The new technology for heterogeneous ion-exchange membrane production

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Introduction

The optimization of production technology is the main goal of all companies. The main reasons of this process is increasing production quality, capacity and decreasing cost. Our main goals were replace old calender kneading technology by new one according to next requirements.

- Increase product quality and capacity
- Decrease cost per kg of final membrane mixture
- Improving environmental condition in production hall and increase work safety

Kneading process

For choosing of proper kneading machine we need to define priorities of technical parameters. The first one is obviously throughput and investment costs. Others are operating costs, health and safety conditions, durability, service etc.

Firstly we need keep in mind there is no universal kneading machine for all application. Also throughput for same device varies according to application. Therefore one of our goals was approve maximum throughputs and composite quality for different kneader types for our application.

The main kneading issue is a shear rate. This parameter is very important when temperature or shear sensitive material is being processed. The Figure 1 describes the problem of shear rate for different kneaders. This figure show that for constant shear rate the co-rotating twin screw extruder need to run more than three times slower than Buss co-kneader. This leads to more than three times lower throughput for the same screw size.

Other benefits of co-kneader are constant shear rate independent of size and larger free volume which can help incorporate large amount of lightweight filler type. The shear rate of calender is also very low. Together with very low kneading area this lead to poor kneading efficiency according to other kneaders.

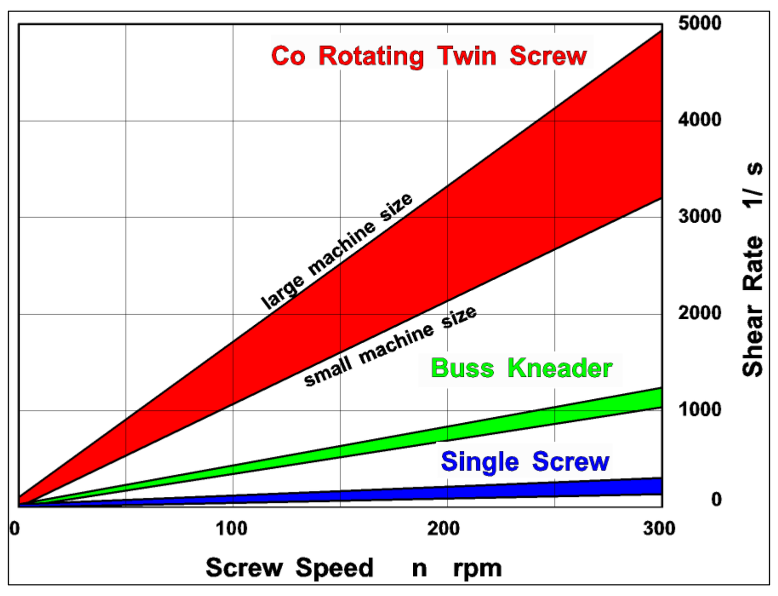


Figure 1: : Shear rate dependences on screw speed for various kneader

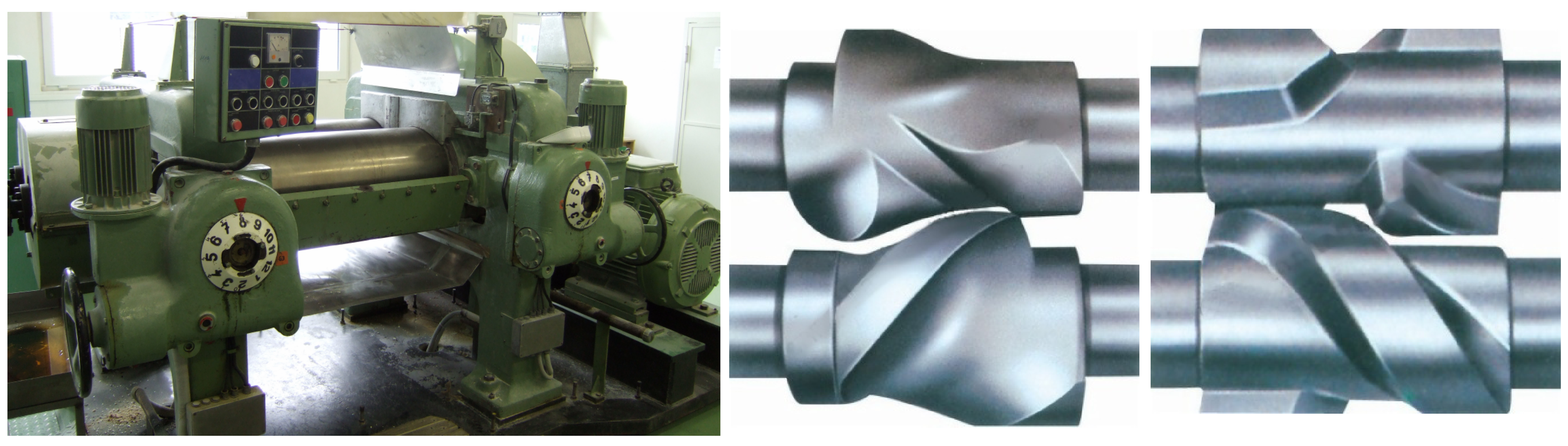
The membrane mixture is one of the highest filled composite (by volume) in the world. While the common highly filled master batches uses very ease flowing polymer grade, for the membrane the higher molecular weight polymer are most beneficial. Low molecular weight polymers are often very brittle causes some damages during membrane swelling. Therefore these polymers can be added only as flow modificator. The higher molecular weigh polymers have often lower melt flow rate and they are sensitive to shear.

Kneading technology

For basic comparing all kneader type we chose following main parameters mentioned in the table 1. The co-rotating twin screw kneader is most common kneader in the world. This kneader has highest kneading efficiency among of all kneaders. But there is some limitation for temperature sensitive application due to extremely high shear rate of co-rotating screws. The banbury mixer/kneader has many disadvantages. The kneading principle is the same as calender which we are need to replace. There is only one differences, the banbury mixer/kneader has closed mixing chamber and can use intermeshing rotor like on the picture 1.

Table 1: Main parameter of different kneaders

	calender	banbury mixer/kneader	twin screw kneader	single screw co-kneader
regime	discontinuous (batch)	discontinuous (batch)	continuous	continuous
configurable roll/screw	no	no	yes	yes
throughput	low	low	high	medium
size	medium	large	small	small
weight	heavy	too heavy	low	low
capital cost	high	high	low	medium
resident time	long	long	short	short
shear rate	low	low	high to extremely high	low to moderate

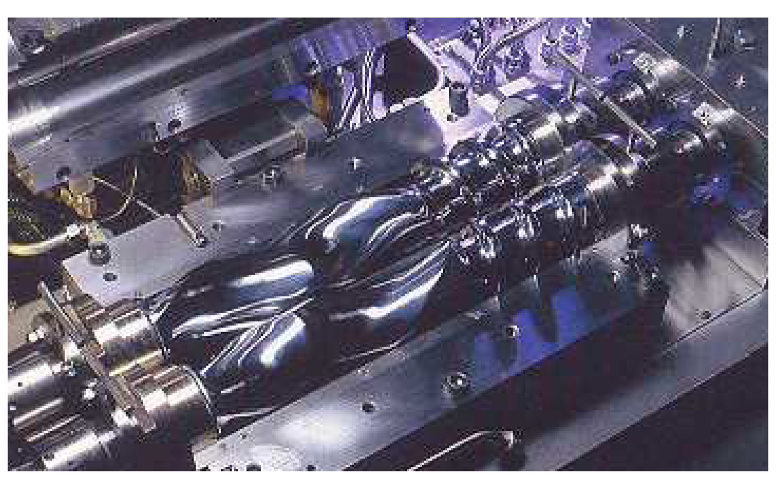


Picture 1: Calender with two smooth roll vs. intermeshing roll for banbury mixer/kneader (on the right)

The first result is very clear. The batch type kneader are not suitable for our application. They are too big, too heavy and too expensive according to very low throughput. Also the universality is quite low than screw type kneader. There is only one benefit for batch type kneader. This is very low shear and also very low mixing temperature but at the expense of all other disadvantages. To fulfill our requirements the continuous kneader is necessary.

On the market there is some special kneader which combine low shear and low temperature mixing properties with continuous process. Its called as continuous mixer (CM) or compact processor (CP). It combine special non intermeshing rotor (see picture 2) with single or twin screw extruder at the second stage.

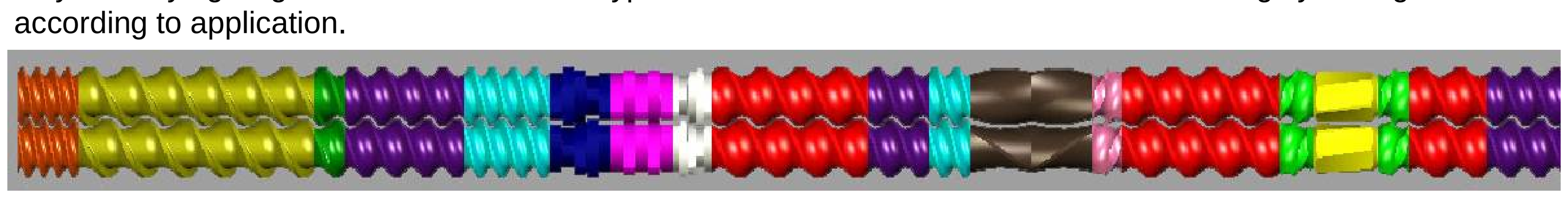
The another disadvantages such as robust design and high capital cost remains. Therefore this CM are used primarily for special application where continuous kneader cannot be used.



Picture 2: Non intermeshing rotors for CM

Twin screw kneader vs. co-kneader

Twin screw kneader is also called as twin screw extruder (TSE). It is only one kneader usable directly for extrusion. Kneading TSE is equipped with special segments for intensive mixing (see picture 3). Standard TSE has obviously only conveying segments. Therefore this type of kneader are much universal due to highly configurable screw according to application.

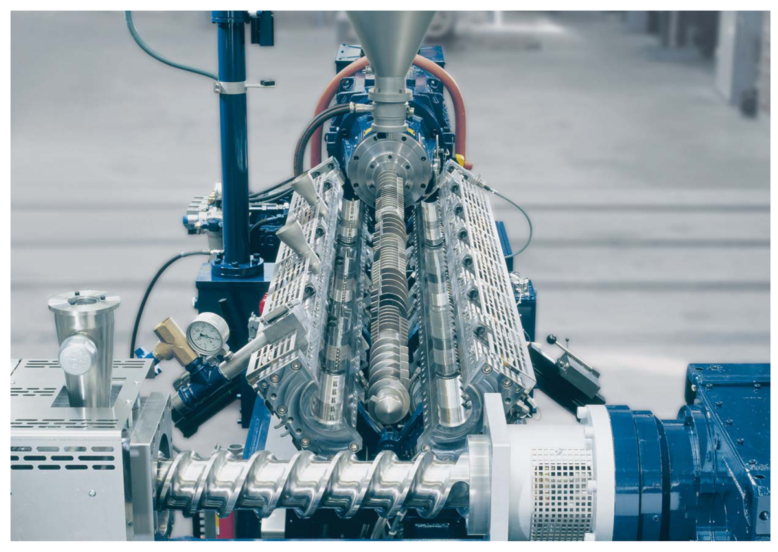


Picture 3: Twin screw with different segment type: kneading (white, purple and blue, dark grey continuous mixer, yellow polygon), backward (light green) and fast and slow conveying

Single screw co-kneader are design as two stage kneader: kneading stage and extrusion. Co-kneader has low intensive mixing properties but without any pressure and temperature peak compared to TSE. Also co-kneader has stable shear rate independent on screw size. This is very useful for up scaling from laboratory data.

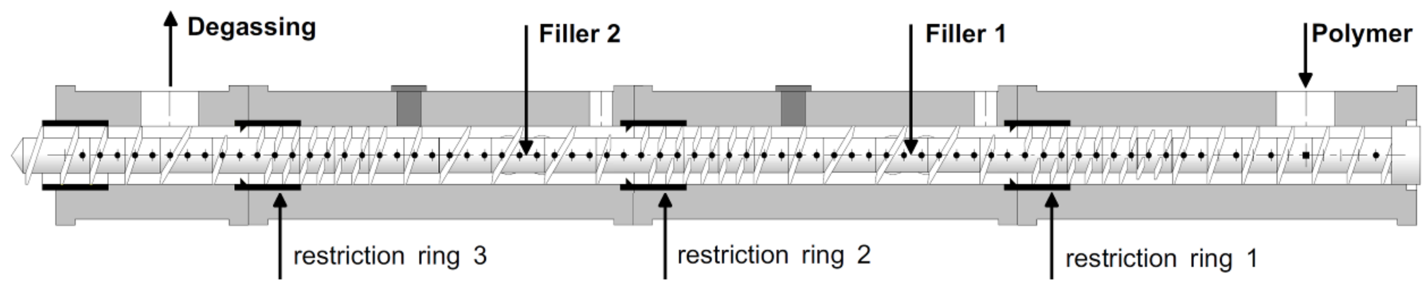
Same as TSE the co-kneader can has modular design. The barrel and screw could be segmented according to application.

The second stage could be realized by single screw with higher dimension or by melt pump. Single screw design are much universal. Melt pump are not suitable when shear sensitive and high viscosity material are processed.



Picture 3: Two stage co-kneader

Although the co-kneaders has lowest shear rate of all other kneader type, the optimization of screw configuration is also needed. Too much kneading elements rapidly increase stock temperature; on the other side too less kneading element is not enough for high quality kneading. On the Picture 5 there is preview of one configuration for three stages filling. The co-kneader use many types of screw elements; basically fast and slow conveying, short kneading and kneading elements for restriction ring. Additionally elements with increased core diameter, kneading element with backward flowing characteristic and others are also usable. The restriction ring is special bore element with lower core diameter which increase melt pressure for high quality mixing. The diameter of restriction ring also need to be optimized for reducing shear rate and stock temperature.



Picture 4: Preview of co-kneader screw configuration with three filing ports

Kneader process comparison

We validate kneading process of our composite on the following kneader mentioned in the table 2. There are two size TSE in co-rotation version, one short counter rotation TSE and two size of co-kneader. For comparison there is also two roll calender. For process validation we use two mixture with 60 wt % of filler and two polyethylene type: medium flow able LDPE (mixture 1) and LLDPE (mixture 2). These PE have different shear sensitivity and also different flowability. The quality of mixture vas performed by optical method and measurement of ion-exchange capacity (IEC). Also we checked the rheological properties of prepared mixture.

Table 2: Kneader process comparison

kneader	calender	Brabender DSE20	Brabender DSK 42/5	Werner & Pfleiderer ZSK 40	Buss PR 46-11D	Buss MKS 30-20D
screw type and size (mm)	2x400 mm	2x20 mm co-rot.	2x42 mm counter rot.	2x40 mm co-rot.	1x46 mm	1x30 mm
length		40D	5D	33D	11D	20D
nominal throughput (kg/h)	not available	25	5	250	20-40	25
max installed drive power (kW)	55	12	12	45	30	10
number of inlet ports	1	2	1	2	2	3
real throughput mixture 1 (kg/h)	10	2	2	20	12	20
real throughput mixture 2 (kg/h)	10	not tested	not tested	not tested	12	15
% of nominal throughput mixture 1 (%)	not available	8	40	8	30	80
% of nominal throughput mixture 2 (%)	not available	not available	not available	not available	30	60

Results

- Low kneading efficiency of celender results more aggregate contents. Aggregates from screw kneaders wasn't observed. All of screw kneader have very high kneading efficiency.
- Due to define size of granule which can be also smaller than granule from caleneder the followed extrusion is much stable.
- Due to low shear stress of co-kneader the mixture has better and stable rheological properties compared to mixture from calender (see figure 2).
- For twin screw kneader the stock temperature strongly depends on screw speed (see figure 3). This lead to higher stock temperature increasement per revolution due to higher shear rate. The stock temperature is higher for mixture two and therefore maximum throughput is lower. Stock temperature increasement for co-kneader is much lower results utilize maximum screw speed and throughput.
- Feeding in more inlet ports results higher throughput per screw revolution.

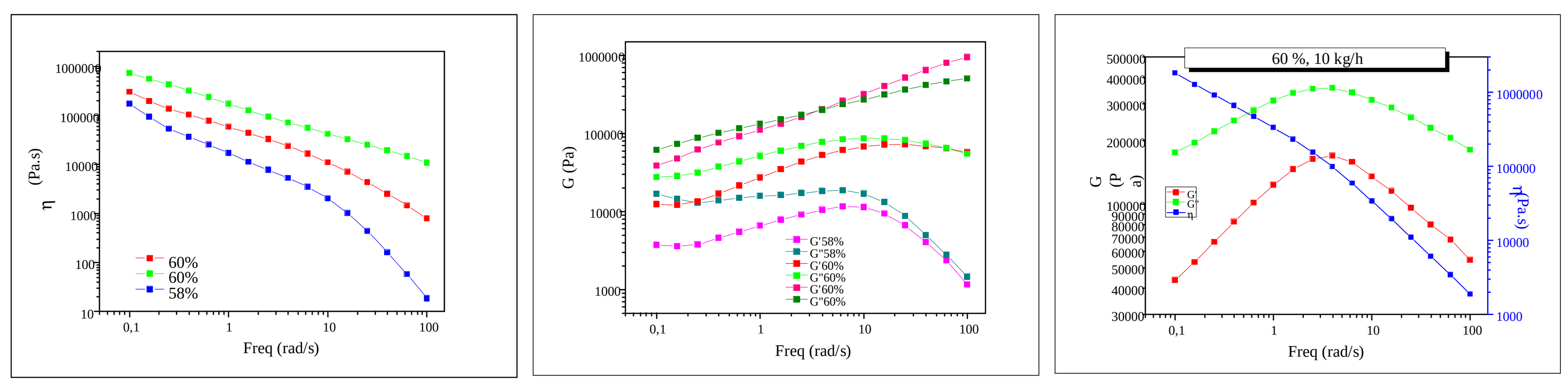


Figure 2: Rheological properties of mixture 1 for calender (two left) graph) and for co-kneader (righ graph) measured at 140°C by oscillating rheometer

Conclusions

- We approved the twin screw kneader has too high shear for kneading of highly filled and temperature sensitive membrane mixture
- The co-kneader has best overall kneading performance for ion-exchange membrane mixture among of all kneader type.
- There is no universal co-kneader screw configuration for all membrane mixture type.
- Co-kneader has more than four times lower energy consumption per kg of mixture than calender.

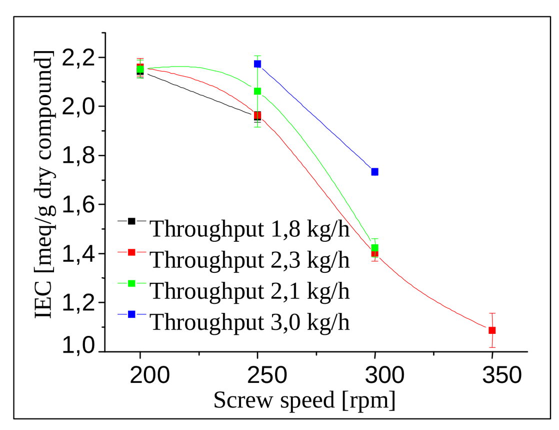


Figure 3: Dependence of IEC on twin screw speed

- We approved the co-kneader has best price/compounding performance for our application. The bigger sized twin screw kneader running at lower screw speed to avoid higher shear is much expensive than much smaller screw diameter co-kneader.
- Finally we found optimal kneading conditions including screw configurations for compounding highly filled ion-exchange membrane mixtures.

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