

# High Viscosity Polyester – New Solid and Melt Phase Process Approaches

U.K.Thiele, Consulting Dr.Thiele Polyester Technology, Bruchköbel/Germany

The production processes for high viscosity polyester are driven by two fast growing market segments – the packaging materials especially the polyester bottles and the technical yarn production. Both areas are fortunately excluded from Chinese polyester fiber predominance yet and growing round the World between 6 and 12%/a. Not to forget PET-foam which is growing fast but from a lower level. It is interestingly to observe in this development area the antagonism between plain process economy and complex process comfort which is finally also part of the overall economy for the consumer. And it is becoming more complicated when IV lift up and removal of acetaldehyde are depending each other which is the case especially in all packaging applications. If we are asking for the eligible innovations in high IV PET production processes we can easily count a hand full. The most important are

- ~ Reduction of conversion cost, mainly labor and energy consumption
- ~ Increase of single line unit capacities safely above 1000 t/d
- ~ Increase of line flexibility
- ~ Reduction of undesired side products like AA or dust
- ~ Improvement of quality like reduced IV fluctuation and lower crystallinity

The problem of this wish list is that some topics are ostensible controversy. But main target of innovation is to solve such extremes applying innovative new technical approaches.

The new developments we can classify in the following categories:

1. New SSP processes and further developments
  - ~ The new horizontal SSP process
  - ~ Further developed state of the art SSP (disadvantage of existing technology and new approaches)
2. High viscosity resin without SSP and its further treatment
  - ~ Technology status of different vendor companies
  - ~ Direct crystallization and AA removal
3. Direct converting of melt to preform or yarn
  - ~ Advertised direct performing processes of Uhde-Inventa-Fischer and ZIMMER-AG
  - ~ AA-scavenger - the still existing hurdle
  - ~ Direct spinning of tire cord
4. What public is able to distill from limited available information base about IntegRex®?

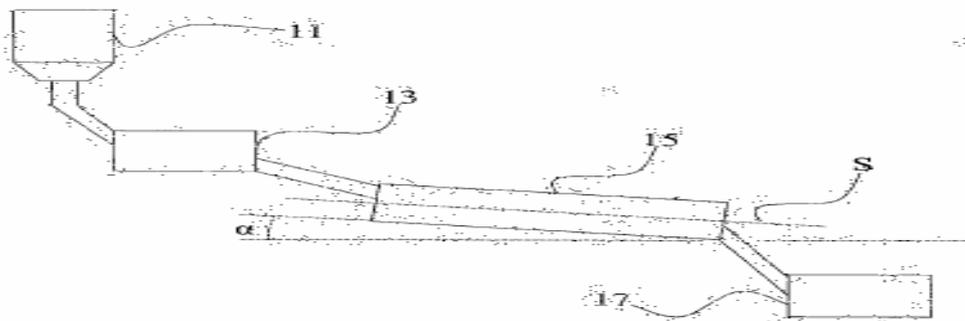
## **New SSP processes and further developments**

~ *The new horizontal SSP process*

Until last year capacity increase of SSP above 1000 t/d in one single line was still a dream because tube reactor diameter and reactor height are inherently at a capacity of 700 t/d at the physical limits. Especially plug flow conditions and even gas distribution are becoming in such a huge vertical tube reactor an increasing problem not to mention the time until the process is running under steady state conditions which is connected to inflexibility regarding throughput and IV-change. A new invention in this field came with the patent publication

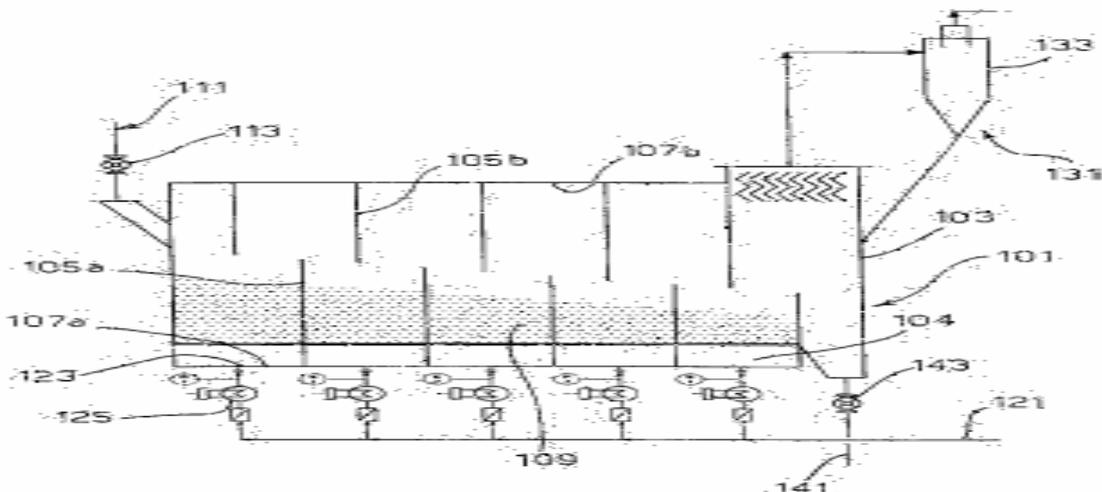
WO 2004/018541[1] where a completely new way of material flow is suggested. When state of the art continuous SSP exists of a vertical tube reactor where the polymer chips are moved by gravity flow from top to the bottom under counter current nitrogen flow the new process is suggesting the principle of inclined rotary kiln which is mechanically a matured technology of the cement industry. The polymer particles are gently moved by gravity differences triggered by slow rotation of the reaction tube whereat the reaction gas is flowing over the steadily renewing granulate bed surface and removing the split off products like water and glycol. It is to prescind that in difference to the vertical tube reactor the plug flow conditions of a kiln type reactor is comparable to a series of large numbered equal sized back-mix tanks. The principle is demonstrated in figure 1.

Figure1: "WO 2004/018541 - Continuous Process for Solid State Polymerization of Polyesters"



For the treatment of even small sized granules of low IV-precursor which are additionally abrasion sensitive and brittle the same inventor suggested in WO 2004058852 a reactor containing a serial of fluid beds which is providing with its limited bed heights a gentle treatment together with intensive gas exchange [1]. Figure 2 is showing the schematic principle.

Figure 2: "WO 2004058852 Reactor and process for Solid State Polymerization of Polyethylene Terephthalate"



Unlike other inventions which need a lot of time between publication and technical

realization the interested professional could read in public papers [2], that M&G head of technology Guido Ghisolfi talked during Nova-Pack -January 2005 (Bal Harbour, Miami, USA) about the new kiln reactor type SSP of a capacity above 1000 t/d . And he already announced this technology named “EasyUp” as proprietary to M&G. Meanwhile an industrial sized Horizontal (kiln type) SSP has already been successfully started-up in one of M&G PET production sites since June 2005 [3]

*~ Further developed state of the art SSP*

One hurdle of the common SSP technology is dust generation especially during second crystallization. Mainly the mechanically moved horizontal crystallizers are not able to treat the polymer pellets as gentle as desired and especially at the peripheral rim and near the stirrer mechanical forces are high. To overcome this problem a new kind vertical second crystallizer is described in WO 03046045 [1]. The improved process exists of a first fluid bed crystallizer which is about state of the art and a second crystallizer which is vertical and the top part of the crystallizer is gently moved by a specially shaped stirrer. By an optimal L:D selection of the crystallizer tube diameter vertical flow movement and horizontal agitation complementing each other which guides to a minimum of mechanical forces. Another feature is the spitted gas movement in the crystallizer tube by introducing the gas into the agitated area and split the flow in an up and downwards portion. The new process should generate less dust and provides further advantage to use the second crystallizer volume as additional SSP space. In figure 3 the crystallizer is demonstrated.

Figure 3: WO 03046045 “Method and Device for Production Highly Condensed Polyesters in the Solid Phase”

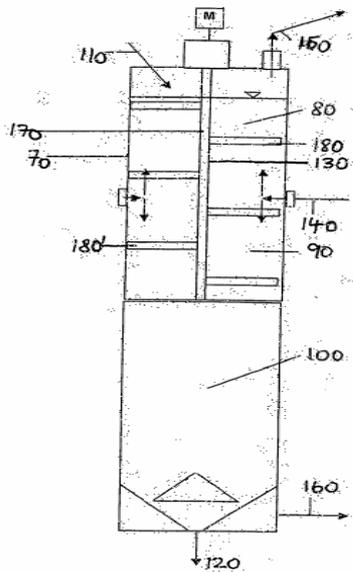


Fig. 2

By assembling fluid bed pre-crystallizer and second crystallizer in parallel to the SSP tube and conveying the hot crystallized chips to the top of the SSP tube the building height might be also possible to be reduced.

## 2. High viscosity resin without SSP and its further treatment

### *~ Technology status of different vendor companies*

Within the last two years we are observing conflicting statements regarding the best way to produce polyester resin of high IV and low AA for packaging. As seen in the first chapter there is significant cost saving potential in some new SSP technology. At the same time there is increasing advertisement about the direct conversion of the melt to the desired processing viscosity for bottles which is between 0,75 – 0,85 dl/g.

The knowledge to polymerize polyester in the melt phase up to an IV of 1,00 dl/g is more than 30 years old. For instance published Zimmer-AG several high IV-reactor process principles which are executed as well in high IV PBT production as in tire cord direct spinning [4]. With further development of finisher technology meanwhile high viscosity melt phase processes of high capacity are offered from the leading engineering companies. Two technical problems for high IV melt phase processes are still left. First problem to be solved is to compete with the meanwhile huge melt phase plant capacity which is at normal IV of 0,60 dl/g safely between 800 and 1200 t/d. And the second problem to be solved is how to get rid of the acetaldehyde.

The solution of the first problem is on a good way because Uhde-Inventa-Fischer announced on July 14, 2005 - that its Melt-To-Resin-technology in a capacity of 200 000 t/y will in part be utilized in the recently announced expansion of the DAK Americas' Cape Fear Manufacturing Site near Wilmington, N.C. (USA) [5]

### *~ Direct crystallization and AA removal*

For the second problem to remove the AA are different methods of resolution in process. When transferring the polymer melt to chips one is receiving under normal strand cutter conditions amorphous granulate which is for the processing in preform machines to crystallize anyhow. It is self evident to combine now the cutting and the crystallization step to gain the heat of the polyester melt to trigger the crystallization process and to remove at the same thermal treatment the main portion of AA. This idea was base of several patents in the past like direct crystallization by stretching in USP 5,292,865 [6] or in connection to a standard cutter in EP 0822214A3 [1] where the melt is only cooled to a temperature between 160° and 220°C where the crystallization is taking place. Similar approaches are described in PCT-WO-EP 00/06691 [1] and WO 94125239 [1]. The usage of this principle and its adaptation to under water die face pelletizing is described in WO 2005044901A1 [1]. It will be interesting to see which of the patented ideas will finally be outlived as granted.

Independent on technical lay out the high viscosity polycondensation has to be combined to the direct crystallization because there is at one side the need to reduce the acetaldehyde content which is possible only at elevated temperature and at the other side the PET resin granulate must be dealt crystallized to enable the simple drying prior preform production. So the removal of acetaldehyde is possible during cutting and crystallization and during pre-drying prior preforming. Knowing the strong demand regarding low acetaldehyde for water packaging it would be advisable to remove it as much as possible prior trading which means on needs residence time and gas treatment where we are back to a tube reactor, a gas circuit and respective equipment which is similar to simple drying. To avoid or minimize this equipment another way out is the addition of AA-scavenger which includes drawbacks like running scavenger cost and the possible diffusion of scavenger traces to the packed liquid. Another way to reduce AA is described in USP-Appl. 20050014929 [6] and USP-Appl. 20050049391 [6] by adding a catalyst during the melt phase which destroys acetaldehyde and reduces in this way the overall AA- content.

Melt to resin process is of advantage from downstream processing quality aspect especially

because of the relatively low degree of crystallization of this polyester resin granulate which provides gentle melting and reduced AA regeneration.

Because today the first melt to resin project is still under execution one has to wait until this plant will be started up and the first results from the field are available. Besides all skepticism this technology will be one of the further polyester process developments which will become of significant impact to the polyester industry.

### **3. Direct converting of melt to preform or yarn**

*~ Advertised direct performing processes of Uhde-Inventa-Fischer and Zimmer-AG*

The advertisement of the direct preforming or melt to preform process was actively performed by the leading engineering companies during the last year. On the occasion of 9<sup>th</sup> World Congress "Polyester PET Chain" in Zurich in 2004 Uhde-Inventa-Fischer gave the public the possibility to observe the melt to preform pilot facility in Domat/Ems. Zimmer-AG demonstrated its direct performing to selected customers. Several companies are possessing respective process patents like USP 5,656,221 [6] and DE 10356298 [1] from Zimmer-AG, USP 5,656,719 [6] from Uhde-Inventa-Fischer or WO 97/31968 [1] from Eastman.

To transfer this innovative process to the industry two main problems are still existent. First problem is the melt distribution and preform processing logistic. Different to direct spinning which is the paradigm process each high output preforming machine is consuming between 2000 and 5000 kg melt per hour. This is a factor x 20 -250 compared to spinning where each spinning position is processing between 20 and 100 kg/h. Each stop of one preforming machine is causing significant melt flow differences and process discomposure which are in DE 10356298 [1] suggested to be compensated by a complicated side stream cutting and melt recycling system. This could mean the continuous melt phase process connected to a direct preforming plant would be in general less stable and the preform producer becomes at the same time a resin producer with unpredicted amounts of granulate. May be the solution might be another way around when in the future a resin producer who is running a melt to resin process will connect one or two high output preform machines to produce a certain amount of standard preforms.

*~ AA-scavenger - the still existing hurdle*

The second and more severe problem is the removal of acetaldehyde. For the time being most of the developments are focussing on the addition of AA scavenger. But unfortunately these substances are mainly of smaller molecule size which permits their diffusion from bottle wall to the packed liquid. Other disadvantages of the scavenger technology are the running additive costs and the tendency of those nitrogen-based additives to discoloration in presence of air and at elevated temperature during recycling. Because AA is a highly volatile substance one should not forget the physical AA-removal via vacuum, surface renewing or gas stripping like described in USP 5,656,221 [6] and WO 97/31968 [1]. As an outlook about direct preforming technology one can sum up that all necessary technology parts are available today. Missing is the entrepreneur who will locate the right combination of technologies together with intelligent plant operation and available market potential.

*~ Direct spinning of tire cord*

Another interesting field of high melt viscosity polyester is direct spinning of tire cord. Here an Intrinsic Viscosity of 0,90 – 1,05 dl/g at the outlet of the finisher is desired. Also this technology is executed in production units of about 40 – 60 t/d which are still running in the US and France. Problems here are the long time performance especially regarding reactor

fouling, increasing discoloration and creation of black spots and the desired low level of carboxyl end-groups in the yarn. Reactor fouling could be terminated by applying latest melt phase technology existing of whipped wall finisher. That equipment is complicated and expensive compared to the common SSP/extrusion-technology. The reduction of COOH-groups is a hurdle similar to acetaldehyde in bottle grade. Termination of COOH-groups applying additives like imidazoles or oxazolines is possible but it makes the process more complicated and expensive. And similar to direct preforming there is a conflict between tire cord production related plant size and economically feasible plant size of polycondensation facilities. Economical short term calculations with amortization periods of 4 – 5 years as they are often applied for new installations are not applicable to exculpate the relatively high investment.

#### 4. Future outlook

The announcement of Eastman's new IntegRex process was made at September 02, 2004. A number on newer and older patent publications like USP-Appl. 20020137877 [6] and USP-Appl. 20040044170 [6] or US-patents 3,250,747 [6] and 3,545,938 [6] are hinting for instance to a melt to resin process. One can assume that Eastman will build a large scale state of the art polycondensation unit of about 1000 - 1200 t/day and introducing all possible process savings and innovations including the interlocking with the PTA-process and the option that one finisher might also be a MTR-process based on existing technology. More important than process technology is seemingly the high production capacity at one production site where PTA is produced which enables the company to reconstruct and concentrate its worldwide production to some core points.

IntegRex = registered trademark

#### References

- [1] [http://ep.espacenet.com/search97cgi/s97\\_cgi.exe?Action=FormGen&Template=ep/EN/home.hts](http://ep.espacenet.com/search97cgi/s97_cgi.exe?Action=FormGen&Template=ep/EN/home.hts)
- [2] (<http://www.mgpolymers.com/Final%20NovaPack%20Jan2005.pdf>)
- [3] See D. Giordano - M&G Global R&D VP presentation paper at PETNOLOGY Forum - Berlin June 6th, 2005.)
- [4] (see: Polyester Producing Plants, Verl. Moderne Industrie, 1996, S33/34)
- [5] [ <http://www.uhde-inventa-fischer.com/pages/global/news.cfm?id=44&db=en>]
- [6] <http://www.uspto.gov/patft/index.html>

