KNEADER TECHNOLOGY FOR THE DIRECT DEVOLATILIZATION OF TEMPERATURE SENSITIVE ELASTOMERS

Boyd T. Safrit, LIST USA, Inc., Charlotte, NC
Andreas E. Diener, LIST AG, Arisdorf, Switzerland

Abstract

Synthetic elastomers have been produced for over 50 years. Advances in catalyst systems and polymer formulations have been somewhat diminished by the continued use of the same processing technology. In particular, the use of coagulation, steam stripping, mechanical dewatering, and convective drying for the devolatilization of temperature sensitive elastomeric solutions can be replaced with direct devolatilization using kneader technology. A two-step, direct devolatilization process has demonstrated energy savings and advantages in environmental emissions and process/product flexibility when compared to the conventional steam stripping process.

Introduction

The reaction of one or more monomers to produce synthetic elastomers is normally exothermic. In many of these reactions, the reaction temperature must be controlled since side reactions and degradation can occur at elevated temperatures. Controlling the reaction temperature can become very difficult due to the viscosity increase of the reaction mass as molecular weight is built during the polymerization. The development of a process to produce elastomers has been guided by the limitations of temperature control under high viscosity conditions. Typical processes used to make synthetic elastomers include emulsion, suspension, or solution polymerizations.

For example, styrene-butadiene rubber (SBR) is made by solution polymerization of styrene and butadiene in a solvent (hexane, cyclohexane, toluene, etc.) The concentration of SBR in the solvent is kept low (10-25%), which keeps the viscosity low. Stirred tank reactors can therefore be used to provide the required mixing and temperature control. Once the reaction is complete, the resulting cement solution is coagulated and stripped with steam in hot water in order to remove the solvent from the rubber. The so-called "rubber slurry" is then subjected to a series of mechanical dewatering processes (expellers, expanders) to remove the majority of the water. Belt dryers are typically used to remove the final residual amount of water from the rubber particles (crumbles). The removal of volatiles (solvent and water) from the rubber is called finishing.

This process for finishing elastomers has both benefits and disadvantages. The technology has been used and proven for over 50 years. The equipment and process are also well known and understood. The coagulation and stripping steps may also provide a washing of the rubber. Spent catalyst, surfactants, and other components present in the reactor product can often be removed from the rubber crumbles.

There are however several significant disadvantages of this finishing technology. A large amount of steam is used for coagulation and stripping. The solvent recovered during the stripping process must be refined, as it contains significant amounts of water. And as the final solvent residual concentration target is lowered, the amount of steam that must be used goes up dramatically. Polymers that stick to the jacket of the stripping vessel or strongly foam cannot be steam stripped (1). The hot air exiting the rubber crumb dryers will contain solvent that typically must be treated in an incinerator for environmental reasons. Many pieces of equipment are also required for this process, which will require more maintenance, a larger plant footprint, and more difficult cleaning.

In order to address these disadvantages, a new process for the direct devolatilization of elastomers was developed. At the core of this new process is kneader reactor technology (2), which has been used over 40 years for a variety of high viscosity applications including drying, polymer/rubber devolitization, solvent recovery from sludge, and liquid based reactions and polymerizations. Figure 1 shows the relationship of kneader reactor technology to other industrially known technologies in the areas of contact heat transfer, power input, and residence time. The unique blend of these characteristics was key in using kneader reactor technology for devolatilization of elastomers. Heat transfer area provided in the reactor casing, shaft, and shaft kneading elements can add or remove energy as required. The kneading/cleaning elements of the kneader reactor serve several functions. They continually clean the reactor casing and shafts in order to prevent polymer buildup and degradation, while also providing excellent mixing and surface renewal. Surface renewal is vital to polymer devolatilization because volatile components in the polymer matrix must be transported to the surface of the polymer to be evaporated and removed. But another key role of the kneading characteristic of this technology is the ability to input power (mechanical energy) into the polymer under low shear conditions. The interaction of the static and dynamic kneading elements in the reactor due to the rotation of the shaft(s) provide the kneading

action, which under viscous conditions, can add significant amounts of mechanical energy to the polymer.

A continuous two-step process (see Figure 2) for the direct devolatilization of temperature sensitive elastomers was developed and demonstrated on a semi-works scale at the Fraunhofer Pilot Plant Center for Polymer Synthesis and Processing in Schkopau, Germany. The first step was the main evaporation of the butadiene rubber (BR) cement in a 100-liter single shaft kneader reactor. The goal of the main evaporation step was to concentrate the cement solution that had been polymerized in a stirred tank reactor and recover the solvent directly for recycle back to the reactor. The concentrated cement, roughly 90-95% BR concentration, was continuously discharged from the main evaporator and fed to the 200-liter twin shaft finisher. The function of the finisher was to reduce the residual volatile concentration down to the necessary volatile level of 500-2000 ppm. Results from the demonstration showed reduced energy consumption and minimal environmental emissions when compared to the conventional steam stripping finishing process.

Experimental

Cement solution of 10% BR in cyclohexane solvent was polymerized in a stirred tank reactor. The temperature limitation of this particular product was 100°C. The cement was fed continuously at 400 kg/hr to the 100-liter kneader single shaft main evaporator, which has 2.1 m^2 of heat transfer area. A residence time of approximately 15 minutes was targeted for the main evaporator using Equation 1.

$$t_r = \frac{V_r \phi_r \rho_p}{F_p} \qquad (1)$$

Due to the temperature limitation of the elastomer, the main evaporator was operated at approximately 300 mbar absolute. At this pressure, the boiling point of cyclohexane is 45°C. The temperature of the hot oil that was circulated through the reactor casing, shaft, and kneading elements was approximately 80°C. As the cement was conveyed down the axis of the kneader, solvent was removed and the remaining cement became more viscous, which enabled more mechanical energy to be added to the cement by the rotation of the shaft (RPM = 50-80). The evaporated solvent was removed from the kneader via the vapor dome and condensed externally. The solvent concentration of the rubber discharged from the main evaporator was approximately 5% and was discharged from the kneader using a twin-screw discharge device that then fed into the twin shaft kneader finisher.

The 200-liter twin-shaft finisher, which has 7.0 m^2 of heat transfer area, was operated at 60 mbar and hot oil was circulated through the jacket and shafts at 80°C. The shafts were rotated at 60 RPM and formed rubber crumbles. A unique combination of shaft RPM and filling level was used to transfer the rubber crumbs into a agitated and tumbled bed, much like a fluidized bed, for the final devolatilization and direct solvent transfer out of the crumble into the gas phase. The formation of rubber crumbles in a smaller finisher can be seen in Figure 3. The rubber crumbles were discharged using a twin-screw discharge device. The evaporated solvent was removed from the kneader via the vapor dome and condensed externally.

Results and Discussion

Main Evaporator

By carrying out the main evaporation predominantly in the viscous and pasty phase, the energy that was required to evaporate the solvent was supplied mainly by mechanical means instead of contact heat transfer. Using Equations 2 and 3, the measured hydraulic pressure, P_{load}, was converted into torque and then into mechanical energy input, Q_{mech}, where M_{spec} is the specific torque of the kneader/hydraulic drive combination, P_{empty} is the hydraulic pressure of the empty kneader (bearings, tightness of stuff box packings, etc. will affect P_{empty}) and n is the shaft RPM. The calculated main evaporator torque was 43 Nm/liter and the Q_{mech} was 27 kW. The energy required to evaporate the solvent in the main evaporator was 35 kW. The remaining 8 kW energy was added to the evaporator by contact heat transfer. 79% of energy required for the solvent evaporation was provided mechanically, meaning scaleup to a larger capacity can be done with more confidence as the process is not heat transfer area limited.

$$M_r = M_{spec}(P_{load} - P_{empty}) \qquad (2)$$

$$Q_{mech} = M_r n \qquad (3)$$

Figure 4 shows the temperature profile of the main evaporator. In the first 50% of the main evaporator, the temperature of the cement is constant at approximately 55°C. As the cement becomes more and more concentrated in the end of the kneader, the temperature increased due to the mechanical energy input but remained below the 100°C discharge target temperature. The hot oil provides both a heating and cooling function in the feed and discharge end of the kneader respectively.

Finisher

The rubber in the finisher was in the form of crumbles due to the unique agitated bed characteristics within the finisher. Therefore, a small amount torque or mechanical energy was added to the crumbles and the crumbles were protected from overheating. The resulting torque was measured to be 3.7 Nm/liter and Q_{mech} was calculated to be 4.6 kW.

Figure 4 shows the measured temperature profile within the finisher. As can be seen, there was an approximate 10°C temperature rise in the finisher and the final temperature of the finished rubber was still less than the 100°C maximum. The hot oil circulated in the finisher provided a cooling function by removing most of the mechanical energy that was added to the finisher. Some of the mechanical energy provided the necessary energy to evaporate the final amount of solvent (~0.5 kW).

The residual solvent in the discharged crumbles was approximately 1000 ppm and the size of the crumbles was 3-6 mm. Under the operating conditions of the finisher and physical form of the rubber crumbles, the solvent evaporation from the rubber is governed by desorption and diffusion of the solvent from within the rubber crumble particle. For a fixed crumble size, the final residual solvent concentration can be controlled by adjusting the vacuum level and residence time. Vacuum level will determine the final equilibrium concentration of solvent in the rubber. Equilibrium cannot be achieved instantaneously and residence time is required in order to approach this equilibrium condition.

Conclusions

A two-step process for the direct devolatilization of a temperature sensitive elastomer cement solution was developed and demonstrated on a pilot plant scale using kneader reactor technology. The target of this process was to address some of the disadvantages of the conventional steam stripping process that has been in use for over 50 years. Some of these disadvantages include: high water and steam consumption, high energy consumption, environmental problems due to high level of emissions, solvent purification, and high maintenance and cleaning costs due to amount of equipment required. The first step, single shaft main evaporator, was carried out under vacuum in order to maintain a low cement temperature. The continuous operation was done in the viscous and pasty phase so that a large portion of the required energy could be provided by mechanical means. The second step, twin-shaft finisher, was operated at an even lower vacuum to reach low equilibrium residual solvent concentrations in the rubber. The rubber was processed in the finisher as small particles or crumbles, which minimized the mechanical energy that was added to the rubber. This protected the rubber from overheating during the final processing step.

The overall energy balance of the demonstrated process is shown in Figure 5. It has been estimated that the direct devolatilization process will reduce energy consumption by 76% when compared to the conventional steam stripping and drying process. It was also estimated that the consumption of water would be decreased by 66%.

The direct devolatilization process has shown many advantages compared to the conventional steam stripping and drying process. By removing water from the finishing process, energy can be saved, emissions reduced, and purification of the solvent can be eliminated. Trace amounts of water in the recycled solvent will also be eliminated, which may also permit new catalyst or polymer development that was previously not possible due to water sensitivity.

Nomenclature

F	flow rate
M	torque
n	shaft RPM
Q	energy rate
t	residence time
T	temperature
V	volume
ρ	density
ϕ	fill level

Indices:
empty	empty reactor
load	full reactor
mech	mechanical
p	polymer
r	reactor/reaction
spec	specific

References

1. P. A. Fleury, D. U. Witte, H. Schildknecht, "Comparison of Devolatilization Technologies for Viscous Polymers", ANTEC 2005 Technical Paper #100655 (2005).

2. D. U. Witte, "Computer Scale-up Model for Desolventizing Highly Viscous Polymers in Kneader Equipment", ANTEC 2005 Technical Paper #100656 (2005).

Key Words

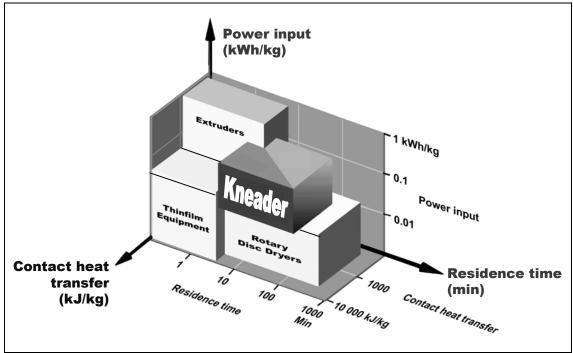kneader reactor, polymerization, rubber, devolatilization, elastomer, high viscosity, heat transfer, torque, scaleup.
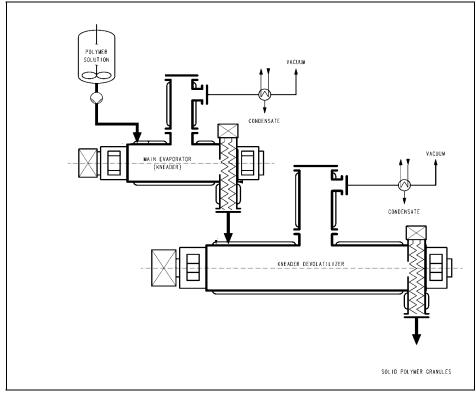
Figure 1: Working Area of Kneader Reactor Technology

Figure 2: Two-Step Process for Direct Devolatilization

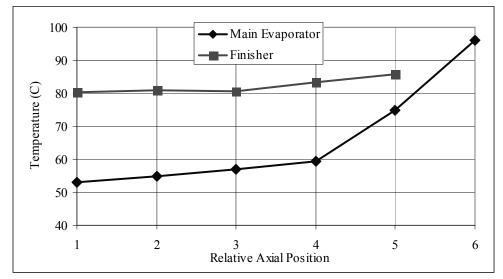**Figure 3:** Rubber Crumble Formation in Finisher
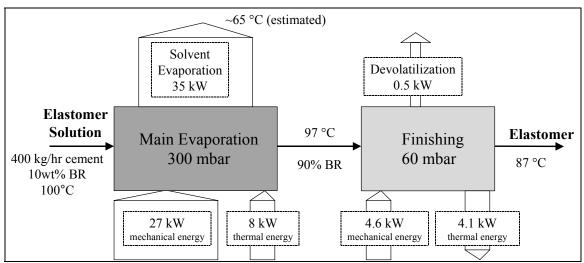

Figure 4: Temperature Profile in Main Evaporator and Finisher

Figure 5: Overall Energy Balance for Two-Step Process