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Upscaling of a Mechanochemical Devulcanization Process for EPDM Rubber Waste from a Batch to a Continuous System

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Abstract: The present work is a comparative study of the effects of mechanical shear, temperature, and concentration of a chemical agent on the devulcanization process of post-industrial ethylene propylene diene (EPDM) rubber waste. Devulcanization was carried out in a heating press (no shear), an internal mixer (low shear), and a co-rotating twin screw extruder (high shear) at temperatures ranging from 100 to 200 °C. The efficiency of pure dibenzamido diphenyl disulfide (DBD) and a commercial devulcanizing agent, Struktol A89[®], containing DBD were studied. Based on the results, the devulcanization process was upscaled from 40 g per batch to a continuous process with a capacity of 270 g/h. The parameters were fine-tuned regarding flow rate, screw speed, and temperature. Blends of virgin rubber (VR) and 25, 50, and 75 wt% recyclates were compared with blends of VR and 25, 50, and 75 wt% of untreated RWP. The quality of the recyclate was determined by rheometer tests, SEM images, TGA, and mechanical properties. The best results were obtained with 2 wt% DBD in the extruder with a temperature profile of 120 to 80 °C, 50 rpm, and 4.5 g per minute (gpm). The tensile strength and strain at break of the recyclate already met the requirements of DIN EN 681-1:2006 for the production of sealing systems. The compression set and Shore A hardness were restored by mixing recyclate with 25 wt% VR.

Keywords: recycling; EPDM rubber; devulcanization; twin screw extruder



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1. Introduction

Recycling rubber waste reduces environmental impact, ensures compliance with government regulations, and reflects how we manage our resources. The easiest way to reuse rubber waste is to grind it into small rubber waste particles (RWP) and process it into asphalt, thermoplastics, or other rubber products [1,2]. However, the amount needed to replace virgin rubber (VR) material in high-value rubber products is limited. Further modification of RWP is required to increase the replaceable amount and minimize property deterioration.

A promising recycling method for modifying rubber waste is devulcanization. It aims to reverse the vulcanization process and selectively break the S-S or C-S crosslinks in the rubber network. Despite intensive research, the main drawback of this technique is the deterioration of properties caused by the scission of the main chain, i.e., the C-C scission of the polymer. Devulcanization processes employ high temperatures, microwave energy, ultrasound, shear, microorganisms, and chemicals [3]. The methods are usually combined to achieve a high degree of devulcanization and to increase the selectivity for the scission of crosslinks [4–6].

In many cases, the recycled material is mixed with VR due to the inferior properties of the devulcanized RWP. The substituted amount of VR depends on the method used, the type of rubber, and the desired properties depending on the application [7–9]. Ghorai et al. replaced 30% of raw natural rubber (NR) [10] and styrene butadiene rubber (SBR) [11] by mechanochemically devulcanized rubber using a silane-based tetrasulfide. A diphenyl

disulfide (DPDS)-devulcanized NR waste could replace up to 40% VR with acceptable mechanical properties [12]. Pirityi et al. substituted 25 to 50 wt% virgin EPDM rubber by thermo-mechanical devulcanized RWP and prepared revulcanized rubber with slightly inferior mechanical properties [13]. Dierkes et al. mixed 50% rubber-devulcanized particles by thermo-chemical devulcanization with 5 wt% DPDS into VR and used it industrially for the production of roofing sheets [14].

DPDS is the most common devulcanization aid; however, its efficiency is low for EPDM [15]. The major disadvantage is their sulfur-specific odor which occurs during devulcanization and in the final products. When compared to other disulfide, the devulcanizing agent dibenzamido diphenyl disulfide (DBD) is more efficient for devulcanizing EPDM [15] and is a better alternative concerning odor [16–18]. That's one more reason to carry out devulcanization in an extruder, regarding reduced odor and gas emissions and increased productivity. Many studies with DBD investigated the devulcanization of NR at mild temperatures between 150 and 180 °C [19,20]. In contrast, the devulcanization of EPDM waste rubber with disulfides was performed at temperatures above 200 °C [15,21–24]. Each polymer type requires different conditions [14,25]. Generally, the devulcanization process at mild temperatures produces good-quality recycle [26]. In addition, life cycle assessment studies have shown that devulcanization performs poorly regarding energy consumption [27,28].

This study investigates how devulcanization with DBD should be designed for low energy consumption and still produce good-quality recycle by replacing large amounts of virgin rubber. It is a challenge to use crosslinked rubber waste as a substitute for virgin rubber instead of filler. The effect of mechanical shear, temperature, and concentration of DBD on the devulcanization of EPDM RWP was studied. The devulcanization process was carried out in a heating press (no shear), an internal mixer (low shear), and a co-rotating twin screw extruder (high shear) at temperatures ranging from 100 to 200 °C and different concentrations of DBD (0.4 to 3.9 wt%).

Devulcanization in the heating press was performed as a blind experiment using DBD to devulcanize the surface of crumb rubber particles. On the one hand, we investigated the influence of temperature and pressure on the degradation of DBD and the devulcanization process and, on the other hand, the simultaneous devulcanization and revulcanization process in the presence of DBD under the influence of temperature and pressure. This is similar to the proposal by Hunt and Kovalak, which monitored the devulcanization of rubber surfaces by treatment with a solvent selected from the group consisting of alcohol and ketones between 150 and 300 °C at a pressure of at least 3.4 MPa for 20 min [29]. Reported data on surface devulcanization experiments showed a preferential breakage of S-S and C-S bonds, with minor breakage of the main chains, and good retention of mechanical properties in blends with virgin rubber.

The devulcanization efficiency of pure DBD and a commercial devulcanizing agent, Struktol A89[®], containing DBD, was compared with respect to the devulcanization temperature in the internal mixer. The best results were used to upscale the devulcanization process of EPDM waste rubber from batch to continuous processing in the extruder. The continuous process was fine-tuned in terms of time (flow rate), temperature, and shear (screw speed). The influence of these devulcanization parameters on the devulcanization efficiency and the final product quality was evaluated by rheometer tests and mechanical properties. Finally, a comparable study was carried out on blends containing 25, 50, and 75 wt% virgin rubber and recycle or untreated RWP, respectively. The relationship between vulcanization characteristics, mechanical properties, TGA, and SEM images of the blends was evaluated and discussed.

2. Results and Discussion

2.1. Devulcanization with No Shear

The concentration of DBD and temperature were varied in a blind experiment in a rheometer and heating press, respectively, to study devulcanization. The mechanical properties of the devulcanizates were evaluated on the test plate obtained with the heating press.

The mixture's rheological behavior was monitored by the torque moment in a rheometer (Figure 1). The samples were exposed to heat for the first time in the rheometer, which led to the initiation of devulcanization. The sharp drop at the beginning of the curves reflects the network degradation reaction caused by DBD [30]. With increasing concentration and temperature, the decrease is more pronounced, and the final value of the torque is lower, indicating an increase in network degradation. The same tendency, the decrease in torque correlated with the crosslink density reduction measured by temperature scanning stress relaxation, was observed in our previous study [30]. Figure 1a shows the rheological behavior of sample S1-4%-B without a curing system at a temperature between 100 and 200 °C. No decrease can be observed for 100 °C; only at 120 °C does the curve start to decrease. After a sharp drop at 200 °C, the curve rises again, indicating crosslinking. Consequently, at least 120 °C is required to start the degradation reaction, and for 200 °C, 15 min of devulcanization time is sufficient.

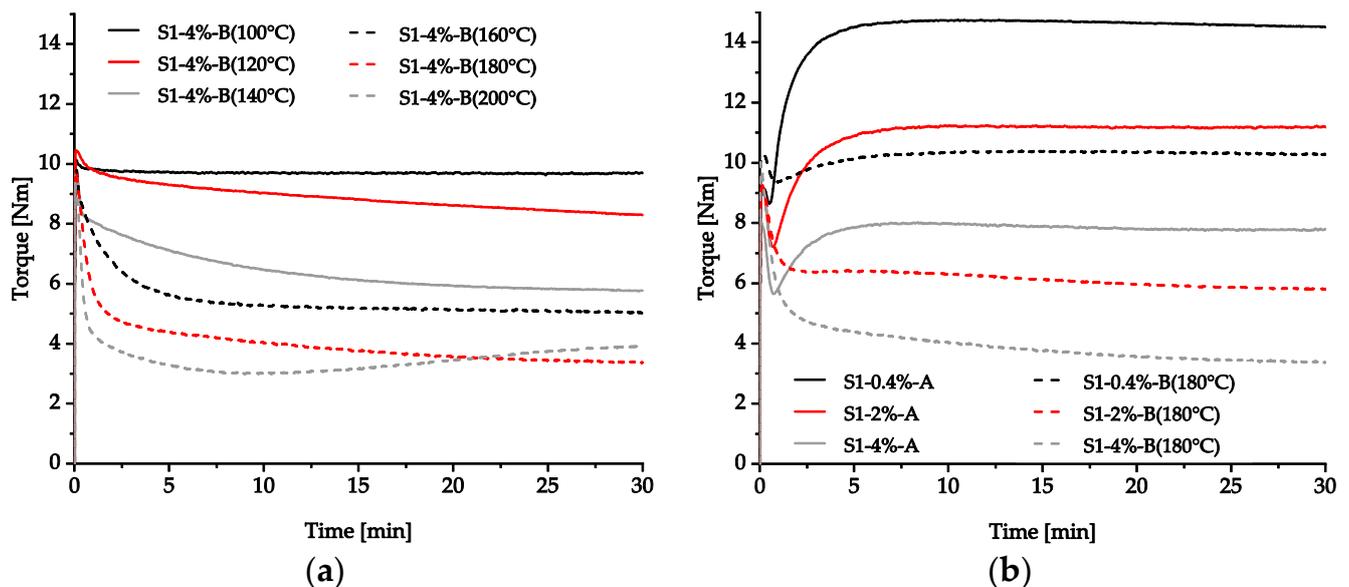


Figure 1. Rheometer curves recorded at 100 to 200 °C for S1-4%-B (a) and 180 °C for S1-0.4%, S1-2%, and S1-4% with (A) and without (B) a curing system (b).

In comparison, Figure 1b shows the effect of DBD concentration on the curing behavior at a constant temperature of 180 °C (the typical crosslinking temperature) of samples with (A) and without (B) the curing system. S1-0.4%-B (180 °C) shows a slight increase in torque after the drop, indicating crosslinking. Studies have found that the sulfur is inactive after devulcanization but not the curing assistants [26], and that crosslink precursors and cyclic sulfides still attached to the RWP from the first vulcanization cycle interact with the redevulcanization process [31]. The reason for the formation of crosslinks, i.e., an increase in torque, could be due to the rearrangement or recombination of the sulfur bridges or the contained sulfur in the cyclic bonds in combination with the residues.

For the samples with curing system (A), devulcanization takes place in the same process step as vulcanization. The curve starts to rise again after less than a minute, with the curve rising fastest at the lowest DBD concentration, indicating crosslinking. However, the degradation reaction was not yet complete compared to the specimens without a curing

system, so after one minute, more crosslinks were formed than broken. The revulcanization reaction overlaps with the devulcanization reaction. Thus, devulcanization occurs first, presumably due to crosslinking intermediates forming for the curing reaction [32]. The scorch time t_{S2} increases from 0.9, 1.8, and 3.6 min for 0.4, 2, and 4 wt% DBD, respectively. ΔM is a measure of crosslink density, which decreases with increasing DBD concentration. This confirms the results of our previous studies showing that DBD interacts with crosslinking intermediates [30].

Tensile tests were performed on test plates compression molded at 180 °C of the specimens with the curing system (A) (Figure 2a). With increasing DBD concentration, i.e., network degradation, tensile strength and strain at break increase. Low chain mobility and network inhomogeneities are mentioned in the literature as reasons why low devulcanized specimens exhibit low mechanical properties [25,33–35]. This is due to the crosslinked areas in the compound, which are weak spots regarding stress transfer.

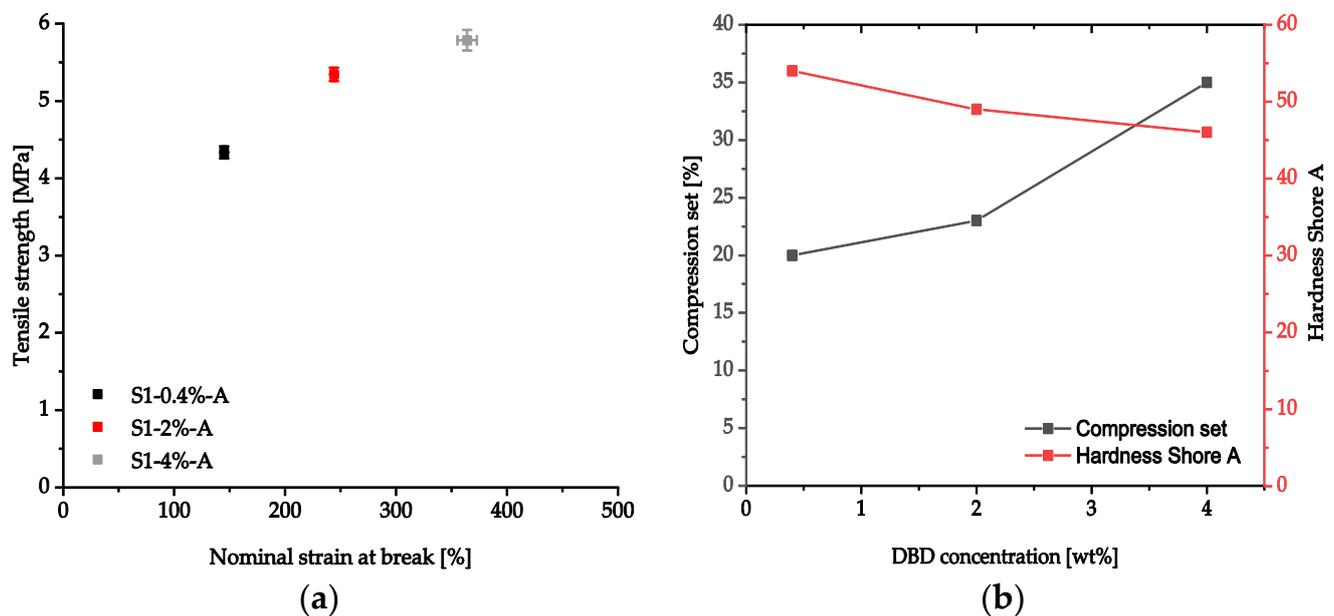


Figure 2. Tensile strength and nominal strain at break (a) and compression set and hardness Shore A (b) of S1-0.4%-A, S1-2%-A, and S1-4%-A.

The hardness decreases and the compression set increases with increasing DBD concentration (Figure 2b). The high compression set reflects the plasticity of the devulcanizate due to the degraded network, DBD, or less formed crosslinks.

2.2. Devulcanization with Low Shear

Samples were devulcanized in an internal mixer with varying DBD concentrations at 160 °C and mixed with the curing system. The rheometer characteristics such as torque minimum (M_L), torque maximum (M_H), the difference between maximum and minimum (ΔM), scorch time (t_{S2}), and time when the sample is 90% crosslinked (t_{90}) are shown in Table 1.

Table 1. Results of rheometer curves recorded at 180 °C for samples S1-0.4%-C (160 °C), S1-2%-C (160 °C), and S1-4%-C (160 °C).

	t_{90} [min]	t_{S2} [min]	M_L [Nm]	M_H [Nm]	ΔM [Nm]
S1-0.4%-C (160 °C)	3.4	0.9	7.6	14.3	6.7
S1-2%-C (160 °C)	4.0	1.3	5.8	10.6	4.9
S1-4%-C (160 °C)	4.1	1.6	4.1	8.1	3.9

The minimum torque decreases due to the degradation of the network in the RWP. ΔM also decreases, indicating that fewer crosslinks are formed during the revulcanization process. The scorch time increases. This curing behavior was also observed for the samples in the heating press, indicating that DBD interacts with the revulcanization process despite devulcanization before revulcanization.

Mechanical tests were performed on compression molded test plates (Figure 3). The increase in tensile strength and strain at break (a) is more pronounced with increasing DBD concentration than for the heating press samples. The compression set also increases, and the hardness decreases (b). A high compression set is obtained for 4 wt% despite the network degradation and the curing system. The same is observed in the heating press. Thus, the shear in the mixer does not improve the compression set. Since the compression set is an important property for evaluating the function of seals, 4 wt% is not reasonable.

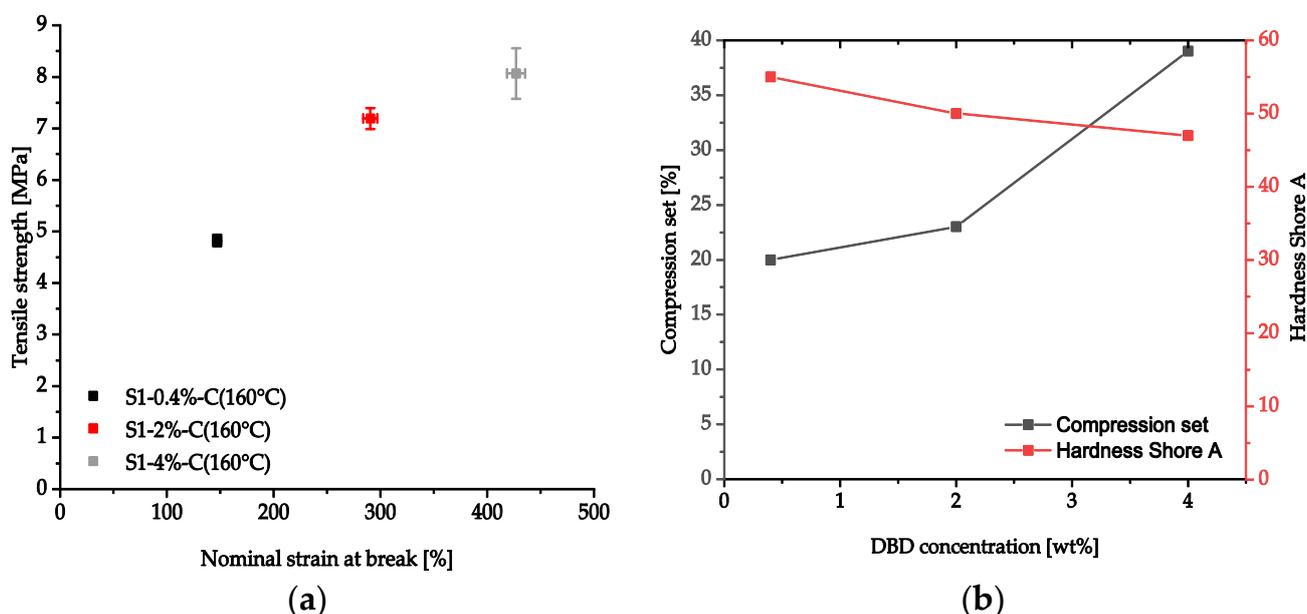


Figure 3. Tensile strength and nominal strain at break (a) and compression set and hardness Shore A (b) of S1-0.4%-C (160 °C), S1-2%-C (160 °C), and S1-4%-C (160 °C).

The long scorch, high compression set, and strain at break were also observed in another study, which was attributed to the interference of DBD in the crosslinking reaction [30].

Based on the previous results, the temperature was varied from 120 to 200 °C, and 2 wt% DBD was used. For comparison, a commercial product, Struktol A89 (S2), containing DBD and a mixture of iron complexes and dispersants, was tested. The effect of the additives on the EPDM network degradation was studied. According to the manufacturer, A89 contains 25–50% DBD. 5 wt% of S2 was used, and, assuming 40% DBD, this corresponds to 2 wt% DBD relative to the RWP.

In Figure 4a, rheometer curves are depicted. The minimum torque decreases with increasing temperature, indicating higher network degradation. At the same temperature, S2 has lower torque values than S1. Dispersants are contained in A89, which are known to decrease the viscosity without degrading the network. A substantial decrease is observed at 120 °C, showing the network degradation by DBD [30]. This indicates that the degradation reaction was not completed at 120 °C and 15 min.

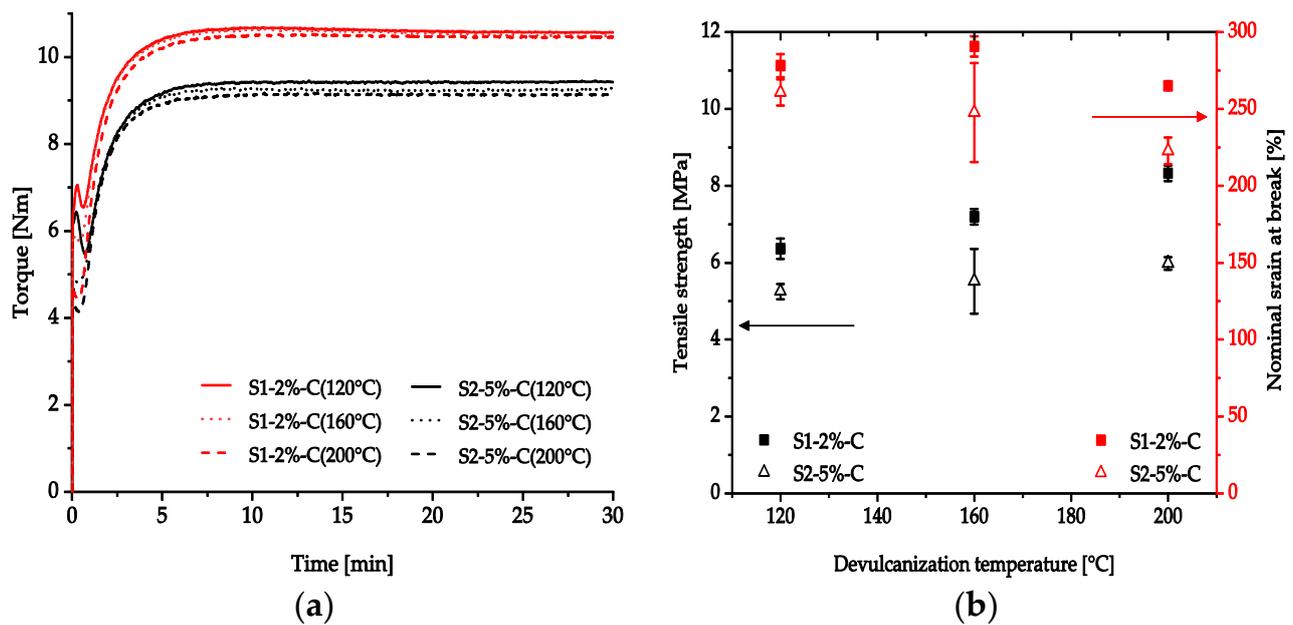


Figure 4. Rheometer curves recorded at 180 °C (a), tensile strength (black), and nominal strain at break (red) (b) for S1-2%-C (■) and S2-5%-C (Δ) as a function of devulcanization temperature.

A higher devulcanization temperature leads to stronger network degradation (minimum torque in the rheometer curves) and better tensile strength (Figure 4b). The strain at break decreases slightly. For a good quality recyclate, low temperatures are preferable [26]. The tensile strength and nominal strain at break are higher for all temperatures in S1 compared to S2. The additional components in S2 do not lead to a higher degree of devulcanization or better mechanical properties. For cost and environmental reasons, S1 should be used over S2 to devulcanize EPDM.

2.3. Devulcanization with High Shear

In addition to the technical aspects, such as a higher degree of devulcanization, the transfer to the extruder also involves practical aspects, such as throughput, and handling of materials due to automatic feeding, which is particularly relevant for the industry [36]. The aim was to further reduce the temperature by optimizing the screw speed and throughput in the extruder. Based on the previous findings in the batch system, a constant concentration of 2 wt% DBD was used for all subsequent tests.

First, the temperature was varied from 120 to 160 °C in the first heating zone. Table 2 shows the minimum torque, tensile strength, and nominal strain at break. There is no significant effect on the properties concerning the temperature, possibly related to the fact that the rubber is not yet fully heated to the set temperature due to its poor thermal conductivity. Since the properties are similar to those in the mixer, no other temperature profiles were tested, and the first heating zone (HZ1) was set to 120 °C.

Table 2. Torque minimum, tensile strength, and nominal strain at break of sample S1-2%-E (100 rpm, 3 gpm) as a function of temperature in the first heating zone (HZ1).

X HZ 1 [°C]	Torque Minimum [Nm]	Tensile Strength [MPa]	Nominal Strain at Break [%]
120	4.1	8.3 ± 0.8	243 ± 20
140	4.4	8.5 ± 0.8	235 ± 16
160	4.5	8.6 ± 0.3	257 ± 3

Subsequently, the screw speed and flow rate were varied. The screw speed influences the shear rate in an extruder [37]. The flow rate is often used to determine the mean residence time [38]. The residence times at flow rates of 1.4, 3, and 4.5 g per minute (gpm) were about 56, 26, and 17 min, respectively. Based on the literature, the residence time is also affected by the screw speed [36], but the flow rate was constant for different screw speeds in this study.

After the devulcanization in the extruder and the addition of the curing system in the mixer, rheometer curves were recorded (Figure 5). As the flow rate decreases and the screw speed increases, the minimum torque, a measure of viscosity, decreases (a). So, increasing shear and residence time leads to a higher devulcanization effect, i.e., more network degradation. Especially regarding subsequent processing steps such as injection molding, a low minimum torque indicates better material processing.

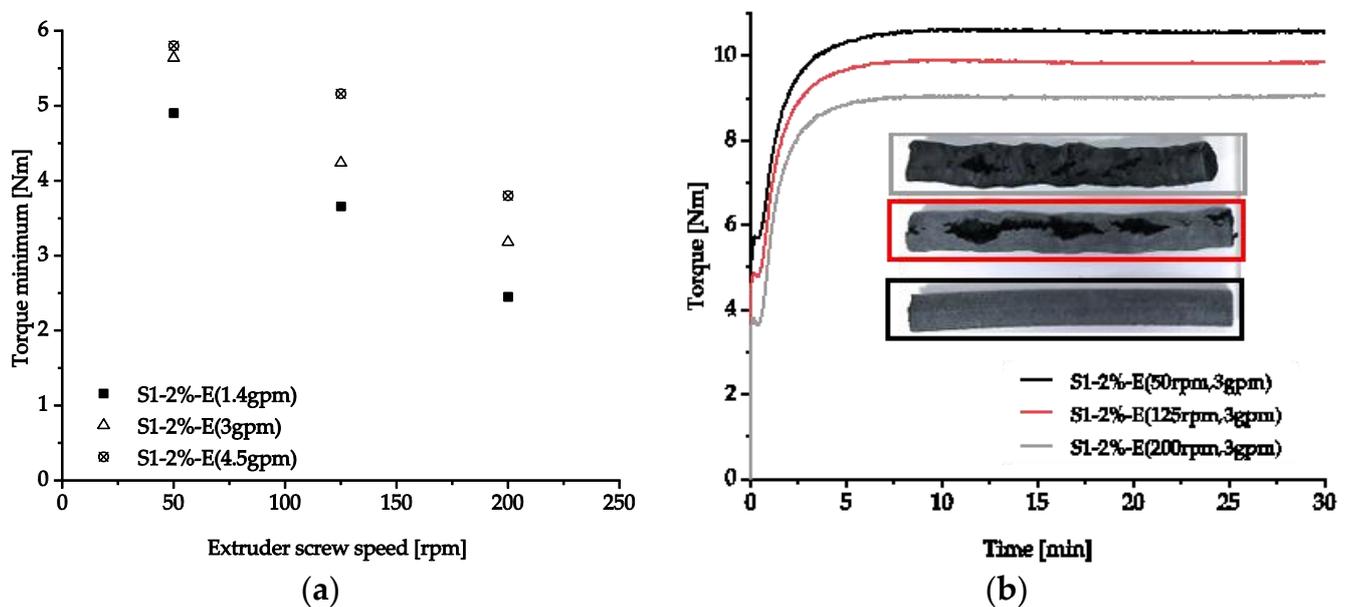


Figure 5. Torque minimum of S1-2%-E as a function of screw speed and flow rate (a) and rheometer curves recorded at 180 °C of S1-2%-E (3 gpm) with pictures of the extruded material (b).

In Figure 5b, the rheometer curves for 3 gpm and different screw speeds are shown. The maximum torque decreases with increased screw speed. So, the vulcanizate is less stiff as the network is degraded. The extruded material has a smoother surface at lower screw speeds.

The mechanical properties were determined on compression-molded test sheets. The tensile strength (Figure 6a) increases at higher screw speeds for 1.4 gpm and decreases significantly for higher flow rates, i.e., a lower residence time. The strain at break (b) also decreases with higher screw speeds. Literature reports polymer chain degradation as a reason for the deterioration of properties [39,40]. Thus, high screw speeds result in high plasticity of the material but poor properties.

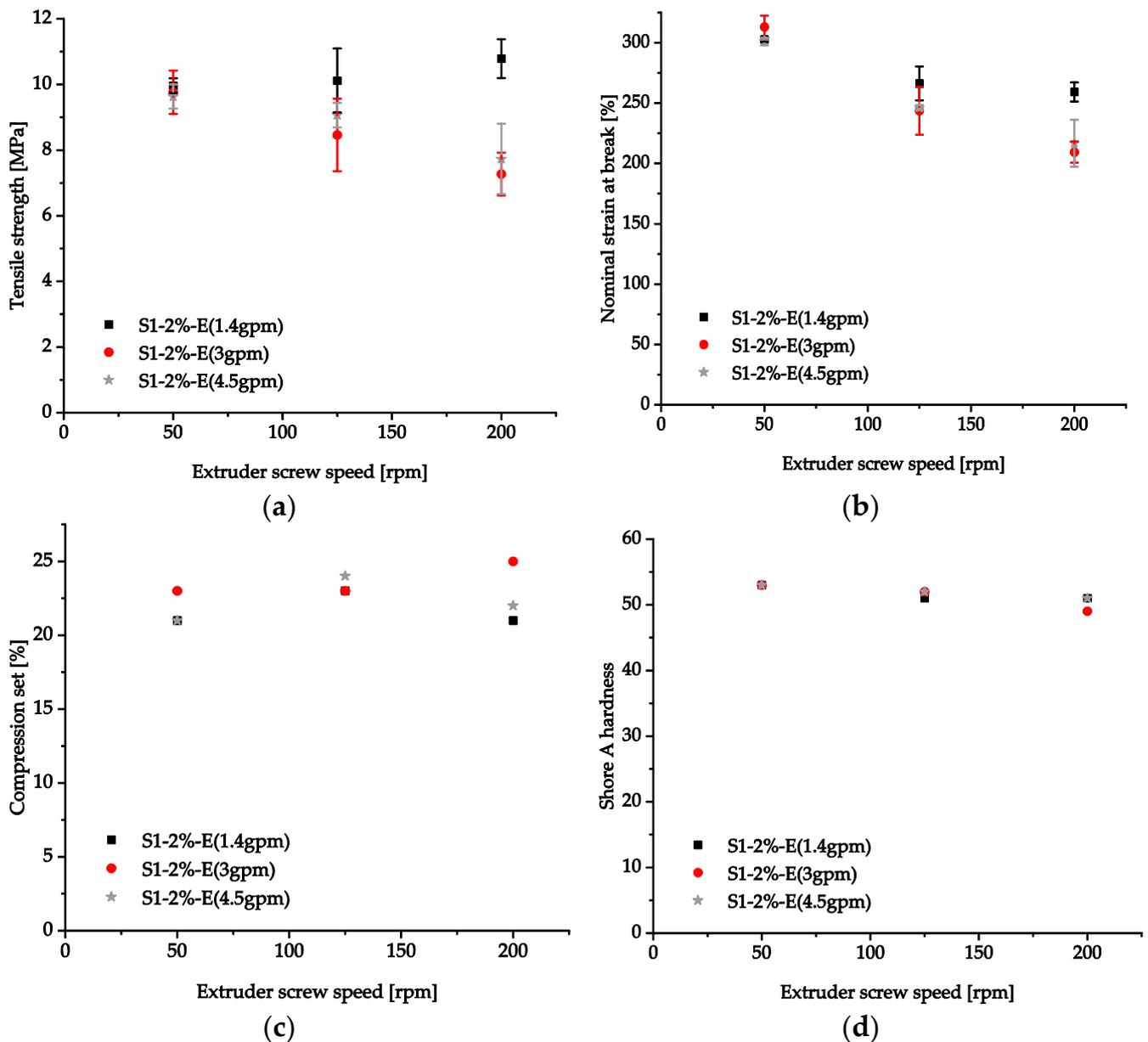


Figure 6. Tensile strength (a), nominal strain at break (b), shore A hardness (c), and compression set (d) of samples S1-2%-E as a function of screw speed and flow rate.

The compression set (c) is independent of extruder parameters and ranges between 20 and 25%. Hardness (d) is hardly affected by screw speed and flow rate, and it tends to decrease slightly.

2.4. Comparison between Batch and Continuous Systems

The difference between high shear in a twin screw extruder and no/low shear in the heating press and mixer were investigated. At 120 °C in the mixer, the devulcanization reaction was not yet complete. Therefore, to compare the devulcanization effect, rheometer curves at 120 and 180 °C of S1-2%-B, S1-2%-D (120 °C), and S1-2%-F (50 rpm, 4.5 gpm) without a curing system were recorded (Figure 7). The curve of S1-2%-B reflects the devulcanization process in the heating press. The samples in the mixer and extruder have similar residence times.

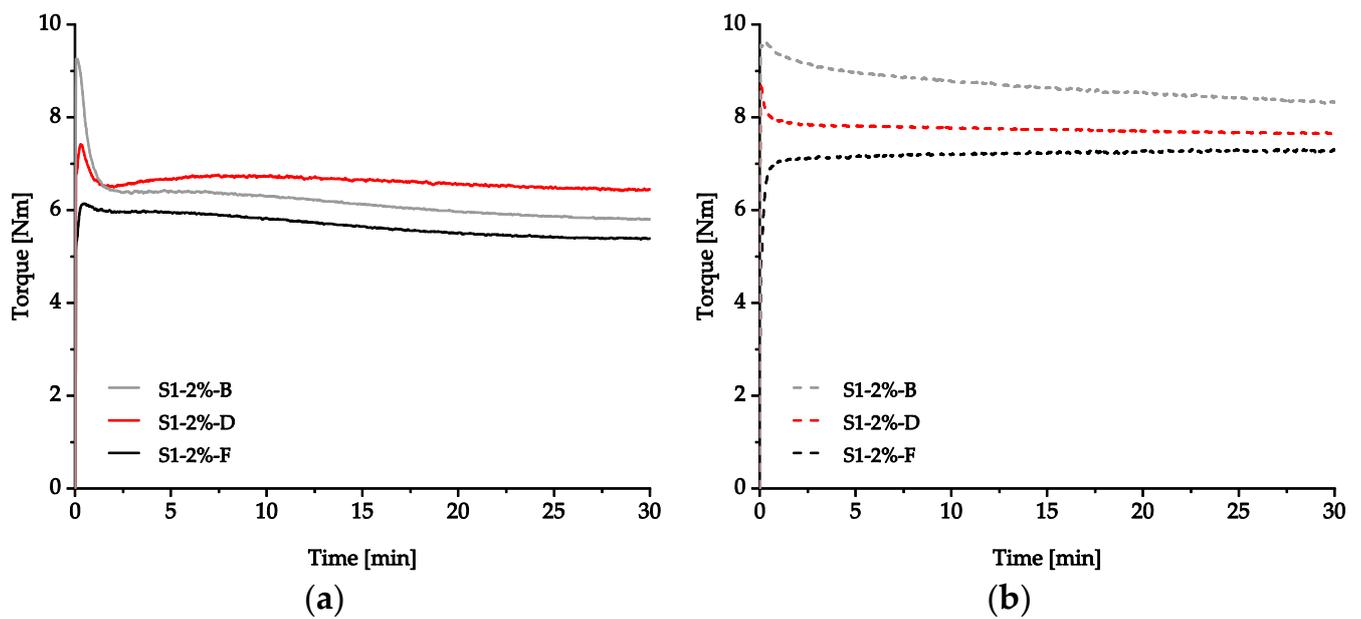


Figure 7. Rheometer curves recorded at 180 °C (a) and 120 °C (b) of S1-2%-B, S1-2%-D (120 °C), and S1-2%-F (50 rpm, 4.5 gpm).

Contrary to S1-2%-F, S1-2%-B, and S1-2%-D show a steep drop at the beginning of the curves (Figure 7a) due to the degradation reaction of DBD [30]. The difference in height between the mixer and the heating press shows that the degradation reaction has already started in the mixer but has not yet been completed. The lower torque level indicates a higher devulcanization effect in the extruder than in the batch, which agrees with the literature [36]. Seghar et al. found that the rubber's self-heating due to the polymer molecules' friction causes an increase in local temperature, which affects the devulcanization process [41]. However, the local temperature, a result of external heating and heat generated by shear, was relatively low at lower temperatures (≤ 160 °C) despite the heat generated at high screw speeds [42]. In contrast, at higher temperatures, the effect of screw speed was significant, resulting in severe degradation. Local temperature changes along the screw cannot be monitored with this setup, but the mass thermocouple on the extruder die only indicated a temperature 9 °C higher than the set temperature for 50 rpm (Table 3). Consequently, self-heating and local hot spots do not affect the process.

Table 3. The mass temperature in the extruder die and the calculated shear rates for S1-2%D (120 °C) and S1-2%-F (4.5 gpm) for different rotational speeds.

	Rotational Speed [1/min]	Shear Rate [1/s]	Mass Temperature [°C]
S1-2%-D(120 °C)	150	183	125
S1-2%-F(4.5 gpm)	50	263	89
	125	656	99 (HZ 5–7)
	200	1050	114

The increase in S1-2%-D indicates crosslinking, which is why the curves are also recorded at 120 °C (Figure 7b), which corresponds to the devulcanization temperature and is insufficient for crosslinking. The higher torque of S1-2%-F recorded at 120 °C can be attributed to the decrease in viscosity at lower temperatures. A decrease from 180 to 120 °C in the rheometer leads to a slowdown of the reaction rate, so S1-2%-B shows only a minimal decrease. S1-2%-D (120 °C) has a lower torque level than S1-2%-B at 15 min. This relates to the devulcanization effect in the mixer due to low shear. S1-2%-D (120 °C) shows no decrease in torque even though the degradation reaction was not complete and the sample

was subjected to heat for an additional 30 min at 120 °C in the rheometer. Consequently, not all 2 wt% DBD is consumed during devulcanization at low shear and low temperature.

A higher devulcanization effect is also observed at 120 °C for S1-2%-F compared to S1-2%-D. Literature reports that shear in the extruder is used to recover and pulverize RWP [43–45] and to promote devulcanization [3,46]. Since the temperatures are the same, the shear rate was calculated for comparison purposes (Table 3). In the extruder, the shear rate γ_E , which is highest in the nip section, was calculated using Equation (1) [47] with the center distance A_w , the rotational speed n , and the distance in the nip section δ_{zw} . δ_{zw} of the extruder was calculated with Equation (2) with D_A outer diameter of the screw [48].

$$\gamma_E = \frac{A_w * 2 * \pi * n}{\delta_{zw}} \quad (1)$$

$$\delta_{zw} = D_A - A_{th} \quad (2)$$

Intermeshing kneading elements were used in the extruder, and a tangential cam rotor in the mixer. The shear rate γ_M of the mixer was calculated with Equation (3) from the quotient of the circumferential velocity u and the gap distance δ , i.e., the distance between the rotor and the chamber wall [48,49]. u was determined with Equation (4), with D as the diameter.

$$\gamma_M = \frac{u}{\delta} \quad (3)$$

$$u = D * \pi * n \quad (4)$$

The filling level of the mixer is a crucial parameter for the shear rate in the mixer [36]. Since the filling level was 0.5, the calculated shear rate is probably higher than the actual one. Although there are usually shear rate ranges, the calculations show comparatively higher shear rates in the extruder than in the mixer (Table 3). Macsiniuc et al. assume that higher shear rates prevail in the extruder than in the mixer, leading to different breakages of the crosslinks [50]. The results show that the high temperatures required at low shear to complete the degradation reaction can be compensated by high shear in the extruder when using low temperature.

In the literature, a melting point of 140 °C is reported for DBD [16,20], which was used in other studies as a criterion for selecting the devulcanization temperature. This study shows that devulcanization is possible below the melting point.

Comparing the properties, the heating press has the lowest properties (A). The properties for S1-2%-C (160 °C) and S1-2%-E (50 rpm, 4.5 gpm) are compared, as the samples have similar residence times and the DBD degradation reaction was complete. The compression set, hardness, and strain at break do not differ, but the tensile strength increased from 7.2 MPa to 9.8 MPa for S1-2%-E. The temperature in the extruder can be lowered, and better mechanical properties are obtained due to a higher shear.

An exact mechanism is difficult to elucidate due to the complexity of rubber compounds. Based on the literature, a devulcanization mechanism is proposed for the three systems in Figure 8. Joseph et al. suggested that the disulfides are thermally degraded into radicals that break sulfur crosslinks by attacking the double bond next to the crosslink, and then new active crosslinking sites are formed [3]. Tripathy et al. also suggested that crosslinks are broken on heating during sintering in a press [51]. Devulcanization in a heating press [30,51] or autoclave [52,53], where there are no shear forces but high temperatures or pressures to produce a devulcanized material, supports the mechanism proposed by Joseph et al. [3]. This is depicted in the scheme (I). Other studies have suggested that disulfides and crosslinks are broken by shear, and the disulfide radicals react with the broken crosslinks to avoid recombination of the crosslinks [21,54,55]. In the case of shear in the mixer and extruder, either (I) or (II) is applicable for the devulcanization mechanism.

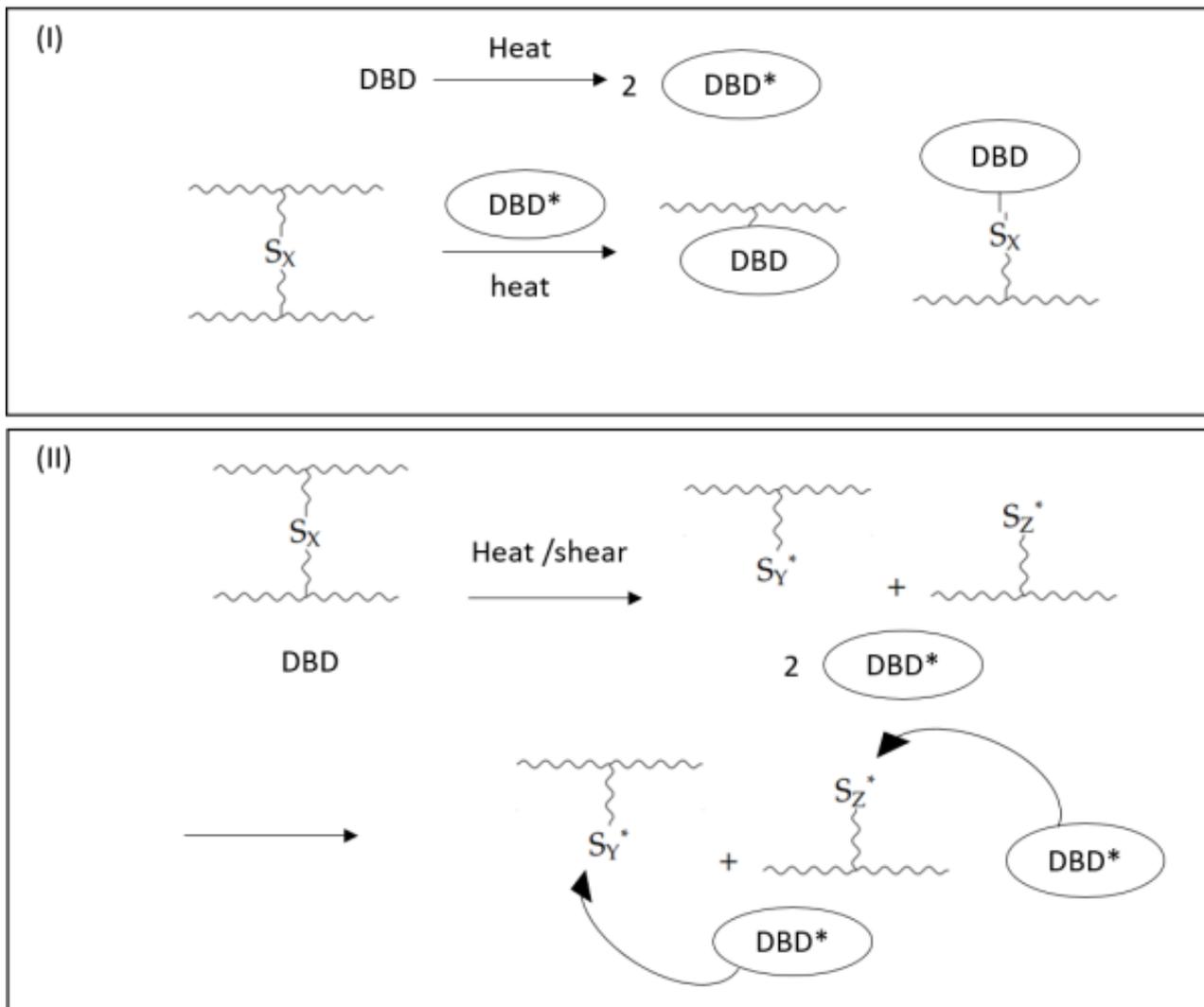


Figure 8. A proposed mechanism of DBD in the presence of heat (I) and heat/shear (II), which is supported by the literature [3,21,51,54,55].

2.5. Preparation of Virgin Rubber Blends

The aim is to produce high-quality products and close the loop in the circular economy. This study investigated how much devulcanized material can replace the virgin rubber compound. The better the quality of the recyclate, the more VR can be replaced by it without deterioration of the product properties.

Some of the recyclate properties do not meet the specifications of DIN EN 681-1:2006 for producing sealing systems in the industry. 25, 50, and 75% of the VR formulation were replaced with S1-2%-E (50 rpm, 4.5 gpm), yielding the best mechanical properties. For comparison, the untreated RWP was also used to replace the VR formulation to evaluate the quality of the devulcanizate. In the industry, RWPs are normally used as fillers, and unlike this study, no crosslinking system is added to the rubber in the RWPs.

The rheometer curves are shown in Figure 9. With the increasing amount of untreated RWP (a), the minimum and maximum torque increase because the RWP are strongly crosslinked.

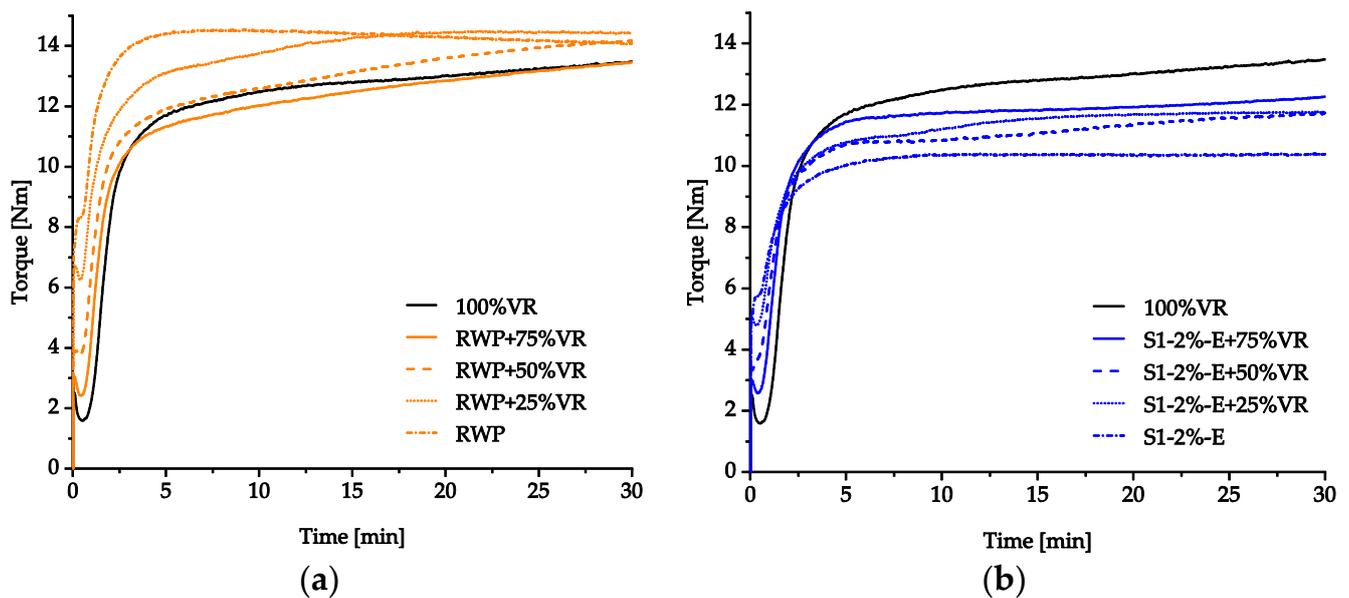


Figure 9. Rheometer curves of VR blends with untreated RWP (a) and S1-2%-E (50 rpm, 4.5 gpm) (b).

An increase in the S1-2%-E (b) amount reduces the maximum torque. The S1-2%-E blends have a lower torque minimum compared to the untreated RWP, so devulcanization is particularly necessary for the processability of the material. Lepadatu et al. had a similar torque minimum and produced sealing systems via injection molding [56,57]. The difference between the minimum and maximum torque decreases, indicating fewer newly formed crosslinking points. The scorch time decreases for both blends due to curing system residues attached to the RWP [31].

Gaskets are divided into different hardness categories in the industry, and the original product (100% VR) has a hardness of around 60 Shore A. The requirements for the 60 Shore A hardness category according to DIN EN 681-1:2006 were given in the plots of the mechanical properties (Figure 10a–d).

The tensile strength (a) for S1-2%-E exceeds the requirements at all blend ratios, while for untreated RWP the tensile strength decreases, and the specifications are no longer met at ratios above 50 wt% RWP. As indicated in the experimental part, the nominal strain at break was determined here (b), but the given elongation at break in the DIN EN 681 applies to the determination with an extensometer. Since the nominal strain is 30% lower and all values for S1-2%-E are around 300%, the DIN requirements were thus fulfilled. For the RWP specimens, the requirements were met only up to a maximum of 50 wt%. This deterioration of the properties of the RWP is related to the formation of a second phase by the immiscible crosslinked particles, in which a different stress distribution prevails due to this heterogeneity [58]. Another cause of the revulcanizates' inhomogeneity is the diffusion of sulfur into the RWP [59,60].

The compression set (c) increases with S1-2%-E. To obtain values according to the DIN, at least 25 wt% VR is required. The RWP specimens meet the requirements in all ratios. The RWP blends with up to 25 wt% VR, like the reference sample, have a compression set of about 10%. The hardness (d) decreases due to devulcanization, and a lower amount of VR results in a decrease in hardness. 25 wt% VR is needed to achieve a hardness of 55 Shore A. All blend ratios meet the requirements since the RWP have a higher hardness than the devulcanized particles due to their still crosslinked network.

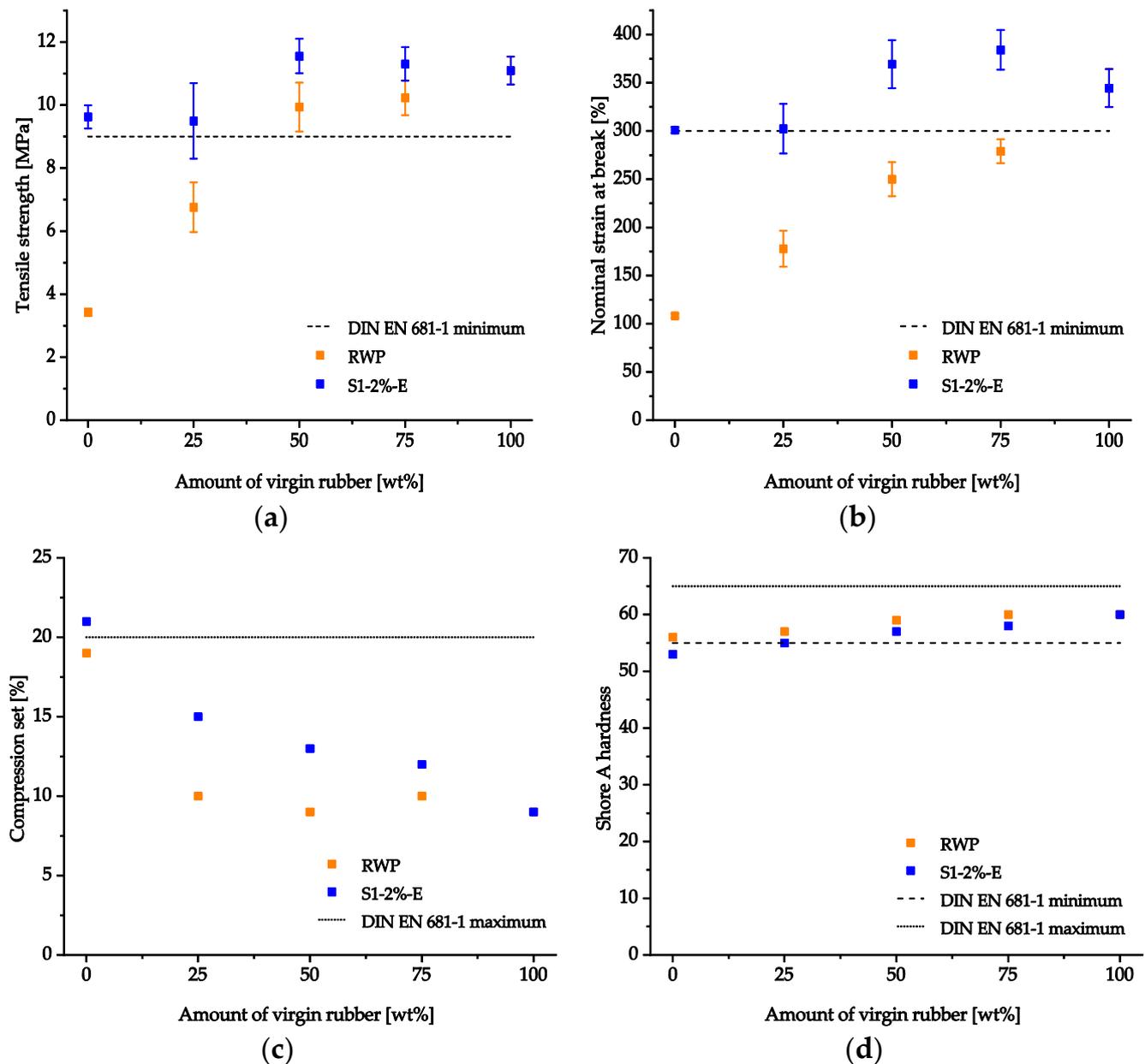


Figure 10. Tensile strength (a), nominal strain at break (b), compression set (c), and shore A hardness (d) of VR blends with untreated RWP (orange) and S1-2%-E (50 rpm, 4.5 gpm) (blue).

In Figure 11, SEM images of the blends are depicted. The RWP (a) shows a rough fracture surface, indicating the size of the original particles [30]. The devulcanized RWP S1-2%-E (b) shows an irregular surface with smooth structures, suggesting that the particles have decreased in size due to devulcanization. The reference shows a smooth surface with only small fissures (c).

By increasing the VR amount in the blends, the surface becomes smoother and more similar to the reference surface structure. 75 wt% VR and S1-2%-E (f) hardly differ compared to 100% VR. 25 wt% and 50 wt% (d + e) are more similar to the surface fracture of S1-2%-E. For untreated RWP, the surface is rough up to a proportion of 50%, with smooth surface structures in between. 75 wt% VR and untreated RWP (i) have a rougher surface compared to 100% VR and S1-2%-E. The reference shows the best properties, so this fracture pattern is equivalent to good tensile strength and strain at break. The rough structures are due to low mechanical properties, as the highly crosslinked RWP provides poor stress transmission and low adhesion [19,33]. The smoother surface of the devulcanizates reflects better properties.

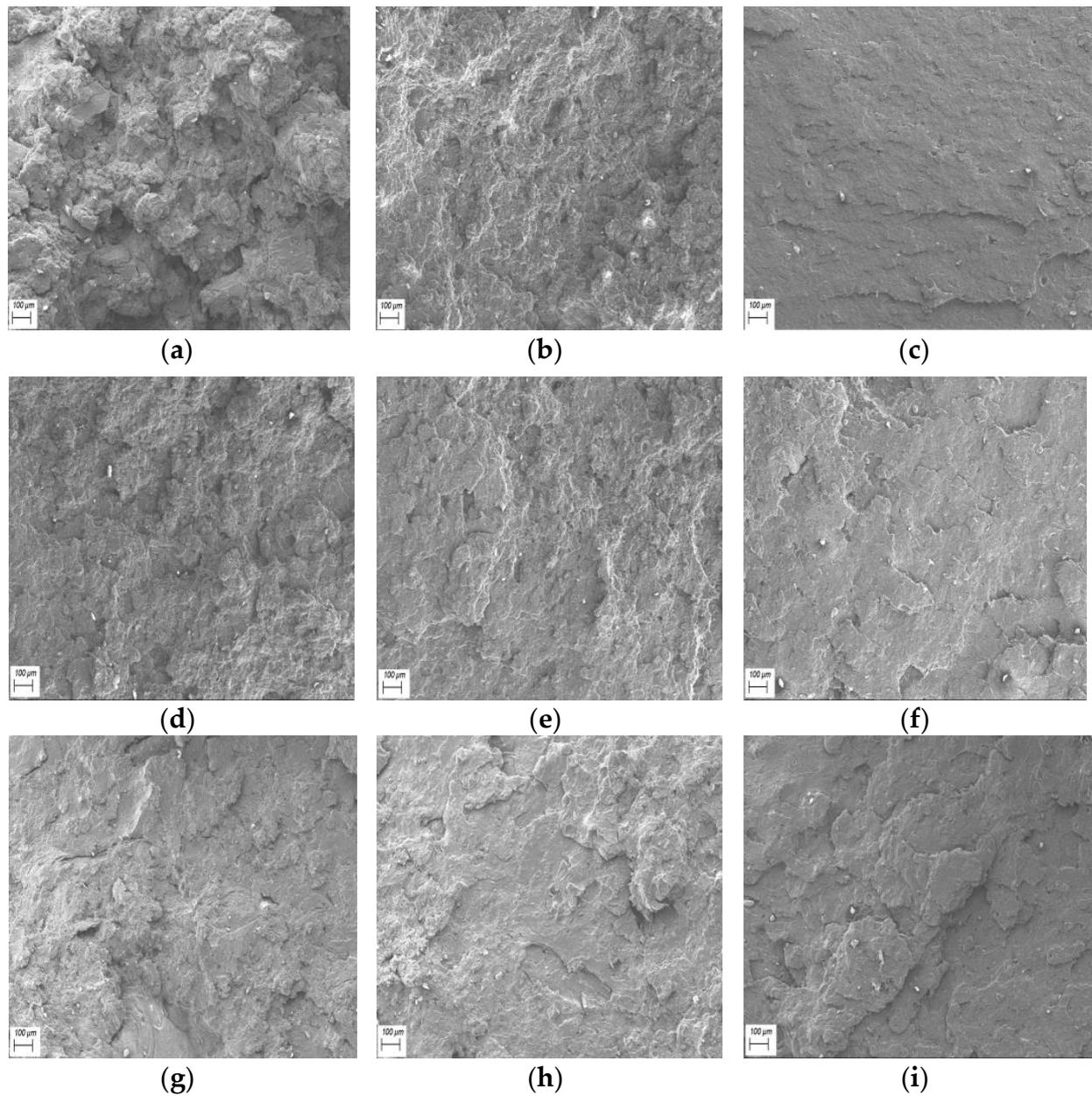


Figure 11. SEM images of RWP (a), S1-2%-E (50 rpm, 4.5 gpm) (b), 100%VR (c), S1-2%-E (50 rpm, 4.5 gpm) with 25 wt% (d), 50 wt% (e), and 75 wt% (f) VR, and untreated RWP with 25 wt% (g), 50 wt% (h), and 75 wt% (i) VR.

Figure 12 shows the results of the TGA measurements for 100% VR, untreated RWP, S1-2%-E (50 rpm, 4.5 gpm), and virgin rubber blends with 50 wt% RWP and S1-2%-E (50 rpm, 4.5 gpm), respectively. Three major steps can be distinguished in the mass loss curve (a). At 240 °C, a small peak can be observed in the DTG curves of the samples with DBD (b). The degradation peak at 300 and 460 °C can be assigned to oils and polymer and carbon black combusts at temperatures higher than 650 °C, which is also reported in other literature [56,61]. There is no difference in the peak temperature of maximum degradation of the polymer or the onset temperature. Thus, the thermal stability of the polymer in the RWP, devulcanizates, and raw rubber is not changed by grinding or devulcanization at our devulcanization conditions.

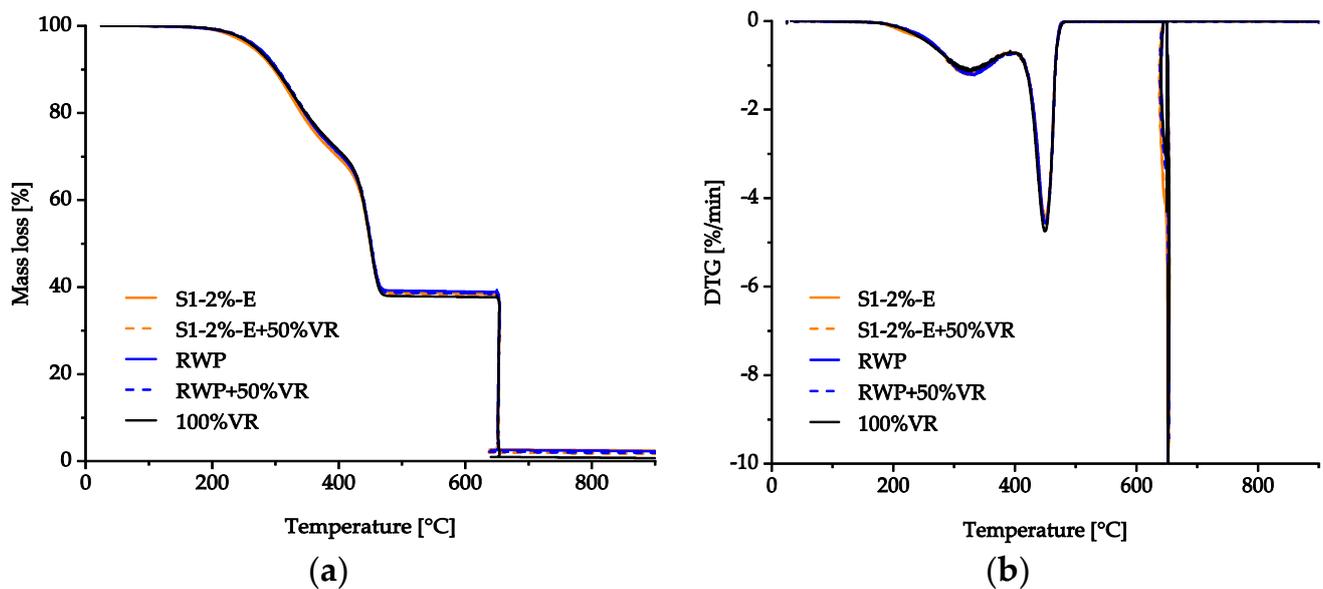


Figure 12. TGA mass loss (a) and DTG (b) curves of 100%VR, untreated RWP, S1-2%-E (50 rpm, 4.5 gpm), and virgin rubber blends with 50 wt% RWP and S1-2%-E (50 rpm, 4.5 gpm).

3. Materials and Methods

3.1. Materials

Post-industrial EPDM waste powder with a particle size distribution smaller than 1 mm [30], derived from sealing system production, the curing system zinc oxide, sulfur, stearic acid, N-cyclohexyl-2-benzothiazole sulfenamide (CBS), zinc bis(dibenzyl dithio carbamate) (ZBEC) and EPDM Keltan 9650Q, carbon black of type N550, and paraffinic oil Mabanol Base oil 500 MSN were provided by M.D.S. Meyer GmbH (Bakum, Germany).

Pure DBD with trade names Struktol 424[®] and Struktol[®] A89 were kindly supplied by Schill and Seilacher GmbH (Hamburg, Germany).

3.2. Preparation of Samples and Blends

The formulation of dry blends consisting of RWP and different amounts of DBD and Struktol A89 are shown in Table 4 and were prepared for 10 min in a KCC9061S household blender from the company KENWOOD (Frankfurt am Main, Germany).

Table 4. Formulation of dry blends consisting of rubber waste particles (RWP) mixed with different amounts and types of devulcanizing agents.

Sample Name	S1-0.4%	S1-2%	S1-4%	S2-5%
RWP	100 wt%	100 wt%	100 wt%	100 wt%
DBD	0.4 wt%	2 wt%	4 wt%	
A89				5 wt%

Devulcanization was carried out in three different systems: an electrically heated hydraulic press, Polystat 200T (Schwabenthan, Germany), an internal mixer, Plastograph S350 (Brabender GmbH, Germany), and a lab compounder, DSE Ketse 40/20 twin screw extruder with a screw diameter of 20 mm and a barrel length of 40 D (Brabender GmbH, Germany).

An overview of samples with and without shear and the curing system are displayed in Figure 13. For the samples in the heating press (A), the curing system was added after the preparation of the dry blends. The mixtures consisting of RWP, DBD, and curing system were treated in the heating press at a temperature of 180 °C and 10 MPa for t_{90} time + 2 min.

C and E were first devulcanized. Subsequently, the crosslinking system was added with the mixer, and then test plates were prepared in the heating press.

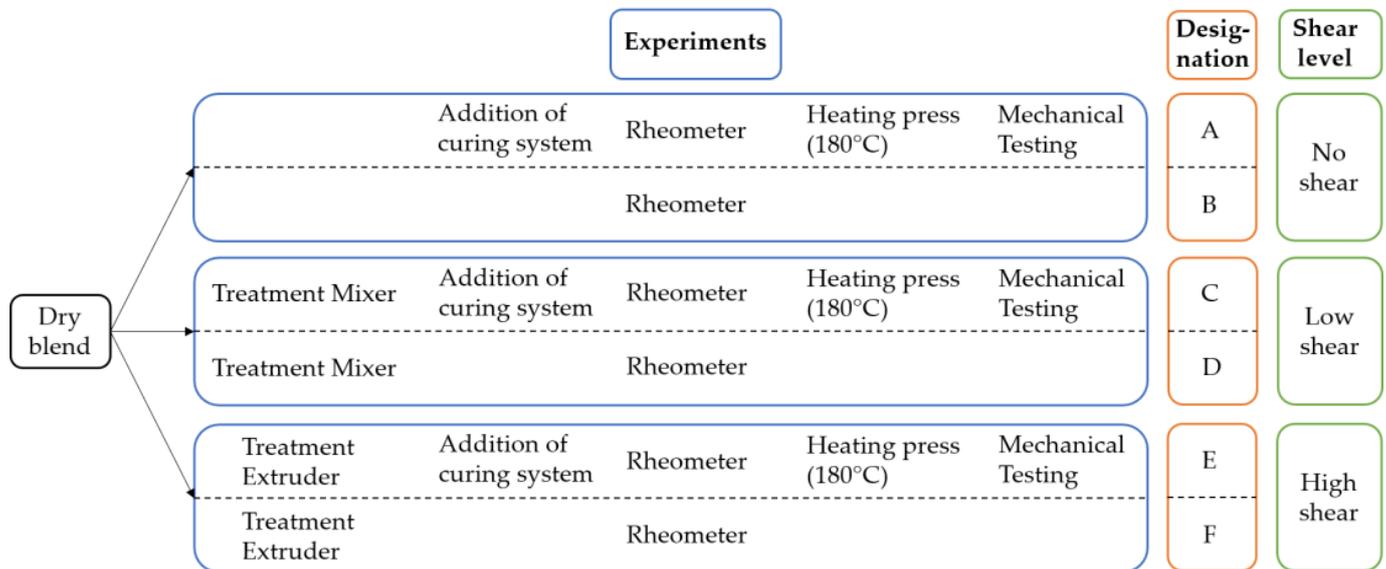


Figure 13. Overview of experiments, designation, and shear level.

The samples prepared in the mixer were devulcanized at 120, 160, and 200 °C at 150 rpm for 15 min, with a filling factor of 0.5.

In the extruder, temperatures of 120, 140, and 160 °C were tested for the first heating zone (HZ1) at 100 rpm and 3 gpm (Figure 14). The other heating zones were set to a constant temperature (110, 90, 80, 80, 80, 80 °C). The parameters were varied from 1.4 to 4.5 gpm flow rate and 50 to 200 rpm screw speed with 120 °C in the first heating zone. For dosing the RWP, a DDSR20 (Brabender GmbH, Germany) was used. The screw comprises three repeating sections consisting of conveying, inverse, and kneading elements. Round strands were obtained through a nozzle with a diameter of 6 mm.

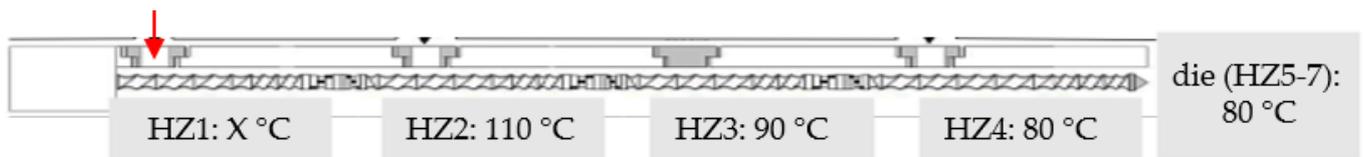


Figure 14. Extruder screw, temperatures of heating zones (HZ), and feeding section (red arrow).

The curing system was added to the samples from A, C, and E and the untreated RWP with an internal mixer type Haake PolyLab QC (Thermo Scientific, Dreieich, Germany) at 90 °C, 40 rpm, and a filling factor of 0.5 for 7 min according to Table 5. The amount of curing system for all samples refers to 100 phr polymer.

Table 5. The compound formulation for samples with a curing system.

Ingredients	Amount [phr]
Polymer	100
Zinc oxide	4
Stearic acid	2
CBS	2.5
ZBEC	0.7
Sulfur	1.2

A reference sample consisting of 100 phr EPDM Keltan 9650Q, 120 phr carbon black of type N550, 100 phr paraffinic oil mabanol base oil 500 MSN, and a curing system was mixed for 15 min with a filling factor of 0.6 in an internal mixer type Haake PolyLab QC (Thermo Scientific, Germany) at 90 °C and 40 rpm. Blends containing 25, 50, and 75 wt% devulcanized rubber or 25, 50, and 75 wt% untreated RWP, raw rubber formulation, and a curing system were prepared with the same parameters as the reference.

Test plates were prepared in the heating press (180 °C, 10 MPa) with the optimal t_{90} time + 2 min (curing characteristics from rheometer curves).

3.3. Characterization of Samples

The devulcanization effect and the curing properties were evaluated by rheometer curves recorded at 180 °C for 30 min according to DIN 53529-1/-2/-3:1983 using a dynamic moving Die Rheometer type D-MDR 3000 (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany). Group B specimens were also tested at 100, 120, 140, 160, and 200 °C, and those in groups D and F at 120 °C.

TGA measurements were performed on the VR blends under an argon atmosphere between 25 and 650 °C and an oxygen atmosphere from 650 to 900 °C at a 5 K/min heating rate using a TG 209 F1 Libra[®] from Netzsch GmbH (Selb, Germany). For the gas transition, an isothermal segment was used, with 5 min per gas at 650 °C.

The compression set was measured based on DIN ISO 815-1/-2:2016 at 70 °C for 24 h on test pieces (three test pieces on top, each 13 mm in diameter and 2 mm thick).

Hardness was determined according to DIN ISO 7619 with a Shore A hardness tester (Karl Frank GmbH, Germany) on three 2 mm-thick test pieces.

Tensile tests were carried out based on DIN 53504:2017-03 and ISO 527-1 using a universal testing machine, the Zwick BZ2.5/TN1S (Zwick GmbH and Co. KG, Ulm, Germany), with a preload of 1 N and a constant speed of 200 mm/min. The mean value and standard deviation of the three S2 specimens tested are displayed. As no extensometer was used, the nominal strain at break was determined according to Equation (5), with L the initial gripping distance after applying the initial force F_0 and ΔL the increase in the gripping distance from the test start. Random tests have shown a systematic deviation between the two setups, where the elongation at break, according to DIN 53504:2017-03, is approximately 30% higher than the nominal strain at break. Still, the determined nominal strain is suitable for comparison within the test series.

$$\epsilon_t = \frac{\Delta L}{L} \quad (5)$$

4. Conclusions

This work investigates the influence of temperature, concentration of the devulcanizing agent DBD, and shear on the devulcanization process of EPDM rubber waste. The devulcanization process was carried out at temperatures between 100 and 200 °C in three different systems (a heating press, an internal mixer, and a twin screw extruder) with varying levels of shear. The optimal parameters were determined in the batch process and transferred to the continuous process to produce composite materials for the injection molding of sealing systems.

A 2 wt% DBD concentration has a significant impact on network degradation, which affects the mechanical properties of composite material. High tensile strength and strain at break and low compression set are obtained. A high compression set is achieved by doubling the DBD concentration (3.9 wt%), but this is not applicable for sealing systems.

The influence of temperature is shear rate dependent, and the shear rate influence on the composite material was fine-tuned in the extruder by screw speed and flow rate. The formation of radicals through the decomposition reaction of DBD starts at 120 °C but is not complete at this temperature after 15 min in the mixer. Devulcanization at 120 °C required high shear to complete the degradation reaction of DBD. A high shear in the extruder compensates for the effect of temperature, and the process can be carried out at moderate

temperatures. An increase in screw speed leads to a decrease in viscosity, i.e., plasticization of the material, but also to a deterioration of the mechanical properties, which is more pronounced at higher flow rates. At low screw speeds, the mechanical properties are independent of the flow rate. The best mechanical properties are obtained at 4.5 gpm and 50 rpm. Hardness, strain at break, and compression set are the same compared to the mixer at 160 °C, but tensile strength is improved. In summary, the shear in the continuous system can compensate for the temperature needed in the batch system without deteriorating the properties.

Due to the high quality of the recycle, large quantities of VR can be replaced in the compound. While the tensile strength values already meet the DIN EN 681 requirements, at least 25 wt% virgin rubber had to be added to achieve the required compression set and Shore A hardness. The results show that the material recycled in a continuous system at low temperatures with only a small amount of virgin rubber achieves similar properties to the reference compound and can be used for sealing systems.

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References

1. Karger-Kocsis, J.; Mészáros, L.; Bányai, T. Ground tyre rubber (GTR) in thermoplastics, thermosets, and rubbers. *J. Mater. Sci.* **2013**, *48*, 1–38. [[CrossRef](#)]
2. Myhre, M.; Saiwari, S.; Dierkes, W.; Noordermeer, J. Rubber Recycling: Chemistry, processing, and applications. *Rubber Chem. Technol.* **2012**, *85*, 408–449. [[CrossRef](#)]
3. Joseph, A.; George, B.; Madhusoodanan, K.; Alex, R. Current status of sulphur vulcanization and devulcanization chemistry: Devulcanization. *Rubber Sci.* **2016**, *29*, 62–100.
4. Zedler, L.; Kosmela, P.; Olszewski, A.; Burger, P.; Formela, K.; Hejna, A. Recycling of Waste Rubber by Thermo-Mechanical Treatment in a Twin-Screw Extruder. *Proceedings* **2021**, *69*, 10.
5. Colom, X.; Canavate, J.; Formela, K.; Shadman, A.; Saeb, M.R. Assessment of the devulcanization process of EPDM waste from roofing systems by combined thermomechanical/microwave procedures. *Polym. Degrad. Stab.* **2021**, *183*, 109450. [[CrossRef](#)]
6. Ostad Movahed, S.; Ansarifard, A.; Zohuri, G.; Ghaneie, N.; Kermany, Y. Devulcanization of ethylene-propylene-diene waste rubber by microwaves and chemical agents. *J. Elastomers Plast.* **2016**, *48*, 122–144. [[CrossRef](#)]
7. Nabil, H.; Ismail, H.; Azura, A.R. Compounding, mechanical and morphological properties of carbon-black-filled natural rubber/recycled ethylene-propylene-diene-monomer (NR/R-EPDM) blends. *Polym. Test.* **2013**, *32*, 385–393. [[CrossRef](#)]
8. Vahdatbin, M.; Jamshidi, M. Using chemical agent in microwave assisted devulcanization of NR/SBR blends: An effective recycling method. *Resour. Conserv. Recycl.* **2022**, *179*, 106045. [[CrossRef](#)]
9. Xiankui, Z.; Huihui, S.; Chuansheng, W. Experimental Research on Seal Ring in the Pipeline Mixed with r-EPDM. *Adv. Mater. Res.* **2011**, *221*, 490–494.
10. Ghorai, S.; Mondal, D.; Hait, S.; Ghosh, A.K.; Wiessner, S.; Das, A.; De, D. Devulcanization of Waste Rubber and Generation of Active Sites for Silica Reinforcement. *ACS Omega* **2019**, *4*, 17623–17633. [[CrossRef](#)]
11. Ghosh, J.; Hait, S.; Ghorai, S.; Mondal, D.; Wießner, S.; Das, A.; De, D. Cradle-to-cradle approach to waste tyres and development of silica based green tyre composites. *Resour. Conserv. Recycl.* **2020**, *154*, 104629. [[CrossRef](#)]
12. Saiwari, S.; Waesateh, K.; Lopattananon, N.; Thititammawong, A.; Kaesaman, A. Study on reuse of diphenyl disulfide-devulcanized natural rubber from truck tires. *Macromol. Symp.* **2015**, *354*, 155–162. [[CrossRef](#)]
13. Pirityi, D.Z.; Pölöskei, K. Thermomechanical Devulcanisation of Ethylene Propylene Diene Monomer (EPDM) Rubber and Its Subsequent Reintegration into Virgin Rubber. *Polymers* **2021**, *13*, 1116. [[CrossRef](#)] [[PubMed](#)]

14. Dierkes, W.K.; Dijkhuis, K.; Hoek, H.V.; Noordermeer, J.W.M.; Reuvekamp, L.A.E.M.; Saiwari, S.; Blume, A. Designing of cradle-to-cradle loops for elastomer products. *Plast. Rubber Compos.* **2019**, *48*, 3–13. [[CrossRef](#)]
15. Dijkhuis, K.A.J. Recycling of Vulcanized EPDM-Rubber—Mechanistic Studies into the Development of a Continuous Process Using Amines as Devulcanization Aids. Ph.D. Thesis, University of Twente, Enschede, The Netherlands, 17 April 2008.
16. Davis, A.R. Plasticizing GR-S and natural rubber. *Ind. Eng. Chem.* **1947**, *39*, 94–100. [[CrossRef](#)]
17. Rajan, V.V.; Dierkes, W.K.; Joseph, R.; Noordermeer, J.W.M. Effect of Diphenyldisulfides with Different Substituents on the Reclamation of NR Based Latex Products. *J. Appl. Polym. Sci.* **2007**, *104*, 3562–3580. [[CrossRef](#)]
18. van Hoek, J.W.; Heideman, G.; Noordermeer, J.W.M.; Dierkes, W.K.; Blume, A. Implications of the use of silica as active filler in passenger car tire compounds on their recycling options. *Materials* **2019**, *12*, 725. [[CrossRef](#)] [[PubMed](#)]
19. Rajan, V.V.; Dierkes, W.K.; Joseph, R.; Noordermeer, J.W.M. Recycling of NR based cured latex material reclaimed with 2,2'-dibenzamidodiphenyldisulphide in a truck tire tread compound. *J. Appl. Polym. Sci.* **2006**, *102*, 4194–4206. [[CrossRef](#)]
20. van Hoek, H.; Noordermeer, J.; Heideman, G.; Blume, A.; Dierkes, W. Best Practice for De-Vulcanization of Waste Passenger Car Tire Rubber Granulate Using 2-2-dibenzamidodiphenyldisulfide as De-Vulcanization Agent in a Twin-Screw Extruder. *Polymers* **2021**, *13*, 1139. [[CrossRef](#)]
21. Ostad Movahed, S.; Ansarifar, A.; Karbalaee, S.; Athary Far, S. Devulcanization and recycling of waste automotive EPDM rubber powder by using shearing action and chemical additive. *Prog. Rubber Plast. Recycl. Technol.* **2015**, *31*, 87–116. [[CrossRef](#)]
22. Jalilvand, A.R.; Ghasemi, I.; Karrabi, M.; Azizi, H. A study of EPDM devulcanization in a co-rotating twin-screw extruder. *Iran. Polym. J.* **2007**, *16*, 327–335.
23. Salimi, A.; Abbassi-Sourki, F.; Karrabi, M.; Reza Ghoreishy, M.H. Investigation on viscoelastic behavior of virgin EPDM/reclaimed rubber blends using Generalized Maxwell Model (GMM). *Polym. Test.* **2021**, *93*, 106989. [[CrossRef](#)]
24. Sabzekar, M.; Zohuri, G.; Chenar, M.P.; Mortazavi, S.M.; Kariminejad, M.; Asadi, S. A new approach for reclaiming of waste automotive EPDM rubber using waste oil. *Polym. Degrad. Stab.* **2016**, *129*, 56–62. [[CrossRef](#)]
25. Saiwari, S. Post-Consumer Tires Back into New Tires. Ph.D. Thesis, University of Twente, Enschede, The Netherlands, 23 May 2013.
26. Guo, L.; Lv, D.; Ren, D.; Qu, L.; Wang, W.; Hao, K.; Guo, X.; Chen, T.; Sun, J.; Wang, C.; et al. Effectiveness of original additives in waste rubbers for revulcanization after reclamation with a low-temperature mechanochemical devulcanization method. *J. Clean. Prod.* **2021**, *297*, 126620. [[CrossRef](#)]
27. Li, W.; Wang, Q.; Jin, J.; Li, S. A life cycle assessment case study of ground rubber production from scrap tires. *Int. J. Life Cycle Assess.* **2014**, *19*, 1833–1842. [[CrossRef](#)]
28. Costamagna, M.; Brunella, V.; Luda, M.P.; Romagnolli, U.; Muscato, B.; Girotto, M.; Baricco, M.; Rizzi, P. Environmental assessment of rubber recycling through an innovative thermo-mechanical devulcanization process using a co-rotating twin-screw extruder. *J. Clean. Prod.* **2022**, *348*, 131352. [[CrossRef](#)]
29. Hunt, L.K.; Kovalak, R.R. Devulcanization Of Cured Rubbe. US005891926A, 6 April 1999.
30. Gschwind, L.; Jordan, C.S.; Vennemann, N. Devulcanization of EPDM rubber waste. Effect of diphenyl disulfide derivate as devulcanizing agent on vulcanization, and devulcanization process. *J. Appl. Polym. Sci.* **2022**, *139*, 52141. [[CrossRef](#)]
31. Joseph, A.M.; George, B.; Madhusoodanan, K.N.; Alex, R. Cure characteristics of devulcanized rubber: The issue of low scorch. *Rubber Chem. Technol.* **2017**, *90*, 536–549. [[CrossRef](#)]
32. Joseph, A.; George, B.; Madhusoodanan, K.; Alex, R. Current status of sulphur vulcanization and devulcanization chemistry: Process of vulcanization. *Rubber Sci.* **2015**, *28*, 82–121.
33. de Sousa, F.D.B.; Zanchet, A.; Marczyński, E.S.; Pistor, V.; Fiorio, R.; Crespo, J.S. Devulcanized EPDM without paraffinic oil in the production of blends as a potential application of the residues from automobile industry. *J. Mater. Cycles Waste Manag.* **2020**, *22*, 273–284. [[CrossRef](#)]
34. Tao, G.; He, Q.; Xia, Y.; Jia, G.; Yang, H.; Ma, W. The effect of devulcanization level on mechanical properties of reclaimed rubber by thermal-mechanical shearing devulcanization. *J. Appl. Polym. Sci.* **2013**, *129*, 2598–2605. [[CrossRef](#)]
35. De, D.; Maiti, S.; Adhikari, B. Reclaiming of rubber by a renewable resource material (RRM). III. Evaluation of properties of NR reclaim. *J. Appl. Polym. Sci.* **2000**, *75*, 1493–1502. [[CrossRef](#)]
36. Saiwari, S.; van Hoek, J.W.; Dierkes, W.K.; Reuvekamp, L.E.A.M.; Heideman, G.; Blume, A.; Noordermeer, J.W.M. Upscaling of a batch de-vulcanization process for ground car tire rubber to a continuous process in a twin screw extruder. *Materials* **2016**, *9*, 724. [[CrossRef](#)] [[PubMed](#)]
37. Sutanto, P.; Picchioni, F.; Janssen, L.P.B.M. Modelling a continuous devulcanization in an extruder. *Chem. Eng. Sci.* **2006**, *61*, 7077–7086. [[CrossRef](#)]
38. Yun, J.; Yashin, V.V.; Isayev, A.I. Ultrasonic devulcanization of carbon black-filled ethylene propylene diene monomer rubber. *J. Appl. Polym. Sci.* **2004**, *91*, 1646–1656. [[CrossRef](#)]
39. Ma, L.; Zhang, Z.; Peng, Z.; Formela, K.; Wang, S. Dynamic mechanical properties and flexing fatigue resistance of tire sidewall rubber as function of waste tire rubber reclaiming degree. *J. Appl. Polym. Sci.* **2021**, *138*, e51290. [[CrossRef](#)]
40. Lv, X.L.; Huang, H.X.; Lv, B.Y. Balancing mechanical properties and processability for devulcanized ground tire rubber using industrially sized single-screw extruder. *J. Appl. Polym. Sci.* **2016**, *133*, 43761. [[CrossRef](#)]
41. Seghar, S.; Asaro, L.; Rolland-Monnet, M.; Ait Hocine, N. Thermo-mechanical devulcanization and recycling of rubber industry waste. *Resour. Conserv. Recycl.* **2019**, *144*, 180–186. [[CrossRef](#)]

42. Simon, D.Á.; Bárány, T. Effective thermomechanical devulcanization of ground tire rubber with a co-rotating twin-screw extruder. *Polym. Degrad. Stab.* **2021**, *190*, 109626. [[CrossRef](#)]
43. Bilgili, E.; Arastoopour, H.; Bernstein, B. Pulverization of rubber granulates using the solid state shear extrusion process: Part II. Powder characterization. *Powder Technol.* **2001**, *115*, 277–289. [[CrossRef](#)]
44. Bilgili, E.; Arastoopour, H.; Bernstein, B. Pulverization of rubber granulates using the solid-state shear extrusion (SSSE) process: Part I. Process concepts and characteristics. *Powder Technol.* **2001**, *115*, 265–276. [[CrossRef](#)]
45. Tozzi, K.A.; Canto, L.B.; Scuracchio, C.H. Reclaiming of Vulcanized Rubber Foam Waste from the Shoe Industry Through Solid-state Shear Extrusion and Compounding with SBR. *Macromol. Symp.* **2020**, *394*, 2000094. [[CrossRef](#)]
46. Mouri, M.; Sato, N.; Okamoto, H.; Matsushita, M.; Honda, H.; Nakashima, K.; Takeushi, K.; Suzuki, Y.; Owaki, M. Continuous devulcanisation by shear flow stage reaction control technology for rubber recycling. Part 4. Devulcanisation mechanism for EPDM. *Int. Polym. Sci. Technol.* **2000**, *27*, T17–T22.
47. Grundler, M. Optimierung der Thermischen Leitfähigkeit Hochgefüllter Graphit-Polymer-Compounds zur Wärmeableitung. Ph.D. Thesis, Universität Duisburg-Essen, Duisburg, Germany, 15 July 2021.
48. Irfan, M.S.; Umer, R.; Rao, S. Optimization of Compounding Parameters for Extrusion to Enhance Mechanical Performance of Kenaf-Polypropylene Composites. *Fibers Polym.* **2021**, *22*, 1378–1387. [[CrossRef](#)]
49. Kohlgrüber, K. *Der Gleichläufige Doppelschneckenextruder—Grundlagen, Technologie, Anwendungen*, 2nd ed.; Carl Hanser Verlag: München, Germany, 2016; pp. 290+470.
50. Macsiniuc, A.; Rochette, A.; Rodrigue, D. Understanding the regeneration of EPDM rubber crumbs from used tyres. *Prog. Rubber Plast. Recycl. Technol.* **2010**, *26*, 51–81. [[CrossRef](#)]
51. Tripathy, A.R.; Morin, J.E.; Williams, D.E.; Eyles, S.J.; Farris, R.J. A novel approach to improving the mechanical properties in recycled vulcanized natural rubber and its mechanism. *Macromolecules* **2002**, *35*, 4616–4627. [[CrossRef](#)]
52. Mohaved, S.O.; Ansarifard, A.; Nezhad, S.K.; Atharyfar, S. A novel industrial technique for recycling ethylene-propylene-diene waste rubber. *Polym. Degrad. Stab.* **2015**, *111*, 114–123. [[CrossRef](#)]
53. Dobrota, D.; Dobrota, G. Reducing of Energy Consumption by Improving the Reclaiming Technology in Autoclave of a Rubber Wastes. *Energies* **2019**, *12*, 1460. [[CrossRef](#)]
54. Mandal, S.K.; Alam, N.; Debnath, S.C. Reclaiming of ground rubber tire by safe multifunctional rubber additives: I. Tetra benzylthiuram disulfide. *Rubber Chem. Technol.* **2012**, *85*, 629–644. [[CrossRef](#)]
55. Ghosh, J.; Ghorai, S.; Bhunia, S.; Roy, M.; De, D. The role of devulcanizing agent for mechanochemical devulcanization of styrene butadiene rubber vulcanizate. *Polym. Eng. Sci.* **2018**, *58*, 74–85. [[CrossRef](#)]
56. Lepadatu, A.M.; Asaftei, S.; Vennemann, N. Investigation of new composite materials based on activated EPDM rubber waste particles by liquid polymers. *J. Appl. Polym. Sci.* **2015**, *132*, 42097. [[CrossRef](#)]
57. Lepadatu, A.M. Recycling of EPDM Rubber Waste Particles by Chemical Activation with Liquid Polymers. Ph.D. Thesis, University of Osnabrück, Osnabrück, Germany, 2015.
58. Barbosa, R.; Ambrosio, J.D. Devulcanization of natural rubber compounds by extrusion using thermoplastics and characterization of revulcanized compounds. *J. Polym. Res.* **2019**, *26*, 160. [[CrossRef](#)]
59. Herrmann, V.; Hanning, S.; Kreyenschmidt, M. Untersuchung zur Diffusion des Schwefels in Rezyklat-Kautschukmischungen Teil 1: Bestimmung des Diffusionskoeffizienten. *GAK Gummi Fasern Kunstst.* **2018**, *71*, 232–241.
60. Herrmann, V.; Hanning, S.; Kreyenschmidt, M.; Wolff, A. Untersuchungen zur Diffusion des Schwefels in Rezyklat-Kautschukmischungen Teil 2: Schwefeldiffusion in Mischungen mit Gummimehl. *GAK Gummi Fasern Kunstst.* **2018**, *71*, 232–241.
61. Pistor, V.; Scuracchio, C.H.; Oliveira, P.J.; Fiorio, R.; Zattera, A.J. Devulcanization of ethylene-propylene-diene polymer residues by microwave—Influence of the presence of paraffinic oil. *Polym. Eng. Sci.* **2011**, *51*, 697–703. [[CrossRef](#)]

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