TECHNIUM
Technium Vol. 28, pp.1-16 (2025)
ISSN: 2668-778X
www.techniumscience.com

Direct Tire Rubber Recovery into Malleable Mixture through Sequential Mixing

Moshe Z. Rakhman*

Highlights

Problem: The phase-dispersed tire rubber induces sharkskin, voids, and high viscosity.
Finding: A super-filled GTR blend turns into a malleable mixture due to fragmentation into invisible micrograins, which interlock with the linear polymer, ensuring green strength and flowability.
Implementation: Direct rubber recovery with adequate quality using a scale-up mixer.

Abstract. Pressurized shear and stretch-induced softening were used to recover a coarse-grained GTR into a processable super-filled mixture. The promoted mixing generates the effects of oxidative splitting of crosslinks with subsequent fragmentation of the softened grains. The formed interphase could comprise cross-linked micrograins. The surface texture and related properties were improved when a scale-up mixer was used with higher power per unit volume. The surface texture and related properties were improved when a scale-up mixer was used with higher power per unit volume. Comparative semi-quantitative testing validates that visualizing the surface texture is reliable for monitoring the viscosity, interfacial adhesion, cavitation, and elastic memory during mixing. These markers control the interphase and effective volume of rubber. The process eliminates the need for a reclaim step and prevents the gas release.

Keywords: recycling; rubber; oxidative desulfuration; roughness; adhesion; interphase.

Abbreviations

GTR - ground tire rubber NR - natural rubber SBR - styrene-butadiene rubber	EVA- vinylacetate ethylene copolymer GRmix- grain-coarsed mixture ModMix – modified mixture	AODS - aerobic oxidative desulfuration CB - carbon black EVR - Effective volume rubber

1. Introduction: Terminology Overview

A new insight on rubber recycling. The question that must be asked is: What is the maximum content of the GTR phase that can be used in a mixture? How will GTR be converted directly into a malleable mixture? Increasing the GTR content above 50 wt% hinders mixing. The excess of the limit of loading so-called ‘dense’ suspension means a super-filled GTR mixture with a fraction close to the maximum.

Effect of elastic memory on melt distortion of in mixture. The GTR-based mixture exhibits spring-like behavior during shearing, deforming a melt. The elastic fragments retain some memory of the previous structure in the melt. Therefore, these granules in rubber blends lead to defects/cracks that can be quantified from tear and abrasion measurements [Gibala et al., 1999]. *Cavitation* induces interfacial failure via the elastic recovery of GTR, and weak adhesion [Henzel et al., 2022].

Surface roughness is the most common tool for measuring the morphology of a mixture [Lonardo et al., 2002] and has been proposed as an indirect indicator of filler dispersion [Putman, 2002]. The large GTR granules, whose strength and elasticity exceed those in the molten matrix, induce surface roughness, inter-phase voids, and high viscosity of polymer blends. Breakage of 70-75% of crosslinks in GTR ensures processing and mechanical properties comparable to the neat control mixture [Teixeira 2021].
Desulfuration is the transition of a carbon-sulfur C = S bond to a carbon-oxygen C = O bond [Morrison, Porter, 1984]. Also, the oil assists in the transfer of the catalyst [Hossein et al., 2019], as confirmed by the effect of swollen GTR oxidation in oil as the C=O and the S=O absorption peaks [Wang et al., 2019]. The transfer redox reaction decreases the bond dissociation energy from 420 kJ/mol for C=C to 270 kJ/mol for CS-SC [Luo 2003]. The catalytic gas-phase O_2 oxidation of an sulfide bond is considered as absent of adsorption before the reaction [Kiani, Wachs 2024].
The strategy for functionalizing ground tire rubber (GTR) is based on the oxidation of electron-deficient unsaturated chains and the restoration of double bonds (Datta et al., 2007). Mechanochemical modification has been shown to increase surface oxygen content and interfacial bonding while reducing cross-linking density (Liu et al., 2020). During the mastication of natural rubber (NR), dibenzamido-diphenyl disulfide (DBD) is used as a radical acceptor, typically applied at levels of up to 0.3 parts per hundred rubber (phr) (Fries & Pandit, 1982). However, excessive amounts of DBD can break down the main chains of NR. The peptizer is composed of 40% active ingredient, also zinc soap, and iron acetylacetonate as a booster (US Patents, 1958, 1972). Thermochemical recycling involves the use of up to 30 mmol of DBD as a devulcanization agent at temperatures above 200°C (Van Hoek et al., 2021).
The study aims to create a strong bond between GTR and matrix by triggering fragmentation and chemical coupling reactions. The evolution of the super-filled GTR mixture during sequential mixing was investigated. The discussion will focus on the relation of interphase morphology, voids, and surface roughness with the processing of the mixture.

2. **Materials and Methods**.

2.1. *Constituents*. GTR was used ASTM D5603 Grade 1: Truck tire tread (based NR), 60 wt% granules has size 250-420 μm, 40 wt% size was below 250 μm is produced by Tyrec Recycling Industries. The moisture content of GTR is below 1% after drying. Elastomers are natural rubber TSR-20 and ESBR as Europrene 1500. EVA is a copolymer comprising 19% of VA. *Homogenizers* include oligomer (C9 resins), RAE oil Plaxolene 50 (Total), and flow improver. The semi-reinforcing carbon black is N-772. Antidegradants 6PPD and TMQ were used. A rubber-functionalizing promoter R-394 (Tyrec) is used for the selective oxidation of GTR.
Formulation design. GTR-matrix is a physical mixture of structurally different constituents with fixed ratios of GTR to matrix and viscosity modifiers. The elastomers are distinguished by long, flexible chains possessing unsaturation. The GTR is a thermoset with limited mobility of chains. The approximate hydrocarbon content was estimated at 50 parts by weight for 100 wt% by weight of ground rubber. The ratio GTR to total polymer blend (GTR+NR+EVA) is 68.5 wt%. Carbon black SRF 772 was used at 50 phr. Operational factors as mixing order and fill factor are selected before mixing. Operational parameters are selected before mixing and changed to control the ram position, temperature, residence time, and mixer peak torque. The melt mixing generates bulk morphology depending on operational parameters, as shear rate, viscosity and elasticity ratio of polymers. The internal mixer is an optimal reactor, ensuring the balance between temperature, pressure, and timing.

2.2. *Methodology*. In an approach to macro-composite, quantitative and semi-quantitative methods were used to characterize mixtures evolution. *Comparative methods* of lower- and higher-quality mixture characteristics should help to make a fast evaluation and further decisions to adjust the process [Ishimura et al., 2021]. Whatever the testing mode, any technique implies the simultaneous assessment of pressure, torque, rate, and temperature [Leblanc, 2023]. The GTR mixture is characterized by the extent of surface roughness and porosity. The macro-dispersion and fragmentation of the granules can be categorized as ranging by surface roughness according to the set of samples. The surface-building tack or T-Peel test was used to test the experimental blend, and the second neat NR/SBR mixture was used. Textile reinforcement is used as support. The sample was performed at 150^{o}C for 1 minute under the pressure of 0.21 MPa. *Sharkskin.* Elastic memory and size of GTR induces the sharkskin on a rolled surface. The visualization provides a realistic approach to the analysis of the macroscopic change in GTR-elastomer mixtures. A score of 10 indicates a regular surface with invisible particles. A semi-quantitative visualization of surface relief is proposed as the indirect characteristic of the evolution of fragmentation, dispersion, suppression of cavities, and elastic memory.

3. **Results**

3.1 *Staged mixing.* There is no simple way to incorporate a major dispersed GTR phase with a bulk density of 345 kg/m^3 in the minor matrix phase. In such compositions, the content of a GTR can reach up to 75 wt%, and the polymer matrix plays the role of a binder. The phase transition includes the evolution of the dense suspension of thermoset granules in a malleable mixture. Highly filled mixtures belong to a class of dense suspensions, approaching the limit of volume filling. Single-step mixing leads to overheating; therefore, the sequential steps are used: compactness, drop, cooling, re-milling, drop. A comparative feasibility analysis was done to examine the efficiency of the promoter-modified ModMix mixture relative to the unmodified coarse-grain mixture GRmix and reference NR/SBR blend, as shown in *Table 1*.

Table I. Effect of modification on properties of mixtures

Compactness step	GRmix	ModMix	Reference NR
Form factor of first batch	Medium piece	semi-dense	dense
After re-milling step	Large pieces	dense	dense
Oil migration	spots	no	no

3.2. Compactness. GTR aggregates are wrapped with a minor matrix phase as soon as they are incorporated. Jamming is the transition from a granular rubber flow-like state to a solid packing state when the GTR is compressed. The process depends on the adhesive interaction of the thermoset aggregates. The applied driving force of mixing is weaker than the resistance to crack growth of the elastically linked, deformable structure of GTR.

3.3. *Mixer torque peak and wetting time.* A mixer peak torque reflects the adhesive dispersion rate and degree of melt strength [Abeykoon et al., 2020]. The modified mixture exhibits higher peak mixer torque, shorter wetting time, and dense batch form factor than rough structure of the unmodified coarse-grained mixture, as shown in *Table I, Figs. 1 and 2*.

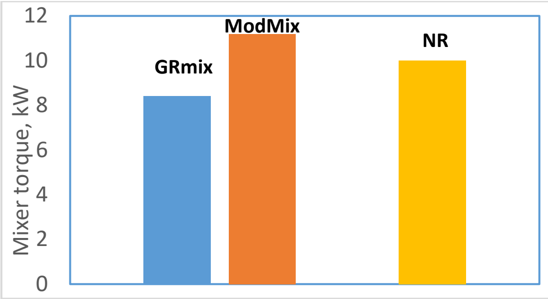

Figure 1. Effect of modification on mixer peak torque

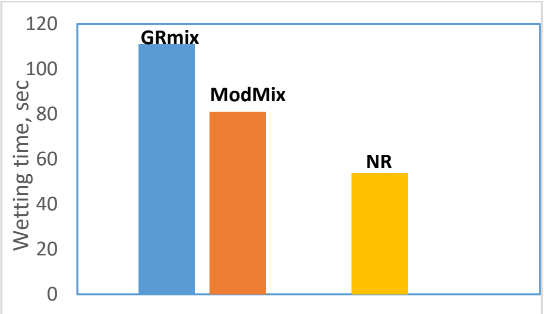

Figure 2. Effect of modification on wetting time

The point at which the jamming of the mixture reaches the packing state depends on the extent of GTR wettability, interfacial adhesion of the constituents [Gotten, 1987], viscosity of the matrix, and pressure. The termination of the ram "dancing" indicates a decrease in the volume due to the compaction of the batch in the chamber. The fusion of resin, EVA, during mixing ensures bonding under pressure. The effect of the deficient interface interaction plays the dominant role on low adhesion and high stiffness of the unmodified coarse-grained GRmix related to the retention of the initial GTR structure and inert surface, the form of the dumped pieces is indicated in *Table I*. The modified ModMix mixture is demonstrated in *Figs. 1 and 2* with a higher mixer torque and shorter wetting time. The adhesive dispersion of GTR is compressed in a jammed batch of ModMix. The pressure-induced jamming implies shear stress due to tightly packed and deformed soft grains so the mixture can continue to flow [Tapia et al., 2024]. The jamming transition reveals the essential effect of achieving dense packing [Zhao et al., 2024] and transition assisting the exchange of crosslinks [Tsuruoka et al., 2020].
Cooling impact. The stress imparted onto the rubber mix generates considerable frictional heat. Subsequent cooling as mill sheeting and storage is a minimum of 180 minutes, ensuring more viscous mixtures in the next step.
3.4. *Effect of temperature on static swelling of thermoset rubber*. The swelling index reflects the RAE oil sorption by the reference NR rubber, which is determined to range between 120–180°C for 1 and 4 hours and is depicted in *Fig. 3*.

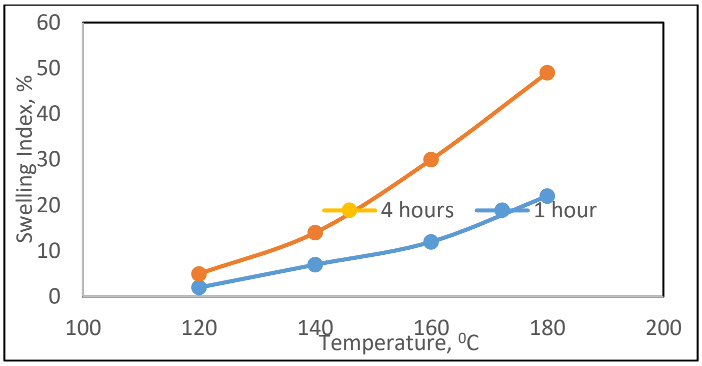

Figure 3. Effect of temperature, and time on swelling of tire rubber in aromatic oil

The swelling index is a function of contact time and temperature. It is increased starting from 140°C, as shown in *Fig. 3,* and achieved a maximum at 180°C. The rubber stiffness in oil was measured by swelling at 180°C for 4 hours by the resistance to penetration of the indenter. The hardness ranged from 48 to 51 Shore A for the swelled rubber, contrary to 63 Shore A for the initial sample; rubber became softer due to absorption. Thus, the high-temperature swelling promotes the softening of the thermoset rubber.

The oil migration from uncured mixtures. The proposed aromatic oil transport mechanism in the unmodified GRmix depends on low solubility and concentration gradient; therefore, the added components migrate to the surface during short-term storage. FT-IR analysis of the chemical composition of the surface spots (*Table I*) showed the presence of oil and fatty acids.

3.5 *Master step*. The densified mixture from the first step is returned to the mixer. The molten matrix is essentially a viscous, inelastic liquid. The disordered and spatially extended GTR granules are a coarse-grained phase of the GRmix; thus, macroscopic distortions of the flow are observed. The mixture exhibits a dispersed morphology, confirmed by SEM testing [Zhao et al., 2019]. GTR dispersion proceeds efficiently when the blend is continuous.

Stretch-induced softening. Stretching causes drawing and thus thinning the GTR granules. Softening of the hard domains (GTR) is due to the stress-stretch behavior of the occluded NR (soft domain). The GTR granules and the matrix phases thus become inevitably continuous. The super-filled rubber mixing in this step is based on the combined effect of inward pressure, shearing, and stretch-induced softening [Mullins, 1969; Denora, Marano, 2022]. Factors governing this mixture morphology are the thermal weakening of intermolecular forces in the swollen coarse-grained GTR and its pulverization under pressurized stretching.

Processing stabilization was achieved by minimizing the oxidative degradation of a blend. The antioxidants stabilize the mixtures during mixing and storage, inhibiting degradation by metal ions [Kawakubo et al., 2005]. Surfactant stabilizes the mixture, reducing free volume as much as possible. The efficient energy transfer strategy due to using a promoter as an energy donor, total thermal history, and work input (energy) is the combined effect of temperature and time [Van Buskirk et al., 1975]. As the mixture considered here is highly viscous, internal viscous heat dissipation is expected due to the internal friction of GTR. It added the mix equivalents faster, improving the melt viscosity and the surface regularity (*Figs. 6 and 9*). The master sheared-stretched mixing presumes interlocking of coarse-grained and swollen GTR fragments through the adhesive strength, which varies with mixing temperature and time.

Technium Vol. 28, pp.1-16 (2025)
ISSN: 2668-778X
www.techniumscience.com

3.6. *Compounding in mixer 160 L*. Optimization of upscaling involves adjusting the process to increase recycling efficiency. The developed two-stage mixing tool is capable, as shown in *Fig. 4 and Table 1* for medium-value parts.

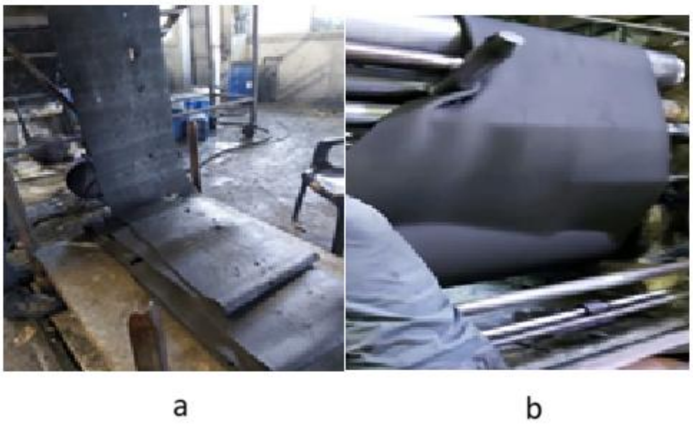

Figure 4. Steps of compounding GTR-functionalized macro-composites
a) Compaction step: 'tears' on rolled web; b) Re-milling process, regular surface (adapted from Rakhman, 2023).

The temperature of the master step rises faster in an industrial mixer; it is higher than that of the same mixture in a lab mixer. The tears on the rolled web after the first step validated the low degree of integrity and weak melt strength, as is seen in *Fig. 4a*. The re-milling generates further fragmentation of GTR, improving dispersion, surface regularity (Fig. 4b), and viscoelastic torque (Figs. 6 and 9) due to the higher melt strength. The properties distinctly improved due to higher power per unit volume. The moderate mixing temperature prevents the gas release.
3.7. Molding of cow comfort mats. The other recycled masterbatch was produced on a kneader.
In compression molding, the GTR recycled mixture was sheeted and cut into blanks. The cow comfort mats, a weight of 11 kg, were molded on press 2000 tons, as depicted in *Fig. 5*.

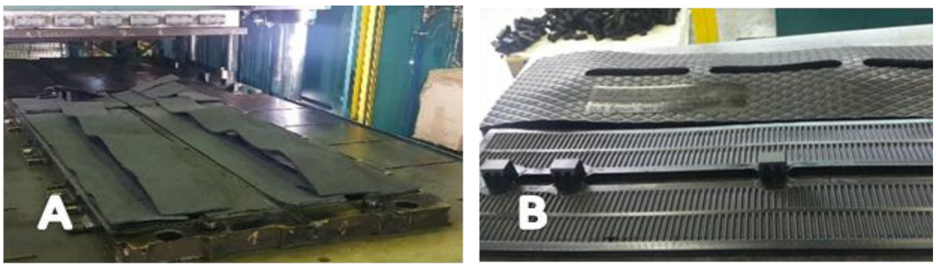

*Figure 5***.** Molding steps of cow comfort mats from GTR recycled mixture
(A) Sheeted blank; (B) Molded cow-comfort-mat.

Flow in the mold was better than regular mixture, it is possible due to the used copolymer and lower viscosity than of the currently used mixture. Therefore, less material was used for molding and more precise dimensions should be obtained. Visual inspection did not find any surface defects.

3.8. *Effect of modification on functional properties*. The gross melt fracture of the mixture, comprising more than 50 phr of GTR, is accompanied by flow instabilities such as surface sharkskin and interphase voids [Kissi et al., 1997]. The evolution of the surface and interface properties strongly depends on the mixing conditions and elastic-plastic state.

Cavitation. The shear-induced mixing, the coarse-grained GTR form, the high moisture content, and the oil volatility cause interfacial macro-voids, which are defined using ASTM D2734. The evolution of macro-voids during the mixing steps is depicted in *Figure 6.*

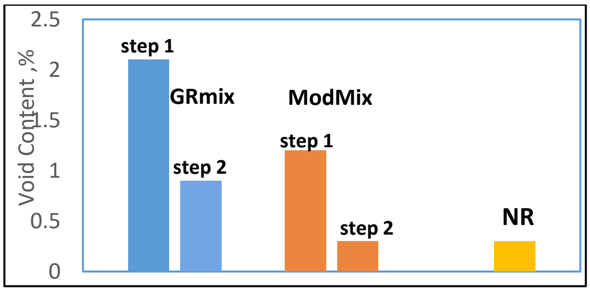

Figure 6. Effect of the modification on cavitation

The void content was characterized stepwise: unmodified GRmix retains porosity even after re-milling, as shown in *Fig. 6.* The modified ModMix induced decohesion of GTR and adhesive dispersion of fragments with subsequent suppression of voids up to a level below 0.4%, and this result is close to NR reference blend after single mixing. It is shown that the nature of the compaction behavior in the unmodified granular mixture has pronounced differences from the compressed densification observed for the modified mixture. The GTR cavitation extent depends on the relationship between the size, softness of fragments, and packing density.

Effect of GTR modification on MDR viscoelastic torque. A moving die rheometer roughly measures the viscoelastic torque; this test simulates force-dependent use and *shear stress* [Ramini, Agnelli, 2020]. Viscoelastic torque controlled the extent of GTR modification, as shown in *Fig. 7.*

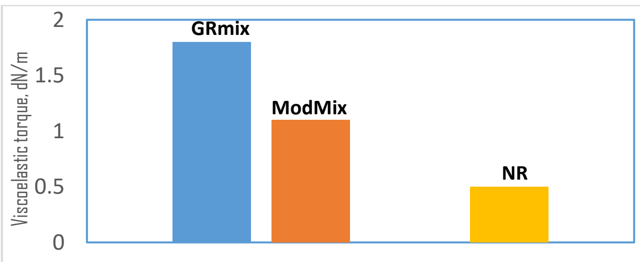

Figure 7. Effect of GTR modification on viscoelastic torque

The adequate surface texture and viscosity, as shown in *Figs. 7 and 9* of the modified ModMix, evidenced a more favorable relationship between integrity and shearing forces than the GRmix.

The behavior of the mixture itself is elastic and ranks below the NR reference blend, even though it involves the pseudoplastic flow.
The interfacial adhesion (building tack). The structural factors governing the interfacial adhesion of the GTR fragments interacting with the matrix depend on constituent wettability. The blends were characterized using a building tack and green strength, as they are crucial indicators of rubber compatibility. The effect of composite type on peel strength is depicted in *Fig. 8*.

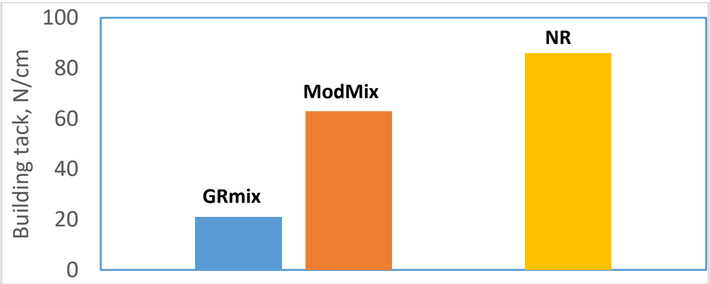

Figure 8. Effect of macro-composite type on peel strength

The unmodified GRmix with relatively higher stiffness and rough surface has indicated inferior tack strength, as shown in *Figure 8*, termed 'interfacial knotty tearing', which is related to the inability of the GTR grains to flow. The GTR modification increases interfacial adhesion and raises building tack; however, it gives in the reference NR blend. The higher temperature mixing and curing promoted higher adhesion and green strength of the mixture, filled with high-reinforced carbon black [Rakhman 2023], due to an assumed enhancement of phase integrity.
Effect of GTR modification on green strength. The green strength indicates how compatible the matrix is with GTR. The *Fig. 9* depicts green strength of composites.

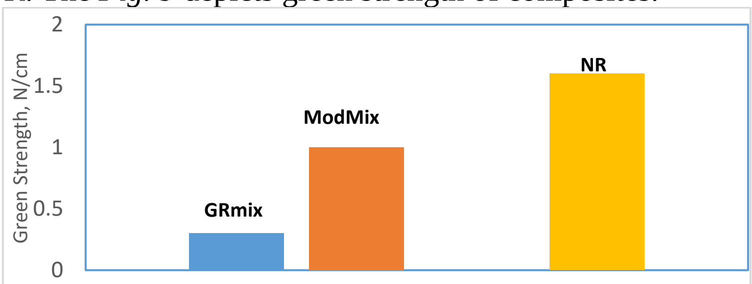

Figure 9. Effect of macro-composite type on green strength

The green strength of the modified ModMix is higher than the granular GRmix and lower than the NR reference as shown in *Fig. 9*. The green strength of the modified ModMix blend is sufficient for rolled sheeting. The building's tack and green strength are critical indicators of the evolution of melt strength, integrity, and pseudoplastic flow.
Melt distortion and surface texture of GTR-polymer melt. Non-destructive inspection of surface relief is proposed without damaging material. The evolution of surface texture is shown in *Fig. 10*.

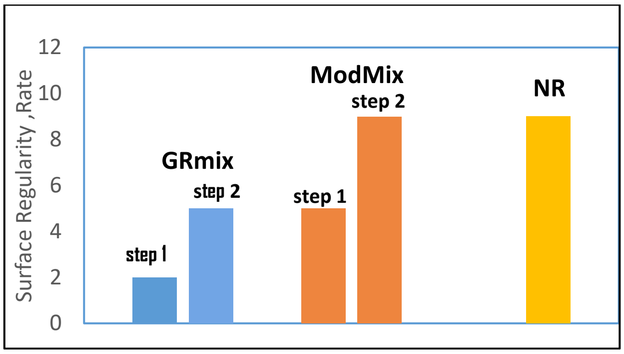

Figure 10. Effect of GTR modification on surface roughness

The evolution of the initial disordered and macro-granular phase-separated mixture into a co-continuous phase is controlled visually, as depicted in *Fig. 10.* The grain elastic memory and its size in unmodified GRmix induce the sharkskin on the surface of the rolled mixture. In the case of a modified ModMix mixture, after crosslink split, the macrodomains interlock with a linear polymer, and profiles do not appear in Dispergrader. Therefore, this tool is ineffective for quantitatively measuring GTR macro-dispersion. The rolled ModMix during the master step and NR reference after a single step develop the regular surface in comparison to the rough unmodified GRmix. The surface roughness of a rolled mixture is suggested as a function of the degree of fragmentation of GTR, elastic memory, and grain size. The melt fracture study can directly estimate the effect of modification *in situ* on the evolution of the modified mixture. Surface texture analysis offers a low-cost and practical test to assess the evolution of GTR in a mixture.

3.8. *Comparative analysis of rheological behavior using combined methods*.

Although it was impossible to directly assess the GTR fragmentation, the viscosity [Clarke, Freakley, 1994] and the surface texture could be used. A semi-quantitative visualization of surface texture is proposed as the most reliable indirect marker of the structure and physical properties of the mixture. Thus, experimental analysis and comparison of results validate the transition of the dispersed GTR phase in a continuous state. In this study, a set of parameters is defined that are anticipated to assess the fragment macro-dispersion. The analysis of viscoelastic torque, interfacial adhesion, and suppression of inter-phase voids are functions of split fragment size, as depicted in *Figs. 6-10*. Complex markers boost the reliability of the test, even if the assessment of the defined interplay is not rather certain.

4. ***The restoration of vulcanization***. Reducing the size of the rubber fragment assumes a substantially lower cross-link density due to oxidative network scission and assists in the restoration of unsaturation [Datta et al., 2007]. Low unsaturation, less than 5%, is sufficient for vulcanization [Coran, 2013]. The semi-efficient curing package was used with an S/Acc. ratio of 0.75. The physical properties are shown in *Table II*.

Table II. Effect of copolymer on static properties of rubber blends

	GRmix	ModMix	NR reference
Delta torque MH - ML, dNm	5.5	7.9	8.6
Hardness Shore A	65	61	60
Tensile, Mpa	8.8	13.3	15.8
Elongation, %	173	336	474
Tear - Type C, N/mm	28±1.31	54±1.03	43±0.81
Abrasion loss, mm^3	361	223	232
Aging 70oC/7 days, change			
Hardness Shore A, rise	6	4	5
Tensile, %	-7	-4	-3
Elongation, %	-19	-15	-20

The rise of the delta torque of the modified ModMix relates to the adequate content of the double bonds able to re-curing as shown in *Table II.* The ModMix is distinguished by the ability to co-cure with matrix elastomer as verified by improved tensile strength, contrary to the strength of the granular GRmix structure. However, the residual cross-link density assists to lower elongation at break than the NR reference. The low tolerable standard deviation in tear strength verified the structural integrity of the ModMix. Summarizing the higher abrasion and tear resistance suggests the retarding crack destruction due to the matrix-spring network. The retention of physical properties exhibits the resistance of the vulcanizates to aging, as the NR reference does (*Table II*).

5. Discussion.

Network topology refers to the spatial features of macroscopic granular chains. Studied macro-composites vary in their heterogeneity, porosity, and viscoelastic properties. Linear structures of matrix exhibit a higher hydrodynamic volume and reduced viscosity [Hartquist et al., 2025].

5.1. Proposed model of structural evolution. The initial coarse-grained GTR mixture creates strong intrinsic heterogeneity in structure. The spatial heterogeneity in networks of unmodified blends is common in such mixtures and minimizes the necessity for breaking all bonds [Tang & Jiang, 2022]. The shear-activated tool provides the conversion of a dispersed GTR phase [Argun & Staff, 2024] into a functionalized core-shell configuration, as illustrated with a model in *Figure 11*.

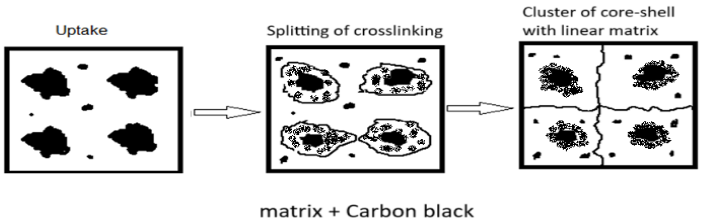

*Figure 11***.** The assumed model of thermoset GTR transition into clusters

The process of pulverizing GTR within a matrix under stress-induced pressure generates the oxidative splitting of the sulfide network, resulting in abundant active sites on the surface of

the GTR. The bond scission defines the malleable properties of the GTR fragments [Jin et al., 2019]. It is suggested that the functionalization of GTR significantly enhances the uniformity of the mixture under optimal operational conditions.
5.3. Synthesis of hybrid clusters. When a certain stress limit is exceeded, the increased melt strength promotes the interlocking of the linear matrix with the thermoset micro-grain [Huang et al., 2021], which enhances the interfacial adhesion [Liu et al., 2020]. Chemical (topological) clusters are presumed to be stiff core covalently linked to “soft” interphase, which immobilizes the matrix. The oxidative and stretched mixing significantly weakens the chains of thermoset grains, and, like a knotting rope, it breaks on at the entrance to the knot under tension. The matrix NR 85% of the elasticity is knot-like structures within its molecular chain formed by cyclization [Mark, Erman, 2007]. The presence of a well-defined core in a linear polymer chain substantially increases the rate of scission of the polymer (≥2.6× faster) because of the deformation of the polymer backbone [Zhang et al., 2024]. The building blocks of the interphase interconnected through matrix linkers are macroscopic clusters that do not break up because of the flow.
5.4. *Expected volume of the interphase*. Crucial factors are the volume of the interphase and core micro-grains. Rubber quality depends on GTR stock, its moisture and content. The size of micro-grains depends on mixing conditions and scale of mixer. The interphase is formed by the diffusion of the surrounding linear matrix chains into the activated GTR fragment chains, which increases the efficiency of the rubber mixture compared with the unmodified composite. The thickness of the interphase is increased due to a thinner thermoset core [Huang et al., 2022], which requires a lower matrix volume fraction to maintain continuous interphase [Jesson & Watts, 2012]. The surface texture, interfacial adhesion, viscosity, voids and tear strength are regarded as indirect markers that validate the evolution of the interphase. The modified mixture has a regular surface and was softer than the bulk stiff phase of the unmodified GRmix (*Figs. 6, 10*, *Table II*) due to the assumed transition of initial granules to interphase. The small cores and thick interphase significantly improve the composite processing.
5.5. Effect of the non-fusible cores size. The controlled regular surface of the modified mixture ModMix confirm the reduction in the thickness size of non-fusible cores (micro-grains) below their invisibility limit of 40 μm [Rose, 1948]. The thickness of an invisible core presumes a critical size below 40 μm for the mixture [Deblieck et al., 2020], thermoplastic vulcanizate [Martin et al., 2009], and this limit also precludes the elastic melt memory [Schmid, 2023]. Essentially, the critical size of 40 μm allows for non-invasive and real-time studies of the phase transition dynamics in the composite, which cannot be achieved through conventional optical microscopy. This capability aids in controlling the evolution of the coarse-to-fine. On the other hand, capillary testing of these mixtures proves impossible [Li et al., 2019] due to the narrow gaps between the residual stiff cross-linked micro-grains and the testing channel's diameter. Thus, the micro-grains do not hinder extrusion, calendering, and compression molding, despite being the primary barrier to capillary flow during injection molding.
The formed interphase could comprise cross-linked micro grains.
5.6. *Effective volume rubber* (EVR) is the key parameter evidencing the transition of the GTR phase into a continuous interphase, directly impacting the level of chain mobility. The interphase is taken into account of the effective volume fraction of rubber. The interphase configuration is the key parameter controlling the integrity of the mixture and EVR, which is responsible for the pseudoplastic flow.
5.7. *Elastic memory of macro-composite*. Initial roughness and increased viscosity are induced by coarse-grained GTR, which retains the elastic memory of the previous state [Kuhn, 1946].

The extent of elasticity (nerve) retention depends on the size of the grains and heat-mixing history. The network splitting improves the mobility of linked domains and, due to this, presumes a decline in the elasticity memory of GTR.

6. ***Modeling the network catalytic scission*** through oxidation by transition metal oxide is the reverse to the cross-linking of elastomer. A conceptual approach considers the catalytic oxidative reaction between a sulfide network of the GTR [Nicolas, 1982] and O_2 gas phase, which was not previously adsorbed. Here, an end-capped metal oxide [US Patent, 2021] splits crosslinks in GTR and scavenges sulfidic residues.
Combining zinc oxide and acid as curing activator vs metal soap. Zinc oxide acts as an activator where only 10 wt% is converted to soap and thiolate during vulcanization. Zinc soap/thiolate are derivatives incapable of replacing zinc oxide and ligands to activate S_8 [Heideman et al., 2006]. Unfilled transparent NR vulcanizate comprising 1 phr of ZnO demonstrates snowflakes of soap arising to unfilled NR vulcanizate inside after a short curing time and storage [Feldstein et al., 1968].
Catalytic oxidation of the sulfide network. The direct recovery GTR proposed selective splitting of the sulfide bonds to restore the rubber tackiness and unsaturation. Aerobic oxidative desulfuration (AODS) in the presence of a true polynuclear transition metal cluster and air oxidant O_2 acts as an energy donor and Lewis acid to split S-S bond [Choi et al., 2023]. The main chains are retained, and residual sulfides are scavenged by metal oxides [Zhang et al., 2013]. The splitting of load-supporting links in the NR blend and more bonds broken at higher strains [Kawakubo et al., 2005].
Factors controlling catalytic oxidation of sulfides. A simplified recycling model implies a sequential cascade of network scission depending on component melting. The reaction rate changes stepwise according to the melting points of resin and polyolefin (>110°C) and promoter (>140°C). Shear mixing speeds up the cleavage of cross-links of GTR [Wang et al., 2020] and induces the radical cascade reaction responsible for oxygenation.
The author stressed that it does not contend against any of the well-known mechanisms of recycling but instead tries to elucidate the need to understand this method.

7. **Conclusions**

The direct recovery of a super-filled and coarse-graining blend into a malleable and re-vulcanizing mixture was achieved through shear-induced compaction and crosslink splitting via promoted stretch-softening mixing. The linear polymer matrix and surrounding fragments diffused and generated interphase consisted of micro-grains. This approach considers how the structural conformation of the GTR and subsequent evolution can influence surface and interface properties of the mixture. The surface texture and related properties were improved using a scale-up mixer with higher power per unit volume. The controlled regular surface of the mixture is achieved with the evolution of coarse-grained GTR in invisible micrograins with a size below 40 μm. Comparative semi-quantitative testing shows that analyzing surface texture is the most reliable method for a complex assessment, even if the specific interactions are not precisely quantified. These parameters are markers controlling the interphase formation and effective volume rubber evolution.

***Corresponding author** Moshe Z.Rakhman: morak777@gmail.com
Tyrec Recycling Industries, Israel
ORCID identification number for the author can be found under https://orcid.org/0000-0001-5388-6771

Acknowledgments*:* The author greatly thanks to Mr. Adam Schwartz from IPRC, Mr. Dekel Lang from Duram, Israel, Mr. Kamal Amer, Mr. Beni Mhadeker, and Ms. Hagit Ihie from IPRC for the preliminary experiments, discussions and suggestions.

References

Abeykoon, C., Pérez, P., Kelly, AL, (2020). The effect of materials rheology on process energy consumption and melt thermal quality in polymer extrusion. *Polymer Eng. Science*, 60(6), 1244-1265, https://doi.org/10.1002/pen.25377

Amash A., Giese U., Shuster RH. (2002). Interphase Grafting of Reclaimed Rubber Powder. *Kautsch Gummi Kunst*., 55, 5, 218-226.

Argun, B. R., Statt, A. (2024). Interplay of Spatial and Topological Defects in Polymer Networks. *ACS Engineering Au*, *4*(3), 351. https://doi.org/10.1021/acsengineeringau.3c00072

Banks, H., Hood, J., Medhin, N., Samuels, Jr., J. (2008). A stick-slip/Rouse hybrid model for viscoelasticity in polymers. *Nonlinear Analysis: Real World Applications*, 9(5), 2128-2149. https://doi.org/10.1016/j.nonrwa.2007.06.015

Chai, A., Andriyana, A., Verron, E., & Johan, M. (2013). Mechanical characteristics of swollen elastomers under cyclic loading. *Materials & Design*, *44*, 566-572. https://doi.org/10.1016/j.matdes.2012.08.027

Chen, L., Malollari, KG., Uliana, A., Sanchez, D., Messersmith, PB., Hartwig, JF. (2021). Selective, Catalytic Oxidations of C–H Bonds in Polyethylene Produce Functional Materials with Enhanced Adhesion. *Chem*, *7*(1), 137-45. https://doi.org/10.1016/j.chempr.2020.11.020

Choi, AES., Roces, SA., Dugos, NP., Wan, MW. (2023). A comprehensive process optimization study of the mixing assisted oxidative desulfurization of diesel oil. *Environ. Techn. Innovation*, *31*, 103144. https://doi.org/10.1016/j.eti.2023.103144

Clarke J; Freakley PK, (1994), Reduction in Viscosity of an SBR Compound Caused by Mastication and Disagglomeration during Mixing, *Rubber Chem. Techn,* 67:4: 700–715. https://doi.org/10.5254/1.3538705

Cotten GR, (1987), Mixing of carbon black with rubber: IV. Effect of carbon black characteristics, *Plast. Rubber Process. Appl*. 7, 173–178. doi:10.1007/s13233-014-2119-5.

Datta RN, Huntink NM, Datta S, Talma A. (2007). Rubber Vulcanizates Degradation and Stabilization, *Rubber Chemistry Technology*, 80(3):436-480. DOI: 10.5254/1.3548174

Deblieck, R., Remerie, K., & Boerakker, M. (2020). A Morphology-Based Model to Describe the Low-Temperature Impact Behaviour of Rubber-Toughened Polypropylene. *Polymers*, *13*(13), 2218. https://doi.org/10.3390/polym13132218

Denora I, Marano C. (2022), Fracture behavior of filled elastomers: how do strain induced softening and its thermally induced recovery affect the fracture toughness? *Constitutive Models Rubber* XII 321–327, https://doi.org/10.1201/ 9781003310266-53.

Dickens, C. F., Montoya, J. H., Kulkarni, A. R., Bajdich, M., & Nørskov, J. K. (2019). An electronic structure descriptor for oxygen reactivity at metal and metal-oxide surfaces. *Surface Science*, 681, 122-129. https://doi.org/10.1016/j.susc.2018.11.019

Dumont D, Houze M, Rambach P, Salez T, Patinet S, Damman P. (2018). Emergent Strain Stiffening in Interlocked Granular Chains, Phys. Rev. Lett. 120, DOI: https://doi.org/10.1103/PhysRevLett.120.088001

Dunstan, DE., & Harvie, DJ. (2020). Shear Induced Interactions Cause Polymer Compression. *Scientific Reports*, *10*(1), 1-7.

Mark JE.; Erman B., (2007). *Rubberlike elasticity: a molecular primer* (2. ed.). Cambridge Univ. Press. ISBN 9780521814256

Heideman, G., Noordermeer, J. W. M., Datta, R. N., & van Baarle, B. (2005), Effect of Zinc Complexes as Activator for Sulfur Vulcanization in Various Rubbers, *Rubber Chemistry Technology*, 78 (2): 245–257. https://doi.org/10.5254/1.3547881

Henzel T., Nijjer J., Chockalingam S., Wahdat H, Crosby AJ, Yan J., Cohen T., (2022), Interfacial cavitation, *PNAS Nexus*, 1, 1– 8, DOI:https://doi.org/10.1093/pnasnexus/pgac217

Huang, J., Zhou, J., & Liu, M. (2022). Interphase in Polymer Nanocomposites. *JACS Au*, *2*(2), 280. https://doi.org/10.1021/jacsau.1c00430

Huang, Y., Müller, M. T., Boldt, R., Zschech, C., Gohs, U., Wießner, S. (2021). A new strategy to improve viscoelasticity, crystallization and mechanical properties of polylactide. *PolymerTesting*, *97*, 107160. https://doi.org/10.1016/j.polymertesting.2021.107160

Jesson DA., Watts JF., (2012), The Interface and Interphase in Polymer Matrix Composites: Effect on Mechanical Properties and Methods for Identification, *Polymer Reviews*, 52(3-4); DOI: 10.1080/15583724.2012.710288

Jiang N, Zhang H., Tang P., Yang Y. (2020). Linear Viscoelasticity of Associative Polymers: Sticky Rouse Model and
the Role of Bridges. *Macromolecules* 53(9). DOI:10.1021/acs.macromol.0c00312.

Jin, Y., Lei, Z., Taynton, P., Huang, S., & Zhang, W. (2019). Malleable and Recyclable Thermosets: The Next Generation of Plastics. *Matter*, *1*(6), 1456-1493. https://doi.org/10.1016/j.matt.2019.09.004

Ishimura, T**.,** Iwai, I., Matsui, K., Mattonai, M., Watanabe, A., Robberson, W., Cook, A., Allen, H. L., Pipkin, W., Teramae, N., Ohtani, H., &

Gibala D, Hamed GR (1994) Cure and mechanical behavior of rubber compounds containing ground vulcanizates. Part I: cure behavior. *Rubber Chemistry Technology*, 67(4): 636–648. https://doi.org/10.5254/1.3538699

Feldstein MC, Rakhman MZ, (1968). The action of zinc oxide as a vulcanisation activator, *Sov. Rubber Technology (En)*,1968, 27, 2,.17-20, *Rubber J.* 1969, 151;

Fries H, Pandit RR. (1982) Mastication of rubber, *Rubber Chem Technol*, 55: 309–327, DOI 10.5254/1.3535880

Kawakubo M., Tsunoda K., Yajima H., Ahagon A., (2005). Reactions of Radicals in Filled Rubber Compounds: II. Generation and Subsequent Reactions of Radicals Upon Deformation, *Rubber Chemistry Technology* 78(4):659-673. DOI: 10.5254/1.3547904

Kissi NE, Piau J, Toussaint F,(1997). Sharkskin and cracking of polymer melt extrudates, *J.Non-Newt.Fluid Mech*., 68,271-90.

Kumar SK.; Jimenez AM. (2020), Polymer adsorption–reversible or irreversible?. *Soft Matter*, 16, 5346–5347. 10.1039/D0SM90097D

Kuhn, W. (1946) Dependence of the Average Transversal on the Longitudinal Dimensions of Statistical Coils Formed by Chain Molecules. *J. Polym. Sci. 1*, 380–388.

Lang M, Scholz R. (2024). On the Swelling of Polymer Network Strands, *Macromolecular Rapid Communications*, 45(10):e2400025 DOI:10.1002/marc.202400025

Leblanc, JL. (2002). Rubber–filler interactions and rheological properties in filled compounds. *Progress in Polymer Science*, *27*(4), 627-687. https://doi.org/10.1016/S0079-6700(01)00040-5

Li, S., Ding, M., & Shi, T. (2019). Spatial distribution of entanglements and dynamics in polymer films confined by smooth walls. *Polymer*, *172*, 365-371. https://doi.org/10.1016/j.polymer.2019.04.010]

Liu, H., Wang, X., Jia, D. (2020). Recycling of waste rubber powder by mechano-chemical modification. *J.Cleaner Production*, *245*, 118716. https://doi.org/10.1016/j.jclepro.2019.118716

Liu, S., Li, T., Shi, F., Ma, H., Wang, B., Dai, X., Cui, X. (2023). Constructing multiple active sites in iron oxide catalysts for improving carbonylation reactions. *Nature Communications*, *14*(1), 1-13. https://doi.org/10.1038/s41467-023-40640-z

Lonardo, P.M., Lucca, D.A. and de Chiffre, L, (2002), Emerging trends in surface metrology, *CIRP Annals – Manufacturing Technology*, 51 (2), 701–723. DOI: 10.1016/S0007-8506(07)61708-9

Luo YR (2003). Handbook of Bond Dissociation Energies in Organic Compounds. *CRC Press; Boca Raton*,FL, USA: Table 11.3.1.

Manas-Zloczower I, Nir A, Tadmor Z., (1982), Dispersive mixing in internal mixers—a theoretical model based on agglomerate rupture. *Rubber Chemistry Technology*, 55, 1250-1285; https://doi.org/10.5254/1.3535929

Mark JE., Erman B. (2007). Rubberlike elasticity: A molecular primer *(2. ed.). Cambridge Univ. Press.* ISBN 9780521814256.

Morrison NJ; Porter M, (1984). Temperature effects on the stability of intermediates and crosslinks in sulfur vulcanization, *Rubber Chemistry Technology* (57 (1): 63–85. https://doi.org/10.5254/1.3536002.

Mullins L, Softening of rubber by deformation, (1969). Rubber Chem. Technol. 42:339–362, https://doi.org/10.5254/1.3539210.

Nicholas PP, (1982). The Scission of Polysulfide Cross-Links in Rubber Particles through Phase-Transfer Catalysis, *Rubber Chemistry Technology*, 55:5: 1499–1515. https://doi.org/10.5254/1.3535945

Noorvand, H.; Kaloush, K.; Medina, J.; Underwood, S., (2021). Rejuvenation Mechanism of Asphalt Mixtures Modified with Crumb Rubber, *Civil Eng*, 2, 370–384. https://doi.org/10.3390/

Pierard, O., LLorca, J., Segurado, J., & Doghri, I. (2007). Micromechanics of particle-reinforced elasto-viscoplastic composites: Finite element simulations versus affine homogenization. *Int J. Plasticity*, *23*(6), 1041-1060. https://doi.org/10.1016/j.ijplas.2006.09.003

Putman J., Putman M., (2002). An improved method for measuring filler dispersion of uncured rubber, *Rub. World*, 225:6:30-36

Rakhman MZ. Feldstein MC. (1968). The action of metal oxides on the sulfur vulcanization of rubbers, *Sov. Rubber Technology (En)*, 27, 11, 15-7, *Rubb.J.*1970, 152, 9, 12

Rakhman MZ, Improvement of Workability and Integrity for Ambient Ground Rubber as Elastomer Alternative: Direct Incorporation and Functionalization, *J. Appl. Sciences Technium*, **2021**, 3:7, 32-45, ISSN: 2668-778

Rakhman MZ, (2023), Blends Comprised Waste Tires and Reinforcing Carbon Black: Effect of Mixing Sequence on Processing and Physical Properties, *J. Solid Waste Technology Management*, 49:2, 91-102, doi.org/10.5276/jswtm/iswmaw/492/2023.91

Rakhman MZ, (2024). Direct Recycling of rubber: Effect of Staged Mixing on Bulk and Surface Properties of Thermoplastic Macro-Composites, *Technium* 24:.26-38 DOI: 10.47577/technium.v24i.11693

Ramini M; Agnelli S, (2020), *Shear heating parameter of rubber compounds* useful for process control in *injection molding machine, Rubber Chemistry Technology*, 93:4: 729–737; https://doi.org/10.5254/rct.20.79954

Scholz H., Poetschke P., Michael H., Mennig G, (2002), Morphology and Mechanical Properties of Elastomeric Alloys from Rubber Crumb and Thermoplastics, *Kautschuk Gummi Kunststoffe*, 55 (11), 585

Schmid F., (2023). Understanding and Modeling Polymers: The Challenge of Multiple Scales, *ACS Polymers Au*, *3* (1), 28-58, DOI: 10.1021/acspolymersau.2c00049

Tang, Z., & Jiang, L. (2022). Visualization of single crosslinks and heterogeneity in polymer networks. *Giant*, *12*, 100131 https://doi.org/10.1016/j.giant.2022.100131

Tapia F, Hong CW, Pascale Aussillous P, Élisabeth Guazzelli E. (2024). Rheology of Suspensions of Non-Brownian Soft Spheres across the Jamming and Viscous-to-Inertial Transitions. *Phys. Rev. Lett*, 133 (8), pp.088201. doi.org/10.1103/PhysRevLett.133.088201

Teixeira, FA. (2021). EP Patent, 19849001, Rubber devulcanization method

Tsuruoka, A., Takahashi, A., Aoki, D., & Otsuka, H. (2020). Fusion of Different Crosslinked Polymers Based on Dynamic Disulfide Exchange, *Angew. Chem. Int. Ed.*, 59, 11, 4294-4298. https://doi.org/10.1002/anie.201913430

US Pat. 2,860,116 (1958). Pikl J,, Process for peptizing diene hydrocarbon elastomers and products thereof

US Pat. No *4129538 (1972).* Kaplan E, Pinto F., Peptizing agent for natural rubber and SBR,

US Patent 9902831 (2018), Re-Processed Rubber and a Method for Producing Same

US Patent 11,034,822, (2021**),** Method for producing recycled thermoplastic rubber masterbatch with improved green strength

Van Buskirk P, Turetzky S, Gunberg P., (1975), Practical Parameters for Mixing, *Rubber Chemistry Technology*, 48:4:577–591 doi.org/10.5254/1.3539661

Van Hoek, H., Noordermeer, J., Heideman, G., Blume, A., Dierkes, W. (2020). Best Practice for De-Vulcanization of Waste Passenger Car Tire Rubber Granulate Using DBD as De-Vulcanization Agent in a Twin-Screw Extruder, Polymers, *13*(7), 1139. doi.org/10.3390/polym13071139

Wang, H., Apostolidis, P., Zhu, J., Liu, X., Skarpas, A., Erkens, S. (2020). The role of thermodynamics and kinetics in rubber–bitumen systems: a theoretical overview. *Int. J. Pav.Eng. 22*(14), 1785–1800. https://doi.org/10.1080/10298436.2020.1724289

Wang X, Fan Z, Li Li, Wang H, Huang M, (2019). Durability Evaluation Study for Crumb, Rubber–Asphalt Pavement: *Appl. Sci*. 9, 3434; doi:10.3390/app91634344

Zhang, X., Dou, G., Wang, Z., Li, L., Wang, Y., Wang, H., Hao, Z. (2013). Selective catalytic oxidation of H_2S over iron oxide supported on alumina-intercalated clay catalysts, *J. Hazard.Mat*, 260, 104-111, https://doi.org/10.1016/j.jhazmat.2013.05.008

Zhao, Y., Hu, H., Huang, Y., Liu, H., Yan, C., Xu, C., Zhang, R., Wang, Y., & Xu, Q. (2024). Elasticity-controlled jamming criticality in soft composite solids. *Nature Communications*, *15*(1), 1-8. https://doi.org/10.1038/s41467-024-45964-y