Continuous polymerisation

Kneader-reactor produces solid granular polymers at low temperature

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Various types of reactor have been developed to date for improving the stability of the polymerisation process. This review describes a few examples of heterogeneous and homogeneous polymerisation, focusing particularly on viscosity control and heat removal. The production of solid polymer granules directly in a kneader-reactor with evaporative cooling is one efficient and reliable polymerisation technology.

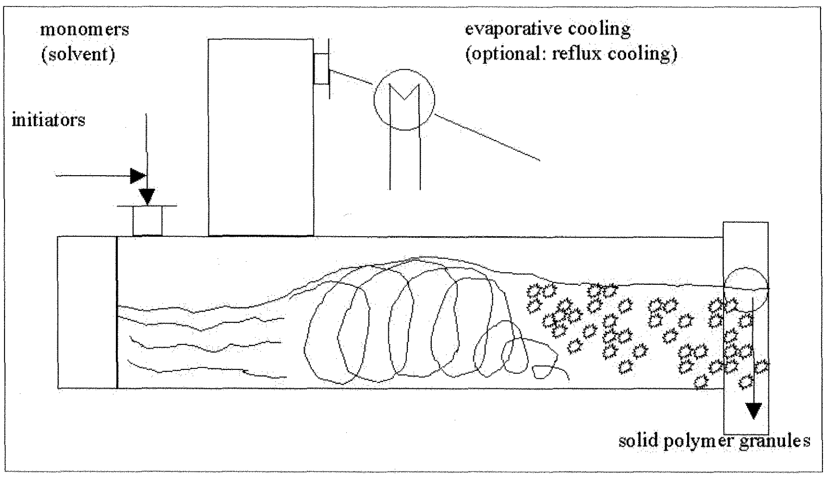

Fig. 1 Kneader-reactor for continuous polymerisation producing solid granular polymers. If the solvent is not used, the reflux of monomer is applied. Temperature adjustment by vacuum operation.

Several processing systems based on conventional techniques have been suggested to overcome the mixing problems associated with highly viscous polymer masses. One such system involves thermodynamic segregation of the polymer mass into two phases (a solid phase dispersed in a liquid phase) in order to reduce the apparent viscosity. Heterogeneous polymerisation systems, such as suspension/emulsion, precipitation and crosslinking processes, are commonly employed for polymer production. Due to the low apparent viscosities, the agitator provides efficient mixing without excessive mechanical heat input and the monomer continues to polymerise in the solid particles. Furthermore, the liquid phase is especially beneficial if evaporative cooling is used to remove the reaction heat.

Heterogeneous polymerisation systems

The standard, agitated tank reactor is suitable for suspension and emulsion polymerisation. The shearing action of the agitator maintains the polydispersive state of the segregated mass.

One of the first commercial-scale precipitation polymerisation technologies was the belt reactor process for polyisobutylene. Liquid ethylene was used not only as a precipitant but also as a medium for evaporative cooling. The evaporated ethylene was condensed externally and simultaneously separated using the reaction heat as a driving force. The benefits of combining evaporative cooling with liquid separation made this continuous process highly innovative with respect to the energy balance.

Acetal polymers have poor solubility. Crystalline polyoxymethylene, for example, is insoluble in its monomer at low temperature. The Celanese Corporation has developed a continuous polymerisation process in a twin-shaft extruder (100% filled, 47 °C, atmospheric, 18 rpm, barrel diameter 50 mm, trioxane feed rate 160 g/min, conversion 80%, net power 224 W) equipped with intermeshing elliptical and parallel paddle blades in the second extruder section.

Continuous polymerisation of syndiotactic polystyrene has also been described. This polymer likewise has poor solubility in its monomer. KRC (1 l total volume) and SCR kneader-reactors were used for continuous pilot testing (100% filled, 70 °C, atmospheric, 50 rpm, barrel diameter 50 mm, total length 660 mm, mean residence time 30 min, monomer feed rate 2 l/h, conversion 40%, net power 100 W).

Crosslinking polymerisation

Crosslinked polyacrylates or polyacrylamides are efficient water absorbers prepared by free radical-initiated polymerisation of the monomer with a crosslinker in aqueous solution (minimum of 50% water). This special type of polymerisation is included under heterogeneous polymerisation because the polymer network is insoluble in water. List's continuous twin-shaft kneader-reactors are especially suitable for this process. During the course of polymerisation, the viscosity of the liquid mass increases as a gel is formed (Fig. 1). The intermeshing of the kneading elements, as shown in Figure 2, granulates this mass into free-flowing gel particles

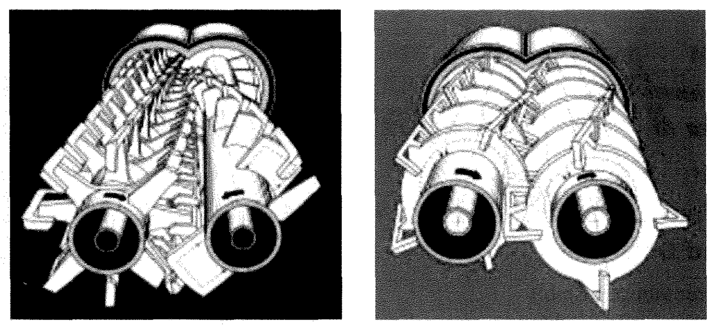

Fig. 2 Intermeshing zones of the twin-shaft kneader-reactors: ORP = opposite rotating processor and CRP = co-rotating processor. The angle of the kneading elements ensures axial conveying of the pasty polymer.

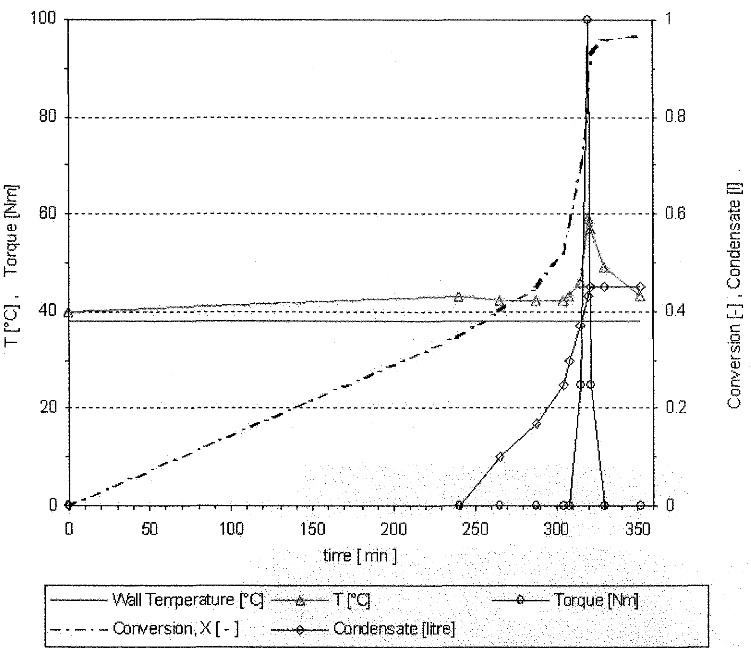

Fig. 3 Free-radical polymerisation of MMA in solution in a CRP 2.5 batch kneader-reactor at 30 rpm and atmospheric pressure. 0.45 kg of solid granules were discharged (conversion 97%, residual solvent 7%). The loss in the mono-screw was 0.19 kg.

which are discharged at a conversion rate of nearly 90%. Evaporative cooling is used to remove the heat of reaction, especially when auto-acceleration of the reaction rate occurs (gel or Trommsdorff-Norrish effect). Approximately 10% of the water is evaporated to remove the high reaction heat of the acrylate monomer (70 kJ/mol).

Homogeneous polymerisation at high temperature

The Sulzer Chemtec tubular loop reactor equipped with static mixers was developed for continuous and homogeneous polymerisation of styrene and methyl methacrylate. This technology uses a high temperature (higher than the glass transition temperature) in order to reduce the melt viscosity. The tubular loop reactor removes the reaction heat by contact only, because evaporative cooling is not possible. A few parameters, such as the ceiling temperature at which equilibrium between polymerisation and depolymerisation occurs, the degree of syndiotacticity of certain polymers and the formation of by-products (oligomers), may affect the process at high temperature, however.

Low temperature

Based on a patented technology, an optimised continuous kneader-reactor has been developed to overcome the mixing problem associated with highly viscous and homogeneous polymer masses (Fig. 1). The thermodynamic segregation described above is no longer used to restrict the apparent viscosity to a reasonable level.
The innovative feature is homogeneous polymerisation below the glass transition temperature to directly produce solid polymer granules. This principle entails mechanically transforming the homogeneous polymeric mass into free-flowing solid granules before the viscosity becomes too high. Direct mechanical granulation eliminates the need for a high power input which always means a risk of mechanical overheating. Not only crystalline but also amorphous polymers can be produced in this way. Evaporative cooling is used to remove the reaction heat.
Figure 3 demonstrates the feasibility of this technology for batch polymerisation of methyl methacrylate monomer (MMA) in diethyl ether with the initiator Perkadox 16 (Elf Atochem).
The conversion profile shown here was estimated on the basis of the final conversion and the measured condensation rate. After 200 min, the polymer mass was observed to wrap around the shafts (Wickel effect). The profiles in the figure point to a strong gel effect. The maximum specific torque of 33 Nm/l is about average for a continuous List kneader-reactor, the upper limit being 60 Nm/l.

Advantages of the kneader-reactor technology

List kneader-reactors were designed to improve radial/axial self-cleaning and axial conveying of viscous polymers. The aim was to avoid complete filling and plugging of the reactor whilst working continuously. The kneading energy is between 0.1 and 1 MJ/kg and the maximum specific torque 60 Nm/l. Torque is very sensitive to compression zones, especially with regard to solid particles. The twin-shaft kneaders have been optimised in order to avoid compression zones between the barrel and the kneading elements on the one hand and the intermeshing zones of the kneading elements on the other hand (Fig. 4).

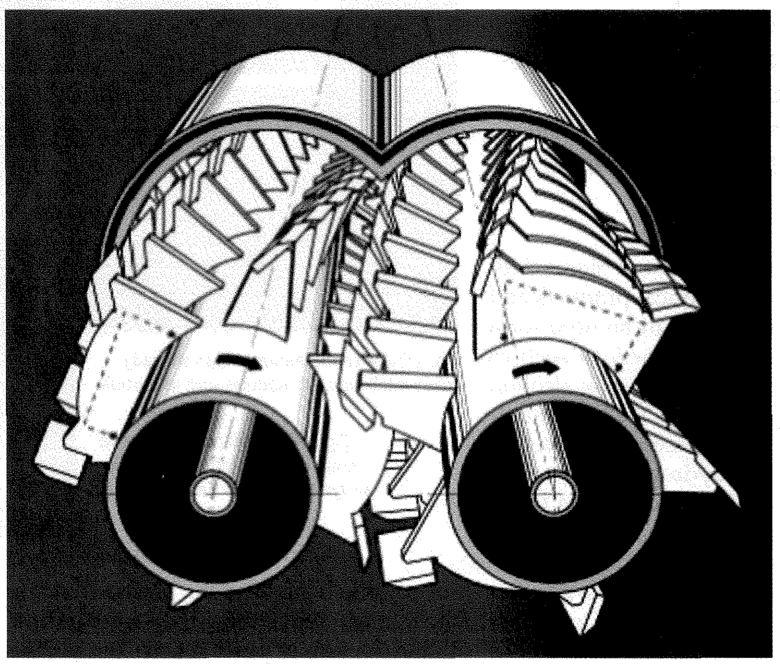

Fig. 4 Improved continuous kneader-reactor

The success of the kneader reactor for PMMA polymerisation indicates that it should be suitable for all the heterogeneous polymerisation systems described here, with significant improvements in qualitative and economic performance.
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