

Abstract

A review of the existing polymerisation processes is proposed, with particular attention to the control of viscosity and heat removal. Up to the present time, different types of reactor have been developed in order to improve the stability of the polymerisation process. A review of these reactors is presented for the heterogeneous and homogeneous polymerisations. The production of solid polymer granules directly in a kneader reactor under evaporative cooling is seen as an efficient and reliable polymerisation technology.

HETEROGENEOUS POLYMERISATIONS

To overcome the mixing problems associated with highly viscous polymer masses, several processing systems have been suggested in the earlier processing techniques. 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 polymerisation systems such as the suspension/emulsion, precipitation and crosslinking processes are commonly employed for polymer production. Due to low apparent viscosities, the agitator provides efficient mixing without too much mechanical heat input and the monomer continues to polymerise in the solid particles. Furthermore, the liquid phase is especially beneficial when the evaporative cooling is used for removing the reaction heat.

a. Suspension / emulsion polymerisations

The standard agitated tank reactor is suitable for suspension and emulsion polymerisations. Shearing provided by the agitator maintains the polydispersive state of the segregated mass.

b. Precipitation polymerisations

Poly(acetal) polymers have poor solubility. For example,

crystalline poly(oxyethylene) is insoluble in its monomer at low temperature (POM, Brandrup et al., 1989 [4]). The Celanese Corporation (Semanchik et al., 1978 [5]) 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 section of the extruder.

The continuous polymerisation of syndiotactic poly(styrene) has been described by Idemitsu Petrochemical Co. (SPS, Yamamoto et al., 1993 [6]). This polymer also has poor solubility in its monomer. The kneader reactors KRC (1 litre 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 50 mm, total length 660 mm, mean residence time 30 min, monomer feed rate 2 l/h, conversion 40%, net power 100 W).

c. Crosslinking polymerisations

Crosslinked poly(acrylates) or poly(acrylamides) are efficient water absorbers prepared by free-radical initiated polymerisation of the monomer with a crosslinker in aqueous solution (minimum 50 % water). This special type of polymerisation is included under heterogeneous polymerisations because the polymer network is insoluble in water. The continuous twin-shaft kneader reactors of the company LIST AG are ideal for this process (List AG, 1997 [10]). During the course of polymerisation, the viscosity of the liquid mass increases as a gel is formed (figure 3). The intermeshing of the kneading elements in figure 1 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 of reaction, especially when the autoacceleration of the reaction rate occurs (gel or Trommsdorff-Norrish effect).

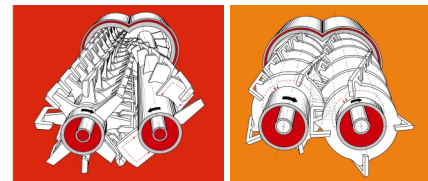


Figure 1: ORP as opposite rotating processor and CRP as counter rotating processor. Orientation angle of the kneading elements assures the axial conveying of the pasty polymer.

HOMOGENEOUS POLYMERISATIONS

a. At high temperature ($T > T_g$)

The company Sulzer Chemtec developed a tubular loop reactor equipped with static mixers for the continuous and homogeneous polymerisation of styrene (Nguyen et al., 1985 [8]) and of methyl methacrylate (Fleury, 1993 [9]). This technology uses a high temperature (above the glass transition temperature) in order to decrease the melt viscosity. The tubular loop reactor removes the reaction heat only by contact, evaporative cooling not being possible. However, some parameters such as the ceiling temperature at which equilibrium between polymerisation and depolymerisation occurs, the degree of syndiotacticity for some polymers and the formation of by-products (oligomers) may affect the process at high temperature.

b. At low temperature ($T < T_g$)

Based on a new patented technology, an optimised continuous kneader reactor has been developed to overcome the mixing problem associated with highly viscous and homogeneous polymer masses (figure 3). The above described thermodynamic segregation is no longer used to maintain the apparent viscosity at a reasonable level.



Kneading shafts of LIST-ORP 6300 CONTI

The innovation is homogeneous polymerisation below the glass transition temperature which directly produces solid granules of polymer. The principle is to transform mechanically the homogeneous polymeric mass into free-flowing solid granules before the viscosity becomes too high. This direct mechanical granulation eliminates the need of a high power input which always risks mechanical over-heating. Not only crystalline but also amorphous polymers can be produced in this way. Evaporative cooling is used for removing the reaction heat. Figure 2 demonstrates the feasibility of this new technology by the batch polymerisation of methyl methacrylate monomer in diethyl ether with the initiator Perkadox 16 (Elf Atochem).

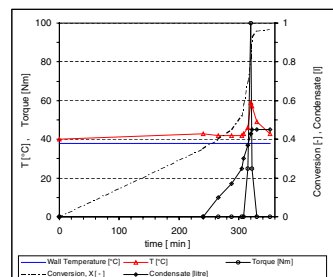


Figure 2: Free-radical polymerization of MMA in solution, in a LIST-kneader reactor CRP 2.5 BATCH, at 30 rpm, atmospheric pressure. 0.45 kg solid granules were discharged (conversion 97%, resid. solvent 7%).

The conversion profile in figure 2 has been estimated based on the final conversion and measured condensation rate. At 200 min, the polymer mass was observed to wrap around the shafts (Wickel effect). The profiles in figure 2 point to a strong gel effect. The maximum specific torque of 33 Nm/litre is reasonable for a continuous LIST-kneader reactor, the upper limit for which is 60 Nm/litre.

LIST

LEADERS IN
HIGH VISCOSITY PROCESSING TECHNOLOGY

LIST- Continuous Kneader Reactor (LIST- CKR) for continuous polymerisations producing solid granular polymers.

P.-A. Fleury, J. List, LIST AG, 4422 Arisdorf (CH)

Keywords

LIST-continuous kneader reactor, self-cleaning, cooling, polymerisations.

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 whilst working continuously. Torque is very sensitive to the compression zones, especially with regards to solid particles. LIST twin-shaft kneaders have been optimised in order to avoid compression zones between the barrel and the kneading elements, and the intermeshing zones of the kneading elements (figure 1).

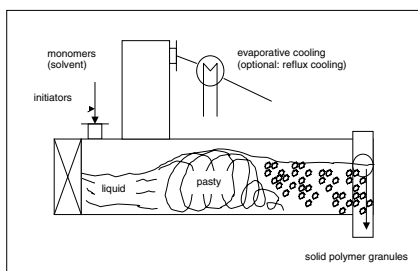
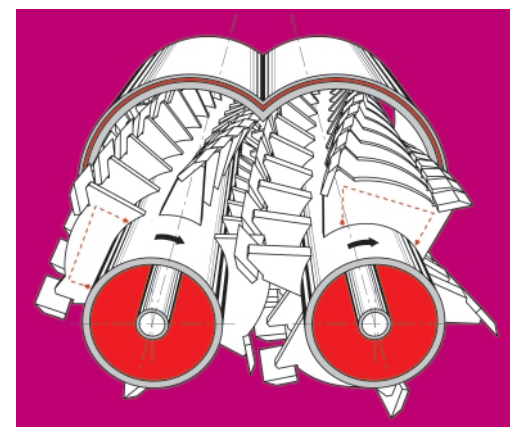


Figure 3: LIST-kneader reactor for continuous polymerisations producing solid granular polymers. If the solvent is not used, the reflux of monomer is applied. Temperature adjustments by vacuum operation.

The success of the LIST-kneader reactor for the polymerisation of PMMA indicates that it should be suitable for all the described heterogeneous polymerisation systems with significant improvements in qualitative and economic performance (figure 3). Table 1 gives a comparison between the different processes.



New LIST-Continuous kneader reactor

Mercier et al., 1993 [11] described polycondensation systems for the production of high glass transition temperature engineering polymers: PEEK, PES, PPE, PPSU, PI, PEI, PEBA, PEI, LCP. Reference to Mercier et al., 1993 [11] in respect of high glass transition temperature engineering polymers suggests that the new LIST technology could also be useful for these materials.

Polymer				Reactor						
name	T _g [°C]	T _c [°C]	-ΔrH MJ/kg ²	soluble at T	type	T [°C]	cooling	e [MJ/kg ²]	discharged polymer	kneading effect
PVBE			0.60	no	belt		evaporating	-		-
PVC	85		1.6	no	tank + screws	50 / 60	reflux	0.49	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 granules	granulation

Table 1: Homogeneous and heterogeneous polymerisation systems for the continuous production of polymers (* melting temperature; ° based on pure polymer, dry basis; e : specific kneading energy; T_g : glass transition temperature; T_c : ceiling temp.; -ΔrH : heat of polymerisation). Data refer to the above described processes.