Crumb rubber as a secondary raw material from waste rubber. A short review of processing methods.

Vjaceslavs Lapkovskis 1*, Viktors Mironovs 1, Andrey Kasperovich 2, Vadim Myadelets 2 and Dmitri Goljandin 3

1 Riga Technical University, Scientific Laboratory of Powder Materials, 6B Kipsalas str., Lab. 110, LV-1048, Riga, Latvia; vjaceslavs.lapkovskis@rtu.lv
2 Belarussian State Technological University, Department of Technology of Petrochemical Synthesis and Polymer Materials Processing, Sverdlova str. 13a, 220006, Minsk, Belarus; myadelets.vadim@gmail.com
3 Tallinn University of Technology (TalTech), Ehitajate tee 5, 19086, Tallinn, Estonia; dmitri.goljandin@taltech.ee

* Correspondence: vjaceslavs.lapkovskis@rtu.lv; Tel.: +371-29536301

Abstract: Despite the development of technologies, modern methods of disposal of end-of-life tires most often represent either the incineration in cement kilns or the destruction of tires in special landfills, showing a lack of sustainable recycling of this valuable material. The fundamental role of recycling is evident, and the development of high-efficiency processes represents a priority for the European market. Therefore, investigation of end-of-life rubber processing methods is of high importance for manufacturers and recyclers of rubber materials. In this paper, methods of processing of end-of-life tires are reviewed in order to obtain rubber crumb, which can later be used in the production of new industrial rubber goods and composite.

The processes of separation end-of-life tire into fractions by type of materials using mechanical processing methods along with mechanochemical and mechanical processes of processing the materials of used tires in order to obtain crumb rubber of various fractions and chemical reactivity are considered.

Keywords: rubber, environmental sustainability, end-of-life tires, critical raw materials, rubber processing, disintegrator, reclaiming, devulcanisation, ozone cutting, grinding.

1. Introduction

Processing of end-of-life tires and rubber is one of the critical aspects for up-to-date waste management. End-of-life tyres (ELT) and elastomer products are recognised by the European Union as a critical, valuable resource for the circular economy. In this regard the use of the principles of sustainable development requires a smart approach to waste using environmentally-friendly concepts of secondary raw materials manufacturing from end-of-life tires.

End-of-life tires have a complex composition, containing rubber, steel, textiles and additives. According to U.K. Waste and Resources Action Programme (WRAP) and the European Tyre & Rubber manufacturers’ association (ETRMA) report the composition of passenger and light truck tires are given in Figure 1 and Table 1.
Table 1. Crumb rubber uses in technical applications

| Application areas                        | wt%  |
|------------------------------------------|------|
| Level crossings                          | up to 80 |
| Extruded pipes                          | 5-10 |
| Garden (watering) hoses                  | 5-40 |
| Silicone caps for spark plugs            | 10-30 |
| Pads for car pedals                      | 10-30 |
| Components of a self-leveling roof       | 10-30 |
| Floor coverings                          | 10-100 |
| Shoe soles                               | 10-100 |
| Components of a sheet roof               | 20-40 |
| Foundation pads                          | 30-50 |
| Mudflaps                                  | 50-60 |
| Automotive gaskets and seals             | 50-60 |

End-of-life tires have a complex composition, containing rubber, steel, textiles and additives. According to U.K. Waste and Resources Action Programme (WRAP) and the European Tyre & Rubber manufacturers’ association (ETRMA) report, the composition of passenger and light truck tires are given in Figure 1 and Figure 2.
Figure 2. Typical composition of passenger and truck tires, wt%.

Most of the end-of-life tyres collected in the E.U. are subjected to recycling with the energy of materials recovery. However, the manufacturing of materials and products with added value which are based on recycled ELTs can be considered as a critical issue for the European circular economy. One of the known approaches to recycle ELTs is to process them through mechanical shearing/grinding. Thus producing crumb rubber that can be used as a material to entirely or partially replace mineral aggregates, producing more environment-friendly composite materials such as rubberised asphalt pavements. Binder modification with crumb rubber is an up-to-date technology for asphalt production with lower ductility. One of the environmentally friendly approaches for tire recycling is devulcanisation.

2. Processing methods for rubber wastes

The current review is devoted to waste rubber processing methods, which can be classified according to the modifications that occur in the elastomeric matrix during processing Figure 3.

Figure 3. Waste rubber processing methods.
Chemical processing methods lead to irreversible changes in the structure of the elastomeric matrix and other rubber components. In most cases, these processes of chemical processing of rubber waste proceed at high temperatures and consist of thermal destruction of polymers, which occurs in a specific environment.

Mechano-chemical methods make it possible to preserve the valuable properties of elastomers to a greater extent in comparison with chemical ones because there is no complete decomposition of the polymer. These methods allow, due to thermal, mechanical and chemical action, to partially destroy the three-dimensional structure of rubbers and obtain a product that has plastic properties, is capable of cross-linking during vulcanisation and can partially replace rubber in rubber compound formulations.

The original structure and properties of the elastomers that are part of the waste are most fully preserved when using mechanical processing methods. The primary method of this class is grinding.

New methods of improving rubber processing products are continually being developed - surface treatment, catalytic regeneration, ultrasonic and chemical devulcanisation and many others. Studies have shown that such process parameters as temperature, the intensity of mechanical action, parameters of the reaction medium are essential.

Shredding tires and separating components are essential processes to recover useful recycled materials. Moreover, preliminary grinding of the material is necessary to select the processing method. Figure 4 demonstrates a two-stage grinding concept for end-of-life tires, showing the possible use of different particle sizes of rubber as secondary raw materials.

**Figure 4.** Staged grinding of end-of-life tires with the indication of the options for using individual fractions of rubber.

2.1. Mechano-chemical processing

2.1.1. Reclaiming

Rubber reclaiming is a technological process of converting mainly worn-out tires, as well as vulcanised rubber waste into reclaimed rubber, a product with predominantly plastic properties,
characterised by the ability to mix with rubber, ingredients and undergo re-vulcanisation. The use of reclaim in the production of elastomeric materials and products saves rubber, carbon black, softeners.

When the regenerate is obtained by the water-neutral method, devulcanisation of rubber occurs in an autoclave in an aqueous medium having an acidic reaction, with continuous stirring. As a result, the conditions for the swelling of rubbers in the softener and heat transfer from the walls of the autoclave to the rubber are improved, the remnants of the tissue contained in the crumb are entirely destroyed, and the degree of contamination of devulcanisation decreases.

The most widespread is the continuous thermomechanical method. Due to the continuity, speed, complete mechanisation and significant automation of the devulcanisation process, this method of obtaining reclaim is the most technologically advanced in comparison with other applied methods of rubber reclamation.

2.1.2. Devulcanisation

During the mechanical processing of crushed vulcanizate in the presence of a reducing agent (thiuram, amines, bisphenols, benzoyl peroxide etc.), the process of devulcanisation can occur. When using alkylphenol-formaldehyde resins, surface devulcanisation of various crushed vulcanizates with a particle size of 0.5 to 5 mm can be carried out on rollers. The introduction of SBR-based elastomeric compositions into the composition leads to an increase in resistance to ageing and abrasive wear in comparison with untreated rubber powder.

The paper reviews tensile, curing, viscoelastic, morphology and thermal properties of natural fibre reinforced rubber composites and reclaimed rubber. The thermal-mechanical devulcanisation has been studied in work. The effects of different proportions on the vulcanisation process parameters of reclaimed rubber and natural rubber. The impact of the dosage of the reclaimed rubber and the cure rate and time of compounds.

Devulcanization of sulphur-crosslinked nitrile butadiene rubber can be carried out in a nitrobenzene medium at a temperature of 200 °C for 3 hours.

It is proposed to use benzoyl peroxide as a devulcanising agent for rubbers based on natural rubber. The process can be carried out at a temperature of 80 °C in a xylene medium with a dosage of benzoyl peroxide 2 g, as well as in a rubber mixer.

A state-of-the-art in rubber devulcanisation was recently reviewed demonstrating an alternative for end-of-life tire conversion into products with added value. Mechanochemical devulcanisation process in two-roll mixing mill with the addition of devulcanising agent is proposed in, thiol acid is suggested by Jana et al. Obtained devulcanised rubber materials represent a powder- and sponge-type aggregates Figure 5.

Figure 5. Crumb rubber (left) and devulcanised crumb rubber (right) after mechano-chemical processing in multi-roll system (author’s images).

2.1.3. Ozone cutting
The rubber products are subjected to the simultaneous action of mechanical stress and ozone, which leads to cracking of the rubber and the separation of reinforcing elements from it without mechanical cutting or crushing.

The main technological line is an ozone disintegration unit. Ozone acts as a “chemical knife”, and the rubber is separated from the metal frame and textile frame. Cracking of rubber in the presence of ozone occurs primarily in the places of stress concentration, i.e. along growing cracks. Therefore, the ozonation process goes along the cavities of the “cut” while the rubber practically retains its properties.

Benefits of ozone technology:
- low energy consumption (5 - 10 times less than mechanical crushing);
- environmental friendliness (low gas emission);
- the process takes place at room temperature.

The ozone method of rubber destruction can be considered as one of the promising techniques, in which the energy consumption per 1 kg of the obtained crumb rubber does not exceed 0.02 kW per hour. This method does not destroy the metal cord and synthetic cord of the tire, there are no costs for cutting the tire into pieces.

Ozone is used as an active agent for surface oxidation and modification of rubber (tire) crumb. The crumb rubber reacts with ozone to produce CO\(_2\) in the initial stages, resulting in a surface oxidised product. The reaction rate constant between ozone and crumb rubber is determined by Fourier transform infrared spectroscopy, which monitors the absorption of ozone in the gas phase in the presence of crumb. The oxidation state is determined using the intensity of the ketone band at 1710 cm\(^{-1}\) as a reference. The ratio between the amount of ozone (in milligrams) reacted with crumb rubber (in grams) is used as a parameter for the surface oxidation state. Thermogravimetric analysis, differential thermal analysis, and pyrolysis gas chromatography showed that ozonation of crumb rubber exclusively occurs on the surface and does not affect the properties in the mass. The surface of the oxidised crumb is characterised by surface acidity and hydrophilicity.

2.2. Mechanical processing

When recycling waste, it is essential to preserve the original structure and properties of the polymers they contain. From this position, the best way to process rubber waste is mechanical shredding.

2.2.1. Grinding at negative temperature

It has been established that the grinding of polymers occurs under conditions when they have the least deformability, i.e. at low temperatures or high speeds. At low temperatures, a minimum of specific work is observed, which is spent from the onset of deformation to fracture.

Cryogenic grinding consists in cooling the rubber below the glass transition temperatures and subsequent mechanical action. For cooling liquid nitrogen or supercritical CO\(_2\) are used. Most preferred is liquid nitrogen, which allows for sufficient physical contact and maintains an inert medium during grinding, preventing oxidative processes. Mechanical action during cryogenic grinding can be carried out by the impact, abrasion, compression, as well as due to the work of an electromagnetic pulse.

The ground vulcanizate obtained by cryogenic grinding has, as a rule, a smooth process surface, which reduces the level of interaction with the elastomeric matrix, but at the same time contributes to good flowability and miscibility when it is introduced into rubber compounds.

The advantages of the cryogenic grinding method include the absence of thermal or oxidative destruction of the powder, fire and explosion safety and efficiency of separation of metal and textiles from crumb rubber after grinding.

The disadvantage of the cryogenic method is the high consumption of refrigerant, especially for obtaining rubber powders with particles less than 0.25 mm in size.
Preferred methods of grinding waste rubber at positive temperatures. One of the necessary conditions determining the possibility of polymer grinding at positive temperatures is the creation of a temperature regime, the lower limit of which would be equal to 80–100 °C.

Mechanical grinding at positive temperatures can be carried out by the abrasion, shear, compression, shear, cutting and impact.  

2.2.2. Abrasive grinding

The process is carried out by supplying the material to the abrasive tool, which is usually made in the form of a tape or a circle, at negative and positive temperatures. To prevent sticking of the crushed material on the tool and to ensure intensive cooling of the treatment zone, water is supplied to the product to reduce the temperature in the contact zone of the instrument.

The fineness of the resulting product and the performance of the equipment is mainly influenced by the tool rotation frequency and the rubber feed rate. The quality of the material obtained affects the subsequent possibility of its use in the production of industrial rubber goods.

This method makes it possible to grind tires without preliminary crushing of the tire, which is a distinct advantage. However, the need to dry the resulting product and the significant heterogeneity of particle sizes limit the industrial use of grinding by attrition.

2.2.3. Compression shear grinding

Compression shear grinding is usually carried out on crushing and grinding rollers operating in a closed cycle with a classifier. The disadvantages of this method comprise the low efficiency of using the surface of the working bodies, which makes it necessary to repeatedly pass the crushed material through the gap, as well as low productivity and high energy consumption.

An increase in the efficiency of grinding rubbers on roller machines can also be achieved by changing the ratio of rolls rotation frequency. Since the simple act of destruction on the rollers is due to the creation of ultimate stresses in the particles of the crushed material, which arise due to the difference in the speeds of rotation of the rollers. It has been found that an increase in roll friction leads to an increase in productivity. To increase the yield of grinding crumbs to 1.0 mm. and increasing the productivity of equipment, the grinding of vulcanised waste can be carried out on a roller mill in the presence of an aqueous solution of a copolymer of (meth) acrylic acid and acrylonitrile. In this case, the friction is 1: 100–1: 400. Copolymer dosage per 100 wt. including secondary rubber is equal to 0.2–0.6 mass. hours (on the dry matter). With an increase in friction to a value of 1: 100 or more, the mechanism of rubber destruction changes. In this case, the destruction of the material occurs in the surface layer of the rubber being crushed in contact with the surface of the high-speed roll with the formation of individual rubber particles of small size.

It is possible to carry out grinding in a complexly deformed (combination of compression and shear in different directions) state using extruders equipped with various types of grinding heads. In these units for grinding, screws with a small clearance to the cylinder can be used as working elements.

Research is being carried out to determine the effect of a crushed vulcanizate, which is obtained by the method of high-temperature shear deformations. This method is based on the phenomenon of multiple cracking of a solid and its destruction into separate particles under conditions of intense compression and simultaneous shear deformation carried out at high temperatures. This grinding method makes it possible to obtain a ground vulcanizate with a bimodal particle size distribution. The first maximum is observed in the range of 350–370 µm, the second, 1400–1500 µm. In this case, in dosages of 5-10 mass. including IV obtained by this method can be used in mixtures based on rubbers SBR, N.R., I.R. and NBR without a significant reduction in the conventional tensile strength and elongation at break. This method is also applicable for grinding vulcanizates of ethylene propylene diene and silicone rubber.
For high-speed grinding of complexly deformed rubber composite, the grinder SD-25 was designed for modelling the grinding process of intact tyres and for producing rubber crumbs in size of 1-3 mm. This result was achieved using special compound tool. The preliminary results enable to design a compound grinder that can process tyres to 1-3 mm rubber powder directly. Tyres can be worked up saving tyre-beads and extracting spikes.

Processing of rubber composites is particularly effective, in which textiles and metal cords become stress concentrators and facilitate fracture 37.

The results of changing the size of the rubber composite and separating the constituent components from it using the example of processing the tread of a car tire using the SD-25 setup are shown in Figure 6.

Figure 6. Grinding at ambient temperature by the grinder SD-25: initial pieces (a), pre-crushed (b) and milled tyre (c), separated wire (d) and rubber (e).

2.2.4. Cutting

Cutting is the process of dividing the body into parts by stress concentrators (knives).

The production and use of highly dispersed active rubber powders have significant advantages in comparison with reclaimed, therefore, in many countries, reclaim plants are being closed, and a transition to processing rubber waste into crushed vulcanizates is taking place 38.

In paper 39 the possibility of producing composites is shown by joint crushing of rubber crumb and textile cord in a disk grinder. The resulting material contains from 5 to 20% cord. In this case, the effect of joint grinding makes it possible to increase the strength of the composite by approximately 1.5–2.0 times in comparison with the vulcanised mixture of rubber crumb and cord, which have not been jointly processed.

The paper describes a method for crushing rubber waste using an ultra-high-pressure water flow (180–300 MPa). This method can be used to obtain IV with a particle size of 100–800 µm. This facilitates the separation of metal reinforcing materials from rubber waste, and also reduces the degree of degradation of the elastomeric matrix because water is at the same time is also a cooling agent 40.

The destruction of the material under the action of a mechanical shock 37 (constrained or free) is destroyed due to the conversion of the kinetic energy of the working body of the equipment into the energy of deformation of destruction 41.

With a constrained impact, the destruction of the material occurs between two colliding surfaces. The destructive effect depends on the impulse of the working fluid.

With a free impact, destruction occurs due to the collision of material particles between themselves and the working parts of the equipment. Therefore, the destructive effect depends on the inertial forces of a piece of crushed material.
On impact grinders, processing of rubber waste can be carried out at negative and positive temperatures. They are used to obtain lumps from the bulky waste and their further processing into fine powders.

The known method, which allows you to reduce energy consumption during crushing by the impact. In this case, crushing and crushing of rubber-based material, for example, car tires are performed with simultaneous or preliminary deformation of the rubber base in a plane perpendicular to the direction of impact. This allows when the impact speed is exceeded by 20% or more over sound in rods and plates, to reduce energy consumption by about 2.5 times.

2.2.5. Processing in disintegrators.

The disintegrator is an impact grinder that refines material by collisions (Figure 7), where the elementary colliding contact of the material piece with the tool is $10^{-3} - 10^{-5}$ s and the processing time in the machine for each element does not exceed 0.1 s. This avoids any heating of the material to be treated.

Unlike the traditional grinding methods, disintegration breaks up the material by a series of high-speed impacts, which generate stress within the material particle tens of times greater than its ultimate strength. Combined with a built-in inertial separation system makes it possible to produce powders of materials that are generally considered impossible to obtain using such types of mills.

A variant of such built-in inertial separation system (selective grinding mode in Figure 8) also makes it possible to separate the components of complex composites released by impact from each other.

The processes accompanying disintegration also significantly alter the mechanical and chemical properties of the material. When the particles are rapidly destroyed, surface oxide films are torn off, and a large amount of new unoxidised surface is formed, which has exceptionally high chemical reactivity. The spatial pattern of the grains of the material is distorted, numerous defects emerge. So mechanochemical processes are taking place not only on the freshly formed surfaces but also in the volume of ground grains.

The disintegration is especially useful for grinding elastic materials (such as rubber and its composites) using low temperatures when the rubber becomes brittle and rapidly degrades. The shortness of the process avoids heating of the processed material. Low temperature milling of...
3. Applications of crumb rubber as a secondary raw material for new products manufacturing

Crumb with particle sizes from 0.1 to 0.45 mm is used as an additive (5...20%) in rubber mixtures for the manufacture of new car tires, massive tires and other rubber products. The use of rubber powder with a highly developed specific surface area of particles (2500-3500 cm²/g), obtained by mechanical grinding, increases the resistance of tires to bending and impact, increasing their service life. Also, the obtained crumb is used for the production of reclaim. The reclaim is widely used in rubber compounds and the manufacturing of new tires as a rubber substitute, but at the same time reclaimed from tire crumb is four times cheaper than rubber. Consequently, there is a reliable and permanent economic factor for the use of reclaim in the domestic rubber and tire industry.

Crumb with particle sizes up to 0.6 mm is used as an additive (up to 50...70%) in the manufacture of rubber footwear and other rubber products. Moreover, the properties of such rubbers (strength, deformability) practically do not differ from the properties of ordinary rubber made from raw rubbers. Also crushed vulcanisate with a particle size of up to 0.6 mm can be used in a dosage of up to 50 mass. h. in compositions for the production of automotive glass seals.

Crumb with a particle size of up to 1.0 mm can be used for the manufacture of composite roofing materials (roll roofing and rubber slate), rubber-bitumen mastics, vulcanised and non-vulcanised roll waterproofing materials. Powdered rubber is used in the manufacture of rubber mats, rubber tiles for roofing.

Crumbs with particle sizes from 0.5 to 1.0 mm allow increasing the strength of the road surface, as well as their impact resistance, frost resistance and resistance to cracking of the canvas at temperature extremes. The volume of crushed rubber in such improved coatings should be about 2% by weight of the mineral material, i.e. 60...70 tons per 1 km of the roadbed. In this case, the service life of the roadway increases by 1.5 - 2 times. In Western Europe, more than 900,000 kilometres of roads require periodic repairs, in the USA more than 700,000 km, in Canada 100,000 km, and Japan 130,000 km. To replace the old road surface with a new one, using rubber powder, only in the listed countries will require about 25 million tons of crumb rubber of fine fractions.

Such powders are also used as a sorbent for collecting crude oil and liquid petroleum products from the surface of water and soil, for plugging oil wells, green waterproofing layers, etc. Composite material based on finely dispersed rubber powders with a highly developed specific surface (2500-3500 cm²/g) and other free-flowing organic additives. Powders have a high ability to crude oil and liquid oil products with all other known sorbents of oil and oil products based on rubber powders. The mass ratio of absorbed oil or oil products by this sorbent is 6.5-7.0 : 1. They do not sink in water, although the raw material for the production of its main component - finely dispersed rubber powder - worn out pneumatic tires and technological waste rubber, have a mass density of more than 1.3. As a result of the sorption of oil or liquid petroleum products, sorbents are collected on the water into large agglomerates weighing up to several kilograms, which remain on the surface in any condition for several months and are relatively easily collected mechanically without leaving any traces, even in the form of thin oil films. Sorbents are non-toxic and environmentally friendly.

Research has been carried out to determine the effect of crumb rubber with an average particle size of 0.6 mm on the properties of wood-based composite materials obtained by hot pressing.

Rubber crumb with particle sizes from 2 to 10 mm is used in the manufacture of massive rubber plates for completing tram and railway crossings, characterised by long-term operation, excellent weather resistance, low noise level and modern design; sports grounds with a comfortable and safe surface; livestock buildings, etc.
Porous boards are obtained by hot pressing rubber powder mixed either with the addition of vulcanising agents or with powder of polyethene, PET, etc. Such slabs are used in residential construction as thermal and sound insulation layers in wall panels, as well as for flooring and insulating coatings. A promising application of powdered rubber is its use as fillers for various synthetic thermoplastics. These compositions undergo dynamic vulcanisation and have rubber-like properties at room temperature, and are processed at elevated temperatures. Studies have been carried out to assess the possibility of using tire crumbs in compositions based on a combination of butyl rubber and chlorosulphonated polyethene. The resulting compositions with crumb rubber have increased thermal stability. Studies of the properties of compositions based on natural rubber and devulcanised BNK showed a decrease in the degree of swelling in an aggressive environment.

The research is being carried out on thermoplastic compositions, where polyethene is used as a binder, polypropylene, polyamide, maleated polyethene. It should be noted that the strength properties of these compositions deteriorate with an increase in the content of crushed vulcanisate. A mixture of polyethene and crumb rubber in a 50:50 ratio has properties similar to compositions based on a mixture of natural rubber and polyethene.

There is material based on thermoplastic polymers (polystyrene, etc.) containing rubber crumb in a dosage of 15–20 phr. The strength of this composite is 6–8 MPa. This thermoplastic elastomeric material can also be used for the preparation of conveyor belts, drive belts, flooring and walkways, floor tiles, rugs, mounting flanges, shock absorber covers, sound barriers, safety guards, carpet backing, car bumpers, wheel arch gaskets, car door and window seals, sealing rings; gaskets, irrigation systems, pipe or hose materials, flower pots, building blocks; roofing materials, geomembranes, etc.

Based on partially vulcanised waste rubber mixtures, it is possible to make massive rubber products. When the dosage of vulcanised waste is 20–35% of the mass, vulcanisates have a strength of 7.0–8.0 MPa and a relative elongation of 250–300%.

Rubber crumb 2-3 mm in size can be used as an adsorbent for fuel components. Intensive processing in disintegrators of rubber crumb and devulcanized rubber crumb with additional components allows to obtain composite mixtures material for environmental applications.

The use of crumb rubber in flexible polyurethane foams has a significant effect on the structure of the material: the density of cross-linking increases significantly. This increases the thermal stability of the material, while the decomposition temperature increases by 14 °C in comparison with the sample without crumb rubber.

In paper the possibility of manufacturing a water-repellent material based on crushed rubber is reported. The water-repellent properties of the resulting material are due to the air that accumulates in the pores of the ground rubber surface.

5. Summary

The methods reviewer in the article make it possible to obtain crushed rubber from waste tires of various fractions, which can later be used in the production of industrial rubber goods and composite materials.

Unfortunately, it is not possible to distinguish from the described rubber processing methods the one universal or optimal method that would be considered the best for all situations. It would be useful for everyone if the best methods were known in the search for an optimal solution to a particular technological problem and some methods were excluded to avoid confusion. It is also useful to know the alternatives from which the appropriate method could be chosen based on cost-benefit analysis, environmental impact and feasibility.

The rapid development of production, the ever-increasing requirements for the technological properties of products, as well as the tightening of requirements for their processing and re-use, lead to the rejection of one technological process in favour of combining them from two or more processing methods.
Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used “Conceptualization, V.L.; methodology, V.L., V.M.; investigation, V.L., A.K., V.M., D.G.; resources and; data curation, V.L., A.K., V.M., D.G.; writing—original draft preparation, V.L.; writing—review and editing, V.L., V.M., A.K., V.M., D.G.; visualisation, V.L., V.M.; supervision, V.L., V.M.; project administration, V.L.; funding acquisition, V.L. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: This work has been supported by the European Regional Development Fund within the Activity 1.1.1.2 “Post-doctoral Research Aid” of the Specific Aid Objective 1.1.1 “To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure” of the Operational Programme “Growth and Employment” (No. 1.1.1.2/VIAA/1/16/175).

This work was supported by the Estonian Research Council grants PRG643 and PRG665 and by the Environmental Investment Center Foundation grant KIK19019.

Conflicts of Interest: The authors declare no conflict of interest.

References

(1) ETRMA. Annual Report 2017: Moving Innovation That Cares. *Annu. Rep. 2017*, 32.

(2) Bulei, C.; Todor, M. P.; Heput, T.; Kiss, I. Directions for Material Recovery of Used Tires and Their Use in the Production of New Products Intended for the Industry of Civil Construction and Pavements. *IOP Conf. Ser. Mater. Sci. Eng. 2018*, 294, 012064. https://doi.org/10.1088/1757-899X/294/1/012064.

(3) ETRMA. End-of-Life Tyre Report 2015. *2015*, 36.

(4) Torretta, V.; Rada, E. C.; Ragazzi, M.; Trulli, E.; Istrate, I. A.; Cioca, L. I. Treatment and Disposal of Tyres: Two EU Approaches. A Review. *Waste Manag. 2015*, 45, 152–160. https://doi.org/10.1016/j.wasman.2014.07.018.

(5) Wang, T.; Xiao, F.; Amirkhanian, S.; Huang, W.; Zheng, M. A Review on Low Temperature Performances of Rubberized Asphalt Materials. *Constr. Build. Mater. 2017*, 145, 483–505. https://doi.org/10.1016/j.conbuildmat.2020.118577.

(6) Picado-Santos, L. G.; Capitão, S. D.; Neves, J. M. C. Crumb Rubber Asphalt Mixtures: A Literature Review. *Constr. Build. Mater. 2020*, 247, 118577. https://doi.org/10.1016/j.conbuildmat.2020.118577.

(7) Bressi, S.; Fiorentini, N.; Huang, J.; Losa, M. Crumb Rubber Modifier in Road Asphalt Pavements: State of the Art and Statistics. *Coatings 2019*, 9 (6), 384. https://doi.org/10.3390/coatings9060384.

(8) Asaro, L.; Gratton, M.; Seghar, S.; Aït Hocine, N. Recycling of Rubber Wastes by Devulcanization. *Resour. Conserv. Recycl. 2018*, 133, 250–262. https://doi.org/10/gdf23q.

(9) Gheni, A. A.; Lusher, S. M.; ElGawady, M. A. Retention Behavior of Crumb Rubber as an Aggregate in Innovative Chip Seal Surfacing. *J. Clean. Prod. 2018*, 197, 1124–1136. https://doi.org/10/gd5mtn.

(10) Dick, J. S.; Annicelli, R. A. *Rubber Technology: Compounding and Testing for Performance*, Hanser Publishers, 2001.
Shi, J.; Jiang, K.; Ren, D.; Zou, H.; Wang, Y.; Lv, X.; Zhang, L. Structure and Performance of Reclaimed Rubber Obtained by Different Methods. *J. Appl. Polym. Sci.* 2013, 129. https://doi.org/10.1002/app.38727.

Rajan, V. V.; Dierkes, W. K.; Joseph, R.; Noordermeer, J. W. M. Science and Technology of Rubber Reclamation with Special Attention to NR-Based Waste Latex Products. *Prog. Polym. Sci.* 2006, 31 (9), 811–834. https://doi.org/10.1016/j.progpolymsci.2006.08.003.

Ghorai, S.; Bhunia, S.; Roy, M.; De, D. Mechanochemical Devulcanization of Natural Rubber Vulcanizate by Dual Function Disulfide Chemicals. *Polym. Degrad. Stab.* 2016, 129, 34–46. https://doi.org/10.1016/j.polymdegradstab.2016.03.024.

Lewandowski, W. M.; Januszewicz, K.; Kosakowski, W. Efficiency and Proportions of Waste Tyre Pyrolysis Products Depending on the Reactor Type—A Review. *J. Anal. Appl. Pyrolysis* 2019, 140, 25–53. https://doi.org/10.1016/j.jaap.2019.03.018.

Zhang, X.; Saha, P.; Cao, L.; Li, H.; Kim, J. Devulcanization of Waste Rubber Powder Using Thiobisphenols as Novel Reclaiming Agent. *Waste Manag.* 2018, 78, 980–991. https://doi.org/10.1016/j.wasman.2018.07.016.

Sabzekar, M.; Chenar, M. P.; Mortazavi, S. M.; Asadi, S.; Zohuri, G. Influence of Process Variables on Chemical Devulcanization of Sulfur-Cured Natural Rubber. *Polym. Degrad. Stab.* 2015, 118, 88–95. https://doi.org/10.1016/j.polymdegradstab.2015.04.013.

Carli, L. N.; Bianchi, O.; Mauler, R. S.; Crespo, J. S. Accelerated Aging of Elastomeric Composites with Vulcanized Ground Scraps. *J. Appl. Polym. Sci.* 2012, 123 (1), 280–285. https://doi.org/10.1002/app.33666.

P, M.; Te, M. Natural Rubber and Reclaimed Rubber Composites—A Systematic Review. *Polym. Sci.* 2016, 2 (1). https://doi.org/10/gft77n.

Zhao, X.; Hu, H.; Zhang, D.; Zhang, Z.; Peng, S.; Sun, Y. Curing Behaviors, Mechanical Properties, Dynamic Mechanical Analysis and Morphologies of Natural Rubber Vulcanizates Containing Reclaimed Rubber. *E-Polym.* 2019, 19 (1), 482–488. https://doi.org/10.1515/epoly-2019-0051.

Masaki, K.; Ohkawara, S.-I.; Hirano, T.; Seno, M.; Sato, T. Devulcanization of Nitrile Butadiene Rubber in Nitrobenzene. *J. Appl. Polym. Sci. - J APPL POLYM SCI* 2004, 91, 3342–3353. https://doi.org/10.1002/app.13546.

Rooy, S.; Basak, G.; Mapi, P.; Bhowmick, A. New Route for Devulcanization of Natural Rubber and the Properties of Devulcanized Rubber. *J. Polym. Environ.* 2012, 19, 382–390. https://doi.org/10.1007/s10924-011-0293-5.

Markl, E.; Lackner, M. Devulcanization Technologies for Recycling of Tire-Derived Rubber: A Review. *Materials* 2020, 13 (5), 1246. https://doi.org/10.3390/ma13051246.

Ozernovs, O.; Jevmenovs, I. Method for Devulcanization of Rubber and Devulcanization Catalyst for Such Purpose. Patent Application PCT/IB2014/066580, October 7, 2015.

Jana, G. K.; Mahaling, R. N.; Das, C. K. A Novel Devulcanization Technology for Vulcanized Natural Rubber. *J. Appl. Polym. Sci.* 2006, 99 (5), 2831–2840. https://doi.org/10.1002/app.22984.

Lapkovskis, V.; Mironovs, V.; Goljandin, D. Suitability of Devulcanized Crumb Rubber for Oil Spills Remediation. *Energy Procedia* 2018, 147, 351–357. https://doi.org/10/gfft7kx.

Khodos, D.; Mirmov, N.; Vassiliev, A.; Vernyi, A. Plant for Reprocessing Waste Tires and for Modifying Rubber Crumb. EP2106893A1, October 7, 2009.
Kakroodi, A. R.; Rodrigue, D. Impact Modification of Polypropylene

Hassan, M. M.; Badway, N. A.; Gamal, A. M.; Elnaggar, M. Y.; Hegazy, E. Studies on Mechanical, Thermal and Morphological Properties of Irradiated Recycled Polyamide and Waste Rubber Powders. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 2010, 268 (9), 1427–1434. https://doi.org/10.1016/j.nimb.2010.01.021.

Kakroodi, A. R.; Rodrigue, D. Impact Modification of Polypropylene-Based Composites Using Surface-Coated Waste Rubber Crumbs. Polym. Compos. 2014, 35 (11), 2280–2289. https://doi.org/10.1002/pc.22893.
590  (60) Nevatia, P.; Banerjee, T.; Dutta, B.; Jha, A.; Naskar, A.; Bhowmick, A. Thermoplastic Elastomers from Reclaimed Rubber and Waste Plastics. *J. Appl. Polym. Sci.* **2002**, *83*, 2035–2042. https://doi.org/10.1002/app.10115.

593  (61) Resmini, E.; Tirelli, D.; Galbusera, M. Thermoplastic Elastomeric Material Comprising a Vulcanized Rubber in a Subdivided Form. WO2005097887A1, October 20, 2005.

595  (62) Bartsevich, V. A. E.; Kazak, I. M.; Konojko, V. V.; Krotova, T. J. V.; Lejzeronok, M. E. E.; Marusova, S. J. N.; Rusetskaja, I. G. E.; Rusetskij, D. V. E.; Rusetskij, V. V.; Tolstik, S. M. Composite Material for Making Large Industrial Rubber Articles. RU2492194C2, September 10, 2013.

598  (63) Alamo-Nole, L. A.; Perales-Perez, O.; Roman-Velazquez, F. R. Sorption Study of Toluene and Xylene in Aqueous Solutions by Recycled Tires Crumb Rubber. *J. Hazard. Mater.* **2011**, *185*(1), 107–111. https://doi.org/10.1016/j.jhazmat.2010.09.003.

600  (64) Lapkovskis, V.; Mironovs, V.; Irtiseva, K.; Goljandin, D. Study of Devulcanised Crumb Rubber-Peat Bio-Based Composite for Environmental Applications. *Key Eng. Mater.* **2019**, *799* KEM, 148–152. https://doi.org/10.4028/www.scientific.net/KEM.799.148.

604  (65) Piszczyk, Ł.; Hejna, A.; Formela, K.; Danowska, M.; Strankowski, M. Effect of Ground Tire Rubber on Structure, Mechanical and Thermal Properties of Flexible Polyurethane Foams. *Iran. Polym. J.* **2015**, *24*, 75–84. https://doi.org/10.1007/s13726-014-0301-4.

607  (66) Bormashenko, E.; Goldshtein, V.; Barayev, R.; Stein, T.; Whyman, G.; Pogreb, R.; Barkay, Z.; Aurbach, D. Robust Method of Manufacturing Rubber Waste-Based Water Repellent Surfaces. *Polym. Adv. Technol.* **2009**, *20*(7), 650–653. https://doi.org/10.1002/pat.1323.