Turning liquid into solids

Different types of continuous polymerization kneader reactors in comparison

Over time, different types of reactors have been developed in order to improve the stability of the polymerization process. This article reviews those reactors designed for heterogeneous and homogeneous polymerization. It then explores the production of solid polymer granules directly in a kneader reactor under evaporative cooling, which is seen as an efficient and reliable polymerization technology.

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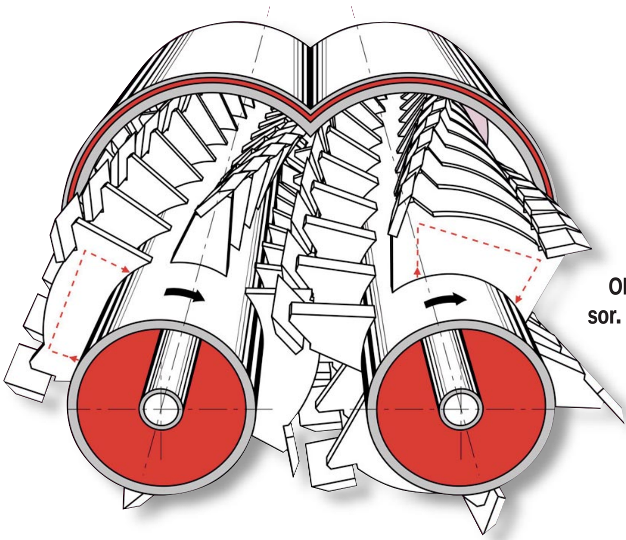

Intermeshing zones of the List twin-shaft kneader reactors: ORP as opposite rotating processor. Orientation angle of the kneading elements assures the axial conveying of the pasty polymer. Form of kneading elements facilitates compressing, or shearing, between the intermeshing zones.

Several processing systems were suggested in earlier processing techniques to overcome the mixing problems associated with highly viscous polymer masses. Among these systems are the use of thermodynamic segregation of the polymer mass in two phases (a solid phase dispersed in a liquid phase) in order to decrease the apparent viscosity. Heterogeneous polymerization systems, such as the suspension/emulsion, precipitation and cross-linking processes, are commonly employed for polymer production. Due to low apparent viscosities, the agitator provides efficient mixing without too much mechanical heat input, allowing the monomer to continue polymerizing in the solid particles. Furthermore, the liquid phase is especially beneficial when evaporative cooling is used for removing the reaction heat.

Suspension/emulsion polymerizations

The standard agitated tank reactor is suitable for suspension and emulsion polymerizations. Shearing provided by the agitator maintains the polydispersive state of the segregated mass. Large vapor passages above the agitated mass allow reflux cooling, and the water evaporation assures the best temperature control of the exothermic process, especially during auto acceleration of the reaction rate (gel or Trommsdorff-Norrish effect). The downside is that large quantities of water have to be separated after the reaction step.

Precipitation polymerizations

One of the first commercial precipitation polymerizations was the belt reactor process for poly(isobutylene) developed by BASF. Liquid ethylene was not only used as a precipitant but also as a medium for evaporative cooling.

The discharged polymer at -40 °C was described as a “sandy mass.” As such, it can be imagined that the standard stirred tank reactor is no longer suitable for agitating such a precipitated polymer.

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Poly(acetal) polymers also have poor solubility. For example, crystalline poly(oxymethylene) is insoluble in its monomer at low temperatures. The Celanese Corporation developed a continuous polymerization process in a twin-shaft extruder (100% filled, 47 °C, atmospheric, 18 rpm, barrel diameter 50 mm, trioxane feed rate of 160 g/min, conversion 80%, net power 224 W) equipped with intermeshing elliptical and parallel paddle blades in the second section of the extruder.

This polymer also has poor solubility in its monomer. The kneader reactors KRC (1 liter total volume, Kurimoto Ltd.) and SCR (Mitsubishi Heavy Industries Ltd.) have been used for continuous pilot testing (100% filled, 70 °C, atmospheric, 50 rpm, barrel diameter of 50 mm, total length of 660 mm, mean residence time of 30 min., monomer feed rate of 2 l/h, conversion 40%, riet power of 100 W).

Cross-linking polymerizations

Cross-linked poly(acrylates) or poly(acrylamides) are efficient water absorbers prepared by free-radical initiated polymerization of the monomer with a cross-linker in aqueous solution (minimum of 50% water). This special type of polymerization is included under the category of heterogeneous polymerizations

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Homogeneous and heterogeneous polymerization systems for the continuous production of polymers.

Polymer					Reactor					
name	Tg [°C]	Tc [°C]	–ΔrH MJ/kg**	Soluble at T	Type	T [°C]	cooling	e [MJ/kg**]	Discharged polymer	Kneading effect
PIB	–73	175	0.96	no	belt	–104/–40	evaporating	–	"sandy"	–
PVBE	–	–	0.60	no	belt	–	evaporating	–	–	–
PVC	85	–	1.6	no	tank + screws	50/60	reflux	–	fine particles	–
POM	178*	120	0.26	no	kneader	47/90	contact	0.11	fine particles	grinding
SPS	170*	–	0.67	no	kneader	50/90	contact	0.49	fine particles	grinding
SAP	230	–	0.81	no	List Kneader	80/100	evaporating	0.07	gelly granules	granulation
PS	100	395	0.67	yes	tubular	140/200	contact	0.004	melt	–
PMMA	105	198	0.56	yes	tubular	130/160	contact	0.005	melt	–
PMMA	105	198	0.56	yes	List kneader	40/80	evaporating	0.35	solid granuels	granulation

* melting temperature; ** based on pure polymer, dry basis; e-specific kneading energy; T_g-glass transition temperature; T_c-ceiling temp.; –ΔrH-heat of polymerization.

because the polymer network is insoluble in water. The continuous twin-shaft kneader reactors of the company List AG are ideal for this process. During the course of polymerization, the viscosity of the liquid mass increases as a gel is formed (see principle drawing). The intermeshing of the kneading elements granulates this mass into free-flowing gel particles, which are discharged at a conversion of nearly 90%. Evaporative cooling is used to remove the heat generated by the reaction, especially during auto acceleration of the reaction rate (gel or Trommsdorff-Norrish effect).

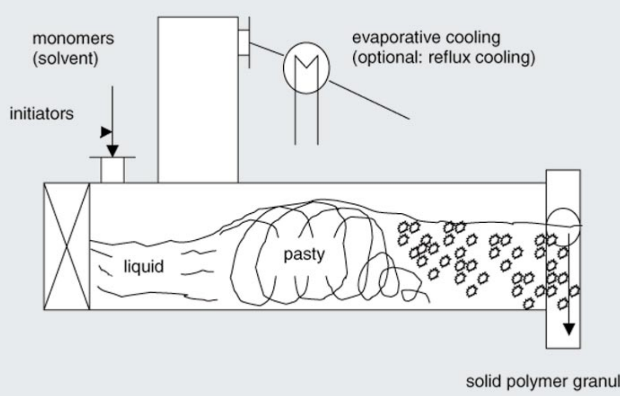
Homogeneous polymerizations

At high temperature (T > Tg)

The company Sulzer Chemtec developed a tubular loop reactor equipped with static mixers for the continuous and homogeneous polymerization of styrene and methyl methacrylate. This technology uses a high temperature (above that of glass transition temperature) in order to decrease the melt viscosity. Keeping in mind that the tubes of the loop reactor are designed for a pressure drop of 100 bar, the maximum allowable mixing energy is Ap/p = 0.01 MJ/kg, which is 100 times lower than that of a kneader reactor. The tubular loop reactor removes the reaction heat only by contact; evaporative cooling is not possible. However, with some parameters, such as when the ceiling temperature at which equilibrium between polymerization and depolymerization occurs, the degree of syndiotacticity for some polymers and the formation of by-products (oligomers) may affect the process at high temperature.

At low temperature (T < Tg)

Based on a new patented technology, an optimized continuous kneader reactor has been developed to overcome the mixing problem associated with highly viscous and homogeneous polymer masses (see principle drawing). Thermodynamic segregation as described above is no longer used to maintain the apparent viscosity at a reasonable level. The innovation is homogeneous polymerization below the glass transition temperature, which directly produces solid granules of polymer. The principle is to mechanically transform the homogeneous polymeric mass into free-flowing solid granules before the viscosity reaches too high of a level. This direct mechanical granulation eliminates the need for high power input, which always runs the risk of mechanical overheating. Not only crystalline, but also amorphous polymers can be produced in this way. Evaporative cooling is used for removing the reaction heat. Tests demonstrate the feasibility of this new technology by the batch polymerization of methyl methacrylate monomer in diethyl ether with the initiator Perkadox 16 (Elf Atochem). At 200 min., the polymer mass was observed to wrap around the shafts (Wickel effect). The profiles point to a strong gel effect. The maximum specific torque of 33 Nm/liter is reasonable for a continuous List kneader reactor, the upper limit of which is 60 Nm/liter.



List kneader reactor for continuous polymerizations producing solid granular polymers. If the solvent is not used, the reflux of monomer is applied. For temperature adjustments, the process may operate under vacuum. Low vacuum for polycondensations is also possible.

Figures: List, Arisdorf, CH

New kneader reactor technology

List kneader reactors have been designed to improve the radial/axial self-cleaning and the axial conveying of viscous polymers. The aim has been to avoid the complete filling and plugging of the reactor while working continuously. Kneading energy is in the range of 0.1 to 1 MJ/kg, with a maximum specific torque of 60 Nm/liter. Torque is very sensitive to the compression zones, especially as regards solid particles. List twin-shaft kneaders have been optimized in order to avoid compression zones between the barrel and kneading elements, as well as the intermeshing zones of the kneading elements.

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