COMPUTER SCALE-UP MODEL FOR DESOLVENTIZING HIGHLY VISCOUS POLYMERS IN KNEADER EQUIPMENT

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Abstract

A concentrated rubber solution (less than 20 % solvent) is fed to a high volume kneader in order to remove the solvent down to ppm level. A simulation program has been developed to describe this devolatilization step.

The program predicts final solvent content, the filling level and the mechanical torque build-up. The program can be used to refine process control and the scale-up of this type of process.

Introduction

Polymerization reactions of rubber solution usually take place in diluted form, either suspended or dissolved in a suitable solvent. The solvent acts both to absorb the heat of reaction, which is then removed by external loop heat exchanger and to decrease the viscosity of the mixture to limit the dissipation of heat in the stirred tank reactor.

After the polymerization the solvent has to be removed to a very a low level. In the past, this solvent removal took place in steam stripping equipment. This process has been developed a long time ago and increasing pressure of environmental restrictions has lead to a gradual improvement of the technology to remove the solvent. These improvements targeted two main goals:

1. Reduce the amount and toxicity of solvent lost during the stripping process by substituting solvents,
2. Simplify the process steps, where leaks can occur and reduce the amount of energy needed to produce the finished rubber.

Today hexane and toluene are commonly used solvents compared to benzene 20 years ago. Solution polymerization has increased in popularity due to the development of metallocene based catalyst technology.

During the 60tees and 70tees a new type of process was developed so called “direct devolatilization”. This technology means that the rubber solution is pre-concentrated by boiling off or flashing the rubber solution until it becomes very viscous (for TPE’s around 80 to 90 % rubber in solvent) and then be concentrated in high viscosity equipment. Extruders were equipped with vent domes to perform this task. The rubbery solution is 1st flashed to atmospheric conditions (102325 Pa abs) and then alternately compressed while stripping agents like water are mixed into the rubber and relaxed to an always lower pressure in order to repeat that flash step up to 5 times.

Since 20 years a new generation of devolatilization equipment has been developed especially for rubbery solutions: the high viscosity kneader. In this equipment, there are no pressurizing zones and a much larger gas room then in extruders. Since the gas room is interconnected over the whole length, the gas amount generated by the flash can be distributed over a larger dome area than in extruders. As a consequence, the flash of the feed solution can be performed down to 2000 Pa This paper describes how such a process is scaled up and presents a simulation tool allowing to size the necessary kneading equipment including drive power, heating/cooling capacity and achieved final volatile content for a given feed stream.

Experimental

We developed the simulation program in steps using different kneaders of different sizes (see figure 1):

- Single shaft batch kneader of 0.007 m^3 process volume
- Single shaft batch kneader of 0.17 m^3 process volume
- Single shaft continuous kneader of 0.017 m^3 process volume
- Single shaft continuous kneader of 5 m^3 process volume

All units were equipped with a hot oil system connected to the heating jackets of the kneader. Both shafts and outer walls of the units were heated or cooled.

We filled the batch unit with polymer up to 30 % of the kneader volume. We added hexane at 40 C and atmospheric pressure and compounded it into the polymer mass. The hexane partly evaporated and returned by reflux condensation into the kneader during 15 min. By then, we shut off the reflux condenser redirected the gas flow to a straight forward condenser and vacuum station. We heated up the mixture by kneading the polymer plus contact heat through the jackets, until we reached the target temperature for the diffusion of the test. At this point, we stopped the kneader, opened the unit and took a sample. We closed the unit again, pulled vacuum of 2000 Pa and broke the vacuum immediately thereafter by nitrogen. We took another sample, closed the unit again and pulled vacuum to 2000 Pa. We started the agitator of the kneader. This was the starting point of the diffusion. We repeated this step - stopping, braking vacuum and taken a sample, closing the unit, pulling vacuum and restarting the unit – another 5 times.

For the continuous trials, we used polymerized and stopped cement pre-concentrated upstreams to 80 to 90 % rubber. The cement entered the kneader at 2000 to 3000 Pa, where a part of it flash-evaporates. The rubber is devolatilized in the unit and discharged through a screw into a gear pump followed by a pelletizer. Samples were taken from the final pellets.

Solvent content was determined by dissolving the rubber in an inert solvent and analyzing hexane content through GC measurement.

Results and discussion

The simulation program targets designing (scale-up) the continuous evaporation of rubbers from cement only. For this purpose, we divided the calculation in 2 sections, the flash evaporation due to the pressure drop of the feed and the diffusion controlled devolatilization of the remaining solvent. For the flash evaporation step, the kneader acts as a self cleaned receiving flash pot.

The flash step in programs, which are commercially available (Chemcad etc.) only takes into account the change of physical-chemical data of solvent as function of pressure and temperature. Since the pressure drop in the kneader can be neglected between point of flash and dome, the flash temperature can be determined using the vapor pressure curve of the solvent. However, in the case of high concentrated solution, the solid, non-volatile material (the rubber) influences the equilibrium between solvent in the cement and the gas phase, since the available interphase is reduced. The equilibrium replacing the vapor pressure curve has to be determined empirically for each rubber/solvent system, described by the Flory-Huggins interaction parameter χ:

$$\frac{p_S}{p_{0S}(T)} = e^{\ln(X_S)+1-X_S+\chi(1-X_S)^2} \tag{1}$$

The flash at these rubber concentrations is not complete. Therefore, the flash concentration as function of temperature is not described completely by the equilibrium, but:

$$w_{S,\,flash} = f\left(w_{S,eq}, \eta_{Cement}, geometry, \Delta p\right) \tag{2}$$

The mentioned geometry describes how the feed inlet is set up (pipe diameter etc.) and Δp is the minimal required pressure drop between the flash pot upstream and the kneader. Considering the change of equilibrium and physical-chemical data to be negligible in the energy balance, we get a modified flash formula:

$$\frac{\partial T}{\partial w_S}\left(c_{rubber} + c_{P,s}\frac{w_S}{1-w_S}\right) = \Delta h_{V,s}\frac{1}{(1-w_S)^2} \tag{3}$$

Formula 3 has to be integrated between solvent concentration and temperature before and at the flash point.

Formula 2 and 3 can be modified to include several solvents as well. In this case the composition of the resulting gas stream determines the partial pressure of each solvent (co-current flow). Note that the resulting gas stream will increase in temperature with decreasing solvent concentration.

The cement after the flash has decreased in temperature and has now to be heated up to shift the equilibrium allowing the polymer to be further desolventized. The heat input is realized nearly exclusively through the mechanical kneading action. The heated jacket and shaft is used to flatten the temperature profile in the kneader thus avoiding cold or hot spots. Kneaders have reduced shear rates compared to extruders, thus the residence time has to be longer than in extruder to heat the polymer up. This necessary residence time is used to permanently renew the interphase between the polymer and the gas phase. The gap between theoretical equilibrium and solvent content in the polymer decreases over the length. Thus no pressure staggering is necessary to achieve a good devolatilization. The local mass transfer can be described by:

$$\frac{dm_S}{dt} = -k_{S,bulk,I}A_I\rho_{cement}\left(w_{S,bulk} - w_{S.I}\right) \tag{4}$$

We neglect static diffusion. The interphase is renewed each time the product is squeezed between static elements of the machine (housing and counter hooks, see figure 1) and dynamic elements of the shaft. In this case the mass transfer coefficient (penetration theory [1]):

$$k_{S,bulk,I} = 2\sqrt{\frac{D_S}{\pi t_{contact}}} \qquad (5)$$

The “contact time” can arbitrarily be chosen as long as we describe the intersurface A_I as the renewed surface during this time period. For practical reasons, the reverse of frequency is the most convenient. In this case the surface A_I is described as the renewed surface during one rotation of the shaft. This parameter is dependent on how the product is distributed in the kneader, the number of interactions between elements, the size of the equipment and the filling level. The only reliable source of this data is to videotape the product behavior during devolatilization and apply the observations for different product grades. Generally, we distinguish between:

- Film forming on mowing parts, which is renewed by dipping into a melt bath at the bottom of the kneader. At low viscosities gravity impacts the surface renewal
- The polymer wraps around the shaft and forms “chunks” of product before the kneading elements.
- The polymer granulates due to the kneader action at very high shaft speed and low filling level. This working point is desired for very temperature sensitive rubbers only.

By applying equations 4, 5 and 6 on a batch test, we can determine the diffusion coefficient of this polymer/solvent system as function of temperature. This diffusion coefficient is slightly dependant on solvent content at higher solvent concentration (higher than 2000 ppm). The equilibrium concentration is negligible for the batch tests, since the gas in the kneader is frequently replaced by nitrogen.

The continuous kneader has nearly plug flow behavior. The simulation divides the reactor volume in finite elements over the length. We apply the mass and energy balance in differential form. The contact heat transfer is considered to be the same as during the batch test. Mechanical heat input is described as function of rotation speed, filling level and the viscosity of the polymer.

Figure 2 shows the typical behavior of solvent removal during a batch test. The diffusion coefficient is typically around 10^{-9} m^2/s for n-hexane in EPDM-rubber. This value is about 10 times lower for cyclohexane.

Figure 3 shows the simulated behavior of solvent content over the kneader length. As clearly can be seen there is a maximum of driving force at about one third of the length of the kneader.

As a result of this simulation development, we can scale-up various sizes of kneaders up to 10 m^3. The accuracy of the prediction of final volatile content was initially about 30%. The validation of the data on the 5 m^3 industrial line allowed us to further improve this prediction to around 10 to 15 % accuracy. Since results are well conform to the model prediction, we are confident that these results can be used for various polymer/solvent systems.

The industrial unit in operation, the program predicts final volatile and power consumption for the devolatilization. The kneader allows to run melt viscosities of some hundred to 10,000 Pa s. This high degree of flexibility is possible, because the kneading action and devolatilization is continuous throughout the machine length. In order to use this feature best, the customer can use the simulation program to predict the optimal working parameters for new polymer grades. The only parameters needed are:

- Operational parameters: feed composition and throughput, targeted final temperature
- Physical chemical parameters: melt viscosity as function of shear rate, Flory-Huggins interaction parameter or other equilibrium data, diffusion coefficient (typically similar for different grades).

The program will calculate final volatile content, fill level in the machine and the required mechanical power as function of the shaft rotation speed.

Summary

A simulation program for devolatilization of solvent from rubbers and other polymers has been developed. The program can be used for scale-up to any appropriate kneader size up to 10 m^3 using pilot scale data and physical chemical data.

Another feature of the program is to predict the behavior of new polymers on existing kneader lines. Thus, the user of the equipment gains a great degree of flexibility.

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Nomenclature

A	area
c	specific heat (polymer)
c_P	specific heat
D	diffusion coefficient
Δh_V	specific evaporation heat
k	mass transfer coefficient
m	mass
p	pressure
p_0	vapor pressure
t	duration
T	temperature
w	mass content
η	viscosity

indices:

I	interphase
S	solvent

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Key Words

Polymer devolatilization, modeling, simulation, diffusion, flash, kneader, high viscosity, rubber

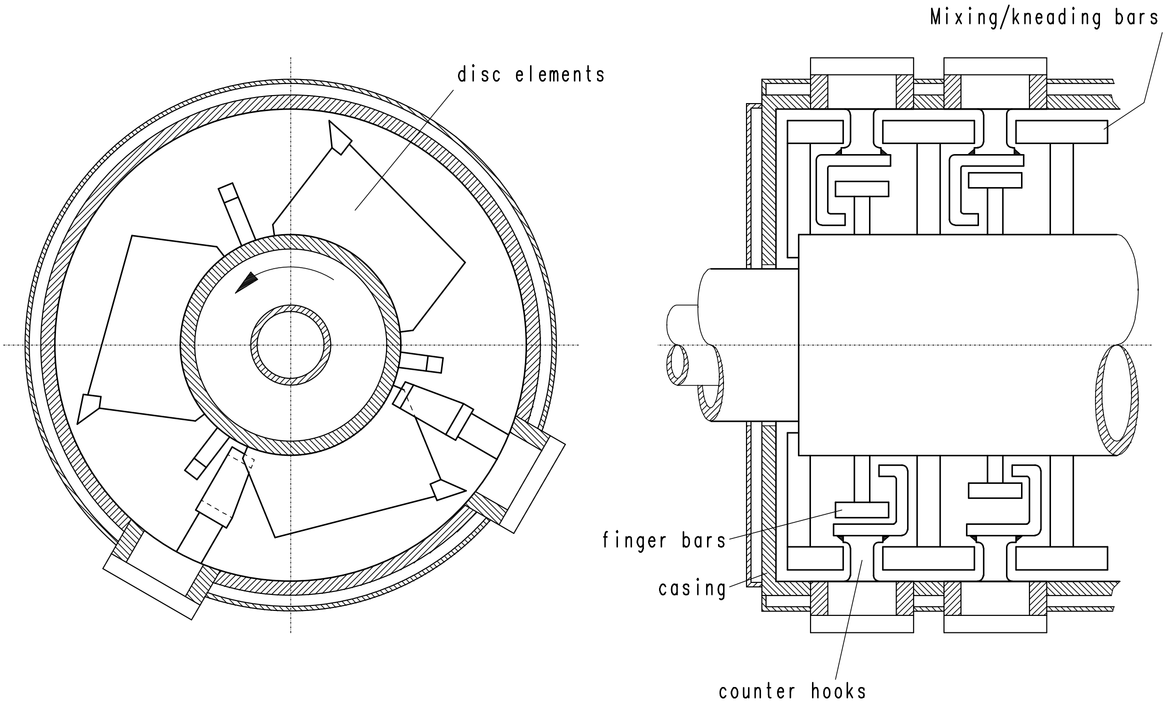

Figure 1: Single shaft kneader devolatilizer

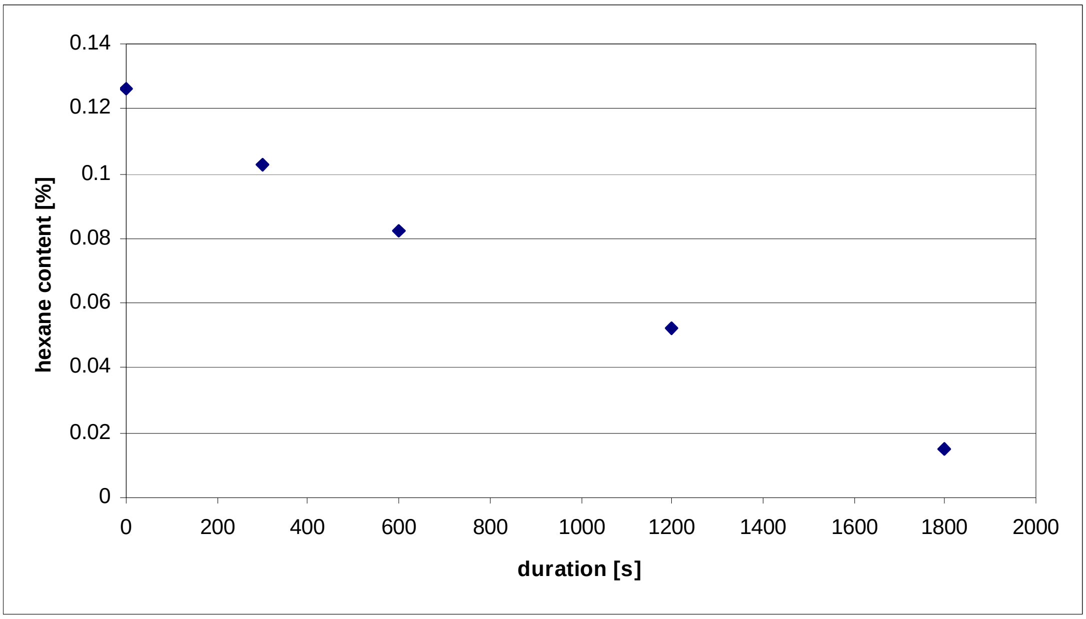

Figure 2: Solvent content reduction at 2000 Pa pressure in 7 L single shaft batch kneader

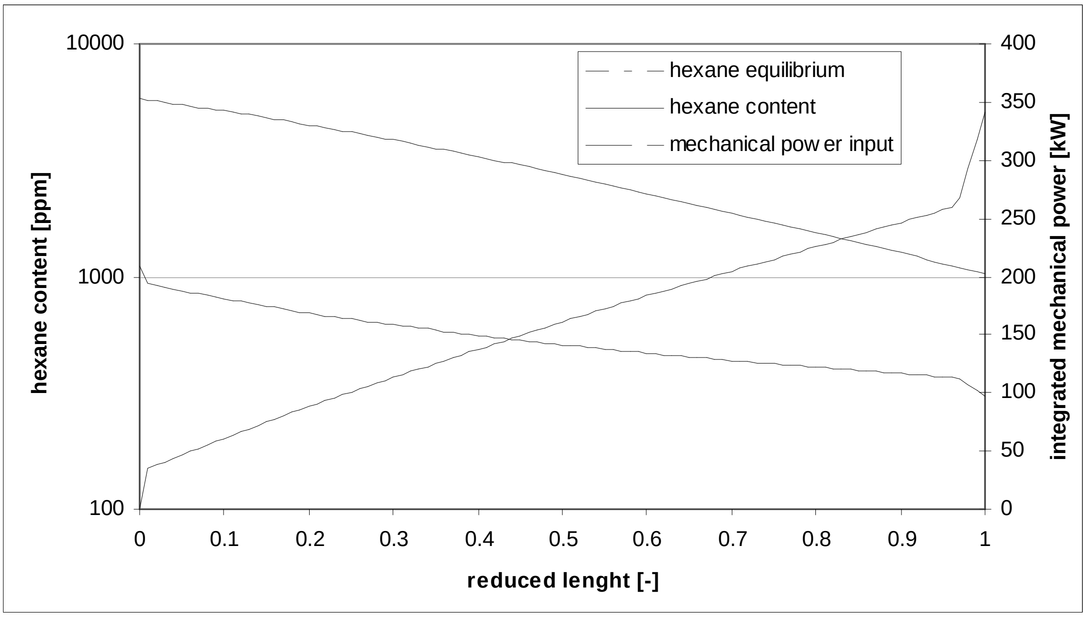

Figure 3: Simulated data of devolatilization in 5 m^3 kneader