

Bulk Polymerisation or Copolymerisation in a Novel Continuous Kneader Reactor

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Summary: A new type of kneader reactor is proposed for the continuous radical (co-) polymerisation without solvent, based on the proven design of mature (kneader-) dryer technology. The reactor has been developed to satisfy all major aspects required for (co-) polymerisation while maintaining the safety and reliability of the previous mechanical design. The new kneader reactor offers a perfect combination of surface renewal and evaporative cooling to control temperature to high conversion (85 to 95%), even for bulk systems that have a strong gel effect (Trommsdorff's effect) and high exothermicity. The reactor can be tested batch-wise to optimise the recipe, as shown in this work for bulk free radical polymerisation of methyl methacrylate (MMA). A simulation program was correlated to the experimental batch data to determine the optimum concentrations of initiator and of chain transfer agent to target a given molecular weight of PMMA. Design of a continuous kneader reactor to optimise the conversion as a function of residence time, to eliminate foam formation, and to produce copolymers without composition drift, is also presented.

Keywords: back-mixing; bulk free radical polymerisation or copolymerisation; kneader reactor; methyl methacrylate; PMMA

Introduction

Generally speaking, the kneader is a closed operation unit based on a self-cleaning mechanism. It operates partially filled, containing a pasty phase and a vapour phase. Typical fill levels are comprised between 40 and 70% of total volume. Since 1966, the kneader technology was developed as a drying operation unit. A typical (kneader-) dryer^[1–6] has one rotating shaft supporting the kneading elements and static cleaning elements^[1,2] fixed on the casing. The intrinsic self-cleaning properties of the kneader are the consequence of the intermeshing between kneading elements welded on the rotating shaft and static counter hooks^[1,2] fixed on the casing. The continuous (kneader-) dryer^[1–6] has a length over diameter ratio of roughly 5, which provides the best compromise between solidity and

specific heat transfer area A/V . The system is today a proven mechanical design.

Up to now, different attempts have been made to use the (kneader-) dryer^[1–6] for continuous polymer applications.^[8,15] A major problem has been fluctuations of the fill meaning fluctuations of the residence time. This phenomenon is the well known “pumping effect” and effects the polymer quality. Designers have tried to overcome this “pumping effect” in polymer applications by creating sophisticated self-cleaning mechanisms. The specific heat transfer area was still considered as the most important parameter and the ratio L/D of roughly 5 was maintained. The result was the emergence of twin-shaft kneaders, in which one shaft cleans the opposite one.^[7] Some of these designs are very interesting for polymer processes^[9–15] requiring a plug-flow behaviour. An example is the continuous production of super absorbent polymers (SAP) based on a cross-linking reaction, which requires efficient intrinsic

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self-cleaning and good control of particle size of the discharged gel-like polymer^[9–14] to improve the drying process. Typical conversion is 90% after 12 minutes residence time in the twin-shaft kneader reactor.^[7] All the patents^[9–14] refer exactly to the same twin-shaft kneader reactor.^[7] The residual monomers, acrylic acid and acrylate salt, are further converted up to 98% with a residence time of roughly 36 minutes in a post curing reactor of simple design, that just moves the free-flowing product. In the following drying step, the residual acrylic acid ends down with 500–1000 ppm.

However, the reality of the mechanical design is that the more efficient the self-cleaning the less robust the design. For example, we can imagine a very sophisticated twin-shaft kneader with very detailed/thin intermeshing of complicated elements. Should one of those complicated elements bend for any reason, the complete kneader is programmed for self-destruction within seconds based on the well known “domino effect”: one bended element will not intermesh correctly with the next coming element and will bend it, a process that will repeat itself in both the downstream and in the upstream directions. Thus, the improvement of efficiency in intrinsic self-cleaning is limited by the mechanical design itself.

Last but not least, we observed that the product itself can improve the global self-cleaning of the kneader. To do so, the product viscosity has to be homogeneous everywhere into the reactor. Kneading interactions push small product volumes that will push other product volumes. In the plug-flow, the viscosity profile upon the length from liquid to pasty may create a “pumping effect” where the “push-push” actions in the liquid region are only activated when that liquid is converted. Once the liquid is converted, the “push-push” actions clean that region and deliver more converted product to the discharge. The fill level of the plug-flow reactor may fluctuate with time and depends on the intrinsic self-cleaning properties of the

reactor itself. This phenomenon is well known as the “pumping effect”. Based on these observations, a new back-mixed kneader reactor^[16] can be designed with a single shaft that has medium intrinsic self-cleaning properties, as the product itself will improve the global self-cleaning due to homogeneous polymer viscosity in the reactor chamber (back-mixing).

Design of a Novel Kneader Reactor

Historically, the high volume kneader technology was developed as a closed drying operation unit^[1–6]. It operates batch-wise or continuously. The batch geometry has a small L over D ratio (length/diameter = 2.5) and the continuous has a large L over D ratio ($L/D = 5$ giving a plug-flow behaviour). Both drying geometries are based on the compromise between solidity and specific heat transfer area A/V . The drying process starts with a liquid phase that becomes more viscous and finally transforms into a free-flowing material. Crust formation and high torque demand are common during the phase transformation from viscous to free-flowing material. Over the last 40 years, the mechanical design of the dryer has proven its capability to handle strong and local kneading forces. Those forces are known to be specifically strong because of the transformation to solid material. The static cleaning elements^[1,2] are the weakest parts and are removable from outside based on a nozzle design. Fatigue cracks and bending were common problems on those static cleaning elements. In case of incident, particular design allows the static element bending in an open direction resulting in a reduction of kneading forces and in the absence of intermeshing with dynamic elements connected to the rotating shaft. A control system was developed to stop the shaft rotation in case of a broken static cleaning element. Pressurized nitrogen is distributed in all static cleaning elements as one circuit with connecting pipes. In case of a broken element the nitrogen circuit loses pressure and gives a signal to stop the rotation of the shaft. To summarize, the

design of the static cleaning elements^[1,2] was improved over the last 40 years based on the worst case: drying process with a transformation to solid. The mechanical design of that single-shaft kneader^[1–6] is today a proven technology.

The new generation of kneaders^[16] has been developed for (co-) polymerisation processes. We do not call them (kneader-) dryers anymore, but kneader reactors. The idea was to use the proven characteristics of the mature dryer technology^[1–6] such as self-cleaning and solidity, and to modify the global geometry in order to satisfy the process requirements of the (co-) polymerisation systems. Such a reaction system has following specification:

- requires heat to initiate the reaction
- is exothermic
- tends to foam at dilute polymer concentration
- becomes very viscous in absence of solvent
- viscosity may create an auto-acceleration of reaction rate (Trommsdorff's effect)
- removal of reaction heat becomes very delicate if combined with an auto-acceleration of reaction rate, conventional heat transfer is strongly limited with regards to scale-up
- solvent is to be abandoned if possible; solvent elimination makes the cost structure very attractive
- water is to be abandoned too if possible; emulsion or suspension processes need additives that contaminate the end product, non negligible monomer losses are also observed, resulting in an unattractive cost structure.

In Table 1, we can see the global modification of the mature dryer technology^[1–6] to transform it into a new kneader reactor^[16] satisfying all major requirements of a radical (co-) polymerisation reaction system. This transformation is mainly a reduction of the L over D ratio from 5 down to 1.1–2 (2 for the smallest pilot because of construction constraints). We abandon the plug-flow behaviour and concentrate on the

back-mixing geometry. Per analogy, we duplicate the conventional CSTR but for high viscous medium (radicals have a very short living time: for this reason, back-mixing is not problematic for the radical system). The internal geometry has been slightly modified in order to improve the back-mixing. A typical continuous dryer^[1–6] has a shaft designed for the best axial conveying with the smallest axial dispersion. The new kneader reactor^[16] focuses on the best axial dispersion, but must still assure an axial conveying in order to feed the discharge twin-screw. This compromise was achieved by testing.

Self-cleaning and surface renewal are particularly appreciated to carry out bulk (co-) polymerisations. The self-cleaning assures that product will not stay in dead zones and avoids any thermal time dependant degradation. The surface renewal allows the monomer to evaporate homogeneously from the viscous phase to cool down the exothermic reaction and the kneading dissipation energy. The evaporative cooling has the major advantage of being independent of the reactor's heat transfer area. This aspect is very important for two reasons:

- it allows the designer to reduce the L over D ratio focusing only on the requirements of the chemical process, without any compromise with regards to the cooling surface of reactor (the “dryer age”^[1–6] focused on specific heat transfer area, a large L/D was beneficial to get the biggest area per unit of volume)
- scale-up is only based on residence time and not on surface any more; this explains the potential benefits on the cost structure for a production line (very compact reactor^[16]).

Description of Reactor

Reactor is partially filled at levels between 40 and 90% of total volume (depending on viscosity). Two phases are present in the reactor chamber: pasty phase and vapour phase. In the continuous mode, the control

Table 1.

The development of a new continuous kneader reactor^[1-6] specifically designed in order to meet the requirements of the free radical (co-) polymerisation systems, based upon the proven mechanical design of the existing (kneader-) dryer.^[1-6]

Radical (co-) polymerisation	Continuous (kneader-) dryer (mature mechanical design), $L/D = 5^{[1-6]}$	Continuous kneader reactor (new global geometry based on mature mechanical design), $L/D = 1.1-2^{[6]}$
Requires heat to initiate the reaction	Has a large L over D ratio: plug-flow needs heat transfer to heat up the feed, limitation in scale-up.	By using a small L over D ratio, we create back-mixing to let the feed warm up when it contacts the already hot reacted polymeric mass: no limitation in scale-up.
Is exothermic	Evaporative cooling. No limitation in scale-up.	Evaporative cooling. No limitation in scale-up.
Tends to foam at dilute polymer concentration	Somewhere between feed and discharge foam can form, limiting the capacity.	Back-mixing creates a high polymer concentration everywhere in process chamber so that foam cannot form.
Becomes very viscous in absence of solvent	The proven/mature mechanical design can handle high viscosities. The viscosity profile from liquid to paste cannot improve the global self-cleaning and ends up with the "pumping effect".	The proven/mature mechanical design can handle high viscosities. The homogeneous polymer viscosity improves the global self-cleaning.
Viscosity may create an auto-acceleration of reaction rate (Trommsdorff's effect)	Evaporative cooling. No limitation in scale-up.	Evaporative cooling. No limitation in scale-up.
Removal of reaction heat becomes difficult if combined with an auto-acceleration of reaction rate, conventional heat transfer is strongly limited with regards to scale-up	Evaporative cooling boils out one monomer at a given axial position of the plug-flow. This monomer may condense back to another axial position, leading to heterogeneity in the copolymer recipe. Heat removal is not limited in scale-up.	Back-mixing mixes again the condensate homogeneously into the polymeric mass. Heat removal is not limited in scale-up.

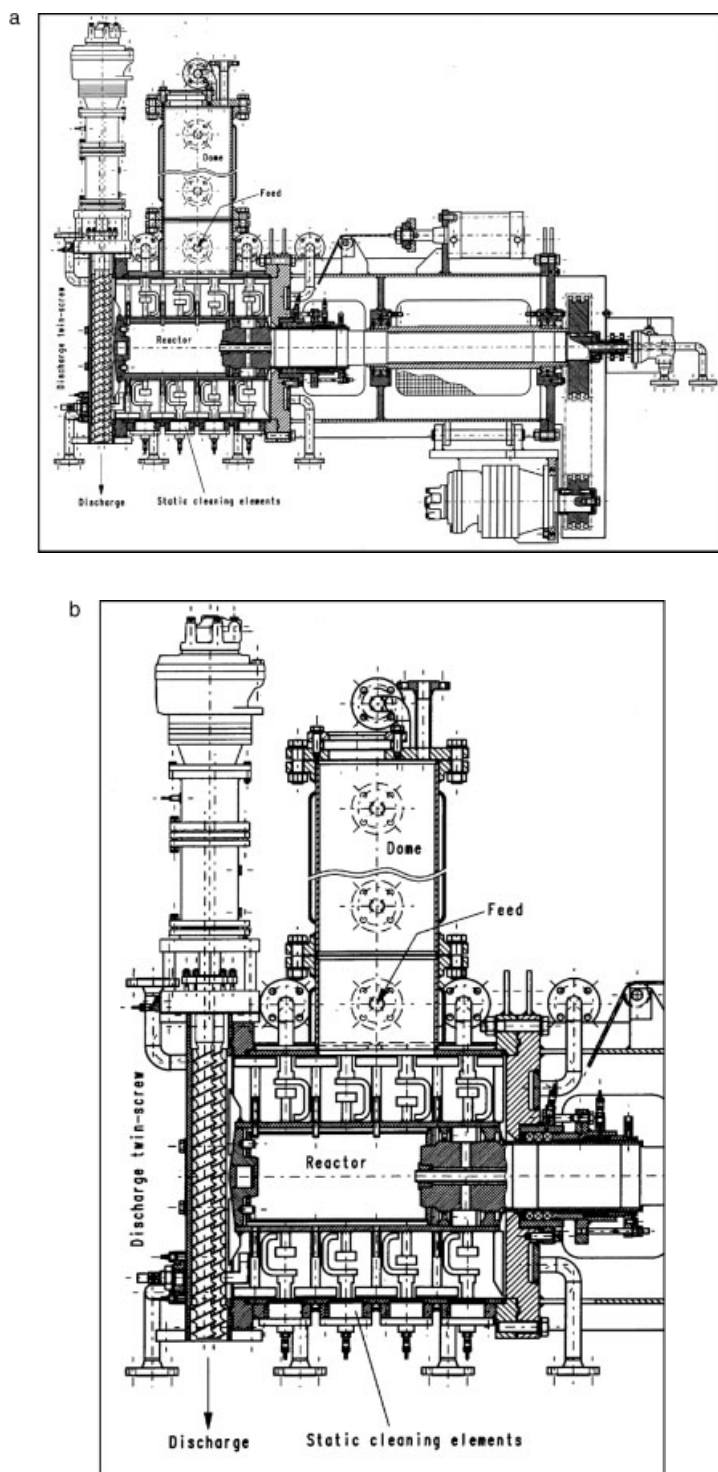


Figure 1.

Side view of a 100 litre kneader reactor^[16] – complete view (figure 1a) and zoomed view. (figure 1b)

of fill level to keep residence time constant is realised by using two different techniques.

The first one is the use of a static deflector mounted on the discharge front plate (see bottom part of inside reactor, on the left of Figure 1). The deflector is adjustable from outside the reactor. Depending on desired fill or on viscosity, the deflector can be adjusted in a position far or near the discharge window, thus changing the rate at which product exits to feed the discharge twin-screw. The second technique is used when the first does not

operate with satisfaction. In such a case, a valve placed after the discharge twin-screw is throttled by a control system reading signals such as torque and temperatures of reactor (option is to regulate the rotation speed of a discharge gear pump, Figure 3). The aim is to get constant torque and constant product temperature in the reactor.

Figure 1 shows the continuous kneader reactor^[16] with its single-shaft supporting the dynamic elements and the static cleaning elements^[1,2] fixed on the casing based on a nozzle construction. The goal is to provide active heating to the shaft and all

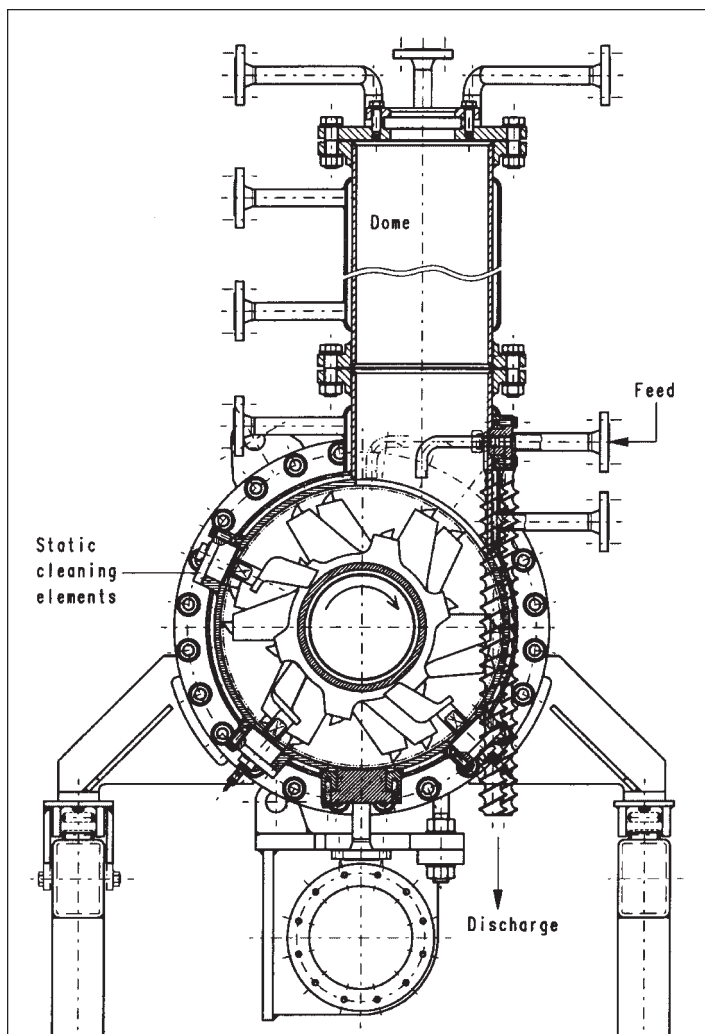


Figure 2.
Front view of a 100 litre kneader reactor.^[16]

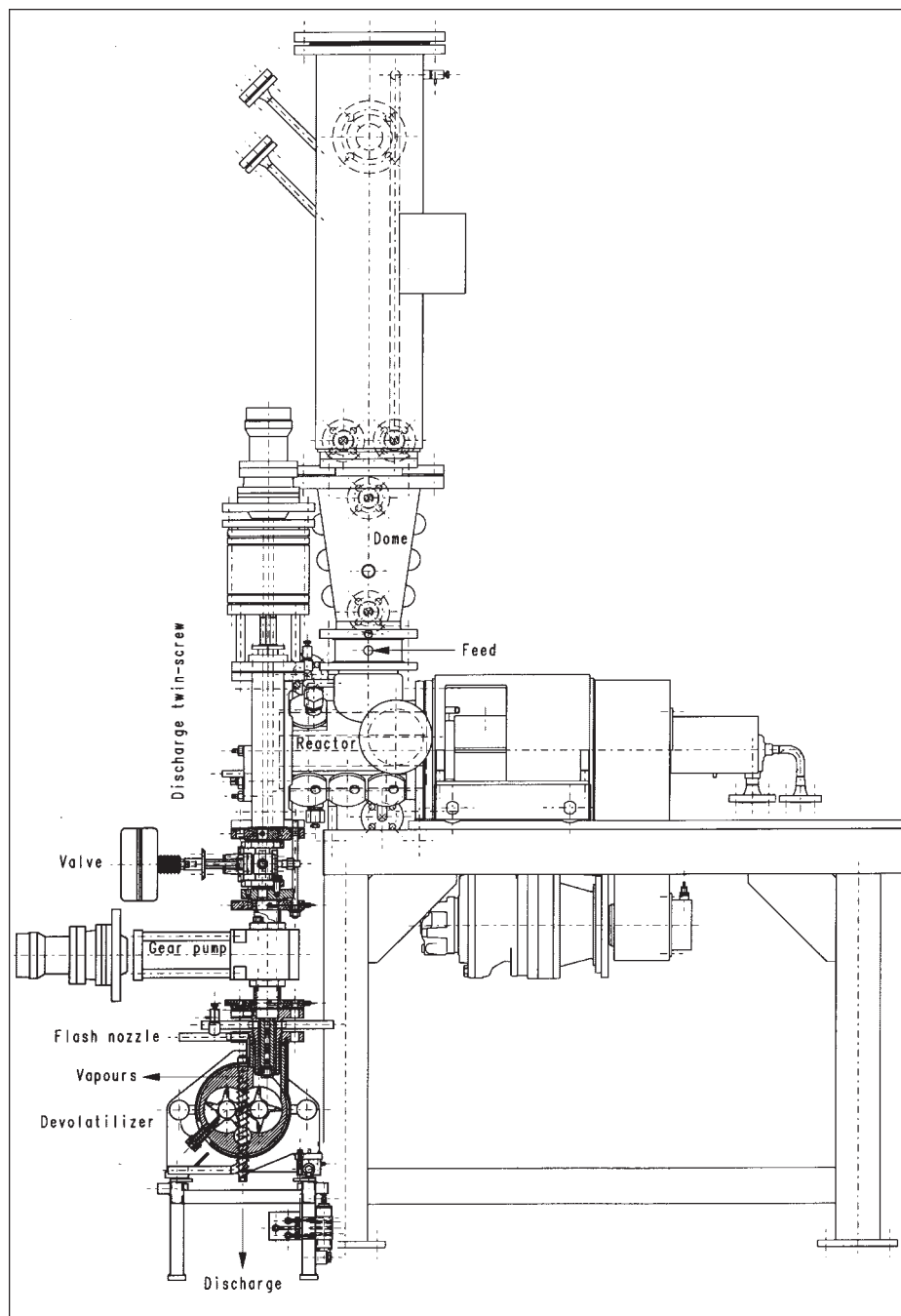


Figure 3.

Side view of a 6 litre pilot kneader reactor^[16] and front view of a 3 litre devolatiliser.

other metal parts that contact the polymer. This is especially important for polymers with a glass transition temperature near to the process temperature, as for PMMA. With a glass point of 110 °C and a process temperature between 130 and 160 °C, PMMA will block any reactor which does not have all metal parts actively heated.

Self-cleaning and surface renewal are particularly important for bulk (co-) polymerisation processes. The self-cleaning assures that product will not stay in dead zones and avoids any thermal time dependant degradation. The surface renewal allows the monomer to evaporate homogeneously from the viscous phase to cool down the exothermic reaction and the kneading dissipation energy. The evaporated monomer is condensed in a dome (Figures 1–3) positioned just above the kneader reactor.^[16] The monomer reflux goes back to the reactor and is mixed again into the reaction mass. This so-called “evaporative cooling” is a powerful technique to scale-up reactors with the guarantee of a controlled product temperature. But it is clear that the evaporative cooling can only be efficient if the monomer can be evaporated from any local portion of polymeric mass. This is the technical advantage of the kneader reactor^[16] to assure a constant and homogeneous surface renewal even at high conversion and especially when the Trommsdorff's effect occurs. The same principal can be realised for copolymerisation. One monomer evaporates to maintain the product temperature constant and is condensed back (reflux) to the reaction mass after the cooling effect.

The kneader reactor^[16] can operate in a batch mode or in a continuous mode. The batch mode is optimal to carry out experimental studies for developing recipes and to get time dependant profiles such as temperature, torque, conversion and molecular weight. The continuous mode operates with a rotating discharge twin-screw, which discharges the polymer continuously out of the kneader reactor. During the evaporative cooling, the back-mixing geometry allows the refluxed monomer to mix homogeneously into the polymeric mass, avoiding any shifting of recipe in the copolymer composition.

A (co-) polymerisation above the glass point allows the possibility to devolatilise the discharged melt by flashing into a devolatiliser directly after the reactor (Figure 3). The gear pump delivers pressure to force the polymer going through a heated die positioned in the near region of the dynamic cleaning elements of the devolatiliser. Residual volatiles of 0.3% have been measured. In order to avoid too high of torque in the reactor and the devolatiliser, the temperature should be kept at least 20 °C above the glass transition temperature of the polymer. The devolatiliser is a twin-shaft kneader operating with a very low fill and at a higher temperature compared to the reactor, designed to clean its flashing chamber at low fill and high temperature in order to minimise the torque and the residence time. The devolatiliser feeds a twin-screw in order to discharge the polymer out of the vacuum chamber, with vapours collected at the top of the devolatiliser.

Table 2.

List of MMA bulk batch experiments, conducted with DtBP initiator and n-DDT chain transfer agent. All polydispersities were 2.0–2.3. Symbols described in text.

N °	[mol/m ³]	[mol/m ³]	[°C]	[mb abs]	[°C]	Mw [kg/mol]		
	Cl	CT	Tw	p	T	exp1	exp2	calc
1	25	0	180	3500	142–162	175	265	194
2	12.5	17.5	155	3500	130–160	—	78	66
3	34	50	145	4700	170–181	22	28	25
4	34	100	145	3700	162–177	15	19	17
5	34	116	151	4500	161–171	—	19	13

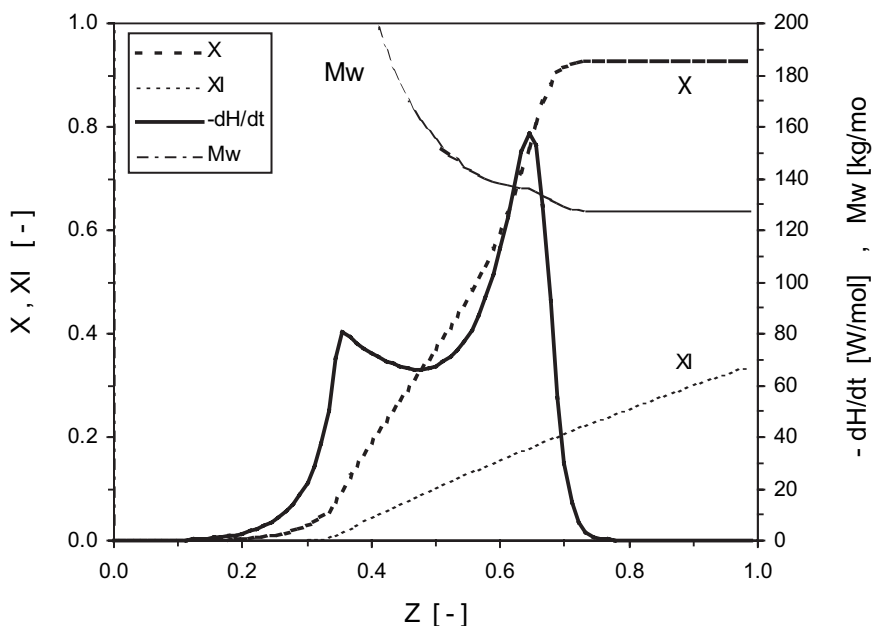


Figure 4.

Calculated profiles for MMA bulk polymerisation, Experiment 1 from Table 2, total reaction time = 25 min at $Z = 1$.

For the case of PMMA, the pressurised reactor^[16] establishes the targeted temperature by adjusting nitrogen pressure. In continuous operation mode, the discharge twin screw is combined with a gear pump to seal the reactor at the outlet (Figure 3). Oxygen contamination is eliminated due to overpressure in the reactor. Other (co-) polymerisation systems for which vacuum operation is necessary to target a given reaction temperature might be exposed to oxygen leakage into the reactor. A simple solution to this problem is to cover the lanterns (Figure 1) of the reactor and of the discharge twin-screw and to purge them with nitrogen. The nozzle construction of the static cleaning elements may also be covered and purged with nitrogen.

Pilot Experiments

The pilot kneader reactor^[16] (Figures 3 and 5) can be tested batch-wisely to optimise the PMMA recipe, such as concentrations of initiator and of chain transfer agent. A simulation program^[17] was correlated to experimental batch data to determine the

optimum concentrations of initiator and of chain transfer agent to target a molecular weight M_w of 70 kg/mol.

Table 2 summarises the reaction conditions tested in this study. The experiments were carried out at a temperature above the glass point and were initiated with di-tertbutyl peroxide (DtBP). The monomer is from Roehm, 30 ppm HQME (inhibitor was not removed). All experiments conducted with a chain transfer agent were made with lauryl mercaptane (n-dodecanethiol, n-DDT). The concentrations of initiator (CI) and of chain transfer agent (CT), the wall temperature of jacket and shaft(s) (T_w), the absolute pressure in the reactor (p) and the product temperature during the evaporative cooling up to the end of reaction (T) are all given. Two different external laboratories executed the molecular weight analysis (M_w values exp1 and exp2). The calculated weight-average molecular weights (M_w calc) are from a computer simulation that integrates the molecular weight curve as a function of conversion.^[17] In general all batch experiments

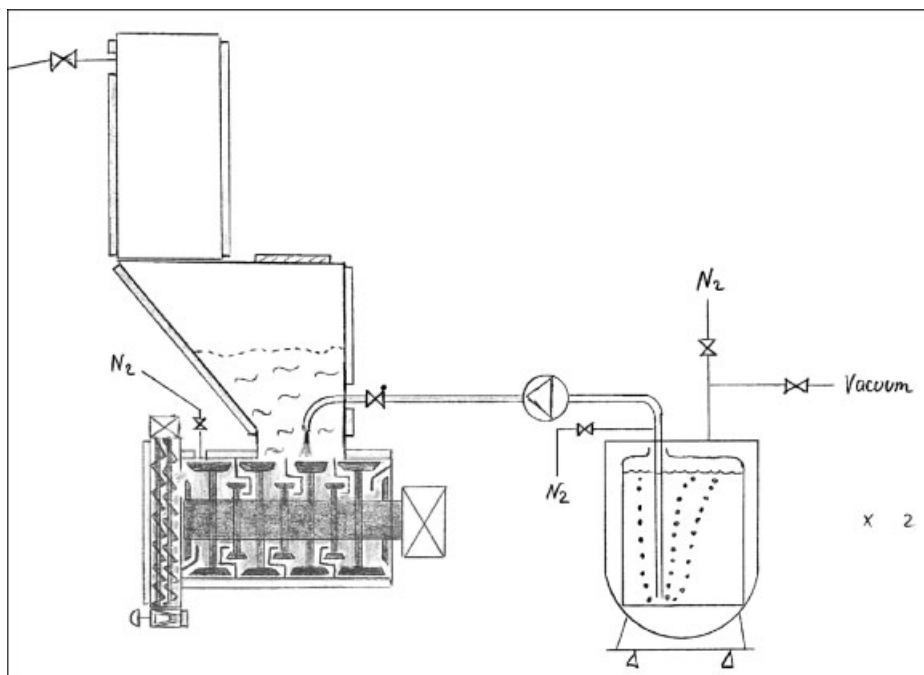


Figure 5.

Set-up for the continuous experiments. The pilot kneader reactor^[16] has a back-mixing configuration (CSTR). This device can operate as a batch (feed stopped and no discharge) or as a continuous reactor (continuous feed and discharge with twin-screw).

delivered high conversions of 90 to 95%. Above the glass point, the depolymerisation rate also limits the final conversion.

The continuous kneader reactor^[16] presented in Figure 5 has a back-mixing configuration based on a single-shaft design. The intrinsic self-cleaning properties of the reactor are the consequence of the intermeshing between kneading elements welded on the rotating shaft and static counter hooks fixed on the casing. The dome is cooled to operate as a reflux condenser during the evaporative cooling process. The process pressure is set using nitrogen pressure to control the reaction temperature at the desired value. Vacuum operation is also possible but requires nitrogen purging on the seals to avoid oxygen contamination. The feed tank, containing the initiator and the chain transfer agent, has a double envelop and is duplicated. Vacuum is pulled to remove oxygen and nitrogen is fed to break vacuum: this operation is repeated three

times to eliminate oxygen. The nitrogen nozzle at the top is open during feed operation.

The mechanical transition between the cooled dome and hot reactor chamber requires particular attention. Effectively, the vertical room from the dome's nozzle up to the reflux condensation dome is not mechanically self-cleaned. The condensed monomer is flowing from reflux condensation dome back to the process chamber. If that monomer gets into contact with a hot and vertical part of steel it will form high molecular weight deposits (due to the absence of initiator and of chain transfer agent). In the vertical direction of the dome's nozzle, the wall should be cold up to the very bottom part of that nozzle to avoid the thermal initiation of the reaction. Another possibility is to distribute the feed containing the premixed initiator and chain transfer agent on the internal perimeter of the condensation dome. The idea is to allow the initiator and chain transfer agent

flowing on vertical and hot metallic wall to avoid any hard molecular weight deposits. A combination of both designs is the best. Effectively, the vapours going up are hot and may initiate thermally a reaction on the long term. A distribution of the cold monomer mix on those surfaces will eliminate any hard deposits on the long term. Based on recipe number 2 of Table 2, the continuous pilot experiment delivered PMMA of 78 kg/mol with a residence of 34 min and at a final conversion of 90%. The residence time was controlled by using the deflector to maintain constant fill during testing.

Another reaction system was tested without solvent. The recycable water-soluble copolymer of styrene and acrylate^[18] was produced using the continuous pilot kneader-reactor.^[16] Conversions above 95% were obtained. The initiator and the chain transfer agent were premixed in the feed tank. Further work will be carried out in order to target a given molecular weight.

Some other reaction systems do not allow the premixing of a fast reacting initiator in the monomer(s) feed tank (Figure 5). For those systems, the initiation of the (co-) polymerisation would already start in the feed pipe and block the feed after some hours of operation. Due to the fact that the kneader reactor is not a micro-mixer but a macro-mixer, the fast reacting initiator can not be fed separately into the reactor. Doing so, a poor micro-mixing would be achieved for the initiator before the initiation starts. The solution to this problem is the use of a “tube in tube” pre-mixer having the function to feed the initiator in the centre of the monomer(s) feed pipe. Both tubes are concentric, the smallest feeds the initiator and ends up some centimetres just before the chamber of the kneader reactor. The mixing length can be varied to optimise the process. The surface of the pipes should be smooth to allow the feed pumps to push any polymer plug into the process chamber. The duplication of such a pre-mixer allows any process optimisations during the experi-

ment without disturbing the steady state conditions.

Conclusion

This study proposes a new technique for the bulk polymerisation of methyl methacrylate (MMA) or for the bulk copolymerisation of acrylate/acrylic based monomer recipes. As a result, the new continuous back-mixed kneader reactor has double the production capacity compared to a plug-flow configuration. The back-mixing configuration minimizes copolymer composition drift, eliminates any foaming problems, and improves the global self-cleaning.

Absence of solvent, increased continuous production capacity, elimination of any foaming, compact reactor size, low manufacturing costs, and a reliable reactor design are strong arguments for the novel back-mixed kneader reactor in the (co-)polymerisation systems.

Nomenclature

A	heat transfer area of the kneader, m ²
CI	concentration of initiator, mol/m ³
CT	concentration of chain transfer agent
D	casing inside diameter of reactor, m
L	length of process chamber, m
IP	index of polydispersity, -
M _w	weight-average molecular weight, kg/mol
p	absolute pressure in reactor, mbar abs
T _g	glass transition temperature, glass point, °C
T	temperature of polymer, °C
T _w	wall temperature of reactor
X	monomer conversion, -
XI	initiator conversion, -
V	total internal volume of kneader, m ³
φ	fill, -

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