The Reactive Processing will need a whole book to cover the work done in the field besides discussion on suitability of the type of machine best suited for the job. This presentation only hopes to provide an introduction to the subject.

We would touch upon the following aspects:
- Why use an extruder?
- Major considerations in use of an extruder.
- Characteristics of Single and Twin Screw extruders relevant to reactive processing.
- Which of the two types will you choose?
- Some commercial production examples – Controlled Rheology PP, Maleic Anhydride grafted PE, Caprolactam polymerization to nylon-6 and nylon alloys.

1. INTRODUCTION

Reactive processing of polymers involves carrying out a designed chemical reaction where a major component is a polymer.

Prior to the use of an extruder such reactions would be carried out in a stirred tank reactor either in solution or emulsion form. And rarely on solids.

Kowalski has presented the following figure in Reactive Extrusion (Ed : Xanthos). The advantages of the extruder reactor over the alternative need no explanation. For detailed economics please refer to the said reference.
Compared to the tank reactor an extruder offers several advantages and also has some limitations:

**Advantages:**
- It is a continuous (nearly) plug flow reactor which may also be adapted to a degree of back mixing.
- Easy to convey and mix high viscosity materials.
- Wide ranges of temperatures and pressures possible.
- Relative ease of operation and safety.
- Post reaction modification possible.
- Control over residence time distribution.

**Limitations:**
- Mixing could be difficult due to high viscosity
- Heat transfer out of the system is poor.
- High cost for long reaction times.

Over the years the extruder design has improved to eliminate mixing as a limitation but heat transfer (cooling) may still cause concern in some reactions.

### 2. PROCESS PARAMETERS

#### 2.1 Residence Time

Reasonable reaction times for selection of a process to be carried out in an extruder shall be from tens of seconds to about 10 min. However, longer times have been reported. Total cycle time of a batch reaction could be misleading when considering a switch from a batch kettle to an extruder. More intensive mixing in an extruder itself could cut reaction time.

#### 2.2 Energy Requirements

Addition polymerizations involve large heat of reactions and are generally ruled out. A ring opening reaction is usually not highly exothermic. Caprolactam to nylon 6 is a good candidate for extruder reaction.

Grafting with vinyl monomers is not a problem since such monomers are used only to the extent of 1-10% of the total reactants.

Energy going into the extruder is of two types. The first is the heat input to melt the usually solid polymer feed and other reactants. The second results from mechanical energy dissipated as heat during the movement of melt from one end to the other, including mixing. Power consumption ‘G’ of the second type may be shown to be

\[ G \propto D^2 L N^2 \eta \]

Where D is diameter, L the length of the screw, N the rpm and \( \eta \) the polymer viscosity at the processing temperature.
For a shear thinning polymer it may be modified to

\[ G \propto K D^2 L N^{1+n} \]

Where \( K \) is a proportionality constant at shear rate \( \gamma = 1 \) and \( n \) is the slope of shear stress vs. shear rate.

The graph below qualitatively shows the effect of screw speed on energy balance in an extruder.

Heat transfer through viscous polymers is poor. Running the screw faster to renew the boundary layer can be counterproductive, since a more viscous layer at the barrel surface could actually cause increase in energy input. (Seen by higher motor currents)

**Material Feed and Removal**

Material feed in reactive extrusion is a major concern when compared to a batch reaction kettle. Material movement through the extruder is plug flow. There may be back mixing depending upon the design. The extent of this length may be worked out either by ‘freezing’ the equilibrium and taking out the screw or by adding a coloured tracer and seeing over what ‘distance’ the material exits in mixed conditions.

It, therefore, becomes necessary to keep uniformity of feed of all the components over short periods of time.

The materials may need to be fed as solids, liquids or gases and may be at normal or high pressures. Safety is a consideration with certain components like peroxides, maleic anhydride, etc.
After the reaction, unreacted components or degraded products will need to be removed either at atmospheric pressure or under vacuum.

Additionally inert gases (or liquids) may be used as stripping aids for removal of unreacted monomers / additives or reaction by products.

Machine design today provides solutions for all the above. Some examples are provided in the text.

3. EXTRUDER DESIGN AND CONFIGURATION

3.1 Single Screw Extruder

Feed is likely to be in solid form. Other reactants / additives may be added at the hopper or downstream. Reaction is unlikely to occur until the polymer is molten. A good mixing section is required and the reactants may also be injected at this point. Hereafter, adequate residence time must be provided for the reaction to complete. This is followed by a section to generate pressure for extrusion.

The extruder may be run in flooded or starved mode. Nitrogen blanket may be used. If a good uniform premix can be obtained a SSE may be adequate for a lot of applications. Feeding of low melting or liquid components will have to be downstream of feed hopper to prevent feed problems.

Should some unreacted components or by products have to be removed, this can be done just before the final pumping section.

The schematic figures below give some possible configurations.
3.2 Twin Screw Extruder (TSE)

TSEs have been extensively used for compounding and over the years the technology has been developed to provide excellent mixing and control of other functions such as residence time, devolatilisation and pressure.

Further, variations of geometries like
- Tangential counter – rotating
- Intermeshing counter – rotating
- Intermeshing co rotating

provide additional possibilities including self wiping characteristics. The latter reduces long residence time tail, sometimes undesirable in reactive extrusion.

The figures below give schematic representation of the three types.

- Counter rotating non intermeshing
- Counter rotating intermeshing

A = Conveying / Feed
B = Melting
C = Mixing
D = Pumping / Metering
4. SELECTION OF AN EXTRUDER

4.1 What type of extruder to choose? This question has no simple answer. We will try to put across some broad considerations.

Unlike most approaches, I like to start with funds available.

There is no point in thinking about a TSE if all the money available is, say Rs. 10 lakhs. In the range of 20-70 lakhs a choice of Indian TSEs are available and you could get a customised one for your needs. Should your resources be greater than this you could certainly look for the state of the art machine from abroad.

4.2 At Rs. 25 k to 100 k

You could get a good local fabricator in any of the metros to make a 25-35mm SSE of L/D 30-36. Vented. Variable speed drive. A good mixing section and screw to your design. Frills like PID controls may be possible.

So what will I ask for in this price range? A screw of the following design: With an excellent feed hopper throat cooling. The figure shows length of various zones in terms of diameters.

If I could get a 35mm machine in this price I will go for L/D=36 and breakup of screw section shall be

<table>
<thead>
<tr>
<th>Feed</th>
<th>Compression + melt</th>
<th>Mixing + Reaction</th>
<th>Vent</th>
<th>Metering</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 D</td>
<td>5</td>
<td>10</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

- Feed: 6 D
- Compression: 6
- Mixing + Reaction: 13
- Vent: 4
- Metering: 7
A longer screw in small diameters is not practical since the root of the screw does not have adequate mechanical strength to transfer the power from the motor into the polymer.

4.3 At Rs. 20-70 lakhs

This budget will get you a good to excellent TSE with some limitations on feeders. Since TSEs are generally worked in starve mode you will need to be careful with your volumetric metering devices. You could get a good data recording facility with a PLC controller. You should look at a minimum L/D of 40 and preferably 44 or higher. Two vacuum ports and at least one liquid injection point. A range of elements will be available and you shall not be limited in your choice of configuration for any reaction.

But currently only co-rotating TSEs are available.

4.4 At Rs. 1.5 crore or higher

You could either upgrade the best Indian machine and still be under Rs. 1.0 crore or look for an imported machine.

In the latter case you have a choice between counter – and co-rotating machine. I would be hard pressed to choose one over the other.

Other considerations that will apply are:
Is it going to be a primarily research machine or one for production?
Will you want to do some compounding also?
What are the service back up of the supplier?

4.5 A second hand machine?

In my view at lower end of the price scale this is not an option. At the upper end it is a definite alternative. Even in this case you need to have good engineering support in-house – both mechanical and Electrical & Electronics.

Pluss Polymers started its technology development on a Rs. 25,000 machine. This set up was also used for initial commercial production. Today we operate with a good Indian TSE modified in-house to suit Reactive Processing and soon hope to graduate to a world class machine.
5. COMMERCIAL EXAMPLES

5.1 Polypropylene Degradation

PP as produced in earlier years was difficult to process due to the presence of very high molecular weight ‘tail’. This tail, it was shown, could be preferentially reduced by thermal cracking in an extruder and later shown to be better by use of a peroxide degradation process.

Sketch below is the schematic of the manufacturing setup.

For kg scale laboratory production the peroxide can be simply tumble blended and fed into a SSE of L/D, 24 upwards. Vent and stabiliser addition can be done away with. The granules can be devolatalised in a vacuum oven and additives tumble blended at the next processing step.

In a commercial situation you may want a nitrogen blanket to exclude atmospheric oxygen, remove by products under vacuum and inject antioxidant and other additives prior to granulation to make the process economic.

5.2 Maleic Anhydride Free Radical Grafting on PE

5.2.1 An early setup (mid ‘60s) using a SSE is shown below:

The features / problems to note are:

- All the reactants are added through the main feed hopper.
- The reaction has to be over before the vent.
- A melt seal is essential before the vent.
- Reaction takes place at a variable temperature profile.
Quality of mixing is uncertain.
Addition of MAH in the hopper is an environmental hazard.
Post reaction additive injection not possible.

5.2.2 Improvements Desirable

Inject Maleic Anhydride and peroxide where it is needed (via closed system to keep environment clean)
Material handling – e.g., line blockages by MAH or safety with peroxides.

The modified system to take care of the above is shown below:

Points to note

A thorough mixing of liquid MAH takes place in the polymer before peroxide enters.
Peroxide should contact the polymer and mix in quickly taking into consideration its half life at that temperature.
Can not delay peroxide injection too long since it means excessive extruder length.
Nitrogen blanket to prevent atmospheric air getting in.
A Single Screw extruder may be used but will have limitations and will only be a marginal improvement over the previous setup.
Counter current nitrogen stripping of MAH within the extruder. Clearly a TSE is necessary for this and a non intermeshing machine will be even better.
5.3 Caprolactam Polymerisation

Nylon-6 from Caprolactam using counter rotating non intermeshing TSE has been described by Thomas Bash in Plastics Compounding. It is not clear whether the process is being followed commercially.

Points to note:

CRNI machine allows 25% more free volume which aids volatiles removal.

Higher free volume allows counter current cooling of melt by fluids (gas or inert liquids)

Higher free volume in a co-rotating TSE may also be obtained by suitable modification of the screw elements. Such modification will tend to make the elements weaker but this may not be important when you are working with unfilled polymers and in starve fed mode.

5.4 Modification of Nylon

For Nylon to form alloys with any other polymer the added polymer must have functionality that is compatible with nylon. Thus the ester, acid or anhydride group containing polymers may be reacted with ammonia or other aminating agents to give groups compatible with nylon. Such polymers having acrylates, acrylic acid, anhydride groups may be part of copolymer macromolecule, e.g., SMA grafted on to polyolefines.

Nylon may then be blended with another incompatible polymer using a compatibiliser derived from any of the above imidized material or the amine end group from the nylon molecule itself may be reacted with the reactive group on the added polymer to form an alloy.
The majority of commercially important polymers are immiscible with one another. When mixed and extruded to make a blend, one polymer will form a dispersed phase in a continuous matrix of the other polymer. Generally, the more viscous polymer forms the dispersed phase. When subjected to further processing the dispersed phase will usually agglomerate into larger domains.

Such a problem also occurs in Nylon blends with polyolefin and other polymers. Phase agglomeration is prevented by bonding the dispersed phase to the matrix by chemical or physical means as indicated above.

For toughening of nylons maleic anhydride / Acrylic acid grafted polymers are used to lower interfacial tensions between the two phases and achieve stabilisation of the blend. The Anhydride/Acid react with -NH2 end groups of the nylon to form a block copolymer. This block copolymer then provides stabilisation of the morphology of the bulk of the two polymers in the blend. To further get a good blend following points need to be borne in mind:

1. Mixing machine used must provide efficient mixing to get desired morphology of one phase in another.
2. Residence time in the machine should be greater than that required for completion of the reaction.

Due to the above requirements, twin screw extruders rather than single screw extruders are often more efficient for blend formation. Internal mixers will generally not provide high enough temperatures required for chemical reaction. Problems may also result due to poor thermal stability of the nylon in presence of air. For non reactive blends these are a strong contender as a suitable machine for the purpose.

6. INDIAN SCENARIO

Silane grafted LDPE for XLPE cables has been produced in India since the mid eighties. Currently, several companies produce silane grafted PE for cables.

We know of attempts made by several companies to produce maleic anhydride grafted polyethylene in India, starting around 1990. SRF probably were the first.

Pluss Polymers are the major producers of maleic anhydride and Glycidyl methacrylate grafted polyolefines. Approx 25 products based on PP, HDPE, LDPE, LLDPE, ULDPE, EVA and EPDM are available. Vin Enterprises is another company that started production a few years back. We believe presently they have one grade each based on PP and PE.

We estimate total current consumption of grafted polymers could be about 100-200 tpa, excluding that used for multilayer nylon films.

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