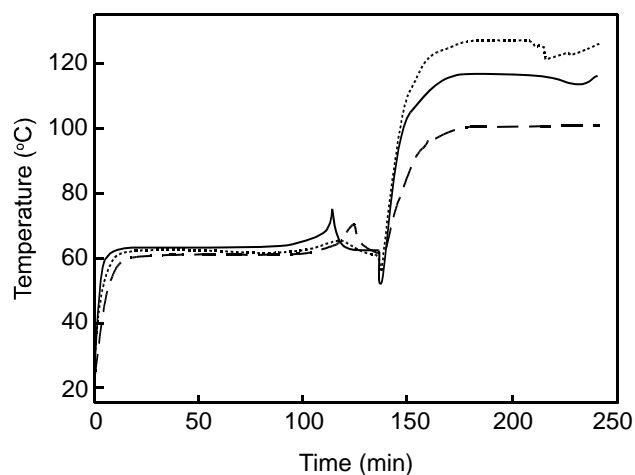
Figure 3. Overlay plot of temperature-time profile and percentage of monomer conversion for samples polymerized at 62°C using 0.030 wt.% ADVN.

monomer conversion and the optimal production time (determined from the procedure such as that shown in Figure 3) for samples polymerized in the one-step (water) process at 60, 62, 65, 68, and 70°C, respectively, using either 0.030 or 0.038 wt.% ADVN, respectively. Specifically, the ultimate percentage of monomer conversion for samples polymerized using 0.030 wt.% ADVN was found to be in the range of ca. 87 to 90%, while that for samples polymerized using 0.038 wt.% ADVN was in the range of ca. 88 to 90%. From the results obtained, there is no obvious correlation between the polymerization temperature used and the ultimate percentage of monomer conversion obtained. On the contrary, the optimal production time for samples polymerized using 0.030 wt.% ADVN was found to decrease monotonically from 176 min at the polymerization temperature of 60°C to 107 min at 70°C on average, while that for samples polymerized using 0.038 wt.% ADVN was found to decrease monotonically from 150 min at 60°C to 95 min at 70°C on average.

Two-Step (Water-Air) Isothermal Process

The as-prepared MMA syrup (% monomer conversion ≈ 7 to 10% and viscosity ≈ 245 centipoise at 25°C), after it was mixed with ADVN at a compositional ratio of either 0.030 or 0.038 wt.%, was degassed and later poured into a glass mould having the cavity thickness of 3 mm. The polymerization step was carried out at temperatures of 60, 63, and 65°C, respectively, using water as the heat transfer medium. The optimal production time for this step was determined according to the method already described in the previous section after the polymerization step was considered complete, the samples were immediately transferred to a hot-air oven, the temperatures of which were set at 105, 115, and 125°C, respectively, in order to allow the polymerization reaction to further occur (by raising the sample temperature above the T_g of PMMA). The total observation time for both polymerization and annealing steps was, again, 4 h, during which both the temperature-time profile and the percentage of monomer conversion as a function of observation time for each sample were recorded for further analysis.

Figure 4 shows the temperature-time profile of samples polymerized in different temperature schemes (e.g., 63-105, 63-115, and 63-125°C) using 0.038 wt.% ADVN. Discrepancy in the temperature-time profile



(--) 3W-0038-63105; (—) 3W-0038-63115; (···) 3W-0038-63125.

Figure 4. Temperature-time profile for samples polymerized in different temperature schemes (e.g., 63-105, 63-115, and 63-125°C) using 0.038 wt.% ADVN.

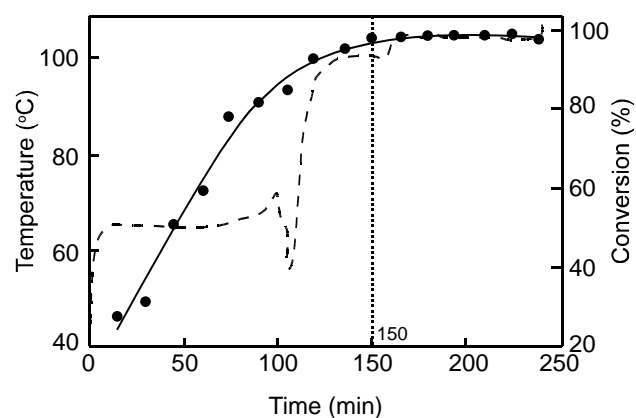
during polymerization step among the three curves is evident. This may attribute to the differences in the initial percentage of monomer conversion of the syrup, the exact position of the thermocouples relative to one another, etc. However, the discrepancy is well within the experimental error (Table 1). After the polymerization step, the samples were transferred to a hot-air oven, of which temperature was set at ca. 105, 115, and 125°C, respectively, in order to anneal further. As soon as the samples were transferred to the hot-air oven, it took around 30 min for the temperature of the samples to gradually increase to the pre-set annealing temperature. The transfer of a sample from the warm-water bath to the hot-air oven took around 5 min on average. Naturally, during 5 min in air, the temperature of the sample had to decrease and it would increase again when the sample was completely transferred to the hot-air oven. A sudden drop in the temperature-time profile was, therefore, a result of the exclusion of the data collected during the transfer period.

The temperature-time profile and the percentage of monomer conversion for samples polymerized in the 65-105°C temperature scheme using 0.038 wt.% ADVN are plotted side by side in Figure 5. According to the data shown, the ultimate percentage of monomer conversion of ca. 98% was achieved soon after the temperature of the samples reached the pre-set annealing temperature (Table 2). For this particular process condition, the optimal production time was ca. 150 min.

Similar to the case of the one-step process, the experimental fact enables the determination of the optimal production time for the two-step process to be as easy as a reading from the much-easier-to-obtain temperature-time profile data, rather than from the time-consuming percentage of monomer conversion data.

Table 2 summarizes the ultimate percentage of monomer conversion and the optimal production time (determined from the procedure such as that shown in Figure 5) for samples polymerized in different indicated temperature schemes using either 0.030 or 0.038 wt.% ADVN, respectively. Specifically, the ultimate percentage of monomer conversion for samples polymerized using 0.030 wt.% ADVN was found to be in the range of ca. 95 to 99%, while that for samples polymerized using 0.038 wt.% ADVN was in the range of ca. 96 to 99%. From the results obtained, there is no significant correlation between the temperature scheme used and the ultimate percentage of monomer conversion observed. The optimal production time for samples polymerized using 0.030 wt.% ADVN was found to decrease monotonically from 200 min for the temperature schemes of 60-105, 60-115, and 60-125°C to 130 min for the temperature scheme of 68-125°C, while that for samples polymerized using 0.038 wt.% ADVN was found to decrease monotonically from 190 min for the temperature schemes of 60-105, 60-115, and 60-125°C to 120 min for the temperature scheme of 68-125°C.

It has been hypothesized that the reason for the ultimate percentage of monomer conversion for samples



(···) Temperature (°C); (—) Conversion (%).

Figure 5. Overlay plot of temperature-time profile and percentage of monomer conversion for the sample polymerized at 65-105°C temperature scheme using 0.038 wt.% ADVN.

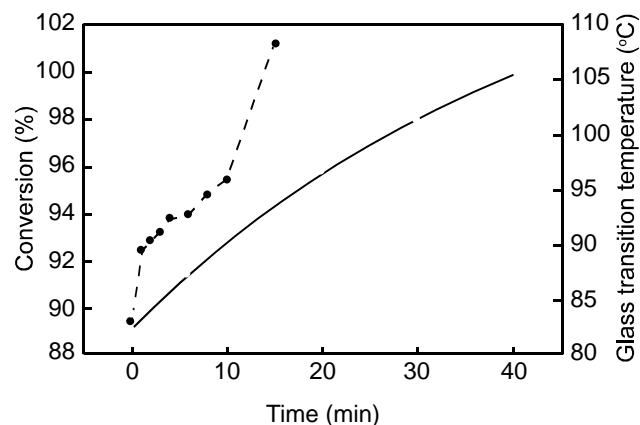
Table 2. Ultimate percentage of monomer conversion and optimal production time for PMMA sheet samples polymerized in the two-step (water-air) process at different temperature schemes using either 0.030 or 0.038 wt.% ADVN.

Temperature scheme (°C)	Monomer conversion (%)		Production time (min)	
	ADV N, 0.030 (wt %)	ADV N, 0.038 (wt %)	ADV N, 0.030 (wt %)	ADV N, 0.038 (wt %)
60-105	97.5 ± 0.5	96.9 ± 0.9	200 ± 6	190 ± 7
60-115	95.0 ± 0.8	96.2 ± 1.6	200 ± 8	190 ± 8
60-125	99.0 ± 0.8	99.7 ± 0.3	200 ± 5	190 ± 6
63-105	95.8 ± 2.2	97.3 ± 1.0	180 ± 7	170 ± 7
63-115	98.3 ± 1.3	97.2 ± 0.5	180 ± 8	170 ± 5
63-125	98.7 ± 0.9	96.8 ± 1.8	180 ± 8	170 ± 8
65-105	98.3 ± 1.3	98.1 ± 1.0	170 ± 5	150 ± 5
65-125	98.5 ± 1.4	98.8 ± 1.0	170 ± 6	150 ± 7
68-125	96.9 ± 1.0	97.5 ± 1.2	130 ± 8	120 ± 6

prepared in the one-step process (i.e., ranging from 87 to 90%) being much lower than that for samples prepared after being annealed at an elevated temperature (i.e., ranging from 95 to 99%) is a direct result of the T_g of PMMA increasing to exceed the reaction temperature after the optimal production time for the one-step process is reached. To verify the above hypothesis, a separate experiment was carried out. In this experiment, the MMA syrup (% monomer conversion ≈ 7 to 10% and viscosity ≈ 245 centipoise at 25°C) was first mixed with 0.15 wt.% of AIBN (equivalent to ca. 0.032 wt.% of ADVN) in a mixing tank, and the mixture was degassed before being poured into a glass mould having the cavity thickness of 3 mm. The polymerization step was carried out at 60°C for 180 min and the annealing step was carried out at 120°C. A Rheometric Scientific DMTA5 dynamic mechanical analyzer was used to measure the T_g value for samples collected after the completion of the polymerization step and after being annealed for various annealing time intervals, ranging from 1 to 40 min. The percentage of monomer conversion of each sample was also determined.

Figure 6 illustrates percentage of monomer conversion and T_g for samples polymerized at 60°C as a function of annealing time, ranging from 0 to 40 min, at an annealing temperature of 120°C. Obviously, the T_g value for sample collected immediately after the completion of the polymerization step was found to be ca. 83°C, which is much higher than the polymerization temperature. The T_g value was found to increase appreciably when the samples were further annealed at

120°C. Specifically, the T_g value was found to increase from ca. 83°C for unannealed sample to ca. 108°C (cf. the referenced value of 105°C [9]) for sample annealed for 15 min. According to Figure 6, the percentage of monomer conversion was also found to be an increasing function with the annealing time interval. Specifically, it was found to increase from ca. 90% for unannealed sample to ca. 99% for sample annealed for 40 min. It should be noted that the sample annealed for 15 min exhibited the percentage of monomer conversion of ca. 94%. From the results shown here, it can



(○) Conversion vs time; (●) Glass transition temperature vs time; (—) Conversion vs time (regression).

Figure 6. Percentage of monomer conversion and glass transition temperature for samples polymerized at 60°C using 0.15 wt.% AIBN (equivalent to about 0.032 wt.% ADVN) as a function of annealing time at an annealing temperature of 120°C.

now be concluded with a higher level of confidence that the increase in T_g value of PMMA during polymerization, when it exceeds the present polymerization temperature, was responsible for the low ultimate percentage of monomer conversion being observed for samples prepared in the one-step process and further annealing at an elevated temperature is required for attaining samples having a higher ultimate percentage of monomer conversion value.

Comparison Between PMMA Sheets Produced By One-step and Two-step Processes

Table 3 summarizes the ultimate molecular weight characteristics for selected PMMA sheet samples produced by the one-step and the two-step isothermal processes in various process conditions using 0.038 wt.% ADVN. For samples polymerized in the one-step process, all of the average molecular weight values were found to decrease slightly with increasing polymerization temperature, with the average values of the different molecular weight averages being $\bar{M}_n \approx 5.2 \pm 0.7 \times 10^5$ Da, $\bar{M}_w \approx 2.1 \pm 0.2 \times 10^6$ Da, $\bar{M}_z \approx 4.1 \pm 0.3 \times 10^6$ Da, and $\bar{M}_{z+1} \approx 5.8 \pm 0.2 \times 10^6$ Da. The decrease in the average molecular weights is expected when the polymerization temperature or the initiator concentration increases. For samples polymerized in the two-step process, average values of the different molecular weight averages are $M_n \approx 5.3 \pm 0.4 \times 10^5$ Da, $M_w \approx 1.9 \pm 0.1 \times 10^6$ Da, $M_z \approx 4.0 \pm 0.1 \times 10^6$ Da, and $M_{z+1} \approx 5.7 \pm 0.1 \times 10^6$ Da. Obviously, the molecular weight characteristics for these samples were not much different.

Figure 7 compares the surface hardness (shore D)

Table 3. Ultimate molecular weight characteristics for selected PMMA sheet samples produced by the one-step (water) and the two-step (water-air) isothermal processes in various temperature schemes using 0.038 wt.% ADVN.

Temperature (°C) scheme	\bar{M}_n ($\times 10^5$)	\bar{M}_w ($\times 10^6$)	\bar{M}_z ($\times 10^6$)	\bar{M}_{z+1} ($\times 10^6$)	MWD
60a	5.9	2.2	4.3	5.9	3.7
62a	5.2	2.1	4.2	5.9	4.0
65a	4.6	1.9	3.8	5.5	3.9
60-105b	5.4	2.0	4.1	5.8	3.7
63-105b	5.6	1.9	4.0	5.7	3.3
63-125b	4.9	1.9	4.0	5.6	3.8

and the impact resistance for PMMA sheet samples produced by the one-step and the two-step isothermal processes in various process conditions using 0.038 wt.% ADVN. The surface hardness for samples produced by the one-step process was found to range from ca. 90.6 to 91.3, while that for samples produced by the two-step process was from ca. 94.2 to 95.1. On the other hand, the impact resistance for samples produced by the one-step process was found to range from ca. 15.5 to 16.0 kJ.m⁻², while that for samples produced by the two-step process was from ca. 18.4 to 23.1 kJ.m⁻². It is obvious from the results shown that PMMA sheet samples produced by the two-step process exhibited much

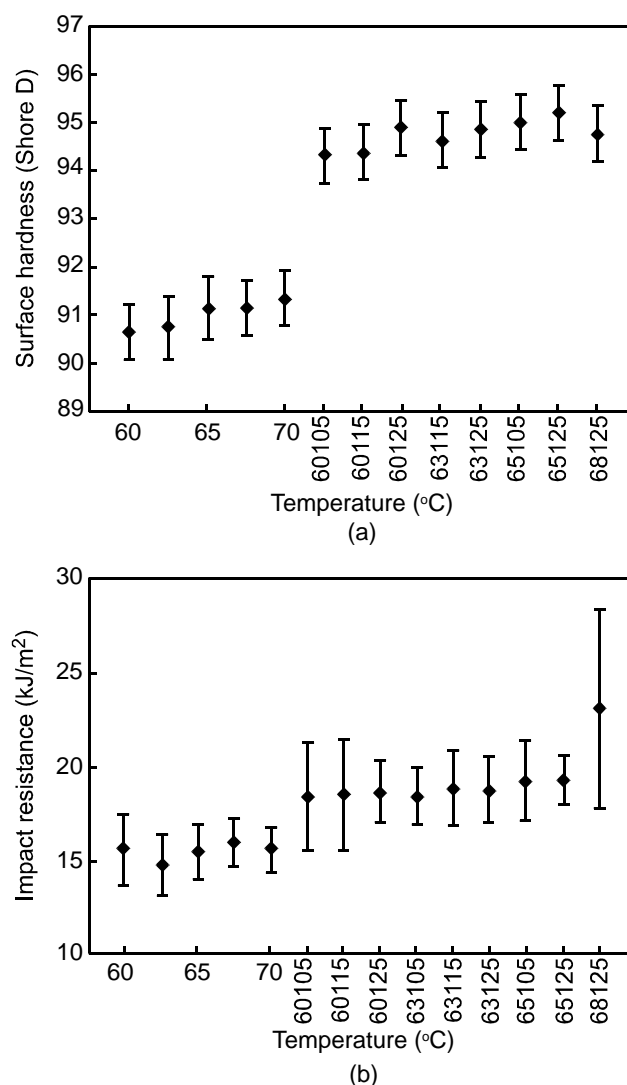


Figure 7. (a) Surface hardness and (b) impact resistance properties of PMMA sheet samples polymerized by one-step (water) and two-step (water-air) isothermal processes using 0.038 wt.% ADVN.

superior mechanical integrity to those produced by the one-step process. Since the molecular weight characteristics for the samples produced by both processes were not much different, the reason for the much difference in the mechanical properties observed must be from much greater ultimate percentage of monomer conversion for the samples produced by the two-step process (i.e., $97.6 \pm 1.1\%$, for samples prepared by using 0.038 wt.% ADVN) as compared to that for the samples produced by the one-step process (i.e., $88.6 \pm 1.1\%$, in samples prepared by using 0.038 wt.% ADVN).

CONCLUSION

In the present contribution, one-step and two-step isothermal sheet-casting processes for producing poly(methyl methacrylate) (PMMA) sheets, based primarily on water and water-air systems, were studied and compared. The overlay plots of the temperature-time profile and the percentage of monomer conversion suggested that the optimal production time for both one-step and two-step processes can simply be determined from the temperature-time profile data, in which it is taken as a time interval after the temperature of the sample reverts to that of the polymerization temperature (in case of the one-step process) and as the time interval after the time of the sample reaches that of the annealing temperature (in case of the two-step process). The results showed that the ultimate molecular weight characteristics of PMMA sheet samples prepared by both one-step and two-step processes were not much different (despite a slight decrease in all of the average molecular weight values with increasing polymerization temperature was observed for samples polymerized in the one-step process), while the ultimate percentage of monomer conversion was found to be marked different (i.e., ca. 88.6% for samples prepared by the one-step process and ca. 97.6% for samples prepared by the two-step process). The annealing step in the two-step process was responsible for the much higher ultimate percentage of monomer conversion achieved in the finished products, which, in turn, was responsible for the much better mechanical integrity that these products exhibited.

ACKNOWLEDGEMENTS

P.S. would like to acknowledge a financial support provided by the Commission on Higher Education, Ministry of Education (formerly Ministry of University Affairs) through the Support Grant for Cooperative Research between Governmental and Private Sectors Project. Partial supports from the Petroleum and Petrochemical Technology Consortium (through a governmental loan from the Asian Development Bank) and the Petroleum and Petrochemical College are gratefully acknowledged.

REFERENCES

1. Bryson J.A, in *Plastics Materials*, 3rd ed., Newnes-Butterworths, London, 330-333 (1975)
2. Balke S.T and Hamielec A.E, Bulk polymerization of methylmethacrylate, *J. Appl. Polym. Sci.*, **17**, 905-949 (1973).
3. Seth V. and Gupta S.K., Free radical polymerizations associated with the Trommsdorff effect under semibatch reactor conditions: An improved model, *J. Polym. Eng.*, **15**, 283-326 (1995).
4. Ghosh P., Gupta S.K., and Saraf D.N., An experimental study on bulk and solution polymerization of methyl methacrylate with responses to step changes in temperature, *Chem. Eng. J.*, **70**, 25-35 (1998).
5. Ahn S.-M., Chang S.-C., and Rhee H.-K., Application of optimal temperature trajectory to batch PMMA polymerization reactor, *J. Appl. Polym. Sci.*, **69**, 59-68 (1998).
6. Ramaseshan V., Trivedi M.K., and Raghunathan T.S., Polymerization control in coating of methylmethacrylate, *Polym. Int.*, **32**, 275-281 (1993).
7. Zhou F., Gupta S.K., and Ray A.K., Modeling of the sheet-molding process for poly(methyl methacrylate), *J. Appl. Polym. Sci.*, **81**, 1951-1971 (2001).
8. Fleischer. D, in J. Brandrup and E.H. Immergut, Eds, *Polymer Handbook*, 3rd ed. Wiley-Interscience, New York, p. III/7, (1989).
9. Peyser. P, in J. Brandrup and E.H. Immergut, Eds. *Polymer Handbook*, 3rd ed. Wiley-Interscience, New York, p. VI/219, (1989).