New Concepts for the Continuous Mixing of Powder Rubber

by

Ali Amash*, Martin Bogun and Robert-H. Schuster
Deutsches Institut für Kautschuktechnologie e. V.,
Eupener Straße 33, 30519 Hannover, Germany

and

Udo Görl and Martin Schmitt
Pulver Kautschuk Union GmbH (PKU), 45772 Marl, Germany

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Abstract

The development of a continuous mixing process for NR powder rubber compounds on the twin-screw extruder requires an appropriate screw configuration taking advantages of various types of screw elements used for conveyance, dispersiv and distributive mixing. Further target of the study was a significant increase in the output with still good quality of process behaviour and material properties. Under the given machine capacity limit, a gradual raise of the feed rate was successfully achieved with increasing screw speed at clearly moderate mixing temperatures. A markedly high filler dispersion degree of >95% was determined for all compounds produced by the varying process parameters. Consistently, rheological and mechanical measurements revealed only negligible to weak differences between the sample properties. For comparison of results, compounds based on NR in bale and powder form were prepared by the discontinuous mixing process.

Introduction

One of the most desired developments is still a reliable continuous compounding process of conventional rubber compounds. It gains an increasing interest, due to the related attractive advantages including economic efficiency, as compared to the nowadays mostly widespread multi-stage rubber compounding technology. In recent years, a real progress towards the continuous mixing process, which primarily requires a continuous feed state of all compound ingredients, occurred by manufacturing of new powder rubber types based on E-SBR and NR [1-3] as well as on gas-phase EPDM [4-6]. These free-flowing rubbers are suggested to replace the conventional rubber supplied in bale form.
The distinctive characteristic of the granular batches produced from polymer emulsions (SBR, NR) and non-pelletized carbon black (fluffy) is the markedly constant rubber-filler ratio, and that their both components are homogeneously distributed in an intimate mix with a high degree of filler dispersion [1]. Compounds on the basis of carbon black filled E-SBR types, prepared by the discontinuous kneader mixing process, revealed an unique combination of favourable mixing behaviour, high dispersion and good in-rubber properties.

In previous works, remarkable efforts are made on the development of an appropriate continuous mixing process for powder rubber based on SBR by using the twin-screw extruder (TSE) and considering several aspects such as the influence of mutual process parameters [7-9]. Twin-screw extruders cover a large variety of configurations including (i) co-rotating, (ii) counter-rotating and (iii) partially or fully intermeshing screws as well as (iv) with constant or variable helix angle [10]. In order to improve mixing performance, TSE design may include special mixing sections and conventional or modified kneading blocks for dispersiv and distributive mixing. It is noteworthy that the various types of twin-screw extruder as well as of mixing elements are primarily designed for processing plastics. The real challenge lie in the transfer of the overall extrusion technology to powder rubber processing. Due to recent progress in gravimetric and volumetric proportioning technology, powder materials and fillers can nowadays also be fed with high accuracy.

This paper is a further contribution of advanced concepts to the development of an appropriate continuous rubber mixing process for powder rubber compounds on the basis of NR by using the twin-screw extruder. The main target of the work is the optimization of mixing parameters, such as feed rate, screw speed, temperatures and energy input. In addition to these a screw configuration should be optimized, in order to improve the extrudate output with a still high dispersion degree and homogenous distribution. An important aim is also the study of the physical behaviour of the materials. A comparison of powder to bale rubber compounds produced by discontinuous process is done.

Experimental

Material and Feeding

Powder rubber (PR) on the basis of 100 phr natural rubber (NR) and 47 phr carbon black (CB) was supplied from PKU GmbH (Marl / Germany) for performance of investigations. The average particle size of the granules lie in the range of 0.5-3 mm. For producing compounds and vulcanizates, different ingredients including anti-oxidants and curing system have to be incorporated. *Table 1* shows the compound recipe used. It should be noticed that the chemicals were premixed and separately added to the powder rubber during mixing process.

Table 1: Formulation of compound

	Ingredients	phr
Powder rubber	NR	100
	N234	47
Premix	Stearic acid	2
	ZnO	4
	6PPD	1.5
	TMQ	1
	Wax	1
	TBBS	1
	Sulphur	1.5
	CTP	0.15

A gravimetric single screw loss-in-weight-feeder (screw diameter 35mm; Brabender flex wall) was used for proportioning powder rubber and similar one (screw diameter 20 mm) for metering chemical premix. The gravimetric feeders handle precise throughput rates and can respond to fluctuation in bulk density via differential weighing scales and an appropriate screw speed control device.

Twin Screw Extruder

Compounding Experiments were performed by using the twin-screw extruder (TSE; Farrel FTX80) equipped with co-rotating screws [11]. Key data about the machine are given in *Table 2*. The extruder barrel consists of nine replaceable parts of 4 L/D Length, respectively. The first metering zone barrel should be permanently cooled by water to prevent material caking. The following eight processing segments are mainly used for mixing and can be heated up to temperatures of 370°C, where open cylinders are suitable for feeding additional ingredients and for degassing purpose.

Table 2: Technical data of the twin-screw extruder

Max. process length	36 L/D
Extruder hole diameter	37 mm
Screw outer diameter	36.5 mm
Screw inner diameter	23.5 mm
Diameter ratio	1.55
Channel depth	6.25 mm
Alignment	31 mm
Max. screw speed	500 min^{-1}
Max. Power	18.5 kW
Max. torque per screw	176 Nm

Discontinuous Compounding

Compounds on the basis of the new powder rubber as well as of a conventional NR type obtained in bale form were produced by the multi-stage discontinuous mixing process carried out on a 1.5 l laboratory internal mixer for mixing time of 6 min. The test formulation is given in Table 1, where the bale rubber type SMR10 (100 phr) and CB N234 (50 phr) would replace the powder rubber/filler-batch used also for extrusion. In the case of bale rubber compound, all ingredients were mixed at 140°C after the necessary mastication of the matrix, while the curatives were added in a separated mixing stage at 115°C. Powder rubber compounds were prepared in a similar manner, however, no separated mastication is ever needed, the curing system and antioxidants are added in the second stage, the mixing time was varied and the loading degree of PR slightly increased (10%).

Sample Preparation and Measurements

All materials produced by extrusion and kneader were shortly threaded over a roll mill of a large nap (5 mm) at 70°C, in order to get rolling hides.

The vulcanization of the compounds was performed at 150°C in a press for yielding sheets of 2 mm thickness. The vulcanization time was chosen in view of an almost complete cross-linking procedure up to 90% of the maximum torque found in vulcameter measurements (Monsanto), which also deliver other important data, such as the scorch time.

The filler dispersion degree was quantified by the so called DIK-method based on the luminous reflectance of razor blade cuts (light optical roughness measurement). The light source is placed inside the optical microscope, the cut is illuminated by a vertical light beam and the reflected image is recorded by a CCD camera. Size distribution and fraction of the undispersed agglomerates (>6 µm) are determined by a computerized image analysis.
The Mooney viscosity of the rubber compounds was detected for an evaluation of the processing behaviour. This important property depends on filling degree, dispersion and the decrease of the molecular weight (i.e. mixing time) during the mixing cycle.
Stress-strain measurements were performed on Dumbbell specimens of vulcanizates at room temperature. Tensile strength, elongation at break, modulus and hardness were determined.

Results and Discussion

Discontinuous Rubber Mixing

Table 3 gives some results for the compounds of the internal mixer. In general, only weak to moderate differences can be established between their properties. The powder rubber compound mixed for 6 min exhibit the lowest Mooney viscosity and the highest dispersion degree of 98.5%, while its mechanical behaviour is comparable to that of the bale rubber vulcanizate. This mixture yields also a good dispersion degree of ca. 95.5% and a clearly higher viscosity in comparison to the two-stage PR mix. Reducing mixing time of powder rubber to 4.5 min, only marginal changes can be observed in the compound properties. The one-stage PR-compound mixed for 3 min exhibits values of dispersion and Mooney viscosity comparable to those of the conventional bale rubber compound. The latter depends on the decrease of the molecular weight during compounding, and, consequently, the mixing time. Considering the results of the vulcameter measurements, bale rubber compound shows a slightly higher value of maximum torque than powder rubber. This indicates a slightly lower cross-linking density, which may be attributed to differences in the molecular weight of both polymers and to reduced absorption capability of the curatives due to the high filler dispersion.

Table 3: Properties of NR compounds produced by discontinuous internal mixer

	Bale rubber	Powder rubber

Mixing time	mastication + 6 min	6 min	4.5 min	3 min one stage
Dispersion degree [%]	95.6	98.5	97.6	95.3
Mooney viscosity (ML_{1+4})	60	55	56	64
Vulcam. torque $S`_{max}$-$S`_{min}$ [dNm]	17	16	16	16.3
Tensile strength, σ_{max} [MPa]	30.5	30.1	30.3	31
Elongation at break, ε_b [%]	532	537	533	540
200% modulus [MPa]	7.8	7.5	7.7	7.3
Hardness (shore A)	67.5	68.8	69.5	70

The whole results clearly show, that the powdered NR/filler-batch used for the investigations does not require a bale rubber-like mastication and even long mixing time, in order to achieve properties similar to those of compounds based on bale rubber. This is due to the suitable pre-treatment and the high filler dispersion of the powder rubber during production and compounding process.

Continuous Mixing Process on Extruder

Screw Elements and Configuration

It is well known, that the geometrics for co-rotating screw were basically developed by Erdmenger, with the objective of screw's touching at any screw angle for self-cleaning purpose [12]. In this work, various types of screw elements were available for varying and optimizing screw configuration. *Figure 1* illustrates these “loose” screw parts:
(Fig. 1a) single-flighted undercut elements of long pitch for particulate feed handling; (1b) forward pumping conveying elements of Erdmenger-profile and various pitches; (1c) kneading blocks for dispersiv mixing, made up of five disks turned by 45° and taking up a total length of 1 L/D (overall offset of 180°; outer diameter 36 mm); (1d) Farrel Asymmetric Modular Mixing Element (FAMME or CME) for dispersiv mixing, which is a variation of the Erdmenger profile exhibit a very steep pitch; FAMME and kneading blocks can be designed as forward-pumping or reverse-pumping elements; (1e) distributive turbine mixing elements for the homogenization and dispersion of low-viscosity additives at low shear rates; (1f) non-intermeshing elements of polygon profile, primarily, for distributive mixing.

The behaviour of the rubber compounding process on extruder is essentially determined and influenced by the chosen screw configuration [4]. The available screw elements allow modification of screw geometry and great variety of mixing sections longitudinally from the feeding zone towards the screw tip. However, the optimization of the screw assembly and the overall continuous mixing process has to be based on principles applied by discontinuous compounding in an internal mixer or on the roll mill. With other words, suitable extrusion concepts require that the powder rubber goes through regions of high shear forces and long duration, alternating with sections of low shear exposure and short residence time. The former can be realized by dispersiv and distributive mixing elements at low temperatures for fully rubber mastication and high filler dispersion.

In this work, several screw configurations composed of different screw elements and varying arrangement were basically tested. Preliminary extruder experiments were performed on the free-flowing powder NR-rubber/filler batch (PR) by using screw configurations of 24 or 36 L/D process length with mostly conveying elements and up to four mixing elements designed for forward- and reverse-pumping. The results of these initial stages were relatively insufficient regarding material properties, but, important test points and improvement options of the process could be defined as well as useful effects were observed during compounding. Therefore, the next step lie in the development of a screw configuration based on the overall establishment. Further investigations revealed that a certain arrangement and a minimum number of all types of the available screw elements with a process length of 36 L/D, would result in a considerably efficient use of the individual distinctive mixing and other advantages of the different elements.

In *Figure 2*, an optimized screw configuration is illustrated for the continuous mixing process of the powder rubber compounds based on NR. It can be seen, that a kneading block placed in the plasticizing zone at 80°C and one FAMME in the following section are needed for a highly level of mastication and filler dispersion. Both block types consist of forward-pumping and reverse-pumping elements, respectively, in order to expose the granular rubber to high shear stress for long residence time. After material conveyance, turbine elements are useful for the homogeneous incorporation of the chemical premix at clearly low shear and temperatures. The compound goes through conveying elements, alternating with a FAMME and a polygon element, which are suitable for further dispersion and effective distribution, respectively. In the last screw segment, conveying elements of small pitch and Erdmenger profile are placed.

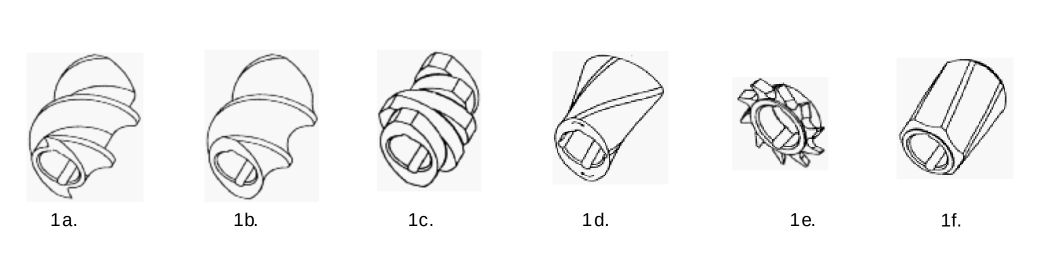

Figure 1: Available screw elements [11]

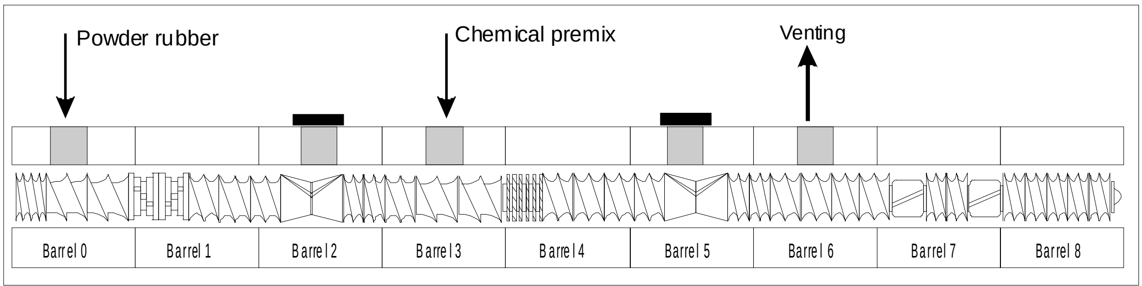

Figure 2: Screw configuration optimized for the continuous mixing process of powder rubber based on NR.

Process Parameters and Properties

The above optimized screw configuration is used for the performance of the experiments on powder rubber compounds. All important extruder process parameters chosen or detected during compounding process, as well as various measurement results corresponding to different properties of the extrudates and vulcanizates are summarized in *Table 4*.

Table 4: Properties of NR compounds produced by the continuous mixing process.

Feed rate [kg/h]	10	20	30	40	50
Screw speed [rpm]	150	220	310	390	460
Specific energy input [kWh/kg]	0.505	0.374	0.348	0.332	0.313
Temperature [°C]	76	88	107	120	132
Mooney Viscosity @100°C [MU]	55.5	57	59	61.5	63
Dispersion degree [%]	98.5	98.0	97.2	96.0	95.3
Torque $S`_{max}$-$S`_{min}$ [dNm]	15.5	15.4	15.0	14.4	13.7
Scorching time, T_{S1} [min]	3.3	3.3	3.1	3.0	2.8
Tensile strength, σ_{max} [MPa]	31.4	31.2	30.7	30.3	30.0
Elongation at break, ε_b [%]	523	520	522	519	517
200% modulus [MPa]	8.4	8.2	7.6	7.6	7.4
Hardness (shore A)	67.5	67	67.5	68	68

We primarily varied the overall feed rate of the materials mixed according to the formulation in Tab. 1, and successfully reached a markedly high output of 50 kg/h at very moderate mixing temperatures. However, this gradually output enhancement was only feasible with a simultaneous increase of the screw speed, in order to remain under the upper torque limit of the twin-screw extruder. Consequently, the real mass temperature conducted for the out going extrudate by push-in thermocouple, also gradually increased up to ca. 130°C, although a maximum cooling for the extruder barrels was adjusted (excepted plasticizing zone). However, vulcameter measurements revealed an obvious scorching safety for all samples of the tested throughput rates, where a reasonable scorching time higher than ca. 2.8 min was recorded. It is assumed, that the short residence time of the compound in great shear regions, due to high screw speed and conveying capability, would compensate the eventual scorching effects of increasing temperature. A further effect observed on the vulcameter curves is a gradually small reduction of the corresponding maximum torque with increasing output and screw speed. This can be primarily attributed to the slightly decreasing cross-linking density, as the mixing time becomes shorter and, consequently, the quality of diffusion and homogeneity of the chemicals in the entire rubber matrix is also marginal lowered. Certainly, metering some chemicals (i.e. zinc oxide) in an earlier stage for better dispersion would improve the cross-linking density, since the later absorption and homogeneity of the curatives can be considerably facilitated.

An important advantage of raising feed rate and screw speed is doubtless the overall reduction in specific energy input needed for the continuous mixing process.
Increasing feed rate, screw speed and temperature results in a certain enhancement of the Mooney viscosity, which is determined by the screw configuration and mixing quality. Short duration of the powder rubber at the mixing elements imposing high shear forces, lowers the level of mastication and, consequently, the Mooney viscosity. However, this important process property still lie in a clearly good value range, as compared to that of internal mixer compounds. An analogous interpretation is given for the slight decrease observed in the filler dispersion of the extrudates by increasing the mentioned parameters. In dependence of the screw speed, the residence time of the material in the high shear regions becomes shorter as well as the duration of dispersion and distribution. But also in this case, the values of the dispersion degree remain in a narrow range of 95-99%. This is evidentially referred to a great suitability and capability of the optimized screw configuration (Fig. 2) to meet important requirements of the continuous rubber mixing process, i.e., good dispersion at maximized output.

The above mentioned effects are consistent with the mechanical properties of the various vulcanizates. Increasing process parameters results in very weak differences between the values of the tensile strength, elongation at break and hardness. The

tendency of the slight σ_{max} decrease may be attributed to the marginal differences in cross-linking density and filler dispersion of the compounds.
However, all effects observed for morphology, rheological and mechanical behaviour of the extrudates, indicate a considerably weak influence of the considered parameters on the process and material behaviour. This is, particularly, due to the good initial properties of the powder rubber as well as to the well-aimed optimization of the screw configuration.

Conclusions

The development of an appropriate continuous mixing process for NR- powder rubber compounds on the twin-screw extruder requires a simultaneous pursuit of several mutual aims, including the achievement of a good quality of morphology (filler dispersion and distribution) and related final properties as well as a maximization of the output at low to moderate temperatures for scorching safety. However, the most important basis of the mixing process is an optimum extruder screw configuration containing various types of screw elements having different functions. A significant raise of the throughput rate is achieved by increasing screw speed without a negative influence on the process and final material properties. These are comparable to the properties of compounds produced by discontinuous mixing. The defined limits of the extruder, i.e., screw speed, torque and cooling are crucial for the optimization of continuous mixing concept.

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