Continuous Mixing of Silica based Rubber/Filler-Composites in Twin Screw Extruder

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Preface

This work was carried out in German Institute of Rubber Technology (DIK) under the supervision of Prof. Dr. R. H. Schuster and Prof. Dr.-Ing. H.-J. Radusch from September 2004 to August 2007.

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1. Introduction

The art of rubber mixing was started from Goodyear's discovery of sulphur vulcanization of natural rubber in 1839 [1]. The mixing of sulphur and rubber are required to achieve satisfactory vulcanization and hence the technology of rubber mixing may be said to have started some 140 years ago. The main aim of mixing is to make a homogeneous mixture from different ingredients. Mixing is generally referred to as the distribution of single volume elements in a specified volume, where those single volume elements differ in atleast one property [2]. The ingredients may differ in structure, viscosity, concentration and rheological behaviour. Apart from ingredients, mixing also depends on the type of mixing equipment. The mixing efficiency depends upon the type, design and process parameters of the equipment used.

The mixing of rubber compounds is traditionally carried out in batch wise mixing equipments, such as roll mills or in internal mixers [3-5]. As the rubbers are available as bales, the batch wise mixing equipments are used until today. Until the development of internal mixers, two roll mills were the major mixing equipment in the rubber industry for many years. Two roll mills are used exclusively in rubber compounding especially for mastication as well as for mixing chemicals. The normal internal mixer is a discontinuous compounding machine which requires high mixing energy [6]. The discontinuous mixing in internal mixer has some advantages, for example: high flexibility regarding different recipes and mixing orders. A major disadvantage of this process is that the batch mixing in internal mixer leads to differences in mixture quality from one batch to another [7-8].

In contrary, continuous mixing processes shows high consistency in mixing quality and needs low mixing energy [9]. Continuous mixing aggregates are state of the art in plastics compounding and extrusion industries for several decades [10]. The availability of plastic raw materials as granules or powders in free-flowing form is practically suitable for feeding in continuous mixing aggregates. As rubbers are available as bales, the applications of continuous mixing aggregates are not yet widely used in rubber industry. But, continuous mixing process is preferable because of cheaper labour costs and better uniformity in quality [9]. Today, a considerable variety of different continuous mixing aggregates are applied for rubber mixing such as planetary roller extruder, twin screw and multi-screw extruder [11-13]. Most of the continuous mixing aggregates originate from the principle of the screw extruder. The continuous mixing aggregates however need rubber materials as free flowing materials for feeding continuously.

Recently, powdered and granulated rubber materials became available as feeding materials for continuous mixing aggregates. Some of them are EPDM from Dow [14] and Rubber/Filler-Composites (RFC) from Degussa AG (Evonik AG) [15-17]. Since 1998, Degussa AG has developed a number of rubber products where the essential rubber ingredients such as carbon black, silica, extender oil and other chemicals can be incorporated during the production process of Rubber/Filler-Composites [18]. The use of special RFC production techniques leads to a significant reduction of the tackiness of the rubber and additionally helps to keep the material in a free flowing form during storage for longer time. Several RFC products are today available commercially or as development products to the rubber user such as E-SBR/carbon black [16], NR/carbon black [19] and E-SBR/silica/silane [17]. These materials are available either in free flowing powder form or in granule form for feeding any continuous mixing aggregate.

During the middle of 90’s, a new system of compound formulation was introduced by the tire industry for making passenger car tire tread compounds. In the new technology, carbon black as filler is replaced by precipitated and highly dispersible silica. The silica is however highly incompatible with the rubber matrix and hence the silica surface should be modified with a coupling agent called organosilane. The mixing of silica with organosilane along with rubber in the internal mixer involves several mixing stages and long mixing time of 10-15 minutes. This is necessary to react chemically the silica and the organosilane during the mixing process. To avoid this mixing process, a new RFC material was introduced by Degussa AG where the silica is silanized during the production process of RFC [17]. Also, the filler in RFC is fully incorporated in the rubber matrix which additionally promotes less mixing time and better material quality.

Several studies were carried out with continuous mixing aggregates and free flowing raw materials such as EPDM in twin screw extruder [20], RFC containing carbon black in twin screw extruder [21], RFC containing silica in planetary roller extruder [22] and RFC containing silica in twin screw extruder [23]. These studies proved that the continuous mixing is possible with rubber compounds in comparison to discontinuous mixing. The development of a continuous rubber compounding process for the purpose of saving energy is without doubt a great challenge for the tire industry. With such Rubber/Filler-Composites containing carbon black or silica, it is one of the most promising approaches to change to continuous mixing process and it is a chance for the rubber industry in the near future.

2. Aim of the work

Until today, several studies were carried out with continuous mixing aggregates and free flowing rubber materials. The mixing of RFCs containing carbon black and silica in co-rotating twin screw extruder were intensively studied by M. Bogun [21]. The mixing of RFCs based on E-SBR and NR with carbon black in twin screw extruder were quite successful and the material properties were even better than the mixtures obtained from the internal mixer. But, the mixing of RFCs based on E-SBR with silica in twin screw extruder were showing poor compound and material properties compared to the mixtures obtained from the internal mixer. Along with that, the silica based compounds lead to higher outlet temperature in twin screw extruder which limited the throughput to a maximum of 37.5 kg/h. In order to overcome these difficulties in mixing of silica based RFCs, the present work is a further step carried out to improve the compound and material properties as well as to optimize the processability in a co-rotating twin screw extruder.

With respect to this, the first goal of this work is to develop a screw configuration in a co-rotating twin screw extruder optimum for mixing RFCs based on E-SBR/silica/silane. Special screw designs were configured with different mixing elements to study the influence on dispersion and distribution of silica particles. By using mixing elements such as forward, reverse and neutral kneading elements, studies were carried out to compare the mixing performance of different kneading elements influencing the compound properties such as filler-filler interaction and mooney viscosity. Along with that, the studies were comparing the mixing efficiency of different kneading elements with respect to specific energy input, residence time as well as outlet temperature of the extrudate.

The mixing performance depends not only on optimum screw design, but also on optimum dosing assembly. As in internal mixer, the ingredients should be dosed in twin screw extruder in right order. There are different barrel sections which can be modularly configured and the dosing of ingredients can be designed to take place along the extrusion direction. The screw configuration and dosing assembly should match each other, so that the incorporation of ingredients easily takes place as well as the compound gets maximum mixing and cooling simultaneously. In order to accomplish optimum incorporation of RFC, filler, plasticizer, activators, antioxidants and cross-linking chemicals, several dosing assemblies were investigated. The influences of dosing assemblies on outlet temperature, specific energy input as well as on compound properties were studied.

Continuous mixing in twin screw extruder gives the possibility to mix all the ingredients in one mixing step. The efficiency of mixing depends upon optimum screw configuration and dosing system. At the same time, the productivity depends upon the maximum throughput possible by the twin screw extruder. On increasing the throughput, the compound temperature increase drastically and it may lead to pre-mature scorching. Taking into account the outlet temperature limit, it is intended to show the possibility of increasing the throughput with one step continuous mixing process while maintaining constant material quality.

The maximum throughput is however limited in one step continuous mixing process due to the influence of higher outlet temperature. On exceeding the outlet temperature limit, pre-mature scorching of the rubber takes place and cross-linking starts during mixing in the twin screw extruder. Hence, a two step continuous mixing process is studied. Here, the first step of mixing is carried out in twin screw extruder and the second step in two roll mill. This leads to increasing the throughput further than the one step continuous mixing without sacrificing the quality of the material properties.

A further goal of this work is to study mixing parameter such as filling degree in the twin screw extruder. The degree of mixing and the material outlet temperature can be greatly controlled by filling degree. Here, the filling degrees are studied in two ways: by keeping the throughput constant and varying the screw speed as well as by keeping the screw speed constant and varying the throughput.

An additional goal of this work is to simplify the continuous mixing process. This has been developed by introducing a new RFC compound where most of the rubber ingredients including some cross-linking agents were mixed during the production process of RFC. This compound is finally available as a single mixture where it requires only one dosing system. All the ingredients are pre-mixed and hence high degree of dispersion between the components can be achieved. The maximum throughputs were studied by this new RFC compound by one step and two step continuous mixing process.

The last part of the work will discuss on continuous mixing of rubber blends based on E-SBR/BR and S-SBR/BR with silica as filler. Different possibilities for mixing blends including the addition of cross-linking chemicals in a one step mixing process were discussed. The influences of extruder parameters and dosing assemblies on the mixing performance of blends were studied. The properties of rubber blends produced in an internal mixer were finally compared.

3. Theoretical background

3.1. Rubber reinforcement with special attention to silica as filler

3.1.1. Background of rubber reinforcement

A material which more than five centuries ago was discovered by natives of Haiti as rebouncing ball and used for playing their favourite game. This gave the introduction to a new material called Caoutchouc. The first material as Caoutchouc (comes from the Indian word "caa-o-chu" or "weeping tree") is polyisoprene recovered from the sap of Hevea Brasiliensis. Today, this material is referred to as Natural Rubber (NR), in contrast to the synthetically produced rubbers. NR can be crosslinked at high temperature with sulphur [1]. It can be transformed either from a sticky or largely plastic state into a highly elastic one and it can be transformed from caoutchouc to an elastomer or rubber.

A distinction is made between raw rubber or caoutchoucs and crosslinked rubbers which mean elastomers. Raw rubber or caoutchoucs do not have a rigid network structure [24]. They are completely deformable in a plastic-like manner, especially at higher temperatures. On the contrary, the crosslinked rubbers are transformed into three dimensional networks and this restrains the movement of macro-molecular chain molecules [25]. Therefore, the crosslinked rubbers do not have a plastic transition section. These materials can only be deformed like a plastic after some chemical or physical structural changes, caused by chemorheological effects due to ageing, decomposition, or rearrangements or they can be deformed after cleavage of the chemical or physical crosslink’s [26].

Most of the elastomers are not used in their pure form. They are generally reinforced by fillers. The crosslinked rubber in their pure form does not possess sufficient material properties for several applications. Hence, they are mixed together with fillers and additives to increase the reinforcement property as well as increase in ageing resistance, UV resistance etc. [27]. The incorporation of fillers in rubbers leads to a non-linear behaviour as well as unique material properties. The addition of increasing amounts of reinforcing fillers influences various properties of an elastomer such as high elasticity with high strength. Hence, reinforcement is defined as the ability of fillers to increase the stiffness of unvulcanized rubber compounds and to improve a variety of vulcanizate properties, e.g. abrasion resistance, compression set and tensile strength. The modulus and viscosity of the rubber compound increases with increase in concentration of the filler. Also, the reinforcement depends upon the type of filler [28] and the reinforcement effects can be explained by stress-strain diagrams [29].

3.1.1.1. Influence of filler on reinforcing effects

Despite several investigations on effects between filler and elastomer [30-35], the reasons for the reinforcement are not completely understood. But, it has to be assumed based upon the statements from above references that the filler reinforcement is the interaction between filler particles and the rubber matrix. These lead to different conditions ranging from van der Waals forces to chemical bonds [36]. The chemical composition of the filler surface, its special structure and the reactivity of elastomers affects the filler-elastomer interactions. The active centres of the filler surface can lead to polarisation of double bonds in the rubber molecules and can thus influence reactions.

Fillers can have chemically or adsorptively bound functional groups on their surface. When carbon black is mixed with rubber, the carbon black surface consists of phenolic, hydroxyl, quinone, carboxyl, lactone groups and reactive hydrogen bonds and others [37-39] which can react with rubber molecules chemically. Hence the level of physical interaction is high [30]. In contrast to this, the silica consists of silanol and siloxane groups on its surface. As silica is polar in nature, its interaction towards non-polar rubber is very less. The interaction can be improved by using a coupling agent between the filler and rubber.

Apart from the rubber-filler interactions, filler-filler interactions occur predominantly above a critical filler concentration called the percolation threshold. The material properties changes drastically above this critical filler concentration due to filler-filler network. These results for example, in an over-proportional increase of electrical conductivity in a carbon black filled SBR compound [40]. The filler-filler interactions influence the material characteristics even at lower concentrations, as shown by Payne effect [41-43].

3.1.1.2. Hydrodynamic effect

Einstein described the hydrodynamic effect by studying the flow behaviour of spherical particles in solutions. The incorporation of particulate fillers to a viscous fluid results in an increase in the viscosity of the fluid, designated as the hydrodynamic effect described by the following equation [44-46]:

$$\eta_f = \eta_0(1+2.5\phi) \qquad \text{Equ. (1)}$$

In this equation, η_f is the viscosity of the fluid containing the particles, η_0 is the viscosity of the pure fluid and ϕ is the volume fraction of particles. Later, Smallwood brought into the concept of modulus [47] and Guth and Gold extended it through a term that is related to the interaction between the particles [48-49]. It is expressed by the following equation:

$$G_f = G_0(1+2.5\phi+14.1\phi^2) \qquad \text{Equ. (2)}$$

The addition of filler concentration increases the shear modulus of the elastomer G_0 and results in a shear modulus G_f for the filled compound. It was experimentally shown that equation (2) was limited for very large particles with spherical shape and filler concentration with ϕ smaller than 2. Another approach was proposed by considering the asymmetry of the filler when the volume fraction of the particle ϕ was corrected by an adjustable shape factor f [50-51]:

$$G_f = G_0(1+0.67\phi+1.62f^2\phi^2) \qquad \text{Equ. (3)}$$

A correction for non-spherical shape of the filler particles, a shape factor f_s was added by Guth, expressed by the following form:

$$G_f = G_0(1+0.67f_s\phi+1.62{f_s}^2\phi^2) \qquad \text{Equ. (4)}$$

The shape factor f_s represents the ratio of the longest and shortest dimension of the particle. From equation (2) and (4), the modulus can be calculated independent of the applied strain. The effective filler volume fraction ϕ_{eff} [52-53] which substitutes the ϕ leads to:

$$G_f = G_0(1+2.5\phi_{eff}+14.1{\phi_{eff}}^2) \qquad \text{Equ. (5)}$$

The rubber could be occluded in the filler aggregates and partly shielded from an external deformation [52]. Apart from occluded rubber, a good interaction between the polymer and filler can occur if the effective filler volume fraction is high enough. That means that at the filler surface, the rubber that is fixed in a layer is reduced and then the hydrodynamic effect occurs. The effective volume fraction however depends upon the testing temperature, the strain deformation and also on the surface activity of the filler used.

3.1.1.3. Filler-polymer interaction

The filler-polymer interactions are strongly determined by the structure and surface of the filler and its interaction with the polymer. During the filler dispersion in the polymer matrix, the polymer tends to be partially immobilised in the form of occluded rubber where the polymer chains are trapped in the voids of the filler aggregates and agglomerates [52]. The occluded or bound rubber, sometimes termed "carbon gel", is defined as the rubber portion in an uncured compound which cannot be extracted by a good solvent due to the adsorption of the rubber molecules onto the filler surface. The filler-polymer interaction leads to the formation of bound rubber due to physical adsorption, chemisorption and mechanical interaction. As far as filler is concerned, the bound rubber is not only affected by the physicochemical characteristics of the filler surface, but also by filler morphology. With regard to polymer, both the chemical structure of the molecules (saturated vs. unsaturated, polar vs. non-polar) and their microstructure (configuration, molecular weight and its distribution) influence the bound rubber. Moreover, bound rubber also shows a strong dependence on the processing conditions of the compound, such as mixing and storage time. The bound rubber behaves like the filler rather than like the polymer matrix. They do not contribute to the elastic behaviour of the matrix because their properties are similar to the rigid filler particles. The bound rubber leads to increase in effective filler loading and thus the strain independent contribution to the modulus [57-58].

3.1.1.4. Polymer network contribution

The polymer network formed during rubber vulcanization is the third strain-independent contribution to the modulus. This modulus G_0 is proportional to the concentration of the elastic active network chains υ and the absolute temperature T, with the Boltzmann proportionality constant k_B:

$$G_0 = \upsilon \; k_B T \qquad \text{Equ. (6)}$$

3.1.1.5. Filler-filler interactions

The filler-filler interaction was first brought into focus by Payne where he showed that the filler-filler interaction affects the strain-dependent contribution to the modulus [42-43]. Payne effect considers the decrease of the storage modulus as a function of double strain amplitude in logarithmic scale in a varying amplitude range from zero until a plateau is reached (Figure 3-1). The main contribution to the complex shear modulus arises from the hydrodynamic effect, the filler-polymer interaction, the polymer network and the filler-filler interaction.

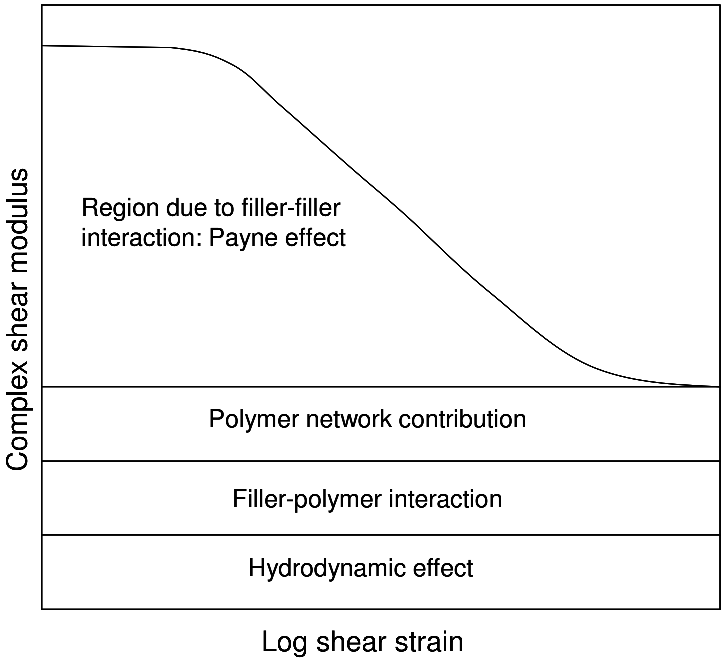


Figure 3-1. Effects contributing to the complex shear modulus for filled rubber compound [42]

The decrease in storage modulus is due to the breakage of physical bonds between the filler particles. These physical bonds could be van der Waals forces. The Payne effect is dependent on the type of filler and is independent of the type of polymer. The Payne effect is stronger for silica than for carbon black as the interparticle forces between silica particles are strong [54-55]. If filler and polymer are highly incompatible, as in the case of silica and a non-polar rubber, the filler particles are in direct contact with each other. The filler network formed by direct contact between the silica particles are more rigid and starts to break at low strain amplitudes. The filler particles act as large multifunctional cross-link sites causing non-affine deformation leading to strain amplification [54].

According to Payne effect, it is assumed that the filler-filler contacts are periodically broken and reformed under a periodic sinusoidal strain γ. As the strain amplitude is increased, an increasing number of contacts will be broken. The rate of breakage, R_b is a function of the maximum amplitude of the strain γ_0 and is proportional to the number of contacts N_c:

$$R_b = k_b \; \gamma_0^m \; N_c \qquad \text{Equ. (7)}$$

where k_b is the rate constant for the breakage process. The rate of agglomeration R_a is proportional to the number of broken filler contacts, which is expressed as the difference between the number of elastically active contacts at zero deformation N_0 and the remaining contacts N_c at a given strain γ and is assumed to vary according to γ_0^{-m}:

$$R_a = k_a \; \gamma_0^{-m} \; N_0 - N_c \qquad \text{Equ. (8)}$$

where k_a is the rate constant of the agglomeration process. From equations (7) and (8), Krauss derived equations describing the storage modulus G' and loss modulus G'' of the agglomerate network at any strain amplitude [44].

It is believed that for a given rubber and cure system, filler networking is a main parameter which governs the dynamic behaviour of the filled rubber. Thermodynamically, the driving force for filler networking is the difference in the surface energies between filler and polymer. The greater the difference in their surface energies, the lower the interactions between polymer and filler and this leads to higher networking tendency in the polymer [56]. This filler networking is carried out by the nature of filler which are favourable to self aggregation or flocculation forming a three dimensional network. This leads to drastic increase in viscosity and modulus which affects the physical properties of the rubber compound [57].

3.1.2. Properties and surface characteristics of silica

Silica has been used as an important reinforcement agent in rubber compounds together with carbon black [58-60]. The structure of filler network influences the visco-elastic properties like elasticity, hysteresis and loss modulus. The silica is characterised by weaker polymer-filler interactions and stronger filler-filler interactions. The stronger filler-filler interactions lead to stronger filler network where it shows a higher modulus at low strain amplitudes. Hence, the reinforcing effect of silica is much higher compared to carbon black.

The silica surface consists of acidic silanol and different siloxane groups: geminal, vicinal, clustered and isolated groups [55]. In the silanol groups, the precipitated silica has a unique characteristic of having hydroxyl groups on its surface [61]. Because of strong intermolecular hydrogen bonds between hydroxyl groups, silica can aggregate tightly [60-62]. This aggregation can cause poor dispersion of silica in a rubber compound. The silica particles tend to agglomerate and hence it can re-agglomerate after mixing. During storage, re-agglomeration takes place which leads to reduction in processability where the viscosity of the rubber compound increases during storage [55]. This effect further increases at higher temperatures. The tendency of the re-agglomeration is influenced also by the water content of the silica. A higher water content in silica leads to lower rate of viscosity increase during storage because of the shielding effect of the water molecules which reduces the filler-filler interaction forces [63]. The silica surface has a hydrophilic character and hence has the tendency to absorb moisture. This adversely affects the curing reaction and hence the properties of the final product.

3.1.2.1. Surface modification of silica

Silica has a hydrophilic nature and rubbers have a hydrophobic nature and hence are highly incompatible materials. This incompatibility can be overcome by modifying the surface of silica [54]. Hence, the silica surface is modified by means of a coupling agent called silane where the silane is bonded chemically to the surface of the silica. Silane coupling agents are silicon based chemicals that contain two types of reactivity namely inorganic and organic in the same molecule. Silanes are the key to providing a method of effectively bonding the inorganic silica to organic rubber as shown in Figure 3-2.

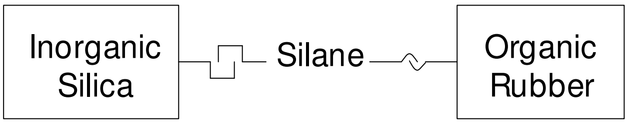


Figure 3-2. Schematic representation of coupling mechanism

A silane that contains atleast one carbon-silicon bond (CH_3-Si-) structure is known as an organosilane. Several organosilanes are developed and evaluated over the years. The silanes are chosen from the groups of sulphur rich silanes namely bis(triethoxysilylpropyl)disulfane

(TESPD) and bis(triethoxysilylpropyl)tetrasulfane (TESPT). The use of silica as filler in combination with bi-functional organosilanes such as TESPD and TESPT are becoming more and more important in rubber applications [64]. In tires, more precisely in passenger tire tread compounds, the two product groups are increasingly being used to reduce rolling resistance.

The silane is usually added during the mixing process of rubber and silica to treat the silica in-situ in the internal mixer. The chemical bonding process between silica and silane is called silanization reaction [54, 65-69]. On one hand, the triethoxysilyl group of TESPT or TESPD reacts with the silanol groups of the silica during mixing with loss of ethanol. On the other hand, the coupling agent also contains a rubber reactive group which allows the formation of covalent bonds between the rubber and coupling agent providing a chemical link between silica particles and rubber during vulcanization [64, 70]. In order to obtain optimum in-rubber properties, it is necessary to ensure that both reactions take place under specific, closely-controlled conditions. The loading level of silane on the filler surface is a function of surface area of the filler. However, the optimum level of silane treatment should be determined experimentally. When the TESPT treated silica is compared with the TESPD treated silica, both lowered the viscosity of rubber compound. But, the effect is more significant on the S2 (silica-TESPD-rubber) compound than on the S4 compound (silica-TESPT-rubber). And also, both compounds improve the mechanical properties after vulcanization. But the stiffness of the compound is more significant on the S4 than the S2 compound [54]. The rate of reactivity to spread and react the silane over the silica surface takes place under controlled mixing temperature and mixing time. The mixing temperature should be under control so that the reactive group in the silane does not react with rubber during mixing. During vulcanization, the rubber is chemically bonded to filler which leads to higher reinforcing effect and different dynamic mechanical properties compared to carbon black. The technology of silanizing the silica is used in "green" tires to impart better abrasion resistance, reduced rolling resistance and improved fuel economy as well as better grip on wet and snow. An optimized tire rolling resistance contributes to fuel efficiency which can be identified by measuring tan delta at 60 ℃. Beneficial heat built-up, abrasion and ice grip characteristics can be identified by measuring tan delta at -10 ℃. New polymers are developed with chain-end modifications, for example, styrene-butadiene copolymers modified with amines, epoxides, silanes or siloxanes to increase affinity to silica filler [71]. This leads to further improvement in tan delta values when compared to non-modified S-SBR compounds. Hence, functionalized S-SBR with silica further increases the interaction between the silica and rubber leading to low tire rolling resistance (less fuel consumption), low tire abrasion and better grip on wet and snow.

3.2. Mixing of rubber compounds

3.2.1. Mixing mechanisms

In case of processing of rubbers, some of the main tasks of mixing are [72]:

- incorporation of additives and fillers
- blending two different or similar type of rubbers
- homogenisation and plastification

The mixing of different ingredients involves basic mechanisms such as laminar, distributive and dispersive mixing irrespective of the type of mixing equipment. In the following sections, the main mixing mechanisms and mixing possibilities with different aggregates will be discussed.

3.2.1.1. Laminar mixing

Rubber compounds are high viscous materials and mixing takes place in a laminar flow. The primary mechanism of this mixing process is the deformation of the high viscous matrix. This mixing is otherwise called extensive mixing where mixing takes place even at low shear rates or elongation rates. In the laminar flow, simple shear or elongational flow patterns, no transverse mixing takes place. Mixing efficiency can be increased, in addition to deformation; the flow is divided and rearranged [72]. The rearrangement is vital for the actual mixing process in laminar flow. The pattern and frequency of rearrangement depends upon the type and geometry of mixing aggregate.

3.2.1.2. Distributive mixing

The process of distributing different components or properties within a matrix homogeneously in the considered volume is expressed as distributive mixing. Distributive mixing is shown schematically in Figure 3-3.

Figure 3-3. Schematic representation of distributing mixing in laminar flow [72]

Two components are distributed finely in the whole cross section of the specified volume by bringing several rearrangement processes. The distributive mixing is dominant during distribution of non-agglomerated fillers and incorporation of soluble and compatible additives. If the mixing time is very long, theoretically a homogeneous distribution can be achieved where the distribution is limited by the smallest particle size of molecules or fillers.

3.2.1.3. Dispersive mixing

The dispersive mixing involves break-up of solid particles and their aggregates which is in contrast to the process of distributive mixing. In case of rubber compounds with filler, the filler agglomerates breakdown into smaller aggregates and primary particles. To deform the filler agglomerates, large forces from the flow must be exhibited. The stress level to deform should exceed the cohesive forces or surface tension forces of the agglomerates. The major part in rubber mixing is the dispersion of filler particles. The higher the dispersion, the better the material properties, but the dispersion should not be completely to the primary particle size. Hence, an optimum particle size should be reached in order to get the optimum final rubber properties [73].

The dispersion of solid particles can be explained by an example with the development of forces on particle in a simple shear pattern. On a shear flow, the correlation:

$$\tau = \eta \dot{\gamma} \qquad \text{Equ. (9)}$$

can be derived, where τ is the shear stress, η the viscosity of the fluid and $\dot{\gamma}$ the local shear rate. It has to be mentioned at this point that the rubber compounds show shear thinning and hence the viscosity cannot be constant as implied in equation (9), but it is a strong function of the shear rate $\dot{\gamma}$. The viscosity drops with increase in shear rate.

The shear rate $\dot{\gamma}$ in a simple drag induced flow between two parallel planes can be calculated from the relative velocity w and the distance of the planes Δy :

$$\dot{\gamma} = \frac{w}{\Delta y} \qquad \text{Equ. (10)}$$

In case of distributive mixing, the mixing process depends only on the flow path, independent of the viscosity. But in dispersive mixing, the mixing process is strongly dependent on the viscosity. In order to break up a solid particle aggregate, a minimum shear stress is necessary. The dispersion of solid particles is therefore more effective in a high viscous medium than a low viscous medium. Furthermore, the shear stress is dependent on the shear rate itself. Hence, high shear stress can be induced by high rotational speed or narrow clearance which causes high shear rates. This aids obviously to higher dispersion rates.

3.2.2. Discontinuous mixing aggregates

The major discontinuous mixing aggregates used since 19th century are two roll mills and internal mixers. These two mixing aggregates are well suitable for mixing any kind of material trade form such as bales, powders, granules and liquids. These two mixing aggregates are capable of mixing bales and powders and hence find its application even today. Two types of extensively used discontinuous mixing aggregates were discussed in the following.

3.2.2.1. Two roll mill

Two roll mills are used for special mixing areas and obviously for cooling and shaping the batches of compound dumped from the internal mixer [74]. Heating is achieved by circulating steam under pressure, hot water or heated oil through the rolls, or by electric resistant heaters, and cooling may be effected by circulating cooling water. Once the required heating has attained, the rolls can be set in motion and the nip can be adjusted to required thickness. For improving the mixing action and possibly for removal of compounded material, two doctor blades are provided, one for each roll. These are commonly operated manually, although hydraulic operation is usual on larger machines. The mixing action of a mill has three components:

1. a nip action, which means high localized shear stress.
2. rolling action in the bank and elongational shearing as the material enters the nip.
3. cutting and folding of the sheet on the mill roll by the operator aided usually by a travelling stock blender.

Mill mixing is the oldest method of rubber mixing where it is a relatively slow method and its batch size is limited. In today’s tire production industries, the two roll mills are operated in a continuous feeding method. However, the skill of the operator is the determining factor for the quality of the product [74].

3.2.2.2. Internal mixer

Since the patenting of the internal mixer for rubber in the year 1914 [75], the advancements were carried out mostly in modifications of rotor geometries or variation of distance between the axes [76-77]. The principle components of an internal mixer are schematically shown in Figure 3-4 a. Internal mixers consists of intermeshing and tangential rotor geometry as shown in Figure 3-4 b, c.

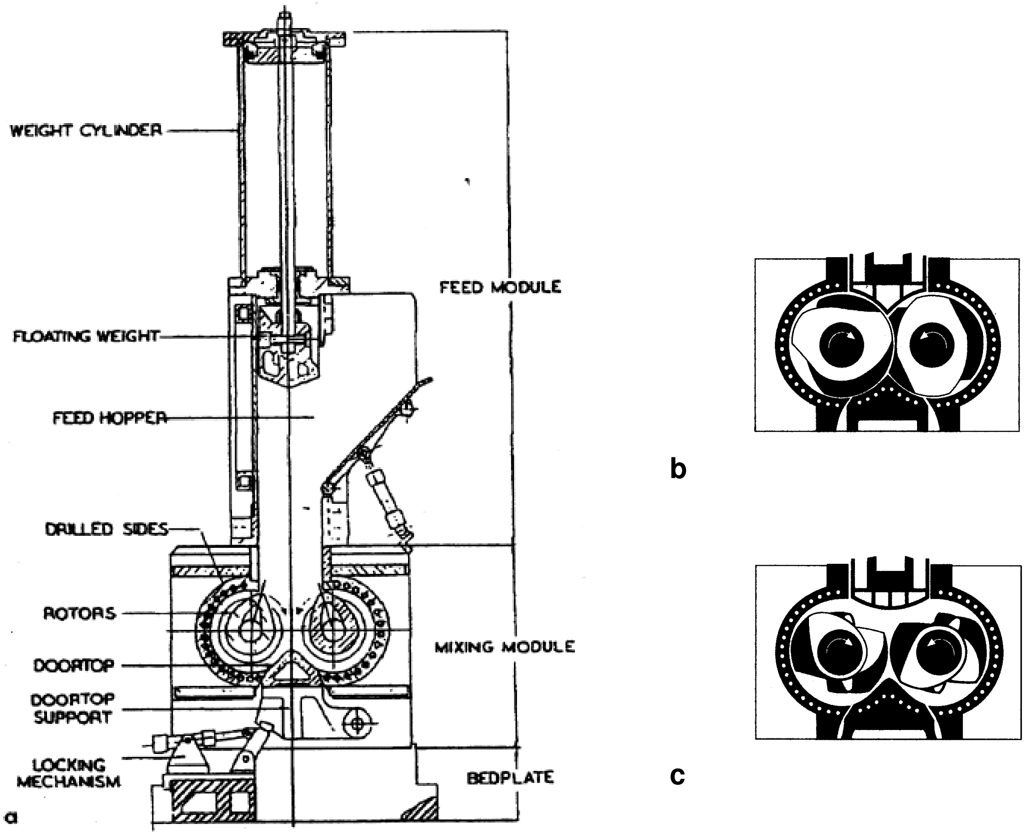


Figure 3-4. Schematic representation of a. Internal mixer [5], b. Intermeshing rotor geometry and c. Tangential rotor geometry [21]

The first internal mixers used in the rubber industry were equipped with tangential rotors, with the main characteristic that the circumferences of the two rotors do not interfere with each other and they also turn at uneven speed. The mixing efficiency of intermeshing rotors is higher than tangential rotors which are due to the enforced formation of thin layers between the rotors. In an intermeshing process particular attention is placed upon interaction between one screw and the other, cutting and folding process, screw shape of the rotor which allows the material move in the opposite direction. In recent years, the manufacturers made great investigations to improve the rotor design of the intermeshing and tangential rotors.

The following general points show the difference between tangential rotor machines and intermeshing rotor machines. The advantages and disadvantages of these two types of rotors depend upon the application of the specific compound being mixed. Therefore, it is not possible to say which system is the better one [78]:

- tangential rotor machines accept ingredients faster and discharge mixed compound faster. In this case, unproductive time in the cycle is less.
- intermeshing rotors have a larger volume and needs more material for the chamber space. The batch size is greater than a tangential mixer.
- intermeshing machines achieve a better degree of dispersion in a given mixing time because of the more intensive mixing action.
- because of the more contact between rubbers and cooled metal surfaces, intermeshing rotor machines control the batch temperature better.

The tangential rotor machines are mostly preferred for tire mixes, where high productivity is important. But the intermeshing machines can perform better with difficult to mix compounds. Other process parameters which influence the quality of mixing are fill factor, rotor speed, temperature control and ram pressure. Many manufacturers produce machines with both types of rotor. The batch sizes are from few kilograms up to 600 kg [74].

3.2.3. Continuous mixing aggregates

Rubber compound production with continuous process has been carried out for about 60 years. Because of the rising price pressure and quality requirements, the continuous production process of rubber compounds is applied in industrial scale production. The advantages of a continuous process as opposed to a batch process are:

- less energy requirement. The existing compounds quality improves.
- the processing area in the mixing unit is smaller. This improves the process control.
- process control, raw materials dosing achieves a better product consistency with a lower personnel requirement.
- continuous recording of measurement data for simpler quality control.
- improved productivity.

Several mixing aggregates are nowadays applied for continuous mixing of rubbers. Some of them are twin screw extruder, planetary roller extruder and multi-screw extruder. During the last few years, several investigations have been carried out which deal with the simplification of compounding process using continuous mixing aggregates [79-87]. Some of the continuous mixing aggregates are discussed in the following.

3.2.3.1. Twin screw extruder

A device of co-rotating twin screw extruder type was first patented by Easton 70 years ago [88]. Similar machines were developed by Erdmenger and his co-workers [89-91] by Bayer in Germany and by Colombo [92] in Italy during the 1940's intended for thermoplastics. Erdmenger also developed an intermeshing kneading disc continuous mixer in this period [93-94]. Later Erdmenger devised a modular intermeshing twin screw extruder containing both screw and kneading disc elements [95]. These efforts were summarised by Erdmenger in papers in the early 1960s [96-97]. The Erdmenger invention was developed commercially by the Werner & Pfleiderer Company [98-101]. The development of technology for twin screw extruders has recently been reviewed by White [102]. They have been gradually increasing in importance in plastics compounding because of superior mixing capabilities and better control over residence time distribution [103].

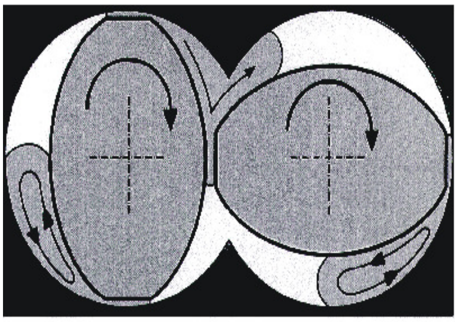


Figure 3-5. Schematic representation of screw in a co-rotating twin screw extruder [104]

Depending upon the direction of screw rotation, number of screws in the machine and the manner of contact of screws, there are three types of twin screw extruders. They are non-intermeshing counter-rotating twin screw extruders, intermeshing counter-rotating twin screw extruders and intermeshing co-rotating twin screw extruders. The modular design of an intermeshing co-rotating twin screw is shown in Figure 3-5. The modular design means that several screw elements can be flanged together and this leads to possibility of desired screw configuration. Intermeshing twin screw extruders can vary in the degree of intermeshing to extent of being fully self-wiping. The self-wiping feature is of particular value if a long residence time tail is deleterious to the reactive extrusion process, as material in the root of the screw may otherwise become stagnant. One of the advantages of twin screw extruders is the additional mixing which happens because of the interaction between the screws. There are interchangeable slip-on mixing elements to make the mixing efficiently [122].

3.2.3.2. Planetary roller extruder

The planetary roller extruder was invented 40 years ago by Mr. Wittrock of Messrs. Chemische Werke Hüls AG [105]. Since then, this extruder has been widely used in compounding of PVC, which is basically a thermal sensitive material which requires excellent temperature control in the compounding process. Besides, planetary roller extruders are also used for compounding other thermoplastics such as polypropylene, polyethylene, thermoplastic polyurethane as well as duroplasts and powder coatings. Nowadays, these extruders find its application in continuous mixing of rubbers [22]. The planetary roller part is the constructive and dominating barrel section regarding to process technique. The planetary roller part is constructed similar to a planetary gear as shown in Figure 3-6.

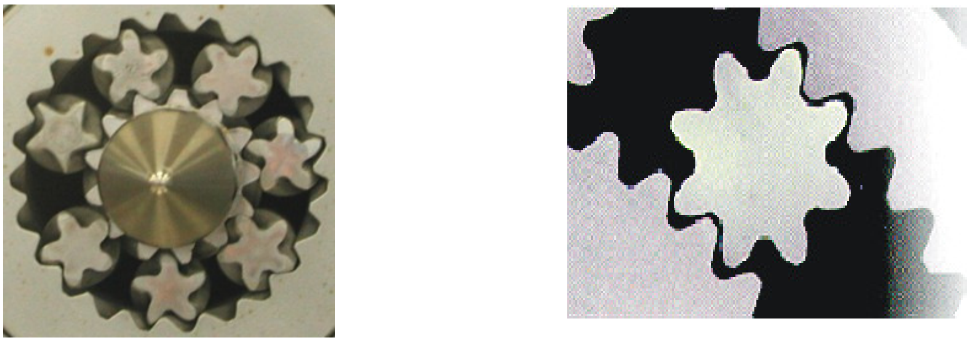


Figure 3-6. Schematic representation of the screw of a planetary roller extruder [104]

The drive is carried out via the central spindle which, in turn, distributes the torque to the planets. These roll off in the 45° helical toothed cylinder. Due to the helical gearing of the planetary system a continuous rolling out of the material is built up at simultaneous discharge in direction outlet of the roller part. This guarantees the best self-cleaning effect of all compounding extruders. Due to extremely thin wall thickness of the cylinder assembly and the central spindle, an excellent temperature control in the contact surface can be obtained. The central spindle is covering the whole processing length. Hence, every module can be equipped with different number of planetary spindles. The single cylinder sections are connected to each other via intermediate stop rings. The planetary spindles are running against these stop rings. Due to the planetary spindles and the variation of the stop ring diameter, the dwell time of the melt and pressure build-up can be changed. Planetary spindles with different tooth geometry are also available. The free cross-sectional area can be adjusted over grooves in the central spindle or the diameter of the dispersion rings [105].

3.2.3.3. Ring extruder

Extruders like the Bühler ring extruders are applied for continuous mixing process for rubbers as well [106]. This extruder type is in fact an extension of a co-rotating twin screw extruder. Here, several screws are arranged in a ring and two adjacent screws intermesh each other, creating relatively more shear barrel sections than twin screw extruders at similar throughput rates. The material is exposed to a large surface area. The large surface area is particularly important for applications which need de-volatilization of solvents and efficient heat exchange for optimum temperature control. The elongational flow is high in ring extruders which are known to have better mixing characteristics than shear flows as in single screw extruders [107-109]. The schematic representation of screw in a multi-screw extruder is shown in Figure 3-7.

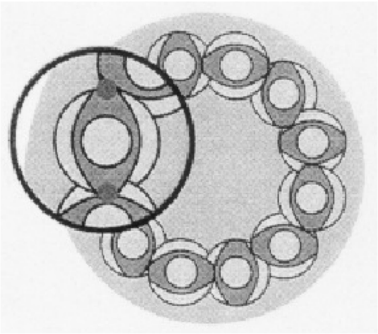


Figure 3-7. Schematic representation of the screw geometry of a ring extruder [104]

The same mixing degree can be achieved by means of a shorter extruder with respect to twin screw extruder. The ring extruders are expected to have better mixing characteristics than a twin-screw extruder. Several investigations have been carried out with ring extruder flow characteristics [110-112]. The ring extruder has a higher specific area building rate and a better surface area-to-volume ratio compared to twin screw extruders. It also has a higher degassing efficiency and a significantly higher throughput rate with shorter residence times.

3.3. Continuous mixing in co-rotating twin screw extruder

3.3.1. Working principle

The modular intermeshing co-rotating twin screw extruder is given the most importance of twin screw machines. Intermeshing co-rotating twin screw extruders are extruders which have same screw rotation direction and generally have self wiping profiles. Fully intermeshing co-rotating screws form lengthwise open channels and crosswise closed chambers, when the mechanical clearances are dis-regarded. Material conveyance in general depends on the drag flow. Forced conveyance is the angle of conveyance based on screw intermesh, where material is conveyed forward by each screw rotation for atleast the screw crest width. Because of the un-interrupted open channel, material exchange can take place lengthwise in the machine. This results in a mixing system based on the drag flow within the lengthwise open screw channel [97]. In the twin screw extruder, the "second screw" wipes the "first screw" which prevents slippage and forward conveying takes place (Figure 3-8) [113].

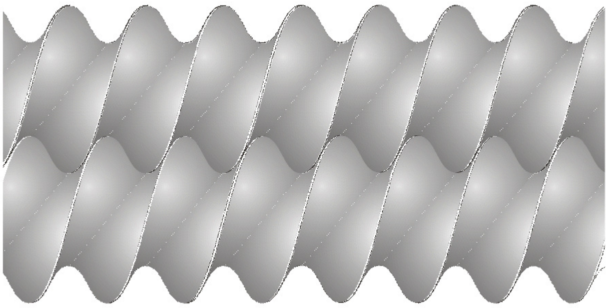


Figure 3-8. Closely intermeshing co-rotating twin screws [113]

There are different types of feeding screws tailored to handle different types of material. These screw designs are in different diameters and pitches to cover any required feed range. The extruder screw controls the metering device. For the control of constant material usage rate, the screw speed has to be controlled. With this also the product average thickness or weight per unit length is cleared. Two-flight screws can have deep screw channels, which result in a large free volume per unit length and a low average shear rate. Two-flight screws are used for processing materials like fibrous components, powders with a low bulk density and for shear-sensitive or temperature-sensitive material that do not require high shear force. Because of the requirement that one screw wipes the other screw, the cross section of the screw has a unique shape for a given diameter, pitch, centreline distance and number of tips. Screw element terms from a single screw are shown in Figure 3-9.

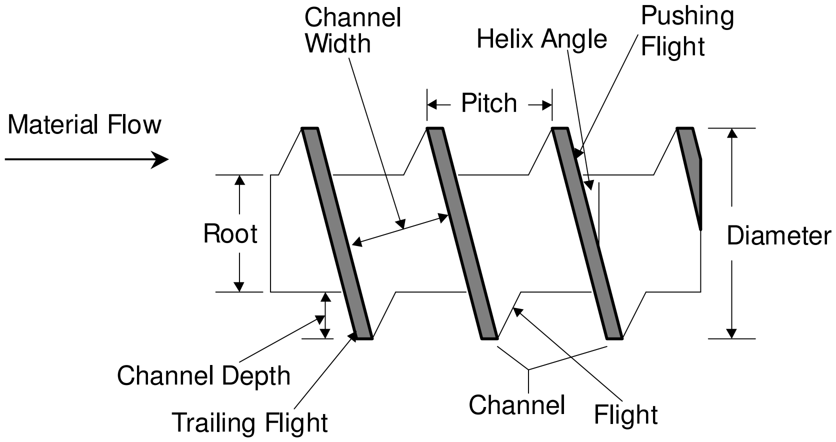


Figure 3-9. Definition of screw elements [135]

Earlier patents such as those of Easton [88], Pease [114], Colombo [115] and Meskat and Erdmenger [116] show the mechanisms of operation of a fully intermeshing co-rotating twin screw extruder. Co-rotating screw elements convey the material from one screw to the other. The material is first conveyed to the lower wedge where the material is compressed and then transported to the other screw. Later on, the material is turned over to the original screw through the upper wedge. The forced conveyance happens at the intermesh and imposes a twist restraint on the material.

The mathematical expressions to calculate the geometry of fully wiped co-rotating twin screw extruders are done by Booy [119, 130]. Due to the constraints on the screw geometry, the screw has a relatively large channel width compared to the flight width. Due to this, hardly any decrease of the channel area is found in the intermeshing barrel section between the two screws. Hence, a screw channel continues from one screw to the next, giving one continuous channel. Due to the multiple thread starts that are common practice for the co-rotating twin screw extruders, several parallel channels exist; the number can be calculated from the number of thread starts. The flow in a screw channel is commonly represented by relating the idea of an infinite channel. The flow in a co-rotating intermeshing twin screws can be envisaged as several parallel channels, with the barrel wall sliding as an `infinite plate´ over the channel (Figure 3-10). The mathematical basis for describing self wiping profile was first patented by Zimmermann in

1965 [118]. It was later taken by Booy where he derives the geometric relations for the shapes of the screws allowing them to become fully intermeshing and self wiping [119].

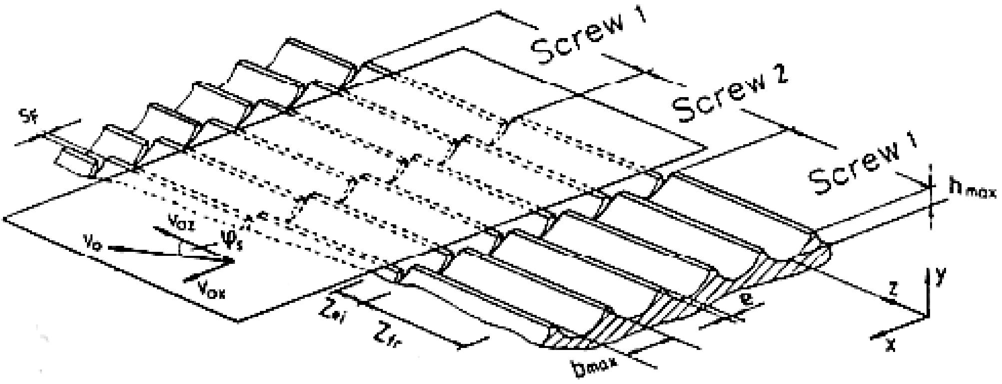


Figure 3-10. Parallel channel representation of a closely intermeshing co-rotating twin screws [120]

Booy shows that the channel depth in a self wiping screw profile which is continuous and maintains a monotonic second increasing derivative must vary according to:

$$H(\theta) = R_s(1+\cos\theta) - \sqrt{C_L^2 - R_s^2 \sin^2\theta} \qquad \text{Equ. (11)}$$

where R_s is the outer radius of the screw, θ is the angle of rotation of the screw and C_L is the centre line distance between the screws. For screw elements, the angle θ may be expressed in forms of the axial distance along the length of the screw z:

$$\theta = 2\ \pi\ z\ (p/S) \qquad \text{Equ. (12)}$$

where S is the pitch and p is the number of thread starts [130].

3.3.1.1. Conveying elements

Conveying (screw) elements can be configured with different pitches and helix angles. Screw pitch can be used to influence residence time in the conveying sections. Screw pitch is also used to control degree of fill with constant throughput and screw speed. With a large screw pitch, a low degree of fill in the vent area can be created and even the residence time is reduced. A small screw pitch is used to produce high degree of fill for heat transfer processes. This maximises the contact between the material and the barrel surface. The conveying elements are available in single, double and triple start configurations as shown in Figure 3-11.

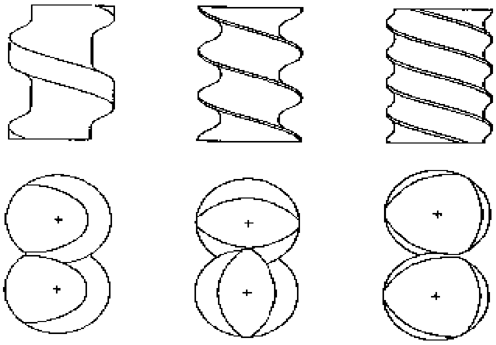


Figure 3-11. Single, double and triple lobe intermeshing conveying elements [122]

The conditions in the wedge area are shown in Figure 3-12 by a parabolic velocity profile. In co-rotating twin screw extruder systems, the entire flow volume is transferred via the open wedge area to the opposing screw. The pressure conditions on both sides of the wedge gap are equal, and as both screws are turning in the same direction, no calendering effect takes place [117].

From Figure 3-12, it can be observed that there is a linear distribution of velocity in the wedge area. This means that the melt or the material is subjected to a constant shearing velocity and that all the particles in the melt are subjected to even stresses. The velocity distribution in a co-rotating twin screw extruder can be influenced by changing the throughput or by changing the screw speed as well as by changing the screw pitch [123].

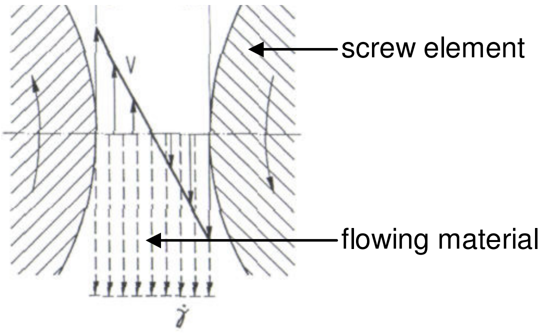


Figure 3-12. Conditions in the wedge area (velocity distribution ν and shearing velocity distribution $\dot{\gamma}$) [123]

The throughput of an extruder in a drag and a pressure flow term is expressed basically by:

$$Q = Q_{drag} + Q_{pressure} = AN - \frac{B}{\eta}\frac{dP}{dL}\sin\varphi \qquad \text{Equ. (13)}$$

The equation (13) states that the net throughput Q in an extruder equals the maximum drag flow capacity (AN) minus the pressure flow, which occurs in the opposite direction. The pressure flow is proportional to the pressure build-up capacity divided by the viscosity. The above equation (13) can be derived from a momentum balance over a screw channel. The constants A and B are specific for an element type and represents the curvature of the screw channel.

The leakage flows can be taken into account by adapting the above equation (13):

$$Q = AN - \frac{B}{\eta}\frac{dP}{dL}\sin\varphi - Q_L \qquad \text{Equ. (14)}$$

Of all the leakage flows possible in a co-rotating intermeshing twin screw extruder, the leakage over the flights predominates [124]. The other leakage gaps which are possible in the intermeshing barrel section are less important, as these consist of small leakage area. The leakage over the flight can be introduced using a pressure and a drag flow term [126]:

$$Q_L = u\left(\overbrace{\frac{v_0}{2}\sin\varphi\cos\varphi\delta_R}^{Drag} + \overbrace{\frac{\Delta P}{\Delta L}\sin\varphi\frac{w+e}{|\tan\varphi|}\frac{\delta_R^3}{12\eta_{flight}e}}^{\Pr essure}\right) \qquad \text{Equ. (15)}$$

$$u = 2(D + 2\delta_R)(\pi - \Psi) \qquad \text{Equ. (16)}$$

The pressure driven leakage flow would seem to be a small contribution to the leakage flow due to the small gap size δ_R. However, for the non-Newtonian fluids, the leakage flow over the flight is of importance; the high shear rate over the flights results in a low apparent viscosity causing the pressure driven leakage flow to become important. To take into account, the non-Newtonian behaviour of the polymer in the screw channel, the average or the local shear rate must be known.

For a one-dimensional approach, the average shear rate in the channel can be expressed as:

$$\dot{\gamma} = \frac{\pi \; N \; D}{H} \qquad \text{Equ. (17)}$$

so that the equation (14) becomes:

$$Q = AN - \left(\frac{\pi \; N \; D}{H} \right)^{-n} \frac{B}{k} \frac{dP}{dL} \sin \varphi - Q_L \qquad \text{Equ. (18)}$$

3.3.1.2. Mixing elements

The mixing task in the co-rotating twin screw extruder is achieved by using staggered kneading blocks which are known as mixing paddles. The kneading elements have the same cross-section like screw elements. There are different axial lengths available and the configuration can be made with different stagger angles. The conveying effect can be forward, neutral, or reverse overall. The extent of backflow which is determined from the combination of two can be generated in these elements. Intermeshing co-rotating twin screw extruders have the screw and disc elements which prepare the self-wiping effect. Two basic types of elements are conveying and kneading elements. The two tip screw and two lobe kneading disc assemblies are shown in Figure 3-13.

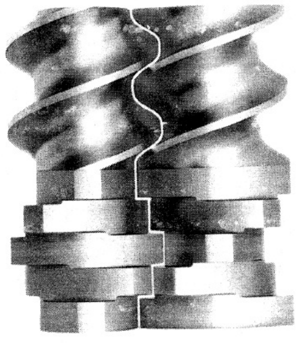


Figure 3-13. Self wiping two-tip screw and two-lobe kneading disc assembly [121]

An axial mixing in a lengthwise direction is provided by the open screw channel. This channel can be crosswise closed with the screw elements or crosswise open with the kneading discs. According to the mixing requirements, various combinations can be arranged. The narrow distribution of residence time causes difficulties for the material to stay at the barrel surface or screw flanks and roots. This is one special characteristic for self-wiping co-rotating twin-screw extruder [121]. The twist restraint depends on the number of flights per unit length and the width of the screw crest. The less the flight number is, the wider the screw crest becomes.

The literature on analysis of flow in an intermeshing co-rotating twin screw extruder is limited in extent [91, 123-130]. Only Werner has attempted to analyse flow in kneading disc regions [131]. There is similarity between kneading paddles and screws. They have the same meridional profile, but kneading paddles have 90° helix angle. The same characteristics of the arrays of kneading paddles with screws are shown in Figure 3-14. The drag flow is very similar. In the other hand, the pressure flow is much more sensitive. This sensitivity comes from the leakage paths in the gaps between offset paddles.

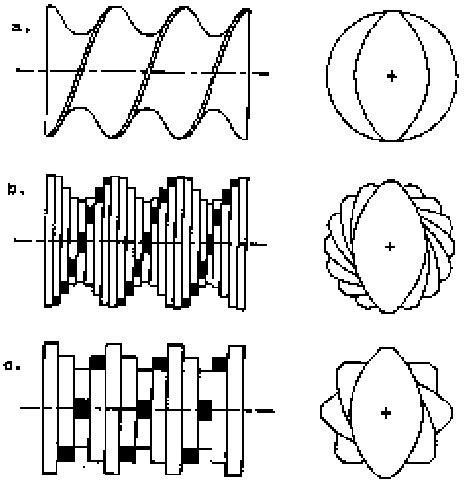


Figure 3-14. The same characteristics between kneading paddles and screws a. square pitch bi-lobe screw, b. same pitch with D/16 thick paddles at 22.5° offset, c. same pitch with D/8 thick paddles at 45° offset [122]

Figure 3-15 shows the different stagger angles and conveying direction of different kneading blocks. The smearing action of the kneading paddle tip against the barrel wall and the opposite paddle effects the dispersive mixing.

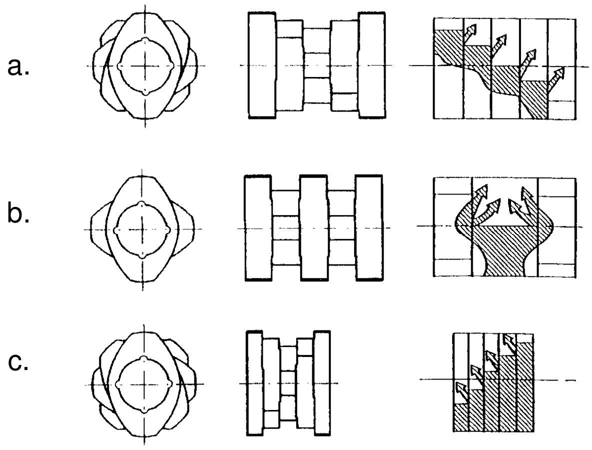


Figure 3-15. Kneading blocks with different stagger angles and conveying direction [21]

a. forward kneading block, $\varphi_K = 45°$

b. neutral kneading block, $\varphi_K = 90°$

c. reverse kneading block, $\varphi_K = -45°$

Co-rotating paddle elements are responsible for the compression/expansion mixing effect (Figure 3-16). With the rotating of the shafts, firstly the arc-shaped portions expand and then later they are recompressed. The contents are squeezed. The force to the contents is axial. If it is upstream or downstream depends on the orientation of the next adjacent paddles.

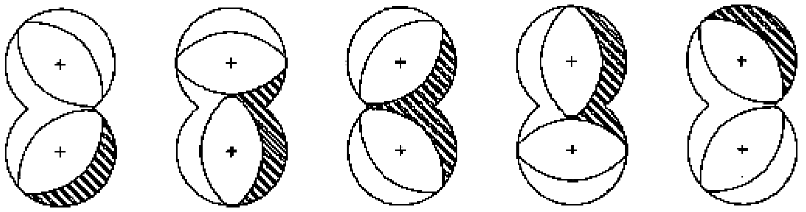


Figure 3-16. Compression/expansion mixing effect with intermeshing co-rotating twin screw extruder [122]

The easiest way describing a kneading block is to consider as modified transport element. In that case, the equations that are used to calculate the transport capacity of a transport element can be used, with few modifications:

$$Q = AN - \frac{B}{\eta}\frac{dP}{dL}\sin\varphi - Q_L - Q_{L,stag}$$ Equ. (19)

In comparison to equation (13), an extra leakage flow is introduced due to the staggering of the kneading paddles.

In the kneading disc block, the flow moves in three directions as expressed by Szydlowski et al. [132]. One may define Q_L as the main forward conventional flow, Q_b a reverse flow caused by the staggering of the discs and Q_C the inflow above the kneading disc tip. Szydlowski et al. define the fractions f_L, f_b and f_C as:

$$f_L = \frac{Q_L}{Q_L + Q_b + Q_C} \qquad \text{Equ. (20)}$$

$$f_b = \frac{Q_b}{Q_L + Q_b + Q_C} \qquad \text{Equ. (21)}$$

$$f_C = 1 - f_L - f_b \qquad \text{Equ. (22)}$$

f_b should tend to characterise distributive mixing and f_C dispersive mixing.

As the paddle on one shaft slices between the next upstream and downstream paddles on the opposite shaft, a cutting mixing effect occurs (Figure 3-17).

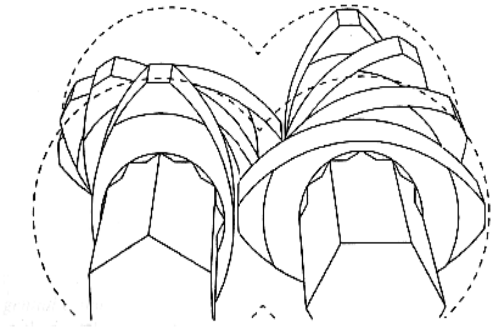


Figure 3-17. Cutting mixing action of kneading paddle arrays [122]

The kneading blocks produce high and low shear region. The high shear rate is generated at the screw flight tips, the low shear in the screw channels. High shear regions also exist in the intermesh area between the two screws. The constrained cross section geometry of the kneading block is responsible for the self-wiping. The pressure between the screws produces axial forward and reverse flows. As it is shown in Figure 3-16 and 3-17, the most effective mixing action happens when that cross section of barrel completely full is. Opposite hand screw or paddle sections prepare fill control. An assured complete filling can be obtained by utilising reverse screw or paddle elements. An alternative method is to use blister rings which require some pressure development for the polymer to pass through, thus causing complete filling for some portion of the upstream screw or paddles. Due to the intermeshing, the blister rings require some axial offset [122]. The amount of resistance is determined by the axial length and radial clearance of the blister rings. Both reverse elements and blister rings provide fixed resistances.

Due to narrow tip clearances only a small fraction of the material has high shear rates. The materials transformation from one screw to the other with stream splitting, recombination and backflow is provided by kneading elements for surface renewal. The kneading block geometry and degree of staggering ordains the extent of backflow. Different kneading block geometries can effectively help for extensive mixing, unchanged self-wiping cross section and the tendency to generate local high shear levels and hot spots. This kneading action is most beneficial in causing solids to melt by rubbing them against each other. The action also enhances mixing of fully molten volumes by repeated reorientations of the laminar layers.

Another point is the percentage of fill at any location along the extruder screw. The filling degree in the partially filled zones is necessary for calculating the residence time as given by the general expression:

$$f = \frac{Q_{feed}}{Q_{\max}} \qquad \text{Equ. (23)}$$

Q_{feed} is the feed rate of the material. For $Q_{\max}$, the AN term of the right side of the equation (13) may be used. If other types of screw elements are taken into consideration, the A-factor for $Q_{\max}$ changes.

The length of each fully filled barrel section is dependent on the pumping characteristics of both the back pressure (for ex. reverse kneading elements) and forward pressure creating screw elements. Each conveying channel may be only partially filled with solid or molten polymer which depends upon the screw element helix angle and screw pitch length. The degree of fill also varies in kneading block regions with respect to the stagger angle and conveying direction. Hence, the *residence time* is defined as the total time a given particle spends in the extruder from the moment it enters the extruder feed throat until it exits the die [135]. *Residence time distribution* is the range in time various particles spend in the extruder. Some particles, depending on their path through the metering section, spend a longer time in the extruder compared to other particles. At a given screw speed, there is an average residence time materials spend in the extruder; some are longer and some are shorter. The material in the extruder experiences a residence time distribution depending upon the fill which is based on the screw design, extruder type, L/D ratio, as well as feed rate and screw speed. The residence time θ_i, can be determined in each section of the extruder as [133]:

$$\theta_i = \frac{V_i}{Q} \qquad \text{Equ. (24)}$$

where V_i is the occupied volume in each section and Q is the volumetric flow rate per unit time. The average residence time is defined by t_{mean} given by [135]:

$$t_{mean} = \frac{V}{Q} \qquad \text{Equ. (25)}$$

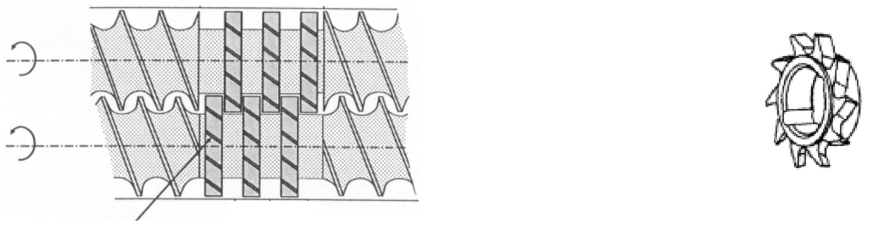
where V is the free volume used and Q is the volumetric flow rate per unit time.

The power and torque also depends upon how much the screw flights are filled which is given by the specific mechanical energy input. The specific mechanical energy input is an important processing parameter of the twin screw extruder which is given by [128]:

$$P_{specif.mech} = \frac{2\ \pi\ n\ M_D}{Q} \qquad \text{Equ. (26)}$$

where n is the screw speed, M_D is the torque and Q is the throughput.

Special mixing elements such as turbine elements or gear mixers are used for distributive and dispersive mixing. The effectiveness of mixing varies upon number of teeth, the conveying angle and the spacer width. Figure 3-18 shows schematically the turbine elements. They split the melt stream in numerous places and then recombine it on the other side of the gear in the spacer area. The main function of these elements is to provide the maximum amount of distributive mixing with minimal energy input. The self-wiping version is an evolution of the design to meet ever increasing quality standards. The elements that do not wipe the entire barrel wall provide a low velocity zone for material stagnation and potential degradation.


Conveying angle in forward direction

Single turbine element

Figure 3-18. Schematic representation of turbine or gear mixer elements [134]

Sometimes three or four successive turbine elements can be used to break and recombine the melt. They are particularly used for mixing oils, liquid additives into the polymer stream [134].

3.3.1.3. Screw configuration

The configuration of a screw depends upon primarily on the objective to be accomplished with the extruder. The barrel and screw are modular in co-rotating twin screw extruder. The barrel and screw can be designed simultaneously depending upon the necessity. The screw designs can be made with respect to the length, number and type of barrels and screw elements. The designs were made with help of screw design software called *Screwcon2* from the company Berstorff GmbH. Different barrel sections were combined together with screw element arrangement with respect to melting, mixing, conveying, venting and pumping etc. A typical screw configuration designed for our experiments is shown in Figure 3-19. All the screw elements can be named for the complete screw configuration and the respective barrel sections can be modularly arranged with closed, feeding or venting barrel sections. Here, the polymer is feed in barrel section one and venting is provided in barrel sections eight and eleven. The open barrels can be used for venting or for dosing additives, fillers and liquid chemicals.

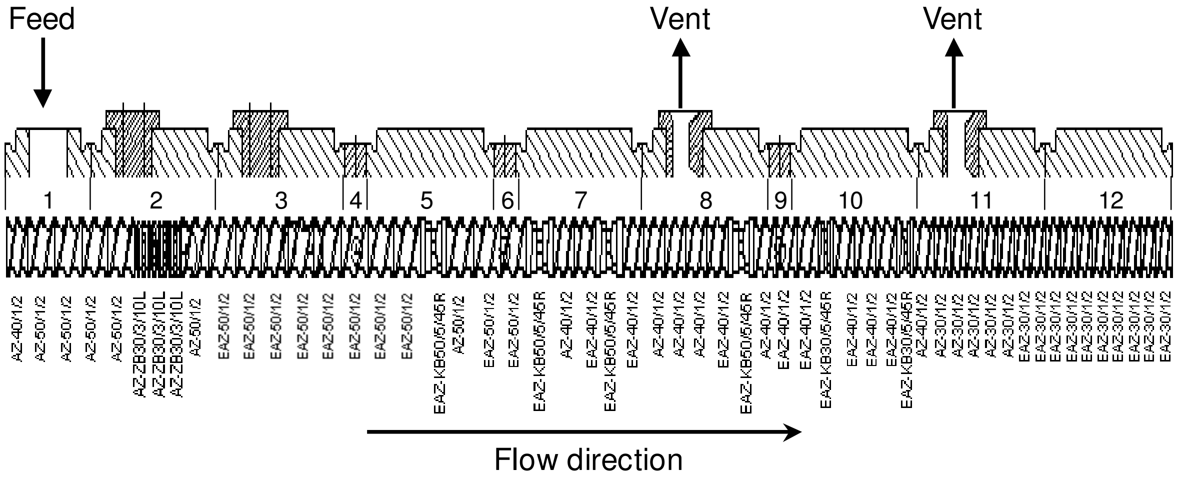


Figure 3-19. Schematic representation of barrel and screw configuration with 12 barrel sections and screw element orders used in this study

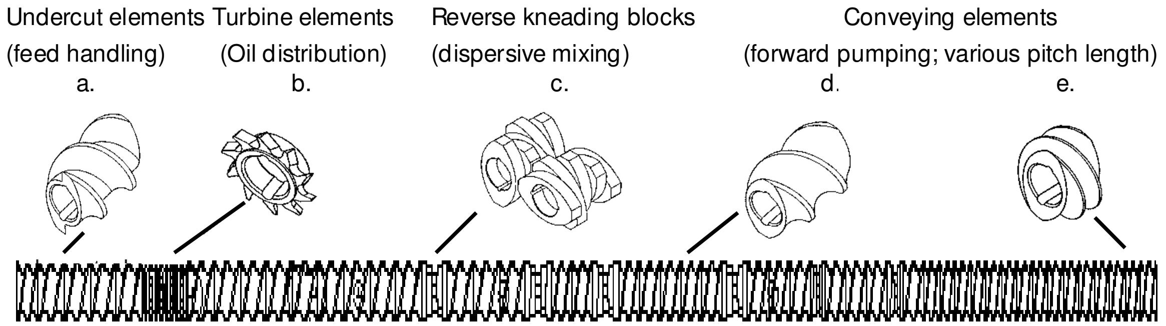


Figure 3-20. Schematic representation of screw configuration and element types used in this study

The screw configuration represented consists of different screw element types as shown in Figure 3-20. It consists of conveying elements with various pitch lengths and undercut types. The undercut elements are used to handle high outputs with variation in pitches. Other elements such as turbine elements and kneading elements are used as mixing elements as discussed in previous sections. The kneading elements consist of forward, reverse and neutral kneading elements. Depending upon the mixing efficiency needed in respective barrel sections, these elements can be arranged along the extrusion direction. Note that whether the mixing sections are composed of kneading elements or turbine type toothed mixing elements, they are more effective when backed up by a restrictive element to increase residence time and degree of fill. Any particular screw design used in a specific compounding needs to be optimised for respective polymer and formulations being produced.

3.3.2. Dosing assemblies

3.3.2.1. Gravimetric feeding

The simplest feed system is gravity-induced solid conveying of polymer pellets, additives, fillers, etc., from the feed hopper into the screw channel. The driving forces are gravity, material weight and the formulation fluidity in the solid state. There are four ways to feed polymer to an extruder: flood feed, starve feed, crammer feed and melt feed [135]. The two solid feed systems that rely on gravity are flood and starve feeding. Starve feeding is typically used in twin screw or multi-screw extrusion as shown in Figure 3-21. Feeders deposit the formulation directly onto the extruder screw, with the screw speed set to remove the formulation at higher rate than it is deposited on the screw. There is no material build-up in the extruder feed throat and the throughput is determined by the feed rate rather than the extruder screw speed.

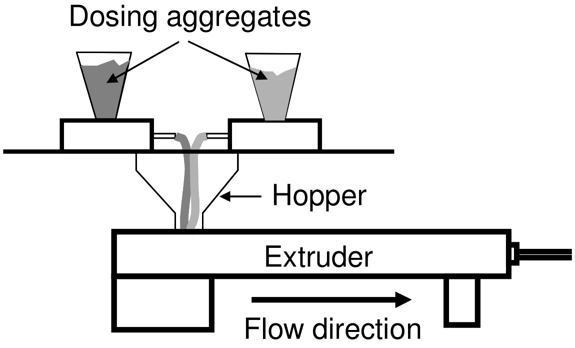


Figure 3-21. Starve-feed extruder [135].

Also, starve feeding has the advantage of depositing all the formulation ingredients in the proper ratio directly onto the extruder screw. The best way to meter materials and guarantee uniform component distribution is to gravimetrically feed each component with different feeders directly above the extruder feed throat. The gravimetric or loss-in-weight feeding ensures that each component is added in the correct proportion, while addition directly above the feed throat minimises any ingredient segregation. Rubber compound consists of several additives including cross-linking agents. This needs a feeder for each ingredient. As a feeder for each ingredient is not available, it requires pre-blending. However, pre-blending depends on the ingredients being mixed and the way material is handled after blending and prior to compounding. Typically, the ingredients in thermoplastic compounding industries are pre-mixed by low intensity blending systems. Typical low intensity blending systems include tumble blenders with wide range of sizes, V-cone blender, ribbon blender, cement mixer, paint shaker and drum roller.

3.3.2.2. Side feeding

Side feeding is possible by twin screw combination with a gravimetric dosing system. In case of continuous rubber mixing, a combination of single screw extruder, gear-pump and multi-screw extruder makes possible the feeding of conventional bale rubber at a constant rate [136]. The schematic representation of single-screw and gear pump combination is shown in Figure 3-22.

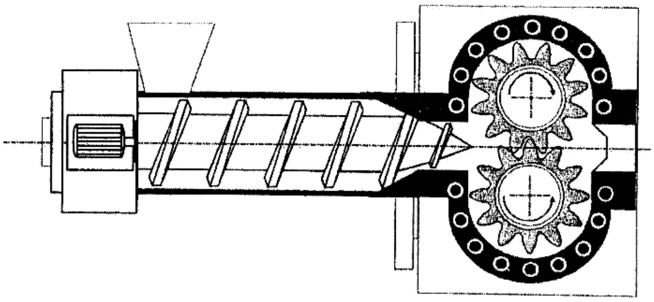


Figure 3-22. Schematic representation of combination of single-screw (transfermix) extruder and gear pump [Maag, Rubicon, Berstorff, Uth]

The transfermix extruder is a single screw extruder consists of a unique barrel and screw configuration where the geometry consists of reducing and increasing flight depths in screw and barrel. The barrel consists of concentric opposite-handed threads which transports the rubber compound back into the pressure build-up section of the screw. The receding flights of the screw interacts with increasing channels of the barrel where the extrudate is partially forced out of the screw into the barrel and hence sheared normal to the flow already transferred into the barrel [137]. The material flow delivered by the gear pump is dependent on the chosen rotor speed and the displacement volume per revolution. Equal volumes of material are transported along the gear pump housing and displaced into the outlet by the meshing of mating gear teeth's. The uniformity and dimensional accuracy of the throughput can be achieved only by a constant delivery of homogeneous plasticized material to the gear teeth cavities. As the gear teeth cavities are completely filled, the pressure fluctuations are highly reduced [138].

The advantages of a single-screw and gear pump combination are as follows [138-139]:

- all conventional bale rubbers can be used.
- constant feed rate with respect to the recipe.
- wide range of entry temperatures into mixing extruders under constant output.
- better incorporation of fillers and additives.
- 20-30 % lower torque for mixing extruder.

3.4. Rubber/Filler-Composites

Historically, the desire to simplify rubber compounding led to suggestions in the 50's and 60's concerning replacement of the usual delivery forms such as bale rubbers by liquid or powder elastomers as raw material. The use of liquid elastomers was never realized due to high cost of its manufacturing process and the need for new machinery. However, elastomers in powder form based on the general purpose rubbers led to the expectation of large simplifications even with the classical compounding technology. Several aspects, possibilities and advantages of using the powder rubber were critically reviewed during this time by many publications [140-143].

The conclusion drawn in many cases was of a possible revolution in classical compounding technologies. Several investigations were carried out in various projects to realize this concept such as powder Nitrile rubber and spray drying of natural latex etc. On getting some promising results, these lead to an optimistic view from the authors. The inflated expectations in the new form of rubber were for example, reflected in the well known Delphi-study of 1972 [144].

To produce smaller particles of rubber, techniques such as spray and freeze drying as well as flash evaporation or grinding processes were used. Due to rubbers tackiness and cold flow of each of the particles, these processes failed. Nevertheless, several investigations were carried out to dust the powdered products with very fine inorganic and organic powders in order to deactivate the cohesion forces. These new measures were unfortunately coupled with the introduction of relatively high amounts of unwanted impurities in the final product. Hence, this procedure, on account of the absence of the filler, led only to a limited simplification of the rubber mixing process.

At the beginning of 70's, it was recognized by Huels AG during the development work on the powder rubber project, that mean difficulties concerning the storage of powder rubber could be markedly reduced if a change to free flowing master-batches produced from premixes of rubber and filler in water emulsion, was carried out [145]. Some of the powder rubber products namely Emulsion-Styrene Butadiene Rubber/Carbon Black were mainly developed by Huels AG during the 70's and 80's of the last century. From 1998 to 2002, Degussa AG developed a number of rubber products called Rubber/Filler-Composites (RFC) based on NR, E-SBR and S-SBR [15, 146]. Rubber/Filler-Composites are defined as free flowing granules consisting of a mixture of rubber, filler and other rubber chemicals used as raw materials for the manufacture of rubber products [18]. The rubber and filler are combined by different processes, jointly processed and produced and maintained in the free flowing form. The filler portion in the product serves, among other things, to reduce the tacky nature of the rubber and thus also ensure long-term stability. Thus the powder or granules of rubber can be conveyed pneumatically and fed directly to the mixing device [147].

In contrast to bale rubber granulation, the raw materials such as rubber and filler can be taken off during their own manufacturing process in the form of pre-stage materials and further processes jointly. Thus, a considerable number of process steps can be eliminated by Rubber/Filler-Composites. Another advantage of Rubber/Filler-Composites is that the filler is already present in the rubber matrix in incorporated condition and therefore need to be no longer incorporated during the compounding process.

Additionally, there are also products based on silica in which the required reaction of the filler with the organosilanes has already been effected by the manufacturer whereby an ethanol release at the user is avoided [69]. In 2003, Degussa AG decided to continue with the development of Rubber/Filler-Composite with the main focus on products based on S-SBR and BR in combination with silica and organosilane. This involves solution polymerisation of rubbers and hence safe handling of organic solvents is necessary. The project was successfully carried out since 2004 with help of a pilot plant for the Rubber/Filler-Composite based on rubber solutions [148].

Several free-flowing rubber/filler batches are today available commercially or as development products to the rubber user are the so-called gas-phase EPDM [149-150], E-SBR/carbon black [16], E-SBR/silica/silane [17] and NR/carbon black [19]. The disadvantage of these products is that today they are not yet available in sufficient quantity and diversity of types on the market. Moreover, unlike bale rubber manufacturers, they are presently available only from a few manufacturers.

With regard to the development of continuous mixing processes, numerous investigations have been published during the last few years [20-23]. The recent announcements of renowned tire makers [82, 151-152] to intend to introduce continuous compounding processes and to have already started with this project clearly show what the trend of the manufacturing processes in the tire industry will be in future.

3.4.1. Rubber/Filler-Composite containing carbon black

The production of a typical bale rubber is made by polymerisation of the monomer in water. After this process, the rubber is coagulated by the addition of acid. The resulting rubber crumbs are dewatered (moisture content 10-15%), dried (residual moisture content < 1%) and it is then pressed into bales [147]. Figure 3-23 shows the production of bale rubber in an aqueous system.

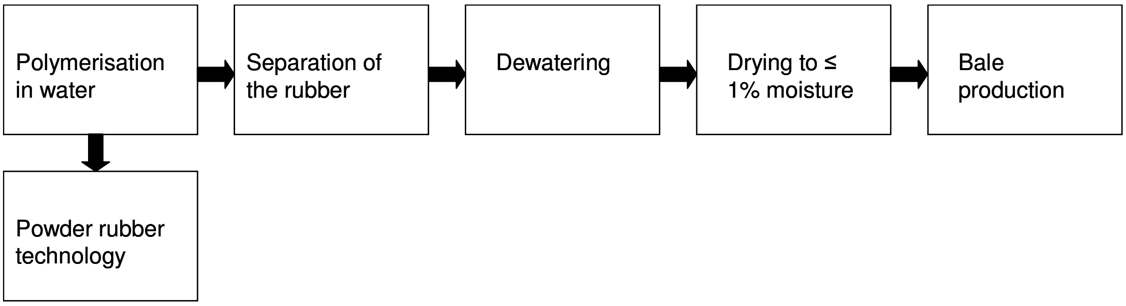


Figure 3-23. Production of bale rubber (aqueous system) vs. powder rubber [147]

All processing steps after polymerisation of rubber can be bypassed in the production of powder rubber which will result in marked reduction in cost to both investment in equipment and energy consumption.

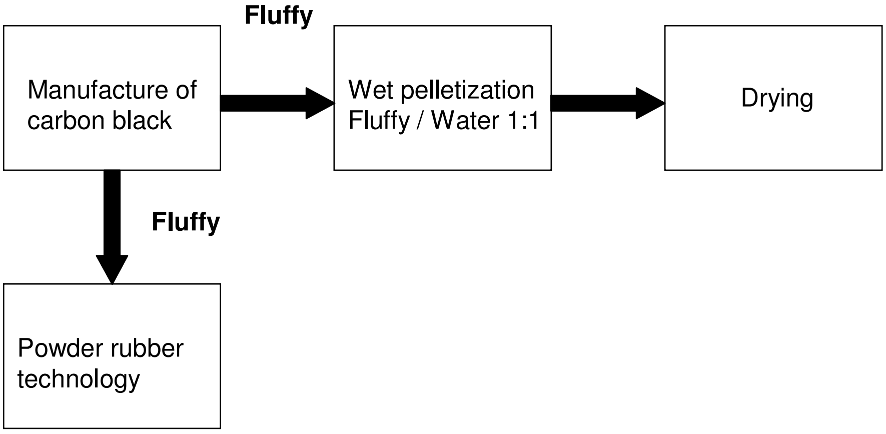


Figure 3-24. Production of wet-pelletized carbon black [147]

Figure 3-24 shows the process steps in the production of wet-pelletized carbon black. After the process of combustion, the carbon black is obtained in fine voluminous form as fluffy carbon black. Since this form cannot be processed in the rubber industry, the fluffy carbon black needs to be pelletized. This can be achieved by addition of large quantities of water and a pelletizing agent. After the production of wet pellets in the so-called pelletizing machines, the carbon black has to be dried to residual moisture content < 1% under high energy input. In the powder rubber process, however, the fluffy carbon black is the form of use. Similar to reduction in rubber processing steps after polymerisation, here too, the energy costs for drying as well as the equipment investments costs can be appreciably reduced. The first process step in the production of powder rubber is the separate production of a stable latex emulsion and a homogeneous filler suspension in water. Both of these pre-stage products are combined via a mixing and grinding unit in an agitator tank. The powder rubber/filler batches are subsequently produced by precipitation of both components (Figure 3-25). Various substances such as acids and bases which influence the pH value of the suspension may be used as precipitants.

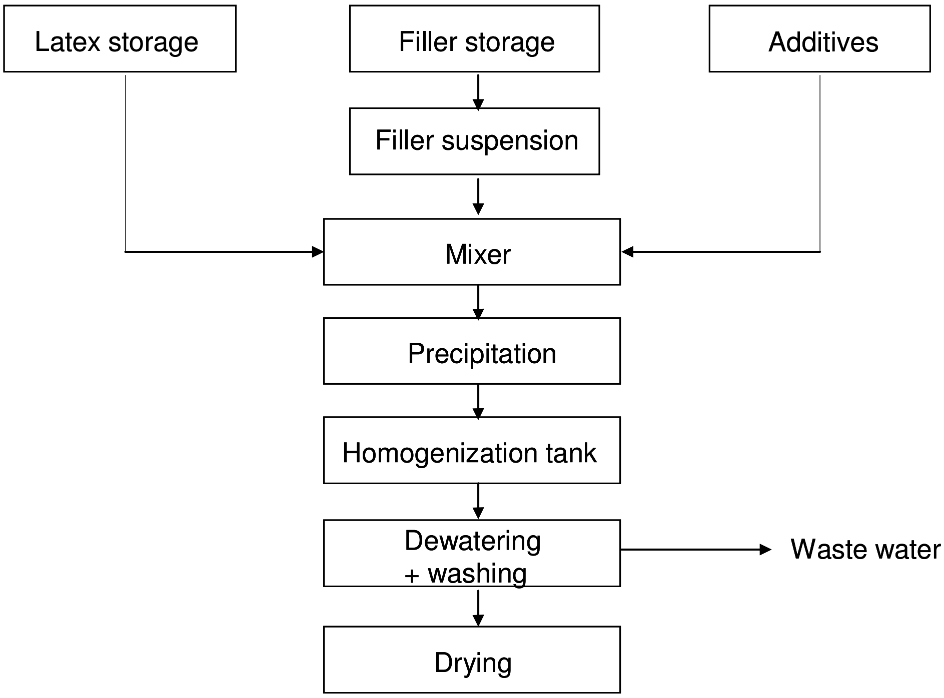


Figure 3-25. Production scheme of carbon black powder rubber [147]

Assisted by further additives, the coagulating latex surrounds each and every individual filler particle. A filler fraction added separately forms an efficient separating layer around each powder rubber particle so that already after precipitation the finished powder rubber is present in the water with its later particle size distribution. The product (in water) if necessary can now be subjected to a maturing process of several hours in a homogenizing tank. Subsequently, the major part of the water is separated and finally, the product is dried to a moisture content of about 1%.

In principle, most of the common rubber types such as emulsion polymers, solution polymers and latex can be converted into the powder rubber form by the general production process described above. In regard to fillers, special attention needs to be directed to different types of carbon black and later also to the precipitated silicas. The carbon fillers can be used in a wide surface area without any problems in the powder rubber process. Even products with a high N_2 surface area can be excellently dispersed in powder rubber compound. The range for possible fill factor adjustments extends from about 40 to 1000 phr. The lower limit is determined by the increase in tackiness of the products. Usually, a powder rubber consists of 100 parts polymer and one carbon black, the type and chosen fill factor being adjusted to the conditions prevailing in the rubber application.

3.4.2. Rubber/Filler-Composite containing silica/silane

Silica has been used more and more as an important reinforcement agent in rubber compounds together with carbon black [58-60]. The structure of filler network influences the visco-elastic properties like elasticity, hysteresis and loss modulus. Due to its stronger filler-filler interactions, it leads to a stronger filler network where it shows a higher modulus at low strain amplitudes. Hence, the reinforcing effect of silica is much higher compared to carbon black. The development of silica based powder rubber in the form of free flowing rubber was initially made with E-SBR. This development were then extended in solution based SBR (S-SBR) together with silica and coupling agent as S-SBR/silica/silane [148]. The same investigations were carried out in combination with BR compounds. This change of filler reinforcement from carbon black to silica along with a exchange of the former used E-SBR/BR with high vinyl S-SBR/high cis BR blends reaches a full balance of properties in tire performance, known as the magic triangle (abrasion, wet grip and rolling resistance). The use of this new rubber/filler system leads to reduction of rolling resistance (less fuel consumption) and better abrasion and wet grip. In the following, the production of Rubber/Filler-Composites based on E-SBR/silica/silane and S-SBR/silica/silane are discussed. The production is explained by means of a flow diagram as shown in Figure 3-26.

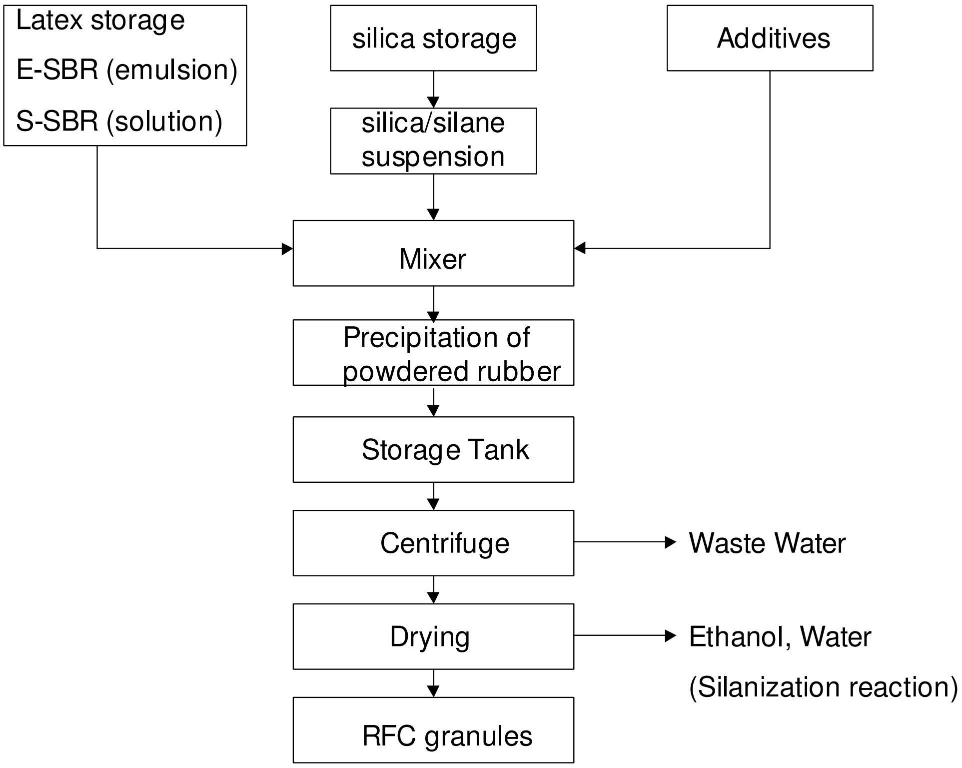


Figure 3-26. Production diagram of Rubber/Filler-Composites based on E-SBR/silica/silane and S-SBR/silica/silane

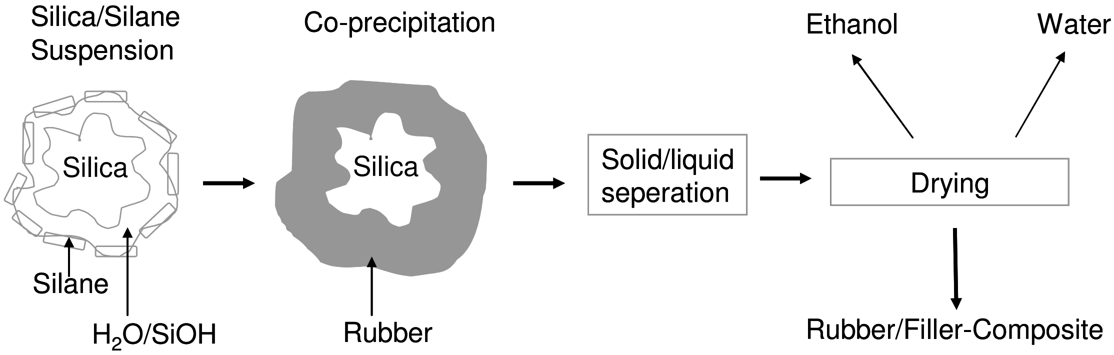


Figure 3-27. Schematic diagram of production of silica based Rubber/Filler-Composite

The first step in the production is to polymerise a stable rubber in water emulsion or solution in organic solvent independent to the type of rubber. Here, SBR is polymerised in two different ways, emulsion and solution SBR. This is followed by the addition of silica with the latex. The silicas used are filter cakes where the moister content is very less. The silica is made as a suspension with silane and a adsorptive agent. The silane is made to adsorb on the silica surface. The particle size of the silica has previously been exactly adjusted to a particular particle size of 5-28 nm. This is followed by addition of additives. All these materials are mixed together by intensive stirring.

In the next step, the precipitation process is completed in a reaction vessel under continuous stirring. It is then transferred to a homogenising tank for further processing. The water or the organic solvent will be removed in a centrifuge and the batch is allowed to dry. The drying temperature is increased to 120 ℃ where the silica is subjected to silanization reaction (Figure 3-27). This leads to release of ethanol and water. The material is dried for a prolonged drying time until the completing of silica and silane reaction. The compound is dried down to rest moister content of less than 1%. The material is then granulated to 3-5 mm and it is in free flowing form. Several types of RFCs such as E-SBR, S-SBR and BR are made with silica/silane combination.

RFCs can also be made with a combination of additives and cross-linking agents. As in the bale masterbatch technology, in powder rubber production, too, softening oils and also various compound ingredients, such as activators, ageing protection agents, reinforcing resins and even cross-linking chemicals, though with restriction, can be incorporated in addition in the rubber phase and dispersed very homogeneously. This next generation compound is called as Finished compound Rubber/Filler-Composite (FC-RFC) as shown in the Figure 3-28.

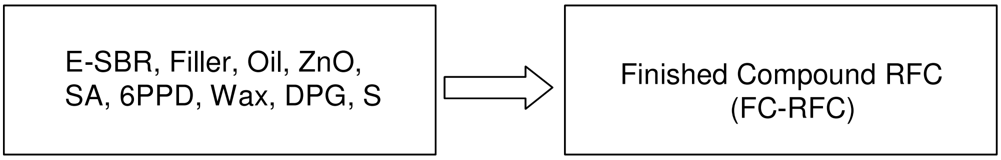


Figure 3-28. Schematic diagram of production of silica based finished compound Rubber/Filler-Composite

This type of material consists of fully incorporated ingredients and hence the degrees of dispersion between the ingredients are high. This leads to further reduction in mixing time and mixing energy. FC-RFC has been developed to reduce the number of dosing systems necessary in the continuous mixing room. As the material is mixed with filler and other ingredients, there is no problem of tackiness of the product. The homogenization of the ingredients in the rubber matrix is quite high and hence can increase the product quality.

3.4.2.1. Silica/silane and silane/rubber reaction

The silica/silane reaction is carried out during drying process of RFC. The addition of coupling agents such as the bi-functional organosilanes, for e.g. bis(triethoxysilylpropyl)disulfane (TESPD) or bis(triethoxysilylpropyl)tetrasulfane (TESPT) with the silica is necessary to achieve compatibilization with rubber. The silane (TESPD) as shown in Figure 3-29 reacts with the silanol groups of the silica [15]. The reaction leads to stable siloxane bonds and ethanol as by-product is evolved. The polysulfide group which is the second reactive group in the silane molecule reacts during vulcanization with rubber to form the so called rubber to filler bonds.

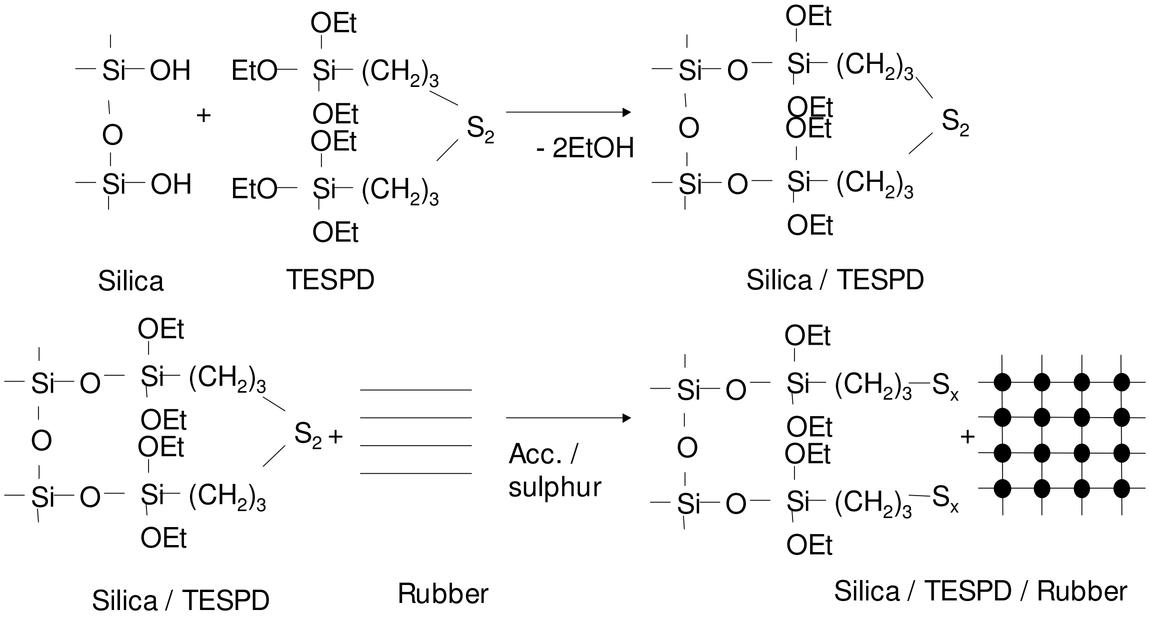


Figure 3-29. Schematic reaction of silica/TESPD and TESPD/rubber [15]

While mixing in the internal mixer, the reaction between the silica and silane is the first reaction which takes place. In case of RFC, this takes place during the drying of RFC, an in-situ reaction. The reaction during drying has to be carefully monitored in order to control the complex reaction and to achieve the completed silanization reaction [67]. Hence, the Rubber/Filler-Composites are highly dispersed compound free from ethanol. Due to this, the Rubber/Filler-Composites are easy to mix and the mixing time can be reduced.

3.4.3. Blends based on Rubber/Filler-Composites

Blending two or more polymers was successfully used to obtain products with desirable property combinations as an alternative route to the synthesis of new polymers [153-155]. Copolymerization and blending are alternative routes for the modification of polymer properties. Blending is the less expensive method. The mixing of two or more rubbers together to achieve a balanced performance of the final product is called rubber blending. The rubber blends are mostly reinforced with fillers such as carbon black or silica. The miscibility of two different rubbers as well as its interaction towards fillers and additives greatly influences the final property of the product. The rubber blends are usually made with different bale rubber combinations by discontinuous mixing aggregates such as internal mixer and two roll mill.

The possibility of blending rubbers by continuous mixing technology however needs free flowing raw materials. This can be achieved by using RFCs where the RFC blends can be made directly during the production process of RFCs or this can take place by mixing two different RFCs in continuous mixing equipment. The RFCs can be dosed gravimetrically in any continuous mixing equipment. As the filler is pre-mixed with the rubber, the number of dosing systems reduces. There are several possibilities in RFC to choose the amount and type of rubber as well as filler. So, the degree of dispersion between the rubber components as well as with filler can be well tuned.

The developments of RFC blends are based on high vinyl S-SBR and high cis BR with silica as filler. This is due to the change of filler reinforcement from carbon black to silica along with an exchange of the former used E-SBR/BR with high vinyl S-SBR/high cis BR blends which reaches a full balance of properties in tire performance showing improved abrasion, wet grip and rolling resistance [71]. The rubber blend combinations along with silica were applied by using RFC production technology. Together with the RFC blend production, the silanization process is finished during the production process of RFC blend. The degree of dispersion and distribution between the components increases significantly which helps further enhancement in dynamic properties. The RFC blend is finally available in granulated form suitable for dosing any continuous mixing aggregate. These types of RFC blends can be mixed both by discontinuous as well as continuous mixing aggregates. In both cases, compared to bale rubber blends, the total mixing time as well the mixing energy reduces drastically.

4. Experimental

4.1. Materials

The RFCs used in this work consists of different rubber types and its compositions are shown in Table 4-1. The chemical features and physical characteristics of the RFC composition were shown in Table 4-2 and Table 4-3. The RFC consists of rubber and filler in suitable proportions and its manufacturing is discussed in Chapter 3.4. The RFCs contain silanized silica and also some of the chemicals as shown in Table 4-1. They are available as free flowing granules and the size of these granules lies in the range of 3-5 mm. As the RFCs are free flowing granules, it can be dosed easily by gravimetric dosing systems in the twin screw extruder. Other ingredients such as oil, activators, antioxidants and cross-linking chemicals should be mixed further with the RFC compound in the twin screw extruder.

Table 4-1. Composition of different RFC materials

RFC type	**Ingredients**			
	Rubber	**Filler**	**Silane**	**Plasticizer/Chemicals**
RFC-1	E-SBR 1712/E-SBR 1721	Silica	TESPD	TDAE oil, 6PPD
RFC-2	E-SBR 1712/E-SBR 1721	Silica	TESPD	TDAE oil, ZnO, 6PPD, SA, Wax, DPG, S
RFC-3	E-SBR 1721	Silica	TESPD	TDAE oil, 6PPD
RFC-4	S-SBR 5025-0	Silica	TESPD	TDAE oil, 6PPD, TMQ
RFC-5	S-SBR 5025-0	Silica	TESPD	DAE oil, 6PPD, TMQ
RFC-6	BR CB 25	Silica	TESPD	6PPD

Table 4-2. Chemical features and mooney viscosity (ML 1+4) of rubbers

Rubber type	**Styrene (wt. %)**	**ML 1+4 (MU)**
E-SBR 1712	23.5	51
E-SBR 1721	40.0	53
S-SBR 5025-0	25.0	65
BR CB 25	----	44

Table 4-3. Specific surface area (N_2-SA) and structure (DBP) of silica used in the RFC

Trade name	**N_2-SA (m^2/g)**	**DBP number ml/100g**	**Remarks**
U 7000 FC	180	260-280	High dispersible silica as filter cakes

The formulation of the rubber compound contains several chemicals where each and every chemical has its own specific functions. These chemicals are necessary for the cross-linking reaction as well as for giving sufficient resistance against degradation processes. In the following Table 4-4, the rubber chemicals and its functions were briefly explained.

Table 4-4. Rubber chemicals and its functions

Chemicals	**Trade name**	**Function**
TDAE Oil	Enerthene 1849-1	Treated naphthenic oil, improves processing
DAE Oil	Naftolen ZD	Naphthenic oil, improves processing
TESPD	Si-75	Bi-functional organosilane
ZnO (Zinc oxide)	ZnO RS	Inorganic activator for vulcanization systems
SA	Stearic acid	Internal and external lubricant
6PPD	Vulkanox 4020/LG	Antioxidant
TMQ	Vulkanox HS/LG	Heat stabilizer
Wax	Protektor G 3108	Ozone and weather resistant
CBS	Vulkacit CZ/MGC	Accelerator
DPG	Vulkacit D/EGC	Accelerator
TBzTD	Rhenogran TBzTD-70	Accelerator
S	Mahlschwefel	Cross-linking agent for rubbers

The rubber chemicals are different in nature with respect to its functions, softening point and supply form. The continuous mixing in a twin screw extruder involves continuous dosing of ingredients in the extruder. Depending upon the function of chemicals, the chemicals are dosed in different barrel sections of an extruder. Other than that, the chemicals have different characteristics according to their supply form and chemistry. Careful selection of supply form (fine powder or granules) and mixing with other chemicals is necessary to make a mixing batch with high quality. Table 4-5 shows softening point and supply form of different rubber chemicals.

Table 4-5. Rubber chemicals softening point and its supply form

Chemicals	**Softening point (°C)**	**Supply form**
Zinc oxide	>>200	Fine powder
Stearic acid	>=69	Coarse powder (free flowing)
6PPD	>=46	Granules ($\phi = 3$-5 mm)
TMQ	85-95	Granules ($\phi = 3$-5 mm)
Wax	>=57	Granules ($\phi = 2$ mm)
CBS	>=96	Fine powder
DPG	>=145	Fine powder
TBzTD	130-135	Granules ($\phi = 3$-5 mm)
S	>=115	Fine powder

4.1.1. E-SBR/silica/silane based Rubber/Filler-Composite

The formulation of RFC-1 is shown in Table 4-6 and the final compound formulation with other ingredients is shown in appendix formulation 1.

Table 4-6. Formulation details of RFC-1 based on E-SBR/silica/silane

RFC-1	**Latex**	**Latex**	**Silica**	**Silane**	**TDAE Oil**	**Antioxidant**
	E-SBR 1712 66.6 phr	E-SBR 1721 33.4 phr	U 7000 FC 76 phr	Si-75 6.2 phr	Enerthene 1849-1 25 phr	6PPD 0.3 phr

4.1.2. E-SBR/silica/silane based finished compound Rubber/Filler-Composite

The RFC based on E-SBR, silica and silane is also available as a mixture with premixed ingredients called as Finished compound Rubber/Filler-Composite (FC-RFC). The formulation of FC-RFC is shown in Table 4-7. The ingredients listed below in Table 4-7 were mixed during the production process of FC-RFC. The final compound formulation is listed in Table 4-8.

Table 4-7. Formulation of RFC-2 (FC-RFC) based on E-SBR/silica/silane

RFC-2 (FC-RFC)	**phr**
E-SBR 1712	66.6
E-SBR 1721	33.4
U 7000 FC	76
Si-75	6.2
TDAE oil	25
ZnO	3
6PPD	1.5
SA	2
Wax	1
DPG	2
Sulphur	2.3

Table 4-8. Formulation of final compound

Ingredients	**phr**
RFC-2 (FC-RFC)	219
TDAE oil	20
CBS	1.5
TBzTD	0.2

4.1.3. Blends of E-SBR based Rubber/Filler-Composite and bale BR

The formulation of RFC based on E-SBR 1721, silica and silane is shown in Table 4-9. The final compound formulation of blend is shown in appendix formulation 3.

Table 4-9. Formulation of RFC based on E-SBR/silica/silane

	Latex	**Silica**	**Silane**	**TDAE Oil**	**Antioxidant**
RFC-3	E-SBR 1721 100 phr	U 7000 FC 76 phr	Si-75 6.2 phr	Enerthene 1849-1 25 phr	6PPD 0.3 phr

4.1.4. Blends of S-SBR and BR based Rubber/Filler-Composites

The formulation of S-SBR/BR blend is typical to a tire tread recipe with S-SBR and BR with silica as filler. Two different types of plasticizer, TDAE and DAE oil were used and tested in bale based and RFC based rubber blends. The S-SBR RFC and BR RFC based material formulations are shown in Table 4-10 and the final formulations are shown in appendix formulation 5.

Table 4-10. Formulation of S-SBR RFC and BR RFC based materials

Ingredients	**RFC**		
	RFC-4	**RFC-5**	**RFC-6**
S-SBR VSL 5025-0 HM	95	95	-
BR CB 25	-	-	95
E-SBR 1712	5	5	5
Ultrasil 7000 FC	76	76	76
Si-75	6.2	6.2	6.2
6PPD	0.3	0.3	0.3
TMQ	0.3	0.3	0.3
TDAE oil	14	-	-
DAE oil	-	20	-

4.2. Mixing aggregates

4.2.1. Internal mixer

For the production of rubber compounds by discontinuous mixing, a laboratory internal mixer from Werner & Pfleiderer GK 1.5 E with a rotor motor power of 24 kW is used. The internal mixer consists of intermeshing rotors and has a mixing volume of 1550 cm^3. The rotors speed can be flexibly adjusted from 20-100 1/min. The temperature in the mixing chambers and rotors can be separately heated upto 95 °C and it can be cooled by water. During mixing, the process data such as power, rotor speed and temperature can be seen online. A thermocouple located in the sidewall of the mixing chamber provides accurate measurement of the compound temperature.

4.2.2. Twin screw extruder

The continuous mixing of RFC compounds are performed by using a co-rotating twin screw extruder from the company Berstorff GmbH, Germany. The technical details of the twin screw extruder used are given in Table 4-11. In a co-rotating twin screw extruder, the barrel sections and screw elements are designed with the building block principle and hence various combinations of barrels and screw elements are possible. Barrel sections with an L/D of four and six are available for the configuration of the modular processing systems. The open barrels can be used for feed barrel sections and those equipped with inserts can be used for degassing, metering and injection barrel sections. The closed barrels can be used for metering and combined barrels can be used for horizontal side feeding of additives or for vertical venting. The extruder barrels can be cooled by steam injection and high pressure cooling. Here, the barrel sections are cooled by a high water flow rate of 3500 l/h for intensive cooling of material.

Table 4-11. Technical details of twin screw extruder ZE 40 A-UTX

L/D ratio	55
Screw outer diameter	43.3 mm
Outer/inner diameter ratio of D/d	1.46
Maximum screw speed	600 1/min
Maximum torque per screw	530 Nm
Power	77 kW

There are various types of screw elements available for the screw configuration. The conveying elements are available with different lengths, pitches, kneading elements in different lengths, offsets and helix angles as well as turbine elements and back-pumping elements. The compound passes through regions of high shear stress where it should be mixed, for example in kneading blocks and through conveying element regions with low shear stress where the material should be only conveyed. The combination of screw elements and barrel systems influences the temperature and compound properties in continuous mixing process.

4.2.3. Transfermix extruder and gear pump

The continuous mixing of blend compounds are performed by using combination of transfermix extruder with a gear pump. The transfermix extruder AZ MCDT 60 is from the company AZ

Formen- und Machinenbau GmbH, Germany. The technical details of the transfermix extruder are given in Table 4-12. Here, the bale rubbers can be cut into stripes with a maximum section of 16x9 mm and can be feed continuously in the transfermix extruder. The transfermix extruder has a heating system where the rubber can be heated to 80 ℃. According to the temperature, the output can differ from 100 to 200 kg/h.

Table 4-12. Technical details of transfermix extruder AZ MCDT 60

Screw speed	0 – 205 1/min
Output	100 – 200 kg/h
Screw diameter	60 mm
Screw length	10 D
Rubber stripes section	max. 16x9 mm

The material conveyed by the transfermix extruder is further conveyed to the twin screw extruder by a gear pump. The pressure in the entrance can be made constant, so that the gear pump helps to convey material at constant output.

The gear pump is from the company Paul Troester GmbH & CO. KG, Germany. The technical details of the gear pump are given in Table 4-13. The material flow delivered by the gear pump is dependent on the chosen rotor speed and the displacement volume per revolution. Equal volumes of material are transported along the gear pump housing and displaced into the outlet by the meshing of mating gear teeth.

Table 4-13. Technical details of gear pump ZP 56/35

Gear pump speed	max. 48 1/min
Output	max. 120 kg/h
min. necessary entrance pressure	20 bar
max. permitted entrance pressure	200 bar
max. permitted operating pressure	500 bar, during run + 100 bar
max. permitted difference in pressure	450 bar, during run + 50 bar
Heating	water heating equipment
Number of gears	28

4.3. Testing methods

4.3.1. Characterisation of rubber compounds

The characterisation of rubber compounds are carried out 24 hours after the mixing.

Rubber process analyser (RPA)

For measuring the filler-filler interaction, the rubber compounds were measured in a RPA at 60 °C with a frequency range of 0.1 Hz and a strain of 0.3-50 deg. The RPA measurements were carried out in Alpha Technologies RPA 2000. The storage modulus G' at low strain is considered as the measurement for filler-filler interaction. The G' decreases to lower value on increase in strain where the rubber compound undergoes shear deformation and filler network breaks down at higher strain.

Mooney viscosity

The mooney viscosity ML 1+4 (100 °C) was measured in Mooney MV 2000E from Monsanto. Mooney devised an instrument to measure the "stiffness" of uncured compounds, otherwise known as the compound's viscosity. For measuring viscosity, the mooney viscometer, in which a knurled knob (rotor) rotates (at two revolutions per minute) in a closed heated cavity, filled with uncured rubber. A shearing action develops between the compound and the rotor, and the resulting torque (resistance of the rubber to the turning rotor) is measured in arbitrary units called Mooney units (MU), which directly relate to torque. The higher the number of mooney units, the higher is the viscosity.

A shorthand language is used to express the results:
e.g. 60 ML 1+4 (100 °C),
where:

- 60 refers to viscosity in Mooney units
- M indicates Mooney
- L indicates that a large rotor was used (S would indicate the use of a small rotor)
- 1 refers to a one minute pre-heating time, after the cavity is closed but before the rotor is switched on, while the rubber warms up to the cavity temperature
- 4 refers to the time in minutes, after starting the rotor, when the reading is taken
- 100 °C is the test temperature

Vulcanization

All materials produced by extrusion and internal mixer are shortly threaded over a two roll mill with a large gap (5 mm) at 50 ℃, in order to get sheets. The vulcanization of all the compounds was performed at 165 ℃ in Rheometer MDR 2000E from Monsanto. The vulcanization time corresponds to t_{90} of the rheometer curve. The time to start the vulcanization is referred as scorch time. The vulcanization of the compounds are performed at 165 ℃ according to DIN 53529 in a compression moulding machine for yielding sheets of 2 mm thickness.

4.3.2. Characterisation of rubber vulcanizates

The characterisation of rubber vulcanizates are carried out 24 hours after the vulcanization.

Tensile test

The tensile strength and elongation at break was measured in Zwick universal testing machine Z010 under DIN 53504 in S2 sample size cut from 2 mm sheets. For each sample, five measurements were made and the average is taken as the final value.

Hardness

The Shore A hardness was measured with respect to DIN 53505 with 6 mm vulcanized sheet under room temperature. The thickness of the sample 6 mm is made by cutting three 2 mm sheets. For each sample, five measurements were made and the average is taken as the final value.

DIN Abrasion test

The abrasion tests were carried out in a cylindrical sample with 16 mm diameter and 6 mm length under DIN 53516. The DIN-Abrasion test is measured according to the loss in volume (mm^3) of the sample. For each sample, five measurements were made and the average is taken as the final value.

5. Results and discussion

5.1. Mixing of E-SBR/silica/silane based Rubber/Filler-Composite

5.1.1. Discontinuous mixing of E-SBR/silica/silane based Rubber/Filler-Composite

The reduction of specific energy input in a mixing room leads to reduction and saving of energy expenses. On the same time, the quality of the product should be achieved. The prime aim of continuous mixing is to reduce the specific energy input considerably compared to discontinuous mixing such as internal mixer and at the same time reaching same or better material properties. Hence, the material properties obtained from the internal mixer is given to be as the reference values for the continuous mixing process. For carrying out the mixing of reference materials, a laboratory internal mixer, Werner & Pfleiderer GK 1.5 E is used. The mixing of reference compounds were carried out with E-SBR based RFC-1 compound.

The conventional mixing time for silica based rubber compounds is 13 minutes and it consists of three steps mixing. This is due to the fact that the silica should undergo silanization reaction in a bale rubber mixture. As the E-SBR based RFC-1 consists of silanized silica as filler, the mixing time can be reduced. Hence, various mixing times were taken for studying reference compounds. The mixing times were varied with 13 minutes, a conventional three step mixing, with seven minutes, a two step mixing and four minutes, a one step mixing. The formulation and mixing steps for mixing the compounds in the internal mixer were shown in appendix, formulation 1. In the mixing steps, the applied process parameters such as rotor speed, temperature, mixing time and addition of raw materials are shown.

The compound and vulcanizate properties obtained from different mixing steps and mixing times were shown in Table 5-1. The conventional three steps mixing with 13 minutes mixing time shows specific energy input of 1.8 kWh/kg. With two step mixing, where all the ingredients except cross-linking agents were mixed for five minutes in the first step and with cross-linking agents for two minutes in the second step, the specific energy input reduces to 0.97 kWh/kg. In case of one step mixing, all the ingredients including the cross-linking agents were mixed together for four minutes. The outcome is reduced specific energy input of 0.64 kWh/kg which is obviously due to the reduced mixing time.

The compound properties such as mooney viscosity (ML 1+4) at 100 ℃ shows 47.61 MU and the scorch time of the compound shows 5.10 min for three step mixing. With two step mixing, the mooney viscosity at 100 ℃ shows 66.5 MU which is higher than three step mixed compound. The scorch time of the compound is 4.87 min which is in good range with the three step mixed compound. With one step mixing of four minutes, the mooney viscosity at 100 ℃ shows 67.63 MU which is higher than the 13 minutes compound but not quite high when compared to two step mixing. The scorch time of the compound is 3.96 min which is lower than the three step and two step mixed compound.

Table 5-1. Properties obtained from materials mixed in internal mixer

Process	**Discontinuous**		
Aggregate	**Internal mixer**		
Type of material	**RFC-1**	**RFC-1**	**RFC-1**
Mixing steps	3	2	1
Mixing time [min]	6+5+2=13	5+2=7	4
Spec. ener. inp. [kWh/kg]	1.8	0.97	0.64
ML 1+4 (100 ℃) [MU]	47.61	66.5	67.63
Vulcameter $\Delta S'$ [dNm] Scorch time [min]	12.31 5.10	13.91 4.87	13.92 3.96
G’ at low strain at 60 ℃ [kPa]	532.71	786.27	863.71
Hardness Shore A	56.86	62.08	62.16
σ 100 % [MPa]	1.9	2.3	2.4
σ 200 % [MPa]	4.8	5.8	5.7
σ 300 % [MPa]	8.9	10.2	9.3
Tensile strength [MPa] Elongation [%]	19.2 508.6	19.5 487.3	20.5 549.4
DIN Abrasion [mm^3]	105.6	95.5	89.7

The filler-filler interaction measured with G’ at low strain at 60 ℃ shows 532.71 kPa for three step mixing. The low G’ at low strain value is an indication that the dispersion of silica has been optimally taken place. With two step mixing, the G’ at low strain shows 786.27 kPa which shows a higher filler-filler interaction than the three step mixed compound. This higher value in G’ at low strain shows that the filler is not optimally dispersed and it also shows an influence in the mooney viscosity of the compound. With one step mixing, the G’ at low strain shows 863.71 kPa which shows a much higher filler-filler interaction than the three step and two step mixed compounds. The reduction in mixing time shows an increase in the filler-filler interaction and hence higher G’ at low strain value. All the other vulcanizate properties are shown in the Table 5-1 which also shows differences in properties with respect to mixing time. Although, the RFC-1 compound contains silanized silica as filler, the amount of mixing time is essential to mix all the ingredients together to achieve optimum degree of dispersion. The vulcanizate properties are consequently influenced from the compound properties. Hence, in a mixing room, the rubber compound should be mixed optimally to achieve optimum compound and vulcanizate properties. The properties obtained from internal mixer with various mixing times will be taken as reference values to compare the continuous mixing process and its material properties.

Further mixing investigations were carried out with E-SBR based RFC-1 compound in internal mixer. The RFC-1 compound mixed as one step mixing for four minutes is taken for our further study. As discussed previously, all the ingredients including cross-linking agents were mixed for four minutes in one step. The temperature of the compound after four minutes mixing is taken as dump or outlet temperature. Here, the outlet temperature of the compound is increased by increasing the fill factor and rotor speed in the internal mixer. This allows studying the maximum critical outlet temperature at which the compound starts to vulcanize. The cross-linking reaction taking place during mixing can be cross-checked by the indication in increase in mooney viscosity and reduction in scorch time. This study will be used as an informative data for limiting the maximum outlet temperature in continuous mixing process, where the cross-linking agents will also be added in one mixing step.

The experiments were performed by keeping the internal mixer starting temperature at 25 °C and the cooling water temperature is kept constant at 25 °C. The outlet temperature is varied by varying the mixer’s filling degree and rotor speed while keeping the mixing time constant for four minutes. After every mixing, the compound is sheeted out in a two-roll mill. After sheeting out, the compound is cooled down for 24 h at room temperature. The materials are then tested for mooney viscosity and scorch time.

Figure 5.1 shows the mooney viscosity and scorch time with respect to compound outlet temperature. As can be seen, the mooney viscosity and scorch time remains constant from outlet temperatures of 100 °C to 140 °C. All the ingredients including cross-linking agents can be mixed with consistent compound properties upto 140 °C. On increasing the temperature further, a critical outlet temperature (T_c) above 140 °C, a sudden increase in mooney viscosity and a sudden decrease in scorch time is observed. The mooney viscosity increases from 60 MU to 120 MU and simultaneously scorch time decreases from 4.5 minutes to 1.8 minutes. This change is an indication of pre-mature scorching in the rubber compound. The cross-linking agents account to make chemical reaction at higher temperatures. This is an indication of sulphur-rubber bonding or scorching where the actual scorch time reduces to lower values. With a mixing time of four minutes, the increase in outlet temperature leads to starting of vulcanization reaction in the compound.

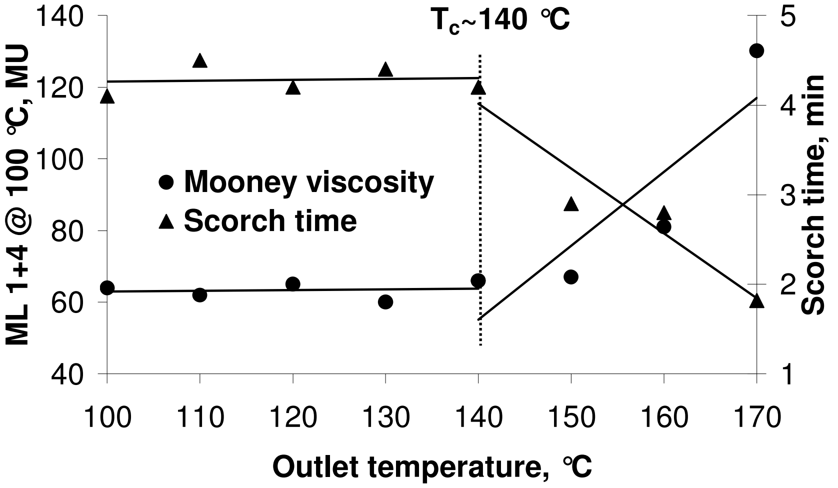


Figure 5-1. Mooney viscosity and scorch time as a function of outlet temperature

The most direct indication for sulphur to rubber bonding is an increase in the compound mooney viscosity and decrease in the scorch time. Hence, this experiment shows that the compound properties such as mooney viscosity and scorch time remain constant below 140 °C. Above the temperature at 140 °C, there is a sudden increase in mooney viscosity and decrease in scorch time. This indicates that the cross-linking reaction takes place during the mixing where the cross-linking agents are mixed together in one mixing step. This influence of outlet temperature on compound properties is very important, in case of mixing rubber compounds in a continuous mixing aggregate such as twin screw extruder. If the cross-linking reaction takes place during mixing in a twin screw extruder, it may lead to poor compound and material properties. Hence, the above obtained results will be taken as a reference for the continuous mixing process to limit throughput at higher outlet temperatures.

5.1.2. Continuous mixing of E-SBR/silica/silane based Rubber/Filler-Composite

5.1.2.1. Development of screw configuration in twin screw extruder

In a co-rotating twin screw extruder, the screw configuration is one of the major parameter for influencing the mixing performance. There are various types of screw elements available for designing the screw configuration. As discussed in the theoretical part in chapter 3, the screw elements can be modularly connected and depending upon the necessity, the screw can be varied and optimised to achieve the maximum mixing level. Especially, mixing elements such as kneading block elements consisting of a discontinuous unit is mainly composed of several discs. There are three basic kneading block elements such as forward, neutral and reverse kneading block elements. The mixing performance can be varied and improved by using these elements in proper combinations. The screw configuration should be configured according to the type of rubber to be mixed. Along with the rubber, other ingredients such as plasticizer, filler, antioxidants and other cross-linking agents which need to be mixed should also be taken into consideration. Hence, the screw configuration is designed according to the type of ingredient mixed and the dosing of ingredients in the respective barrel sections in the extruder along the extrusion direction. During mixing, the temperature in the material increases due to shear or due to external heating from the barrel. This leads some materials to release some volatile gases such as moisture. Hence, venting barrel sections need to be provided to remove the gases and the screw elements with relatively low flight depths are applied in these barrel sections.

The material used in this study is a Rubber/Filler-Composite (RFC-1), a rubber compound based on E-SBR and silica as filler. The dispersion and silanization of silica in the E-SBR rubber compound is already carried out during the production process of RFC-1. However, other ingredients such as plasticizer, antioxidant and other cross-linking agents are further need to be mixed in the twin screw extruder. The homogenization of all ingredients is necessary to have uniformity in quality. The homogenization is influenced by several processing parameters such as screw configuration, dosing of compounds, temperature, screw speed, throughput, filling degree etc. In the following, three different screw configurations are discussed to study the influence of mixing elements on material properties. Three types of screw configurations A, B and C with differences in mixing elements are shown in Figure 5-2 for mixing RFC-1 compound. The screw configuration A consists of forward kneading elements in six places along the extrusion direction. The first four forward kneading block elements are 1.25 L/D and the next two are 0.75 L/D. They are usually intermeshing and self wiping made up of five disks, each turned by 45° relative to the previous one. The screw configuration B is similarly made as screw configuration A except the kneading elements are changed to neutral kneading block elements each turned 90° relative to the previous one. Similarly, the first four neutral kneading mixing elements are 1.25 L/D and the next two are 0.75 L/D. The screw configuration C is made similarly but with reverse kneading elements each turned by -45° relative to the previous one. Similarly, the first four reverse kneading mixing elements are 1.25 L/D and the next two are 0.75 L/D. Figure 3-19 shows the screw configuration C with screw element names and 12 barrel sections.

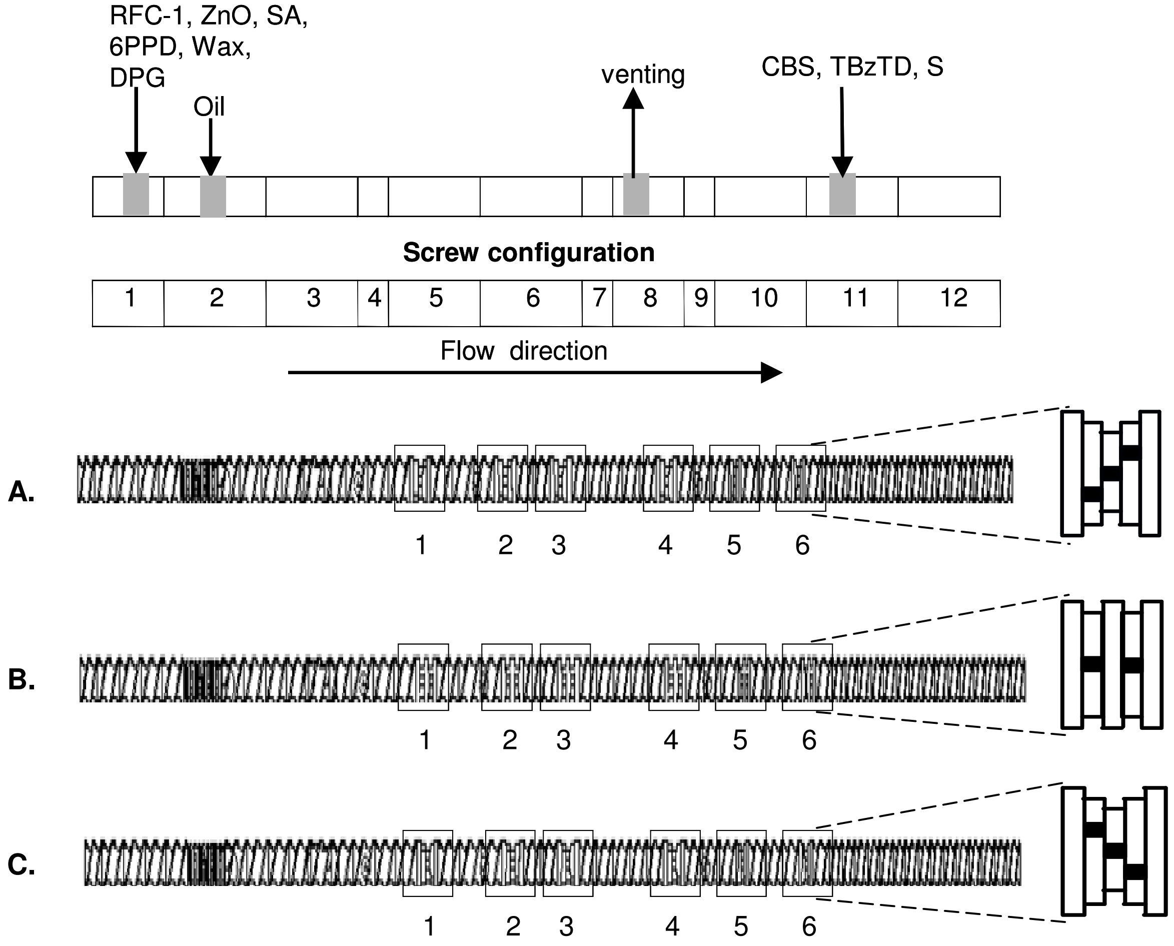


Figure 5-2. Schematic representation of three screw configurations with A. forward kneading elements, B. neutral kneading elements, C. reverse kneading elements

The RFC-1 along with ZnO, SA, 6PPD, Wax, DPG were mixed as a pre-blend and dosed in barrel section one. The plasticizer oil is dosed with a dosing pump in barrel section two. A venting is provided in barrel section eight for the removal of volatile gases. The cross-linking agents such as CBS, TBzTD, S were mixed separately as a pre-blend and dosed in barrel section eleven. All the experiments were carried out at a throughput of 35 kg/h and with a screw speed of 205 1/min. The extruder barrels were cooled maximum by providing cooling by a high water flow rate of 3500 l/h. Previous studies on rubber mixing in twin screw extruder showed that there is high temperature development in the compound in the die section [21]. Hence, to avoid high temperature development in the rubber compound, all the trials were taken without die.

In Figure 5-3, the specific energy input is shown for the extrusion process using three screw configurations A, B and C. The specific energy input reaches 0.28 kWh/kg for screw configuration A with forward kneading elements. The specific energy input increases to 0.36 kWh/kg for screw configuration B with neutral kneading elements and the specific energy input increases further to 0.46 kWh/kg for screw configuration C with reverse kneading elements. This difference in specific energy input is due to the flow paths and forces occurred in the kneading element sections as well as high viscosity of the compound. Although the kneading elements were placed in the same barrel sections for all the screw configurations, the screw configuration C shows the highest specific energy input. This shows that the material undergoes more compression with reverse kneading elements compared to forward and neutral kneading elements.

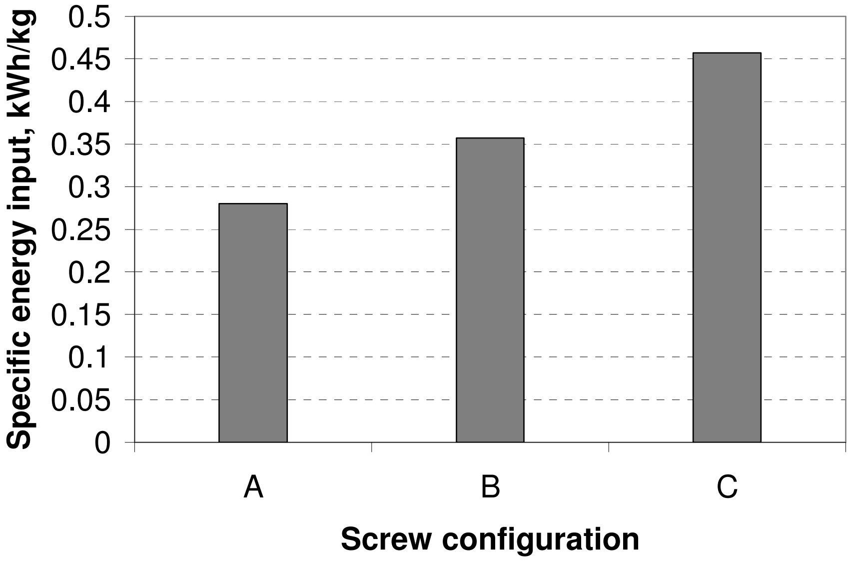


Figure 5-3. Specific energy input of the extrusion process using screw configurations A, B and C

The residence time using different screw configurations A, B and C are shown in Figure 5-4. As discussed in the chapter 3.3.1.2., the residence time is defined as the total time a given particle spends in the extruder from the moment it enters the extruder feed throat until it exits the die [135]. This was measured manually by dosing foreign particles during extrusion, in this case 50g of Kevlar fibre were dosed along with the RFC-1 material in barrel section one. In Figure 5-4, the screw configuration with forward kneading elements gives a residence time of 37 s. The residence time increases to 50 s for screw configuration B with neutral kneading elements. With screw configuration C, the residence time increases further to 64 s.

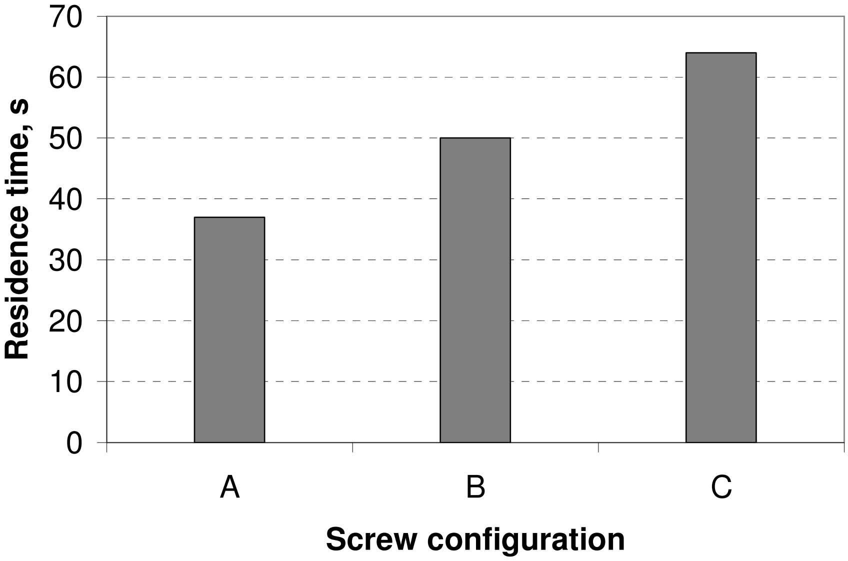


Figure 5-4. Residence time using screw configurations A, B and C

This shows that the material spends relatively more time with the screw configuration C having reverse kneading elements indicating higher degree of filling in the reverse kneading sections. The variation of the degree of filling has a decisive influence on the operating behaviour of the extruder, e.g. on the residence time behaviour and on the shear load acting on the material (ex: temperature). The higher residence time in screw configuration C has also higher specific energy input as shown in Figure 5-3.

The outlet temperature of the compounds was measured manually directly after the extrusion. With a relatively short residence time, the screw configuration A with forward kneading elements leads to a outlet temperature of 112 °C (Figure 5-5). With the application of screw configuration B, the neutral kneading elements, the outlet temperature increases to 113 °C which is almost similar to screw configuration A. This slight increase can be related to the higher residence time for the screw configuration B having neutral kneading elements. The outlet temperature increases drastically to 117 °C for the screw configuration C with reverse kneading elements. This increase can be related to the amount of time the mixing taking place due to the back flow as well as high shear load in the reverse kneading barrel sections. Reverse kneading elements or backward-conveying elements affect the back-pressure length respectively the residence time in the up-channel direction so that the shear deformation increases. As the shear deformation increases, the rubber compound dissipates more heat and hence high outlet temperature.

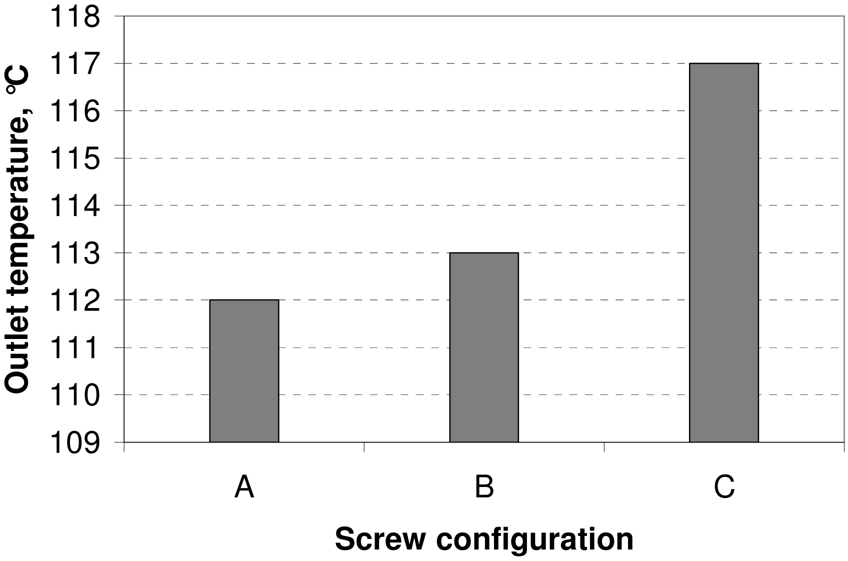


Figure 5-5. Outlet temperature of the compound from the extruder using screw configurations A, B and C

The outlet temperature of the compound depends on the development of compound temperature along the channel direction inside the extruder. In Figure 5-6, the developments of barrel temperature along the channel direction are shown for the extrusion process using screw configurations A, B and C. The barrel temperature increases due to the shear and amount of heat dissipation from the rubber compound although the extruder barrels were continuously cooled to 20 °C. The barrel temperatures for screw configuration B with neutral kneading elements are higher than for screw configuration A with forward kneading elements. This shows that the heat developed due to shear is higher for neutral kneading elements than the forward kneading elements which can be also seen from the compound outlet temperature from Figure 5-5. On using reverse kneading elements, the barrel temperature increases further. As the rubber compound undergoes back flow in reverse kneading sections, the temperature increases due to dispersive and distributive mixing. The dispersive mixing is observed by the shear and elongational stresses created, while the distributive mixing is achieved by frequent stretching and reorientations of the flow. The outlet temperature of the compound from screw configuration C as shown in Figure 5-5 correlates well with the development of barrel temperature as shown in Figure 5-6.

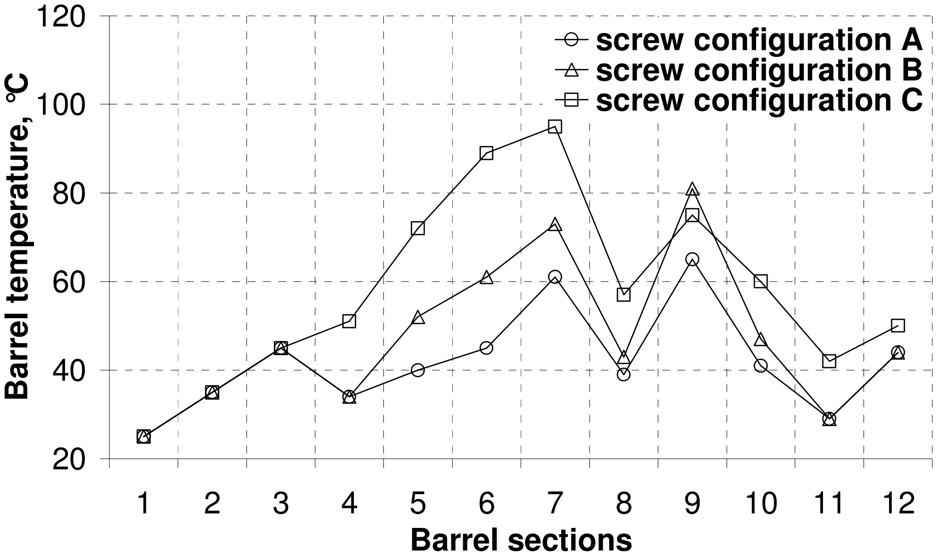


Figure 5-6. Temperature in different barrel sections using screw configurations A, B and C

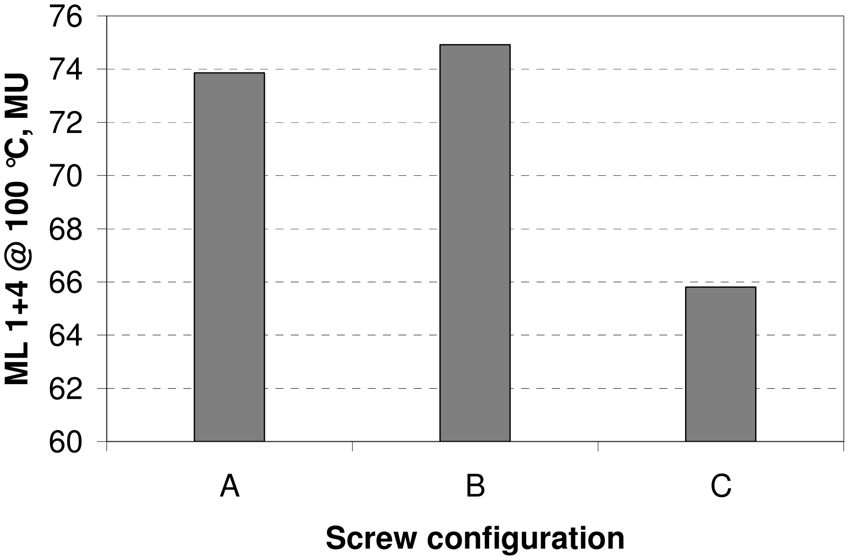


Figure 5-7. Mooney viscosity of the compound using screw configurations A, B and C

The mooney viscosity at 100 °C is measured for all compounds from screw configurations A, B and C. As shown in Figure 5-7, the mooney viscosity of the compound mixed by screw configuration A shows a value of 73.9 MU. With screw configuration B, the mooney viscosity increases slightly to 74.9 MU. The mooney viscosity decreases to 65.8 MU with the screw configuration C. The decrease in mooney viscosity from screw configuration C shows that the compound has undergone dispersive and distributive mixing. The dispersive mixing consists of breaking clumps or aggregates into particles of the smallest size as possible. The distributive mixing consists of a kinematic flow that will provide a uniform concentration of all the components. The dispersion of silica in the rubber compound as well as uniform distribution of all rubber chemicals reduces the mooney viscosity of the rubber compound.

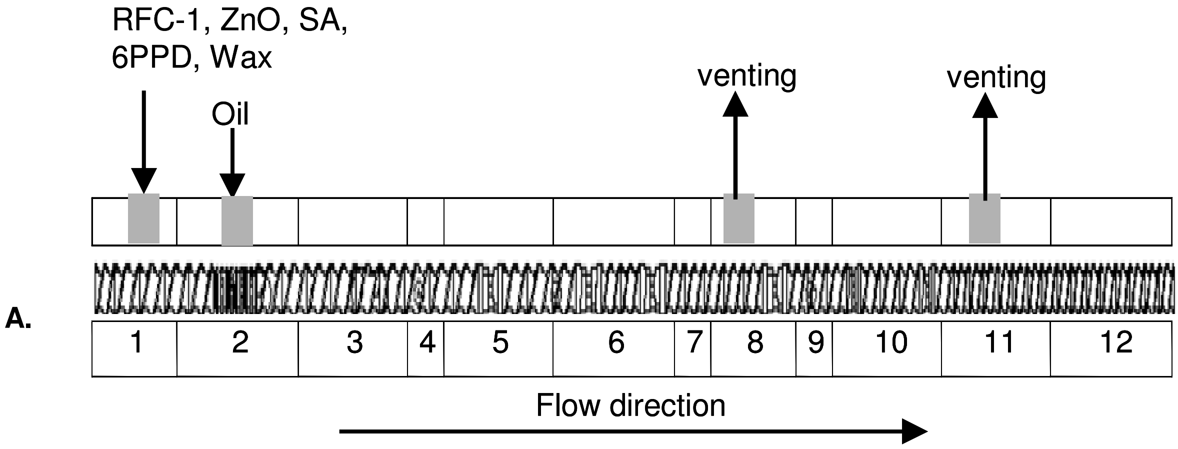
Figure 5-8. Storage modulus at 0.28% strain of the compound using screw configurations A, B and C

The storage modulus G’ at low strain (0.28%) is shown in Figure 5-8 for screw configurations A, B and C. The filler-filler interaction is measured by G’ values where higher the filler-filler interaction, the higher the G’ values at low strain. With screw configuration A, the G’ value reaches to 1304.8 kPa and increases to 1623.1 kPa with screw configuration B. With screw configuration C, the G’ value decreases drastically to 548 kPa. The results of G’ values are similar to mooney viscosity values for all the screw configurations as shown in Figure 5-7. Reverse kneading elements provides significant changes in flow directions breaking and recombining the flow. This leads to a high shear process where the silica particles are dispersed to a high degree reducing the filler-filler interactions. Together, the homogeneity of rubber with filler, oil and additives are increased significantly. This reduces the filler-filler interaction and hence the G’ at low strain.

5.1.2.2. Optimization of the dosing assembly in twin screw extruder

Any type of formulation of a typical rubber compound consists of normally over ten different components. It is of no worth to have individual dosing unit for each component. Hence, some chemicals can be mixed together and made as a pre-blend. As pre-blends, the chemicals can be feed separately in appropriate barrel sections. In case of twin screw extruders, starve feeders are used for dosing ingredients. Feeders deposit the formulation directly onto the extruder screw, with the screw speed set to remove the formulation at higher rate than it is deposited on the screw. There is no material build-up in the extruder feed throat, and the throughput is determined by the feed rate rather than the extruder screw speed. To make starve feeding by gravimetric dosing systems, the components were chosen either as granulates or powders.

The screw configuration used here is screw configuration C consisting of reverse kneading elements as shown in Figure 5-2. The dosing assemblies were studied in a comparative way where it is tried the best possible assembly to achieve high mixing quality. Figure 5-9 shows a schematic representation of different dosing assemblies A, B, C and D for continuous mixing of RFC-1. All the experiments were carried out at a throughput of 35 kg/h and with a screw speed of 205 1/min. The extruder barrels were cooled to 20 ℃ by providing cooling by a high water flow rate of 3500 l/h and all the trials were taken without the die.



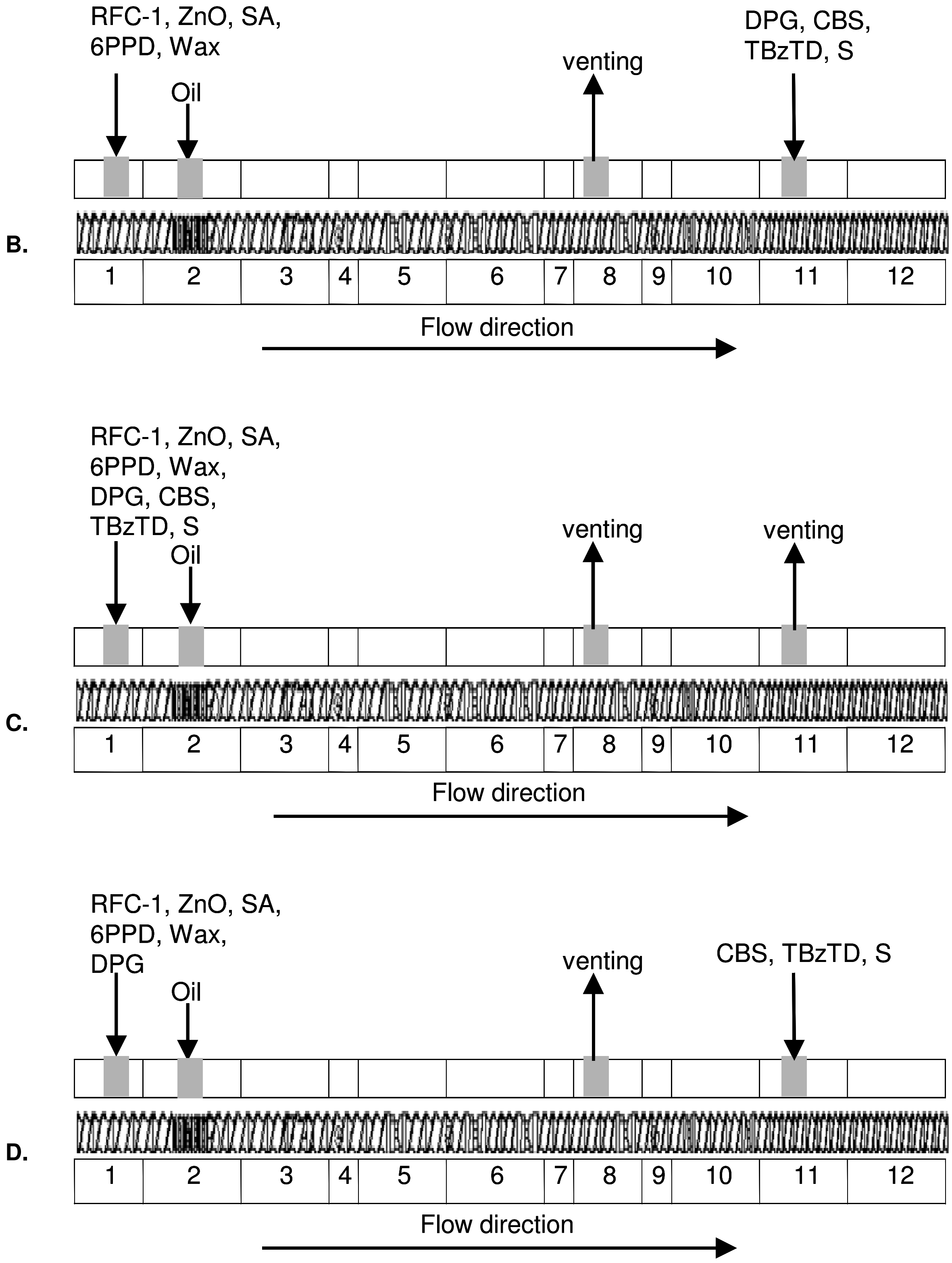


Figure 5-9. Schematic representation of different dosing assemblies A, B, C and D

In Figure 5-9, dosing assembly A shows the mixing of RFC-1 without cross-linking chemicals where the RFC-1 along with ZnO, SA, 6PPD and Wax were mixed as a pre-blend and dosed in barrel section one. The plasticizer oil is dosed for all assemblies with a dosing pump in barrel section two. Venting is provided in barrel section eight and eleven for the removal of volatile gases. In dosing assembly B, all the ingredients were dosed similarly to dosing assembly A, but, here the cross-linking chemicals as pre-blend DPG, CBS, TBzTD and S were dosed in barrel section eleven. In dosing assembly C, the cross-linking chemicals as pre-blend DPG, CBS, TBzTD and S were dosed in barrel section one along with the RFC-1 pre-blend. The dosing assembly D consists of pre-blend of RFC-1, ZnO, SA, 6PPD, Wax along with DPG dosed in barrel section one and the rest of the cross-linking chemicals as pre-blend CBS, TBzTD and S were dosed in barrel section eleven. All the dosing systems were calibrated for every new dosing assembly according to a throughput rate of 35 kg/h.

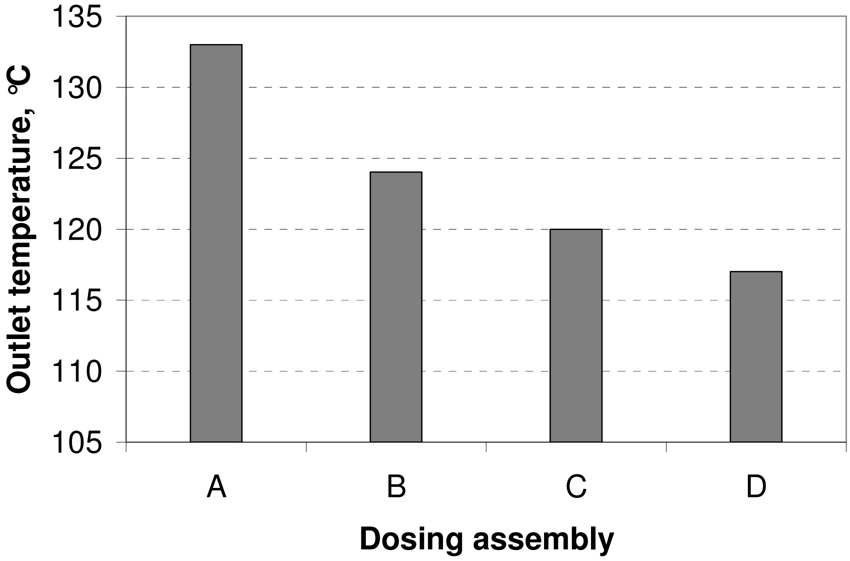


Figure 5-10. Outlet temperature of the compound from the extruder using dosing assemblies A, B, C and D

The outlet temperatures using dosing assemblies A, B, C and D were shown in Figure 5-10. Without cross-linking agents in dosing assembly A, the RFC-1 along with the pre-blend chemicals reaches an outlet temperature of 133 °C. The material undergoes compression and shear leading to high temperature of the compound. With the addition of cross-linking chemicals in barrel section eleven as shown in dosing assembly B, the outlet temperature decreases to 124 °C. The screw elements in barrel section eleven and 12 are forward conveying elements.

On addition of cross-linking chemicals, the friction on the barrel wall in barrel section eleven and 12 is reduced and hence the compound temperature reduces. The outlet temperature decreases further using dosing assembly C. The addition of cross-linking chemicals along with RFC-1 pre-blend in barrel section one acts as a dispersing and lubricating agent leading to decrease in outlet temperature to 120 °C. In dosing assembly D, the dosing of DPG with RFC-1 pre-blend in barrel section one and other cross-linking chemicals CBS, TBzTD and S in barrel section eleven leads to further decrease in outlet temperature to 117 °C. Here, the DPG alone acts as a agent reducing the silica-silica interaction and hence enhancing the silica dispersion [61]. Due to this, the compound is mixed well until barrel section ten. On further addition of cross-linking agents in barrel section eleven, the overall compound temperature reduces to 117 °C.

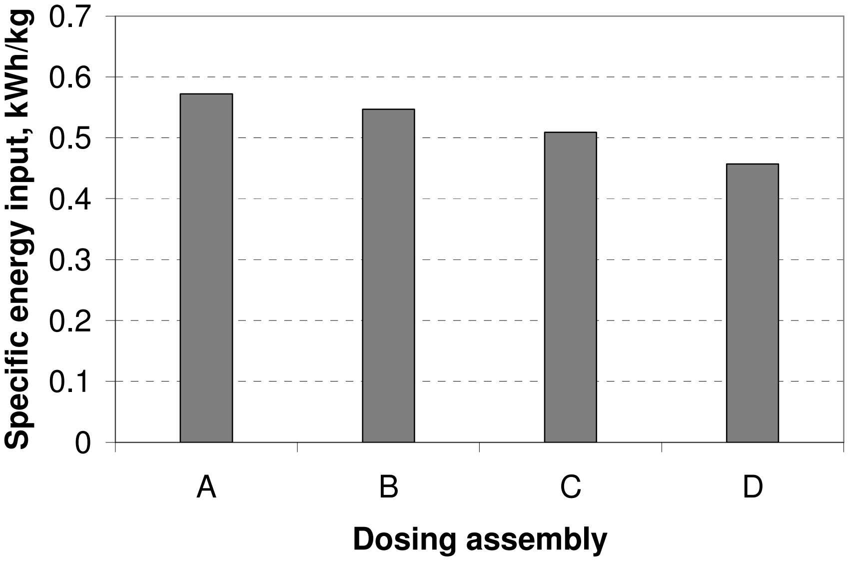


Figure 5-11. Specific energy input using dosing assemblies A, B, C and D

The specific energy input using dosing assembly A shows 0.572 kWh/kg and it decreases to lower value successively using dosing assemblies B, C and D (Figure 5-11). This decrease can be related to the outlet temperature (Figure 5-10) where as the material shows less heat dissipation, the friction between the compound and barrel is minimized. The specific energy input depends upon the overall viscosity of the compound. This can be seen in the values of mooney viscosity as shown in Figure 5-12. With dosing assembly A, the mooney viscosity reaches 102.9 MU. This shows that the material is extremely hard and high shear forces are needed to process this material. Hence, the outlet temperature goes to 133 °C. This is also indicated by a torque value of higher specific energy input. On addition of cross-linking chemicals as shown in dosing assembly B, this value decreases to 87.3 MU. This value further decreases to 68.3 MU using dosing assembly C. Cross-linking agents are basically low molecular weight compounds, also act as internal lubricants which improves micro-dispersion [25]. This leads to a reduced mooney viscosity of 68.3 MU. The incorporation of all the ingredients together however decreases the mooney viscosity. On addition of DPG in barrel section one with RFC-1 pre-blend, the mooney viscosity decreases further to 65.8 MU. The reduction in mooney viscosity could be influenced by the reduction in rubber viscosity, dispersion of silica particles and homogenization of rubber chemicals. In this case, the DPG can be effective in dispersing the silica particles. As the silica dispersion increases, the filler-filler interaction decreases and hence reduces the viscosity of the compound. As the viscosity of the compound decreases, there is a reduction in specific energy input from the extruder and reduction in outlet temperature of the compound.

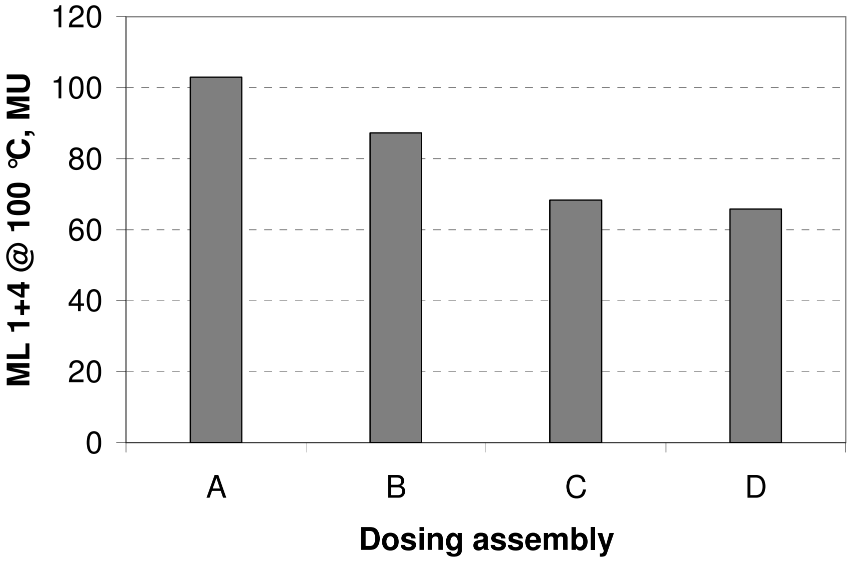


Figure 5-12. Mooney viscosity of the compound using dosing assemblies A, B, C and D

The reduction in mooney viscosity is also influenced by the reduction in filler-filler interactions. According to Payne, the storage modulus at low strain is an indication of filler-filler interaction [43]. The filler-filler interaction reduces with increase in degree of filler dispersion. The agglomerate size of filler reduces during distributive mixing and the distance between the filler particles reduces during dispersive mixing. The effect of filler-filler interaction with variation in different dosing assemblies A, B, C and D can be seen from Figure 5-13. Although, the RFC-1 consists of silanized silica as filler, the optimum dispersion of silica particles takes place in the twin screw extruder. As shown in Figure 5-13, the filler-filler interaction indicated by the storage modulus at low strain decreases drastically from dosing assembly A to D.

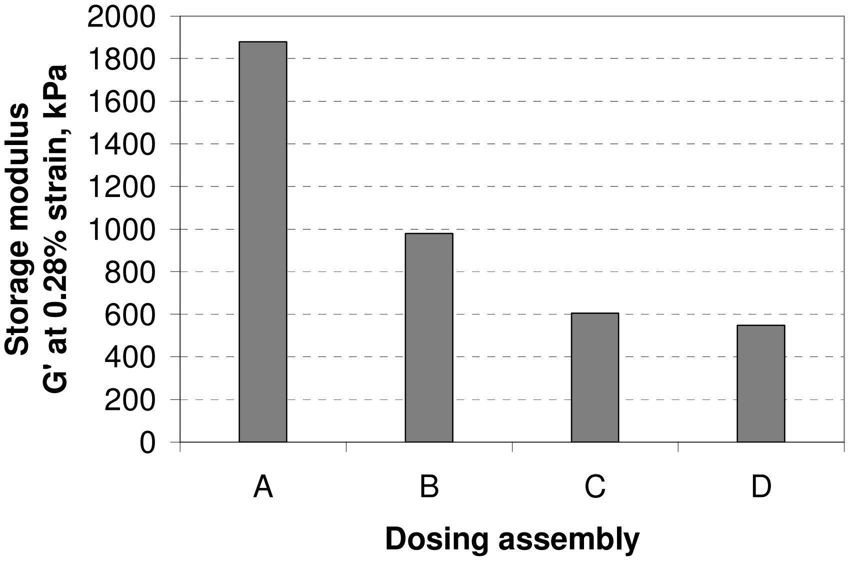


Figure 5-13. Storage modulus at 0.28% strain of the compound using dosing assemblies A, B, C and D

The filler-filler interaction reaches 1879.2 kPa with dosing assembly A without cross-linking agents. Here, the filler-filler interaction is so high which increases the mooney viscosity of the compound. On the other side, the filler-filler interaction reduces drastically with dosing assembly D. This is due to that the RFC-1 pre-blend is mixed with DPG and the rest of the cross-linking chemicals were mixed in barrel section eleven. DPG is used as primary or secondary accelerator. It is a low molecular weight additive which gets on to the filler surface during mixing and hence supports better dispersion of the silica filler [61]. The increase in filler dispersion leads to reduction in storage modulus at low strain. Hence, addition of DPG along with RFC-1 pre-blend in barrel section one is a optimum dosing assembly and rest of the cross-linking agents in barrel section eleven reduces the mooney viscosity and filler-filler interaction of the rubber compound.

The vulcanization mechanism of the rubber compound is tested by vulcameter measurements carried out at 165 °C for 30 min. As there are no cross-linking agents added in dosing assembly A, the vulcameter and scorch time measurement are not carried out. In dosing assembly B as shown in Figure 5-14, the ∆S' reaches 8.51 dNm and scorch time of 9.25 min. These values are due to the addition of DPG in barrel section eleven together with CBS, TBzTD and S. As the melting point of DPG is 145 °C, the degree of incorporation with the rubber compound was difficult in barrel section eleven. This shows that the dispersion of cross-linking chemicals have not taken place sufficiently for proper vulcanization reaction. This may lead to in-homogeneous cross-linking reactions in the compound and hence would lead to poor material properties. With dosing assembly C, the ΔS' reaches a value of 14.86 dNm and scorch time of 2.65 min. Comparing to the reference compound in internal mixer mixed for 4 minutes, the decrease in scorch is an indication of pre-scorch due to high shear in the reverse kneading barrel sections. Here, the vulcanization reaction starts earlier and hence reduces the scorch time. This shows that the compound has undergone pre-mature vulcanization in the extruder.

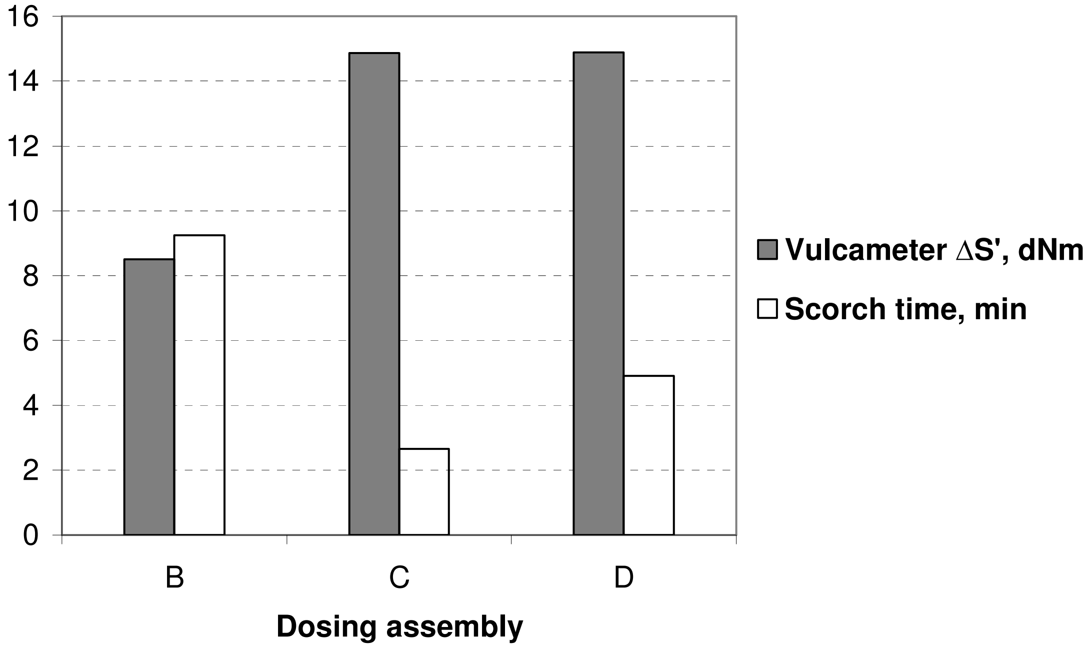


Figure 5-14. Vulcameter ΔS' and scorch time of the compound using dosing assemblies B, C and D

With dosing assembly D, the ΔS' reaches a value of 14.89 dNm and scorch time of 4.9 min. The vulcameter value shows that the dispersion of cross-linking agents was uniform throughout the compound and hence proper cross-linking reaction takes place. The scorch time of 4.9 min shows that the compound is free of pre-mature scorching during mixing process in the extruder. The ΔS' and scorch time values are in comparable range with the reference compounds mixed in the internal mixer. Hence, the dosing assembly D proves to be the optimum for the compound mixing from the above discussed dosing assemblies.

5.1.2.3. Development of one step continuous mixing process

The mixing performance achieved by screw configuration C and dosing assembly D are further investigated to study the mixing performance at higher throughputs. The effectiveness of production depends upon the maximum throughput possible by the extruder. To increase the throughput, the screw speed needs to be increased. With the development of one step continuous mixing process, it is intended to show the maximum possible throughput under controlled outlet temperature. The increase in throughput and screw speed can lead to higher outlet temperature of the compound. In case of rubber compound, higher outlet temperature may lead to pre-scorching or cross-linking reaction happening during the mixing in the extruder. Hence, the maximum throughput and screw speed should be studied within the maximum outlet temperature in order to control pre-scorching as well as to achieve required compound and material properties.

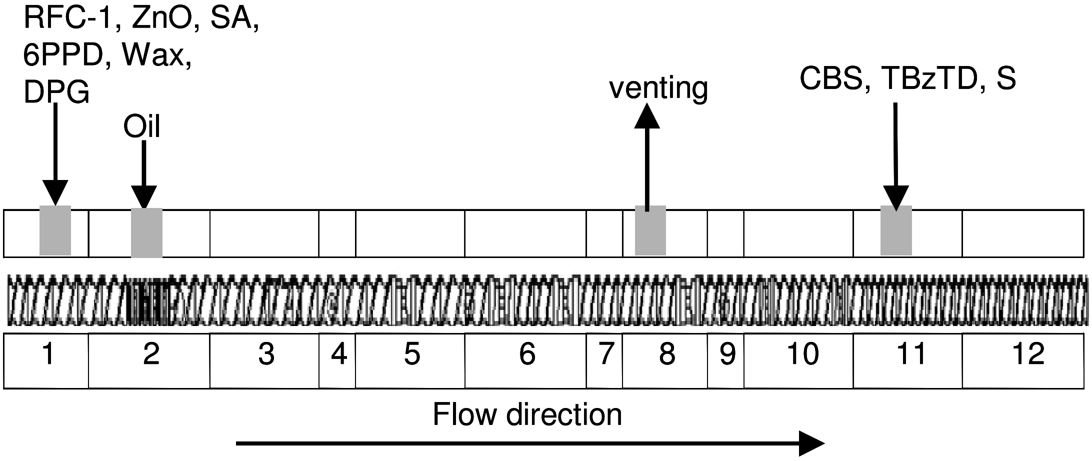


Figure 5-9 (D). Schematic representation of one step continuous mixing process

The schematic representation of dosing assembly D with the screw configuration C is shown in Figure 5-9 (D) for one step continuous mixing process. In our study, the throughput and screw speed were considerably increased under relatively constant filling degree of 21.5 %. The throughputs were increased from 35 kg/h to 50 kg/h and the screw speed from 205 1/min to 260 1/min. The throughput and screw speeds were shown in Table 5-2. The maximum throughput and screw speed were studied accordingly to the maximum allowed outlet temperature of the compound as will be discussed further. As discussed in previous sections, the extruder barrels were cooled to 20 ℃ by a high water flow rate of 3500 l/h and all the trials were taken without the die.

Table 5-2. Process parameters

Parameters	**Data**			
Throughput (kg/h)	35	40	45	50
Screw speed (1/min)	205	215	240	260

The specific energy inputs for different throughputs were shown in Figure 5-15. With a throughput of 35 kg/h and a screw speed of 205 1/min, the specific energy input reaches 0.46 kWh/kg. On increasing the throughputs to 50 kg/h with a screw speed of 260 1/min, the specific energy input decreases to 0.41 kWh/kg. It shows that with increasing throughput and screw speed, the specific energy input decreases.

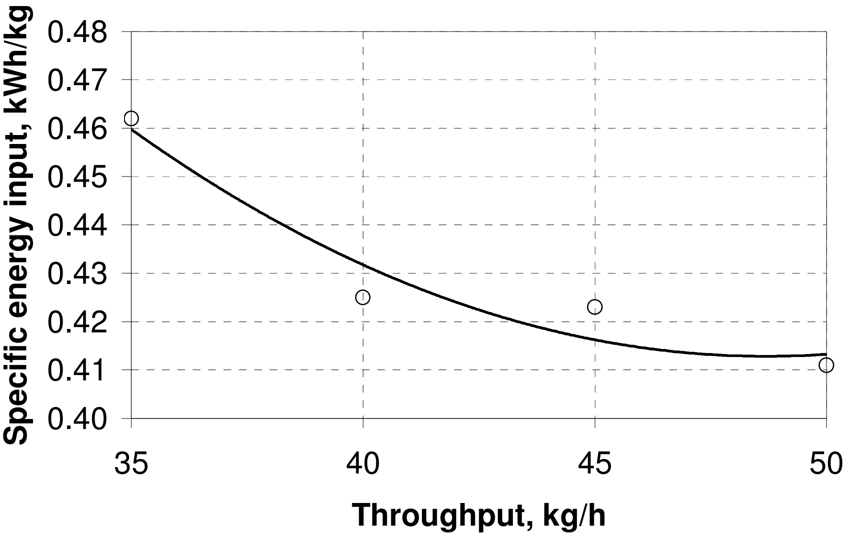


Figure 5-15. Specific energy input as a function of throughput

With increase in throughput and screw speed, the residence time decreases and the outlet temperature increases as shown in Figure 5-16. The increase in throughput and screw speed reduces the residence time of the compound inside the extruder. At the same time, the increase in throughput and screw speed leads to increase in outlet temperature of the compound. When the screw speed increases, the amount of heat introduced into the rubber compound increases due to shear and the temperature of the exiting compound increases also. The shear heat comes from two sources; one is the scraping of the rubber in contact with the barrel wall by the screw, and the other is the individual layers of polymeric materials sliding over or under each other together with the additives and fillers during the laminar flow, generating viscous heat. In the flow, the molecular friction or resistance in one layer as it flows over the molecules in another layer causes heat to be generated which leads to reduction in viscosity and increase in outlet temperature. The increase in compound temperature is also due to the reverse kneading elements which increase the fill factor in mixing sections. Depending on the mixing section and the viscous shear heat generated, the compound temperature as well the barrel section temperatures differ.

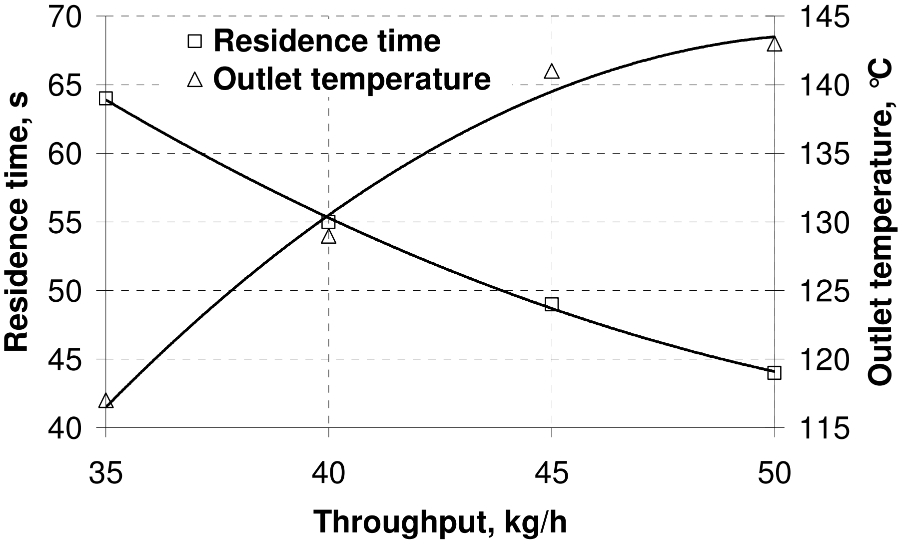


Figure 5-16. Residence time and outlet temperature as a function of throughput

As the die is kept open, the pressure drop is zero in the die barrel section. But the pressure drop is developed in the mixing sections due to reverse kneading elements. This leads to successive distributive and dispersive mixing during the flow of the rubber compound. The viscous shear heat generated can be controlled by the rate of cooling the barrel but also by the degree of fill. If the degrees of fill in the kneading sections are low, they lead to lower outlet temperatures and vice versa. Hence, degrees of fill in kneading sections are directly dependent on amount of throughput and screw speed. A balance of throughput rate and screw speed under controlled filling degree with this screw configuration leads to controlled outlet temperature.

With a throughput of 50 kg/h, the outlet temperature reaches 143 °C. From the experiments from internal mixer, the compound properties remains consistent below 140 °C and above 140 °C the cross-linking reaction takes place, if the cross-linking agents are mixed together in one mixing step. As the outlet temperature reached 143 °C, the experiments in twin screw extruder were stopped with a maximum throughput of 50 kg/h. The compound properties such as mooney viscosity and scorch time are shown as a function of throughput in Figure 5-17. The mooney viscosity stays almost constant and there is little increase in scorch time. This shows that there were no pre-mature scorching upto a throughput rate of 50 kg/h.

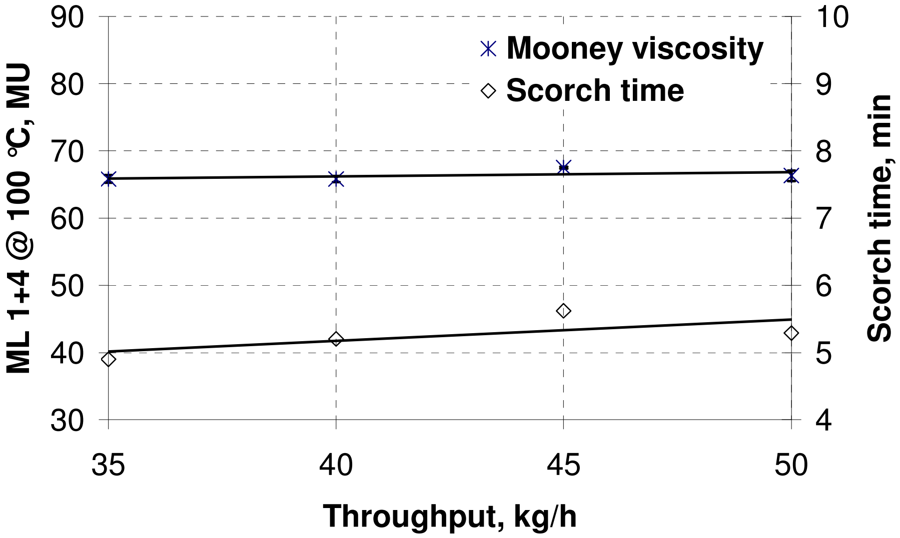


Figure 5-17. Mooney viscosity and scorch time as a function of throughput

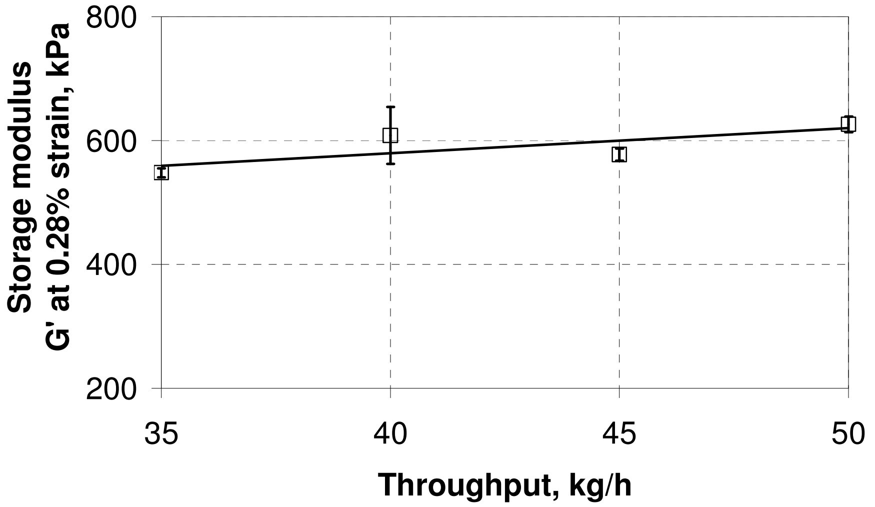


Figure 5-18. Storage modulus at 0.28% strain of the compound as a function of throughput

The storage modulus at low amplitude is used to study the filler-filler interaction which is regularly used to evaluate the micro-dispersion. As shown in Figure 5-18, with increase in throughput, the values show an almost constant storage modulus at low amplitude. This shows that the filler-filler interaction remains constant even under shorter residence times and higher throughput rates.

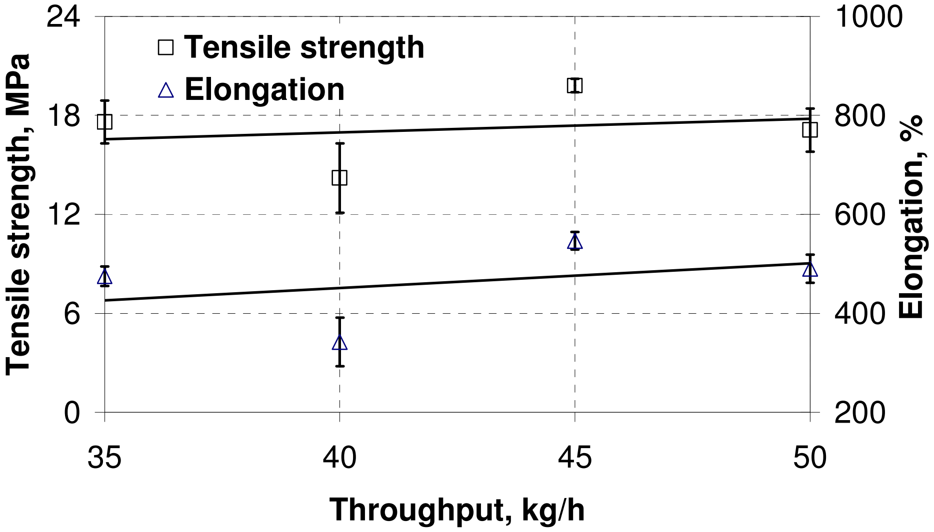


Figure 5-19. Tensile strength and elongation as a function of throughput

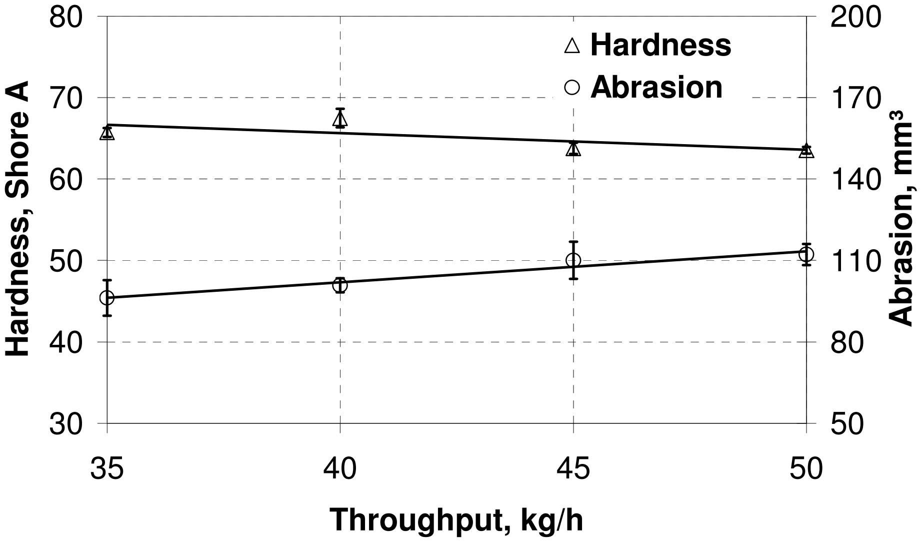


Figure 5-20. Hardness and abrasion as a function of throughput

The vulcanizate properties such as tensile strength and elongation as a function of throughput are shown in Figure 5-19. The tensile strength and elongation are almost constant with increase in throughput. This can be comparable by an almost constant hardness and abrasion as shown in Figure 5-20. This shows that the vulcanizate properties remain almost constant across the entire feed range indicating a consistent quality. Also, the compound and vulcanizate properties correlate well with the one step reference mixture mixed in the internal mixer.

5.1.2.4. Development of two step continuous mixing process

The two step continuous mixing process is developed to increase the throughput in twin screw extruder. As the throughput in one step continuous mixing process is limited to 50 kg/h due to the outlet temperature of 143 °C, experiments were carried out to increase the throughput further by using two step continuous mixing process. The main causes for the throughput limitation are the development of pre-mature scorching due to mixing of silane based compounds and cross-linking agents at high mixing temperatures. For mixing cross-linking agents in one mixing step, the outlet temperature is limited to 140 °C as discussed in chapter 5.1.1. During the mixing of E-SBR/silica/silane compound without cross-linking agents, the sulphur groups in silane will start to react with the rubber forming sulphur bonds with the rubber. This also makes pre-scorching of the rubber and lead to poor compound and vulcanizate properties. The silane used in RFC-1 is a disulfane (Si-75) having high temperature stability of 170 °C [146, 158]. It is suggested that during mixing of rubber compounds, the maximum mixing temperature of the disulfane based compounds should not exceed 170 °C. But, this is allowed only when the cross-linking agents are not mixed together. Hence, in the twin screw extruder, the possibility for pre-mature scorching due to cross-linking agents at higher outlet temperatures can be avoided by mixing the cross-linking agents in the second mixing step, for example in two roll mill. This allows mixing the RFC-1 compound in the extruder at throughputs higher than 50 kg/h and outlet temperatures higher than 143 °C.

Figure 5-21 shows a schematic representation of two step continuous mixing process. The screw configuration used here is screw configuration C consisting of reverse kneading elements as mixing elements. The first mixing step takes place in twin screw extruder where RFC-1 along with ZnO, SA, 6PPD, Wax, DPG were dosed in barrel section one and oil in barrel section two. Venting is provided in barrel sections eight and eleven for the volatile gases. During the second mixing step, the mixed compound from the extruder and cross-linking agents such as CBS, TBzTD and S are mixed together with help of a two roll mill. The experiments are carried out in the extruder with throughputs of 50 to 70 kg/h increased in steps of five with subsequent increase in screw speed (Table 5-3). The throughput and screw speed were considerably increased under relatively constant filling degree of 21.5 %. The extruder barrels were cooled to 20 °C by providing cooling by a high water flow rate of 3500 l/h and all the trials were taken without the die. In two roll mill, the materials are then mixed with cross-linking agents at 50 °C for five minutes. After mixing, the material is sheeted out from the two roll mill.

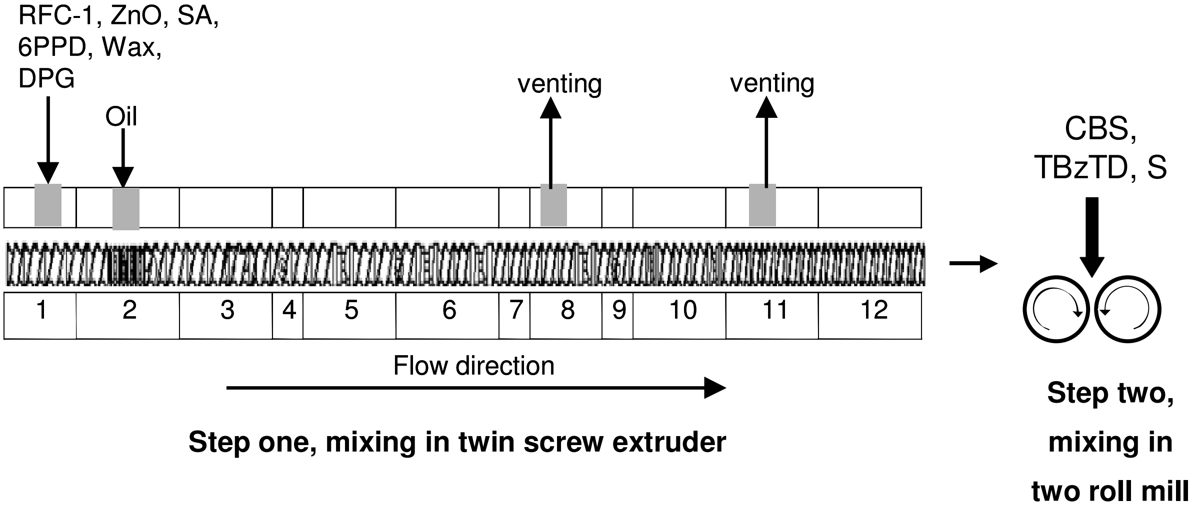


Figure 5-21. Schematic representation of two step continuous mixing process

Table 5-3. Process parameters

Parameters	**Data**				
Throughput (kg/h)	50	55	60	65	70
Screw speed (1/min)	260	280	300	320	340

The specific energy input with increase in throughput and screw speed is shown in Figure 5-22. There is a decrease in specific energy input with increase in throughput and screw speed similar to one step continuous mixing process from previous chapter. At 50 kg/h with 260 1/min screw speed, the specific energy input reaches 0.44 kWh/kg. This value is high compared to the value 0.41 kWh/kg from one step continuous mixing process at 50 kg/h with the same screw speed. As the compound in not mixed with cross-linking agents, the viscosity of the compound remains high and hence the specific energy input is high.

The residence time and outlet temperature as a function of throughput are shown in Figure 5-23. With increase in throughput and screw speed, the residence time decreases. The residence time decreases further from 45 s for 50 kg/h to 32 s for 70 kg/h. The amount of time the material spends inside the extruder for mixing reduces drastically with increase in throughput and screw speed. As in the case of internal mixer, the mixing time for conventional silica based compounds is 13 minutes and for Rubber/Filler-Composite based compounds atleast 4 minutes. In case of twin screw extruder, the mixing of RFC based compounds are done in less than a minute.

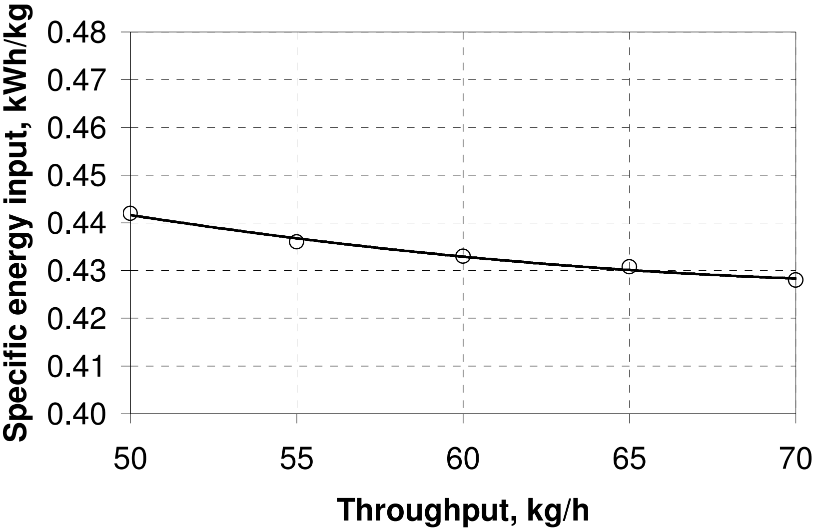


Figure 5-22. Specific energy input as a function of throughput

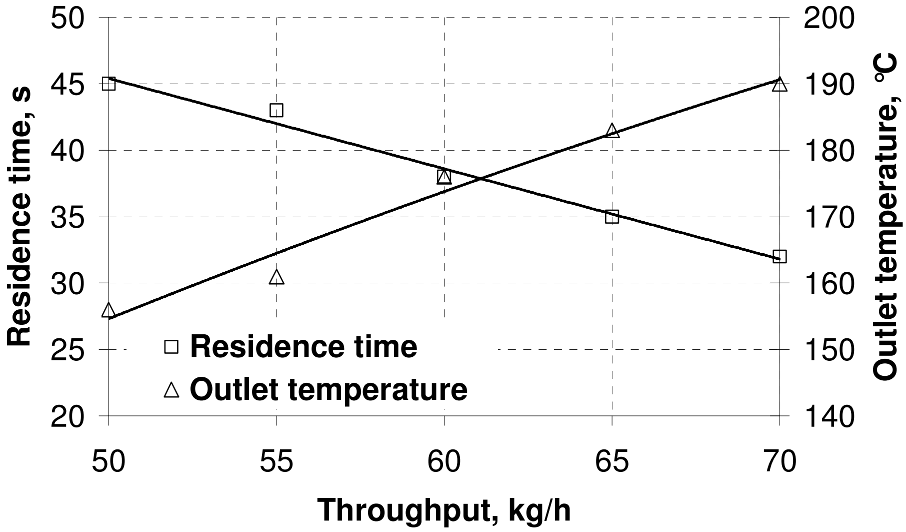


Figure 5-23. Residence time and outlet temperature as a function of throughput

The temperature of the rubber compound during mixing is a critical parameter for the final quality of the vulcanizate. This temperature can be reduced by controlling the extrusion process parameters such as throughput, screw speed and screw design. At a throughput of 50 kg/h, the outlet temperature increases from 143 °C to 155 °C compared to one step mixing process. This drastic increase of 12 °C comes from the development of compressive viscous shear heat without cross-linking agents. In case of one step mixing, the cross-linking agents start melting in barrel section eleven as soon as it comes in contact with the hot rubber compound. As it starts getting mixed, it acts as a lubricant on the surface and there-by lowering the coefficient of friction between the barrel wall and the material and also between the screw and material, leading to lower outlet temperature.

On increasing the throughput in extruder from 50 kg/h to 70 kg/h and screw speed from 260 1/min to 340 1/min, the outlet temperature increases from 155 °C to 190 °C. The compound temperature reaches 190 °C in 32 s residence time. This drastic increase is due to the high throughput and high screw speed although the barrel temperatures were cooled constantly at 20 °C. The rubber compound is subjected to enormous shear and high heat dissipation takes place during mixing. After the material is mixed in extruder, the material is cooled down to 50 °C in the two roll mill for the addition of cross-linking agents. The silane in the RFC-1 compound is a disulfane (Si-75) having high temperature stability of 170 °C. Above this temperature, the silane may undergo reaction with the rubber [158]. The indication of pre-mature scorching could be seen from the mooney viscosity and scorch time. As can be seen in Figure 5-24, the mooney viscosity shows a gradual increase to 70 MU and on the other side, the scorch time increases. If there is a pre-mature scorching happened, the scorch time is supposed to decrease. Hence, it is found that, there is no pre-mature scorching taking place in the extruder upto 70 kg/h.

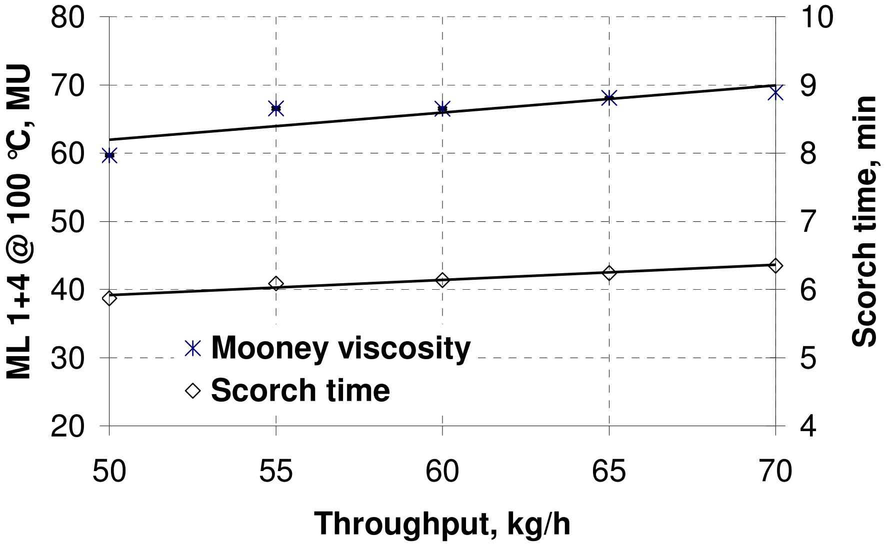


Figure 5-24. Mooney viscosity and scorch time as a function of throughput

The incorporation of cross-linking agents in two roll mill at 50 °C leads to uniform mixing of the chemicals. This also reduces the chance of scorching due to cross-linking agents in the two roll mill. The mooney viscosity and scorch time increases slightly with increase in throughput. The mooney viscosity and scorch time values clearly indicate that the compound is free of any pre-vulcanization reactions. The residence times in the extruder at higher throughputs are very less and hence the there is slight variation in the mooney viscosity and scorch time of the compound. However, the value lies in limit for further processability of the compound.

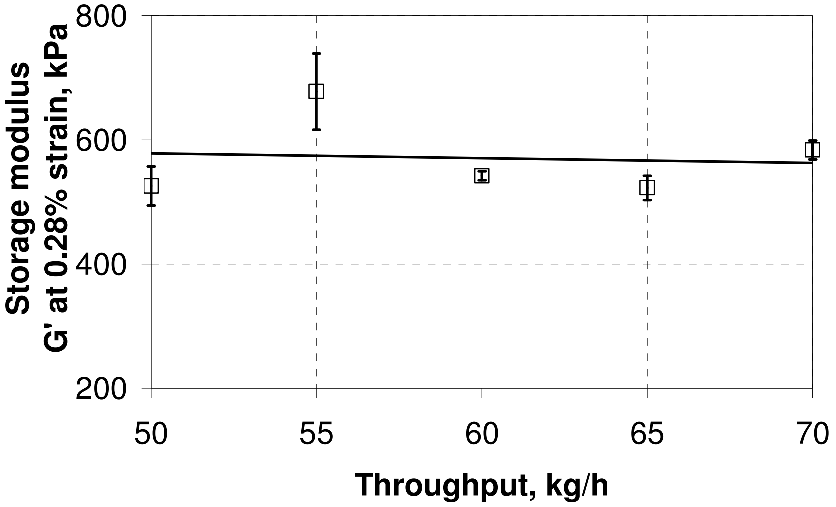


Figure 5-25. Storage modulus at 0.28% strain of the compound as a function of throughput

The filler-filler interaction described by the storage modulus at low strain is shown in Figure 5-25. The storage modulus at 0.28 % strain stays almost constant as well below 600 kPa throughout the entire throughput range. This shows that the filler-filler interaction stays at lower range and hence the degree of dispersion is high. The micro-dispersion is taking place in the twin screw extruder due to the fact that the DPG is mixed with the RFC-1, ZnO, SA, 6PPD, Wax in barrel section one. The addition of oil in barrel section two also plays a major role in mixing. These mixing conditions are accompanied by the optimum screw configuration consisting of reverse kneading elements. The rubber compound is homogenized by the reverse kneading elements leading to optimum filler dispersion. The micro-dispersion of filler is however improved by mixing the compound with cross-linking agents in the two roll mill. The two roll mill brings sufficient shear energy to disperse the cross-linking agents and also the filler. The homogenization of the chemicals in the rubber compound is very important for the consistent quality. With an almost constant storage modulus, the compound indicates uniform filler dispersion as well as no pre-scorching during the extrusion and in two roll mill. Figure 5-26 shows the vulcanizate properties such as tensile strength and elongation as a function of throughput. The tensile strength and elongation values are found to be constant throughout the entire throughput range. At throughput rates upto 70 kg/h, the tensile strength and elongation values show that the rubber chains are free of mechanical and thermal degradation. The values correlates well with one step mixed reference compound mixed in the internal mixer.

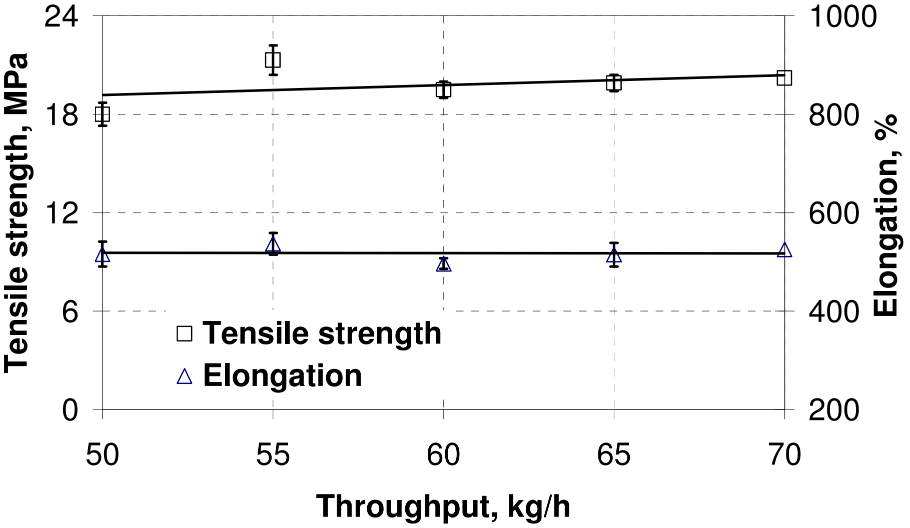


Figure 5-26. Tensile strength and elongation as a function of throughput

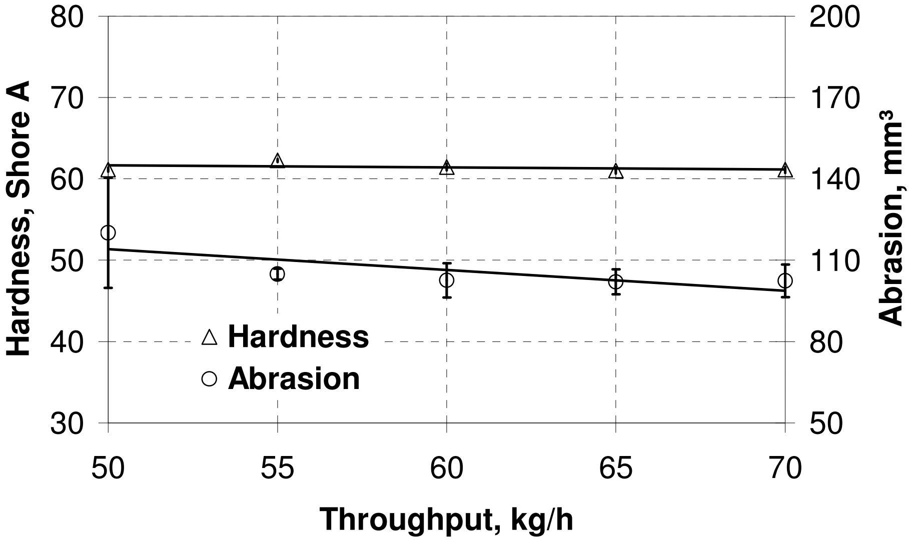


Figure 5-27. Hardness and abrasion as a function of throughput

Figure 5-27 shows the hardness and abrasion as a function of throughput. These properties show very less changes with respect to increase in throughput. The vulcanizate properties show consistent values and hence the quality of the compound and vulcanizate remains unaffected in the above process parameters. This shows that the compound is compoundable in the twin screw extruder up to 70 kg/h without the problem of pre-scorching and without much deviation in the vulcanizate properties.

5.1.2.5. Investigation of extruder filling degree

5.1.2.5.1. Calculation of extruder filling degree

The investigations were carried out to study the influence of filling degree of the extruder on mixing efficiency. Having a constant screw configuration and dosing assembly, the filling degree in the extruder can be varied in two ways: by varying the throughput at constant screw speed and by varying the screw speed at constant throughput. Figure 5-9 (D) shows the schematic representation of the one step continuous mixing process for the production of RFC-1 based rubber compound. The extruder barrels were cooled to 20 °C by providing cooling by a high water flow rate of 3500 l/h and all the trials were taken without the die.

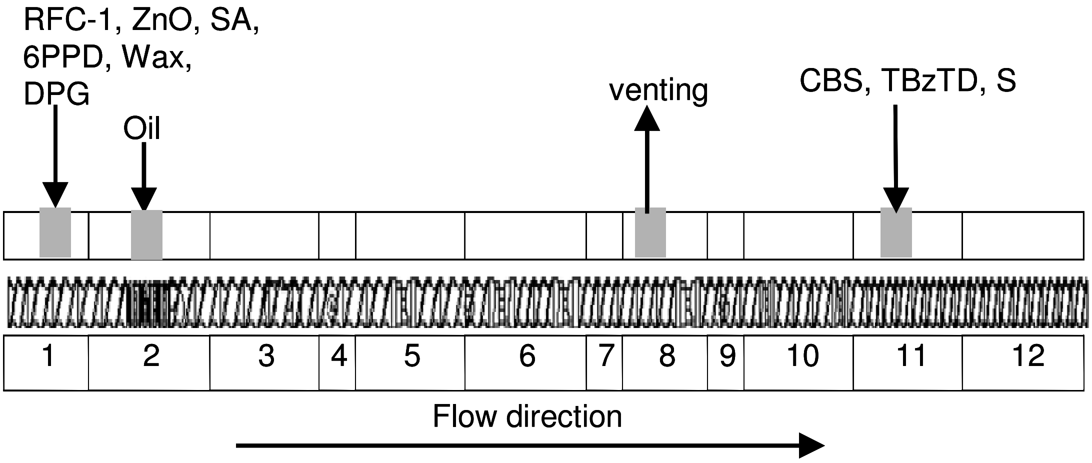


Figure 5-9 (D). Schematic representation of one step continuous mixing process

Here, the filling degree is calculated for the applied extruder excluding the die as:

$$f = \frac{V_m}{V_F} = \frac{\theta\, Q}{V_F\, \rho} \qquad \text{Equ. (27)}$$

where f is the filling degree, V_m is the volume of material inside the extruder, V_F is the empty extruder inside volume, θ is the residence time, Q is the throughput controlled by feeding, ρ is the density of the rubber compound and

$$V_F = V_b - V_s \qquad \text{Equ. (28)}$$

where V_b is the inside volume of the barrel without die and V_s is the volume of the two screws.

In the following, the filling degree is varied by varying the throughput at constant screw speed and by varying the screw speed at constant throughput. The influence of filling degree on material properties is further discussed.

5.1.2.5.2. Effect of varying throughput at constant screw speed

The material properties depend upon how well the rubber, filler and other cross-linking chemicals are mixed. On varying throughput at constant screw speed, the filling degree, residence time, specific energy input and outlet temperature of the compound are also changing. This study is focussed to understand the influence of varying throughput at constant screw speed on machine parameters as well as its effect on material properties. Hence, a constant screw speed of 180 1/min is selected and the throughput is varied from 25 kg/h to 40 kg/h in steps of 5 kg/h.

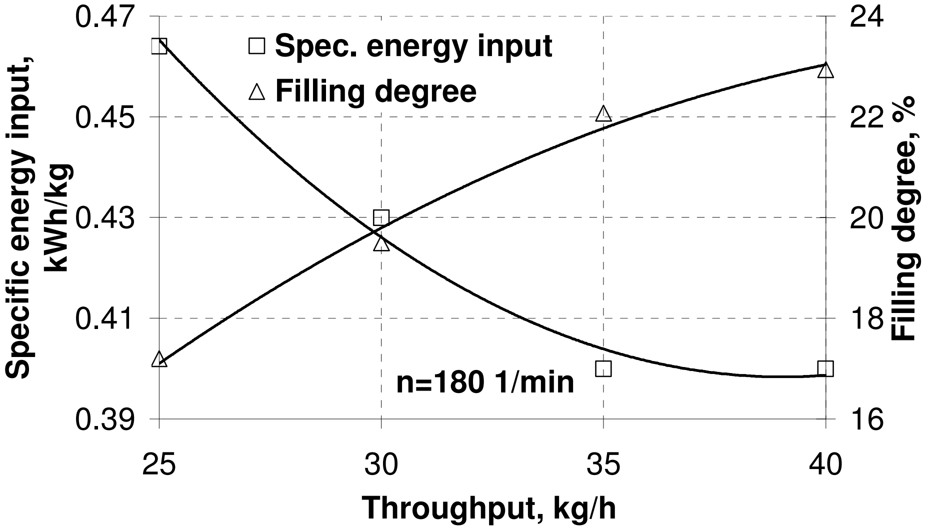


Figure 5-28. Specific energy input and filing degree as a function of throughput

Figure 5-28 shows the specific energy input and filling degree with respect to throughput. With increasing throughput at a constant screw speed, the specific energy input decreases. On the other hand, with increasing throughput at constant screw speed, the filling degree increases. With a throughput of 25 kg/h, the overall filling degree reaches 17 %. On increasing the throughput to 40 kg/h, the filling increases to 23 %. The filling degree is very less as it is a rubber material and there is no real melting takes place like in the case of thermoplastic materials. The rubber compound together with filler is a highly viscous material and hence the filling degree is less. On increasing the filling degree above 23 %, the torque in extruder reaches more than maximum set value and leads to stopping the machine. Figure 5-29 shows residence time and outlet temperature as a function of throughput. With increase in throughput at constant screw speed, the residence time decreases. The residence time decreases from 72 s at 25 kg/h to 60 s at 40 kg/h. This is due to that the residence time in each reverse kneading sections decreases with increase in throughput and hence the mean residence time decreases. The free volume in the extruder decreases and the material is forced to move faster with increase in throughput. The outlet temperature reaches 92 °C at 25 kg/h and increases to 127 °C at 40 kg/h. With higher throughput, the material undergoes compression leading to increase in outlet temperature.

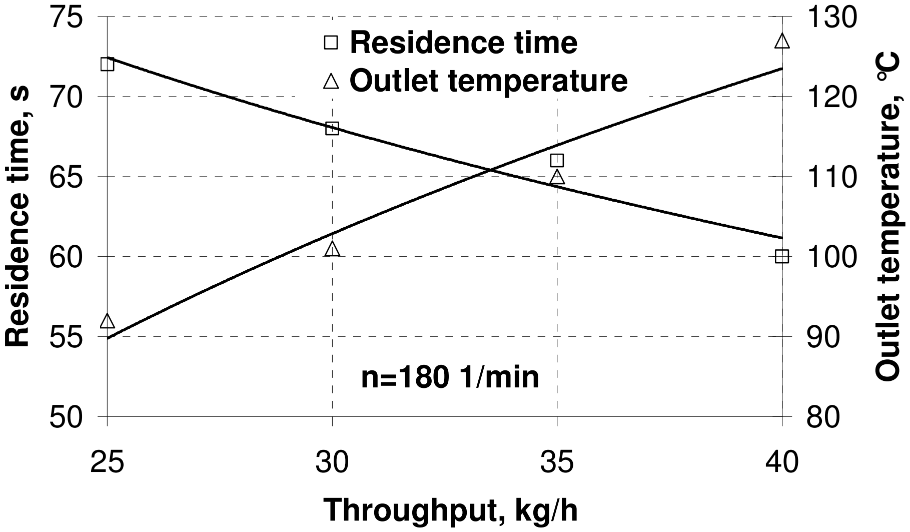


Figure 5-29. Residence time and outlet temperature as a function of throughput

The mooney viscosity and scorch time are shown as a function of throughput in Figure 5-30. The mooney viscosity and scorch time stays almost constant throughout the entire throughput range. This shows that the decrease in residence time to 60 s and increase in outlet temperature upto 127 °C does not show any variation on material property. As the temperature for cross-linking reaction lies around 140 °C for one step continuous mixing, it does not affect mooney viscosity and scorch time. On decreasing the throughput below 25 kg/h at a constant screw speed of 180 1/min, the cross-linking agents cannot be mixed properly. Here, the filling degree becomes less than 17 %. On increasing the throughput above 40 kg/h at a constant screw speed of 180 1/min, the torque of the machine reaches maximum set value and the machine stops. Here the filling degree is above 23 %. Hence, at a constant screw speed of 180 1/min, the experimental window is left to a throughput range of 25 kg/h to 40 kg/h.

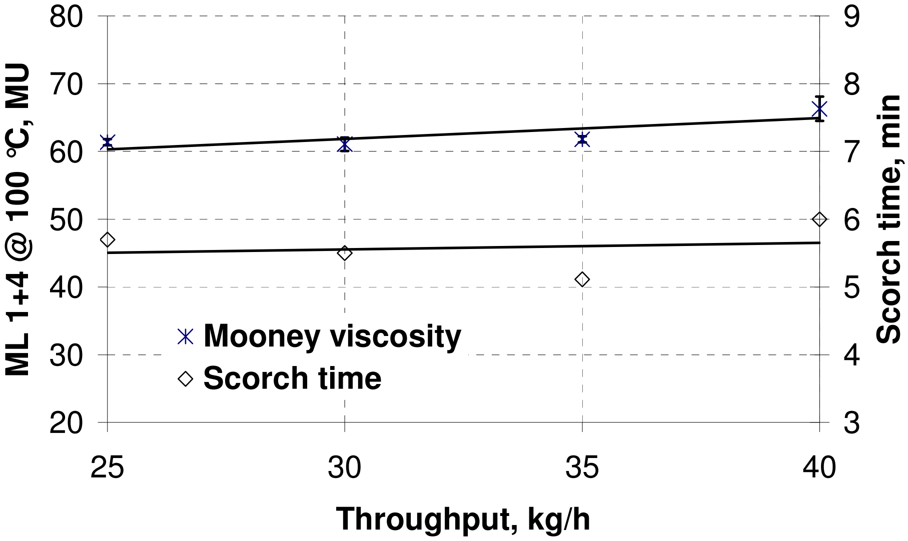


Figure 5-30. Mooney viscosity and scorch time as a function of throughput

The effect of filling degree on filler dispersion is measured by the storage modulus at low strain where it is used to study the filler-filler interaction. As shown in Figure 5-31, with increase in throughput at constant screw speed, the values show a small increase in the storage modulus at low strain. As the filler dispersion is also a function of mixing time, the decrease in residence time may lead to increase in filler-filler interaction. The optimum storage modulus G' at low strain can be achieved at a throughput of 25 kg/h and at a screw speed of 180 1/min.

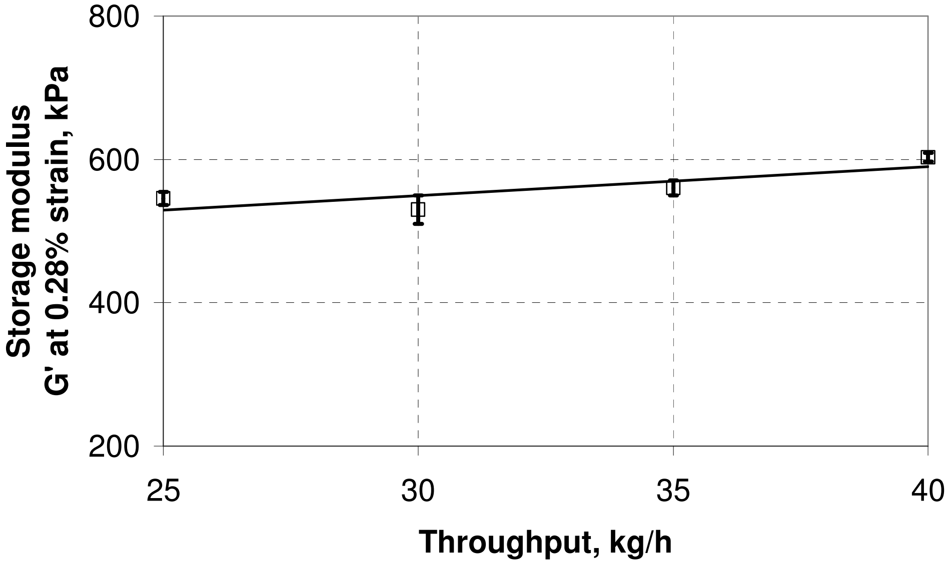


Figure 5-31. Storage modulus at 0.28% strain of the compound as a function of throughput

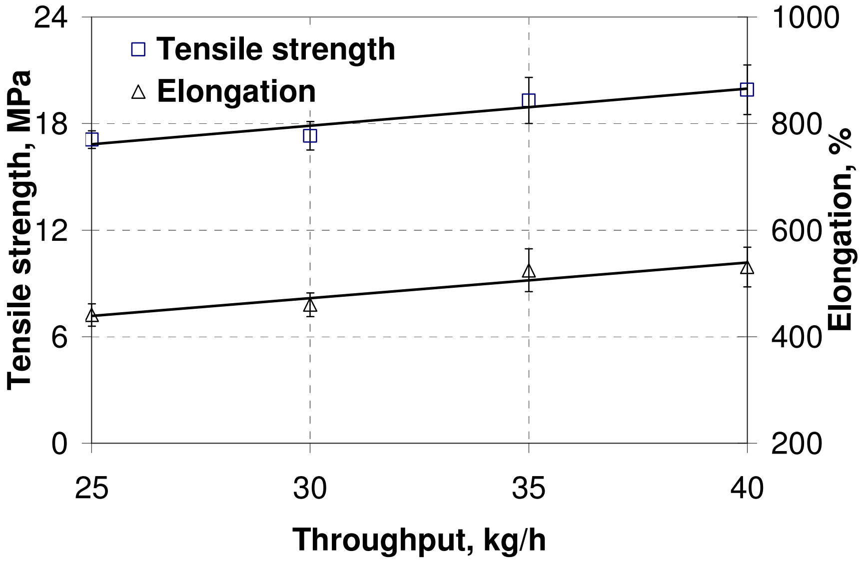


Figure 5-32. Tensile strength and elongation as a function of throughput

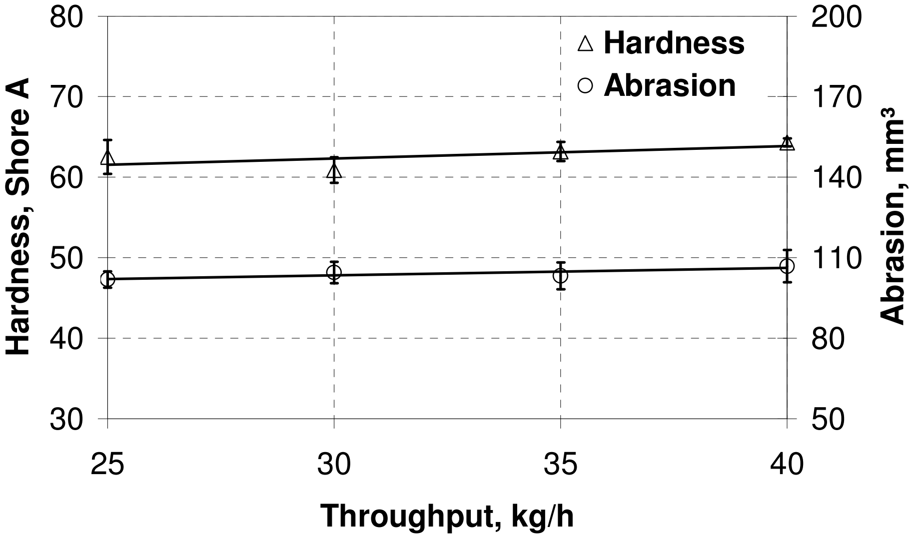


Figure 5-33. Hardness and abrasion as a function of throughput

The vulcanizate properties such as tensile strength and elongation are tested and shown as a function of throughput in Figure 5-32. The tensile strength and elongation increases slightly with increase in throughput. The hardness and abrasion as a function of throughput are shown in Figure 5-33. The vulcanizate properties remain relatively constant at the same level across the entire feed range and the variations in properties are negligible.

5.1.2.5.3. Effect of varying screw speed at constant throughput

Here, the filling degree were varied by keeping the throughput constant at 40 kg/h and varying the screw speed from 180 1/min to 240 1/min in steps of 20 1/min. Figure 5-9 (D) shows the schematic representation of the one step continuous mixing process. Figure 5-34 shows the specific energy input and filling degree with respect to screw speed. It shows that with increasing screw speed at constant throughput, the specific energy input increases. At the same time, with increasing screw speed at constant throughput, the filling degree decreases. In comparison to the previous chapter, the filling degree can be increased or decreased by varying the throughput at constant screw speed. Here, the filling degree can be decreased or increased by the varying the screw speed at constant throughput.

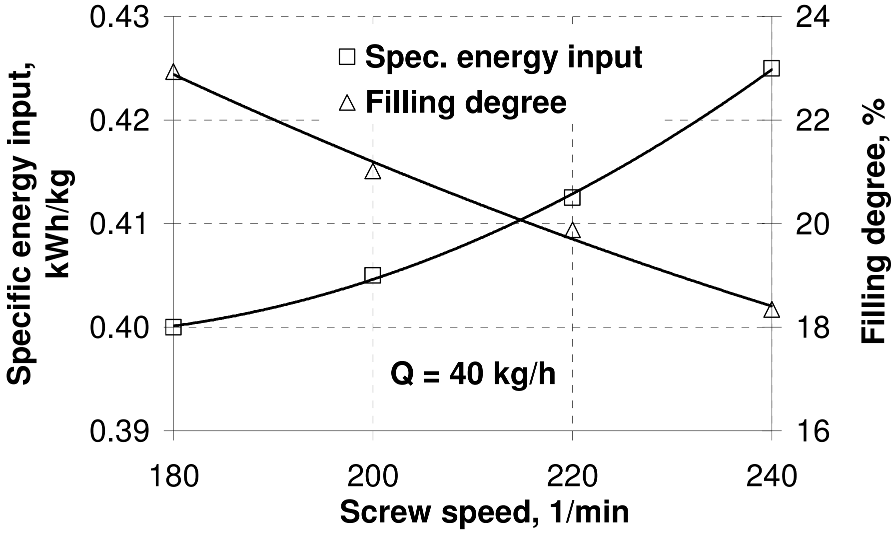


Figure 5-34. Specific energy input and filling degree as a function of screw speed

Figure 5-35 shows residence time and outlet temperature as a function of screw speed. With increase in screw speed at constant throughput, the residence time decreases. The residence time decreases from 60 s at 180 1/min to 48 s at 240 1/min. Here, the residence time in kneading sections decreases with increase in screw speed and hence the mean residence time decreases. The free volume in the extruder increases and the material is forced to move faster with increase in screw speed. The outlet temperature reaches 127 °C at 180 1/min and increases to 135 °C at 240 1/min. Although the filling degree is decreasing, with higher screw speed the outlet temperature increases.

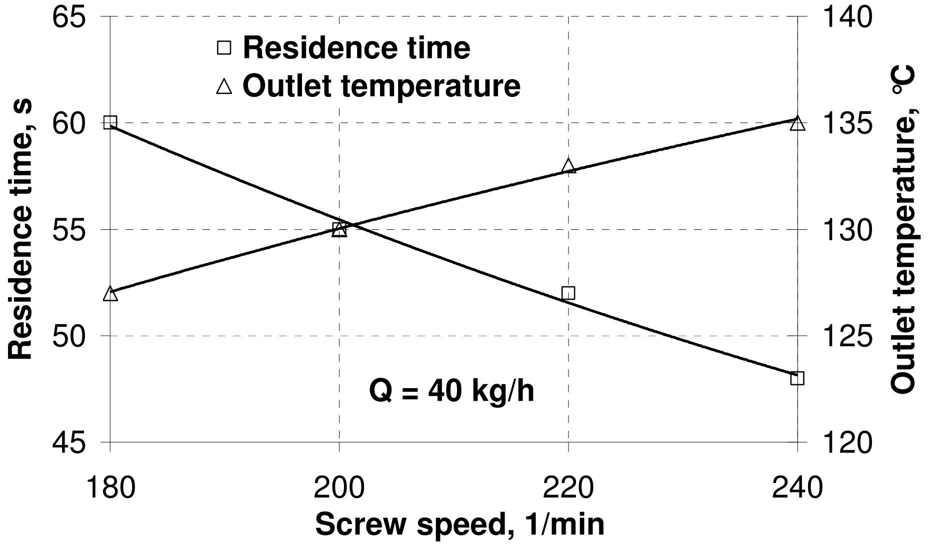


Figure 5-35. Residence time and outlet temperature as a function of screw speed

The mooney viscosity and scorch time are shown as a function of screw speed at constant throughput in Figure 5-36. The mooney viscosity and scorch time values stay almost constant. On increasing the screw speed above 240 1/min, the cross-linking agents cannot be mixed properly. The screw speed is too high and the filling degree becomes lower. On decreasing the screw speed below 180 1/min, the torque of the machine reaches maximum set value and the machine stops. This is similar in the previous chapter where the throughput is increased under constant screw speed.

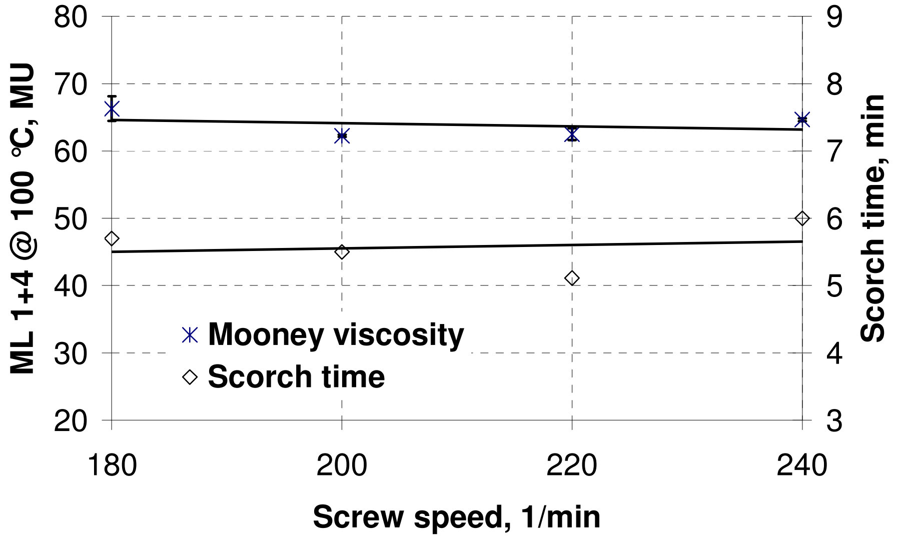


Figure 5-36. Mooney viscosity and scorch time as a function of screw speed

Hence, the experimental window left to a screw speed range of 180 1/min to 240 1/min at a constant throughput of 40 kg/h. The variation of screw speed can also be done at higher throughputs, but the outlet temperature should be taken into consideration. At higher outlet temperatures, the compound may undergo pre-mature scorching. The screw speed and throughput should be optimally selected in order to obtain lower outlet temperature and at the same time, achieving optimum material properties. Here, the experiments were carried out to show the optimum parameters for obtaining optimum material properties.

The degree of filler dispersion measured by the filler-filler interaction is shown in Figure 5-37. With increase in screw speed at constant throughput, the values show a small increase in the storage modulus at low strain. As discussed in the previous chapter, the filler dispersion is a function of mixing time. On increasing the screw speed, the residence time decreases and it may lead to increase in filler-filler interaction. The tolerance in variation of filler-filler interaction is almost constant with increase in screw speed.

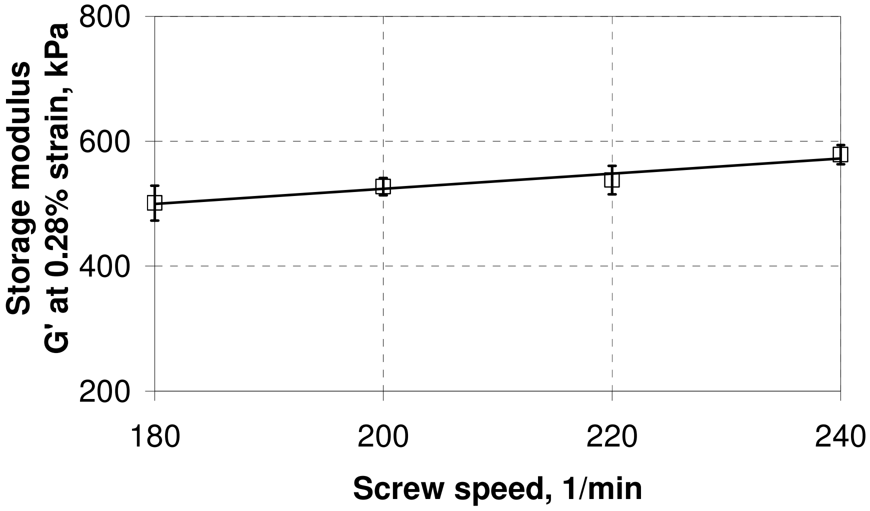


Figure 5-37. Storage modulus at 0.28% strain of the compound as a function of screw speed

The tensile strength and elongation as a function of screw speed are shown in Figure 5-38 and the hardness and abrasion as a function of screw speed are shown in Figure 5-39. The vulcanizate properties remain almost constant at the same level across the entire screw speed range. This shows that within this experimental window, the compound properties and vulcanizate properties are found to be optimum. The calculated filling degree in the extruder varies in-between 17 % to 23 %. Below or above this level, the rubber compound cannot be mixed properly.

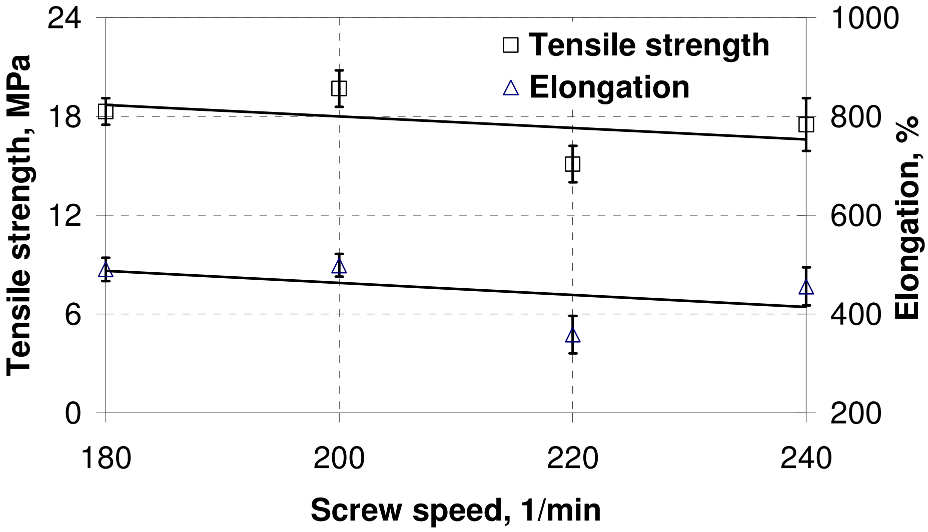


Figure 5-38. Tensile strength and elongation as a function of screw speed

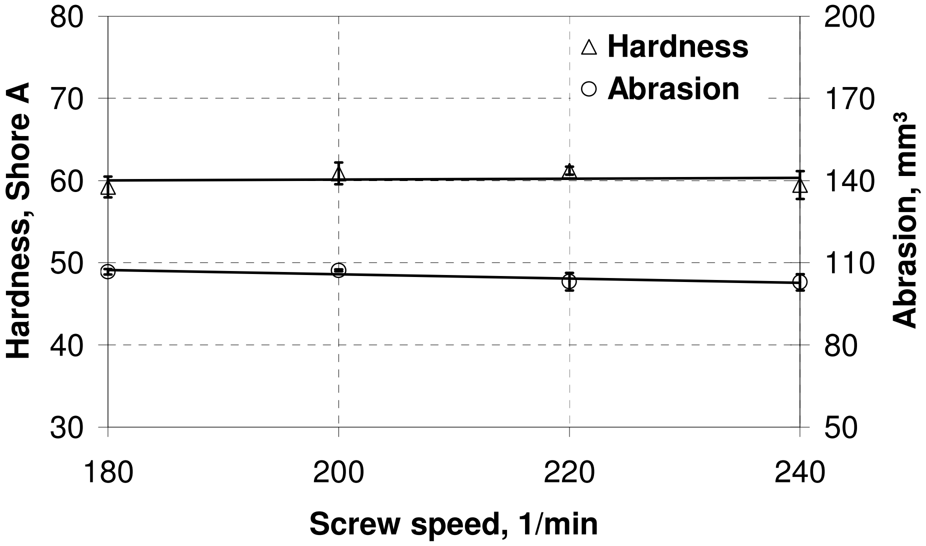


Figure 5-39. Hardness and abrasion as a function of screw speed

Less than 17 % filling degree, the cross-linking agents in barrel section eleven finds difficulty to get mixed and above 23 % filling degree, the machine torque reaches above maximum set value leading the machine to stop. Hence, if the outlet temperature is within the limit, optimum compound and material properties can be achieved between the filling degree ranges of 17 % to 23 %.

5.1.3. Development of process simplification

The continuous mixing process comprises of screw configuration, dosing assembly, carefully selected pre-blend (in case of chemicals) and optimum machine parameters. In case of rubber compounds, there are several chemicals need to be mixed together. These chemicals need to be made either as a pre-blend or should be supported by individual dosing systems. This leads to more parameters which should be controlled and it makes continuous mixing process complicated. In order to prevent complication, the best possible way is to reduce the number of dosing systems. For that, more pre-blend of chemicals should be made. As the RFC is a pre-blend of rubber and filler, the mixtures in the pre-blend can be extended to also some chemicals. Hence, the finished compound RFC (FC-RFC) is developed as a mixture of several ingredients mixed during the production of RFC compound as shown in Figure 3-28.

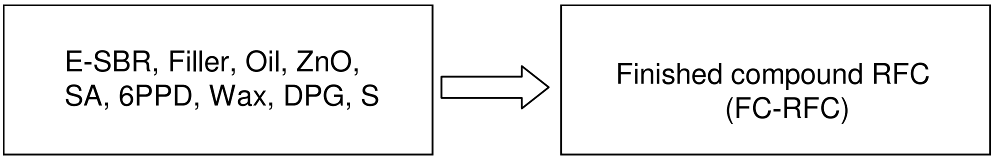


Figure 3-28. Schematic diagram of production of silica based Finished Compound Rubber/Filler-Composite

The FC-RFC is developed to process rubber compound much easier in twin screw extruder. The FC-RFC is a free flowing granulated material with a size of 3-5 mm. The ingredients in FC-RFC include some cross-linking agents such as DPG and sulphur. In our further discussions, FC-RFC will be referred as RFC-2. RFC-2 is easily dosable in the twin screw extruder as most of the components are premixed and granulated. The number of dosing systems can be reduced and there will be high degree of dispersion between the components.

Figure 5-40 shows the schematic representation of one step continuous mixing of RFC-2 compound. Here, three dosing systems are necessary for dosing RFC-2, oil and for CBS and TBzTD. As the RFC-2 is a premixed compound, it requires only one dosing system. The RFC-2 is dosed in barrel section one and oil is dosed separately by a volumetric dosing pump in barrel section two. The CBS and TBzTD were made as a pre-blend and dosed in barrel section eleven. The screw configuration is similar to the previous chapter consisting of six reverse kneading elements in each of the screw configuration.

Figure 5-41 shows the schematic representation of two step continuous mixing of RFC-2 compound. Here, the RFC-2 and oil are mixed in the twin screw extruder. Venting is provided in barrel sections eight and eleven for the volatile gases. The cross-linking agents, CBS and TBzTD were mixed with the help of a two roll mill in step two at 50 °C for five minutes. After mixing, the material is sheeted out from the two roll mill. The experiments were carried out in both cases at 50 kg/h with a screw speed of 260 1/min. The extruder barrels were cooled to 20 °C by providing cooling by a high water flow rate of 3500 l/h and all the trials were taken without the die.

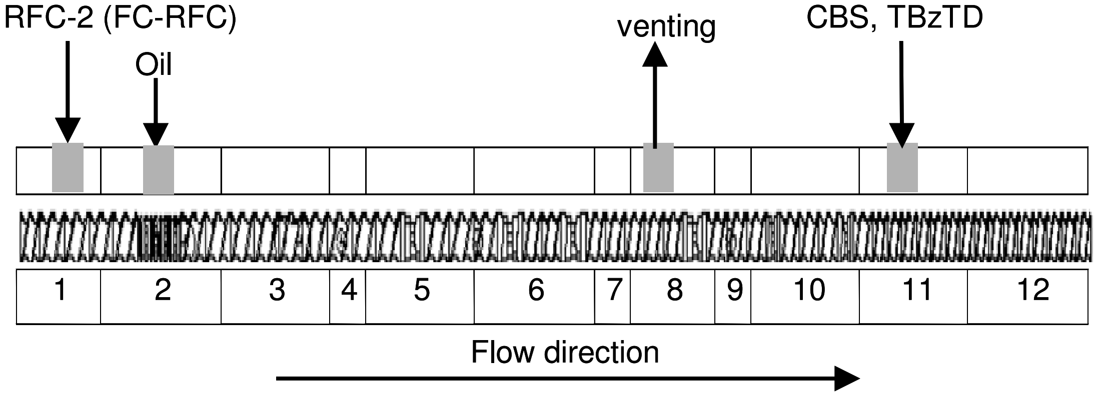


Figure 5-40. Schematic representation of one step continuous mixing of FC-RFC

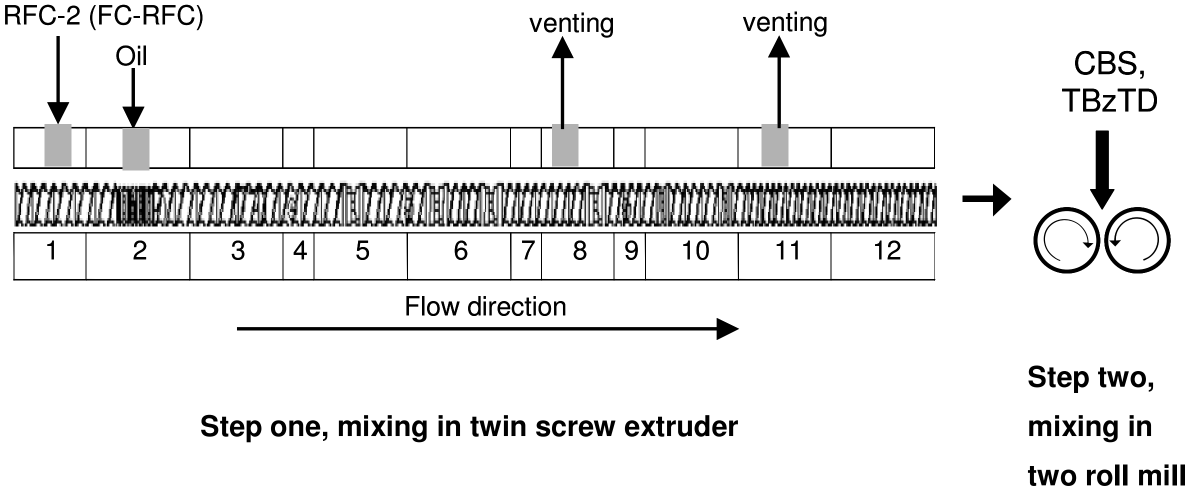


Figure 5-41. Schematic representation of two step continuous mixing of FC-RFC

The compound and vulcanizate properties obtained by one step and two step continuous mixing processes are shown in Table 5-4. The outlet temperature from the extruded compound reaches 136 °C for one step continuous mixing process and increases to 155 °C in case of two step continuous mixing process. This is similar as discussed in chapter 5.1.2.3. in one step and 5.1.2.4. in two step continuous mixing process. The addition of CBS and TBzTD in barrel section eleven reduces the outlet temperature in one step mixing. The mooney viscosity reaches a value of 71.3 MU for one step and 76.4 MU for two step mixing. The scorch time reaches 5.6 minutes for one step and 6.3 minutes for two step continuous mixing. The filler-filler interaction measured by storage modulus at low strain also shows a value of 648.4 kPa for two step mixing compared to 646.7 kPa for one step mixing. This shows that all the compound properties of two step continuous mixing process is lying higher than the one step continuous mixing process. In case of vulcanizate properties, similar deviations can be seen.

Table 5-4. Compound and vulcanizate properties

Properties		**One step mixing**	**Two step mixing**
Screw speed	[1/min]	260	260
Throughput	[kg/h]	50	50
Outlet temp.	[°C]	136	155
ML 1+4 (100 °C)	[MU]	71.3	76.4
Vulcameter ΔS'	[dNm]	13.5	13.1
Scorch time	[min]	5.6	6.3
G' at low strain at 60 °C	[kPa]	646.7	648.4
Hardness	Shore A	63.7	64.3
Tensile strength	[MPa]	22.2	23.2
Elongation	[%]	689.3	622.9
DIN Abrasion	[mm^3]	125	103

The properties remain high quality irrespective of one step or two step continuous mixing process. Thanks to the fact that RFC-2 consists of several ingredients as a pre-blend. This leads to reduction in dosing systems and thus simplifies the process configuration. Additionally, it has homogeneous dispersion of the filler together with the ingredients which leads to the production of high quality rubber compound.

5.2. Mixing of E-SBR based Rubber/Filler-Composite and bale BR blends

The developments of new polymeric materials are basically focussed on minimum cost but also in achieving desired material properties. Hence, polymers are often blended to achieve a balance of properties for successful performance of the product [153-155]. A tire is an representative example of such a complex balance of properties. In tire based compounds, the compound has to be soft and elastic to conform to the road surface and at the same time, it has to be stiff and strong to bear load and be abrasion resistant [158]. Passenger car tire treads are a mixture of rubber blends such as E-SBR/BR, NR/BR and especially S-SBR/BR blends [159]. Blending of unsaturated rubbers, for example, SBR is highly recognised to obtain better wet grip for high performance tires when styrene content is more than 23.5 % [160]. Since different elastomers have different types of responses to stress, required properties can be achieved only by a combination of selected elastomers.

The main objective of an industrial mixing process is production of materials having the desired properties. A number of mixing procedures have been developed over the years to control more precisely the different aspects of overall phase morphology, filler distribution, homogeneity and interaction between different components of rubber blends [161]. Rubber-rubber blends can be prepared by a variety of methods namely by latex or solution blending, during synthesis and by conventional mechanical mixing [162]. Commercial rubber operations employ batch mixing as the rubber is usually obtained in large bales [163-166]. Especially in the manufacturing of tires, batch mixing is used with optimum productivity by increasing the rotor speed as well as the filling degree. Various studies were carried out on rubber mixing in internal mixer [167-169].

This investigation is aimed on development of a new mixing method for the production of rubber blend by using continuous mixing aggregates. Continuous mixing aggregates such as twin screw extruder needs free flowing raw materials and hence RFC based on E-SBR, a free flowing raw material is used. This material can be easily fed in the twin screw extruder. But, bale rubber is difficult to feed in twin screw extruder. Hence, a bale BR rubber made as pre-batch stripes can be fed through a side feeding system into the twin screw extruder. This side feeding system consists of a combination of transfermix extruder and gear pump. The bale based BR is then blended with E-SBR (RFC) in the twin screw extruder. The objective is to show the development of process configuration such as combination of transfermix extruder and gear pump, together with the twin screw extruder as well as sequence of feeding the ingredients including cross-linking agents for the continuous production of rubber blend.

5.2.1. Materials and compound manufacture

The formulation of E-SBR based RFC-3 is shown in Table 4-9. The butadiene rubber (Buna CB 24) is a commercially available grade consists of 98 % cis-1,4 butadiene content. The filler used is highly dispersible silica (Ultrasil 7000 GR, Degussa AG) same as the filler used in E-SBR based RFC-3. For silanization of silica, TESPD as coupling agent is used. The final formulation of E-SBR and BR rubber based compound is shown in appendix formulation 2 and 3.

5.2.2. Discontinuous mixing of E-SBR/BR blend

The E-SBR/BR blend is made in a ratio of 80 parts E-SBR and 20 parts BR and mixed in a 5 l laboratory internal mixer. The formulation and mixing procedure for bale E-SBR and bale BR is shown in appendix, formulation 2. The formulation and mixing procedure for E-SBR based RFC and bale BR is shown in appendix, formulation 3. As the water content in Ultrasil 7000 GR is higher than Ultrasil 7000 FC, the filler content is slightly increased in BR pre-batch. Table 5-5 shows the results for discontinuously mixed rubber blend.

Table 5-5. Properties of E-SBR/BR blend produced by discontinuous mixing

Mixing aggregate	**Discontinuous mixing**	
Blend	**bale E-SBR + bale BR**	**RFC E-SBR + bale BR**
Mixing steps	3	3
Mixing time [min]	13	13
ML 1+4 (100 °C) [MU]	35	51
Vulcameter ΔS' [dNm]	12.8	15.6
Scorch time [min]	4.7	4.97
G' at low strain at 60 °C [kPa]	322.3	448
Hardness Shore A	58.5	62
σ 100 % [MPa]	1.8	1.5
σ 200 % [MPa]	4.3	3.4
σ 300 % [MPa]	7.7	6.2
Tensile strength [MPa]	17.6	22.3
Elongation [%]	554.7	672.6
DIN Abrasion [mm^3]	91	103

In case of bale rubber blends, the mooney viscosity reaches a value of 35 MU. With RFC and bale based blends, the mooney viscosity reaches 51 MU. The storage modulus G' at low strain (0.28%) shows that, with RFC and bale based blends, the filler-filler interaction is high compared to bale based E-SBR/BR blends. The vulcanizate properties like hardness, tensile strength, elongation and abrasion are higher with RFC based E-SBR and bale based BR blends compared to bale based E-SBR/BR blends. Hence, with similar mixing aggregate and mixing time, the bale based E-SBR/BR compounds show better properties than RFC based E-SBR and bale based BR blends.

5.2.3. Development of continuous mixing process configuration

The continuous mixing of rubber blend is carried out by a combination of co-rotating twin screw extruder and a transfermix extruder coupled with a gear pump. The schematic representation of continuous mixing of E-SBR/BR blend is shown in Figure 5-42. The twin screw extruder is provided by screw configuration C (Figure 5-2). 80 parts of E-SBR (RFC-3) is feed in twin screw extruder and 20 parts of BR pre-batch is feed through transfermix extruder. The mixing procedure employed to make BR pre-batch consists of two steps for completion of silica-silane reaction as indicated in appendix, formulation 3. The BR compound without cross-linking agents is taken after two mixing steps for continuous mixing. After the second mixing step, the BR compound was sheeted out and made into stripes manually in a two roll mill. The stripes are made for feeding in transfermix extruder. The transfermix extruder equipped with a single screw extruder is heated to 80 °C. The E-SBR (RFC-3) together with DPG, ZnO, 6PPD, stearic acid and wax were feeded in barrel section one in the twin screw extruder. Oil is volumetrically dosed in barrel section two by oil dosing pump. The BR pre-batch stripes were feeded in transfermix extruder-gear pump which is coupled to the twin screw extruder in barrel section seven. The cross-linking agents such as CBS, TBzTD and sulphur for the total blend were feeded in barrel section eleven. In order to degas moisture and other volatile gases, a vent is provided in barrel section eight.

The experiment was carried out at a throughput of 35 kg/h and at a screw speed of 200 1/min. The extruder barrels were cooled to 20 °C by providing cooling by a high water flow rate of 3500 l/h and all the trials were taken without the die.

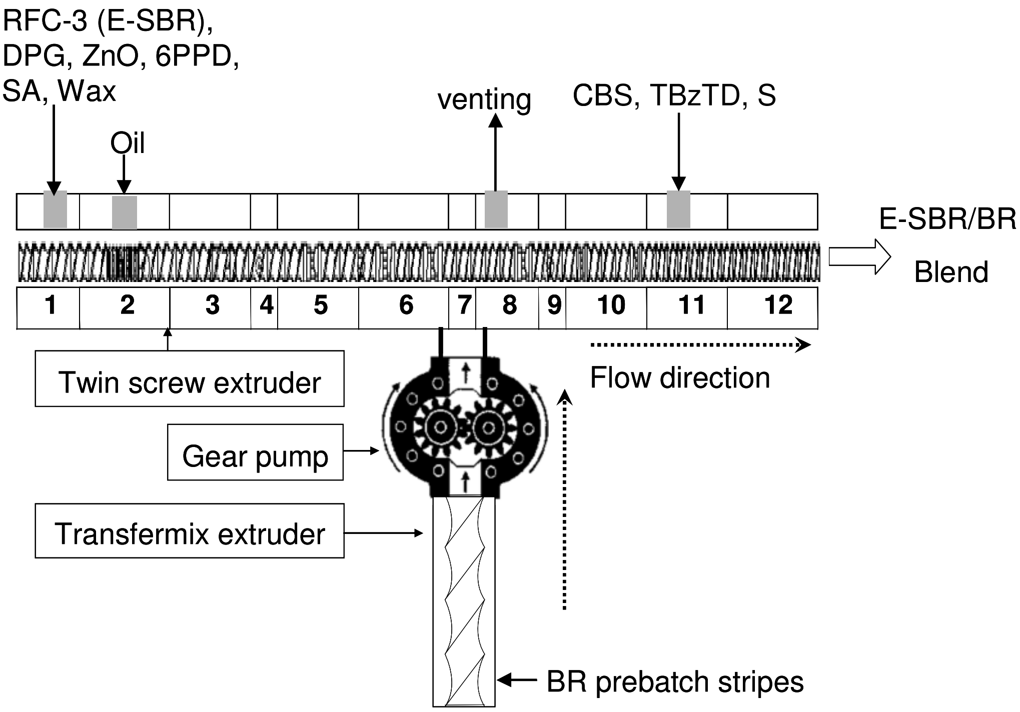


Figure 5-42. Schematic representation of continuous mixing of E-SBR based RFC and bale BR blend

The BR pre-batch with completed silanization reaction, made as stripes were feed through transfermix extruder. The transfermix extruder transports the BR compound and feeds the gear pump. It is then forwarded by the gear pump into the twin screw extruder. The transfermix extruder screw speed is controlled by the chosen inlet pressure set point P_{in} via a Proportional Integral-Differential (PID) controller which regulates the control loop. When changing the throughput of the system by adjusting the gear speed of the pump, the extruder screw speed is automatically regulated in order to deliver the set inlet pressure P_{in} and the corresponding mass flow to the gear pump. Thus the gear pump can run independent of the extruder and various die pressure requirements can be optimised necessary for the system. The minimum required inlet pressure necessary to assure 100 % filling of the gear teeth cavities found to be in the range between 10-30 bar. This is a minimum back pressure required to run the system constantly. As shown in Figure 5-42, the E-SBR and BR is mixed in barrel section seven. In barrel section eleven, the blend is mixed further with the cross-linking agents. The overall throughput from the twin screw extruder and transfermix extruder is calculated together to 35 kg/h and hence the RFC based E-SBR and bale BR blend can be mixed continuously including cross-linking agents in one mixing step.

5.2.4. Influence of continuous mixing on blend properties

The compound and vulcanizate properties of E-SBR/BR blend from continuous mixing are shown in Table 5-6. With this screw configuration and process configuration, it is possible to achieve closely the compound properties attained with the internal mixer as shown in Table 5-5. The main difference is the type of mixing aggregate and mixing time. The outlet temperature reaches to 110 °C at a throughput of 35 kg/h and 200 1/min screw speed. The throughputs can be increased further like in case of E-SBR based RFC-1 compound. The maximum outlet temperature should be shown importance at higher throughputs to avoid pre-mature scorching.

Table 5-6. Properties of E-SBR based RFC and bale BR blend produced by continuous mixing

Properties		**Values**
Throughput	[kg/h]	35
Outlet temp.	[°C]	110
ML 1+4 (100 °C)	[MU]	54
Vulcameter ΔS'	[dNm]	14.5
Scorch time	[min]	4.86
G' at low strain at 60 °C	[kPa]	424
Hardness	Shore A	59
σ 100 %	[MPa]	1.3
σ 200 %	[MPa]	2.7
σ 300 %	[MPa]	5.0
Tensile strength	[MPa]	21
Elongation	[%]	707.7
DIN Abrasion	[mm^3]	109

The mooney viscosity and scorch time are relatively in the same range from continuous and discontinuous mixing. The storage modulus value at low strain of 424 kPa shows that the filler-filler interaction decreases to lower values compared to the reference sample of 448 kPa mixed in the internal mixer. Other vulcanizate properties such as hardness, tensile strength, elongation and abrasion are found to be nearly similar from continuously mixed blend compared to discontinuously mixed blend.

5.3. Mixing of S-SBR and BR based Rubber/Filler-Composite blends

Blends of solution-SBR (S-SBR) and polybutadiene (BR) are used in tire treads to improve wet grip and rolling resistance. In contrast to emulsion-SBR (E-SBR), the molecular weight, molecular weight distribution, microstructure and branching can be controlled well in S-SBR to produce polymers that offer improved end properties. As a component in the polymer blend of car tire treads, grip and rolling resistance can be enhanced by controlling the styrene and vinyl content, especially T_g and shape of the tan delta curve [160]. S-SBR is gradually replacing the E-SBR in special applications and particularly for summer and winter tire treads and low rolling resistance tires especially for the high performance sector. The BR rubbers are highly elastic and have a high degree of resistance to dynamic stress and retain these properties even at extremely low temperatures. S-SBR is often blended with BR to further improve final end properties [159]. Several properties can be improved on blending S-SBR/BR such as resistance to reversion, improved wet grip, crack resistance, low hysteresis, good abrasion resistance and good resilience [158].

Oils and other slippery materials are called plasticizers "a compounding material used to enhance the deformability of a polymeric material". Their function at low levels is to aid in the dispersion of fillers. At higher amounts they reduce uncured compound viscosity, often lower compound cost, reduce vulcanizate stiffness (hardness) and in some cases improve low temperature flexibility. They also improve flow in extrusion and molding by making the uncured compound less elastic and reducing viscosity and friction.

Petroleum oils are one of the major sources of plasticizers. These oils are divided into three categories: aromatic, napthenic and paraffinic. The latter category gives better rebound resilience and lower hysteresis, while aromatics are better for tensile strength and resistance to crack growth. Aromatic oils play a major role in composition of tires because they are required to facilitate the processing of the rubber compounds. Recently, DAE oil (Distillate Aromatic Extract oil), having increased polycyclic aromatic hydrocarbon content were replaced by TDAE oil (Treated Distillate Aromatic Extract oil), having reduced polycyclic aromatic hydrocarbon content, in order to make eco-friendly tires. Hence, a comparative study has been carried out in conventional tire tread recipe to check the properties of rubber with formulations that are identical in all respects except the choice of plasticizer. The results were then compared with newly developed RFC based blends. RFCs based on S-SBR/BR blends used in this study were first of its kind for continuous production.

5.3.1. Discontinuous mixing of S-SBR/BR blend

The blends of S-SBR/BR were made with 70/30 ratio. Two different mixing times, 13 minutes and 4 minutes were taken to compare the effect of mixing time. The formulation and mixing time procedure are shown in appendix, formulation 4 and 5. Table 5-7 shows the compound and vulcanizate properties obtained from bale based and RFC based blends from discontinuous mixing mixed with different types of oils. In this study, the bale blends were made from bale S-SBR and bale BR and the RFC blends were made from S-SBR based RFC and BR based RFC.

Table 5-7. Compound and vulcanizate properties obtained from discontinuous mixing of bale based and RFC based S-SBR/BR blends with different oils

Properties	**TDAE oil**			**DAE oil**		
	Bale blend	**RFC blend**	**RFC blend**	**Bale blend**	**RFC blend**	**RFC blend**
Mixing time [min]	13	13	4	13	13	4
Outlet temp. [°C]	140_{max}	148_{max}	137	140_{max}	140_{max}	137
Spec. ener. inp. [kWh/kg]	1.7	1.7	0.5	1.7	1.7	0.5
ML 1+4 (100 °C) [MU]	37.3	44.2	72.7	30.6	42.6	61.92
Vulcameter ΔS' [dNm]	16.25	14.88	20.65	14.54	14.25	18.55
Scorch time [min]	3.48	2.91	1.09	3.72	3.52	1.67
G' at low strain at 60 °C [kPa]	292.63	263.68	800.27	182.44	254.82	572.88
Hardness Shore A	61.2	58.9	68.5	58.3	59.1	66.1
σ 100 % [MPa]	1.9	1.7	2.5	1.6	1.6	2.2
σ 200 % [MPa]	4.5	4.3	5.5	3.7	3.5	4.5
σ 300 % [MPa]	8.3	8.2	9.1	6.9	6.4	7.4
Tensile strength [MPa]	15.7	15.6	12.6	15.0	14.3	11.8
Elongation [%]	462.3	467.8	392.4	516.6	519.9	453.4

The comparison of properties between bale compounds based on TDAE and DAE oil shows that the mooney viscosity found to decrease and scorch time found to increase in case of DAE oil. Despite the mixing time, all the compound properties shows that DAE oil found to give better compound and vulcanizate properties compared to TDAE oil. The properties obtained from RFC based blends shows that the mooney viscosity is comparatively high and scorch time found to reduce irrespective of type of oil. Although silanization is completed in RFC based compounds, mixing for 13 minutes does not reduce mooney viscosity lower than bale based rubber blends. Also, all the properties from bale based blends are found to be better than the RFC based blends irrespective of type of oil.

5.3.2. Development of screw and process configuration

The screw and process configuration for continuous mixing of S-SBR/BR based RFC blends are shown in Figure 5-43. The screw configuration is specially designed with more mixing elements. The compositions of RFC-4, RFC-5 and RFC-6 are shown in Table 4-10. S-SBR based RFC-4 and BR based RFC-6 were mixed as pre-blend (70/30 ratio) and dosed in barrel section one of the twin screw extruder. All the other chemicals including cross-linking chemicals such as ZnO, SA, 6PPD, Wax, DPG, TBzTD, CBS, S were mixed as a pre-blend and also dosed in barrel section one. The oil is dosed with a dosing pump in barrel section two.

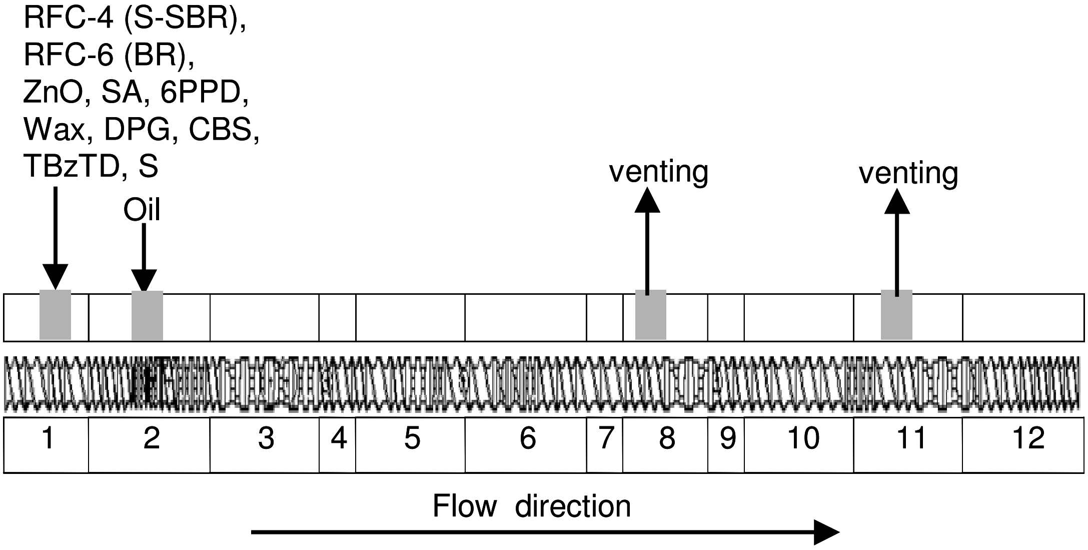


Figure 5-43. Schematic representation of continuous mixing of RFC based S-SBR/BR blend

Two ventings are provided in barrel section eight and barrel section eleven for the removal of volatiles. All the experiments were carried at a throughput of 25 kg/h and with a screw speed of 200 1/min. The extruder barrels were cooled maximum by providing cooling by a high water flow rate of 3500 l/h and all the experiments were carried out without the die. The above experimental set-up was repeated with RFC-5 (S-SBR with DAE oil) in the place of RFC-4 (S-SBR with TDAE oil) in barrel section one of the twin screw extruder.

5.3.3. Comparison of discontinuous and continuous mixing on blend properties

The formulations of RFCs are given in chapter 4.1.4. in Table 4-10 and the final formulations are shown in appendix, formulation 5. The discontinuous mixing of RFC blends was carried out for 13 minutes and 4 minutes mixing time. The 13 minutes mixing time is a three step mixing and four minutes is a one step mixing. In three step mixing, the cross-linking agents were mixed in the third mixing stage. In case of one step mixing, all the ingredients were mixed together from the beginning. The mixing was carried out separately with TDAE and DAE oils. Table 5-8 shows the compound and vulcanizate properties obtained from RFC blends from discontinuous and continuous mixing with different oils. The material properties from the discontinuous mixing are taken as reference for comparing the material properties obtained from continuous mixing.

Table 5-8. Compound and vulcanizate properties obtained from RFC based S-SBR/BR blends from discontinuous and continuous mixing with different oils.

Properties	**Values from discontinuous mixing**				**Values from continuous mixing**	
Used oil	**TDAE oil**	**TDAE Oil**	**DAE oil**	**DAE oil**	**TDAE oil**	**DAE oil**
Mixing time [min]	13	4	13	4	1.35	1.35
Screw speed [1/min]	-	-	-	-	200	200
Throughput [kg/h]	-	-	-	-	25	25
Output temp. [°C]	148_{max}	137	140_{max}	137	75	75
Torque [%]	-	-	-	-	70	64
Spec ener. inp. [kWh/kg]	1.7	0.5	1.7	0.5	0.75	0.68
ML 1+4 (100 °C) [MU]	44.2	72.7	42.6	61.9	107.8	73
Vulcameter ΔS' [dNm]	14.88	20.65	14.25	18.55	20.21	18.68
Scorch time [min]	2.91	1.09	3.52	1.67	0.73	1.54
G' at low strain 60°C[kPa]	263.68	800.27	254.82	572.88	982.54	771.89
Hardness Shore A	58.9	68.5	59.1	66.1	67.6	66.7
σ 100 % [MPa]	1.7	2.5	1.6	2.2	3.1	2.1
σ 200 % [MPa]	4.3	5.5	3.5	4.5	7.2	4.4
σ 300 % [MPa]	8.2	9.1	6.4	7.4	-	7.6
Tensile strength [MPa]	15.6	12.6	14.3	11.8	8.6	14.9
Elongation [%]	467.8	392.4	519.9	453.4	230.6	498.6

The mooney viscosity reaches 44.2 MU for 13 minutes mixing with TDAE oil. The mooney viscosity decreases to 42.6 MU when the RFC blend is mixed with DAE oil. On reducing the mixing time to four minutes, the mooney viscosity increases to 72.7 MU with TDAE oil and decreases to 61.9 MU with DAE oil. With continuous mixing, keeping all the parameters same except the oil type, the mooney viscosity reaches 107.8 MU with TDAE oil and decreases to 73 MU with DAE oil.

The filler-filler interaction measured by storage modulus at low strain shows a lower value at 13 minutes mixing compared to 4 minutes mixing and the values are relatively lower for compounds mixed with DAE oil. The compounds mixed in twin screw extruder are having higher values compared to discontinuous mixing, but the trend decreases with DAE oil. The compound properties are directly comparable with the material properties where the DAE oil based blends are giving better material properties than TDAE oil. The hardness is high in case of shorter mixing times. The hardness is also related to how well the ingredients are mixed. As can be seen from the Table 5-8, when the compound shows a high filler-filler interaction, then the mooney viscosity is also high. The higher filler-filler interaction leads to increase in mooney viscosity of the compound which makes final material hardness to be high. But the filler-filler interaction, mooney viscosity and hardness is lower for the compounds based on DAE oil. The tensile strength and elongation are shown in the Table 5-8, where the σ 100 % is high for compounds showing high filler-filler interaction. For compounds having higher filler-filler interaction, the tensile strength and elongation values are poor.

The blend mixed with DAE oil shows better properties which are almost same irrespective of different mixing aggregates. This shows that the DAE oil has more plasticizing efficiency compared to TDAE oil. The higher plasticizing efficiency leads to better filler dispersion which leads to less filler-filler interaction, less mooney viscosity and consequently improvement in other vulcanizate properties. The less plasticizing efficiency of TDAE oil could be due to the additional extraction treatment of TDAE oil.

The influence of continuous mixing process on compound and vulcanizate properties is not better than properties obtained by discontinuous mixing. This should be further optimized by dosing the ingredients in appropriate barrel sections and by optimizing the screw configuration. As the S-SBR and BR are quite soft rubbers compared to E-SBR rubber, further process optimization is necessary for the continuous mixing process to achieve better properties.

6. Summary

This work brings a contribution to the study of the mixing of rubber compounds in a co-rotating twin screw extruder. The advantages of continuous mixing of rubber compounds in comparison to discontinuous mixing are constant high degree of mixing, less energy requirement, better process control and improved productivity. The disadvantages are high equipment cost, complicated dosing assemblies and need of free flowing raw materials. As the raw materials are available today in free flowing form such as Rubber/Filler-Composites, the aim of the present work is to mix Rubber/Filler-Composites based on silica as filler in the twin screw extruder. In order to increase quality level and productivity of silica based rubber compounds, several parameters were investigated in twin screw extruder and optimal processing window's been set. As quality criteria for the rubber compounds mixed in the twin screw extruder, the properties of rubber compounds mixed in the internal mixer were taken as references.

For the characterisation of the rubber compounds, rubber process analyser and mooney viscometer were employed. From the rubber process analyser, the storage modulus G' value at low strain is considered as a criteria to study filler-filler interaction where lower the G' at low strain, lower is the filler-filler interaction and better is the filler dispersion. From mooney viscosity, the stiffness of the uncured compound is measured. The lower the value, the lower is the viscosity and better is the processability. The indication of pre-scorching can be also seen from high mooney viscosity data. The cross-linking behaviour of the rubber compound was also tested. For the characterization of the rubber vulcanizates, stress-strain behaviour, hardness and abrasion tests were employed in order to control the quality of the obtained vulcanizates.

For the experimental trials in twin screw extruder, E-SBR/silica/silane based Rubber/Filler-Composite (RFC-1) and other chemical ingredients were taken as raw material. The effect on filler dispersion was studied by various screw configurations where the screw configurations were differing in mixing sections with the type of kneading elements such as forward, neutral and reverse kneading elements. Based on the experimental results, it could be established that the application of reverse kneading elements in a screw configuration reduces the filler-filler interaction drastically in comparison to screws with forward and neutral kneading elements. The reverse kneading elements are providing significant changes in flow directions breaking and recombining the flow and additionally their use leads to longer residence time. This leads to high shear process where the silica particles are subjected to high degree of dispersion reducing the filler-filler interaction. It was seen that by using reverse kneading elements based screw, the mooney viscosity reduces significantly compared to forward and neutral elements. It was demonstrated that by using three screw configurations having forward, neutral or reverse kneading elements, the screw configuration with reverse kneading elements (screw configuration C) shows the best mixing performance for mixing E-SBR/silica/silane based Rubber/Filler-Composite.

For studying the right order of dosing the ingredients in the twin screw extruder, four different dosing assemblies were investigated by keeping the screw configuration constant (with reverse kneading elements). The influence of the dosing assembly was found optimal, where RFC-1, ZnO, SA, 6PPD, Wax and DPG were added in barrel section one, extender oil in barrel section two and CBS, TBzTD, S in barrel section eleven (dosing assembly D). The addition of DPG in barrel section one is found to be optimum for achieving better silica dispersion. This leads to reduced filler-filler interaction and lower mooney viscosity. During mixing, the friction between the components leads to increase in temperature of the compound. This increase in temperature (above 145 °C) could lead to pre-scorching of the compound. In order to avoid this, CBS, TBzTD and S were added in barrel section eleven. The use of dosing assembly D shows lower outlet temperature, lower specific energy input, lower mooney viscosity and lower G’ at low strain compared to other dosing assemblies. The cross-linking behaviour was also found to be optimum. Hence, the above results prove that the dosing assembly D is the right order of dosing the ingredients in twin screw extruder for E-SBR/silica/silane based Rubber/Filler-Composite.

The optimization of the productivity in twin screw extruder was carried out in two ways. The aim was to achieve product quality at higher throughputs similar to those of the vulcanizates mixed in the internal mixer. In the one step continuous mixing process, the throughput and the screw speed were increased, while the filling degree was kept constant at 21.5 %. It was demonstrated that by using the right screw configuration (C) and the right dosing assembly (D), the throughput can be increased from 35 to 50 kg/h by keeping the rubber compound and the vulcanizate properties constant. Additionally, the specific energy input and the residence time were decreased; hence a secondary increase of the productivity was achieved. Here, the maximum throughput is limited to 50 kg/h because of the limiting factor: the outlet temperature. By increasing the throughput more than 50 kg/h, the outlet temperature could rise above 145 °C and could lead to pre-mature scorching of the rubber compound.

To further increase the productivity, an additional mixing step was necessary. In case of one step continuous mixing process, the addition of cross-linking chemicals (CBS, TBzTD and S) in barrel section eleven leads to the possibility of pre-scorching at higher outlet temperatures. Hence, in two step continuous mixing process, these cross-linking chemicals were added by using a two roll mill in a second mixing step. Hence, in the twin screw extruder, mixing of rubber, filler and oil without cross-linking agents leads to the elimination of pre-scorching reaction. The two roll mill was cooled enough; hence the pre-scorching reaction was avoided in the two roll mill. Hence, the throughput of the twin screw extruder was increased up to 70 kg/h. In this case too, the limiting factor is again the outlet temperature, where the compound reaches an outlet temperature of 190 °C at 70 kg/h. Above this temperature, the silane may react with the rubber or the rubber mixture will be thermally damaged. By mixing via extrusion followed by the mixing of the cross-linking chemicals in the two roll mill, up to a throughput of 70 kg/h, the rubber compound and also the vulcanizate properties remains in good quality. At the same time, the specific energy input and the residence time decreases further at 70 kg/h and hence a secondary increase of the productivity was achieved.

Further studies were carried out on studying the effect of filling degree in the twin screw extruder. Here, the filling degrees in the twin screw extruder were varied in two ways: by varying the throughput at constant screw speed and varying the screw speed at constant throughput. As in first way, the filling degree were varied by varying the throughput from 25 to 40 kg/h and keeping the screw speed constant at 180 1/min. Here, the filling degree increases with increase in throughput at constant screw speed. The results show that the specific energy input decreases with increase in throughput. The residence time decreases and outlet temperature increases with increase in throughput. The compound properties and vulcanizate properties remains almost constant throughout the entire throughput range under constant screw speed. As in second way, the throughput was kept constant at 40 kg/h and the screw speed was varied from 180 to 240 1/min. The increase in screw speed by keeping the throughput constant shows a decrease in filling degree and increase in specific energy input. The residence time decreases and outlet temperature increases with increase in screw speed. The compound properties and vulcanizate properties remains almost constant throughout the entire screw speed range under constant throughput. In both cases, the optimum compound and vulcanizate properties are achieved within a filling degree range between 17 % and 23 %.

The finished compound-RFC (FC-RFC) was developed to simplify the processing of rubber compound in twin screw extruder. The FC-RFC consists of rubber, filler, oil and extension of cross-linking agents such as DPG and sulphur. Due to this, the complication in dosing assembly was reduced and necessity for pre-blending of the chemicals was eliminated. Experiments were carried out at 50 kg/h by one step and two step continuous mixing process. As the FC-RFC compound consists of pre-dispersed ingredients, there was easy of dosing and mixing in the twin screw extruder and consistent material properties were achieved.

The production of rubber blend by continuous mixing had been carried out in a twin screw extruder with transfermix extruder and gear pump combination. The rubber blend studied here consists of E-SBR and BR rubbers with silica as filler. The E-SBR based RFC was feed in twin screw extruder and the BR pre-batch was feed continuously by a side feeding combination of transfermix extruder and gear pump. The influences of process configuration on compound and vulcanizate properties were studied. The experimental results show that the screw configuration used achieves almost similar material properties in comparison to internal mixer. Also, the addition of BR pre-batch in barrel section seven with the help of gear pump proves to be the right sequence of addition with E-SBR. The E-SBR/BR blend can be continuously mixed at a throughput of 35 kg/h at 200 1/min. The outlet temperature reaches 110 °C for a feed rate of 35 kg/h. The attained blend compound properties and vulcanizate properties correspond to the characteristics of the reference compound mixed in the internal mixer.

Further studies were carried out in mixing rubber blends by using RFC based S-SBR and RFC based BR with silica as filler. Bale rubber blends were taken as reference mixtures mixed by discontinuous mixing. The results show that S-SBR/BR blends can be produced in twin screw extruder. But, the material properties are not better than the properties obtained by discontinuously mixed blends. Investigations were carried out with two different plasticizers namely DAE and TDAE oil. The results show that DAE oil having more plasticizing efficiency than TDAE oil gives superior material properties. In comparison to bale based blends to RFC blends, bale blends shows superior material properties than RFC blends.

The results of this investigation gave an identification of different process parameters in a co-rotating twin screw extruder for mixing silica based RFC compounds by continuous mixing process. But, at the same time, it also raises lot of new questions for further optimization. This area of investigation is still very wide and more effort is necessary to find an answer for all open questions.

Continuous mixing of silica based rubber compounds are state of the art in tire mixing. Traditionally, silica based compounds are mixed in bale form and several mixing steps are necessary for completing silanization reaction in internal mixer. This takes high mixing energy and mixing time. But in case of twin screw extruder, all these can be made continuously with reduced mixing time and mixing energy. This is due to the fact that, RFCs are free flowing granules, based on rubber and filler where the silica is already silanized during the production process of RFC.

The mooney viscosity of silica based rubber compound obtained from twin screw extruder was always higher than that of compounds from internal mixer. It is well known that the mixing time is relatively short in twin screw extruder compared to internal mixer. The relationship between the reduction in filler-filler interaction and its effect on mooney viscosity was a subject of long discussions within the project. The filler-filler interaction in silica compounds can be reduced by silanization reaction, but not completely. Taking into account of the mixing time, the rubber compound needs to be mixed well to further reduce the filler-filler interaction. Hence, this should be further investigated in twin screw extruder by further optimizing process parameters such as screw configuration, dosing assembly, screw speed, throughput and filling degree.

Most of the investigations in this study were made on continuous mixing of E-SBR/silica/silane compound. This should be further extended in studying silica based rubber compounds based on BR, NR, S-SBR in detail. As tire formulations are based on binary or tri-blends, several rubber blends should be further investigated by continuous mixing. Also, the dispersion of filler particles in each of the blend phases in a rubber blend such as SBR/BR should be investigated. The properties such as abrasion will be high, if the BR phase has more filler. On the other side, to obtain better wet grip, SBR phase should have more filler. If the filler is less dispersed in one of the phases, the desired properties cannot be completely achieved. Hence, by continuous mixing, the distribution and dispersion of fillers in rubber blend phases need to be studied.

7. Appendix

Mixing prescription for the production of rubber compound in internal mixer

Formulation 1. E-SBR compound

Nr.	**Ingredients**	**phr**
1	RFC-1	207.5
2	TDAE oil	20
3	ZnO	3
4	SA	2
5	6PPD	1.2
6	Wax	1
7	*Half compound*	*234.7*
8	DPG	2
9	CBS	1.5
10	TBzTD	0.2
11	Sulphur	2.3
12	*Full compound*	*240.7*

- 3 step mixing

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,5,6	6
	2	Two roll mill	16/20	50	-	7	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	7	5
	5	Two roll mill	16/20	50	-	7	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	25	60	0.75	7,8,9,10,11	2
	8	Two roll mill	16/20	50	-	12	2x

- 2 step mixing

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,5,6	5
	2	Two roll mill	16/20	50	-	7	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	25	60	0.75	7,8,9,10,11	2
	5	Two roll mill	16/20	50	-	12	2x

- 1 step mixing

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,5,6, 8,9,10,11	4
	2	Two roll mill	16/20	50	-	12	2x

Formulation 2. E-SBR/BR bale blend

Nr.	Ingredients	phr
1	Bale E-SBR 1721 (80%)	101.6
2	Bale BR 24 (20%)	20
3	Silica U 7000 GR	80
4	Silane Si-75	6.2
5	TDAE oil	23.4
6	ZnO	3
7	SA	2
8	6PPD	1.5
9	Wax	1
10	*Half compound*	*238.7*
11	DPG	2
12	CBS	1.5
13	TBzTD	0.2
14	Sulphur	2.3
15	*Full compound*	*244.7*

- 3 step mixing

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,5,6,7,8,9	6
	2	Two roll mill	16/20	50	-	10	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	10	5
	5	Two roll mill	16/20	50	-	10	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	25	60	0.75	10,11,12,13,14	2
	8	Two roll mill	16/20	50	-	15	2x

Formulation 3. E-SBR based RFC /bale BR blend

Nr.	Ingredients	phr	phr
1	RFC E-SBR 1721		207.5
2	Bale BR 24	100	
3	Silica U 7000 GR	80	
4	Silane Si-75	6.2	
5	TDAE oil	45	
6	TDAE oil		20
7	*Half compound*	*231.2*	
8	*Half compound*		*227.5*
9	ZnO	3	
10	SA	2	
11	6PPD	1.5	
12	Wax	1	
13	DPG	2	
14	CBS	1.5	
15	TBzTD	0.2	
16	Sulphur	2.3	
17	*Full compound**	*240.7*	

* 20% BR compound +80% E-SBR compound + chemicals

- 3 step mixing

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	2,3,4,5	6
	2	Two roll mill	16/20	50	-	7	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	7	5
	5	Two roll mill	16/20	50	-	7	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	50	60	0.75	1,6	3
	8	W&P GK 1.5E	25	60	0.75	7(20%),8(80%), 9,10,11,12, 13,14,15,16	2
	9	Two roll mill	16/20	50	-	17	2x

Formulation 4. S-SBR/BR based bale blend

Nr.	Ingredients	phr	phr
1	Bale S-SBR VSL 5025-0 HM	70	70
2	Bale BR 25	30	30
3	Silica U 7000 GR	80	80
4	Silane Si-75	6.2	6.2
5	TDAE oil	37	
6	DAE oil		37
7	ZnO	3	3
8	SA	2	2
9	6PPD	1.5	1.5
10	Wax	1	1
11	TMQ	0.3	0.3
12	*Half compound*	*231*	*231*
13	DPG	2	2
14	CBS	1.5	1.5
15	TBzTD	0.2	0.2
16	Sulphur	2.1	2.1
17	*Full compound*	*236.8*	*236.8*

- 3 step mixing with TDAE oil

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,5,7,8,9,10,11	6
	2	Two roll mill	16/20	50	-	12	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	12	5
	5	Two roll mill	16/20	50	-	12	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	25	60	0.75	12,13,14,15,16	2
	8	Two roll mill	16/20	50	-	17	2x

- 3 step mixing with DAE oil

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,6,7,8,9,10,11	6
	2	Two roll mill	16/20	50	-	12	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	12	5
	5	Two roll mill	16/20	50	-	12	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	25	60	0.75	12,13,14,15,16	2
	8	Two roll mill	16/20	50	-	17	2x

Formulation 5. S-SBR/BR based RFC blend

Nr.	**Ingredients**	**phr**	**phr**
1	RFC-4	137.76	
2	RFC-5		141.96
3	RFC-6	54.84	54.84
4	TDAE oil	27.2	
5	DAE oil		23
6	ZnO	3	3
7	SA	2	2
8	6PPD	1.2	1.2
9	Wax	1	1
10	*Half compound*	*227*	*227*
11	DPG	2	2
12	CBS	1.5	1.5
13	TBzTD	0.2	0.2
14	Sulphur	2.1	2.1
15	*Full compound*	*232.8*	*232.8*

- 3 step mixing with TDAE oil

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,6,7,8,9	6
	2	Two roll mill	16/20	50	-	10	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	10	5
	5	Two roll mill	16/20	50	-	10	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	25	60	0.75	10,11,12,13,14	2
	8	Two roll mill	16/20	50	-	15	2x

- 3 step mixing with DAE oil

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,5,6,7,8,9	6
	2	Two roll mill	16/20	50	-	10	2x
	3	24 h storage at room temperature					
2	4	W&P GK 1.5E	50	60	0.75	10	5
	5	Two roll mill	16/20	50	-	10	2x
	6	24 h storage at room temperature					
3	7	W&P GK 1.5E	25	60	0.75	10,11,12,13,14	2
	8	Two roll mill	16/20	50	-	15	2x

- 1 step mixing with TDAE oil

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,4,6,7,8,9, 11,12,13,14	4
	2	Two roll mill	16/20	50	-	15	2x

- 1 step mixing with DAE oil

Mixing steps	Process steps	Aggregate	n [1/min]	Tv [℃]	f	Mixing order (Ingredients)	Mixing time [min]
1	1	W&P GK 1.5E	60	60	0.75	1,2,3,5,6,7,8,9, 11,12,13,14	4
	2	Two roll mill	16/20	50	-	15	2x

8. Symbols and abbreviations

Symbol	Description
A	Geometrical constant
B	Geometrical constant
BR	Butadiene rubber
C_L	Centre line distance between the screws
D	Diameter
DAE	Distillate aromatic extract oil
e	Flight land width
EPDM	Ethylene-propylene-diene polymer
E-SBR	Emulsion styrene butadiene rubber
f_b	Represents distributive mixing
f_c	Represents dispersive mixing
FC	Filter cake
FC-RFC	Finished compound-Rubber/Filler-Composite
f	Filling degree
f	Shape factor
f_s	Ratio of the longest and shortest dimension of the particle
G_0	Shear modulus of the pure elastomer
G_f	Shear modulus for the filled compound
G’	Storage modulus at low strain
H	Height of the screw channel
h	Hour
kW	kilowatt
kPa	kilopascal
kg	kilogram
k_a	Rate constant of the re-agglomeration process
k_B	Boltzmann proportionality constant
L/D	Length to diameter of the screw
min	Minute
$_{min}$	Minimum
$_{max}$	Maximum
mm	Millimeter
ML(1+4)	Mooney viscosity after 1 minute of preheating and 4 minutes of measures with a large rotor
MPa	Megapascal
MU	Mooney units
M_D	Torque in twin screw extruder
NR	Natural rubber
Nm	Newton meter
nm	Nanometer (10^{-9} meter)
N_0	Number of elastically active constants at zero deformation
N or n	Screw rotation speed
phr	parts per hundred rubber
P_{in}	Set inlet pressure
p	Number of thread starts
PID	Proportional integral-differential controller

Q_L	Main forward conventional flow
Q_b	reverse flow caused by the staggering of the discs
Q_C	Inflow above the kneading disc tip
Q	Volumetric flow rate per unit time (throughput)
Q_{feed}	Feed rate
R_a	Rate of agglomeration
RFC	Rubber/Filler-Composite
RPA	Rubber process analyser
R_s	Outer radius of the screw
rpm	Revolutions per minute
s	Second
S	Pitch
S-SBR	Solution styrene butadiene rubber
Si	Silane
$\Delta S'$	Difference on vulcameter torque
t	Time
T	Absolute temperature
TESPD	Bis(triethoxysilylpropyl)disulfane
TESPT	Bis(triethoxysilylpropyl)tetrasulfane
T_c	Critical temperature
t_{mean}	Average residence time
U7000	Silica type
u	Circumference of the eight-shaped barrel
V	Free volume
ν	Velocity distribution
V_m	Volume of material inside the extruder
V_F	Free volume inside the extruder
V_b	Volume of the barrel without die
V_i	Occupied volume
V_s	Volume of the two screws
v_0	Circumferential velocity of the screw
w	Width of the screw channel
w	Relative velocity
Δy	Distance of the planes
z	Length of the screw
ZE	Twin screw extruder
Ψ	Intermeshing angle
θ_i	Average residence time in each section
θ	Angle of rotation of the screw
σ	Stress
η	Viscosity
η_f	Viscosity of the fluid
η_0	Viscosity of the pure fluid

ϕ	Volume fraction of particles
ϕ_{eff}	Effective filler volume fraction
υ	Concentration of the elastically active network chains
τ	Shear stress
$\dot{\gamma}$	Shear rate
φ_K	Kneading block stagger angle
δ_R	Clearance between barrel and flight tip

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Eislingen, 25. August 2009 Joseph Wilfred Gnana Mani

Eidesstattliche Erklärung

Hiermit erkläre ich eidesstattlich, das ich die vorgelegte Dissertation selbstständig und nur unter Verwendung der angegebenen Literatur und Hilfsmittel angefertigt habe.

Eislingen, den 25.08.2009 Joseph Wilfred Gnana Mani