Technium Vol. 24, pp.26-38 (2024)
ISSN: 2668-778X
www.techniumscience.com

Direct Recycling of Rubber: Effect of Staged Mixing on Bulk and Surface Properties of Thermoplastic Macro-Composites

Moshe Z. Rakhman*
ORCID https://orcid.org/0000-0001-5388-6771

*Tyrec Recycling Industries
Correspondence: morak777@gmail.com

Highlights

What is the problem? The non-fusible and large-sized GTR, whose strength and elasticity exceed those of the molten matrix, induces surface roughness, interphase voids, and high viscosity of polymer blends.
What are the findings? The relationship was established between the viscosity, surface roughness, voids, and inter-phase adhesion, as well as the link between the above indicators and the fragmentation extent.
What are the implications of the main findings? Direct recycling was achieved using 67 wt% of GTR in the blend.

Abstract

The novel concept was used to upcycle GTR via cleavage of a cross-linked network with subsequent conversion into macro-composite. The pre-blend, which comprised loose 74 wt% GTR, was compacted with the matrix fusing under ram pressure. The final master step ensured the better bulk properties (interfacial adhesion, removal of macro-voids, viscosity) and the regular surface of the D2 blend, comprised of 20 phr SEBS. The extent of fragmentation could not be directly appraised, where traditional testing had failed to identify them. The regular surface quality and reduced viscosity of blend D2 evidence the decrease in size particles, accompanied by improving bulk properties (interfacial adhesion, removal of macro voids). The interactions were quantified using an analysis of peel strength; elastic recovery, tear, and tensile strength. Direct reprocessing via two-staged mixing governed the conversion of GTR to thermoplastic macro-composite., excluding the reclaim step.

Keywords: recycling; rubber; thermoplastic; fragmentation; surface roughness; macro-voids; viscosity; interphase;

1. Introduction

Recycled thermoplastic rubber (TPR). The ground tire rubber (GTR) feedstock varies depending on the composition, grinding type and shape, surface area, cross-linking extent, and aging times. Poor interfacial adhesion in thermoplastic blends filled with low-energy GTR (usually up to 50 wt%) is related to the inhomogeneity of dispersed GTR, and the lack of compatibility between GTR and thermoplastics. The highly GTR-filled blends in a ratio of 70/30 showed drastically decreased tensile strength. Notably, no flow was observed for 80/20 blends [Prut, et al., 2017].
Surface and bulk quality. Surface appearance, among other factors, even if this property may not be functional, defines the perceived quality. GTR of more than 3 wt% impairs the surface fracture morphology in terms of roughness, enclosed cavities, and flaws [L'Ábbee et al., 2010]. These fractures arise from the shear stretching of elastic GTR during mixing [Kissi et al., 1997; Lefevre et al., 2014]. The morphology of the surface fracture is correlated with crack growth rates in dependence on crack velocity and GTR content [Mashita et al., 2023]. Melt fracture is characterized by two distinct

phenomena: a rough surface and high viscosity. Cavitation is another deformation-induced damage process that forms voids at interphase and causes interfacial failure [Henzel et al., 2022].

*Melt Viscoelasticity Effect***.** Dynamic vulcanization of thermoplastic vulcanizates (TPV) increases the EPDM viscosity, which promotes phase inversion [Coran, Patel, 1990; Van Duin, 2006]. The molten ethylene-1-octene copolymer also demonstrates phase inversion during dynamic cross-linking via the increase in melt elasticity induced by dual cross-linking by the peroxide and silane as coagent with hydrolysis of methylol groups and condensation [US Patent, 2009]. Carbon black [Taguet et al., 2014; LeHel et al., 2020], SEBS [Sengupta et al., 2004], and blend GTR/EVA [Saeb et al., 2022] may also increase the melt strength of the composite. The dispersed solid crosslinked phase must be above 64 wt% to provide a reasonable compression set [LeHel et al., 2020]. The large rubber domains above the critical size of 40 µm are not dispersed efficiently. A coarse morphology acts as strong imperfections, ruining the macroscopic properties of the blends [Martin et al., 2009].

TPR matrix. Processing of GTR-filled PP-based matrix requires temperatures well above 200ºC. Therefore, polyolefins EVA, LDPE, and LLDPE are preferable matrices to avoid GTR degradation during injection molding below 200ºC [Koning et al, 1998]. Since EVA shows a better affinity to GTR, it was selected as a main matrix component.

GTR functionalization strategy is based on the oxidation of electron-deficient unsaturated backbone [Baldwin et al, 2008] and the erosion that assisted the restoration of double bonds [Datta et al, 2007]. This process overcomes poor compatibility with thermoplastics and improves the homogeneity of the system [Fazli, Rodrigue, 2023]. Improvement of the mechanical properties is assumed by the interaction between GTR and the thermoplastic matrix [Sonnier et al., 2008]. A low interfacial adhesion of GTR to the substrate is confirmed by the easy removal of rubber from the EVA matrix [Mujal-Rosas et al., 2011]. The mixing temperature depends on the concentration of functionalized groups in SEBS [Rodriguez-Guadarrama, 2020] and polyolefins [Azimi, 2021]. Unfortunately, most research efforts end as soon as successful degradation is shown, and no attention is given to functional parameters with this concept. A disadvantage is that an absence of homogeneous modification of the GTR is not ensured, and, as a result, stable reproducibility of properties is not guaranteed. Besides the processing parameters, the macrostructure of the composite is dependent on the composition ratio, viscoelasticity of the matrix, dispersion, and distribution. Previous studies reported that the surface roughness of the GTR compound correlated to the extent of dispersion of GTR, and unsaturation of rubber [Rakhman, 2023]. This study focused on direct reprocessing of GTR in the thermoplastic composite. The first approach is the functionalization of GTR in situ, which is assumed to offer the desired level of interactions between GTR and matrix. A second conceptual approach involved a comparative study of the evolution of bulk, inter-phase, and surface properties of the thermoplastic composite during staged mixing and GTR .fragmentation

Abbreviations

GTR - ground tire rubber; SEBS styrene-ethylene-co-butylene-styrene copolymer	EVA – ethylene-vinyl acetate copolymer TPR **-** Thermoplastic macro-composite

Descriptions

The interface is the boundary between two layers of different chemistry [Jesson, Watts, 2012] *The interphase* is the activated interface of the ground rubber and adherend [Jesson, Watts, 2012]

2.Experimental

2.1. Compounding ingredients. GTR grade 40B is an ambient-milled truck tread, size below 40 mesh or 425 µm (Tyrec, Israel). SEBS is a Calprene H6174 (Dynasol). EVA is a copolymer comprising 19% of VA - Greenflex FF 55 (Versalis).

Rubber-functionalizing promoter R-394 produced by Tyrec Recycling Industries. Aerobic oxidative desulfurization removed the sulfides and thiophens at the mild conditions [US Patent, 2021; Yuan, et al., 2022].

Antidegradants 6PPD (Vulkanox R 4020), and TMQ (Vulkanox HS/LB) are both LANXESS. Compositions also contain oligomers C5/C9, C9; flow improver; and carbon black SRF 772.

Formulation design. The matrix is a minor continuous phase, and GTR is a major discrete phase. The distinguishing feature of the macro-composite is that the controlled ratio of GTR to SEBS and EVA with the oxygen-containing pendant groups could affect the processing of the blend. Preliminary trials showed that at an excessive GTR-matrix ratio above fourfold, wetting and uptake in the mixer chamber were hindered, and the batch was powdered. The approximate hydrocarbon content was estimated at 100 parts by weight for 200 wt% by weight of ground rubber. The blend, furthermore, comprised an elastomer SEBS (content of 20, 30, and 40 wt% on 200 wt% of GTR) and a copolymer EVA (60 wt%). Carbon black SRF 772 was used at 12 wt% loading.

Basic operational parameters. The internal mixer exhibits an optimal reactor, ensuring the balance between temperature, ram pressure, and timing during staged mixing. The coarseness of the elastic and infusible GTR hindered its occlusion by a binary blend. Operational parameters can readily be observed and may be modified during mixing to somewhat control how the process is going on; there are ram position, temperature and time (of sequences of the procedure), and mixer peak torque.

Mixing design. The model compositions were prepared in a Banbury mixer [Rakhman, 2023]. The process is limited by “time to mix” or a “temperature limit” as fail-safe criteria. The molding cycle for viscosity, peel strength, and mechanical properties included 3 mins of pressure-less preheating, 30 secs of venting; holding pressure for 2 mins at 160°C, and cooling under 6 bars of pressure.

2.2. Methodology. The quality of recycled GTR blends is usually below that of raw elastomer. Comparative methods of lower- and higher-quality composite characteristics should help to make a fast evaluation and further decisions to improve its proper utilization as raw material [Ishimura et al., 2021; Ruiz-Hernandez et al., 2018], Comparison could predict the evaluation of mixing steps by exploiting the extent of macroscopic roughness and viscoelasticity.

The analysis of GTR fragmentation. Industrial quality control of filler dispersion uses methods, that are usually not measured directly. The macro-dispersion can be categorized along a spectrum and quantified by reproducible ranging according to the size of the particles. The preferred approach to indirect estimation of GTR fragmentation should be simple and quick. The extent of fragmentation could be directly appraised, yet the impact of both bulk and surface properties may not be evaluated completely, where traditional testing had failed to identify them. The evolution of macro-dispersion, fragment size, and bulk properties could be characterized by viscosity, inter-phase adhesion, surface roughness, and cavitation.

Surface macro-roughness is characterized semi-quantitatively by direct observation. To ensure the relevant roughness estimation, provision should be made for a suitable roughness set of variables—images formed by a 5X light glass magnifier. A score of 10 indicates a regular surface with invisible particles to the naked eye in size below 40 µm [Rose, 1948], while lower scoring values indicate different degrees of roughness and fragmentation indirectly.

Viscoelastic torque. The direct measurement of shear viscoelasticity of GTR composites was hampered because of a low gap between the large GTR size and the small diameter of the rheometer channel. The minimum viscoelastic torque ML was comparatively measured A moving die rheometer roughly, where its variations could assess the changes in flow [MonTech MDR; Ramini, Agnelli, 2020]. The MDR test at 150°C used a pre-molded disc. Wetting time characterizes the achievement of GTR uptake at the maximum mixer peak torque. The void content was determined using the ASTM D2734 and the density was by the dry/wet weight method ASTM D792 [Montagna et al., 2012]. The composite peel test was used to estimate the interphase adhesion between the GTR pre-blends and the polyolefin matrix. Peel strength is related to surface roughness, therefore, the pre-blends were extra re-milled in Banbury to ensure better uniformity. Matrix adherend – 1.5 mm LLDPE/EVA (1:1) sheet was etched in chromic acid for 2 hrs [Wang et al, 2009]. The specimens of sheets with 1.5 mm thickness were cut with a razor blade using the frame. The matrix adherend and pre-blend were reinforced by fabric and separated with 25 mm wide mylar. T-peel testing of the composite ribbon was performed according to the modified ASTM D6892/D903 at a rate of 25 mm/min for the 127 mm length of the bond line.

3. Results and Discussion.

3.1. Staged mixing. There is no simple way to incorporate large quantities of loose and elastic GTR into a matrix and uniformly disperse it. Composites were prepared using two-stage mixing to ensure that any changes in the GTR-SEBS ratio could be attributed to morphology and controlled fragmentation of GTR. The one-step mixing is accompanied by uncontrolled heating and degradation of the GTR. Staged melt-mixing can overcome this problem. Firstly, the GTR should be compacted and consolidated in a batch without overheating. Next, the pre-blend is returned to the mixer, and the remaining components are added. The weight and volume ratios of the polymer phases and GTR in staged compositions are shown in *Table I*.

Table I **-** Effect of polymer ratio on compositions of two-step mixing.

Pre-blending step	**A1**	**B1**	**C1**	**D1**
Ratio GTR-EVA-SEBS, wt%	200:60:0	200:30:20	200:30:30	200:30:40
Thermoset rubber fraction, wt%	77	80	77	74
Form factor of batch-off	lumps	pieces	large pieces	semi-dense
Master step – EVA, wax, fatty acid added to pre-blend phase				
TPR master step	**A2**	**B2**	**C2**	**D2**
Ratio GTR-polyolefin-SEBS, wt%	200:60:0	200:60:20	200:60:30	200:60:40
Ratio GTR-polyolefin-SEBS, vol%	175:65:0	175:65:22	175:65:33	175:65:44
Thermoset rubber weight fraction, wt%	77	71.1	69	67
Effective rubber volume fraction, vol%	76	66.7	64	61.6
Form factor of batch-off	lumps	large pieces	batch	Dense batch

3.2. Pre-blending. Compaction was intended to consolidate a 74 wt% GTR mix into a batch (*Table I*). At the beginning of mixing, GTR is essentially elastic aggregates with a low bulk density of 345 kg/m^3. Pre-blends comprised half of the thermoplastic and completely the neat elastomer, carbon black, resin, fatty acid, and rubber-functionalizing promoter. The polymers and half of the GTR were added first, and after 30 secs, the remaining GTR was added. The compaction of GTR was estimated by a series of semi-quantitative tests, including the mixer peak torque, wetting time, and qualitative test 'form factor' of the batch. The extent of interaction of GTR with the matrix was evaluated for mixer peak torque, wetting time and voids content. A mixer peak torque characterizes the extent of melt strength [Abeykoon et al., 2020] and the quality of the interface boundary of molten polymer blends [Gotten, 1987; Klie et al., 2015]. The form factor of discharged batch-offs as slabs, pieces, or lumps is implied as a function of the melt strength during mixing. During mixing, the mixer's torque was reduced after the addition of GTR because of partial batch breakdown in the case of binary pre-blend. The effect of the SEBS on the evolution of mixer peak torque and wetting time in the pre-blending stage is depicted in *Figs. 1 and 2.*

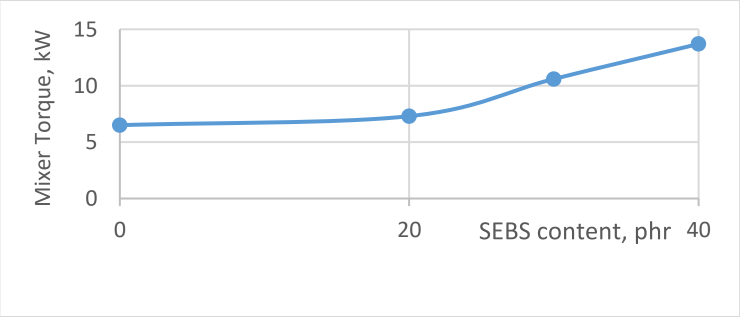

Figure 1. Effect of SEBS content on mixer peak torque of pre-blends

The uptake of GTR by the molten phase is related to the mixer torque passing through a maximum of 60–140 secs due to the polymer/resin fusing. The binary pre-blends A1/A2 (GTR/EVA), were poorly dispersed, and extremely crumbly, since the low values of mixer torque were related to poor dispersion of GTR, which was incapable of producing sufficient mixer torque, and shear force, as shown in *Fig. 1*. By contrast to the coarse textured binary blends, the ternary blends SEBS promoted the uptake of the GTR with decreasing wetting time (*Fig. 2*) and increasing the overall compaction rate.

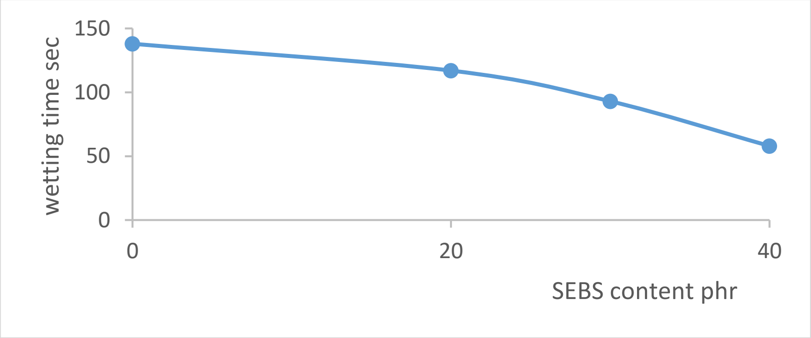

Figure 2. Effect of SEBS content on wetting time of pre-blends

The ram pressure and short-term fusion of the matrix/resin were sufficient to generate GTR wettability. The ternary D1 blend was consolidated, with a denser form factor (*Table I*), a higher mixing peak torque of 64% versus the binary A1 blend. It is related to rising melt strength (melt elasticity) [Munstedt, 2018], which promotes melt elasticity at high shear stresses.

Cooling impact. The blend processing is limited by its low heat transfer capability. Hence, intermediate cooling is needed to improve dispersion. Firstly, an extra GTR step improves dispersion in the matrix. Secondly, in each pass, the batch is remixed at an elevated temperature for a short time, which ensures the thermal stabilization of GTR due to the prevention of overheating of a blend. Prepared pre-blends were cooled for at least 180 mins to increase the melt viscosity, which is well known to be critically dependent on temperature.

3.3. The effect of SEBS on master mixing step. The master blend consisted of a pre-blend and added EVA as a diluent, which was charged into the mixer first. Then a flow improver and surface aids (graphite or wax) helped keep the blend from sticking and minimize the mixing time. The thermal mixing weakens the cross-linked network, assisting selective bond-breaking. A master blend was processed into a mixture that is as uniform as possible. Mixing a binary masterbatch was difficult due to its low melt strength. Added surface aids prevent the blend from sticking and minimize the mixing time.

Processing stabilization implied that GTR fragmentation was achieved with retention of the backbone chains. The temperature stabilization was achieved via fill factor, ram pressure, and shear-force mixing [Manas-Zloczower et al., 1984]. Oxidative shear mixing generated free radicals on GTR chains which could be recombined, if not stabilized. Therefore, at the end of the mixing cycle, adding antioxidants inhibited free radicals to prevent further degradation of the GTR chains and improve their thermal stability.

Heat work history. Work input (energy) is the combined effect of power, temperature, and time during mixing [Van Buskirk et al., 1975]. As can be seen, a limited work heat history was applied during the first step, so the viscosity and surface roughness were poor. The mixing work equivalents operated more rationally at higher temperatures during a master step, the process is mostly governed by SEBS loading, which builds up a discharging temperature of more than 15°C to 25°C comparably to binary blends. It is suggested that cleavage of the cross-links in GTR can be achieved using a range of external stimuli (promoter, shear, temperature) for propagating the fractures and fragmentation of GTR aggregates.

Unsuitable mixing conditions could cause melt fractures due to an inadequate matrix-GTR interaction. In this case, the real duration of mixing could include the added step of re-milling. The master step demonstrated the fragmentation of large aggregates and the suppression of macro-voids. Although it was impossible to assess the extent of fragmentation, the effect on the bulk and surface properties could be estimated.

3.4. Macro-voids. It is suggested that entrapped air, moisture, and volatiles formed in a mixing process play a significant role in void nucleation as a function of the shear mixing-related time. The stretching and shear mixing processes generate macro-voids between unmodified phases that cannot stick together. Macro-voids in the grain-boundary structure result in inter-phase irregularities, stemming from the excessive elastic recovery of GTR [Henzel et al., 2022]. The effect of the SEBS content on the comparative macro-void content evolution is depicted in *Figure 3*.

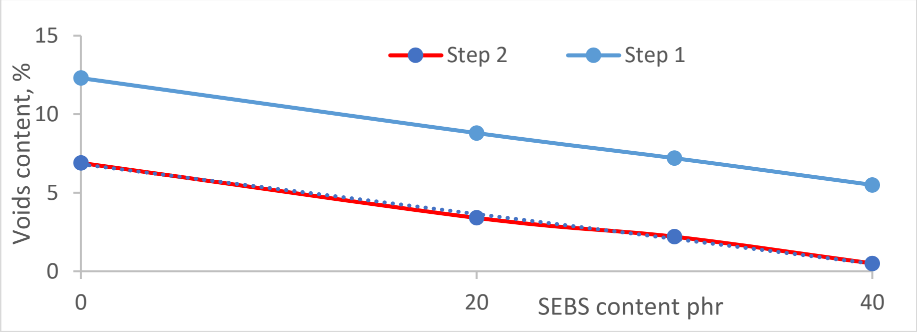

Figure 3. Effect of SEBS on macro-void content in composites

The binary blends A1 and A2 comprised a higher void amount (*Fig. 3*). Denser form factor related to reduced void content of ternary SEBS pre-blend (*Table I and Fig. 3*). The power curve of mixing was flattened as evidence of suppression macro-voids and reduced batch volume. The SEBS-promoted consolidation of composite D2 is notably governed by the reduction of the viscosity of the composite and the subsequent dissolution of voids up to a level 0.5%, as assumed due to the disintegration of GTR. The master step demonstrated the fragmentation of large aggregates and the suppression of macro-voids.

3.5. Surface roughness is the most common tool for measuring the morphology of materials [Lonardo et al., 2002] and has been proposed as an indirect indicator of filler dispersion [Putman, 2002]. The non-fusible and large-sized GTR particles induce surface roughness, inter-phase voids, and high viscosity of polymer blends. The observed evolution of surface texture is a function of GTR disruption. The relevant control of surface texture requires a suitable set of roughness variables. The controlled regular surface could be ensured via the size reduction of non-fusible cores up to their invisibility below 40 µm. On the one hand, the comparative surface roughness method ensured the semi-quantitative estimation of macro-void content (*Fig. 3*), during staged mixing, which was undetected by typical testing. On the other hand, the surface roughness indicated the evolution of the disordered morphology and the gross irregularities of the GTR macro-composite. The measure of surface roughness can be used as an indirect indicator to evaluate bulk properties as a function of fragmentation extent. Observations of surface roughness should become dominant in heterogeneous blends to predict the extent of GTR fragmentation.

Effect of SEBS on web surface texture and viscosity. Although it was not possible to directly assess the fragmentation, the effect of the cleavage of the cross-linked network on the change of viscosity [Clarke, Freakley, 1994] and surface roughness could be used. The surface roughness shows evidence of the changes in the final morphology of disrupted GTR in an elastomer matrix. The effect of the SEBS content on the viscoelastic torque and surface roughness is depicted in *Figs. 4 and 5*.

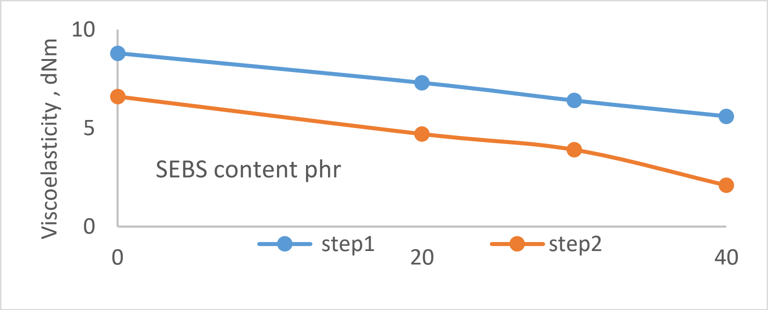

Figure 4. Effect of SEBS content on viscoelastic torque of two steps composites

Figures 4 and 5 illustrate the strong macro-roughness and high viscoelastic torque of binary A1/A2 blends, caused by melt failures. The effect of mixer torque on rheological properties appears to be the opposite of increasing mixing energy, as shown in *Fig. 1*.

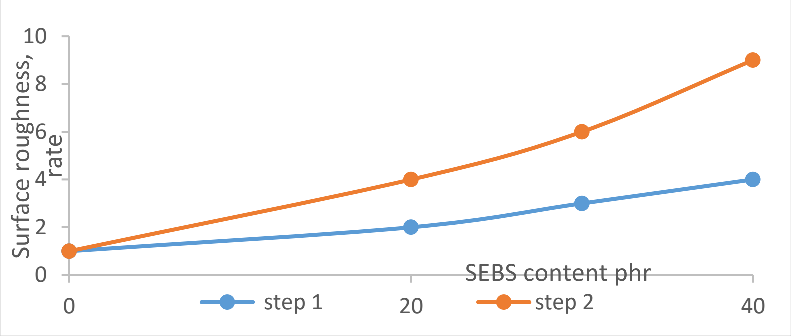

Figure 5. Effect of SEBS content on surface roughness rate of pre-blends and master blends.

Two different methods —surface roughness and viscosity—confirm that the optimal extent of fragmentation is indeed achieved in blend D2. The increase in the SEBS content of blend D2 minimized the surface roughness, and void content, reducing viscoelastic torque, as depicted in *Figs. 3-5* compared with the pre-blend step.

3.6. Effect of the molding temperature on the interphase adhesion. Studies claimed [Candal et al., 2008; Le Mouellic et al., 2021] that increasing the injection temperature of the overmolded TPVs from 190°C up to 260°C raises the peel strength. The effect of molding temperature on adhesion between GTR pre-blends and polyolefin sheets was studied with samples obtained at 160°C and 190°C, as shown in *Figure 6*.

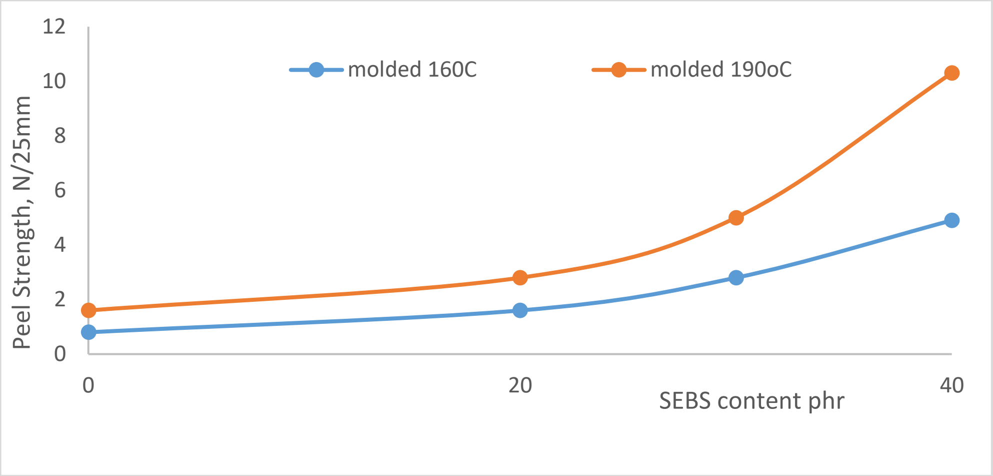

Figure 6. Effect of SEBS and molding temperature on macro-composite peel strength

The rise in peel strength between the PE/EVA sheet and the GTR-based pre-blend, as depicted in Figure 6, is consistent with the SEBS content. The molding temperature at 190°C raised the peel strength compared to 160°C by 58% through the presumed sintering of a thermoset network as a promising approach to overcome the limitation of lower temperatures [Tsuruoka, 2020]. The increase in SEBS in the ternary blend enhanced peel strength, due to the improved viscosity of GTR fragments. The evolution in interphase, presumed to be ruled by the interlocking between restored domains and matrix, also plays an active role in the final morphology stabilization.

3.7. The proposed model of GTR conversion in macro-composite. The subsequent fragmentation of weakened aggregates was governed by mild oxidative cleavage of the sulfidic network below 200°C promoted. In summary, this scission helped to regain the adhesion and unsaturation of main chains [Rakhman, 2023; US Patent, 2021]. A conceptual “onion peeling model" was proposed to explain the erosion mechanism [Shiga & Furuta, 1982]. Evaluation of viscosity, roughness, and an inter-phase adhesion of matrix/rubber (*Figs. 3–6*) presumes the pattern of GTR disintegration, that is illustrated in *Figure 7*.

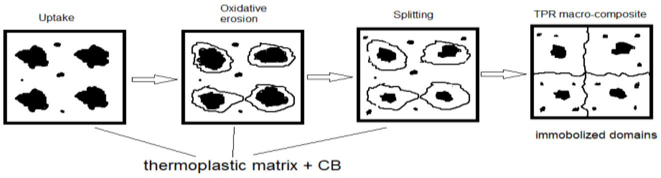

Figure 7. The assumed model of consecutive steps of the GTR conversion to macro-composite [adapted from Fazli, Rodrigue, 2022]. The proposed structure of the macro-composite comprises thermoset cores, which, are surrounded by a gel-like shell (interphase) and carbon black dispersions in the matrix.

The sequential pattern of GTR conversion proposed in *Figure 7*. The borders among the particles break down, expectedly enough (because GTR turns into finely divided macro-gels). Macro-composites are composites in which non-fusible cores have been partially surrounded by an oxidized gel-like shell (inter-phase). Even the relatively moderate functionalization of GTR and matrix polymers, this can achieve good adhesive strength [Chen et al., 2021]. Comparing evolution of surface roughness and viscosity (*Figs. 3 and 4*) suggested that macro-gels immobilized in the matrix demonstrated uniform bulk and surface, as implied via a thicker interfacial region in the GTR/EVA blend [Saeb et al., 2022]. Promoted immobilization of the rubber domains was possible by generating an 'effective' volume of restored rubber.

3.8. Effective volume fraction comprises restored rubber. Promoted oxidative functionalization of the rubber fragments was possible by generating an 'effective' volume of restored rubber. The viscosity-roughness relationship (*Figs. 4–5*) demonstrated the conversion of large-sized aggregates into the 'effective' volume comprising the semi-crosslinked domains and carbon black dispersed in a matrix. Several variables that affect the morphology are identified, including the polyolefin type and thermoset nature of restored 'effective' rubber and its ratio; the ligament's thickness, and the continuous plastic phase [Abdou, Patel, 1991]. The smaller the thermoset core size, the less matrix volume fraction is required for such continuous inter-phase [Jesson, Watts, 2012; Wu et al., 2014]. Thus, the formation of uniform dispersion improves the integrity of the macro-composite.

3.9. Mechanical properties. The macro-composites demonstrated in *Table II* significant improvements in the uniformity of static properties depending on SEBS content.

Table II. Effect of polymer/elastomer matrix on TPR static properties

Macro-composites	**A2**	**B2**	**C2**	**D2**
Hardness Shore A	81	69	65	62
Modulus 100%, MPa	3.2	2.7	2.6	2.4
Tensile Strength, MPa	3.6±1.81	6.3±1.23	6.8±1.16	7.1±1.08
Elongation at break, %	127	231	248	265
Tear - Type C, N/mm	18±1.54	26±1.26	30±1.15	36±1.04
Compression Set at 70°C /22hr, %	ND	26	28	33

The binary blend A2 demonstrated low tensile strength and tear with high standard deviation, as shown in *Table II*. The declining inter-domain gap presumably in this mix leads to greater localization of plastic deformation. The increasing (impairing) compression set from B2 to D2 stems from the reducing semi-cross-linked effective rubber fraction content. The increasing SEBS content improved tensile strength, elongation, and tear resistance of ternary blends, and reduced hardness. The reduced standard deviation of the tensile strength and tear of the D2 blend is accompanied by an improvement in the uniformity of the composite. Thus, the described process can overcome the effect of uncontrolled variations in the GTR feedstocks on the final composite characteristics.

3.10. Structure-property relationship of the macro-composite versus commercial TPV. The EPDM phase was assessed as 70% crosslinked under TPV dynamic crosslinking [Martin et al., 2009]. Further, it also suggested two conceptual models: one is a gel-like lamellar structure up to 10 µm size [LeHel et al., 2020]; another model comprises co-continuous gel-like structures observed up to 200 µm size [Martin et al., 2009; Wu et al., 2014]. On the other hand, the presented macro-composite implies somewhat restored thermosetting gel-like structures up to 10 µm size within a matrix.

4. Summary and recommendation.

The novel concept was used to upcycle GTR via cleavage of a cross-linked network with conversion into macro-composite. The pre-blend, which comprised loose 74 wt% GTR, was compacted with the matrix under ram pressure. The master step assisted in the fragmentation of rubber aggregates and in the removal of the macro-voids due to the controlling shear forces, temperature, and residence time.

Although the degree of fragmentation was not quantifiable, one could estimate its effects on both the bulk and surface properties. Two different methods —surface roughness and viscosity—confirm that the optimal degree of fragmentation is achieved in blend D2 with an added 20 phr of SEBS. The relationship established between viscosity, surface roughness, and inter-phase adhesion. A series of tests, including peel strength, elastic recovery, tensile strength, and tear, quantified the interactions between the GTR and matrix. Direct GTR conversion to a malleable thermoplastic macro-composite is governed by two-staged mixing. The reclaim step was excluded.

Acknowledgments*:* The author thanks Michael Shuster and Michael Gishvoliner for the helpful discussions. The author is grateful to Adam Schwartz and Peter Paneah for their help in the design.

References

Abdou-Sabet S.; Raman P. Patel RP, (1991), Morphology of Elastomeric Alloys, *Rubber Chem Techn*, 64:5: 769–779. https://doi.org/10.5254/1.3538589

Abdou-Sabet S., Puydak RC, Rader CP., (1996), Dynamically Vulcanized Thermoplastic Elastomers, (1996), *Rubber Chem. Technol.*, 69:3: 476–494; https://doi.org/10.5254/1.3538382

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

Azimi M , (2021), Chemical oxidation of high-density polyethylene: Surface energy, functionality, and adhesion to liquid epoxy, *J. Appl. Polymer Science*, 138:39; DOI: 10.1002/app.50999

Babu RR, Singha N., Naskar K., (2011), Effects of mixing sequence on peroxide cured (PP)/ethylene octene copolymer (EOC) thermoplastic vulcanizates (TPVs). Part. II. Viscoelastic characteristics, *J. Polymer Res*, 18:1:31-39; DOI:10.1007/s10965-010-9388-2

Bohin F, Feke DL, Manas-Zloczower I, (1996), Analysis of Power Requirements and Dispersion Quality in Batch Compounding Using a Dispersion Model for Single Agglomerates, *Rubber Chem.Technol.*, 69:1, 1–7. doi:10.5254/1.353835

Byers, JT., (2001), Filler–Non-black. *In: Baranwal, Stephens (Eds.), Basic Elastomer Technology*. *ACS, Rubber, Akron, Ohio*, 82–111; ISBN 10: 091241507X ISBN 13: 9780912415079

Candal, MV.; Gordillo, A.; Santana, OO.; Sánchez, JJ. (2008), Study of the adhesion strength on overmoulded plastic materials using the essential work of interfacial fracture concept. *J. Mater. Sci.* **2008**, 43, 5052–5060. DOI: 10.1007/s10853-008-2667-1

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, *Chemistry*, 7, 137–145; doi.org/10.1016/j.chempr.2020.11.020

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

Colom, X.; Carrillo, F.; Cañavate, J., (2007), Composites reinforced with reused tyres: Surface oxidant treatment to improve the interfacial compatibility. *Compos. A: Appl. Sci. Manuf.* 38(1):44-50 DOI:10.1016/j.compositesa.2006.01.022

Coran, AY.; Patel, RP, (1980), Rubber-thermoplastic compositions - 1. EPDM-PP thermoplastic vulcanizates, *Rubber Chem. Techn*. 53:141–150, http://dx.doi.org/10.5254/1.3535023

Coran AY; Patel, RP, (1996), in: G. Holden, RK Hans, RP Quirk (Eds.), *Thermoplastic Elastomers*, 2nd ed., Hanser Publishers, Munich, 143

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.

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

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

Ishimura, T**.,** Iwai, I., Matsui, K., Mattonai, M., Watanabe, A., Robberson, W., Cook, A., Allen, H. L., Pipkin, W., Teramae, N., Ohtani, H., & Watanabe, C., (2021), Qualitative and quantitative analysis of mixtures of microplastics in the presence of calcium carbonate by pyrolysis-GC/MS. *J. Analytical Applied Pyrolysis*, *157*, 105188. DOI:https://doi.org/10.1016/j.jaap.2021.105188

Fazli, A.; Rodrigue, D. (2020), Waste Rubber Recycling: A Review on the Evolution and Properties of Thermoplastic Elastomers, *Materials, 13*, 782. DOI:https://doi.org/10.3390/ma13030782

Fazli A.; Rodrigue, D., (2021), Effect of Ground Tire Rubber Particle Size and Content on the Morphological and Mechanical Properties of Recycled High-Density Polyethylene/GTR Blends, *Recycling*, 6 (3), 44; doi.org/10.3390/recycling6030044

Fazli A., Rodrige D., (2023), Thermoplastic elastomers based on recycled high-density polyethylene/ground tire rubber/ethylene vinyl acetate: Effect of ground tire rubber regeneration on morphological and mechanical properties, *J. Thermoplastic Composite Mater*, 36(6) 2285–2310; doi.org/10.1177/08927057221095388

Formela K, Korol J., Saeb MR. Interfacially modified LDPE/GTR composites with nonpolar elastomers: from microstructure to macrobehavior, *Polym Test*, **2015**; 42: 89–98. DOI: 10.1016/j.polymertesting.2015.01.003

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

Klie B, Teich S, Haberstroh E, Giese U, (2015), New Method for Evaluating Rubber Mixing Quality by means of alternative Representation of the Fingerprint Chart, *Kautschuk Gummi Kunststoffe*, 10, 31-39

Koning, C.; Van Duin, M.; Pagnoulle, C.; Jérôme, R. (1998), Strategies for compatibilization of polymer blends. *Prog. Polym. Sci*. 23,707–757; doi.org/10.1016/S0079-6700(97)00054-3

l'Abee RMA.,Van Duin M, Spoelstraa AB, Goossens JGP, (2010), The rubber particle size to control the properties-processing balance of thermoplastic/cross-linked elastomer blends, *Soft Matter***,** 6**,** 1758-1768; DOI: 10.1039/B913458A

Le Cam, J-B. (2010), A review of volume changes in rubbers: the effect of stretching, *Rubber Chem. Technology*., 83, 247-269; DOI:10.5254/1.3525684

Le Hel C., Bounor-Legaré V., Catherin M, Lucas A, Thèvenon A., Cassagnau P, (2020). TPV: A New Insight on the Rubber Morphology and Mechanic/Elastic Properties, *Polymers*, 12, 2315; doi:10.3390/polym12102315

Lefèvre V., Ravi-Chandar K., Lopez-Pamies O., (2015), Cavitation in Rubber: An Elastic Instability or a Fracture Phenomenon? *Int. J. Fracture*, 192(1):1-23, https:// doi. org/ 10. 1007/ s10704- 014- 9982-0

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

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

Martin G, Barrès C, Sonntag P, Garois N, Cassagnau P., (2009), Morphology development in thermoplastic vulcanizates (TPV): Dispersion mechanisms of a pre-crosslinked EPDM phase. *Eur. Polymer J*. 45 (11), 3255-3266. ⟨10.1016/j.europolymj.2009.07.012⟩

Mashita R., Bito Y., Uesugi K., Hoshino M, Kageyuki I., Kishimoto H., (2023), Insights into the cavitation morphology of rubber reinforced with a nano-filler, *Scientific Reports***,** 13:5805 https://doi.org/10.1038/s41598-023-33137-8

Montagna LS, Santana RMC, (2012), Influence of rubber particle size on properties of recycled thermoplastics containing rubber tyre waste, *Plastics, Rubber Composites*, 41:6, 256-262, https://doi.org/10.1179/1743289811Y.0000000032

Mujal-Rosas, R.; Orrit-Prat, J.; Ramis-Juan, X.; Marin-Genesca, M.; Rahhali, A., (2011) Study on dielectric, thermal, and mechanical properties of the ethylene vinyl acetate reinforced with ground tire rubber, *J. Reinf.Plast. Compos*. 30, 581–592. DOI:10.1177/0731684411399135

Prut, EV., Zhorina, LA., Novikov, DD., Gorenberg, AY., Vladimirov, LV., Berlin, AA., (2017), Structure and properties of blends based on ground rubber tires and thermoplastics. *Mendeleev Communications*, 27(4), 405-06. https://doi.org/10.1016/j.mencom.2017.07.030

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

Rakhman MZ, (2021), Improvement of Workability and Integrity for Ambient Ground Rubber as Elastomer Alternative: Direct Incorporation and Functionalization, *J. Appl. Sciences Technium*, 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

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

Rodriguez GM, Díaz-Requejo MM, Perez PJ, (2021), Metal-Catalyzed Post-polymerization Strategies for Polar Group Incorporation into Polyolefins Containing C−C, C=C, and Aromatic Rings: *Macromolecules* **2021**, 54, 4971−4985; doi.org/10.1021/acs.macromol.1c00374

Rose A, (1948), The Sensitivity Performance of the Human Eye on an Absolute Scale, *J. Optical Society of America***,** 38, (2)**,** 196-208

Ruiz-Hernandez V, José Roca M, Egea-Cortines M, Weiss J., (2018), A comparison of semi-quantitative methods suitable for establishing volatile profiles, *Plant Methods*, 14:67 I https://doi.org/10.1186/s13007-018-0335-2

Saeb, MR.; Wi´sniewska, P.; Susik, A.; Zedler, Ł.; Vahabi, H.; Colom, X.; Cañavate, J.; Tercjak,A,Formela,K, (2022), GTR/Thermoplastics Blends: How Do Interfacial Interactions Govern Processing and Physico-Mechanical Properties?, *Materials* 15(3), 841; https://doi.org/10.3390/ma15030841.

Sengupta, P., Sengers, WGF., Noordermeer, J. W. M., Picken, SJ., Gotsis, AD. (2004), Linear viscoelastic properties of olefinic thermoplastic elastomer blends: melt state properties. *Polymer*, *45*(26), 8881-891. https://doi.org/10.1016/j.polymer.2004.10.030

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

Seghar, S., Asaro, L., Rolland-Monnet, M., Hocine, N.A., (2019), Thermo-mechanical devulcanization and recycling of rubber industry waste, *Resources, Conservation Recycling*, 144, 180–186; DOI:10.1016/j.resconrec.2019.01.047

Shiga S., Furuta M., (1982), Processability of EPR in an Internal Mixer (II) Morphological Changes of carbon black agglomerates during mixing, *Nippon Gomu Kyokaishi*, 55:491–503. doi:10.2324/gom

Smitthipong, W., Nardin, M., Schultz, J., Suchiva, K. (2009), Adhesion and self-adhesion of immiscible rubber blends. *Int. J. Adhesion Adhesives*, *29*(3), 253-258. https://doi.org/10.1016/j.ijadhadh.2008.06.003

Sonnier, R.; Leroy, E.; Clerc, L.; Bergeret, A.; Lopez-Cuesta, J.M.; Bretelle, A.S.; Ienny, P. (2008), Compatibilizing thermoplastic/ground tyre rubber powder blends: Efficiency and limits, *Polym. Test*. 27, 901–907; DOI: 10.1016/j.polymertesting.2008.07.003

Taguet A., Cassagnau P., Lopez-Cuesta JM, (2014), Structuration, selective dispersion and compatibilizing effect of (nano)fillers in polymer blends, *Progress Polymer Science*, 39:8, 1526-1563; DOI:10.1016/j.progpolymsci.2014.04.002

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

Yuan, B.; Li, X.; Sun, Y. A, Short Review of Aerobic Oxidative Desulfurization of Liquid Fuels over

Porous Materials. Catalysts 2022, 12,129. https://doi.org/10.3390/catal12020129

US Patent 7589154, (**2009**), Process for making thermoplastic vulcanizates,

US Patent 9441099, (**2015**), Olefinic Thermoplastic elastomer composition and process for producing the 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, *Rub. Chem. Techn*, 48:4:577–591
doi.org/10.5254/1.3539661

Van Duin M, (2006), Recent Developments for EPDM-Based Thermoplastic Vulcanisates, *Macromol. Symp*., 233:11–16,
doi:10.1002/masy.200650102

Wang H, Chen S., Zhang J, (2009), Surface treatment of LLDPE and LDPE blends by nitric acid, sulfuric acid, and chromic acid etching, *Colloid Polym Sci*, 287:541–548; DOI: 10.1007/s00396-009-2000-9

Wang, Y.-H., Chen, Y.-K., Rodrigue, D.. (2018). Production of Thermoplastic Elastomers Based on Recycled PE and Ground Tire Rubber: Morphology, Mechanical Properties and Effect of Compatibilizer Addition, *Int. Pol. Process*, 33, 4, 2018, 525, doi.org/10.3139/217.3544

Wu, H.; Tian, M.; Zhang, L.; Tian, H.; Wu, Y.; Ning, N., (2014), New understanding of microstructure formation of the rubber phase in thermoplastic vulcanizates (TPV), *Soft Matter*, 10, 1816–1822; DOI:10.1039/c3sm52375f