

## ARTICLE

# Thermomechanical devulcanization of ethylene propylene diene monomer rubber and its application in blends with high-density polyethylene

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**Abstract**

The recycling of ethylene propylene diene monomer (EPDM) rubber remains a challenge, as its cross-linked structure cannot be broken down reversibly. Devulcanization may offer a breakthrough; however, a 100% decrease in cross-link density (CLD) with no chain degradation has never been reported. In this research, sulfur- and peroxide-cured EPDM rubbers of known compositions were devulcanized on a two-roll mill and in an internal mixer. The CLD of both rubber samples decreased by around 85%, while the sol content of the peroxidic devulcanizate was considerably higher than that of the sulfuric devulcanizate (23% vs. 3%). Horikx's theory revealed that sulfur-cured samples showed excellent selectivity for cross-link scission, while peroxide-cured samples suffered degradation. Uncured, cured, and devulcanized rubber samples were mixed into high-density polyethylene at various compositions. Large EPDM rubber contents impaired the mechanical properties of the blends, indicating insufficient adhesion between the two phases. Compounds containing originally uncured rubber mixtures had the most beneficial mechanical properties.

**KEYWORDS**

elastomers, recycling, rubber, thermoplastics

## 1 | INTRODUCTION

The rubber industry takes up almost 10% of the global polymer market, yet the recycling of rubber waste has remained an unsolved problem to this day. It was already established by 1839 that cured rubber does not melt, nor can it be reprocessed via conventional techniques. This fact is still valid, which means rubber vulcanizates retain their shape and structure as long as their intramolecular forces are intact.<sup>1–4</sup> The most widespread recycling

techniques already emerged in the 1850s, with Goodyear's patent for the addition of ground rubber waste into uncured mixtures, and Hall's patent for heating rubber shoe soles into a mouldable state.<sup>5</sup> In other words, there has been no ground-breaking innovation in rubber recycling since the 1850s, and rubber waste is mostly incinerated or downcycled nowadays.<sup>5</sup> Several techniques have been proposed for rubber recycling, and devulcanization is widely considered a viable solution. It is a process, whereby cross-links of a rubber network are

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selectively cleaved while the polymer backbone remains intact; in other words, the original uncured rubber mixture is regained from rubber waste via devulcanization. It must be noted, however, that current devulcanization processes severely compromise the mechanical properties of the recycled material, due to undesired degradation of the polymer chains as well as oxidation.<sup>6</sup>

The main principle of any devulcanization technique is that the bond energy of cross-links is lower than that of carbon–carbon covalent bonds building up the polymer backbone.<sup>7</sup> When exposed to various stimuli, the sulfur–sulfur and carbon–sulfur bonds in the rubber matrix are affected to a greater extent than carbon–carbon bonds, leading to some selectivity for cross-link scission over polymer degradation. Consequently, it can be hypothesized that rubbers cured with peroxides cannot be effectively devulcanized since their cross-links have the same chemical composition as the polymer itself and hence the breaking of covalent bonds will occur at random.<sup>8</sup> Several studies are available about the vulcanization kinetics of rubbers,<sup>9</sup> but devulcanization has not been modeled that widely.<sup>7</sup>

A number of studies can be found about distinct devulcanization strategies, which include microbiological,<sup>10,11</sup> microwave,<sup>12,13</sup> ultrasonic,<sup>14,15</sup> chemical,<sup>16,17</sup> and mechanical<sup>18,19</sup> treatments. All technologies except microbiological devulcanization involve elevated temperatures. The highest selectivity for cross-link scission can be achieved via microbiological, chemical, and thermomechanical devulcanization, while high productivity is attainable via thermomechanical and microwave treatments.<sup>6,20,21</sup>

Thermomechanical devulcanization has the greatest potential of all strategies, as these procedures are scalable, and offer a high degree of devulcanization with limited chain degradation. Zhang et al.<sup>22</sup> and Dijkhuis et al.<sup>23</sup> used an internal mixer for their research and achieved up to 60% devulcanization. However, most researchers study the applicability of extruders to devulcanization experiments even though they are not as prevalent in the rubber industry as internal mixers. Jalilvand et al.<sup>24</sup> and Movahed et al.<sup>25</sup> achieved almost 90% devulcanization with excellent selectivity for cross-link scission. In general, temperature, shearing rate (screw/rotor speeds), and residence time have a significant influence on the effectiveness of the thermomechanical treatment, and they have to be optimized for both research and industrial purposes.

Horikx<sup>26</sup> developed a well-referenced technique for the evaluation of devulcanization processes in the 1950s. Based on the Flory–Huggins solution theory,<sup>27,28</sup> he constructed a method to illustrate whether the degradation process of a cross-linked polymer is dominated by random chain scission or the selective cleavage of cross-links. He identified two distinct scenarios and derived

theoretical equations, where the sol fraction of a polymer is given as a function of its cross-link density (CLD). The first scenario is characterized by a statistically random distribution of covalent bond cleavages along the polymer backbone. Equation (1) shows the relationship between the sol fraction and the CLD of the polymer for a random degradation process:

$$1 - \frac{v_f}{v_i} = 1 - \frac{(1 - \sqrt{s_f})^2}{(1 - \sqrt{s_i})^2} \quad (1)$$

where  $v_i$  (mol/cm<sup>3</sup>) stands for the initial CLD,  $v_f$  (mol/cm<sup>3</sup>) stands for CLD after degradation,  $s_i$  (–) stands for the initial sol fraction of the polymer and  $s_f$  (–) stands for the sol fraction of the polymer after treatment.<sup>8,26</sup>

Equation (2) shows the change in CLD as a function of the soluble fraction of the polymer, in the case of pure devulcanization:

$$1 - \frac{v_f}{v_i} = 1 - \frac{\gamma_f(1 - \sqrt{s_f})^2}{\gamma_i(1 - \sqrt{s_i})^2} \quad (2)$$

where  $\gamma_i$  (–) and  $\gamma_f$  (–) stand for the initial and the final cross-linking index, respectively.<sup>8</sup> The cross-linking index represents the average number of cross-links per polymer chain and can be evaluated according to Equation (3) by definition:

$$\gamma_x = v_x \frac{M_n}{\rho} \quad (3)$$

where  $\gamma_x$  (–) is the cross-linking index,  $v_x$  (mol/cm<sup>3</sup>) is the CLD,  $\rho$  (g/cm<sup>3</sup>) is polymer density and  $M_n$  (g/mol) stands for the number-average molecular weight of the polymer.<sup>26</sup> In this research, the initial cross-linking index is estimated with the use of Equation (4)<sup>29</sup>:

$$s = \frac{(2 + \gamma_i) - \sqrt{\gamma_i^2 + 4\gamma_i}}{2\gamma_i} \quad (4)$$

According to Forrest and Isayev,<sup>6,30</sup> there are three viable approaches for the utilization of devulcanizates. Devulcanizates may be revulcanised into rubber products with 100% recycled content when mixed with curing agents.<sup>31,32</sup> They can be added to virgin rubber mixtures and thus rubber products with some recycled content can be created.<sup>31,33</sup> Also, they can be blended with thermoplastics, producing thermoplastic elastomers (TPEs).<sup>12,34–36</sup>

As the polymer chains of ethylene propylene diene monomer (EPDM) rubber are mainly built up of ethylene

and propylene constituents, it is typically blended with either polyethylene or polypropylene to form TPEs. Danesi and Porter already investigated the elastomeric behavior of polypropylene/EPDM blends in 1978.<sup>37</sup> They obtained highly elastic materials above 50 wt% EPDM content with elongation at break values above 200% and negligible tensile set. Jalilvand et al.<sup>35</sup> prepared ternary mixtures of high-density polyethylene (HDPE), polypropylene, and various EPDM rubber mixtures. They found that the presence of active vulcanizing agents in the rubber component was crucial for the formation of materials with high elasticity. When 20 wt% devulcanized EPDM was directly mixed with HDPE and PP, the resulting material had an elongation at break value of 15%. When vulcanizing agents were added to the mixture, this value increased to 32%.

We developed a two-step batch devulcanization technique using a two-roll mill and an internal mixer, both of which are widespread technologies in the rubber industry. We performed devulcanization experiments on two almost identical EPDM rubber mixtures: one vulcanized with a sulfur-based, the other vulcanized with a peroxide-based system. We applied Horikx's analysis to evaluate the effects of the curing systems on devulcanization.

Subsequently, we prepared blends of EPDM rubber and HDPE to study the compatibility of uncured, cured and devulcanized EPDM rubbers with HDPE. Our goal was to produce TPEs by mixing the two components in an internal mixer and then hot pressing the resulting mixtures into sheets. We tested the physical and mechanical properties of the blends and assessed their industrial applicability and potential development in the future.

## 2 | EXPERIMENTAL

### 2.1 | Materials

Two sets of samples were prepared based on EPDM rubber according to the compositions described in Table 1. Both rubber mixtures contained the same filling materials and uncured raw rubber; however, their vulcanizing system shows significant differences. One of them was vulcanized with sulfur (hence the symbol EPDM<sub>S</sub>), and the other was vulcanized with the aid of peroxides (EPDM<sub>PO</sub>). It should be noted that Dutral TER 4047, the base polymer in use, has a 54% ethylene, 41.5% propylene, and 4.5% ethylidene norbornene content and its Mooney viscosity is 55 at 100°C. The rubber mixtures were kindly provided by the Palotás Mix Kft. (Kemeneshőgyész, Hungary).

Toluene, produced by the Fisher Scientific UK (Loughborough, United Kingdom), was used as the general solvent and extraction agent for experiments.

**TABLE 1** Ethylene propylene diene monomer (EPDM) compositions used in the experiments

EPDM <sub>S</sub>		EPDM <sub>PO</sub>	
Component	phr	Component	phr
Dutral TER 4047	100	Dutral TER 4047	100
Zinc oxide	4	Zinc oxide	4
Zinc stearate	1	Zinc stearate	1
UltraLube UL160	3	UltraLube UL160	3
PEG 4000	1	PEG 4000	1
Dolomite B	30	Dolomite B	30
N550 CB	45	N550 CB	45
N772 CB	40	N772 CB	40
DK 350 oil	15	DK 350 oil	15
TBTD	0.8	Perkadox 14-40	4
MBT	1.5	TAC DL 50	3
ZDBC	0.8		
Sulfur	3.0		
Total	243.1	Total	246

**TABLE 2** Nomenclature for the ethylene propylene diene monomer (EPDM) compounding experiments

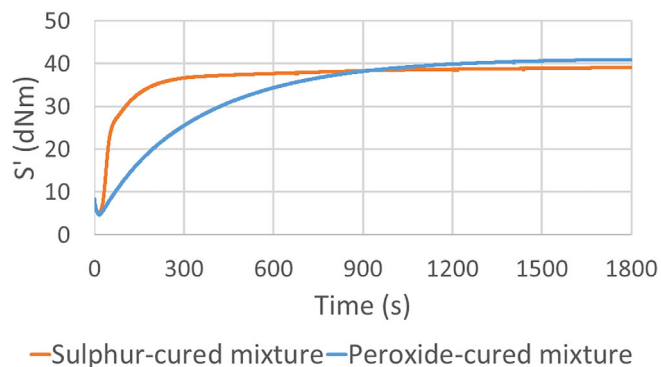
Sample	Description
EPDM <sub>S,u</sub>	Uncured rubber with sulfur vulcanizing system
EPDM <sub>PO,u</sub>	Uncured rubber with peroxide vulcanizing system
EPDM <sub>S,r</sub>	Sulfur-cured rubber (vulcanized)
EPDM <sub>PO,r</sub>	Peroxide-cured rubber (vulcanized)
EPDM <sub>S,d</sub>	Devulcanized sulfur-cured rubber
EPDM <sub>PO,d</sub>	Devulcanized peroxide-cured rubber

TIPELIN BA 550–13 (MFI: 0.35 g/10 min, 190°C/2.16 kg, according to ISO 1133-1; elongation at break: 1180%, according to ISO 527-3; tensile strength: 29 MPa, according to ISO 527-3), a blow molding grade of HDPE, produced by the MOL Petrolkémia Zrt. (Tiszaújváros, Hungary) was used to prepare blends with EPDM at various compositions.

In order to investigate the changes in EPDM during curing and devulcanization, we used various types of EPDM rubber in the compounding experiments. The nomenclature for rubber samples and their respective descriptions are presented in Table 2.

### 2.2 | Preparation of rubber vulcanizates

We determined the necessary curing times ( $t_{90}$ , which stands for the time at which 90% curing is achieved) from



**FIGURE 1** Vulcanization curves of the sulfur-cured and the peroxide-cured ethylene propylene diene monomer compounds [Color figure can be viewed at [wileyonlinelibrary.com](#)]

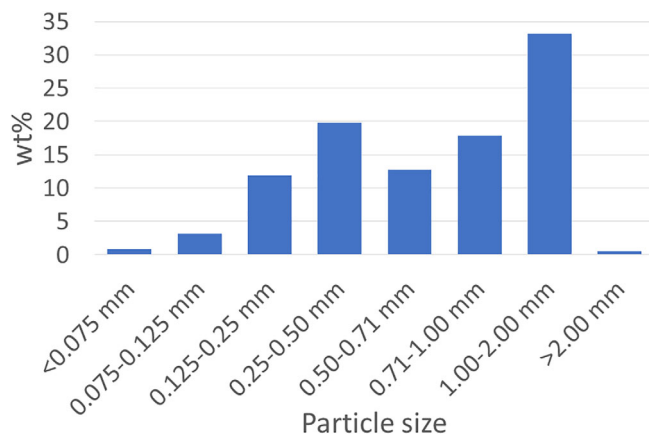
curing curves (Figure 1), which were recorded by a MonTech Monsanto R100S rheometer (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) in isothermal ( $T = 180^{\circ}\text{C}$ ) time sweep mode (1.667 Hz,  $1^{\circ}$  amplitude) for 30 min.

We used a Collin Teach-Line Platen Press 200E (Dr. Collin GmbH, Ebersberg, Germany) type hot press to compression mold and cure the EPDM rubber into 2-mm thick sheets. Process parameters were set at  $180^{\circ}\text{C}$  and 2.8 Mpa. We applied pressure in a stepwise manner, starting at 0.7 MPa and gradually increased it to 2.8 MPa to allow for degassing. We opened the press after  $t_{90}$  was reached.

Cured rubber sheets were ground with a Retsch ZM200 (Retsch GmbH, Haan, Germany) cryogenic mill. The sheets were initially cut into  $10 \times 10 \text{ mm}^2$  pieces and then placed under liquid nitrogen. Once thermal equilibrium was achieved, the frozen rubber shards were fed into the mill, which was also cooled by liquid nitrogen. A cutting speed of 12,000 rpm was chosen for this process. The particle size distribution of the ground rubber vulcanizate is shown in Figure 2. Fractionation took place in a BA200N type sieve shaker (CISA Cedacteria Industrial, Barcelona, Spain), operating with an amplitude of 2 mm for 1 h.

### 2.3 | Devulcanization

The first step of devulcanization was performed on a Labtech LRM-SC-11/3E type two-roll mill (Labtech Engineering Co. Ltd., Samutprakarn, Thailand). Ground EPDM rubber was fed to the mill in batches of 30 g with a fill factor of 85% to insure adequate shearing rates. Rolls were heated to 210 and  $230^{\circ}\text{C}$ , and their speed was set at 4 rpm for the colder and 2 rpm for the hotter roll. The



**FIGURE 2** Particle size distribution of the ground ethylene propylene diene monomer rubber vulcanizate [Color figure can be viewed at [wileyonlinelibrary.com](#)]

gap size between the rolls was gradually decreased to 0.1 mm, and the same operating conditions were maintained for 25 min.

The second step of devulcanization was conducted in a Brabender Plasti-Corder (Brabender Technologie GmbH & Co., Duisburg, Germany) internal mixer with a chamber size of  $50 \text{ cm}^3$ . We treated the rubber for 15 min at  $200^{\circ}\text{C}$  and 140 rpm. We monitored the temperature continuously in order to avoid overheating the sample inside the chamber.

### 2.4 | Preparation of EPDM–HDPE blends

Compounds of HDPE and EPDM rubber were also prepared in the internal mixer. This time, a more conventional filling rate of 70% was used. The operating temperature was set to  $180^{\circ}\text{C}$  and the mixing speed was 40 rpm. The residence time was 10 min, after which the mixture was removed from the chamber.

The tensile test specimens were also prepared with the same hot press that was used for curing experiments before. Mixtures of HDPE and various EPDM samples were molded into sheets at  $180^{\circ}\text{C}$  under 2.8 MPa in 5 min. Table 3 contains the nomenclature and composition of the blends prepared.

### 2.5 | Testing of samples

The sol content of rubber samples was determined via Soxhlet extraction. 10 g of rubber was inserted into the cellulose thimbles and they were sealed with cotton wool. The bottom distillation flask was filled with 200 ml of toluene and continuous water cooling was applied. All

**TABLE 3** Nomenclature and composition of the EPDM-HDPE blends

Sample	Rubber type used (Table 2)	Rubber content (wt%)	HDPE content (wt%)
E2H8u	EPDM <sub>PO,u</sub>	20	80
E2H8r	EPDM <sub>PO,r</sub>	20	80
E2H8d	EPDM <sub>PO,d</sub>	20	80
E4H6u	EPDM <sub>PO,u</sub>	40	60
E4H6r	EPDM <sub>PO,r</sub>	40	60
E4H6d	EPDM <sub>PO,d</sub>	40	60
E6H4u	EPDM <sub>PO,u</sub>	60	40
E6H4r	EPDM <sub>PO,r</sub>	60	40
E6H4d	EPDM <sub>PO,d</sub>	60	40

Abbreviations: EPDM, ethylene propylene diene monomer; HDPE, high-density polyethylene.

extraction experiments were run for 20 h, and the removed specimens were dried at 120°C for 6 h in order to remove the solvent completely.

The sol content was calculated according to Equation (5):

$$\text{sol} [\%] = \left[ 1 - \left( \frac{M_f}{M_i} \right) \right] * 100, \quad (5)$$

where  $M_i$  (g) and  $M_f$  (g) stand for the mass of rubber before and after the extraction, respectively.

However, we needed further correction to find the actual sol fraction of the polymer component of the rubber. We had to decide about each component of the rubber mixture whether it would diffuse into the solvent or remain in the polymer matrix. Consequently, sol fraction values had to be corrected on this basis. We assumed that all oils and polyethylene glycol (PEG) would leave the polymer matrix, accounting for 19 phr of the mixture altogether. We devised Equations (6) and (7) for the sulfuric and peroxidic mixtures, respectively.

$$\text{sol}_{\text{S, corr}} [\%] = \left( \text{sol} [\%] - \frac{19}{243.1} * 100 \right) * 2.431 \quad (6)$$

$$\text{sol}_{\text{PO, corr}} [\%] = \left( \text{sol} [\%] - \frac{19}{246} * 100 \right) * 2.460 \quad (7)$$

CLD was measured according to the ASTM D6814 standard. Rubber samples were immersed into toluene for 72 h (until equilibrium swelling was achieved), weighed, then dried at 80°C until a constant mass was achieved. We used the Flory–Rehner Equation (8) to evaluate CLD based on experimental data:

$$\nu_x = - \frac{[\ln(1 - v_r) + v_r + \chi v_r^2]}{\left[ V_1 \left( v_r^{1/3} - v_r \right) / 2 \right]} \quad (8)$$

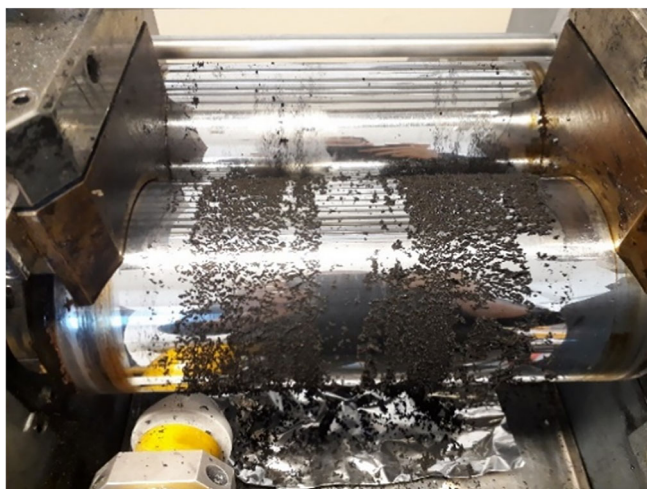
where  $\nu_x$  (mol/cm<sup>3</sup>) denotes CLD,  $\chi$  (–) means the polymer-solvent interaction parameter (which equals 0.496 for an EPDM-toluene system),  $V_1$  (cm<sup>3</sup>/mol) is the molar volume of the solvent (106.13 cm<sup>3</sup>/mol for toluene), and  $v_r$  (–) stands for the volume fraction of rubber in the toluene-swollen rubber sample.<sup>8,38</sup> The latter can be approximated with the following Equation (9), as described in the ASTM D6814 standard:

$$v_r = \frac{\frac{m_r}{\rho_r}}{\frac{m_r}{\rho_r} + \frac{m_s}{\rho_s}} \quad (9)$$

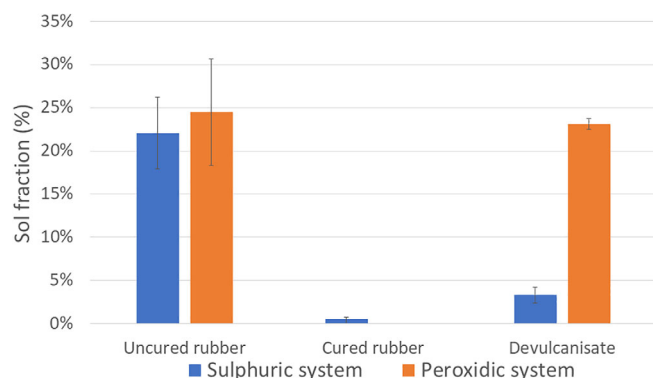
where  $m_r$  (g) stands for the mass of the dried rubber sample,  $m_s$  (g) denotes the mass of the solvent absorbed by the swollen rubber (the difference between the masses of the swollen and dry rubber samples),  $\rho_r$  (g/cm<sup>3</sup>) is the density of the rubber sample (measured as 1.23 g/cm<sup>3</sup>),  $\rho_s$  means the density of the solvent (0.867 g/cm<sup>3</sup> for toluene).<sup>8,38</sup>

Tensile test specimens were die cut out of compression molded sheets, according to the ISO 527 standard. A Zwick Z050 tensile tester was equipped with a 50 kN cell and specimens were secured with 100 kN grips. Clamping distance was 115 mm, test speed was set at 50 mm/min and the room temperature was 22°C with a relative humidity of 33%. We repeated the tests three times in order to reduce the risk of errors.

Fracture energy for compounded mixtures was measured via Charpy impact testing. Specimens were placed horizontally in a Ceast Resil Impactor Junior with a 15 J pendulum. The room temperature was 23°C with a



**FIGURE 3** EPDM<sub>PO</sub> after 10 min of processing on the two-roll mill. EPDM, ethylene propylene diene monomer [Color figure can be viewed at [wileyonlinelibrary.com](#)]



**FIGURE 4** Sol fraction values, corrected for the completely soluble and insoluble components of the rubber samples [Color figure can be viewed at [wileyonlinelibrary.com](#)]

relative humidity of 38%. Test specimens were prepared in accordance with the ISO 179 standard, with a length of 80 mm, a width of 10 mm, and a thickness of 2 mm. A 3 mm deep notch was cut on the specimens for better control of the fracture. Five tests were run for each composition and average fracture energy and its standard deviation were determined.

Scanning electron micrographs (SEM) were taken from cryogenic fraction surfaces of all EPDM-HDPE blends. Surfaces were first sputter-coated with gold and

then placed into a Jeol JSM-6380LA (Jeol LTD., Tokyo, Japan) microscope.

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Devulcanization of EPDM rubber mixtures

Preliminary devulcanization experiments of EPDM rubber were run on an internal mixer and a two-roll mill. We expected that a devulcanized rubber sample should have a consistency similar to that of uncured rubber. Uncured EPDM rubber is highly ductile, and it can be readily morphed into new shapes. Initially, EPDM was put into the internal mixer, but there was no significant change toward such behavior even after 60 min of processing at 240°C. We realized that the distance between the rotors allowed the rubber crumbs to move freely, without much shearing. Therefore, we concluded that a devulcanization step on the two-roll mill should precede processing in the internal mixer, as the adjustable gap size of the two-roll mill allows better shearing.

After some experimenting with the operating parameters of the two-roll mill, the ground EPDM would start sticking to itself, forming aggregates first, then an almost uniform sheet on one of the rolls, as shown in Figure 3.

The samples were then removed from the mill and placed into the internal mixer, where they were also subjected to shearing forces. The resulting material morphed into a few blocks, which showed reduced elasticity. Peroxidic vulcanizates were easier to process, despite almost identical mechanical properties.

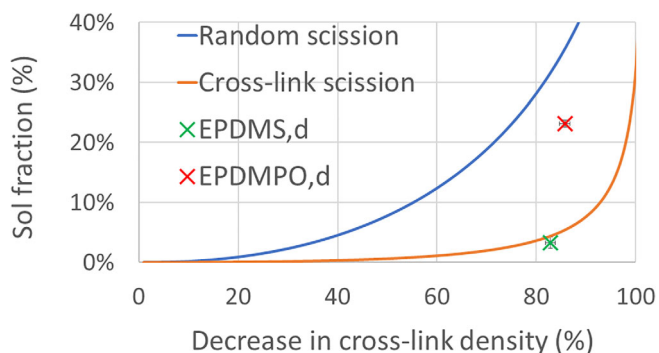
#### 3.2 | Horikx's analysis of the devulcanizates

Figure 4 summarizes the results obtained from the Soxhlet extraction experiments. Uncured rubber samples had a much higher sol content than cured rubbers and sulfuric and peroxidic systems have almost identical behavior. However, devulcanization made a massive impact on the sol content of the peroxide-cured rubber, whereas the sol content of the sulfuric-cured rubber barely increased.

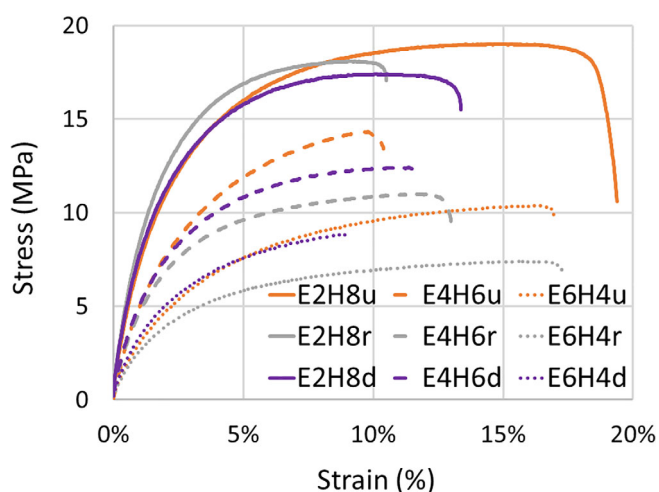
**TABLE 4** Cross-link density (CLD) results for the two vulcanizing systems

Sample	CLD in vulcanizates (mol/dm <sup>3</sup> )	CLD in devulcanizates (mol/dm <sup>3</sup> )	Decrease in CLD
EPDM <sub>S</sub>	3.862 × 10 <sup>-3</sup>	6.610 × 10 <sup>-4</sup>	82.88%
EPDM <sub>PO</sub>	3.668 × 10 <sup>-3</sup>	5.233 × 10 <sup>-4</sup>	85.73%

It is likely that the different cross-link structure of the two systems causes such phenomenon. We assume that the peroxidic matrix goes through a random degradation

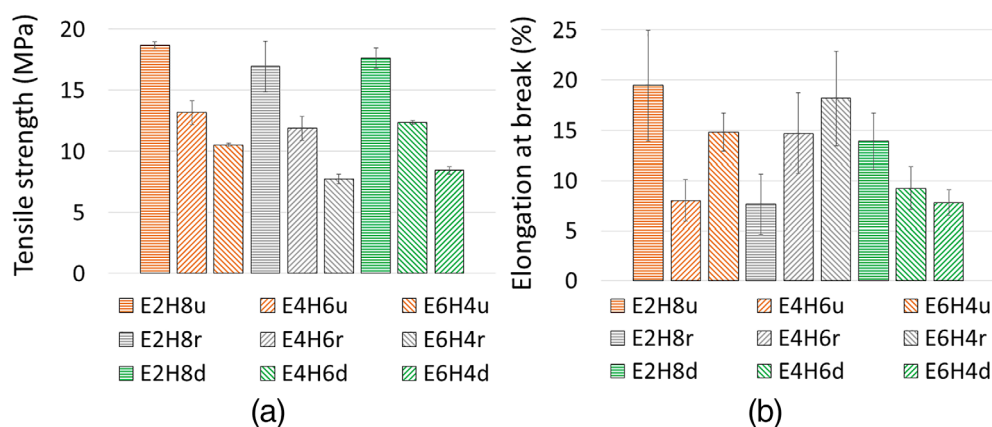


**FIGURE 5** Horikx plot for the devulcanizates [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 6** Characteristic tensile test results of the ethylene propylene diene monomer (EPDM)–high-density polyethylene (HDPE) blends [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**FIGURE 7** Summary of the tensile behavior of the ethylene propylene diene monomer (EPDM)–high-density polyethylene (HDPE) blends: (a) Tensile strength and (b) elongation at break [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



process, as shown by Verbruggen et al.<sup>8</sup> In peroxide-cured rubbers, cross-links are identical to covalent bonds in the molecular chains. When exposed to shearing forces and heat, they are equally likely to break, therefore random degradation occurs. According to Fukumori et al.,<sup>39</sup> the elastic constant of carbon–carbon covalent bonds is 30 times higher than that of sulfur–sulfur bonds. Ultimately, the low elastic constant of the sulfur bonds allows the sulfuric cross-links to stretch further, making them susceptible to selective breaking. Therefore, the different behavior of the two samples can be explained by their chemical makeup.

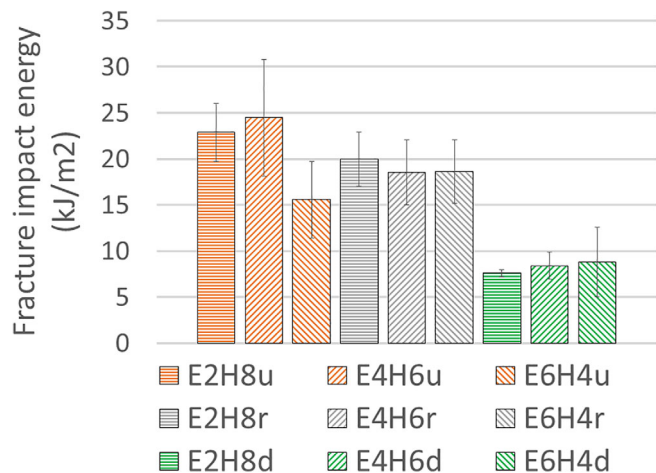
After performing swelling tests in toluene, we applied the Flory–Rehner equation to the results to obtain the CLD values. These data are summarized in Table 4. We found that the two samples went through almost the same degree of devulcanization. CLD decreased by 82.9% and 85.7% for the sulfuric and peroxidic samples, respectively. Though the Flory–Rehner equation carries a high level of uncertainty, the results are comparable with each other since the methodology used is the same.

Figure 5 is a plot depicting Horikx's equations, where the sol fraction is shown on the y-axis, and the proportional decrease in CLD is represented on the x-axis. Two experimental data points were also placed on the graph, representing the devulcanized sulfuric and peroxidic EPDM rubbers. As mentioned earlier, sulfuric samples were expected to show higher selectivity for cross-link scission than peroxidic samples. It can be deduced that the reactions of the peroxidic sample were dominated by random chain scission, whereas the sulfuric sample was devulcanized to a great extent with limited degradation of its polymer backbone.

### 3.3 | Compounding of EPDM with HDPE

Figure 6 shows characteristic tensile curves for all blends. It is visible that tensile behavior of the samples had

similar trends, but they greatly varied in tensile strength and elongation at break. Figure 7 shows tensile strength and elongation at break for each sample. In general,

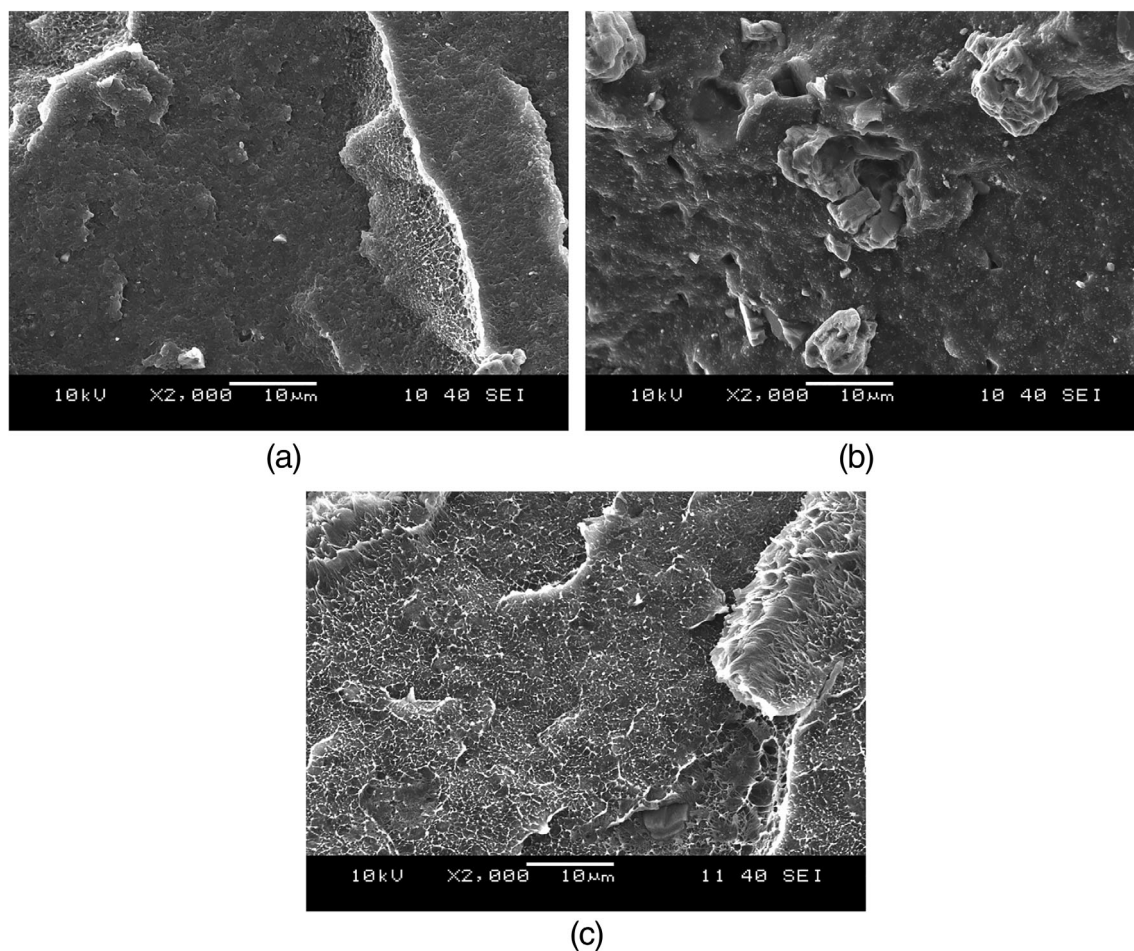


**FIGURE 8** Summary of the Charpy impact tests of the ethylene propylene diene monomer (EPDM)–high-density polyethylene (HDPE) blends [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

specimens containing virgin rubber had the highest tensile stress for each composition. The curing potential in these samples created additional adhesive bonds between the two phases, hence the improved mechanical properties.

Figure 7(a) shows that increasing EPDM content led to a significant loss in tensile strength, which means that EPDM acted as a filler in the HDPE matrix. Similar effects were reported in the literature, too. Blends with devulcanizates and blends with cured rubber content show almost identical tensile strength, though the use of devulcanizates resulted in slightly higher tensile strength.

Figures 6 and 7(b) clearly indicate that the EPDM–HDPE blends did not have rubber-like elasticity. Their elongation at break was as low as 10%–20%, much lower than that of virgin HDPE. Based on Figure 7(b), there is no clear trend between how the various rubber types (uncured, cured, or devulcanized) affect this property differently. Also, rubber content does not seem to influence how elastic the blends are. The elongation at break values show opposing trends for vulcanizate and devulcanizate-containing samples. Increasing vulcanizate content corresponded with increasing elongation at break values,



**FIGURE 9** Scanning electron micrographs of tensile test specimens: (a) E4H6u, (b) E4H6r, and (c) E4H6d



while increasing devulcanizate content caused lower elongation at break values. This phenomenon may be explained by the inability of the vulcanizate to bond to the matrix and the compromised structural integrity of the peroxidic devulcanizate.

Figure 8 summarizes the impact test results. No conclusive trends can be deduced from these results. Uncured rubber seemed to mix with HDPE with ease, and a higher level of homogeneity was achieved. Hence the more substantial impact strength of E2H8<sub>u</sub> and E4H6<sub>u</sub>, compared to blends with similar composition but containing cured and devulcanized rubber samples.

Comparing the static and dynamic mechanical behavior of the samples, we can observe that tensile strength is mainly correlated with the composition of blends, while the elongation at break values does not follow the same trend. The maximum strain values do not seem to have any correlation with the type of EPDM rubber present in the blend. In contrast, we failed to identify any significant difference in the dynamic mechanical behavior within experimental sets (where the same type of EPDM was used). Ultimately, the amount of rubber had no impact on the fracture energy values. Consequently, it can be concluded the pure mixture of EPDM and HDPE does not promote TPE-like behavior. Adding curing agents to the rubber could potentially improve the adhesion between the phases and consequently produce more rubber-like blends.

SEM micrographs were taken of the fracture surfaces of the tensile test specimens. Figure 9 shows some of the characteristic differences between compounds containing uncured, cured, and devulcanized rubber samples. Cured rubber particles segregated from HDPE, indicating weak adhesion between the phases, as seen in Figure 9(b). The EPDM–HDPE interface appears to be smoother (and almost identical) for samples containing uncured and devulcanized rubber as shown in Figure 9(a,c). During devulcanization, rubber becomes more active chemically so devulcanizates can form stronger bonds with HDPE than vulcanizates. We arrived at this conclusion based on the difference between Figure 9(b,c). In Figure 9(b), cured rubber particles are easily distinguishable as sharp objects, whereas devulcanizates seem to merge better with the HDPE matrix in Figure 9(b). Virgin rubber can also merge with HDPE easily due to the presence of vulcanizing agents. Ultimately, devulcanization resulted in a material that is more similar to virgin rubber than to cured rubber.

## 4 | CONCLUSIONS

We used a two-roll mill and an internal mixer for the thermomechanical devulcanization of EPDM rubber. Our aim was to obtain a material that resembles the uncured

mixture the most and we set the treatment parameters accordingly. First, the cryogenically ground rubber was processed at 210/230°C on the two-roll mill for 25 min. Then the devulcanization procedure continued in the internal mixer at 200°C for 15 min. We performed Horikx's analysis on the resulting devulcanizates. We achieved a decrease in CLD of around 85% for both sulfur-cured and peroxide-cured rubber samples. Sol content, however, varied greatly for the two different rubber mixtures. The devulcanizate that was initially cured with peroxides significantly increased in sol content, which indicates chain degradation. On the other hand, the sulfuric system showed excellent selectivity for cross-link scission. In other words, we achieved 83% devulcanization for the sulfuric samples.

We wanted to compare the compatibility of HDPE with uncured, cured and devulcanized EPDM rubber. Consequently, we prepared polymer blends of HDPE and various EPDM rubber samples in an internal mixer with rubber contents of 20, 40, and 60 wt%. Tensile tests revealed that EPDM rubber negatively influenced the mechanical properties of the mixtures. We did not find a clear trend in how the various types of rubber (uncured, cured, and devulcanized) affected tensile behavior differently. The blends did not show much elasticity, with elongation at break between 10% and 20%.

We measured the fracture energy of the compounds via Charpy impact tests. We found that the samples containing uncured rubber had a positive effect on fracture energy. The use of devulcanizates made the material a lot more brittle. The amount of rubber present in the samples had no clear influence on fracture behavior. SEM further demonstrated the difference between samples containing uncured, cured, and devulcanized rubber. The interface of the two phases appeared to be rough for the samples containing cured rubber, while the other two systems had better adhesion between the phases.

The devulcanization procedure that we developed shows great potential for industrial use. A high degree of devulcanization was achieved for sulfur-cured EPDM rubber with technologies widely used in the rubber industry. The application of the devulcanizates requires further experiments to gain industrial relevance.

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