Chapter 4

Scale up Studies on Process for Glycidyl Azide Polymer

4.1 Introduction

Synthetic routes for GAP were studied and experimental trials at laboratory scale were done as explained in chapter 3. Based on the experiments carried out, a synthesis route was selected for scale up of PECH process at 20 kg level and GAP at 10 kg level. Design of a pilot plant reactor requires laboratory data on the reactions involved. The chemical reaction rate is influenced by physical processes like mass transfer and heat transfer which are usually controlled by the size and structure of the reactor. The method of chemical similitude\(^1\)\(^-\)\(^3\) has been used to deal with the complex relation between the overall rate of the reaction, type and size of the reactor. The basis of chemical similitude is the dimensionless groups derived from the application of the laws of conservation of mass, momentum and energy to the chemical reaction system. The principles of similarity should be observed in planning model studies. Four types of similarities are important in most of the chemical systems\(^4\) viz., (i) Geometrical similarity (dimensional proportionality), (ii) Mechanical similarity, which includes (a) Static similarity (deformational proportionality), (b) Kinematic similarity (time proportionality) and (c) Dynamic similarity (force proportionality), (iii) Thermal similarity (temperature proportionality) and (iv) Chemical similarity (concentration proportionality).

Detailed account of model studies are available in the literature.\(^5\)\(^,\)\(^6\) The equality of the magnitudes of the dimensionless groups can be used successfully in certain cases as the scale up criteria, if chemical similitude is applicable to the system. A detailed description of dimensionless numbers used for the analysis of process vessels together with significance of use is available in literature.\(^7\)\(^-\)\(^9\) Dimensional similitude can be used as the criteria in simple reaction systems. In general, it is not practical to have complete dimensional similarity in a chemical
system. This is mainly because the influence of physical parameters on the overall rate of reaction could vary widely in reactors with largely different scales. When the overall rate is controlled by physical rate processes like mass transfer or heat transfer, the dimensionless groups containing force or thermal properties become important. On the other hand, chemical similarity becomes important when chemical reaction rate is the rate controlling step. When identical temperature distribution is to be maintained in model as well as pilot plant reactor, thermal similarity is the scale up criteria. In the scale up trials carried out for polymerisation of ECH, chemical and thermal similarities were maintained.10, 11

Polymerisation of ECH is an exothermic process. For exothermic reactions, stability of the chemical reactor depends on the thermal management of the system. The rate of heat removal by coolant circulation through jacket or cooling coil should be equal or greater than the heat generated due to exothermic reaction. Stability is one of the important factors in the selection of the chemical reactor.12-14 Another important aspect of scale up is the parametric sensitivity. Mathematical treatment for conditions under which, thermal behaviour of a chemical reaction is very sensitive to small changes in process parameters like small variations in concentration of reactant or reactant inlet temperature is available in the literature.15 Parametric sensitivity of the reactor is generally determined from mathematical model of the reactor.

4.1.1 Process optimization

In general, mathematical models are employed to determine the optimum conditions for the process. In the case of polymerization of ECH, the process parameters such as temperature range and concentration of monomer were found to be the most critical parameters through laboratory experiments. For conversion of PECH to GAP, apart from the temperature limit, reaction time and explosive limits of the reactants were also taken into account for the purpose of optimization of the process. A detailed account of optimization methods is reported in the literature.13-16
4.1.2 Selection of the reactor

Reactions involved in the polymerisation are complex as the product distribution is complicated. Due to the interactions of various chemical and physical processes, polymerisation products could have a wide range of chain length and molecular weight. Because of the highly viscous nature of reaction system, stirred tank reactors are used for polymerisation process. A batch reactor is selected in the polymerisation of ECH as relatively small scale of 20 kg level of production is planned. The size of the reactor for scale up of the process was decided based on technical as well as economic considerations resulting from the quantitative requirement of the product. A batch reactor process gives a narrower molecular weight distribution for the product as the residence time distribution is uniform for all reactants. For a slow polymerisation reaction as in the case of PECH, a continuous system may require a battery of stirred tank reactors. Detailed account of selection criteria for reactors employed for polymerisation reactions\textsuperscript{17, 18} and design of polymerisation reactors are available in literature\textsuperscript{19, 20}. Selection of the reactor was done keeping in mind, the optimum conditions that are to be achieved for the polymerisation reaction. Dimensional similarity was maintained while selecting the reactor system. On a similar consideration, the level of scale up for azidation of PECH was fixed at 10 kg. As the conversion process involves azido compounds glass vessels were selected for the azidation process.

4.2 Scale up studies on the process for PECH

4.2.1 Effect of polymerisation time on the polymer properties

From the kinetic considerations as explained in chapter 4, polymerisation was carried out by slow addition of monomer to favour the activated monomer mechanism. This condition was achieved by keeping the instantaneous concentration of monomer as low as possible. The synthetic studies described in chapter 3 show that polymerisation time of 17 to 18 hours is required for achieving the required
range of molecular weight and physical properties for the prepolymer. Study was carried out to find the effect of polymerisation time on the final polymer properties.

4.2.2. Experimental

4.2.2.1 Materials

Epichlorohydrin (ECH) supplied by Qualigens was purified by distillation and fraction collected at 114-118°C. It was kept over molecular sieve prior to use. BF$_3$etherate supplied by Fluka, 1,4-butanediol supplied by Spectrochem, Mumbai and laboratory reagent grade toluene were used for the study.

4.2.2.2 Procedure

A two liter capacity stainless steel reactor was utilised for the polymerisation experiments. The initiator prepared as mentioned in section 3.4.4.2 in chapter 3 was charged along with toluene into the reactor and chilled to -5°C. In all the experiments, the molar ratio of the initiator was maintained constant. Addition time of the monomer was varied over a wide range. The addition of monomer at higher rates reduces polymerisation time. The exotherm generated during the reaction was effectively dissipated by efficient thermal management and the reaction temperature was maintained within -5 to 0°C during the experiments. The polymer was isolated and purified as mentioned under synthetic procedure in chapter 3 and was subjected to detailed analysis.

4.2.2.3 Results and discussion

The analysis results of the polymer synthesised show that, though the reduction in polymerisation time affects the physical and chemical properties of the polymer, required range of polymer properties can be achieved with reduced polymerisation time, by maintaining the reaction temperature in the range -5 to 0°C. Table 4.1 shows the results of the analysis of polymer samples from the experiments.
Table 4.1 Effect of polymerisation time on polymer properties

<table>
<thead>
<tr>
<th>Reaction time (hrs)</th>
<th>Mol. wt (Mn by VPO)</th>
<th>Viscosity (cps)</th>
<th>Hydroxyl value (mg KOH/gm)</th>
<th>Polydispersity</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1990</td>
<td>33000</td>
<td>40.2</td>
<td>2.2</td>
<td>68.2</td>
</tr>
<tr>
<td>12</td>
<td>2045</td>
<td>35400</td>
<td>39.1</td>
<td>1.9</td>
<td>73.1</td>
</tr>
<tr>
<td>15</td>
<td>2090</td>
<td>37600</td>
<td>38.8</td>
<td>1.9</td>
<td>73.4</td>
</tr>
<tr>
<td>20</td>
<td>2140</td>
<td>38700</td>
<td>37.3</td>
<td>1.8</td>
<td>74.8</td>
</tr>
<tr>
<td>24</td>
<td>2200</td>
<td>41000</td>
<td>36.2</td>
<td>1.7</td>
<td>75.5</td>
</tr>
</tbody>
</table>

To confirm the effect of polymerisation temperature on the polymer properties, the experiments were also carried out at different temperatures. An optimised reaction time of 12 hours was followed for these experiments. Table 4.2 shows the variation of molecular weight and yield with temperature of polymerisation.

Table 4.2 Effect of process temperature on molecular weight and yield of polymer

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mol. wt (by VPO)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>790</td>
<td>38</td>
</tr>
<tr>
<td>20</td>
<td>1100</td>
<td>48</td>
</tr>
<tr>
<td>10</td>
<td>1570</td>
<td>68</td>
</tr>
<tr>
<td>0</td>
<td>1700</td>
<td>90</td>
</tr>
<tr>
<td>-5</td>
<td>2100</td>
<td>95</td>
</tr>
<tr>
<td>-10</td>
<td>2120</td>
<td>95</td>
</tr>
</tbody>
</table>

It was noted that molecular weight and yield of the polymer are adversely affected by increase in temperature. Figures 4.1 and 4.2 show the effect of temperature on molecular weight and yield respectively with a polynomial best fit.

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Figure 4.1 Effect of polymerisation temperature on molecular weight

\[ \text{Mol.WT} = 0.239 T^2 - 30.7 T + 1843 \]

where \( T \) is temperature

\[ \text{Yield} (\%) = 0.006 T^2 - 1.09 T + 65.46 \]

Figure 4.2 Effect of polymerisation temperature on yield

4.2.3 Experimental

The data generated during the pre-scale up trials were made use of to fix the scale-up ratio and identify pilot plant reactor. Based on the data generated, thermal
and chemical similarities were considered for the scale up. Figure 4.3 shows the flow chart for the scaled up process of PECH.

*Note: VM- Volatile matter

**Figure 4.3 Flow chart of the scaled up process for polymerisation of epichlorohydrin**
A linear scale ratio of 3 corresponds to a 50 litre capacity reactor capable of producing 20 kg of PECH per batch. The bottleneck is the control and maintenance of polymerisation reaction at -5°C.

4.2.3.1 Materials

The materials used for the process was same as mentioned in section 4.2.2.1.

4.2.3.2 Equipments

A 50 litre jacketed stainless steel reactor meeting the heat transfer requirement for cooling the reactants and also to contain the exotherm generated during the polymerisation reaction was used for the scale up trial. An anchor type stirrer with rpm in the range of 50–100 was selected based on the trial carried out at small scale. A 50 litre capacity rotary flash evaporator was used for evaporation of solvents and isolation of polymer.

4.2.3.3 Procedure

i) Initiator preparation

In a typical process trial, a two litre glass reactor was used as the process vessel for initiator preparation. The vessel was cleaned, dried and purged with dry nitrogen for about 30 minutes with moisture trap at outlet. 562 g of 1,4-butanediol was charged into the reactor with stirring and dry nitrogen purging was continued. 887 ml of BF₃etherate was charged slowly over a period of 1hr. The reactor contents were maintained at 35-40°C. The reaction is continued for 2 hrs. At the end of the reaction, the reactor was connected to a vacuum line (vacuum level of 10 mm Hg) to remove ether completely. The vacuum line was then disconnected and the flask sealed.
ii) Polymerisation

The 50 litre jacketed stainless steel reactor was cleaned thoroughly and purged with dry nitrogen. Required quantity of toluene was charged into the reactor along with the initiator complex with continuous agitation (rpm 50–70). Coolant circulation was started through the jacket to maintain the reactant temperature at \(-5^\circ\text{C}\). Epichlorohydrin was added as a slow stream, using a metering pump. Required amount of epichlorohydrin was added at a rate of nearly 1.4 lit/hr. Rate of addition was fixed based on the heat transfer requirements, to contain the exothermic heat generated and to keep the average temperature of reaction at \(-5^\circ\text{C}\). After the monomer addition, the contents were stirred for \(\frac{1}{2}\) hr and reaction was arrested by adding distilled water. Agitation was continued for another 1 hr and then the contents were charged into a wash tank.

iii) Neutralisation and isolation of polymer

The polymer layer was neutralised with required amount of sodium bicarbonate dissolved in distilled water. The contents were stirred thoroughly for 10-15 minutes and then allowed to settle. The resin layer settles at the bottom and the pH of the resin layer was checked to confirm that the layer had become basic. After removing the water layer, the resin layer was repeatedly washed with distilled water till it became neutral.

The resin layer was charged into a 50 litre capacity rotary flash evaporator and the toluene was removed by evaporation under reduced pressure at 100–110\(^\circ\text{C}\). Volatile content was monitored regularly to ensure the removal of toluene.

4.2.3.4 Results and discussion

After removal of volatiles, the polymer was analysed for physical, chemical and spectroscopic properties. Table 4.3 shows typical analysis results of polymer
batches processed in pilot plant. The polymerisation trial results show that, polymer with consistent properties could be obtained by the process employed. The molecular weight (Mn) determined by GPC by using polystyrene as calibration standard.

### Table 4.3 Properties of PECH batches processed in the pilot plant

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Viscosity (cps)</th>
<th>Hydroxyl value (mg KOH/g)</th>
<th>Volatile matter (%)</th>
<th>Molec.wt.</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>VPO</td>
<td>GPC</td>
</tr>
<tr>
<td>1</td>
<td>31000</td>
<td>40</td>
<td>0.1</td>
<td>2250</td>
<td>2518</td>
</tr>
<tr>
<td>2</td>
<td>30200</td>
<td>41</td>
<td>0.2</td>
<td>2210</td>
<td>2500</td>
</tr>
<tr>
<td>3</td>
<td>31100</td>
<td>40</td>
<td>0.2</td>
<td>2247</td>
<td>2490</td>
</tr>
<tr>
<td>4</td>
<td>29980</td>
<td>41</td>
<td>0.2</td>
<td>2190</td>
<td>2510</td>
</tr>
<tr>
<td>5</td>
<td>31000</td>
<td>41</td>
<td>0.2</td>
<td>2200</td>
<td>2530</td>
</tr>
<tr>
<td>6</td>
<td>30840</td>
<td>41</td>
<td>0.2</td>
<td>2230</td>
<td>2530</td>
</tr>
<tr>
<td>7</td>
<td>30440</td>
<td>41</td>
<td>0.1</td>
<td>2230</td>
<td>2529</td>
</tr>
</tbody>
</table>

The difference in the Mn values determined by GPC and VPO methods is due to the difference in the solution properties of PECH compared to polystyrene. In dilute solutions of PECH, the intermolecular hydrogen bonding causes uncoiling of polymer molecules leading to increase in hydrodynamic volume and corresponding increase in GPC molecular weight.

### 4.3 Scale up of the process for GAP

Study of the kinetics of the chemical process provides important data for the purpose of scale up. The conversion process could be affected by number of factors. Identifying the critical parameters which influence the chemical conversion is an important step in scale up of chemical process. Study of the chemical kinetics leads to the factors that influence the rate of the reaction.21
In this scale up programme, a batch reactor was selected and the kinetic data was collected from small scale experiments. To maximise the yield from a reaction, optimum temperature profile is to be realised by devising the correct mode of heat transfer. Other factors like assessment of hazards, explosion potential and flammability were considered while selecting the reactor set up for azidation. Detailed account on social factors covering ecology and hazards associated with reactor systems are available in the literature.\textsuperscript{10}

**4.3.1 Design of the reaction system**

The kinetics of the reaction between PECH and sodium azide in N,N-dimethyl formamide (DMF) medium was studied in detail. In this reaction, sodium chloride is the byproduct formed by replacing Cl in the PECH by N\textsubscript{3}. Sodium azide has limited solubility in DMF. The progress of the reaction depends on two diffusive transfers of species, namely diffusion of sodium azide into the reaction site, followed by diffusion of sodium chloride out of the reaction site. As the reaction system is of multiphase composition, uniform distribution of the diffused phase is very important. Energy for suspending the solid particles is to be derived from the agitator. The size, shape and density of the particles, the viscosity and density of the liquid affect the settling velocity of the solid particles. Since the particles are kept in motion by currents of liquid, uniformity of suspension requires an adequate circulation rate and pattern of the liquid in the vessel. Hence, the design and speed of rotation of the agitator play a vital role in the performance of the reactor. Correlations are presented in the literature\textsuperscript{22, 23} for estimating the power required to lift particles from reactor vessel floor.

The ease with which solids are suspended in a liquid depends on the settling velocity of the particles. This in turn depends on the size, shape, and density of the particles; the viscosity and density of the liquid and whether settling is hindered or free. In general, small and light particles with a free settling velocity less than
1 ft/min are readily suspended in an agitated vessel, as they tend to follow the circulation pattern of the liquid. Larger and heavier particles tend to settle out against the fluid motion, but if the free-settling velocity is below 10 ft/min, it is possible to have a fairly uniform suspension in an agitated vessel. When the free-settling velocity exceeds 10 ft/min, an ordinary impeller cannot produce a uniform suspension. Settling rates are also generally governed by the volume fraction of solids in suspension. When the solids occupy less than 30% of the volume of the suspension, the particles are free settling. When the volume fraction is more than 50%, hindered settling occurs and the slurry behaves like a viscous non-Newtonian liquid than like separate phases of liquids and solids. With hindered settling, the suspended particles normally settle slowly.

It is a common practice that a large number of laboratory experiments will be carried out to generate data needed for the pilot plant process design. These laboratory experiments are to be carefully planned and executed so as to collect maximum information. Shape factors of the laboratory reactor, agitator type and speed of rotation, baffles are some of the important parameters to be considered in addition to pressure, temperature and concentration, while conducting pre-scale up studies. Product reliability and process repeatability are influenced by these factors adversely. Keeping all these things in mind, laboratory experiments were carried out in a 2 litre round bottom flask fitted with a paddle agitator in order to optimise the process parameters like temperature, reaction time, intensity of agitation. Since the reaction medium is heterogeneous, it can be in dynamic regime, chemical regime or mixed regime. Scale up criteria will vary depending upon the controlling mechanism. Values of kinetic rate constant determined at different temperatures throw light into the rate-determining step. Hence, second sets of experiments were carried out to evaluate the kinetic parameters.
4.3.2 Kinetics of conversion of PECH to GAP

In order to select reactor type from many alternatives, fix the size of the reactor and to optimise process parameters, it is essential to know the rate of the chemical reactions involved, the maximum conversion possible, the variables that affect the process and the nature of physical processes interacting with chemical reactions. It is possible to estimate the rate of mass and heat transfer from the properties of the reactants, the flow characteristics and the reactor parameters. For the determination of rate of chemical conversion, data is to be collected from experiments. The over all reaction rate mainly depends on the rate controlling step. In heterogeneous reactions, the rate controlling step may result from chemical or physical resistance. The factors that affect the rate of heterogeneous reactions include the following;

i) Mass transfer factors like diffusion.
ii) The patterns of phase contact.
iii) Fluid dynamic factors like degree of turbulence.
iv) Interfacial surface area of contact.
v) Reactor shape and size.
vi) Temperature and pressure.
vii) Kinetic factors such as activation energy, concentration of reactants.

In general, heterogeneous reactions consist of several steps. These are

i) Diffusion of reactants from one phase to the interface.
ii) Diffusion of reactants from interface to the bulk of second phase or to reaction site.
iii) Chemical reaction between the reactants at the reaction site.
iv) Diffusion of products out of the reaction site or into the bulk of first phase.
Any one or combination of these steps could be the rate controlling step of the reaction and it shall depend upon the specific nature of the reaction and process conditions. Identification of the rate controlling step of the reaction can be done by number of means. In the present study, kinetics of the reaction was investigated to identify the rate controlling step of the reaction. There are different methods for generating kinetic data. One of the methods is generation of data using a scale down reactor. Detailed criteria for selection of experimental reactor are available in the literature. The experiments simulating the process conditions of actual reactor were carried out using the small scale reactor. Here, the detailed mechanism involved in the reaction is not considered. The rate equations and dependency of the rate constants on the variables like temperature or concentrations were established. By this method, reliable data can be generated for scale up in less time, even for complex reactions.

The temperature coefficient of overall reaction rate is a good measure of the control mechanism. An increase in temperature has more influence on the chemical reaction than on the physical process. The relative difference can be utilised to identify the rate controlling step. The temperature coefficient is usually expressed as the elevation in rate constant caused by a temperature rise of 10°C. The mathematical expression for 10°C temperature coefficient is derived from Arrhenius equation and is expressed as follows.

\[
\ln \left( \frac{K_{T+10}}{K_T} \right) = \frac{E}{R} \left[ \frac{1}{T} - \frac{1}{T+10} \right] \quad (4.1)
\]

Where \( K_T \) is the rate constant at absolute temperature \( T \) and \( K_{T+10} \) is the rate constant at absolute temperature \( T+10 \). \( E \) is the activation energy and \( R \) is the universal gas constant.

For diffusion controlled process, the numerical value of \( (K_{T+10})/K_T \) is 1.1 to 1.2 and for kinetically controlled process it is 2 to 4.
4.3.3 Experimental

A series of experiments were done at different temperatures from 100 to 130°C for evaluating the kinetics of the conversion process.

4.3.3.1 Materials

PECH with molecular weight 2200 (by VPO), synthesised as mentioned under section 4.2 was used for the study. Sodium azide, supplied by Spectrochem, Mumbai was used as such. DMF supplied by S.D. Fine chemicals, Kochi, was purified by distillation and dried over molecular sieves prior to use. Laboratory reagent grade toluene and distilled water were also used for the synthesis.

4.3.3.2 Equipments

A two litre capacity round bottom flask was used as the reaction vessel. A paddle stirrer, driven by an electrical motor with control was used for agitation. The temperature was monitored by a digital control system attaché to the electrical heating system. IR spectra of the samples were recorded using Nicolet 510 P FTIR spectrometer in the range 400 to 4000 cm\(^{-1}\).

4.3.3.3 Procedure

PECH was dissolved in DMF and was mixed with slightly more than equimolar quantity of sodium azide. The kinetic study was conducted at constant temperature of 100, 110, 120 and 130°C. Samples were taken at regular intervals of time (1/2 hour) from the reaction kettle, cooled and filtered. The filtrate was then distilled to remove DMF. After the removal of the solvent, polymer samples were washed with water and dried. The procedure was repeated for 110, 120 and 130°C.

Conversion of PECH to GAP was followed by IR spectra. To follow the extent of conversion of PECH to GAP, C-Cl peak at 747 cm\(^{-1}\) or azide peak at 2100
cm\(^{-1}\) is used. During the course of reaction, the intensity of C-Cl peak at 747 cm\(^{-1}\) decrease as the intensity of azide peak at 2100 cm\(^{-1}\) increase. The hydroxyl peak at 3400 cm\(^{-1}\) originally present at the chain ends of PECH is retained during and after completion of the conversion of PECH to GAP. The reaction was not conducted above 130\(^0\)C because of safety considerations. At temperatures below 100\(^0\)C, the rate of reaction is low and it may take long period for completion of the conversion.

### 4.3.3.4 Results and discussion

With increase in the reaction temperature, time required for complete disappearance of chlorine decreases. Progress of the reaction was monitored by IR spectra. The time required to convert PECH to GAP completely at different temperature is given in table 4.4. IR spectra showing progress of the reaction and reduction in the intensity of the peak due to C-Cl bond is shown as figure 4.4.

#### Table 4.4 Effect of temperature on reaction time

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>110</td>
<td>&lt; 2 ½</td>
</tr>
<tr>
<td>120</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>130</td>
<td>&lt; 1 ½</td>
</tr>
</tbody>
</table>
Figure 4.4 IR spectra of samples showing progress of reaction

The prominent peaks in the spectra are considered for quantitative evaluation and reference. Peaks at 2100 cm\(^{-1}\) and 1281 cm\(^{-1}\) correspond to CH\(_2\)-N\(_3\) and peak due to CH\(_2\)-Cl bond appears at 747 cm\(^{-1}\). Peak due to the C-O-C linkage, which appears at 1125 cm\(^{-1}\) and peak corresponding to hydroxyl groups at 3400 cm\(^{-1}\) remain
unchanged during the course of the reaction. The quantitative investigation of conversion of PECH to GAP was monitored by the decrease in the ratio of intensities of IR peak at 747 cm\(^{-1}\) and 1449 cm\(^{-1}\), \(C_a/C_{a0}\) (where \(C_a\) is the intensity of peak due to CH\(_2\)-Cl and \(C_{a0}\) is the intensity of reference peak due to C-C). From these values, extent of conversion was determined quantitatively. A similar follow up of the reaction can also be done with ultra violet spectroscopic evaluation, TGA and DSC.\(^{26}\)

The concentration gradient as represented by the ratio was used for the evaluation of the kinetics of the conversion process. The data was found to fit well for first order kinetics. First order plot of chlorine substituent concentration at different time intervals are shown in figures 4.5, 4.6 and 4.7.

\[\text{Figure 4.5 First order plot for concentration of chlorine substituent (100\(^\circ\)C)}\]
Figure 4.6 First order plot for concentration of chlorine substituent (110°C)

Figure 4.7 First order plot for concentration of chlorine substituent (120°C)
Excellent linear fit shows that the reaction is first order with respect to chlorine concentration. Since sodium chloride and sodium azide have very low solubility in DMF, concentration of sodium azide can be taken as constant and so, the rate of reaction is dependent only on chlorine concentration. The values of the rate constant at different temperatures, which are the slopes of the first order plot, are shown in table 4.5. These values are in agreement with results reported in literature\textsuperscript{26}

Table 4.5 Variation of rate constant with temperature

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>k (min(^{-1}))</th>
<th>k (hour(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.01625</td>
<td>0.975</td>
</tr>
<tr>
<td>110</td>
<td>0.01842</td>
<td>1.105</td>
</tr>
<tr>
<td>120</td>
<td>0.01968</td>
<td>1.181</td>
</tr>
</tbody>
</table>

Arrhenius temperature dependency is plotted in figure 4.8. Slope is a measure of activation energy (E) of the chemical reaction. The activation energy of the conversion reaction estimated from the slope is 12.6 kJ mol\(^{-1}\).

![Figure 4.8 Arrhenius plot of rate constant](image-url)
10°C temperature coefficient calculated using equation 4.1 is 1.1, which shows that reaction is in dynamic regime and hence diffusion controlled. For diffusion controlled processes, agitation and intensity of mixing are very important. The solid sodium azide should be well suspended in the fluid medium. The agitation speed should be maintained above critical speed ($N_c$) of the particles so that they will not settle to the bottom of the reactor.

4.3.4 Estimation of agitator speed requirement

Kinetic studies show that the reaction between PECH and sodium azide is diffusion controlled. For a diffusion-controlled reaction, dynamic similarity is the most critical issue and can be addressed satisfactorily by maintaining same degree of dispersion in the pilot plant and model. In the pilot plant, geometrical similarity was not maintained, as a glass reactor was modified to suit to the specific requirement. The solvent requirement was also reduced to make the process more cost effective. Chemical similarity was also not maintained due to the change in concentration of the reactants. Physical properties of the slurry in the model and pilot plant are also different. To account for all these factors, a different scale up criterion was adopted. The agitator speed for the pilot plant was estimated for different similarity criteria and also for critical speed requirement. The criteria considered for scale up include (i) constant power/unit volume, (ii) constant tip speed of the agitator and (iii) constant Reynolds number.

The flow pattern in an agitated vessel depends on the geometrical proportions of the equipment. The mechanism of flow is a combination of laminar flow, turbulent flow and boundary layer separation. The dimensions of the tank and the impeller, physical properties of the fluid and the suspended solid, the speed of rotation of the impeller are some of the important design considerations. The designer has the freedom to select the most appropriate agitator type and the various geometrical or shape factors, which depend on the physical properties of the slurry. But the speed of
rotation of the impeller depends on the settling velocity of the solid. In an agitated suspension of free settling solids, some of the particles may never reach the liquid surface. Often the solids are lifted only to a definite maximum height \((Z_s)\) above the vessel floor, which sometimes is much less than the liquid level. Above this level, the liquid is free from solids. The geometrical parameters of the model and pilot plant reactor are tabulated in table 4.6.

Table 4.6 Geometrical parameters of the model and pilot plant reactors

<table>
<thead>
<tr>
<th>Design parameters</th>
<th>Model</th>
<th>Pilot plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>2 litre</td>
<td>50 litre</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Round bottom flask</td>
<td>Cylindrical vessel</td>
</tr>
<tr>
<td>Vessel diameter</td>
<td>16 cm</td>
<td>40 cm</td>
</tr>
<tr>
<td>Agitator diameter</td>
<td>8 cm</td>
<td>20 cm</td>
</tr>
<tr>
<td>Position of the agitator</td>
<td>4 cm</td>
<td>17 cm</td>
</tr>
<tr>
<td>from the bottom</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level of the reactants</td>
<td>12 cm</td>
<td>45 cm</td>
</tr>
</tbody>
</table>

As the impeller speed is increased, \(Z_s\) increases and becomes equal to the liquid depth \((H)\). A large number of empirical correlations are available in literature, to estimate the power \((P)\) required to suspend particles to the required height depending upon the type of agitator used. Such a correlation shown as equation 4.2 was used in the study to fix the speed of agitation for the laboratory experiments:\textsuperscript{27}

\[
P = \frac{\rho g e}{\bar{\rho}_m v_m u_t} = \left[1 - \epsilon_m \right]^{2/3} \left(D_l/D_s\right)^{1/2} \rho^{0.35} \rho^{0.35} (4.2)
\]

where

\[
\rho = \frac{Z_s - E}{D_t} - 0.1
\]

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where $P$ - power delivered by the impeller, $\rho_m$ - density of the suspension, $V_m$ – volume of the suspension, $u_t$ – terminal settling velocity of the particles from Stokes law, $\epsilon_m$ – volume fraction of the liquid in suspension, $D_t$ – diameter of the tank, $D_a$ – diameter of the agitator, $E'$ – clearance between the impeller and the floor of the vessel, $Z_s$ – height of liquid in the vessel, $g$ – the gravitational acceleration and $g_c$ – the Newton’s law proportionality constant.

Volume of suspension is given by the expression

$$V_m = \frac{\pi D_t Z_s}{4} \quad (4.3)$$

Volume fraction of liquid in suspension is given by

$$\epsilon_m = \frac{\text{Volume of liquid in suspension}}{\text{Volume of suspension}}$$

For the laboratory experiments, a paddle agitator with a suitable geometry was selected. Once the power is determined, agitator speed ($n_s$) can be obtained from power number ($P_n$).

$$P_n = \frac{K_c \, n_s^3 D_a \rho}{g} \quad (4.4)$$

Where, $K_c$ is a constant obtained from literature which is a function of the geometry of the agitator (for flat paddle stirrer, $K_c = 1.7$) and $\rho$ is density of the medium.

For the correlation selected for scale up, the agitator speed was calculated from equation 4.2 for a 2-litre laboratory set up. The minimum speed needed for the complete dispersion is 330 rpm and found to be adequate from real time experiments. The agitator speed was also estimated for different similarity criteria. The results are tabulated in table 4.7. It was seen that the agitator speed requirement based on the correlation for critical speed demands for a higher rpm and hence more effective.
Table 4.7 Comparison of speed of agitation by various similarity criteria

<table>
<thead>
<tr>
<th>Scale-up criteria</th>
<th>Agitator speed (rpm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
<td>Pilot plant</td>
</tr>
<tr>
<td>Constant power/unit volume</td>
<td>332</td>
<td>180</td>
</tr>
<tr>
<td>Constant tip speed Constant</td>
<td>332</td>
<td>132</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>332</td>
<td>50</td>
</tr>
<tr>
<td>Present correlation</td>
<td>332</td>
<td>360</td>
</tr>
</tbody>
</table>

4.3.5 Experimental

For the conversion process, glass or glass-lined reactors are mandatory as sodium azide is one of the reactants. As a first step GAP production was scaled-up to a level of 10 kg/batch. A 50 litre glass reactor set up was used as the reaction vessel. Teflon paddle stirrer with glass rod was used as the stirrer. Temperature control was done using an on-off control and cooling water circulation operated manually. Figure 4.9 shows the flow chart for the scaled up process of GAP.

The various steps involved in the conversion process are;

i. Reaction of PECH with sodium azide

ii. Recovery of DMF

iii. Washing and extraction of GAP (in toluene) and

iv. Recovery of GAP from toluene.
Figure 4.9 Flow chart of the scaled up process of GAP
4.3.5.1 Materials

Materials used for the trials were same as mentioned in section 4.3.3.1.

4.3.5.2 Equipments

The scale up reaction was done in a electrically heated 50 litre glass reactor with temperature control. The washing of the reaction products was done in a 100 litre capacity glass vessel. Recovery of solvents and drying of the GAP resin were carried out in a 50 liter capacity vacuum flash evaporator. Completion of the conversion was verified by IR spectroscopy using Nicolet 510 P FTIR spectrometer in the range 400 to 4000 cm$^{-1}$.

4.3.5.3 Procedure

(i) Reaction of PECH and sodium azide.

The 50 liter glass reactor was cleaned and dried. The reactor was purged with nitrogen gas and warmed to 45°C. Required quantity of PECH dissolved in DMF and required quantity of sodium azide suspended in DMF were charged into the reactor. The heterogeneous reaction between sodium azide and PECH will be effective only if the azide particles are suspended uniformly in the liquid medium. The results of the kinetic study helped to select the optimum speed (350-400 rpm) of the stirrer. Temperature was first set at 80°C to avoid over heating and slowly raised. When it reaches around 80°C the rate of temperature rise was found to increase due to initiation of the exothermic reaction. The reaction was carried out in the pilot plant at 120-130°C based on the optimised reaction temperature derived from the kinetic experiments. After 5 hrs of reaction a 50 ml sample was withdrawn and washed with distilled water. The resin layer was separated, moisture and volatiles were distilled off. The IR spectrum of the sample was checked for C-Cl peak at 747 cm$^{-1}$. If the peak was observed, the reaction was continued till the chlorine trace was removed completely.
(ii) Recovery of DMF

The reaction products were discharged into a 50 litre container and allowed to settle. The resin layer was separated from the sodium chloride and unreacted sodium azide and charged into the 50 litre capacity rotary vacuum flash evaporator to recover DMF. At 120°C under a pressure of 20 mm Hg, up to 90% DMF was recovered.

(iii) Washing and extraction

GAP resin layer was washed with distilled water in a 100 litre glass reactor. The contents were agitated vigorously for 30 minutes and allowed to settle for 1 hour. Emulsion layer formed contains GAP. The emulsion layer was repeatedly washed with excess distilled water each time and the water extract is tested with AgNO₃ for complete removal of unreacted NaN₃ and NaCl. When no precipitate was seen the resin layer was extracted with toluene. GAP was repeatedly extracted with toluene for completely separating it from the emulsion.

(iv) Recovery of GAP from toluene

The GAP solution was heated in the 50 litre capacity rotary vacuum flash evaporator at 110°C and 20 mm Hg pressure (absolute) to distil off toluene, which was recovered and reused. Vacuum drying of the GAP was continued till volatile content was below 0.5%. The resin was discharged from the vacuum evaporator and weighed. The yield was approximately 90%.

4.3.5.4 Results and discussion

The resin was stored in sealed containers. The resin batches processed were analysed for chemical and physical properties and were found to be consistent. The analytical results of the resin batches processed in the pilot plant are provided in table 4.8.
Table 4.8 Properties of GAP processed in pilot plant

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Batch size (kg)</th>
<th>Viscosity (cps)</th>
<th>Nitrogen content (%)</th>
<th>Hydroxyl value (mg KOH/g)</th>
<th>Volatile matter (%)</th>
<th>Mole. wt VPO</th>
<th>Mole. wt GPC</th>
<th>Functionality VPO</th>
<th>Functionality GPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>2220</td>
<td>38.4</td>
<td>43.7</td>
<td>0.23</td>
<td>2250</td>
<td>2510</td>
<td>1.75</td>
<td>1.96</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2300</td>
<td>39.3</td>
<td>44.2</td>
<td>0.21</td>
<td>2210</td>
<td>2500</td>
<td>1.74</td>
<td>1.97</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>2250</td>
<td>39.6</td>
<td>44.9</td>
<td>0.22</td>
<td>2190</td>
<td>2480</td>
<td>1.75</td>
<td>1.98</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>2290</td>
<td>39.8</td>
<td>44.1</td>
<td>0.21</td>
<td>2230</td>
<td>2510</td>
<td>1.75</td>
<td>1.97</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>2260</td>
<td>39.4</td>
<td>43.7</td>
<td>0.23</td>
<td>2240</td>
<td>2530</td>
<td>1.74</td>
<td>1.97</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>2240</td>
<td>39.8</td>
<td>43.5</td>
<td>0.21</td>
<td>2260</td>
<td>2540</td>
<td>1.75</td>
<td>1.97</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>2300</td>
<td>40.3</td>
<td>43.9</td>
<td>0.22</td>
<td>2220</td>
<td>2520</td>
<td>1.74</td>
<td>1.97</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>2220</td>
<td>40.1</td>
<td>44.1</td>
<td>0.22</td>
<td>2220</td>
<td>2500</td>
<td>1.75</td>
<td>1.97</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>2250</td>
<td>40.4</td>
<td>44.4</td>
<td>0.23</td>
<td>2200</td>
<td>2500</td>
<td>1.74</td>
<td>1.98</td>
</tr>
</tbody>
</table>

The consistent results indicate the adequacy of the process followed for scale up. The difference in the molecular weight and functionality determined by GPC and VPO is due to the use of polystyrene as the calibration standard as explained in section 4.2.3.4.

### 4.4 Conclusion

Polymerisation of ECH was done under different reaction conditions and based on the trials, the parameters required for producing polymer with required chemical and physical properties were optimised. The optimised process parameters were adopted for scale up of PECH production in a pilot plant batch reactor at 20 kg level. Chemical and thermal similarity was maintained for scale up and the process was successfully scaled up at pilot plant level. Reproducibility of the process was established in the pilot plant.
Experimental study was carried out for conversion of PECH to GAP and kinetics of the process was investigated. Based on the kinetic study results, the rate controlling mechanism of the conversion process was identified and the process was found to be in the dynamic regime. The agitator speed requirement was estimated for different scale up criteria and a correlation based on critical speed of agitation was found to be effective for conversion with reasonable yield. Based on the experimental and theoretical studies carried out, production of GAP was scaled up in a pilot plant batch reactor at 10 kg level. Reproducibility of the process and consistency of the product were established through repeated trials in the pilot plant.

4.5 References


