

Bench-Scale and Pilot Plant Preparation of Chemically Modified Polyester Resins

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SYNOPSIS

The laboratory preparation procedure of a recently developed unsaturated polyester resin was followed to prepare the resin on a large scale (10- and 200-L pilot plant reactors). The process heating rate, reaction temperature, and agitator tip speed were kept constant on scale-up. The resin was successfully reproduced and its properties were unchanged upon scale-up. The effects of reaction temperature and inert gas flow rate on the polyesterification reaction rate were investigated. It was found that a 10°C increase in temperature or a 50% increase in the gas flow rate results in a 50% increase in the reaction rate.

INTRODUCTION

Unsaturated polyester resins are a class of reinforced plastics that have great versatility.¹ Depending on end use, the properties of the polyester resins may be tailored by proper selection of reactants and conditions. Recently,² laboratory preparation procedures of three unsaturated polyester resins were developed. The physical and mechanical properties of the prepared resins were compared with commercially available polyester resins used in greenhouses. It was found that: (1) the partial substitution of the commonly used glycols (propylene, diethylene) by neopentyl glycol improved the resins' mechanical properties; and (2) the replacement of 35% of the styrene used as a thinning fluid by methyl methacrylate improved the resins' optical characteristics. More importantly, the combination of (1) and (2) led to a product that was stable against harsh weather conditions (high temperature, humidity, and UV radiation).

This paper addresses the large-scale (bench-scale and pilot plant) preparation of one of the three developed polyester resins. The paper also discusses the effects of variations in the reaction temperature and the inert gas flow rate on the reaction rate and

the production time cycle of the polyester resin. Both aspects of this study have not been comprehensively covered in the literature, where the emphasis of research work conducted on polyesters was on their chemistry³ and not on their engineering.

EXPERIMENTAL

Materials

Three types of glycols and two types of anhydrides were used in the synthesis of the unsaturated polyester resins. All starting materials used were of technical grade. Neopentyl glycol (NPG) and methyl methacrylate (MMA) were purchased from Hoechst of Germany and ICI of England, respectively. Maleic anhydride (CdF Chimie, France), phthalic anhydride (Cepsa, Spain), and styrene (SABIC, Saudia Arabia) were supplied by the Kuwait Chemical Manufacturing Company (KCMC).

Apparatus

Laboratory-scale experiments were conducted in a 10-L jacketed glass reactor equipped with a multi-speed mixer and connected to a circulator. Nitrogen was bubbled through the reaction mixture using a sparger.

Pilot plant experiments were carried out in a multipurpose resin pilot plant whose major com-

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ponents were (Fig. 1): a 200-L stainless steel jacketed reactor equipped with a 2.5-kW axial mixer, a 20-kW electric heater to heat the thermal fluid, a 24-kW chiller, a packed column, a condenser, and a 500-L thinning tank.

Preparation Procedure

The same preparation procedure was followed in conducting laboratory and pilot plant experiments. Following are the details of the pilot plant preparation.

Glycols and anhydrides were charged in the 200-L reactor at room temperature. Inert gas (nitrogen) was bubbled through the reactor at a rate of 300 L/h. During this step, the agitator was started to ensure a homogeneous mixture. An antioxidant was added and the reactor was tightly closed, nitrogen flow was stopped, and vacuum was applied to degas the reactor. Vacuum was released by starting the flow of

nitrogen. This degassing procedure was repeated three times. The heater was switched on and temperature was monitored as a function of time. After reaching the reaction temperature (200 or 210°C), the flow rate of nitrogen was increased to 750 L/h and was maintained throughout the sampling period. A sample was taken every 1–2 h and its viscosity and acid number (mg potassium hydroxide required to neutralize the acid in g of the sample) were determined. The acid number of the prepared resins was measured according to ASTM D1639. The viscosity of the resins was determined using a Haake CV-100 viscometer (W. Germany). The test was conducted at 25°C using a 1 : 1 weight ratio of resin and ethylene glycol monomethylether. When the desired acid number was reached, the reactor was cooled to 150°C and the nitrogen flow rate was decreased to 300 L/h. Before the contents of the reactor were pumped to the thinning tank, an appropriate amount of inhibitor was added. A mixture of

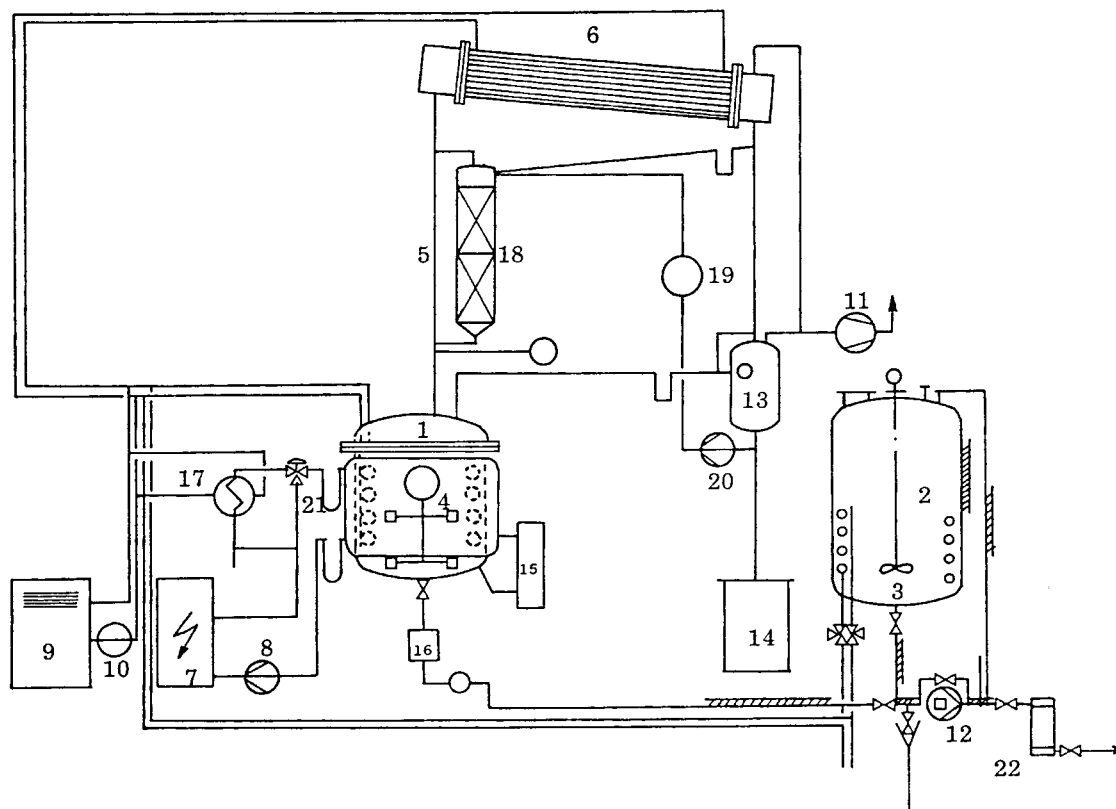


Figure 1 Schematic diagram of the resin pilot plant. 1. Pilot Plant Reactor; 2. Thinning Tank; 3. Stirring Propeller; 4. Agitator; 5. Vapor Tube; 6. Reflux Condenser; 7. Heating System; 8. Circulation System; 9. Water Chiller; 10. Circulating Pump; 11. Fan Vacuum Pump; 12. Positive Displacement Pump; 13. Separator Tank; 14. Collecting Receiver; 15. Hydraulic Lowering Device; 16. Discharge Filter; 17. Heat Exchanger; 18. Packed Column; 19. Reflux Dosing Meter; 20. Reflux Pump; 21. Heating/Cooling Control Valve; 22. Filter.

styrene and methyl methacrylate, whose weight is 40% that of the resin, was blended and cooled to about 10°C. Styrene accounted for 65% of the total weight of the mixture. The reaction mixture was slowly added to the contents of the thinning tank and the temperature was kept below 50°C using chilled water. Finally, the thinned polyester resin was discharged and stored in a closed drum kept in an air-conditioned room.

RESULTS AND DISCUSSION

Three novel polyester resins were developed and prepared in a 1-L reactor.² The large-scale preparation of only one of them is discussed. The other two resins were treated using the same methodology and are not included here.

The large-scale preparation was carried out in two stages. The first stage involved resin preparation in a 10-L reactor, whereas the second stage involved the pilot plant preparation of the polyester resin. The 10-L scale experiments enabled the comprehensive determination of the acid–time curve and the acid number–viscosity curve. Both of these curves are of practical importance. The former is a measure of the reaction rate,⁴ whereas the latter is considered a “resin performance” curve in the sense that if the resin’s viscosity stays within predetermined limits, the resin’s performance in a specific application will be adequate. In addition to the determination of these two curves, the 10-L data were used to estimate the operating conditions of the 200-I reactor of the resin pilot plant. For example, during the stage of heating the reactants from room temperature to the reaction temperature, various heat-

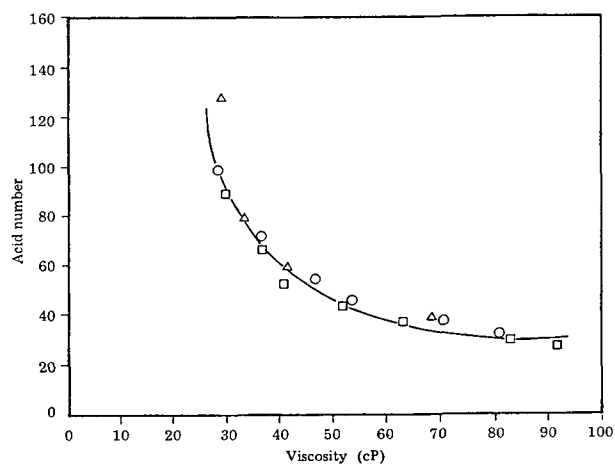


Figure 2 The acid number–viscosity relationship for three 10-L reactor batches.

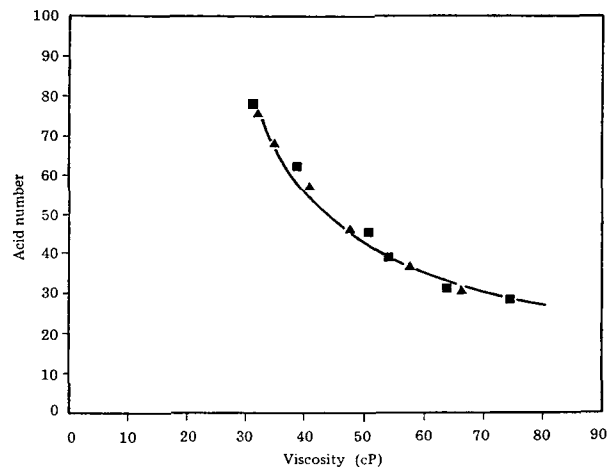


Figure 3 The acid number–viscosity relationship for two pilot plant batches.

ing rates were tried in the 10-L reactor, and a heating rate of 1°C/min produced a resin with optimum properties. Heating rates lower than this value resulted in a longer process time and added to the production cost of the resin, whereas heating rates higher than 1°C/min led to highly viscous resins.

The determination of the agitator speed of the pilot plant reactor is another example of using data collected from a smaller-scale study. The 10-L reactor was equipped with an anchor mixer with diameter and rotational speeds of 0.11 m and 350 rpm, respectively. The pilot plant reactor had an axial agitator with a diameter of 0.37 m. To run the two reactors at the same agitator tip speed,⁵ the agitator’s rotational speed was fixed at 102 rpm. A third example is the determination of the inert gas flow rate. Assuming that the superficial gas velocity⁶ remains constant on scale-up, then the pilot plant’s gas flow rate may be computed from the laboratory gas flow rate using eq. (1).

$$G_p = G_l E \frac{D_p}{D_l} F^2, \quad (1)$$

where G is the gas flow rate, D is the reactor’s diameter, and the subscripts p and l denote pilot plant and laboratory, respectively.

Reproducibility

The unsaturated polyester resins were prepared several times to ensure the reproducibility of the preparation procedure. Figure 2 shows the acid number–viscosity relationship for the 007 resin pre-

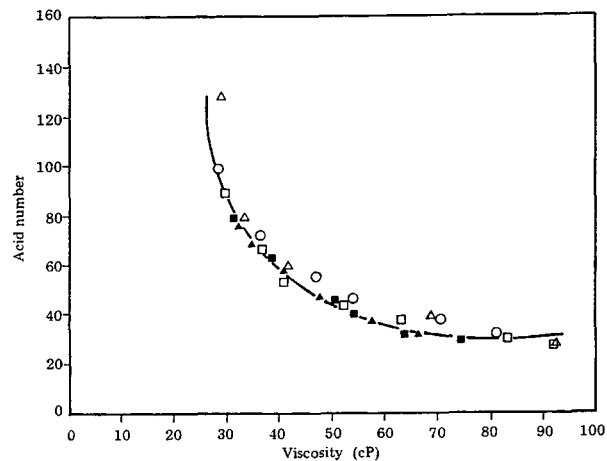


Figure 4 Comparison of the acid number–viscosity data collected from a 10-L reactor (Δ , \circ , \square) and the pilot plant reactor (\bullet , \blacktriangle).

pared in the 10-L reactor. Most of the data points fall on the same “performance” curve. The procedure was repeated on the pilot plant scale and similar results were obtained (Fig. 3). At this point, it is important to compare the acid number–viscosity curves obtained from the two reactors (Fig. 4) since a close agreement in these curves reflects similarity in physical properties. Table I shows that this is the case, especially when it comes to light transmission percentage, which is considered of primary importance for resins used in greenhouses. Reproducibility may also be ensured by examining the acid number–time curve that provides a measure of the reaction rate. Once the reactants, composition, and ratios are fixed, the reaction rate will be a function of the temperature and the inert gas flow rate. The reaction temperature affects the reaction rate constant, whereas the gas flow rate drives the reversible polyesterification reaction to the right through the removal of water.

Table I Comparison of Physical Properties of Resins Prepared in Laboratory and Pilot Plant Reactors

Reactor Size (l)	Light Transmission	Yellowness Index	Haze
10	82.1	9.66	14.1
	81.9	12.83	14.7
	83.1	9.68	15.7
200	84.6	13.57	16.5
	82.1	14.35	20.5
	82.0	11.99	—

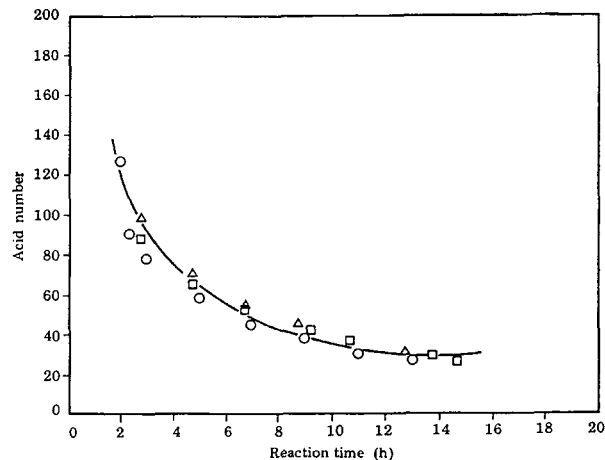


Figure 5 Change of acid number with time for three 10-L reactor batches.

The acid number–time curve of the 007 resin prepared in a 10-L reactor is given in Figure 5. Again, a close agreement within the three batches was obtained. The pilot plant data is presented in Figure 6: The acid number–time curves of the two reactors are not expected to coincide unless experiments are conducted at the same temperature and gas flow rates. In the case presented here, only the first requirement (same temperature rate) was met.

Effect of Inert Gas Flow Rate

Bubbling inert gas through the reaction mixture serves three purposes: it facilitates the removal of the water produced from the polycondensation reaction, enhances the mixing process of the reactants, and prevents the thermal oxidation of the produced

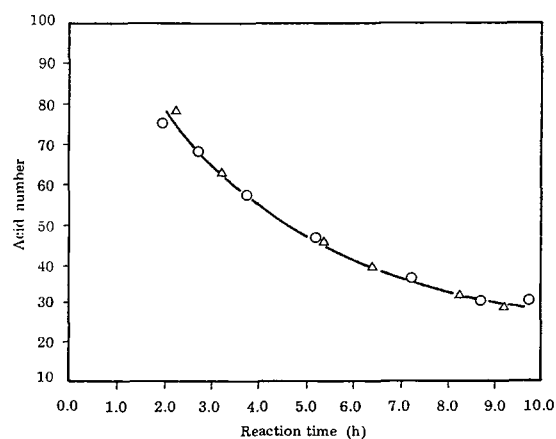


Figure 6 Change of acid number with time for two pilot plant batches.

polyester resin. The optimum inert gas flow rate is the highest rate that does not result in appreciable loss of reactants or low-molecular-weight products.

Three values of the gas flow rate (G) were investigated in the 10 and 200-L reactors. The discussion presented here is limited to the pilot plant case, but similar conclusions can be drawn from the laboratory data. The reaction temperature was 200°C and the values of G were 0.75, 1.125, and 1.5 m³/h. An overall decrease in the reaction time required to reach a certain acid number is expected.⁸ However, Figure 7 does not clearly show such a decrease. The reduction in reaction time can be more readily shown if the function $(AN - AN_f)/(AN_i - AN_f)$ is plotted against the reaction time. AN is the acid number at any time of the reaction, AN_i is the initial acid number, and AN_f is the final acid number. It should be noted that AN_f is not the acid number at infinite time, but rather the desired acid number before the thinning process. Figure 8 shows the plot of this function for three pilot plant experiments.

In these three runs, AN_i and AN_f were selected to be 76 and 28, respectively. The results of this analysis are independent of the choice of AN_i and AN_f . The reason for defining a function that varies from 1 to 0 is to present the results in a way that will eliminate absolute numbers and give a clear relative assessment of the effect of the inert gas flow rate. This procedure is frequently adopted to solve chemical engineering problems.⁹ To obtain a final acid number of 28, reaction times of 17.0, 11.6, and 9.5 h are needed when the inert gas flow rate is 0.75, 1.125, and 1.5 m³/h, respectively.

An important feature of the three curves is that,

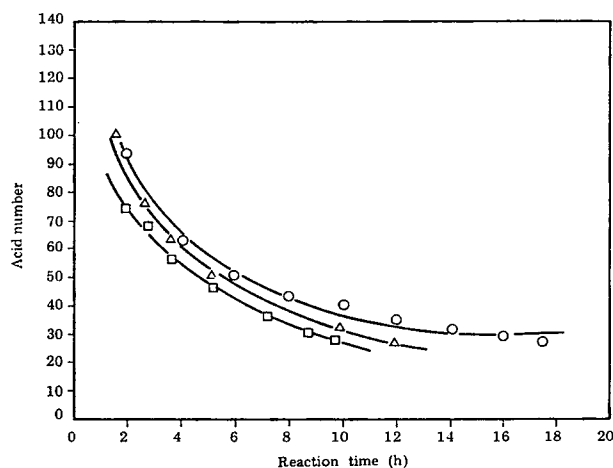


Figure 7 Effect of gas flow rate on the acid number-time relationship for three pilot plant runs: $G = 0.75$ m³/h (\circ), $G = 1.125$ m³/h (Δ), and $G = 1.5$ m³/h (\square).

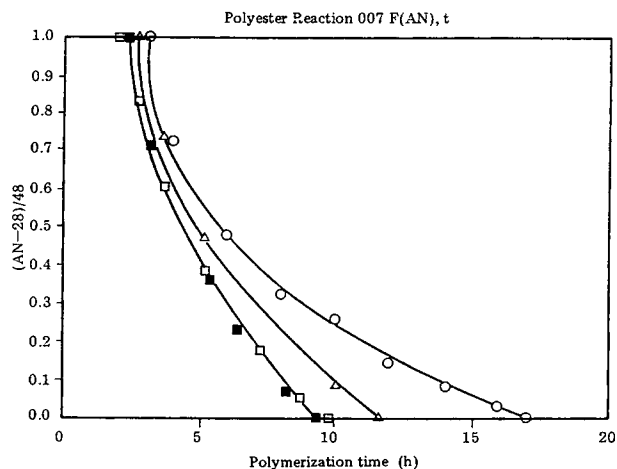


Figure 8 Variation of a dimensionless form of the acid number with time for three gas flow rates: $G = 0.75$ m³/h (\circ), $G = 1.125$ m³/h (Δ), and $G = 1.5$ m³/h (\square).

for large acid numbers (60), they are similar and close to each other; as the acid number decreases, the curves move apart. This can be explained by recalling that the viscosity is low at high acid numbers, so the rate of the polycondensation reaction is high and the water removal from the reactor is fast; therefore, the reaction is driven away from equilibrium at a higher rate. At a lower acid number, however, the viscosity is high, so the polycondensation reaction rate is slower and approaching equilibrium conditions. This phenomenon will result in reduced water evolution, and a high inert gas flow rate will facilitate the stripping of the trapped water and dramatically contribute to reducing the time cycle of the polycondensation reaction.

This type of time dependence of the resin acid number (Figs. 7 and 8) tempts one to stop the reaction at higher acid number values (say, 40 instead of 28) and reduce the resin production cycle that is normally desirable in commercial production. However, such a practice does not give desirable resin properties and results in a glass-reinforced polyester (GRP) panel with lower strength. Polyester resins with various final acid numbers were taken and reacted with styrene to form crosslinked polyesters that were cast in panels, and the tensile strength of these panels were measured. Figure 9 shows the % change in the tensile strength of the cast-filled resin with the acid number. A limiting value is obtained at lower acid number values; however, with increasing AN , the tensile strength drops rapidly. For instance, tensile strength will drop by 50% if the acid number is increased from 23 to 37. The drop can be explained by recalling that higher AN values mean

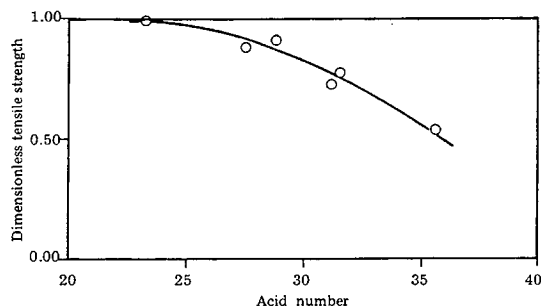


Figure 9 Variation of the dimensionless tensile strength with acid number.

lower molecular weights and fewer unsaturation sites that are needed for crosslinking with the thinning monomer (such as styrene). The decrease in the crosslinking sites leads to GRP panels with lower tensile strength.

Effect of Reaction Temperature

Polyesterification reactions start at a temperature of about 170°C. The higher the temperature, the higher the reaction rate constant and the faster the reaction rate. Figure 10 shows the drop in acid number as a function of reaction time for two reaction temperatures: 200 and 210°C. Since the rate of change in the acid number is directly correlated with the reaction rate,⁴ an increased reaction temperature leads to a higher reaction rate. The reaction temperature cannot be further increased since side reactions and resin degradation become significant at a temperature of approximately 220°C.

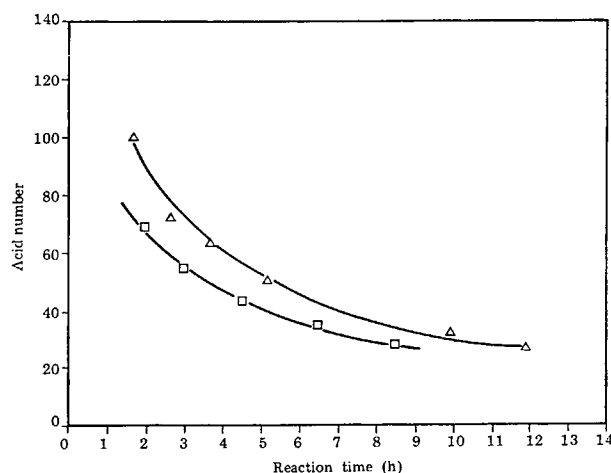


Figure 10 Effect of reaction temperature on the acid number-time relationship: $G = 1.125 \text{ m}^3/\text{h}$, $T = 200^\circ\text{C}$ (\circ), and $T = 210^\circ\text{C}$ (Δ).

The relative importance of the reaction temperature and the inert gas flow rate may be inferred from the analysis of the reaction kinetics. The polyesterification reaction kinetics are given by:

$$\frac{-dAN}{dt} = kAN^m, \quad (2)$$

where k is the reaction rate constant and is a function of the temperature (T) and the gas flow rate (G). The value of the exponent m has been a subject of dispute in the literature³ and will be assumed to be 3.¹⁰ Upon integration, eq. (2) gives:

$$\frac{1}{(AN)^2} - \frac{1}{(AN_0)^2} = 2k(t - t_0). \quad (3)$$

Equation (3) is strictly valid for systems where the ratio of the hydroxyl to carboxylic groups is stoichiometric; in our case, this ratio is 1.07. Nevertheless, at least qualitative information can be extracted from eq. (3). Figure 11 shows a plot of $1/(AN)^2$ vs. $t - t_0$ of five pilot plant experiments where T and G were varied. Since k is proportional to the slope of the best-fit line going through data points, a change in the slope can be taken as a measure of the relative importance of T and G . Figure 11 shows an increase of k with increasing T and G . For example, for a reaction temperature of 200°C, an increase of 33, 50, and 100% leads to an increase of 27, 56, and 98%, respectively, in the k value. When the reaction temperature is 210°C, k increases by 55% for a 33%

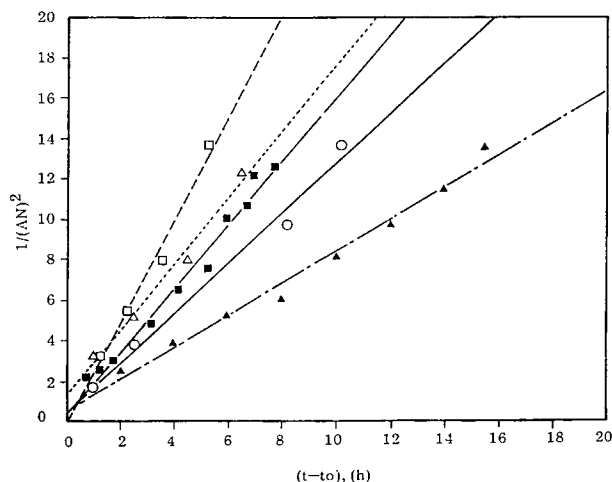


Figure 11 Third-order kinetics plot of pilot plant data: $T = 200^\circ\text{C}$, $G = 0.75 \text{ m}^3/\text{h}$ (Δ); $T = 200^\circ\text{C}$, $G = 1.125 \text{ m}^3/\text{h}$ (\circ); $T = 200^\circ\text{C}$, $G = 1.5 \text{ m}^3/\text{h}$ (\square); $T = 210^\circ\text{C}$, $G = 1.125 \text{ m}^3/\text{h}$ (Δ); and $T = 210^\circ\text{C}$, $G = 1.5 \text{ m}^3/\text{h}$ (\square).

increase in G . Thus, at higher temperatures, the effect of G becomes more pronounced. This observation must be taken into account if one is concerned with modelling the system. One cannot have two separate terms for the dependence of k on T and G , since the G dependence is a function of T .

Thus far, Figure 11 was used to examine the effect of G for a constant T , it can also be employed to study the effect of T for a constant G . For instance, at a gas flow rate of $1.125 \text{ m}^3/\text{h}$, the slope increases by 32% when T is increased from 200 to 210°C , whereas the increase is 61% when G is $1.5 \text{ m}^3/\text{h}$; again, the interdependence of T and G is obvious. Nevertheless, it can be assumed that the 10°C temperature increase results, on the average, in a 50% increase in the reaction rate.

Since the physical properties of the resin and the mechanical properties of the cast-filled resin were not changed as a result of changing the operating conditions (T and G), one has some flexibility in running the plant at a high temperature or at a high gas flow rate. From the economic viewpoint, the former may be more feasible.

CONCLUSIONS

The unsaturated polyester resin was successfully prepared and reproduced in a large-scale reactor. The properties of the resin were unchanged on scale-up. The operating conditions of the 200-L pilot plant reactor were derived from the conditions of the 10-L reactors by assuming a constant heating rate, reaction temperature, and agitator tip speed. The pilot plant gas flow rate was estimated from the laboratory reactor by assuming a constant superficial gas velocity. The effects of the reaction temperature and the inert gas flow rate were determined. It was found that increasing the temperature from 200 to 210°C resulted, on the average, in a 50% increase in the reaction rate. The exact percent increase depends on the operating gas flow rate. It was also shown that increasing the gas flow rate from 0.75 to 1.125 to $1.5 \text{ m}^3/\text{h}$ led to an increase of 50 and 33%, respectively, in the reaction rate when the reaction temperature was 200°C . At a higher temperature,

the percent increase is different. This suggested an interaction between these two parameters that must be accounted for when modelling the polyesterification reaction and process. A semi-empirical model capable of predicting the pilot plant kinetic data from the laboratory data was developed and will be discussed in a later article.

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