



# Recycling of EPDM rubber via thermomechanical devulcanization: Batch and continuous operations

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## ABSTRACT

Thermomechanical devulcanization is a possible solution for the circular economy of EPDM rubber, as it removes covalent crosslinks from vulcanizates, resulting in a material similar to uncured rubber mixes. In this paper, sulfur-cured EPDM rubber was treated with thermomechanical stimuli: a) processing on a two-roll mill and in an internal mixer, and b) twin-screw extrusion. Horikx's analysis indicated a 75 % decrease in crosslink density with little polymer chain degradation. The resulting devulcanizates and non-devulcanized rubber crumb were added to the original rubber mix, yielding samples with 0, 25, 50, 75 and 100 wt% recycled rubber contents. Revulcanizates with up to 50 wt% devulcanizate content retained the tensile strength of the original rubber with a slight increase in modulus. Ultimately, batch devulcanization had the most promising results, and extrusion devulcanization was also more beneficial than using non-devulcanized rubber crumb. Crosslink density and morphological tests also support these findings.

## 1. Introduction

Ethylene propylene diene monomer (EPDM) rubber is the most common synthetic elastomer used outside the vehicle tyre industry [1]. It was developed from ethylene-propylene copolymer in order to make traditional sulfur curing possible. Consequently, a cheap, widely available synthetic elastomer was created. Similarly to other elastomers, it is used in compounds that are heavily filled with inorganic particles such as carbon black, silica, dolomite, etc. Most EPDM products exploit the material's excellent chemical stability, resistance to UV, heat and ozone, allowing outdoor applications with lifecycles reaching up to 50 years [2, 3]. Consequently, the global demand for EPDM rubber has reached 1.5 million tonnes per year, and this sheer volume makes EPDM recycling a hot research topic. Similarly to other elastomers, the circular economy of EPDM rubber cannot be achieved at the moment, as covalent crosslinks do not allow the traditional, value-conserving reprocessing of elastomer products [4,5]. Covalent adaptable networks may offer a long-term solution, but they are not commercially available due to their high costs [6–8].

Current rubber waste management practices revolve around recycling as ground rubber, and incineration [9]. However, full recovery

whereby waste rubber can completely replace primary rubber ingredients has not been achieved. While natural rubber is a renewable, bio-based resource, most synthetic rubbers are crude oil derivatives. Therefore, the waste management of synthetic rubbers is especially critical [10–12]. Devulcanization may become the ultimate solution, as it is the process of converting rubber waste into its original uncured form via the selective scission of covalent crosslinks in the elastomer matrix. Ideally, devulcanization would yield an uncured rubber mixture ready to be vulcanized with intact polymer chains. In practice, however, devulcanization is always accompanied by undesired side reactions such as chain degradation and oxidation, hindering the mechanical properties of devulcanized rubber. The type of curatives also has a significant effect on the devulcanization of rubber. Considering that the bond energy of C–C covalent bonds is larger than that of C–S and S–S bonds, peroxide-cured rubbers are more prone to side reactions (i.e. degradation) during devulcanization than sulfur-cured rubbers [4,13–16]. The reactions occurring during devulcanization are not fully understood yet, but it is generally accepted that radical formation, rearrangement, substitution and oxidation are the main pathways. Devulcanization promoting chemicals can trigger further mechanisms, but their presence limits the application of the devulcanizates. The various reaction types

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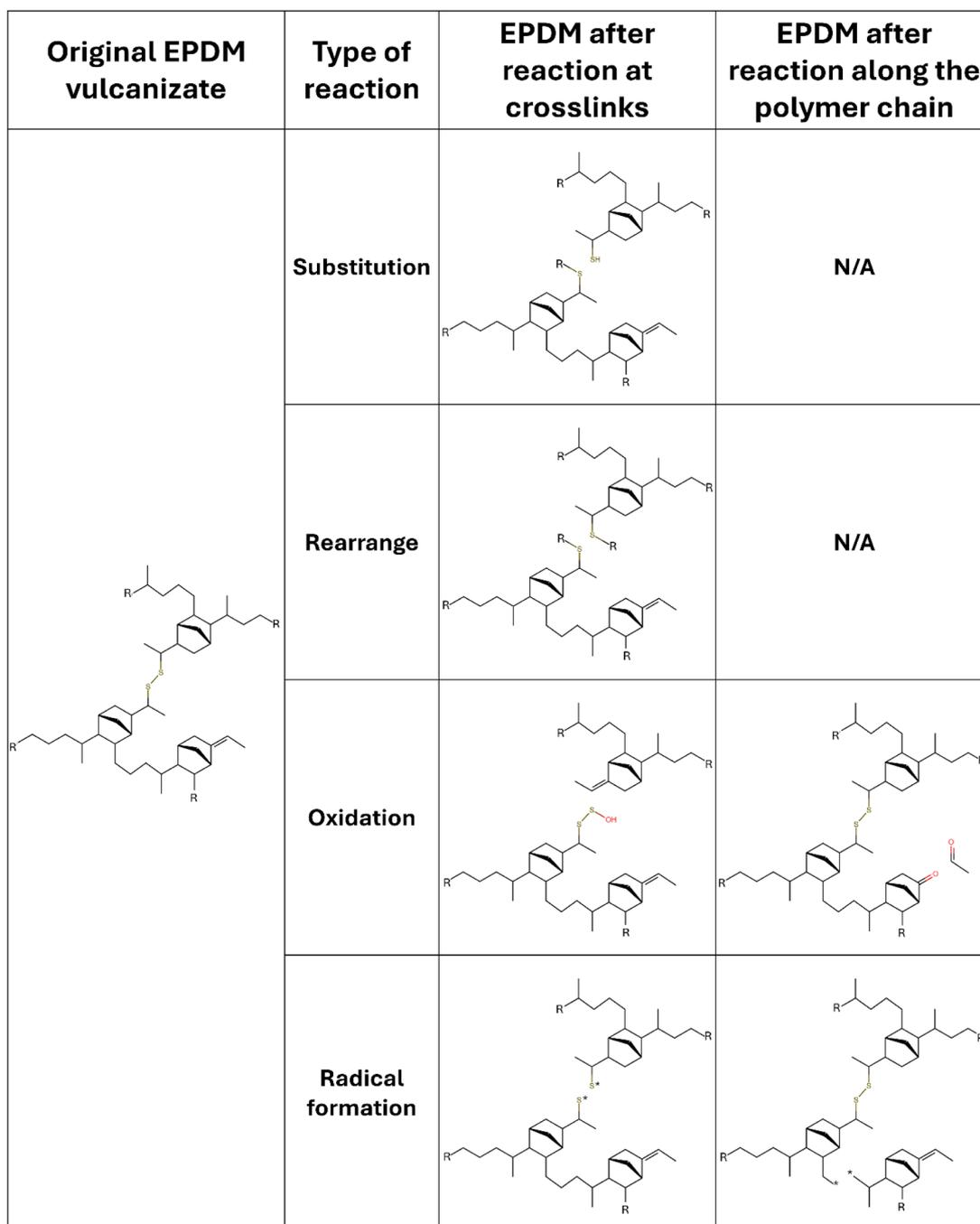


Fig. 1. Reaction mechanisms during EPDM devulcanization.

can occur along the polymer chain or specifically at crosslinks as shown in Fig. 1.

It is impossible to isolate these mechanisms, they are occurring simultaneously. However, processing technologies and conditions have a crucial role in promoting the desired reaction pathways over those that reduce the quality of the devulcanizate. Overall, exposure to air at temperatures above 240 °C is the main driver of oxo-degradation while exposure to temperatures above 280 °C can trigger the random scission of polymer chains via radical formation. Furthermore, Fukumori and Matsushita [15] have suggested that the elastic constants of covalent bonds also affect the selectivity for the breakage of sulfur-containing bonds. Their reasoning is based on the fact that the bond energies of C–C, C–S and S–S bonds are of similar magnitude, the respective elastic constants show a larger variation. Consequently, heating alone causes

the random scission of covalent bonds, while mechanical treatment and shearing can induce the selective breakdown of sulfur crosslinks [15, 17–20].

Several distinct devulcanization techniques have been developed over the past decades, and they can be evaluated based on their yield, conversion rate and selectivity. During microbial devulcanization, certain strains of bacteria digest the sulfur components of rubber to fuel themselves. It is a highly selective process with little side reactions, but it is only effective near the surface of rubber and it is not easily scalable [21,22]. Microwave devulcanization induces uniform heat generation throughout the rubber matrix, thus the surface effect is significantly reduced compared to microbial devulcanization. However, microwave devulcanization is also difficult to scale [23,24]. It is possible to achieve high selectivity and conversion via chemical devulcanization. However,

this technique is difficult to scale and requires the use of organic solvents in many cases, so it has gained little attention from industry lately [22, 25–27]. Several distinct thermomechanical devulcanization techniques have also been developed. They are widely adaptable and can be combined with other stimuli (such as devulcanization agents, ultrasounds or supercritical carbon dioxide). Batch devulcanization normally occurs in conventional rubber processing equipment (two-roll mill or internal mixer), while a continuous operation is normally conducted in extruders. Thermomechanical devulcanization offers a good balance in yield, conversion and selectivity, thus it is regarded as a promising technology. Extrusion devulcanization is often considered the scaled-up version of batch thermomechanical devulcanization [28–32].

Horikx's analysis has been proven as a reliable tool to evaluate the effectiveness of devulcanization [33–35]. This method is based on the Flory-Huggins theory, and correlates the degree of devulcanization (percent decrease in crosslink density) with the sol content of rubber. Two theoretical curves can be generated: a) one corresponding to ideal devulcanization, b) the other corresponding to polymer degradation. Experimental data can be plotted between these curves and the data points' relative distance from these curves can indicate the selectivity of the devulcanization technology.

Sutanto et al. [13,18] developed kinetic models on the thermo-mechanical devulcanization of EPDM rubber. They found that EPDM can be devulcanized even at temperatures exceeding 200 °C, due to its excellent heat resistance. Macsiniuc et al. [30] achieved high degrees of devulcanization: ~75 % in batch operation and ~80 % in continuous operations. However, they did not analyze the extent of side reactions. Other studies reported either lower degrees of devulcanization with a low extent of side reactions or higher degrees of devulcanization accompanied by severe oxidative degradation processes [36,37]. Treatment temperature, residence time, shearing rate and fill ratio have been identified as the most important parameters affecting the success of devulcanization.

Though Horikx's analysis is an excellent tool to analyze devulcanization, it is not adequate on its own without studying the applicability of the devulcanizates. Four distinct uses of devulcanized rubber have been identified [26,38]: (a) blending with thermoset resins to increase their stiffness [39]; (b) blending with thermoplastic polymers to form thermoplastic elastomers [40]; (c) mixing with virgin rubber to form partly recycled rubber products [41,42]; and (d) devulcanization to yield 100 % recycled rubber [43]. However, from a circular economy point of view, waste rubber should end up in recycled rubber products with similar purposes to those of the original product.

Seghar et al. [44] experimented with the application of devulcanizates in virgin rubber. They found that 20 wt% recycled content would result in a 20 % decrease in the samples' Young's modulus and tensile strength. Movahed et al. [45] also reported a quasi-linear decrease in mechanical properties of recycled rubber at increasing devulcanizate contents.

Previously, our research group has reported results on the microwave and thermomechanical devulcanization of ground tire rubber and EPDM rubber [23,46–48]. We have reported up to 80 % decrease in crosslink density during the batch thermomechanical devulcanization of EPDM rubber on a two-roll mill with a low extent of side reactions. The current paper is aimed at scaling up these findings on an extruder while comparing the two thermomechanical technologies based on the obtained recycled materials. Devulcanizates were characterized via Horikx's analysis. Subsequently, they were mixed into virgin rubber mixtures to form partially recycled rubber samples with various recycled contents. Mechanical, morphological and swelling tests were performed on the obtained devulcanizates to investigate the effectiveness of EPDM recycling via batch and continuous thermomechanical devulcanization.

**Table 1**

Composition of the EPDM mixture used for the experiments.

Component	Amount (phr)
Dutral TER 4047	100
Dolomite B	30
N550 carbon black	45
N772 carbon black	40
DK 350 oil	15
UltraLube UL160	3
PEG 4000*	1
Zinc oxide	4
Zinc stearate	1
TBTD**	0.8
MBT***	1.5
ZDBC****	0.8
Sulfur	1
Total	243.1

\* Polyethylene glycol with an average molecular weight of 4000 Da.

\*\* Tetrabutylthiuram disulphide.

\*\*\* Mercaptobenzothiazole.

\*\*\*\* Zinc dibutyl dithiocarbamate.

## 2. Experimental

### 2.1. Materials

Throughout the experiments, the same EPDM-based sulfuric rubber mixture was used. The base polymer was Dutral TER 4047 (ML(1+4 at 125°C): 55) with 54.0 wt% ethylene, 41.5 wt% propylene and 4.5 wt% ethylidene norbornene contents. The rubber mixture was produced and provided by Palotás Mix Kft. (Kemeneshőgyész, Hungary), and its composition is presented in Table 1.

Revolcanization experiments required the use of the same curing agents as used in the original recipe: zinc oxide (produced by S.C. Werco Metal S.r.l., Zlatna, Romania), zinc stearate (produced by Merck KGaA, Darmstadt, Germany), TBTD, MBT, ZDBC, and sulfur (all produced by Ningbo Actmix Rubber Chemicals Co., Ltd., Ningbo, China).

### 2.2. Sample preparation

First, the EPDM reference rubber was cured with a Collin Teach-Line Platen Press 200E (Dr. Collin GmbH, Ebersberg, Germany) hot press. Curing took place at 180 °C with a 2.8 MPa closing pressure. A 2 mm thick mold was used for curing, and the rubber mixture was kept in the mold for  $t_{90}$ , which was previously determined via rheometer measurements. The resulting 2 mm thick rubber sheets were pulverized in a RETSCH ZM200 (Retsch GmbH, Haan, Germany) cryogenic mill at a 12,000 rpm rotor speed. The mill was equipped with a ring sieve with 2 mm trapezoid holes. 55 wt% of the resulting powder had a particle size larger than 710  $\mu$ m, and only this fraction was chosen for devulcanization to maximize the shearing rate during devulcanization [47].

A previously reported two-step devulcanization technique was used for the preparation of batch devulcanizates. This technique was used because of its high degree of devulcanization and low extent of chain degradation [48]. The first step took place on a Labtech LRM-SC-11/3E (Labtech Engineering Co. Ltd., Samutprakarn, Thailand) two-roll mill. EPDM rubber crumb was fed to the rolls in batches of 50 g and each batch was allowed to pass through the gap 20 times. The gap size was 0.5 mm for the first round, which was decreased to 0.1 mm to maximize the shearing rate over the course of the remaining 19 rounds. Roll speeds were set at 4 and 2 rpm for the front and rear rolls, respectively. Three temperature settings were applied: (a) 170 and 190 °C, (b) 190 and 210 °C, and (c) 210 and 230 °C at the front and rear rolls, respectively. The second step of devulcanization took place in a Brabender Plasti-Corder (Brabender Technologie GmbH & Co., Duisburg, Germany) internal mixer. Throughout the procedure, the mixer was equipped with

**Table 2**  
Summary of the devulcanized samples.

Batch samples										
Sample name	Temperature of front roll (°C)				Temperature of rear roll (°C)				Temperature of internal mixer (°C)	
dEPDM <sub>b1</sub>	170				190				N/A	
dEPDM <sub>b2</sub>	190				210				N/A	
dEPDM <sub>b3</sub>	210				230				N/A	
dEPDM <sub>b4</sub>	170				190				180	
dEPDM <sub>b5</sub>	190				210				180	
dEPDM <sub>b6</sub>	210				230				180	
dEPDM <sub>b7</sub>	170				190				200	
dEPDM <sub>b8</sub>	190				210				200	
dEPDM <sub>b9</sub>	210				230				200	
Extruded samples										
Sample name	Extruder zone temperatures (°C)									
	Zone 10	Zone 9	Zone 8	Zone 7	Zone 6	Zone 5	Zone 4	Zone 3	Zone 2	Zone 1
dEPDM <sub>c1</sub>	160	155	155	155	150	150	150	145	145	145
dEPDM <sub>c2</sub>	170	165	165	165	160	160	160	155	155	155
dEPDM <sub>c3</sub>	180	175	175	175	170	170	170	165	165	165
dEPDM <sub>c4</sub>	190	185	185	185	180	180	180	175	175	175
dEPDM <sub>c5</sub>	200	195	195	195	190	190	190	185	185	185
dEPDM <sub>c6</sub>	210	205	205	205	200	200	200	195	195	195

tangential rotors, a 50 cm<sup>3</sup> chamber, and a fill factor of 75 % was applied. This step of devulcanization lasted for 15 min with a 150 rpm rotor speed. Three settings were tested: (a) no treatment in internal mixer, (b) 180 °C, and (c) 200 °C.

The continuous devulcanization took place in a Labtech LTE 26-44 (Labtech Engineering Co. Ltd., Samutprakarn, Thailand) twin-screw extruder. The die was removed from the end of the extruder to decrease the pressure build-up in the barrel. The screw speed was set to 60 rpm, based on our previous results [23]. All devulcanization parameters and the nomenclature of the resulting samples are presented in Table 2.

The applicability of the most promising devulcanizates was tested via reintegration into the original virgin rubber mixture introduced in Table 1. dEPDM<sub>b6</sub> and dEPDM<sub>c6</sub> were selected based on Horikx's analysis (see later in Section 3.1.), and as reference, non-devulcanized rubber crumb was also mixed into virgin rubber to show the positive effects of devulcanization on the recyclability of EPDM rubber. For this procedure, a two-step mixing strategy was applied to make sure that the curatives are adequately dispersed in the recycled rubber crumbs [23, 47]. The devulcanized or non-devulcanized rubber crumbs were first mixed with the original curing system: 4 phr of zinc oxide, 1 phr of zinc stearate, 0.8 phr of TBTD, 1.5 phr of MBT, 0.8 phr of ZDBC and 1 phr of sulfur. The amounts were measured for polymer content, not for the overall weight of the rubber crumbs. Then these mixtures were added to the virgin rubber mixture introduced in Table 1. Mixing took place in a Brabender Plasti-Corder internal mixer for 10 min at 60 °C with a 75 % fill factor and a 45 rpm rotor speed.

Rubber samples with 0, 25, 50, 75, and 100 wt% recycled rubber contents were prepared. These mixtures were tested in the rheometer and vulcanized until their respective  $t_{90}$  values in the hot press mentioned earlier. The devulcanized samples were named based on the type and amount of recycled rubber they contain. crumb\_25, crumb\_50, crumb\_75, and crumb\_100 contain non-devulcanized rubber crumb at 25, 50, 75 and 100 wt%, respectively. rEPDM<sub>b6\_25</sub>, rEPDM<sub>b6\_50</sub>, rEPDM<sub>b6\_75</sub>, and rEPDM<sub>b6\_100</sub> contain the selected batch-devulcanized sample (dEPDM<sub>b6</sub>) at 25, 50, 75 and 100 wt%, respectively. rEPDM<sub>c6\_25</sub>, rEPDM<sub>c6\_50</sub>, rEPDM<sub>c6\_75</sub>, and rEPDM<sub>c6\_100</sub> contain the selected continuously devulcanized sample (dEPDM<sub>c6</sub>) at 25, 50, 75 and 100 wt%, respectively.

### 2.3. Testing

Curing properties were determined with a MonTech Monsanto

R100S (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) rheometer. Isothermal ( $T = 180$  °C) time sweep mode (1.667 Hz, 1° amplitude) was run for 30 min.

For Horikx's analysis, the sol content and the crosslink density of all rubber samples had to be determined. Sol content was measured via Soxhlet extraction in toluene. For each sample, 5 parallel tests were run to minimize experimental error. A correction had to be applied to the measured sol content values to account for the completely extractable rubber components [47]. The crosslink density of the rubber samples was evaluated via swelling tests in toluene according to the ASTM D6814-02 standard [49]. EPDM rubber was immersed into toluene for 72 h, and the crosslink density can be calculated based on the amount of toluene it absorbs, based on the Flory-Rehner equation. The determination of the crosslink density and sol content of rubber samples required the use of toluene (supplied by Fisher Scientific UK, Loughborough, United Kingdom). The polymer-solvent interaction parameter for the EPDM-toluene system was assumed to be 0.496 [16,30,33,50].

Test specimens for tensile and tear strength tests were prepared via die cutting with a ball press. Tensile tests were performed on a Zwick Z005 (ZwickRoell GmbH & Co. KG, Ulm, Germany) tensile tester with a 5 kN load cell, as per ISO 37:2017. The clamping distance was 60 mm, and the crosshead speed was 500 mm/min. The same tensile tester was used for the tear strength tests, which were performed according to ISO 34-1:2015. The clamping distance was 56 mm and the crosshead speed was 500 mm/min. The Shore A hardness of the rubber samples was determined with a Zwick H04.3150.000 (ZwickRoell GmbH & Co. KG, Ulm, Germany) hardness tester, according to ISO 48-4:2018 [51–53].

Scanning electron micrographs (SEM) were taken with a Jeol JSM-6380LA (Jeol LTD., Tokyo, Japan) microscope. The fracture surfaces of tensile test specimens were first sputter-coated with gold, and then analyzed in the microscope.

## 3. Results and discussion

### 3.1. Evaluation of devulcanization

To perform Horikx's analysis, the degree of devulcanization and the sol content of each devulcanizate were determined. To separate the effects of thermomechanical processing from cryogenic milling, the cryo-milled rubber crumbs were also tested accordingly. Cryo-milled rubber crumbs had a 4.5 % sol content, and showed a 2 % decrease in cross-link density. These values make the milled rubber virtually identical to the bulk virgin rubber. Cryogenic milling is proven to be a gentle size-

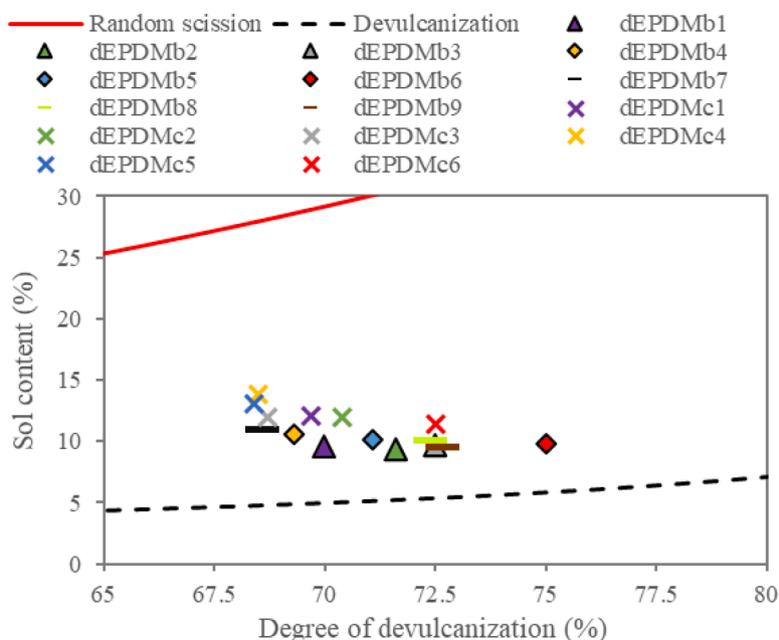


Fig. 2. Horikx's plot for the devulcanizates.

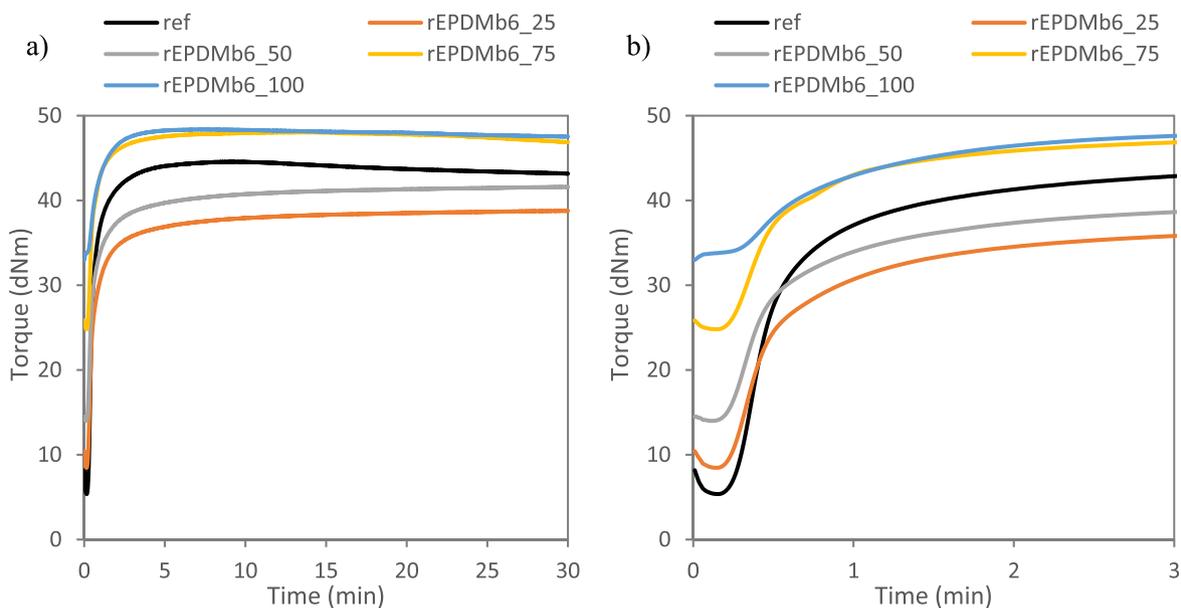


Fig. 3. Curing curves for selected revulcanizates: (a) for 30 min, (b) zoomed in for the scorch period.

reduction method that keeps the molecular structure of rubber intact. The sol content and crosslink density values of devulcanizates are plotted in Fig. 2. In general, both batch devulcanization and extrusion decreased the crosslink density of EPDM rubber by around 70 %. The operating temperature of the two-roll mill had a stronger influence on devulcanization than the temperature of the internal mixer. The higher the temperature of the milling rolls, the higher the degree of devulcanization. All sol content values are in the range of 9–14 %, and extruded samples have a slightly higher sol content than batch devulcanizates. All data points lie between the two theoretical curves, but the ones representing batch devulcanizates are closer to the theoretical curve corresponding to devulcanization than points representing extruded samples. Ultimately, it means that these devulcanization processes eliminate around 70 % of crosslinks from the rubber matrix while keeping the polymer chains mostly intact. Extrusion would cause a slightly larger

extent of polymer degradation than batch devulcanization, which can be attributed to the higher temperatures reached in the extruder. Batch devulcanization took 30 min overall, but the rubber crumbs only stayed in the high-shear zone of the mill for only a few seconds each time they were passed through the rolls, approximately 60–100 s overall. The residence time of rubber crumbs in the extruder were around 80–100 s. While shearing times were comparable for the two technologies, the samples were allowed to cool down between passes through the roll during batch devulcanization. Consequently, the samples would reach a lower maximum temperature during milling than in the extruder. Even though batch devulcanization took place in open air, the lower temperatures limited the risk of oxidation. Overall, it can be concluded that the reaction pathways introduced in Fig. 1 were indeed occurring simultaneously in both cases, since the data points do not lie on either theoretical curve but in between. However, radical formation along the

**Table 3**  
Curing parameters of the revulcanizates.

Sample name	Scorch time (s)	$t_{90}$ (min)	$S_{min}$ (dNm)	$S_{max}$ (dNm)
ref	14	1.8	5.4	44.6
crumb_25	13	3.4	11.3	45.7
crumb_50	14	4.6	15.7	47.8
crumb_75	12	5.7	26.5	51.5
crumb_100	13	2.6	35.4	55.1
rEPDM <sub>b6</sub> _25	15	2.9	8.5	38.8
rEPDM <sub>b6</sub> _50	16	4.8	14.0	41.6
rEPDM <sub>b6</sub> _75	13	4.1	24.8	48.1
rEPDM <sub>b6</sub> _100	17	2.5	33.7	48.5
rEPDM <sub>c6</sub> _25	13	3.2	6.9	34.3
rEPDM <sub>c6</sub> _50	15	4.5	11.9	34.7
rEPDM <sub>c6</sub> _75	13	4.7	25.2	48.7
rEPDM <sub>c6</sub> _100	19	2.7	30.3	41.7

polymer chain was more prevalent during extrusion, due to the higher temperatures arising within the samples.

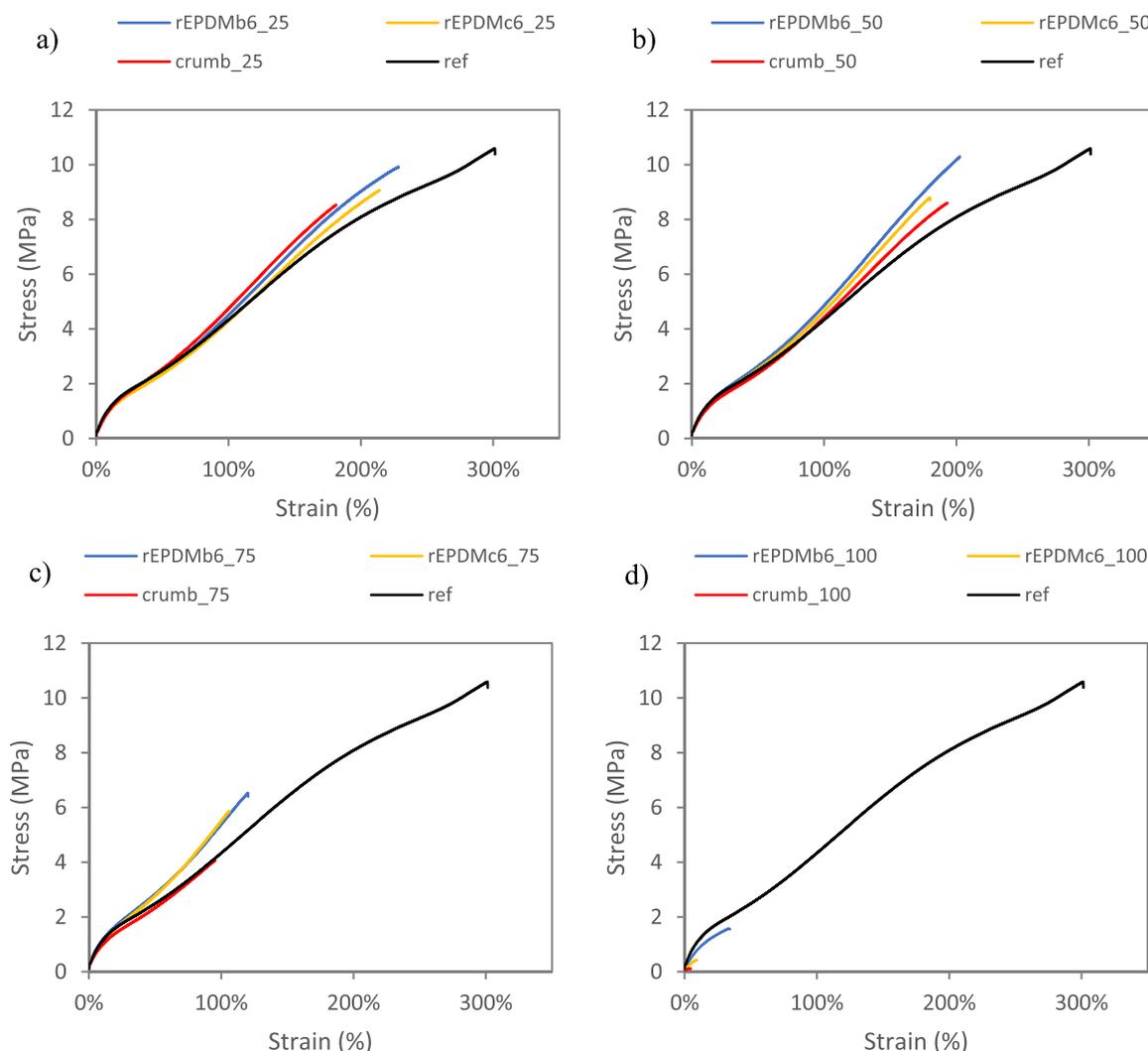
### 3.2. Revulcanization

Based on Fig. 2, dEPDM<sub>b6</sub> and dEPDM<sub>c6</sub> were selected as the most promising samples among batch and continuous devulcanizates, respectively. Along with these two devulcanizates, non-devulcanized rubber crumb was also mixed with the same virgin rubber mixture to

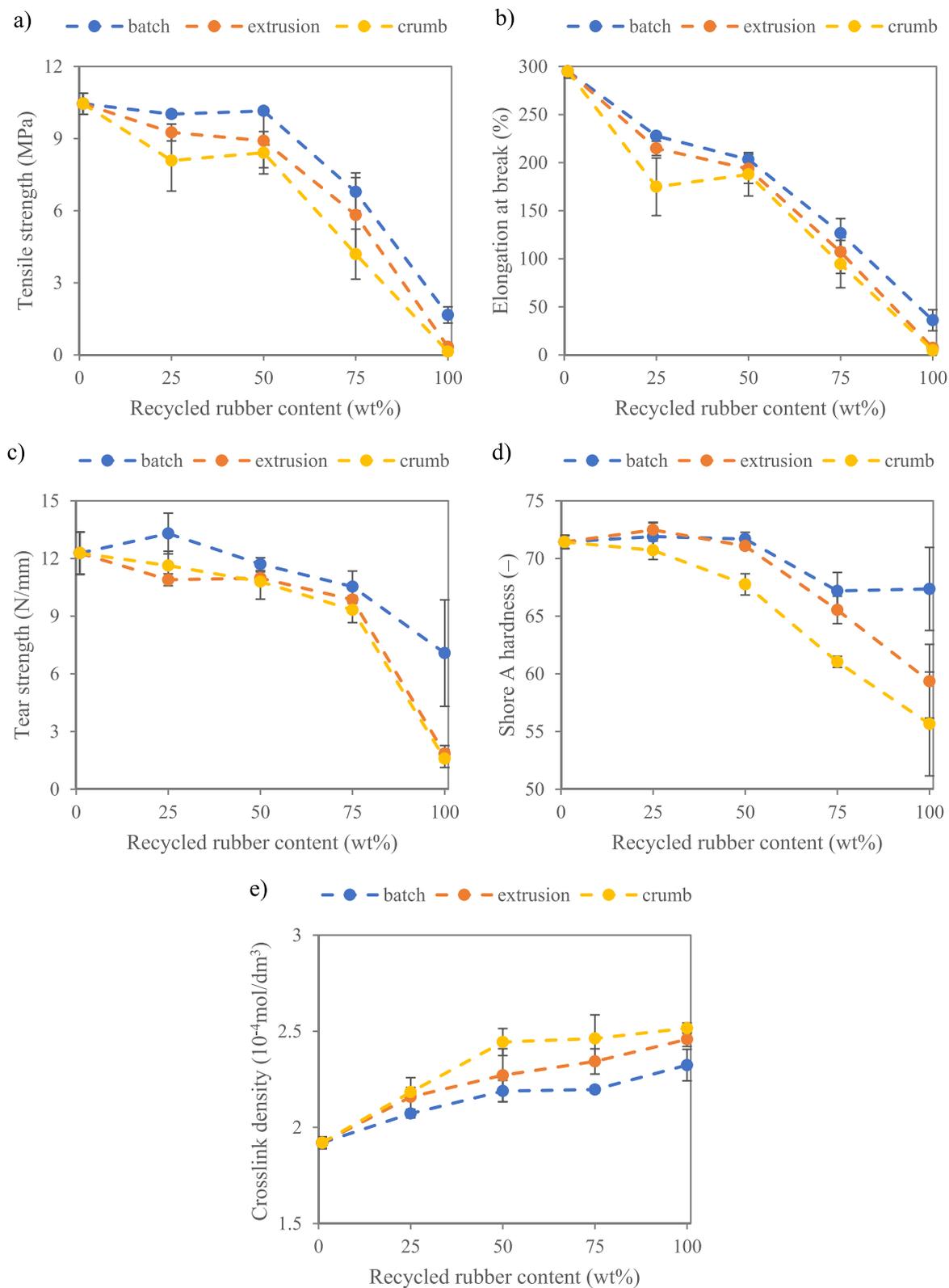
form partially recycled EPDM rubber. In Fig. 3, the curing curves of rEPDM<sub>b6</sub>\_25, rEPDM<sub>b6</sub>\_50, rEPDM<sub>b6</sub>\_75 and rEPDM<sub>b6</sub>\_100 are compared with that of virgin EPDM rubber. The minimum torque value significantly increases at higher devulcanizate contents. Also, the virgin rubber mixture is more prone to reversion than the devulcanizate-containing samples. This phenomenon can be attributed to the migration of curing agents between the virgin and the recycled phases of these samples [54]. Curatives that were initially mixed with the devulcanized rubber particles can diffuse into the virgin rubber phase, thus counteracting the torque-decreasing effects of reversion. Diffusion is more prominent in samples containing large amounts of virgin rubber, consequently the curves of rEPDM<sub>b6</sub>\_25 and rEPDM<sub>b6</sub>\_50 appear marching, while the curing curves of rEPDM<sub>b6</sub>\_75 and rEPDM<sub>b6</sub>\_100 indicate very slight reversion.

The curing properties for all revulcanizates are presented in Table 3. Scorch times showed little variation, while optimal curing times slightly increased at increasing devulcanizate contents. This phenomenon is caused by the diffusion of curing agents between the two rubber phases, as the trend stops for samples containing 100 wt% recycled rubber. Based on the measured minimum and maximum torque values, recycled EPDM content seems to have a hardening effect, and it hinders the processability of rubber mixtures when used in large quantities.

After curing, the revulcanizates were subject to mechanical tests, and the characteristic tensile curves are plotted in Fig. 4. Since all samples have very similar compositions, the onset of the stress-strain curves is



**Fig. 4.** Characteristic stress-strain curves for the EPDM revulcanizates: (a) with 25 wt%, (b) 50 wt%, (c) 75 wt% recycled content, and (d) 100 wt% recycled content.

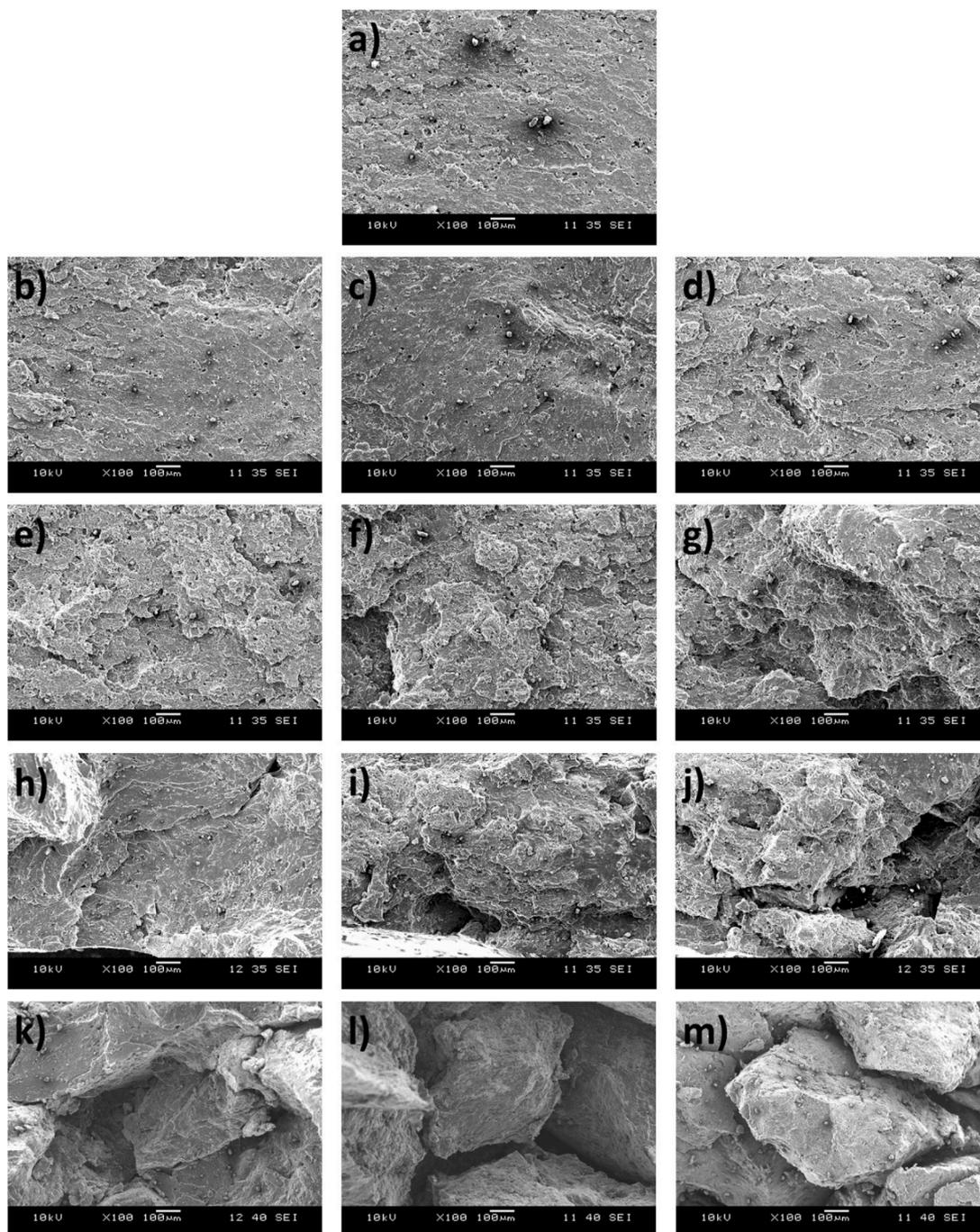


**Fig. 5.** Measured properties of revulcanized rubber vs. recycled rubber content: (a) tensile strength, (b) elongation at break, (c) tear strength, (d) Shore A hardness, (e) crosslink density.

almost identical. Recycled rubber content somewhat increased the modulus, yet it had detrimental effects on the elongation at break values of the samples, especially above 75 wt% content. Samples containing extruded devulcanizates consistently performed worse than the samples with batch devulcanizates, yet still outperformed the non-devulcanized

samples at their respective recycled rubber contents. This can be attributed to the slightly higher extent of degradation during extrusion compared to batch devulcanization.

The tensile strength and elongation at break of the samples are plotted in Fig. 5 against the samples' recycled rubber content. It is shown



**Fig. 6.** SEM micrographs of the fracture surfaces of the revulcanizates: (a) ref, (b) rEPDM<sub>b6\_25</sub>, (c) rEPDM<sub>c6\_25</sub>, (d) crumb\_25, (e) rEPDM<sub>b6\_50</sub>, (f) rEPDM<sub>c6\_50</sub>, (g) crumb\_50, (h) rEPDM<sub>b6\_75</sub>, (i) rEPDM<sub>c6\_75</sub>, (j) crumb\_75, (k) rEPDM<sub>b6\_100</sub>, (l) rEPDM<sub>c6\_100</sub>, (m) crumb\_100.

that revulcanizates containing devulcanized rubber have better tensile properties than samples containing non-devulcanized EPDM rubber crumb. Also, the tensile strength of the reference rubber can be retained up to around 50 wt% recycled content, above which it drops sharply. Revulcanizates with 100 wt% recycled rubber content had barely any strength, some specimens would break under the load of their own weight. Surprisingly, the tensile strength and elongation at break values of crumb\_50 are higher than those of crumb\_25. The corresponding standard deviation values are also higher, indicating irregular sample failures during the tests, which might be due to improper mixing, or a few larger than average rubber crumbs present in one of the test specimens of crumb\_25.

The tear strength values of the recycled samples are shown in Fig. 5c. Compared to the tensile strength, the tear strength of the samples is not hindered as much at increasing recycled contents. Revulcanizates containing batch devulcanizates outperformed the other two experimental sets in this case as well. Crack propagation behaviour does not depend only on the overall mechanical properties of the sample, but also on the dispersion quality of smaller, harder recycled particles within the virgin rubber matrix. Cracks mostly appear within the softer virgin rubber phase along the virgin-recycled interface. At increasing recycled contents, crack propagation is more often obstructed by the hard recycled particles [23,55]. Even though the overall strength of the samples decrease, the tear strength is not impacted as strongly. As adhesion

between the phases is stronger for samples containing batch-devulcanized rubber crumbs, these samples have superior tear strength. Tear strength is only fully compromised when there is no virgin rubber present in the sample, as voids are inevitable in this case.

The Shore A hardness of the revulcanizates is summarized in Fig. 5d. While the hardness of the rubber samples barely changes up to 50 wt% recycled rubber content, a sharp decrease can be observed above 75 wt%. This drop is especially significant in the case of the samples containing non-devulcanized rubber crumbs. The standard deviation of the experimental data increases significantly at larger recycled rubber contents, due to the voids present in the system. The voids can justify the fact why the larger recycled content would decrease the hardness of rubber despite increasing its overall crosslink density. The Shore A probe can inflict cracks in the samples more easily when the adhesion between phases is weaker.

The crosslink density of the revulcanizates was also measured to analyze the curing process further. It is shown that the addition of recycled rubber to the mixture increased the overall crosslink density of the revulcanizates (Fig. 5e). Since the non-devulcanized EPDM crumb had the largest initial crosslink density, crumb\_25, crumb\_50, crumb\_75, and crumb\_100 had larger crosslink densities than their counterparts containing previously devulcanized rubber. A similar trend is observed for the difference between the revulcanizates from the continuous and the batch devulcanization processes. It should be noted that even though the average crosslink density for each sample was evaluated, the crosslink density within partially recycled rubber samples was not homogeneous: the recycled and revulcanized rubber crumb phases are expected to have higher crosslink densities than the virgin matrix, which provides further explanation to the trends of mechanical properties of the partially recycled rubber samples.

Scanning electron micrographs were taken of the fracture surfaces of each tensile test specimen (Fig. 6). The reference sample can be characterized with a smooth fracture surface. This smooth surface is apparent in all samples with up to 25 wt% recycled content. However, when non-devulcanized EPDM crumbs were used, they clearly stood out from the virgin rubber matrix at 50 and 75 wt% recycled contents. The samples containing batch-devulcanized rubber had a more homogeneous surface even at larger filling ratios. However, these devulcanized crumbs did not fully integrate when revulcanized without virgin matrix (Fig. 6k). The morphology observed correlates well with the mechanical tests: the more homogeneous revulcanizates containing batch-devulcanized rubber had better tensile properties than their extruded or non-devulcanized counterparts.

#### 4. Conclusions

A sulfur-cured EPDM rubber, formulated for profile production was subjected to two kinds of thermomechanical devulcanization. The first method involved the combination of batch processes: two-roll milling and mixing in an internal mixer. The second method was twin-screw extrusion. Each devulcanized rubber was tested according to Horikx's theory and it was found that the batch processes were more effective in cleaving the sulfuric crosslinks of the rubber samples. For the batch processes, a 75 % degree of devulcanization was achieved, while extrusion broke 72.5 % of crosslinks. Also, extrusion caused a larger extent of chain degradation events, indicated by the slightly larger sol content of extruded devulcanizates.

To assess the effects of devulcanization further, the devulcanizates were mixed with curing agents and the resulting mixture was added to virgin EPDM rubber in order to produce recycled and partially recycled rubber samples with 25, 50, 75 and 100 wt% recycled contents. The same was performed with non-devulcanized EPDM rubber crumb to see how devulcanization benefits the mechanical properties of recycled rubber. Based on mechanical and morphological tests, batch devulcanization seemed to have outperformed extrusion devulcanization, while both devulcanization processes were more advantageous than the use of

non-devulcanized rubber crumb. The tensile strength barely changed with up to 50 wt% batch devulcanizate content, while the elongation at break value decreased by around 30 %, indicating an increase in modulus. This phenomenon correlates well with the observed increase in crosslink density. Scanning electron micrographs further proved that batch devulcanization resulted in a homogeneous revulcanizate with uniform properties, while extruded and non-devulcanized rubber crumb would introduce local defects in the recycled rubber. These findings are especially pronounced at 75 and 100 wt% recycled rubber contents. However, batch devulcanization is more labor-intensive even on an industrial scale; the only viable thermomechanical devulcanization method that can be economically scaled is extrusion. Consequently, it is vital to optimize shear rates and residence times during extrusion. By controlling the maximum temperature the rubber reaches in the extruder, the adverse effects of degradation can be minimized. Screw design can also play an important role in achieving superior devulcanizate quality.

In summary, the thermomechanical devulcanization of EPDM rubber is suitable for recycling. Batch devulcanization only causes a slight deterioration in product quality at up to 50 wt% recycled rubber content. Its scaled up version of extrusion devulcanization causes a slightly larger reduction in mechanical properties, but extrusion devulcanization is still more beneficial than simply adding non-devulcanized EPDM rubber crumb to virgin rubber.

#### CRediT authorship contribution statement

**Dávid Zoltán Pirtyi:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Tamás Bárány:** Writing – review & editing, Funding acquisition, Conceptualization. **Kornél Pölöskei:** Writing – review & editing, Supervision, Project administration, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### References

- [1] S.A. Roy, Global demand for EPDM (ethylene propylene diene monomer) is set to increase by 1.5 million tons by 2020, *Int. Inst. Procure. Mark. Res.* (2012).
- [2] G. Evanko, A success story - The EPDM industry makes progress with recycling, *ProfRoof* (2010) 50–53.
- [3] J. Kruzelak, R. Sykora, I. Hudec, Sulphur and peroxide vulcanisation of rubber compounds - overview, *Chem. Pap.* 70 (2016) 1533–1555, <https://doi.org/10.1515/chempap-2016-0093>.
- [4] M. Forrest, Overview of the world rubber recycling market, in: D. Potter (Ed.), *Recycling and Re-use of Waste Rubber*, Smithers Rapra, Shawbury, 2014, pp. 17–30.
- [5] A. Fazli, D. Rodrigue, Waste rubber recycling: a review on the evolution and properties of thermoplastic elastomers, *Materials* 13 (2020) 782, <https://doi.org/10.3390/ma13030782>.

- [6] A. Toldy, Recyclable-by-design thermoset polymers and composites, *Express Polym. Lett.* 15 (2021) 1113, <https://doi.org/10.3144/expresspolymlett.2021.89>.
- [7] L.M. Polgar, M. van Duin, A.A. Broekhuis, F. Picchioni, Use of diels-alder chemistry for thermoreversible cross-linking of rubbers: the next step toward recycling of rubber products? *Macromolecules* 48 (2015) 7096–7105, <https://doi.org/10.1021/acs.macromol.5b01422>.
- [8] G. Banhegyi, Reconsidering plastics recycling and bio-plastics, *Express Polym. Lett.* 15 (2021) 685–686, <https://doi.org/10.3144/expresspolymlett.2021.57>.
- [9] Pegoretti, Material circularity in rubber products, *Express Polym. Lett.* 17 (2023) 352, <https://doi.org/10.3144/expresspolymlett.2023.25>.
- [10] T. Tábi, K. Pölöskei, The effect of processing parameters and calcium-stearate on the ejection process of injection molded poly(lactic acid) products, *Period. Polytech. Mech. Eng.* 66 (2022) 17–25, <https://doi.org/10.3311/PPME.18246>.
- [11] G. Lonca, R. Muggé, H. Imbeault-Tétrault, S. Bernard, M. Margni, Does material circularity rhyme with environmental efficiency? Case studies on used tires, *J. Clean. Prod.* 183 (2018) 424–435, <https://doi.org/10.1016/j.jclepro.2018.02.108>.
- [12] M. Costamagna, V. Brunella, M.P. Luda, U. Romagnoli, B. Muscato, M. Giroto, M. Baricco, P. Rizzi, Environmental assessment of rubber recycling through an innovative thermo-mechanical devulcanization process using a co-rotating twin-screw extruder, *J. Clean. Prod.* 348 (2022) 131352, <https://doi.org/10.1016/j.jclepro.2022.131352>.
- [13] P. Sutanto, F. Picchioni, L.P.B.M. Janssen, Modelling a continuous devulcanization in an extruder, *Chem. Eng. Sci.* 61 (2006) 7077–7086, <https://doi.org/10.1016/j.ces.2006.07.012>.
- [14] K. Fukumori, M. Mouri, N. Sato, H. Okamoto, M. Matsushita, Continuous recycling of vulcanisates, *Int. Polym. Sci. Technol.* 28 (2001) 5–11, <https://doi.org/10.1177/0307174X0102800601>.
- [15] K. Fukumori, M. Matsushita, Material recycling technology of crosslinked rubber waste, *R&D Rev. Toyota CRDL* 38 (2003) 39–47.
- [16] M.A.L. Verbruggen, L. van der Does, J.W.M. Noordermeer, M. van Duin, H. J. Manuel, Mechanisms involved in the recycling of NR and EPDM, *Rubber Chem. Technol.* 72 (1999) 731–740, <https://doi.org/10.5254/1.3538830>.
- [17] A.M. Joseph, B. George, K.N. Madhusoodanan, R. Alex, The current status of sulphur vulcanization and devulcanization chemistry: devulcanization, *Rubber Sci.* 29 (2016) 62–100.
- [18] P. Sutanto, F.L. Laksmiana, F. Picchioni, L.P.B.M. Janssen, Modeling on the kinetics of an EPDM devulcanization in an internal batch mixer using an amine as the devulcanizing agent, *Chem. Eng. Sci.* 61 (2006) 6442–6453, <https://doi.org/10.1016/j.ces.2006.05.024>.
- [19] A. Dorigato, D. Rigotti, G. Fredi, Recent advances in the devulcanization technologies of industrially relevant sulfur-vulcanized elastomers, *Adv. Ind. Eng. Polym. Res.* 6 (2023) 288–309, <https://doi.org/10.1016/j.aiepr.2022.11.003>.
- [20] H. Chittella, L.W. Yoon, S. Ramarad, Z.W. Lai, Rubber waste management: a review on methods, mechanism, and prospects, *Polym. Degrad. Stab.* 194 (2021) 109761, <https://doi.org/10.1016/j.polymdegradstab.2021.109761>.
- [21] B. Kaewpetch, S. Prasongsuk, S. Poompradub, Devulcanization of natural rubber vulcanizates by *Bacillus cereus* TISTR 2651, *Express Polym. Lett.* 13 (2019) 877–888, <https://doi.org/10.3144/expresspolymlett.2019.76>.
- [22] L. Asaro, M. Gratton, S. Seghar, N. Ait Hocine, Recycling of rubber wastes by devulcanization, *Resour. Conserv. Recycl.* 133 (2018) 250–262, <https://doi.org/10.1016/j.resconrec.2018.02.016>.
- [23] D.Á. Simon, D.Z. Pirtiyi, T. Bárány, Devulcanization of ground tire rubber: microwave and thermomechanical approaches, *Sci. Rep.* 10 (2020) 16587, <https://doi.org/10.1038/s41598-020-73543-w>.
- [24] P.S. Garcia, F.D.B. de Sousa, J.A. de Lima, S.A. Cruz, C.H. Scuracchio, Devulcanization of ground tire rubber: physical and chemical changes after different microwave exposure times, *Express Polym. Lett.* 9 (2015) 1015–1026, <https://doi.org/10.3144/expresspolymlett.2015.91>.
- [25] M. Myhre, S. Saiwari, W. Dierker, J. Noordermeer, Rubber recycling: chemistry, processing, and applications, *Rubber Chem. Technol.* 85 (2012) 408–449, <https://doi.org/10.5254/rct.12.87973>.
- [26] A.I. Isayev, Recycling of rubbers, in: J.E. Mark, B. Erman, C.M. Roland (Eds.), *Science and Technology of Rubber*, Elsevier, Amsterdam, 2013, pp. 697–764.
- [27] L. Gschwind, C.S. Jordan, N. Vennemann, Devulcanization of ethylene-propylene-diene monomer rubber waste. Effect of diphenyl disulfide derivate as devulcanizing agent on vulcanization, and devulcanization process, *J. Appl. Polym. Sci.* 139 (2022) 52141, <https://doi.org/10.1002/app.52141>.
- [28] L. Asaro, M. Gratton, S. Seghar, N. Ait Hocine, Thermomechanical devulcanization of waste rubber with supercritical CO<sub>2</sub>, in *Workshop On the Multiphysics Behavior of Rubber*, Marseille, France, 2017.
- [29] R. Barbosa, J.D. Ambrósio, Devulcanization of natural rubber compounds by extrusion using thermoplastics and characterization of revulcanized compounds, *J. Polym. Res.* 26 (2019) 160, <https://doi.org/10.1007/s10965-019-1820-7>.
- [30] A. Macsiniuc, A. Rochette, D. Rodrigue, Understanding the regeneration of EPDM rubber crumbs from used tyres, *Prog. Rubber Plast. Technol.* 26 (2010) 51–81, <https://doi.org/10.1177/147776061002600201>.
- [31] L. Guo, D. Ren, W. Wang, K. Hao, X. Guo, F. Liu, Y. Xu, M. Liu, H. Liu, Low-temperature mechano-chemical rubber reclamation using terpinene as a swelling agent to enhance bond-breaking selectivity, *Polymer* 13 (2021) 4272, <https://doi.org/10.3390/polym13244272>.
- [32] Candau, LeBlanc, Maspoch, A comparison of the mechanical behaviour of natural rubber-based blends using waste rubber particles obtained by cryogrinding and high-shear mixing, *Express Polym. Lett.* 17 (2023) 1135–1153, <https://doi.org/10.3144/expresspolymlett.2023.86>.
- [33] M.M. Horikx, Chain scissions in a polymer network, *J. Polym. Sci.* 19 (1956) 445–454, <https://doi.org/10.1002/pol.1956.120199305>.
- [34] M.A.L. Verbruggen, L. van der Does, W.K. Dierkes, J.W.M. Noordermeer, Experimental validation of the Charlesby and Horikx models applied to devulcanisation of sulfur and peroxide vulcanisates of NR and EPDM, *Rubber Chem. Technol.* 89 (2016) 671–688, <https://doi.org/10.5254/rct.16.83776>.
- [35] S. Seghar, L. Asaro, N. Ait Hocine, Experimental validation of the Horikx theory to be used in the rubber devulcanization analysis, *J. Polym. Environ.* 27 (2019) 2318–2323, <https://doi.org/10.1007/s10924-019-01513-z>.
- [36] K.A.J. Dijkhuis, I. Babu, J.S. Lopulissa, J.W.M. Noordermeer, W.K. Dierkes, A mechanistic approach to EPDM devulcanization, *Rubber Chem. Technol.* 81 (2008) 190–208, <https://doi.org/10.5254/1.3548204>.
- [37] X. Colom, J. Cañavate, K. Formela, A. Shadman, M.R. Saeb, Assessment of the devulcanization process of EPDM waste from roofing systems by combined thermomechanical/microwave procedures, *Polym. Degrad. Stab.* 183 (2021) 109450, <https://doi.org/10.1016/j.polymdegradstab.2020.109450>.
- [38] M. Forrest, Characterisation of devulcanised rubber and products containing devulcanised rubber, in: D. Potter (Ed.), *Recycling and Re-use of Waste Rubber*, Smithers Rapra, Shawbury, 2014, pp. 105–134.
- [39] K. Aoudia, S. Azem, N. Ait Hocine, M. Gratton, V. Pettarin, S. Seghar, Recycling of waste tire rubber: microwave devulcanization and incorporation in a thermoset resin, *Waste Manag.* 60 (2017) 471–481, <https://doi.org/10.1016/j.wasman.2016.10.051>.
- [40] M.M. Hassan, R.O. Aly, S.E.A. Aal, A.M. El-Masry, E.S. Fathy, Mechanochemical devulcanization and gamma irradiation of devulcanized waste rubber/high density polyethylene thermoplastic elastomer, *J. Ind. Eng. Chem.* 19 (2013) 1722–1729, <https://doi.org/10.1016/j.jiec.2013.02.012>.
- [41] S.O. Movahed, A. Ansarifar, G. Zohuri, N. Ghaneie, Y. Kermany, Devulcanization of ethylene-propylene-diene waste rubber by microwaves and chemical agents, *J. Elastomers Plast.* 48 (2014) 122–144, <https://doi.org/10.1177/0095244314557975>.
- [42] F. Valentini, A. Dorigato, D. Rigotti, A. Pegoretti, Evaluation of the role of devulcanized rubber on the thermomechanical properties of expanded ethylene-propylene diene monomers composites, *Polym. Eng. Sci.* 61 (2021) 767–779, <https://doi.org/10.1002/pen.25615>.
- [43] F.D.B. de Sousa, A. Zanchet, C.H. Scuracchio, From devulcanization to revulcanization: challenges in getting recycled tire rubber for technical applications, *ACS Sustain. Chem. Eng.* 7 (2019) 8755–8765, <https://doi.org/10.1021/acssuschemeng.9b00655>.
- [44] S. Seghar, L. Asaro, M. Rolland-Monnet, N. Ait Hocine, Thermo-mechanical devulcanization and recycling of rubber industry waste, *Resour. Conserv. Recycl.* 144 (2019) 180–186, <https://doi.org/10.1016/j.resconrec.2019.01.047>.
- [45] S.O. Movahed, A. Ansarifar, S. Karbalaee, S. Athary Far, Devulcanization and recycling of waste automotive EPDM rubber powder by using shearing action and chemical additive, *Prog. Rubber Plast. Technol.* 31 (2015) 87–116, <https://doi.org/10.1177/147776061503100202>.
- [46] D.Á. Simon, D.Z. Pirtiyi, P. Tamás-Bényei, T. Bárány, Microwave devulcanization of ground tire rubber and applicability in SBR compounds, *J. Appl. Polym. Sci.* 137 (2020) 48351, <https://doi.org/10.1002/app.48351>.
- [47] D.Z. Pirtiyi, K. Pölöskei, Thermomechanical devulcanisation of ethylene propylene diene monomer (EPDM) rubber and its subsequent reintegration into virgin rubber, *Polymer* 13 (2021) 1116, <https://doi.org/10.3390/polym13071116>.
- [48] D.Z. Pirtiyi, K. Pölöskei, Thermomechanical devulcanization of ethylene propylene diene monomer rubber and its application in blends with high-density polyethylene, *J. Appl. Polym. Sci.* 138 (2021) 50090, <https://doi.org/10.1002/app.50090>.
- [49] ASTM: ASTM D6814-02: Standard test method for determination of percent devulcanization of crumb rubber based on crosslink density, 2018.
- [50] P.J. Flory, Thermodynamics of high polymer solutions, *J. Chem. Phys.* 10 (1942) 51–61, <https://doi.org/10.1063/1.1723621>.
- [51] ISO: ISO 34-1:2015: Rubber, vulcanized or thermoplastic – Determination of tear strength – Part 1: trouser, angle and crescent test pieces, 2015.
- [52] ISO: ISO 37:2017: Rubber, vulcanized or thermoplastic – Determination of tensile stress-strain properties, 2017.
- [53] ISO: ISO 48-4:2018: Rubber, vulcanized or thermoplastic – Determination of hardness – Part 4: indentation hardness by durometer method (Shore hardness), 2018.
- [54] S.O. Movahed, A. Ansarifar, S. Estagy, A review of the reclaiming of rubber waste and recent work on the recycling of ethylene-propylene-diene rubber waste, *Rubber Chem. Technol.* 89 (2016) 54–78, <https://doi.org/10.5254/rct.15.84850>.
- [55] S. Ghorai, S. Bhunia, M. Roy, D. De, Mechanochemical devulcanization of natural rubber vulcanizate by dual function disulfide chemicals, *Polym. Degrad. Stab.* 129 (2016) 34–46, <https://doi.org/10.1016/j.polymdegradstab.2016.03.024>.