Finishing reaction of PA 6 in the melt phase

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The difference in the production of PA6 in comparison to that of other polymers is the downstream water extraction and drying after the granulation. During these process steps, the monomer and the oligomer contents in the final product are reduced in the 0.2 to 0.6 ww/w range. The installed units for extraction and drying of the final granulated product are characterized by their large energy consumption, which considerably influences manufacturing costs.

In the past there had been attempts to develop a demonomerization process, aiming for the reduction of the monomer and oligomer content in the melt phase without extraction and drying [1,2]. The tested technologies failed to operate with the high viscosity melt. The principal deficiency was the poor surface renewal for the successful demonomerization. Therefore the operating temperature was increased in order to facilitate the demonomerizaton, the equilibrium of the polymerization reaction shifted towards the monomer direction. For this reason the measured monomer content was always high.

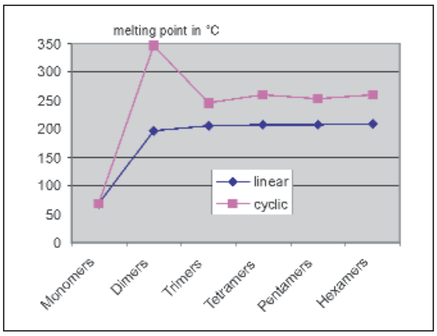

Fig. 2
Diagram of the melting point of the oligomers

Trials with the List Kneader

To overcome the process disadvantages mentioned above, it was necessary to find a processing technology that could operate at lower product temperatures and at higher melt viscosity, thus ensuring a high surface renewal. Such an operation would avoid the degeneration of polymers and would allow for the effective separation of the monomers and oligomers from the melt. The operation should preferably take place under vacuum.

For effective demonomerization, the surface renewal rate has to be faster than the formation of monomer in order to shift the reaction equilibrium to the polymer side. It is generally known that decreasing the reaction temperature the reaction velocity is also reduced. Based on the function of the reaction temperature and taking advantage of the high surface renewal rate of the List processors, trials were planned and carried out at the test center of the List AG.

The polymer melt with a usual extraction content of 9 % at 220 °C was fed to the Continuous Kneader Reactor (CKR) by List and the volatile components were evaporated under low vacuum at approx. 1 mbar (abs.). The polymer was processed in the 220-225 °C temperature range. Fig. 1 shows the process flow diagram of the pilot unit. It was found that within a few minutes the monomer content in the melt was < 0.1 %. Though the friction energy, generated during processing of the high viscous polymer, is remarkable, the unique design of the parts in contact with the product guaranteed the effective removal of the excess energy. This competitive feature of the CKR permitted the close control of the polymer temperature. This was confirmed by the measured DT between feed and discharge. It was 2 °C.

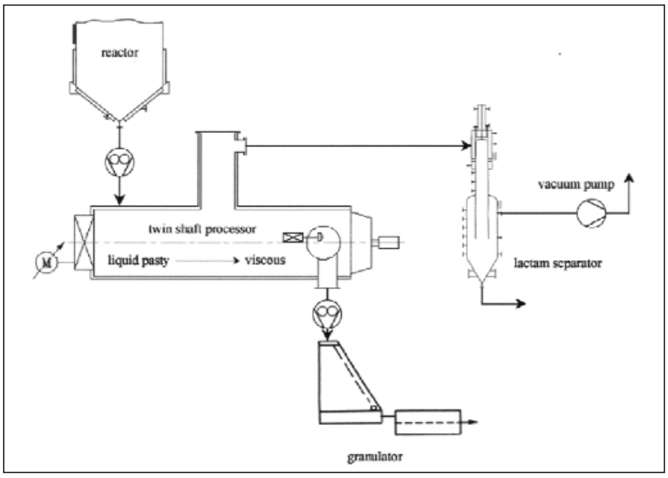

Fig. 1 Process flow diagram of the pilot unit

Composition of the final polymer

The analysis of the final polymer proved that almost exclusively the monomer can be separated using this process (Table 1).

With the decrease of the monomer content and the progress of the polymerization reaction, the viscosity clearly increased. Furthermore, the recovered caprolactam is clean and can be directly recycled to the polymerization process without rectification (Table 2).

Table 1 Product composition after demonomerization

Products	Content in the polymer melt [mg/kg]
Caprolactam	600
Dimers	8.400
Trimers	3.700
Tetramers	4.000
Pentamers	2.700
Hexamers	1.200
Heptamers	650

Table 2 Composition of the condensate

Parameter	Content of extract [mg/kg]
Caprolactam	669.000
Dimers	2.800
Trimers	140
Tetramers	< 10
Pentamers	< 10
Hexamers	< 10
Heptamers	< 10

Summary

The trials proved that the demonomerization in the melt phase is possible. The composition of the final polymer compares well with the composition of the product from the extraction process. The recovered monomer can be recycled to the polymerization process without loss. The oligomers with the higher melting point remain in the polymer. Future trials will investigate the influence of the oligomers with high melting and high boiling points, on the manufacturing process of fibers/filaments and foils as well as on their quality.

Conclusion

The conclusions drawn from those results are:

- The final PA 6 from melt finishing can be used for technical applications
- The technology of melt finishing leads to the simplification of the process, and the reduction of production and energy costs because, the granulation for the extraction, the extraction, and the drying of the wet granules are avoided.

References

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