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Thermomechanical-chemical devulcanization of ground tire rubber

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Abstract. We developed a thermomechanical devulcanization process of ground tire rubber (GTR) by incorporating chemicals to achieve better devulcanization. The samples were devulcanized in a twin-screw extruder with the help of three types of chemicals that aid devulcanization: N-(cyclohexylthio) phthalimide (PVI), dibenzamid diphenyl disulfide (DBD) and dialkyl-pentasulfide (DPS, commercialized as Aktiplast 79). We characterized the resulting devulcanizates by Soxhlet-extraction, and produced vulcanized sheets, which we characterized mechanically and examined the vulcanization process. We found that all chemicals facilitated better devulcanization and the devulcanizate had a more rubber-like behavior during mixing. Vulcanization was also slightly improved and reversion was reduced. When revulcanized, the rubber had improved strain at break and tear strength.

Introduction

The upcycling of elastomers is one of the most critical problems in the recycling of polymers [1]. This is due to the structure of elastomers: their high elasticity is provided by crosslinks between their molecule chains. These crosslinks, however, make them hard to recycle as they hinder reversible meltability. The most pressing issue of elastomer recycling is the recycling of the tire rubbers. Tire rubbers are composite materials consisting of metallic and textile reinforcements and different types of rubbers. First, the elastomeric part must be ground, producing ground tire rubber (GTR). This GTR is easy to handle, and it can be used to toughen different kinds of polymers, for example, thermoplastics [2-5], thermosets [6, 7], and rubbers as well [8-11]. The problem with this kind of use is that the GTR is not compatible with the matrix, so these materials cannot be high-performance materials. While this use of GTR is viable, it cannot be considered optimal as it cannot handle the increasing mass of rubber waste. A better way of recycling is devulcanization and reclamation, both of which aim to break up the crosslinked structure of rubbers, thus enabling primary recycling [12]. Devulcanization achieves this goal by selective crosslink scission; reclamation is also accompanied by significant chain scission [13]. There are several ways of devulcanization, the most widespread of which are the thermomechanical [14-16], thermochemical [17, 18] and microwave [19, 20] methods. The most straightforward of these is thermomechanical devulcanization because it is continuous, highly productive, and does not necessarily involve chemical agents [15]. Thermomechanical devulcanization is carried out mainly in a twin-screw extruder, where combining heat and shear produces enough energy to break crosslinks. [21]. Heat and shear can be altered easily in the extruder as extruder screws are modular and thus easily customizable. Thermomechanical devulcanization can be aided with chemical additives that help break crosslinks and they also influence recombination [13]. The degree of devulcanization can be rated by soluble content and cross-link density. Soluble fraction can be used to quantify the degree of devulcanization since devulcanizates are more soluble than crosslinked elastomers [14, 22, 23].

The main disadvantage of devulcanizates is that if they are revulcanized, their properties are inferior to those of primary rubbers. Researchers also found that revulcanizing is significantly faster than in the



case of conventional rubbers due to the accelerator residue remaining after devulcanization [24]. This fast revulcanization is also facilitated by residual carbon black as it has oxygen, nitrogen, and sulphur on its surface [25]. Fast revulcanization might also result from devulcanization itself, as reduced cross-linking density increases polymeric chain mobility, leading to more effective collisions among molecules and a more rapid revulcanization reaction [26].

In this study, our aim was to improve thermomechanical devulcanization by incorporating different types of devulcanization aids. Additionally, we aimed to improve the consistency of the devulcanizate, to create a more rubber-like material that can be processed more easily by the rubber industry.

Materials and methods

Materials

We used ground tire rubber (GTR) from AquaJet Ltd. (Budapest, Hungary), produced by water jet milling with a particle size under 0.4 mm. The pellets were made from truck tire treads, they were clean and contained only a small amount of contaminants.

We used three types of devulcanization agents:

- PVI: N-(cyclohexylthio)phthalimide
- DBD: Dibenzamid diphenyl disulfide
- Aktiplast 79: Dialkyl-pentasulfide

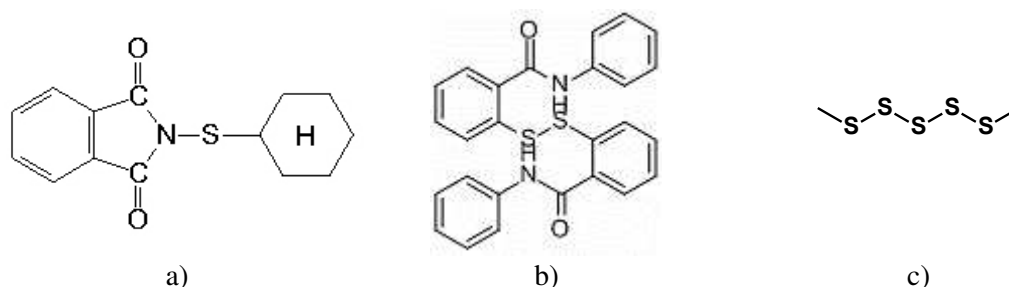


Figure 1.: The chemical composition of the devulcanization aids (a): PVI, b): DBD, c): Aktiplast 79).

PVI is used in the rubber industry as a retarder, DBD is a known peptizer used in the treatment of natural rubber, and Aktiplast 79 is a reclamation agent for natural and synthetic rubbers. We formulated six recipes using these materials (Table 1).

Table 1.: The compounds formulated for devulcanization.

Content	Amount (phr)					
	1	2	3	4	5	6
GTR	100	100	100	100	100	100
PVI	0	2	0	0	1	1
DBD	0	0	2	0	1	0
Aktioplast 79	0	0	0	2	0	1

We constructed a simple recipe for revulcanizing the devulcanized GTRs (dGTRs) (Table 2). Zinc oxide (Werco Metal (Zlatna, Romania)) and stearic acid (Oleon (Ertvelde, Belgium)) were used as activators,

CBS (*N-Cyclohexyl-2-benzothiazolesulfenamide*) (Rhein Chemie (Mannheim, Germany)) was used as accelerator, and sulphur (Ningbo Actmix Polymer (Zhejiang, China)) was used for cross-linking.

Table 2.: Recipes for revulcanization.

Content	Amount (phr)
dGTR (with devulcanization aids)	100
Zinc oxide	5
Stearic acid	2
CBS	1.5
Sulphur	1.5

Methods

The devulcanizing agents were mixed with GTR in a Henschel FM/A10 Fluid Mixer (Henschel (Kassen, Germany) at 1000 rpm for 5 min.

Devulcanization was carried out with a twin-screw extruder LTE 26-44 (Labtech Engineering Co., Ltd., Samutprakarn, Thailand) with unidirectionally rotating screws at a barrel temperature of 190 °C and a speed of 60 rpm.

The vulcanizing agents were mixed to dGTR with a Brabender Lab-Station internal mixer (Brabender GmbH & Co. KG, Duisburg, Germany). We used the Intermix (Mixer type 350 SX) mixing module. Mixing was performed at a speed of 40 rpm for 6 min in a chamber at 50 °C with the chamber filled approximately 60%.

The dGTR samples were characterized by Soxhlet extraction and compared based on soluble content, which allowed a comparison of their degree of devulcanization. Measurements were performed in a Soxhlet extractor with a hot toluene solvent for 18 h and then dried for 12 h. The soluble solid content is given by the formula below:

$$\text{Sol content (\%)} = \left(1 - \frac{M_f}{M_i}\right) \cdot 100$$

where M_i and M_f stand for sample mass before and after extraction.

We used a D-RPA 3000 moving die rheometer (MonTech, Buchen, Germany) to record the vulcanization curves of dGTR samples and determine the vulcanization times. Measurements were performed at 160 and 180 °C.

Then the revulcanized rubbers were tested. Square sheets of 160x160 mm and 2 mm thickness were pressed with a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) hydraulic press at 180 °C for the typical vulcanization time $t_{90} + 30$ seconds. This ensured that the whole volume of the sample was vulcanized. The pressure was 16 bar.

We performed tensile and tear tests to characterize the revulcanized rubbers using a Zwick Z005 (Zwick, Ulm, Germany) universal tensile tester with a speed of 500 mm/min. Tensile strength and elongation at break were calculated with the following equations:

$$\sigma_B = \frac{F_B}{A_0}$$

$$\varepsilon_B = \frac{L_B - L_0}{L_0} \cdot 100$$

where σ_B is tensile strength (MPa), F_B is the force measured at break (N), A_0 is the initial cross-section of the specimens (mm²), ε_B is elongation at break (%), L_B is the length measured at break (mm), and L_0 is the initial gauge length of the specimen (mm). Tear tests were performed on standardized specimens with a 1 mm nick. We characterized the samples by tear strength, which can be calculated in the following way:

$$T_s = \frac{F_m}{a_0}$$

where T_s is tear force (N/mm), F_m is the maximal force (N), and a_0 is the initial thickness of the samples (mm).

Results and discussion

Soluble content

The soluble content of the samples (Table 3) showed that the additives incorporated into the GTR were almost completely dissolved without devulcanization, as the soluble content before devulcanization typically increased by 2%, which was equal to the amount of additives. This suggests that elevated temperatures are indeed required for the mechanism of action of the devulcanization agents. After devulcanization, the soluble content of all devulcanizates increased significantly compared to the reference dGTR, so the devulcanization agents facilitated devulcanization. This effect was most pronounced with DBD, which proved to be the most effective additive, while the least increase was produced by PVI. This can be explained with the fact that DBD decreases the molecular weight of crosslinked elastomers, and this facilitates a better degree of devulcanization.

Table 3.: Soluble content.

Sample (before devulcanization)	Sol content (%)	Sample (after devulcanization)	Sol content (%)
GTR₀	10.8 ± 1.0	dGTR₀	13.3 ± 0.7
GTR_{PVI}	12.3 ± 1.0	dGTR_{PVI}	17.0 ± 1.0
GTR_{DBD}	12.7 ± 0.3	dGTR_{DBD}	20.5 ± 0.9
GTR_{Aktioplast 79}	12.2 ± 0.6	dGTR_{Aktioplast 79}	19.0 ± 0.6
GTR_{PVI+DBD}	12.5 ± 0.9	dGTR_{PVI+DBD}	18.6 ± 0.1
GTR_{PVI+Aktioplast 79}	11.9 ± 0.8	dGTR_{PVI+Aktioplast 79}	17.0 ± 0.7

The increase in devulcanization was also apparent from the consistency of the dGTRs: using devulcanization aids produced a rubber-like devulcanizate instead of rubber granules (Figure 2).

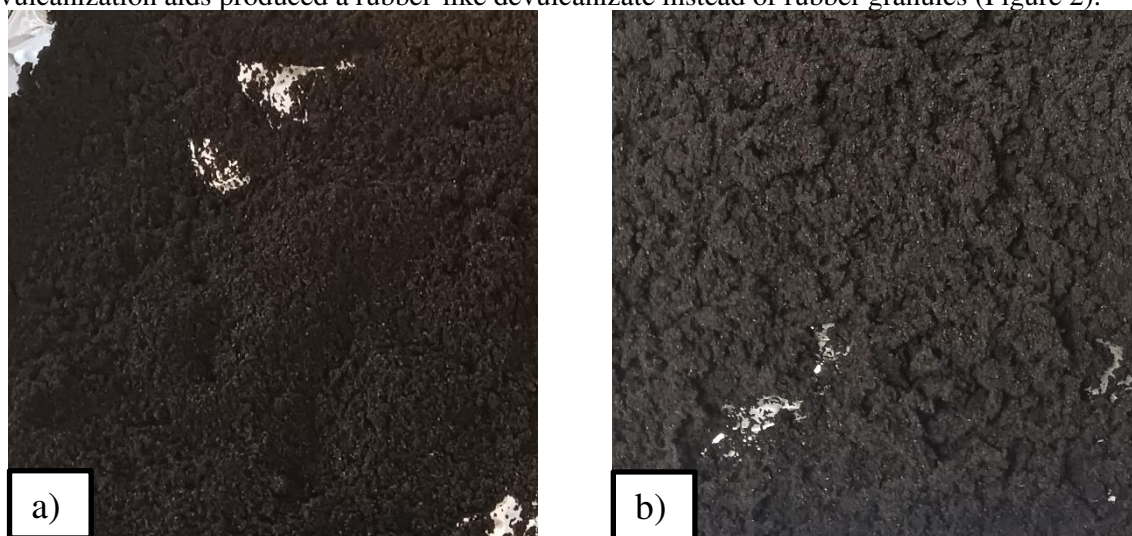


Figure 2.: Comparison of the consistency of devulcanizates (a): without devulcanization aids, b): with devulcanization aids).

Mixing

During the preparation of the rubber mixtures, we registered the torque and temperature of the mixture, and drew conclusions from them. The mixing curves (Figure 3) indicate that all devulcanization agents increased the torque at the end of mixing. This can be attributed to a more rubber-like behavior, since rubbers have higher viscosity than other plastics, and this can increase mixing torque. Increasing torque also results in growing temperatures at the end of mixing. This effect is most pronounced in the case of Aktiplast 79, which seems to increase viscosity of the devulcanizates, and this also showed in the presence of dGTRs: while all others came out of the extruder in a powdery form, the Aktiplast 79 helped to create a more consistent material.

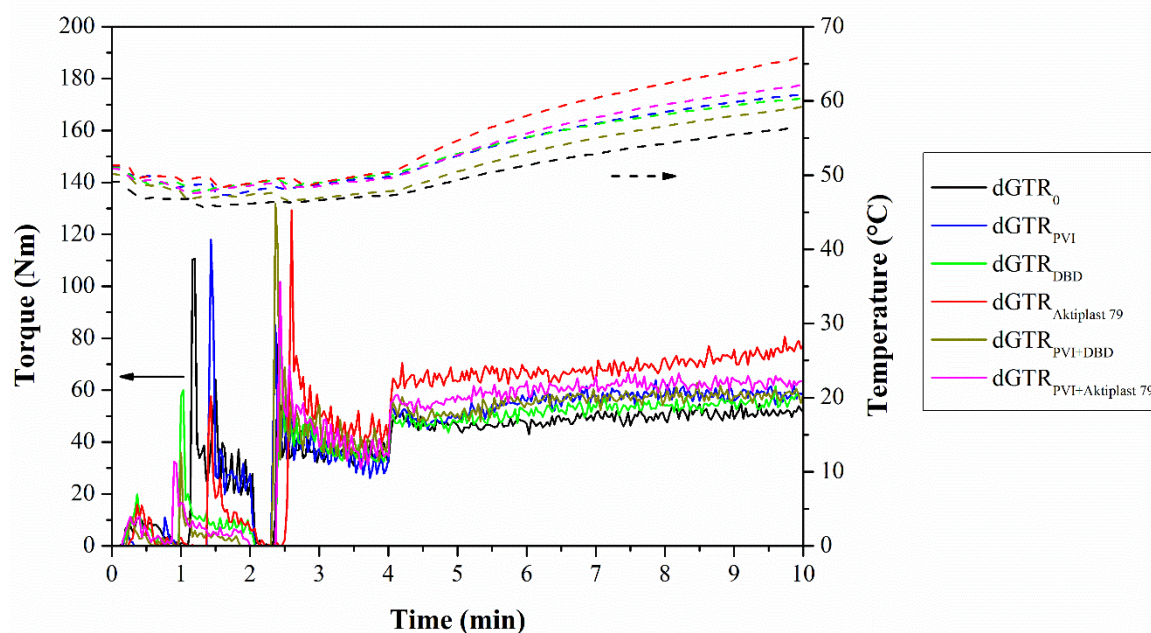


Figure 3.: The recorded plastograms.

Vulcanization

In our analysis of the vulcanization process (Figure 4, Table 4), we observed a consistent decrease in torque with all additives. This decrease suggests that these additives produce a softer behavior in the material, which indicates shorter molecules. Notably, Aktiplast 79 produced the most substantial reduction in torque, showing its significant impact.

However, despite the use of these additives, there was no significant improvement in the vulcanization times of dGTR blends. Only a marginal deceleration was noticed with the application of PVI, failing to alter the inherently rapid vulcanization process notably.

Furthermore, the combined use of PVI with other additives like DBD or Aktiplast 79 did not yield any synergistic effects on the vulcanization process.

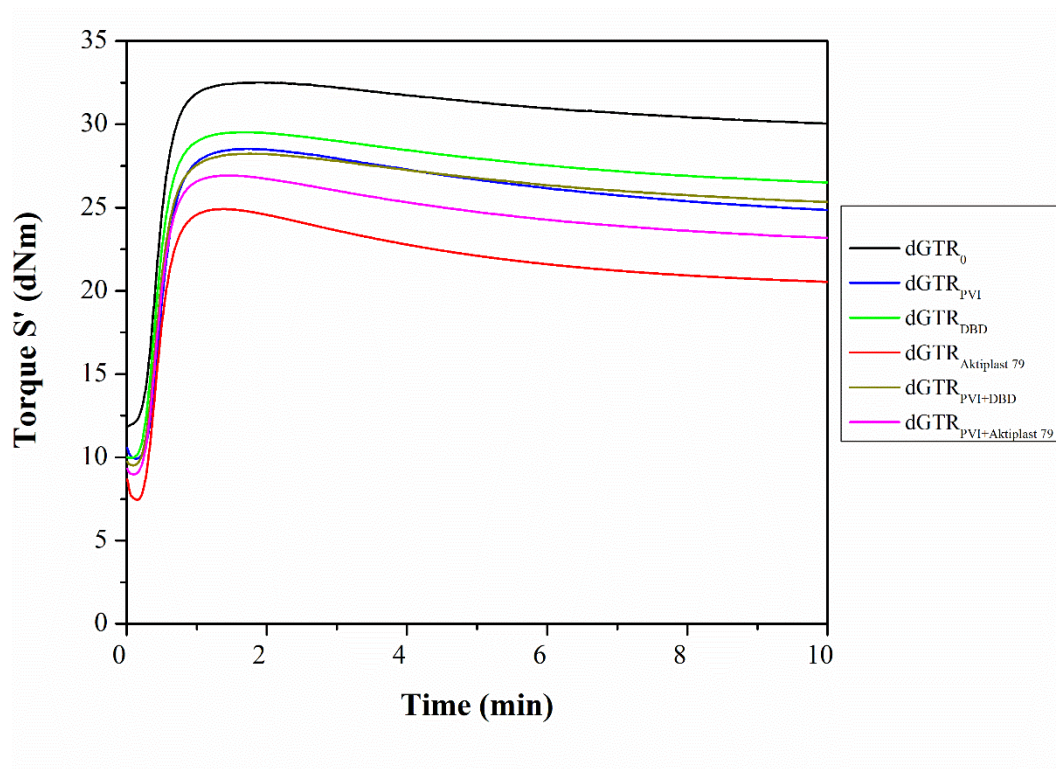


Figure 4.: Vulcanization curves recorded at 180 °C.

Table 4.: Characteristics of the vulcanization process.

Samples	S'_{\min} (dNm)	S'_{\max} (dNm)	t_{10} (min)	t_{30} (min)	t_{50} (min)	t_{70} (min)	t_{90} (min)
dGTR₀	12.07	32.52	0.26	0.36	0.44	0.54	0.75
dGTR_{PVI}	9.92	28.52	0.31	0.41	0.49	0.59	0.81
dGTR_{DBD}	10.03	29.52	0.25	0.35	0.43	0.53	0.73
dGTR_{Aktioplast 79}	7.46	24.91	0.28	0.37	0.45	0.54	0.73
dGTR_{PVI+DBD}	9.53	28.23	0.27	0.37	0.44	0.55	0.76
dGTR_{PVI+Aktiplast 79}	8.98	26.92	0.27	0.36	0.44	0.54	0.72

Tensile tests

The tensile test results (Figure 5, Table 5) showed that the devulcanizing aids led to a noteworthy increase in elongation at break for the revulcanized rubbers. This enhancement, however, came at the cost of reduced tensile strength. Among the tested chemicals, Aktiplast 79 improved elongation at break most, which can be attributed to the enhanced devulcanization produced by Aktiplast 79. Interestingly, there was no synergistic effect observed with the simultaneous use of PVI and Aktiplast 79.

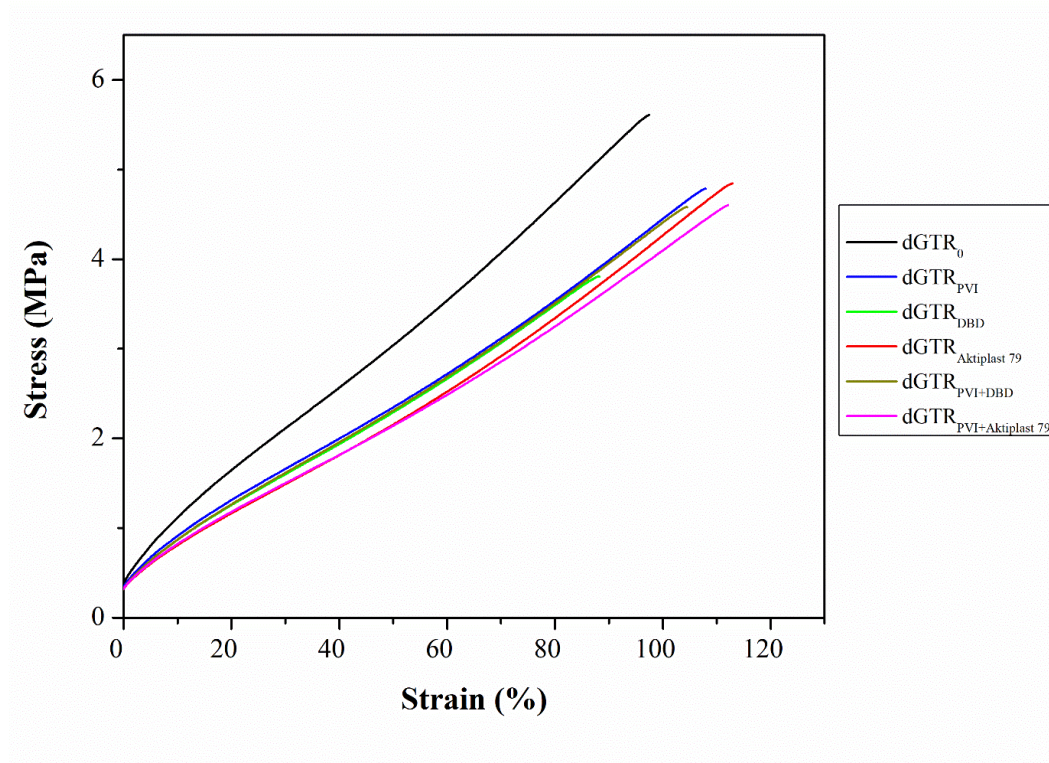


Figure 5.: Typical tensile curves.

Table 5.: Mechanical properties of the revulcanized rubbers.

Samples	Maximal stress (MPa)	Strain at break (%)	Tear strength (N/mm)
dGTR₀	5.4 ± 0.4	98.4 ± 1.5	4.4 ± 0.2
dGTR_{PVI}	4.7 ± 0.3	109.6 ± 6.6	5.2 ± 0.2
dGTR_{DBD}	3.9 ± 0.4	89.7 ± 5.0	5.4 ± 0.6
dGTR_{Aktioplast 79}	4.8 ± 0.1	114.2 ± 8.2	6.1 ± 0.8
dGTR_{PVI+DBD}	4.6 ± 0.4	108.1 ± 7.5	4.9 ± 0.2
dGTR_{PVI+Aktioplast 79}	4.4 ± 0.9	109.1 ± 19.9	5.0 ± 0.1

Tear tests

The results of the tear tests (Figure 6, Table 5) clearly show that the devulcanization aids increased tear propagation strength, and improved resistance against crack propagation in all cases. This improvement was most striking with Aktiplast 79, there was no synergistic effect when it was used with PVI. This behavior was most likely in connection with the higher rate of devulcanization, which yielded better revulcanizates as well.

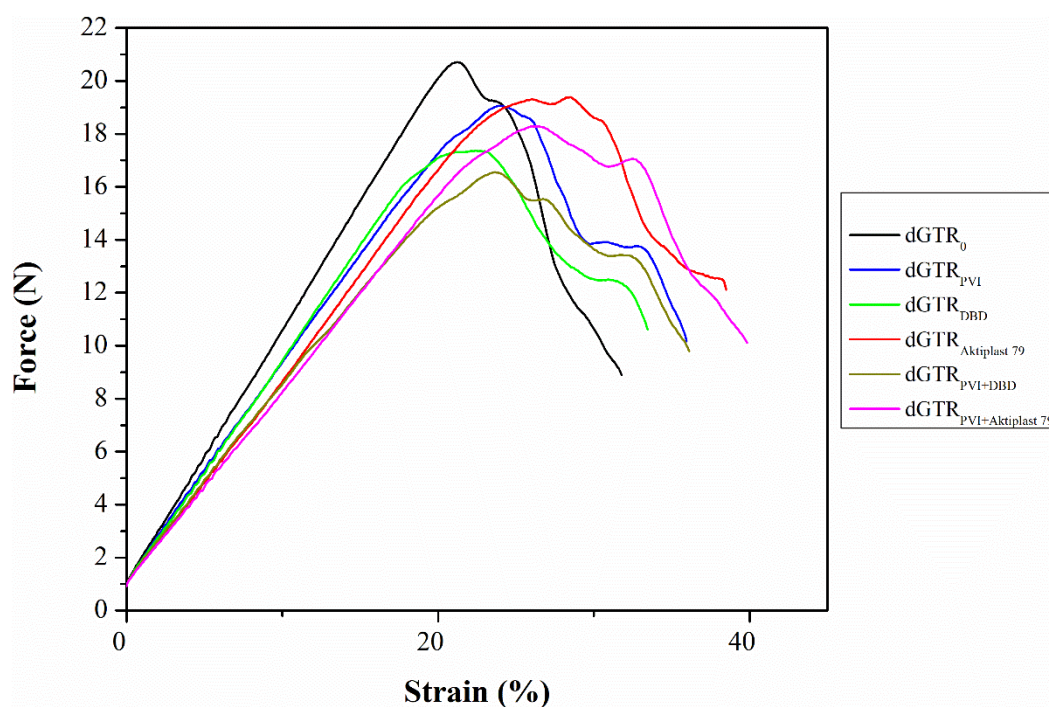


Figure 6.: Typical tear curves.

Conclusions

We presented a way of enhancing thermomechanical devulcanization by using devulcanization chemicals, PVI, DBD, and Aktiplast 79, and examined devulcanization, mixing, and revulcanization. We also characterized the revulcanized rubbers with mechanical tests and concluded that all of the chemicals increased the degree of devulcanization, and the revulcanized rubbers were also improved when devulcanized in the presence of these chemicals. The greatest improvement was observed with Aktiplast 79, which also produced a rubber-like devulcanizate instead of rubber granules.

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