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FINAL REPORT

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Title:

Upcycling of crumb rubber after microwave devulcanization in rubber and thermoplastic elastomer formulations

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1. Introduction

Polymeric materials have gained enormous importance in the last few decades. Thermoplastics and thermosets are extensively used in almost every facet of life, due to their beneficial and diversely customizable properties. However, polymeric materials pose environmental hazards and their waste management is problematic. As a result of their chemically stable structure, the decomposition of polymeric wastes in most cases are excessively slow, so polymeric products may exist for many decades after they are discarded. This problem is more substantial and acute in the field of thermoset polymers, especially with rubbers, because of their chemically cross-linked 3D molecular structure. Rubbers cannot be recycled like thermoplastics via relatively simple and cost-effective reprocessing (remelting, remolding) methods. Therefore, the development of feasible recycling technologies for rubbers attracts a great deal of academic and industrial interest. A straightforward and promising route consists of grinding the used rubber products followed by their subsequent devulcanization. There is a number of methods currently in industrial use to grind rubber waste: mechanical grinding at ambient or cryogenic conditions, and waterjet milling. The latter incorporates a high-pressure water beam that grinds rubber waste. Compared to mechanical grinding, smaller particles can be obtained by this method and rubber degradation can also be avoided, though the final material needs to be dried. Devulcanization is a selective breakdown of the cross-linked structure involving the breakup of the intermolecular sulfuric cross-links formed during the former vulcanization process. There are various methods for rubber devulcanization, including thermomechanical, thermochemical, mechanochemical, physical, and biological techniques, as well as methods using microwaves and ultrasound. Currently, microwave devulcanization is one of the most promising technologies because of the good properties of the treated material and the promise of high productivity. Microwave heating takes advantage of volumetric heating: a fast and uniform rise of temperature can be achieved. The process does not require additional chemicals and is considered an eco-friendly technology. A disadvantage of microwave devulcanization is that nonpolar polymer chains are almost transparent for microwaves. Rubber additives, such as carbon black, can absorb microwaves and dissipate their energy in the form of heat due to their dielectric loss. Therefore, rubber mixtures containing carbon black can be treated with microwaves. Fortunately, tires contain large amounts of carbon black. The process can be considered controlled degradation, so the parameters should be adjusted with care in order to avoid or minimize the chain scission of the polymer backbone. dCR can be rated based on its sol fraction, which can be measured by Soxhlet extraction or by studying the effect of its addition to virgin rubber mixtures: natural rubber (NR) based or styrene-butadiene rubber (SBR) based mixtures. Many studies focused on the exposure time of CR to microwaves. The general conclusion was that the longer exposure time, the larger the soluble fraction (sol-fraction) of the samples, and hence the lower their gel fraction and cross-link density values. The devulcanized rubber thereafter can be used as a feedstock for fresh rubber compounds, or can be blended with thermoplastic polymers and fresh rubbers/curatives to form thermoplastic dynamic vulcanizates (TDVs). TDVs are relatively new members of the family of thermoplastic elastomers (TPEs). TPEs are thermoplastic polymeric materials combining the easy and cost effective processability and reprocessability of thermoplastics and the elastic properties of rubbers. TDVs are produced by the incorporation of rubbers into molten thermoplastics under intensive kneading/mixing during which the rubber is selectively cured and becomes finely dispersed in the thermoplastic matrix. This “dynamic” curing or vulcanization leads to a fine dispersion of the partly or fully cross-linked rubber phase in the thermoplastic matrix, which is often termed as salami or sea-island structure. The thermoplastic “matrix” phase provides processability and reprocessability of the melt, while the rubbery behavior can be attributed to the matrix ligaments between the rubber particles, which may undergo inhomogeneous deformations without plastic deformation (yielding). Though various thermoplastics can serve as matrices, the majority of researchers have used polyolefins (low density polyethylene, linear low density polyethylene, high density polyethylene and polypropylene). This is due to their wide availability (eventually from recyclable waste resources) and reasonable price. Proper adhesion between the rubber and the thermoplastic phase is essential for good overall mechanical performance. Besides the utilization of various compatibilizing agents, another straightforward opportunity to enhance the mechanical performance of scrap crumb rubber-based TDVs is the incorporation of fresh rubber along with the dCR into the thermoplastic matrix.

2. Microwave devulcanization of CR

This chapter is devoted for the introduction and discussion of microwave devulcanization technique used in this project.

2.1. Effect of crumb rubber type, microwave treatment parameters and devulcanization atmosphere

We started this research project with the clarification of the effect of different crumb rubber types (mechanically ground and waterjet milled), parameters of the microwave treatment (heating rate, final temperature, holding time) and the atmosphere present during devulcanization (air or nitrogen). The related results are presented hereby.

Materials

As crumb rubber (CR), waterjet-milled and mechanically ground tire rubber were selected and used. Manufacturers, types and basic properties of the crumb rubbers are listed in Table 1.

Abbreviation	CR_WJ	CR_M
Manufacturer, Type	Aquajet Ltd., Budapest, Hungary	Euro-Novex Ltd., Budapest, Hungary
Main properties	Waterjet milled truck tire tread, CR (CR) with average particle size of 173±9 µm,	Mechanically milled truck tire, max. particle size 4 mm

Table 1. Types and producers of raw materials

Devulcanization process

CR was devulcanized in a BP-125/50 type laboratory microwave oven, produced by Microwave Research Inc. (Carol Stream, Illinois, USA), and in a conventional AVM561/WP/WH type (Whirlpool, Benton Harbor, Michigan, USA) power-controlled microwave oven. In the latter oven, the power of the microwave treatment was set to 650 W. The batch size of the treated CR was 50 g. A motorized stirring system with a speed control was attached to the microwave ovens. The stirring speed was 100 rpm. The parameters of the microwave treatment can be seen in Table 2.

	Treatment time (min)	Heating rate (°C/min)	Final temperature (°C)	Holding time at the maximum temperature (min)
Conventional microwave oven	8.5	~23*	~220	0
Laboratory microwave oven	~30 (+ the holding time)	6	150-250	0, 1, 3, 5
	~15	12	200	0
	~9	18	200	0

*Calculated average value

Table 2. Parameters of the microwave treatment

Characterization technique

The achieved rate of devulcanization of the CR was characterized by Soxhlet extraction in toluene. The testing time was 18 hours. The insoluble fraction, gel fraction of the rubber can be separated from the soluble fraction with this extraction technique. The sol content is a good indicator of processability, which is the ultimate goal of devulcanization.

Devulcanization results

Both types of CR with different particle size ranges were treated in a conventional microwave oven at 650 W without stirring in order to check “microwave devulcanizability” of the CRs. The temperatures (Table 3) were measured with a Testo 875 type thermal camera (Testo SE, Lenzkirch, Germany). CRs with particle size of 1-2 mm and 2-4 mm behaved adversely, as they only needed 30 s to ignite. CR_WJ with a particle size of 0-0.6 mm and CR_M with the particle size of 0-1 mm provided the best results. Based on these results, CR_WJ and CR_M_0-1 were chosen for further investigations.

Sample	**Particle size (mm)**	**Time (s)**			
		30	60	90	120
		Achieved temperature (°C)			
CR_WJ	0-0.6	138	185	248	Ignition
CR_M_0-1	0-1	145	190	Ignition	Ignition
CR_M_1-2	1-2	Ignition			
CR_M_2-4	2-4	Ignition			

Table 3. Microwave devulcanization of CR: behavior and temperature at the end of treatment

CR_WJ and CR_M_0-1 samples were exposed to microwaves in the conventional microwave oven with constant stirring. After several devulcanization attempts, 8.5 min treating time was set in order to prevent ignition of the samples. This duration was chosen according to Table 4, the temperature in the samples did not reach 248 °C at the end of the treatment. The soluble content of the samples was determined by Soxhlet extraction before and after devulcanization (Table 4). There was no significant difference in the sol fraction between the samples, but the devulcanization process was more consistent with CR_WJ than with CR_M. The quality of the dCR_WJ samples was better and during the process, less smoke was generated than in the case of the dCR_M samples. Ultimately, CR_WJ was chosen for further devulcanization experiments.

Sample	**Sol fraction (%)**
CR_WJ	10.1±0.4
CR_M_0-1	7.1±0.5
dCR_WJ	24.6±2.0
dCR_M_0-1	22.0±1.4

Table 4. The sol fraction of CRs before and after treatment in the conventional microwave oven

The devulcanization in a laboratory microwave oven (purchased for the project) can be controlled and monitored better than in the conventional oven, therefore we studied the effects of heating rate, set maximum temperature, holding time and type of atmosphere on the soluble content of dCR. Table 5 shows the sol content of the CR and dCR samples. Devulcanization parameters were set to reveal the minimum temperature of efficient devulcanization, as well as to minimize the degradation of main polymer chains and to eliminate smoke generation. To ensure this, the experiments were repeated in nitrogen atmosphere. The results showed that devulcanization required high temperature (around 200 °C), but above 200 °C the sol content tended to decrease, the devulcanization process was unbalanced and the quality of dCR was uneven.

A nitrogen atmosphere was used to avoid ignition and smoke generation. According to the results, smaller sol contents were achieved in nitrogen atmosphere and there is no significant change in the sol fraction of the samples treated at different temperatures.

After heating CR up, the maximum temperature was held for different durations (1, 3, 5 min). The results reveal that the holding time in an oxidative atmosphere, independently of its length has a decreasing effect on the sol content. In case of inert atmosphere, there is no significant effect of holding time. In conclusion, the heating of CR to a sufficient temperature is more important than longer holding time at the maximum temperature. The increased heating rate also decreased the sol content.

Sol content (%)									
Atmosphere		Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
Heating rate (°C/min)	Maximum temperature (°C)	Holding time (min) 0		1		3		5	
CR_WJ		10.1±0.3	10.2±0.4	-	-	-	-	-	-
6	150	11.5±0.4	10.6±0.3	7.9±0.5	10.7±0.6	10.4±0.5	9.3±0.9	6.7±0.7	9.9±0.5
6	170	11.8±0.2	11.1±0.3	11.0±0.7	10.8±0.3	9.4±0.6	11.2±0.6	6.7±0.9	11.7±0.3
6	190	19.8±0.6	12.5±0.6	13.1±0.5	11.0±0.7	11.3±0.4	11.9±0.5	9.6±0.5	10.1±0.6
6	200	21.2±0.9	13.0±1.2	11.8±0.9	11.1±0.5	13.4±0.7	13.4±1.0	16.5±1.1	10.8±0.8
6	210	18.3±1.2	12.9±0.7	-	-	-	-	-	-
6	230	21.5±1.1	-	-	-	-	-	-	-
6	250	18.4±1.3	-	-	-	-	-	-	-
12	200	10.5±0.4	-	-	-	-	-	-	-
18	200	10.9±0.6	-	-	-	-	-	-	-

Table 5. The results of the Soxhlet extraction before and after the treatment of CR_WJ in the laboratory microwave oven

2.2. Effect of preheating and combined devulcanization techniques

Materials

Based on the results of the previous phase the waterjet milled CR was chosen and used for further investigation (average particle size of 173±9 μm, Aquajet Ltd., Budapest, Hungary) and the devulcanization was carried out under air to a final temperature of 200 °C.

Devulcanization process

Microwave devulcanization of CR was carried out in the previously described laboratory microwave oven. In this study the heating rate was 6 °C/min and the maximum temperature was 200 °C in every case. After the temperature reached 200 °C the material was taken out and cooled down. A motorized stirring system with a speed control was attached to the microwave oven. The stirring speed was 100 rpm. In some cases, a heat treatment on 150 °C was used prior to devulcanization in a Venticell LSIS-B2V (MMM Group, Monroe, Louisiana, USA) oven. The parameters of microwave devulcanization and the abbreviations of the samples can be seen in Table 6.

Abbreviations	**Batch size (g)**	**Achieved temperature (°C)**	**Heat treatment prior devulcanization (hour)**
dCR_M_50g	50	200	-
dCR_M_50g_1	50	200	1
dCR_M_50g_2	50	200	2
dCR_M_100g	100	200	-
dCR_M_100g_1	100	200	1
dCR_M_100g_2	100	200	2
CR_H_2	100	150	2 (heat treatment only)

Table 6. Parameters of microwave devulcanization and the abbreviation of the samples

Thermomechanical devulcanization was carried out in a Brabender Plasti-corder internal mixer (Brabender GmbH & Co., Duisburg, Germany). The duration of the treatment was 10 min and the chamber volume was 50 cm^3. The parameters of thermomechanical devulcanization and the abbreviations of the samples can be seen in Table 7. Prior to both treatments, CR was kept at ambient temperature.

	Rotor speed (rpm)	**Achieved temperature (°C)**
dCR_TM_40_160	40	160
dCR_TM_40_170	40	170
dCR_TM_40_180	40	180
dCR_TM_40_190	40	190
dCR_TM_40_200	40	200
dCR_TM_120_160	120	160
dCR_TM_120_170	120	170
dCR_TM_120_180	120	180
dCR_TM_120_190	120	190
dCR_TM_120_200	120	200

Table 7. Parameters of thermomechanical devulcanization and the abbreviation of the samples

The combination of microwave and thermomechanical devulcanization was also carried out. The parameters of dCR_M_50g sample was used for microwave devulcanization. For thermomechanical devulcanization the parameters of dCR_TM_120_200 sample was chosen. The sequence was the following: microwave then thermomechanical (dCR_M+TM) and thermomechanical then microwave (dCR_TM+M) devulcanization.

Characterization technique

dCR was characterized by Soxhlet extraction described earlier. In addition, FTIR analysis was conducted on the toluene extracts after drying using Bruker Tensor 37 (Billerica, Massachusetts, USA) instrument. All spectra were measured and collected under the same conditions, in transmission mode, with wave frequencies ranging from 400 to 4000 cm^{-1}.

Devulcanization results

The sol fraction values of the samples after microwave devulcanization are listed in Table 8. With the main treatment parameters (6 °C/min heating rate, 200 °C temperature) and 50 g batch size the sol content increased, indicating a successful devulcanization. Batch size of 100 g was also used to improve productivity. The sol content remained unchanged, the power of the microwave oven was enough to heat the CR to 200 °C without the treatment duration would have been increased. Further increase of batch size was not possible because of the instrument size.

As a results of 1-hour heat treatment prior devulcanization, the sol content did not change significantly. But applying a 2 hours heat treatment the results showed a great leap in sol content.

Sample	Sol fraction (%)
CR	11.0±0.7
dCR_M_50g	16.1±0.8
dCR_M_50g_1	16.2±0.6
dCR_M_50g_2	25.1±1.1
dCR_M_100g	15.8±0.7
dCR_M_100g_1	15.7±0.9
dCR_M_100g_2	28.5±1.3
CR_H_2	20.4±0.4

Table 8. The sol fraction of CR after microwave devulcanization

The sol contents of the samples after thermomechanical devulcanization can be seen in Table 9. The trends are clear, higher rotor speed and temperature leads to increasing sol content. This can be interpreted by the increasing stress on the crosslinked molecular structure of the material caused by the increasing external mechanical stress (increasing rotor speed creates higher shear) in one hand and more vigorous molecular segment movement on the other, latter induced by elevated temperatures.

Sample	Sol fraction (%)
CR	11.0±1.2
dCR_TM_40_160	14,4±0.7
dCR_TM_40_170	18.0±0.5
dCR_TM_40_180	19.1±0.6
dCR_TM_40_190	20.3±0.9
dCR_TM_40_200	25.8±0.7
dCR_TM_120_160	16.3±0.6
dCR_TM_120_170	21.6±0.8
dCR_TM_120_180	25.1±0.5
dCR_TM_120_190	24.2±0.4
dCR_TM_120_200	30.2±0.7

Table 9. The sol fraction of CR after thermomechanical devulcanization

The sol contents of the samples after combined thermomechanical and microwave devulcanization can be seen in Table 10.

Sample	Sol fraction (%)
CR	11.0±1.2
dCR_TM+M	34.7±1.0
dCR_M+TM	27.4±0.9

Table 10. The sol fraction of CR after the combined devulcanization

A surprisingly large difference can be observed if one compares the results of the two combined devulcanization tests. When the thermomechanical process takes place first the sol content of the devulcanized material is ca. 25% higher compared to the reverse method. This may be described by the significant chain scissions caused by the thermomechanical process, which was more pronounced on a fresh material, than on a previously microwave devulcanized one as a consequence of the higher viscosity of the former. Higher viscosity led to higher internal shear stresses in the material during thermomechanical devulcanization which resulted in more pronounced bond cleavage. If a microwave step preceded the thermomechanical one the bond cleavage caused by the microwave treatment lowered the viscosity of the rubber resulting in decreasing internal shear during the thermomechanical step.

Figure 1-3. shows FTIR spectra of fresh and treated CR samples. Figure 1. shows the results of a microwave devulcanization process, Figure 2. depicts the effect of thermomechanical treatment and the effect pf preheating can be seen on Figure 3.

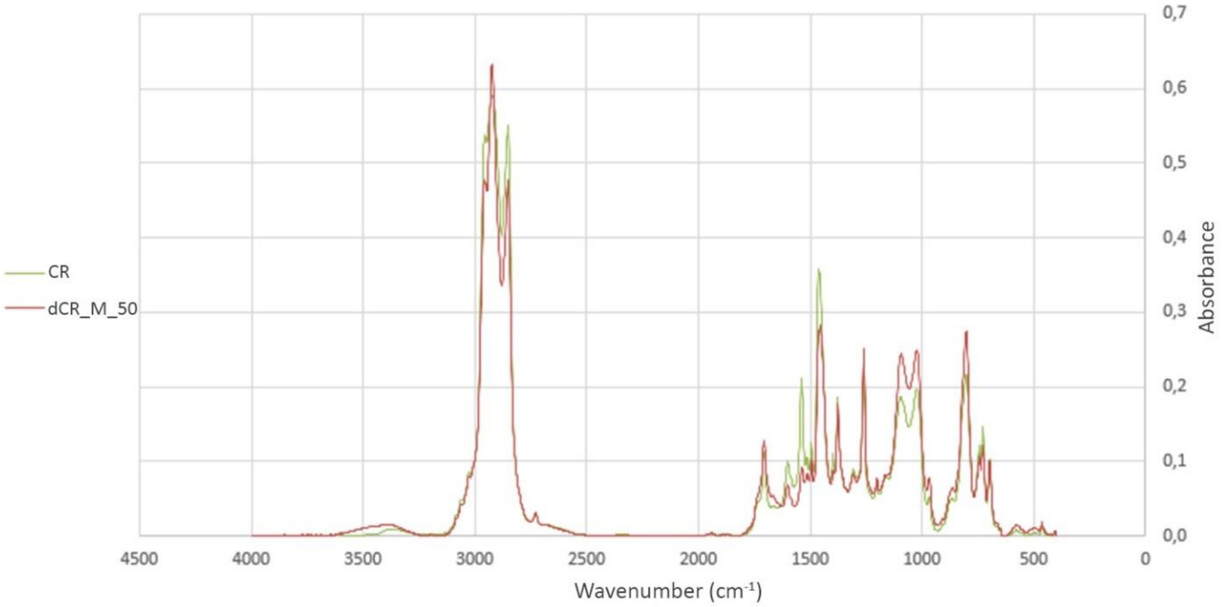


Figure 1. The FTIR spectra of CR and dCR_M_50g sample

Peaks at the 3000-2500 cm^{-1} range correspond to the polymer backbone, the marginal decrease of their intensity can be linked to minor chain scission. Peak at 1539 cm^{-1} decreased significantly which indicates major reduction of C=C double bonds. Peaks with increasing intensity can be associated with the formation of new groups as a result of the recombination of free radicals formed during the devulcanizaion process.

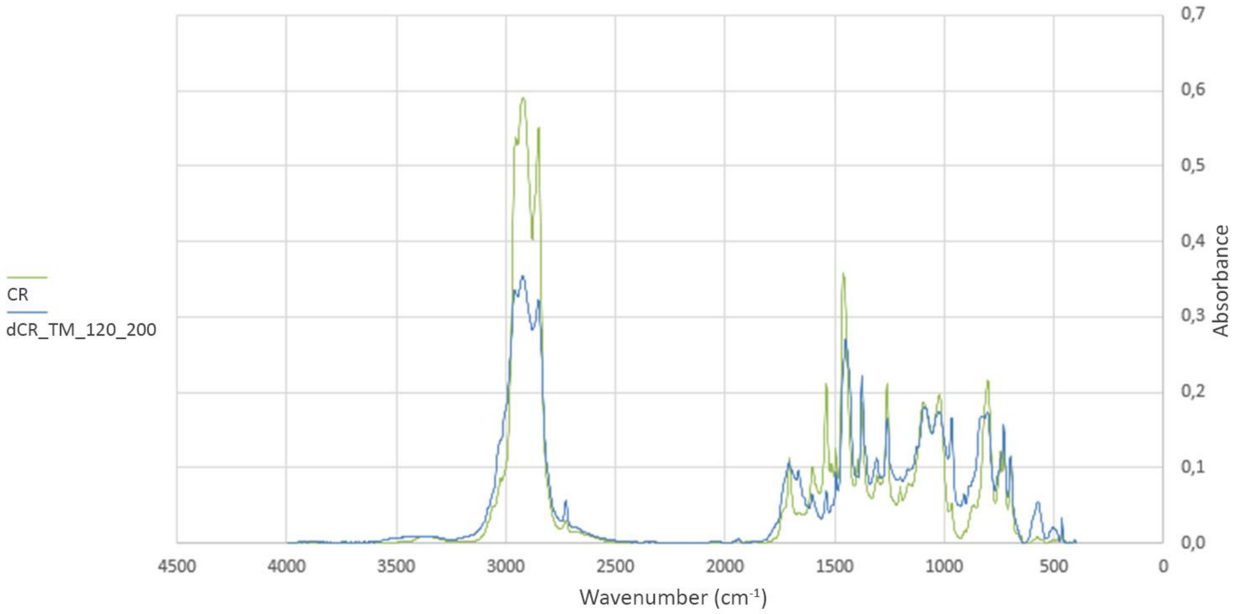


Figure 2. The FTIR spectra of dCR_TM_120_200 sample

In case of thermomechanical devulcanization a considerable decrease of the peaks at the 3000-2500 cm^{-1} range can be observed, which is a sign of remarkable degradation of the chains. The peak related to the C=C double bonds decreased remarkably as well, similarly to the microwave treated sample. The appearance of new peaks is not that prominent than at the microwave treated sample which suggests that the formation of new groups is less emphasized than that during microwave devulcanization.

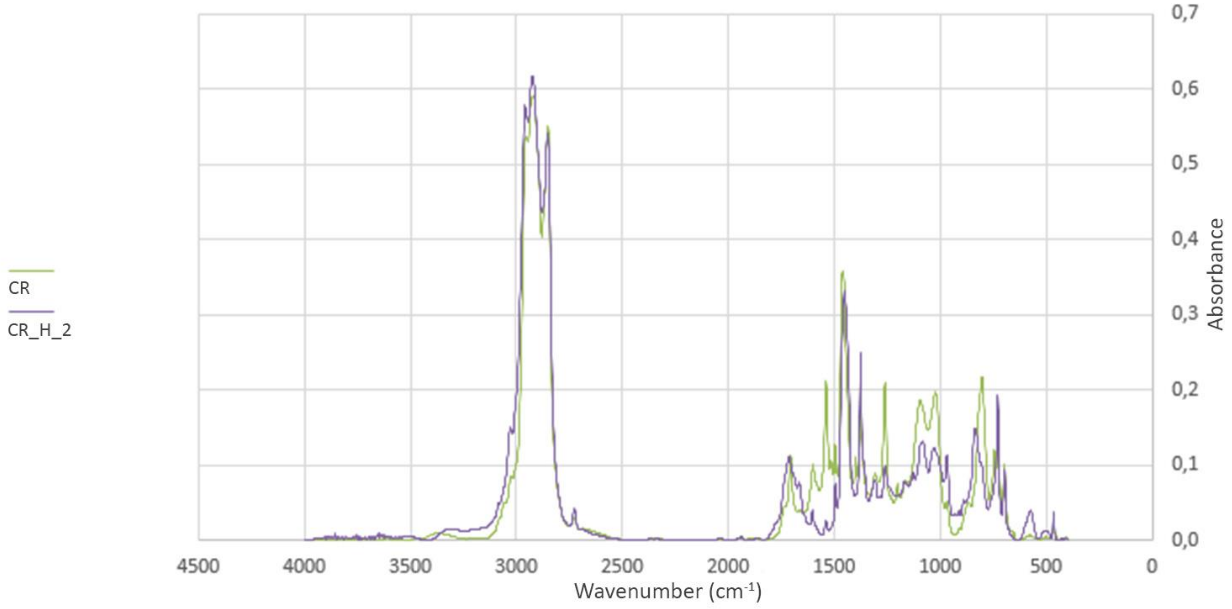


Figure 3. The FTIR spectra of preheated CR

The effect of preheating shows to be similar than that of microwave treatment based on FTIR data. Peaks shoing up near 500 cm^{-1} most likely to be linked to some toluene residues, which was used as a solvent for Soxhlet extraction.

Based on the results we chose the dCR_M_100g_2 sample for further investigation in TDV production. This technique (2 hours of preheating at 150 °C prior to microwave devulcanization, without supplementary thermomechanical devulcanization) led to the highest sol content without the utilization of an additional equipment- and labor-intensive and therefore costly processing step.

3. Using the dCR in rubber compounds

The first pillar of the upcycling of microwave devulcanized rubber waste can be the partial replacement of a fresh rubber compound with dCR without compromising its performance in mechanical and other aspects.

Materials

Materials for this section of the research was chosen according to the formulation of the dCR. Based on the known origin of the CR (waterjet milled truck tire treads and sidewalls) natural and styrene butadiene rubber (NR and SBR) were selected as base rubbers. Their properties are depicted in Table 11. The additives of rubber mixtures were commercially available standardized ones.

Abbreviation	NR	SBR
Manufacturer, type	NR TSR 10 Sud Comoe Caoutchuc, Aboisso, Ivory Coast	SBR 1502, SKS-30 ARKPN, JSC Sterlitamak Petrochemical Plant Sterlitamak, Russia
Main properties	N/A	Mooney viscosity (ML, 1+4, 100°C): 48-58 Bound styrene content: 22-25 wt%

Table 11. Types and producers of raw materials

Processing

In order to assess the usability of dCR in rubbers, different amounts of dCR and CR (as reference) were added to NR and SBR-based compounds. The recipes of the rubber compounds are shown in Table 12. The rubber ingredients were mixed with a Brabender Plasti-corder internal mixer at 50 °C and 40 rpm. The order of the components in Table 12 (left to right) also reflects the order of mixing.

Abbreviation	NR	SBR	ZnO	Stearic acid	Carbon black (N 772)	Carbon black (N 330)	dCR	dCR_x	dGR_2x	CR	Paraffin oil	CBS	TMTD	Sulfur
NR_REF	100	0	10	2	60	0	0	0	0	0	10	1.25	0.6	0.6
NR_dCR50	100	0	10	2	60	0	50	0	0	0	10	1.25	0.6	0.6
NR_dCR100	100	0	10	2	60	0	100	0	0	0	10	1.25	0.6	0.6
NR_dCR185	100	0	10	2	60	0	185	0	0	0	10	1.25	0.6	0.6
NR_dCR100_X	100	0	10	2	60	0	0	100	0	0	10	1.25	0.6	0.6
NR_dCR100_2X	100	0	10	2	60	0	0	0	100	0	10	1.25	0.6	0.6
NR_CR100	100	0	10	2	60	0	0	0	0	100	10	1.25	0.6	0.6
SBR_REF	0	100	5	1	55	9	0	0	0	0	24.5	1	0.8	2
SBR_dCR50	0	100	5	1	55	9	50	0	0	0	24.5	1	0.8	2
SBR_dCR100	0	100	5	1	55	9	100	0	0	0	24.5	1	0.8	2
SBR_dCR185	0	100	5	1	55	9	185	0	0	0	24.5	1	0.8	2
SBR_dCR100_X	0	100	5	1	55	9	0	100	0	0	24.5	1	0.8	2
SBR_dCR100_2X	0	100	5	1	55	9	0	0	100	0	24.5	1	0.8	2
SBR_CR100	0	100	5	1	55	9	0	0	0	100	24.5	1	0.8	2

Table 12. The rubber compounds and their abbreviations (values in phr)

In the case of dCR100_X and dCR100_2X samples the mixing consisted of two phases. In the first step the dCR with vulcanizing agents was compounded (Table 13). Then this untreated dCR mixture (dCR_x and dCR_2x) was added to the rubber mixture.

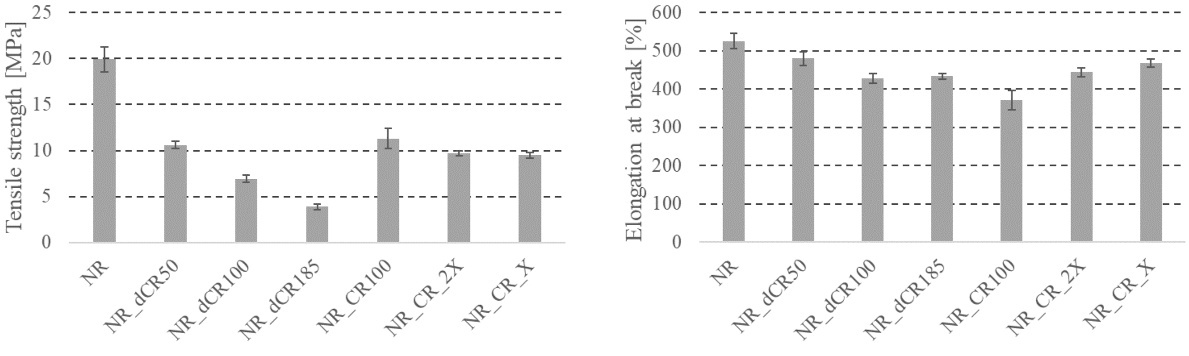
Abbreviation	dCR	ZnO	Stearic acid	Paraffin oil	CBS	TMTD	Sulfur
dCR_x	100	5	1	10	0.625	0.3	0.3
dGR_2x	100	10	2	20	1.25	0.6	0.6

Table 13. The rubber compounds and their abbreviations (values in phr)

The compounds were vulcanized by a hot press. The pressure applied was 2.8 MPa and the temperature was 160 °C.

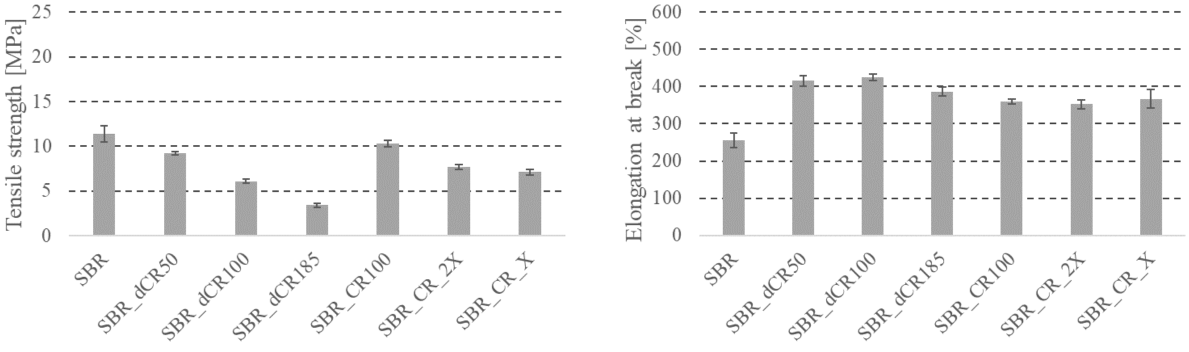
Results

Results of the mechanical tests are summarized in Figure 4 and 5.



a) b)

Figure 4. Tensile strength (a) and elongation at break (b) values of the tested NR compounds



a) b)

Figure 5. Tensile strength (a) and elongation at break (b) values of the tested SBR compounds

Results show that at SBR compounds dCR acts as a plasticizer, lowering tensile strength and increasing elongation at break. At NR compounds both tensile strength and elongation at break values decreased as a result of the addition of dCR in every tested compounds. This plasticizing effect however can be beneficial in TDV production, where plasiticizer oils can be effectively used to enhance the dispersion of the rubber phase in the thermoplastic matrix, which has a positive effect on the mechanical performance of the material.

4. Using the dCR in thermoplastic dynamic vulcanizates

Materials, processing

Based on the results of the phase dealing with fresh rubber compunds, we decided to start the TDV development with an NR-SBR mixture compound as a model rubber for truck tires. The formulation of the model rubber (MR) was: SBR 70 phr, NR 30 phr, ZnO 5 phr, stearic acid 1 phr, naphthenic oil 30 phr, N550 carbon black 60 phr, CBS 1.5 phr, TMTD 1.5 phr, Sulphur 1.5

phr. The rubber ingredients were compounded by Gumiplast Ltd (Nyírmada, Hungary) in a Banbury-type internal mixer.

The applicability of the dCR and the effect of its content in TDV production were studied by partial substitution of the MR by dCR, in 10, 20 and 30 wt% ratios. The component formulations of the TDVs are shown in Table 14.

Designation	60MR	50MR	45MR/5dCR	40MR/10dCR	35MR/15dCR
PP	40	50	50	50	50
MR	60	50	45	40	35
dCR	0	0	5	10	15

Table 14. Abbreviations and formulation of the TDVs produced (amounts are shown in wt%)

The compounding and dynamic vulcanization of the blends were performed on a modular co-rotating twin screw extruder (Labtech LTE 26-44, Labtech Engineering Co. Ltd., Samutprakarn, Thailand) with a screw speed of 180 rpm and two different temperature profiles. The temperature profiles of the twin screw extruder are displayed in Table 15.

Designation	Zones										
	1	2	3	4	5	6	7	8	9	10	Mold
L	160	160	160	165	165	170	170	170	175	175	180
H	170	170	170	175	175	175	180	180	180	180	180

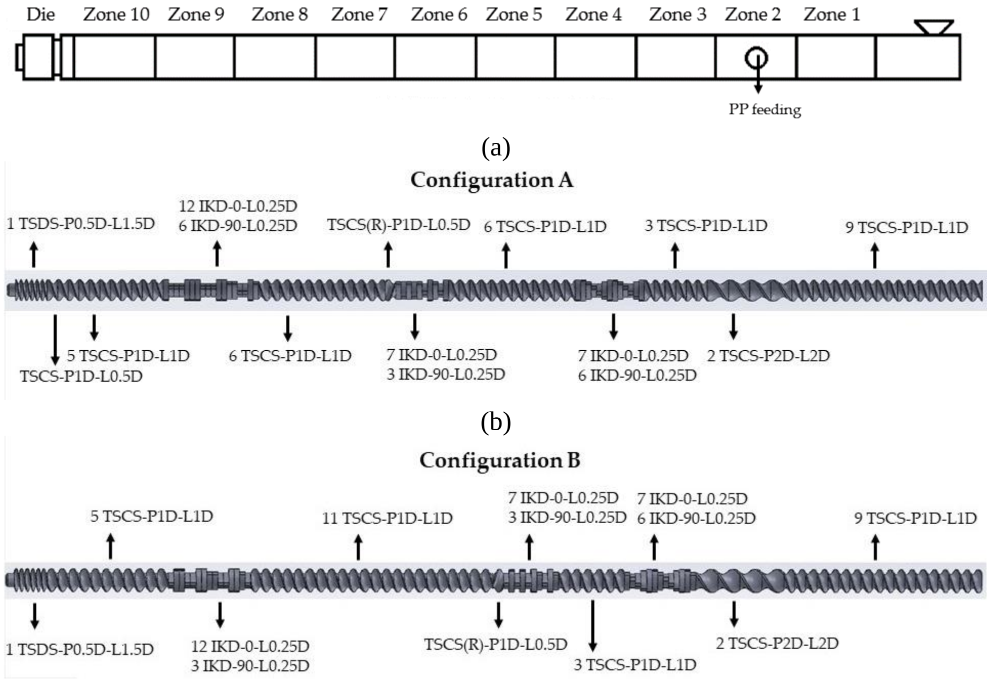
Table1 15. Temperature profiles of the twin screw extruder (temperature values are shown in °C)

Prior to compounding and dynamic vulcanization, the rubber mix was shaped on a single screw extruder (Labtech 25-30C, Labtech Engineering Co. Ltd., Samutprakarn, Thailand, 40 rpm screw speed and 95-105 °C zone temperatures) and a single rubber filament was obtained with a diameter of 3 mm to ensure the precise and reproducible dosing of the rubber during TDV production. The rubber was dosed by feeding the rubber filament continuously into the hopper of the twin-screw extruder. PP was fed in two different ways so that effects of different feeding methods could be studied: i) feeding the PP with the rubber filament through the hopper (H) of the twin-screw extruder simultaneously, and ii) dosing PP in melted state into the second zone of the twin-screw extruder with the help of a single-screw extruder (Labtech 25-30C, Labtech Engineering Co. Ltd., Samutprakarn, Thailand, D=25 mm, L/D=30) and a side feeder (S) adaptor. The given MR/PP ratio was set by the following method: net uncured rubber intake at the given screw speed of the double screw extruder (180 rpm) was measured (4.5 kg/h) and the necessary amount of additional PP was calculated and set by i) utilizing and adjusting the built in hopper feeder of the twin screw extruder to grant 4.5 kg/h feeding of PP granules (in case of hopper PP feeding and 50/50 MR/PP ratio), ii) adjusting the screw speed of the side feeder single screw extruder to obtain 4.5 kg/h (50/50 PP/MR ratio), and 3 kg/h (40/60 PP/MR ratio) throughput for the neat PP melt (in case of side feeding). Three different temperature profiles were set on the single-screw extruder, which are summarized in Table 16. The screw speed of the side feeding extruder was set according to the PP and rubber ratios of the various formulations (cf. data in Table 14.).

Designation	Zones				
	1	2	3	4	Adaptor
1	140	145	155	160	160
2	165	170	175	108	180
3	185	190	195	200	200

Table 16. Temperature profiles of the single-screw extruder used for side dosing of the PP (temperature values are shown in °C)

Effects of different screw configurations was also investigated: the zones of the twin-screw extruder and the different screw configurations are depicted in Figure 6. It can be seen that two of the three kneading blocks on Screw "B" are positioned closer to the PP feeding zone and to the hopper. The concept behind it was to achieve intensive mixing and kneading at an early stage of the curing of the rubber phase, which may lead to finer dispersion and an improvement in the mechanical performance of the resulting TDVs. At the middle kneading block, a conveying element with reverse flight was implemented to decelerate the melt flow and increase the pressure. This way, the preceding kneading block kneaded/sheared the compound even more intensively. Conveying elements with double length and pitch (TSCS-P2D-L2D) were selected for the PP feeding zone, to produce the necessary free volume for the PP melt. At the end of the screw, a conveying element with 1.5D length and 0.5D pitch was used to increase the pressure for more homogenous and more uniform output.



(a)

(b)

(c)

Figure 6. Extruder zones and screw configurations: (a) Location of the zones along the extruder; (b) Screw configuration A; (c) Screw configuration B. Designations of the screw modules (D stands for the diameter of the screw): TSCS-P1D-L1D: twin-start conveying screw, pitch 1D, length 1D; TSCS(R)-P1D-L1D: twin-start conveying screw (reverse flight), pitch 1D, length 1D; TSCS-P2D-L2D: twin-start conveying screw, pitch 2D, length 2D; IKD-0-L0.25D: individual kneading disc, length 0.25D 0° angle; IKD-90-L0.25D: individual kneading disc, length 0.25D 90° angle (each kneading disc can be rotated and positioned in 60° steps on the screw, so utilizing a 0° and a 90° kneading element allowed us to build kneading blocks with individual discs having a 30° angle difference compared to the neighboring blocks: 0°, 60°, 120°; 180°; 240° and 300° was achieved with discs with a 0° angle, while 30°, 90°, 150°, 210°, 270°, 330° was achieved with discs with a 90° angle); TSDS-P0.5D-L1.5D: twin-start discharge screw, pitch 0.5D, length 1.5D

The extruded TDV filaments were cooled by air and pelletized (Labtech LZ-120/VS pelletizer, Labtech Engineering Co. Ltd., Samutprakarn, Thailand) after compounding. From the pellets ISO 3167 A type dumb-bell specimens were injection molded with an Arburg Allround Advance 370S 700-290 injection molding machine (Arburg Ltd. Lossburg, Germany). The related parameters were: barrel temperature range: 170-190 °C, mold temperature: 30 °C, injection speed: 50 cm^3/s, shot volume: 44 cm^3 and holding pressure: 350 bar. Abbreviations and processing parameters of the TDV samples are summarized in Table 17.

Abbreviation	Screw config-uration	PP feeding method	Compounding extruder temperature profile	PP feeding side extruder temperature profile	TDV formulation
A_S_L_1_50MR	A	side, melt	L	1	50MR
A_S_L_1_60MR	A	side, melt	L	1	60MR
B_S_L_1_50MR	B	side, melt	L	1	50MR
B_S_L_1_60MR	B	side, melt	L	1	60MR
A_S_L_1_50MR	A	side, melt	L	1	50MR
A_S_H_1_50MR	A	side, melt	H	1	50MR
A_H_H_0_50MR	A	hopper, granules	H	- (PP was fed at hopper)	50MR
A_S_H_1_50MR	A	side, melt	H	1	50MR
A_S_H_2_50MR	A	side, melt	H	2	50MR
A_S_H_3_50MR	A	side, melt	H	3	50MR
B_H_H_0_50MR	B	side, melt	L	1	50MR
B_H_H_0_45MR/5dCR	B	side, melt	L	1	45MR/5dCR
B_H_H_0_40MR/10dCR	B	side, melt	L	1	40MR/10dCR
B_H_H_0_35MR/15CR	B	side, melt	L	1	35MR/15dCR

Table 17. Abbreviations used for the TDV samples having different compositions and produced with various processing parameters

Results

Characteristic tensile curves of the PP, the cured MR (cured at 180 °C) and the "A_H_H_0_50MR" TDV is shown in Figure 7. It can be seen that the TDV has a higher initial modulus compared to the MR, but after around 25% elongation, a rubber-like, low modulus deformation can be observed.

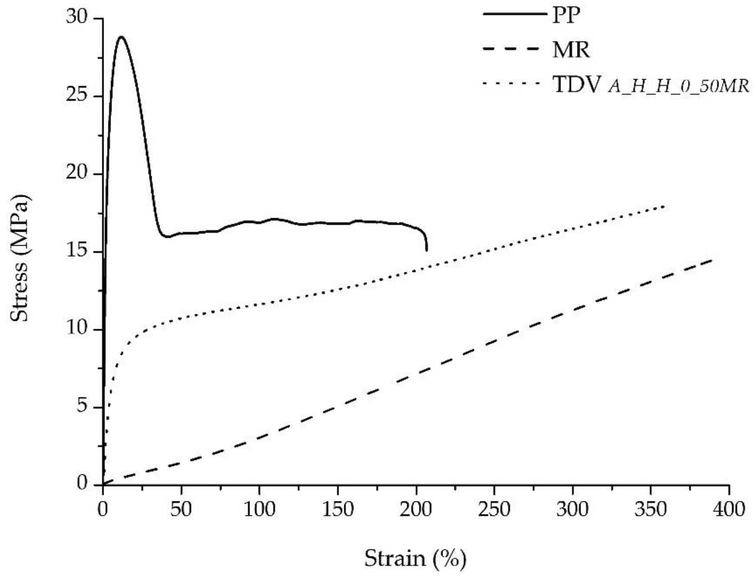
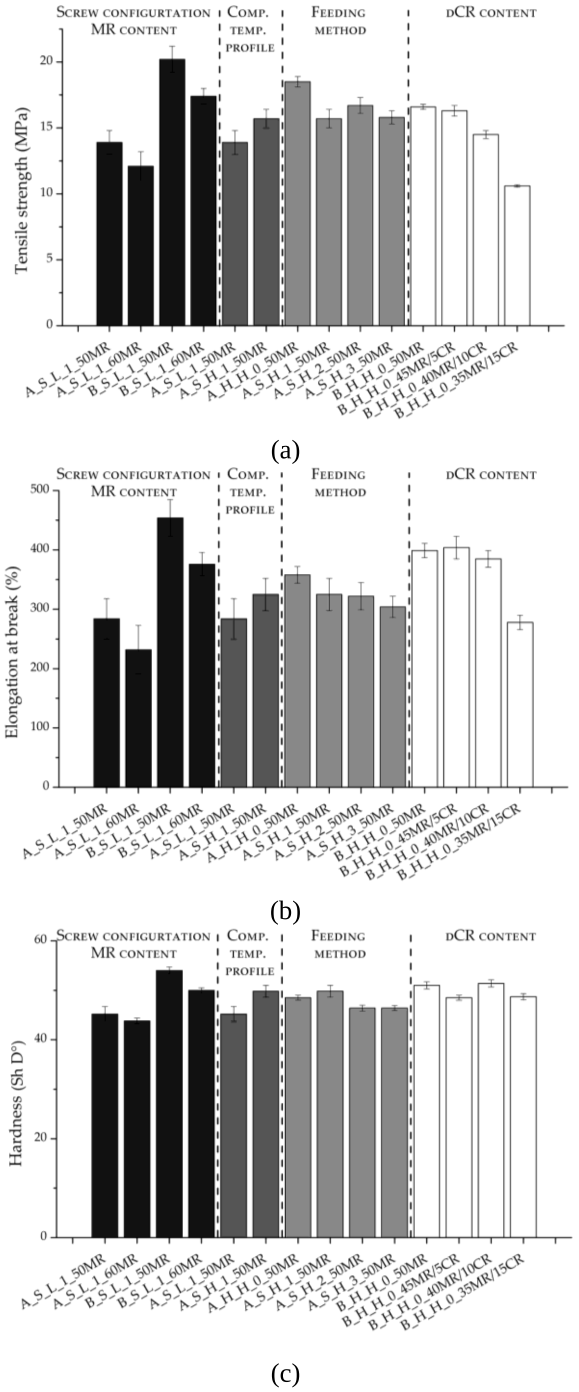


Figure 7. Characteristic tensile curves of the PP, MR and one of the TDVs

The results of the mechanical tests were arranged in four categories based on the various variables studied, namely i) screw configuration and MR content; ii) the temperature profile of the compounding twin-screw extruder; iii) PP feeding method; iv) dCR content. The tensile strength, elongation at break and hardness values of the produced TDVs are summarized in Figure 8.

Similar tendencies can be observed regarding the tensile stress and elongation at break of the investigated compounds. Screw configuration “B” and lower MR content resulted in improved tensile properties (Figure 8/a and b). Higher initial compounding temperature (compounding temperature profile “H”) resulted in improved tensile properties, and the same can be observed in terms of hardness (Figure 8). Feeding the PP at the hopper in a form of granules had a positive effect on the tensile mechanical properties similar to the higher initial compounding temperature.



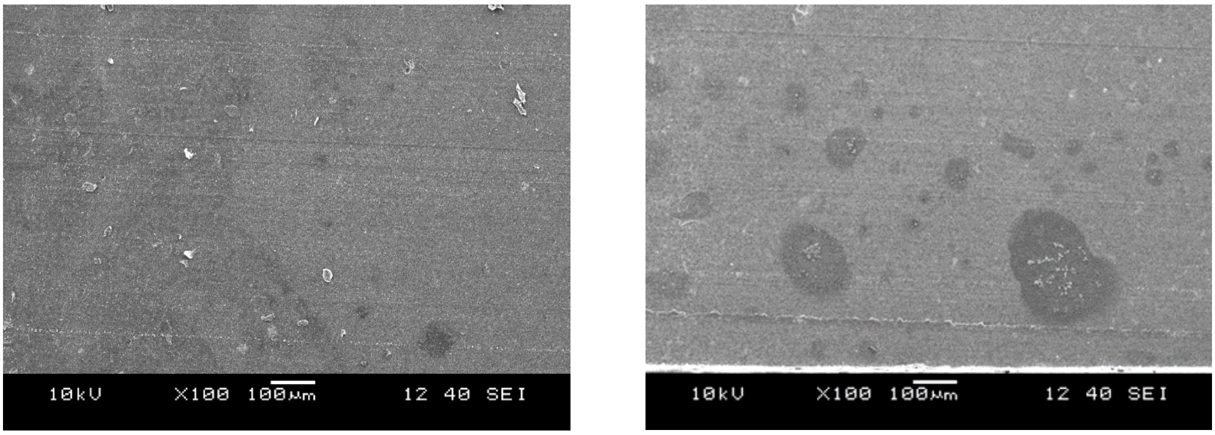
(a)

(b)

(c)

Figure 8. Ultimate tensile properties and hardness of the produced TDVs: (a) Tensile stress; (b) Elongation at break; (c) Hardness.

The melt temperature of the PP in the case of PP side feeding did not have a significant effect on the tensile properties. The processing parameters of TDVs with incorporated dCR were defined by considering the results of the tensile tests of the TDVs containing MR. Therefore, screw configuration “B”, hopper feeding of the PP and a higher compounding temperature profile were used in the production of TDVs containing dCR. Replacing 10, 20, 30 wt% of the MR with dCR resulted in slightly deteriorated tensile behavior, nevertheless at 10 and 20 wt% ratios the decline was very modest. Hardness remained practically unchanged by dCR content (cf. Figure 4). The possible reason behind this finding is that the Shore hardness of dCR was closely matched with that of the resulting TDV in this case (Figure 8). Figure 9 shows typical micrographs from TDVs produced with 50 wt% MR content and different screw configurations. Darker areas belong to the MR, while lighter areas to the PP phase.

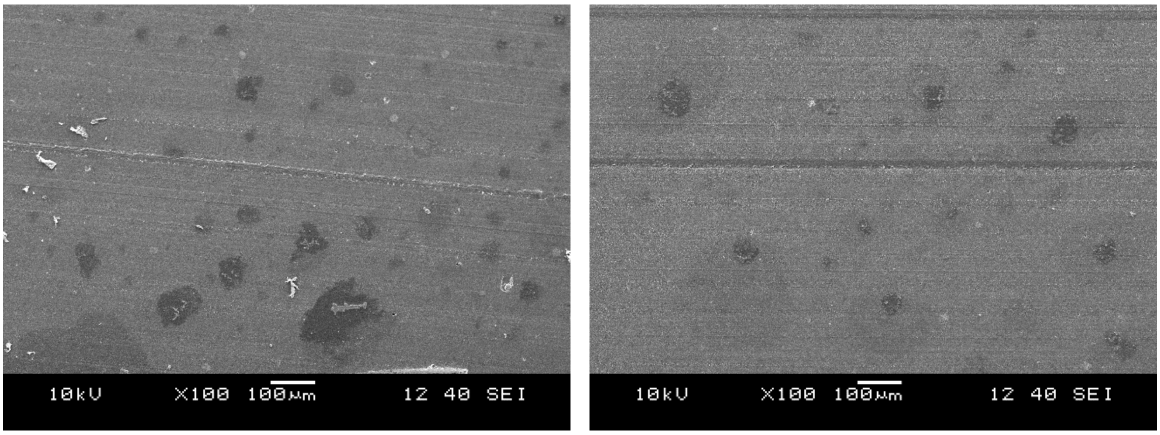


(a) (b)

Figure 9. Cryomicrotomed surfaces of the TDVs produced with different screw configuration: (a) Screw configuration “A” (A_S_L_1_50MR); (b) Screw configuration “B” (B_S_L_1_50MR).

According to the SEM images, screw configuration “B” resulted in better dispersion of the rubber phase, displaying rubber “islands” with small diameter. By contrast, TDVs produced with screw configuration “A” showed a coarser rubber dispersion. At low magnification even hints for local co-continuity can be found. This can be attributed to lower shear stresses, evolved during compounding with “A” compared to “B” screw that delayed the dispersion of rubber (transition to droplets).

Figure 10 shows typical records from TDVs produced with 50 wt% MR content and different PP feeding methods. The comparison of the images displayed in Figure 9 and Figure 10 shows that increasing the compounding temperature (Figure 9/a: compounding temperature profile: L; Figure 10/a compounding temperature profile: H) resulted in a refinement of the rubber dispersion similar to the modification of the screw configuration. Hopper feeding of the PP had a similar, but additional refining effect on the dispersion of the rubber in the TDV. This may be caused by the rapid curing of the rubber phase at the zone, where the PP was introduced to the compounding extruder in the case of side feeding. This rapid vulcanization can be explained by a thermal shock, “suffered” by the rubber when merging with the PP melt coming from the side feeding extruder. Fast curing could hinder the rupture of the rubber particles, and thus the dispersion of the rubber phase.



(a) (b)

Figure 10. Cryomicrotomed surfaces of the TDVs with different PP feeding method and higher compounding temperature profile: (a) Side feeding with 180°C melt temperature (A_S_H_2_50MR); (b) Hopper feeding (A_H_H_0_50MR).

Figure 11 shows a micrograph taken from the surface of a TDV containing 10 wt% dCR in the rubber phase. TDVs with the tested dCR contents had similar rubber particles having seemingly poor adhesion to the embedding matrix. This is the most reasonable explanation for decreasing tensile strength and elongation at break for the related TDVs, especially at higher dCR contents.

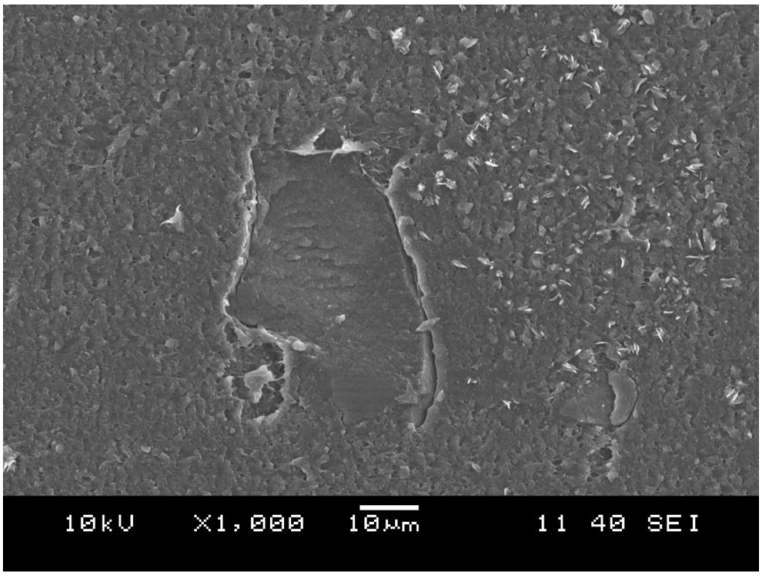


Figure 11. Cryomicrotomed surfaces of the TDV with 10 wt % dCR in the rubber phase

5. Summary

Based on the results of our research, the following conclusions can be drawn:

- the crosslinked 3D molecular structure of rubbers can effectively be broken up by microwave treatment, however the selectivity of the technique (breaking up only the crosslinks and leaving the backbone intact) is not perfect,
- the most important parameter of the devulcanization process is the achieved final temperature of the rubber, the presence of inert atmospheres such as nitrogen decrease the effectiveness of the breakdown,

- a heat treatment or a thermomechanical treatment prior to microwave devulcanization can effectively enhance the efficiency of the latter,
- devulcanized CR can act as a plasticizer in SBR based compounds, decreasing tensile strength and increasing elongation at break of the related compounds,
- in terms of TDV production high quality TDVs can be produced up to 10 wt% dCR content (by replacing 20 wt% of the fresh rubber compound with dCR) with appropriate fresh rubber compound and technological parameter selection.

6. Main results and outcomes of the project

The main result of this project is the successful demonstration of the feasibility of crumb rubber devulcanization. Various parameters and opportunities of devulcanization was tested and characterized. Techniques and parameters resulting in the highest rate of devulcanization was further used to produce dCR to check whether it can serve as a feedstock for either new rubber or TDV production. The outcome of this project showed, that a significant amount of fresh rubber can be replaced with microwave devulcanized crumb rubber, which has a huge economical and ecological potential keeping in mind that the proportion of both rubber waste and TDV production is growing.

7. Project related SSAC papers, BSc, MSc theses PhD dissertations

Project related SSAC papers:

Dávid Kocsis: Polipropilén alapú termoplasztikus elasztomerek fejlesztése dinamikus vulkanizáció segítségével, Polimer Technológia szekció, I. helyezés, Bodor Géza különdíj

Dávid Kocsis: Finomszemcsés gumiőrlemény töltés hatása a polietilén mechanikai jellemzőire, Polimertechnika szekció, III. díj

Project related BSc theses:

Richárd Göbl: A gumiőrlemény hatása duromerek szívósságára (2014)

Anikó Kulin: Epoxi gyanta gumiőrleménnyel történő szívósításának vizsgálata (2014)

Viktor Hliva: A gumiőrlemény hatása az epoxigyanta anyagszerkezeti tulajdonságaira (2015)

Kristóf Szabó: Ismert receptúrájú elasztomerek mikrohullámú devulkanizációja: kaucsuk hatásának vizsgálata (2015)

Tibor Franczel: Gumiabroncs őrlemény devulkanizálása és elemzése (2017)

Bálint Kotró: Ismert receptúrájú térhálós elasztomerek devulkanizációja és elemzése (2018)

Dániel Antunovics: Devulkanizált gumiőrlet alkalmazása gumikeverékekben: receptúra fejlesztés (2018)

Project related MSc theses:

Milán Luketics: Abroncs gumiőrlet értéknövelt újrahasznosítása mikrohullámú devulkanizációt követően gumi keverékekben (2015)

Dávid Kocsis: Polipropilén alapú termoplasztikus elasztomerek fejlesztése dinamikus vuklanizáció segítségével (2016)

Dávid Papp: Mikrohullámú devulkanizációs eljárás fejlesztése hulladék gumiabroncs őrlet értéknövelt újrahasznosításához (2017)

Kristóf Szabó: Devulkanizált gumiőrlemény alkalmazása termoplasztikus dinamikus vulkanizátumok előállítására (2017)

Dávid Brenn: Feldolgozási paraméterek hatása polipropilén alapú termoplasztikus dinamikus vulkanizátumok jellemzőire (2018)

Project related PhD dissertations:

Dániel Ábel Simon: Upcycling of crumb rubber (CR) after microwave devulcanization (in progress) 2017-

Pirityi Dávid: Microwave devulcanization of rubbers (in progress) 2018-

8. Project-related papers, conference abstract

1. Kocsis D., Bárány T.: Polipropilén alapú termoplasztikus dinamikus vulkanizátumok fejlesztése, Polimerek 2: (10) 301-304, 2016
2. Simon D. Á., Tamás-Bényei P., Bárány T.: Gumihulladék mikrohullámú devulkanizációja, ZIP Magazin 7: (7-8) 17-19, 2017
3. Simon D. Á., Bárány T.: The effects of processing parameters on the properties of polypropylene-based thermoplastic dynamic vulcanizates in 'FEMS Junior EUROMAT 2018 Conference, Budapest, Hungary (8.7.2018-12.7.2018).
4. Halász I. Z., Simon D. Á., Bárány T.: A mikrohullámú devulkanizáció, mint a gumiőrlemények egy értéknövelt újrahasznosítási lehetőségének alapja in 'XXVI. Nemzetközi Gépészeti Konferencia – OGÉT, Targu Mures, Romania (26.4.2018-29.4.2018).
5. Bárány T., Simon D. Á.: Application of ground tyre rubber in thermoplastic dynamic vulcanizates in 'German Rubber Conference 2018', Nuremberg, Germany (2.7.2018-5.7.2018), 5 pages
6. Simon D. Á., Halász I. Z., Karger-Kocsis J., Bárány T.: Microwave devulcanized crumb rubbers in polypropylene based thermoplastic dynamic vulcanizates. Polymers, 10, 767-780 (2018).
7. Halász I. Z., Kocsis D., Simon D. Á., Kohári A., Bárány T.: Development of polypropylene based thermoplastic elastomers with crumb rubber by dynamic vulcanization: a potential route for rubber recycling. Periodica Polytechnica Chemical Engineering, (submitted) (2019).
8. Simon D. Á., Pirityi D., Tamás-Bényei P., Bárány T.: Microwave devulcanization of ground tire rubber and applicability in SBR compounds. Journal of Applied Polymer Science, (submitted)
9. Simon D. Á., Pirityi D., Bárány T.: Devulcanization of ground tire rubber: Microwave and thermomechanical approaches, Rubber Chemistry and Technology, (under preparation)
10. Pirityi D., Bíró Z., Pölöskei K.: Thermomechanical devulcanization of EPDM rubber on a two-roll mill, Plastics, Rubbers and Composites (under preparation)