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Improvement of Workability and Integrity for Ambient Ground Rubber as Elastomer Alternative: Direct Incorporation and Functionalization

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Dedicated to the late Mr Ushi Miller

Abstract. The main barriers to the wide use of ambient ground tire rubber (GTR) are the absence of breakdown in shear mixing, lack of compatibility, and co-curing with the polymer matrix. The functionalization of the GTR was realized through dispersive shear-induced mixing, with the disintegration of the aggregates due to the swelling gradient, oxidation of a network and to sequence order. The GTR-functionalized macro-composite comprised a co-cured compatible GTR and an unsaturated elastomer at any ratio, retaining the excellent initial properties, unlike a depolymerized reclaim. This blend had an unexpected integrity effect: the enhanced workability of the roll-processed, self-sustained web with regular surface skin topography and verified integrity for an uncured blend. Functionalization appears to be a more significant factor than GTR size, characterized by lower gel content, improved abrasion, and tear resistance compared to the virgin elastomer blend. Workability and integrity control indicators were selected.

Keywords: Ground rubber functionalization; surface skin; macro-composite, quality indicators

1. Introduction. *The primary recycling step* presents a grinding, *secondary recycling* step using a ground tire rubber (GTR) for reclaiming at 220-280°C to produce a depolymerized material [Adhikari, De 2000] with submicron size thermoset grains [Van Hoek, 2021]. The ambient GTR exhibits slightly oxidized large agglomerates, with a sponge-like convoluted dendritic texture, size ranged from 200 to 500 μm. GTR produced from truck tires retains the better physical properties than reclaim, since it should regarded as a suitable component for elastomer blends. Michelin announced its target to achieve the '2030' tire with a 10% recycled rubber by “2048”, tires will have a 30% recycled rubber [Michelin, 2018]. The direct incorporation of a GTR in an elastomer proposes the ways to solve this problem without cost-consuming secondary recycling.

1.1. GTR-filled blend by technological compatibilization. The GTR-filled blend comprised a curable unsaturated elastomer as a continuous major phase and an inert GTR as a minor no curable disperse phase. The macro-sized GTR had not typically broken under usual mixing shear, the rubber compound bulk heterogeneity influenced the surface topography. Generally, miscibility resulted in one phase, while compatibility created an interphase for which its size and stability were determined by interfacial interactions [Manharaj, 2012, Hermann et al, 2017]. The consequences of this incompatibility are inhomogeneous distribution of GTR in the polymer phase and thermodynamic non-equilibrium after mixing in a blend. The most critical deterrent to the use of GTR is a large aggregate size that exceeded the polymer interchain distance and introduced an area of localized stress. Technological compatibilization method applied GTR with size up to 100 μm, the volume of GTR that could be suitable was limited by the content of coupling agents – copolymers, resins, surfactants that modify the interfacial tension of the GTR [Habibah et al, 2018, Hejna et al, 2020]. It is known that loading more than 5 phr adversely affected the fracture morphology [Hassim et al, 2019]. Ambient GTR-filled compounds were characterized by the melt fracture of the surface that is known as 'sharkskin' [Patcharaphun et al 2014].

1.2. GTR oxidative desulfurization (ODS) in situ was the tool of functionalization. Significant advances have been made involving an ODS for GTR modified asphalt [Houda, 2018]. GTR decomposition continued until it was completely dispersed into the matrix as the swollen polymer gel. ODS catalyst formed from metal oxide and acid [Georgiadis et al, 2020], the metal-catalyzed solvolytic reaction [Liquori et al, 2021] activated the chain-links of polymer. The catalyst raised the domino oxidation effect of the GTR [Zhang et al, 2013], The oil assisted the transport of catalyst [Hossein et al, 2019], the effect of GTR oxidation in oil was observed as the C–O and the S=O absorption peaks by FT-IR for the swollen GTR compared to the untreated GTR that reflected the oxidative fracture of C–S and S–S bonds [X.Wang et al, 2019].

1.3. Swelling GTR Thermodynamics. The desired performance of the GTR-asphalt was achieved by absorption of oil involved in volume rise. The GTR size distribution, surface texture, time, and interaction temperature significantly affected the swelling phenomenon [Makoundou et al, 2021]. The decrease of rubber strength was correlated with the degree of swelling and temperature. Thermally shear-induced GTR-oil interaction accelerated swelling, the selective scission of cross-linked bonds [H. Wang et al, 2020]. Dispersive mixing is intended for the breakdown of the hot, swollen, and weakened agglomerates under the repeated multiaxial stretching of GTR. The effect of mixing [Kawahara et al, 2014] provided a decohesion/cavitation into GTR agglomerates. It is possible that the dynamic swelling rate in Banbury is far from static swelling [Ramarad et al 2015]. The GTR network degradation removed the constraints for the GTR chains that partially dissolved the softener [Yao et al. 2016] but improved the storage stability. The softener assisted the GTR surface modification [Hassan et al, 2014; Zanetti et al, 2015]. GTR was swollen by the absorption of the oily components at 160–220◦C to form a gel-like material [Noorvand et al 2021]. Dynamic swelling of GTR in the presence of EVA, resin, and oils improved the properties of GTR [Rakhman 2016, 2018].

1.4. Migration of softeners and other aids in the uncured and cured GTR blends caused a change in the loss of a tack for GTR-based blends. Limited solubility and the concentration gradient of softener resulted in migration and exudation [Ignatz-Hoover et al, 2003]. Softener and promoter are dissolved at thermal mixing and became supersaturated when the mix cooled down, that resulted in the ''blooming' or exudation' effect.

2. Problem Statement and Objectives.

The goal of the study was to produce integral compound with disintegration of ambient large size GTR to maintain a roll-processed self-sustained web with regular surface skin topography to overcome the poor dispersion and incompatibility of ambient GTR:
- Optimization of the operating conditions to generate a workable and co-cured compound;
- Selection of the industrial workability indicators for the assessment of GTR blends.

3. Experimental program

3.1. Base materials. Rubber buffing powder (TR-40B) from tire truck treads and powder from whole truck tire (TK-40TK} both size less 425 µm, all were supplied by Tyrec Recycling Industries from Israel. The elastomers comprised NR as SMR-10, BR as Europrene Neocis BR-40 supplied by Versalis, LLDPE as Queo 0201 supplied by Borealis.

3.2. Rubber-Functionalized Promoter R-393 (Tyrec Industries) represented an optimal ratio of a transition metal oxo complexes, that are effective:
- The thermo-triggered-shear ensured the oxidation effect on a GTR surface.
- Retained scorch resistance due to prevention of sulfidic residues recombination.

Promoter [Rakhman, 2020] assisted to partial dissolution of swollen GTR and prevented a sulfidic residues recombination due to the anionic group presence.

3.3. Softeners include the melt compounding copolymers, resins, process aids. From the thermodynamic viewpoint, the GTR-softener system is regarded as the high-molecular solvent for thermoset and accelerates the penetration of a promoter into GTR. It also improves the rheology of the blend due to the phase changing. RAE oil Plaxolene 50 (Total), resins C9, LLDPE copolymer was used.

3.4. Preparation of GTR- functionalized compound.

3.4.1. Functionalization of GTR by oxidative degradation of a network. The GTR-functionalized macro-composite comprised an unsaturated elastomer matrix and a compatible GTR at any ratio that exhibited a co-cured integral blend. The intensity of dispersion degree defined the GTR interfacial interaction and the structural integrity which affect the functional properties of the compound [Dierkes et al, 2019].

3.4.2. Mixing parameters. The model formulations were compounded in a Banbury mixer with a chamber volume of 1.6 L, using a 75% fill factor, a chamber temperature setting of 60°C with ram pressure set to 6 bar to provide compaction of a GTR at the start. A three-stage mixing process was used, in which polymer, GTR, softener, promoter, and the processing aid were added in the first pass. In the first two mixing stages, the rotor speed was increased in order to bring the batch temperature to 160˚C to complete the GTR functionalization. The curing group, antidegradants, zinc oxide were added in the final pass. When GTR, polymer, and softener were loaded into the mixer, two forces were found to be competing against each other: the strong crosslinks within GTR aggregates versus the softener with elastomer interaction. NR pre-masticated with 0.15 phr of chemical peptizer and 2 phr of zinc fatty acid salt were added to reduce viscosity so that it can wet the GTR. On the one hand, the swelling and breaking of GTR aggregates, and on other prevention of over-oxidation, and sticking of the compound to rotors required certain residence time. The re-milling applied to broken swollen agglomerates [Klie et al, 2015] in the matrix, improved the macro-dispersion of GTR and eliminated gross heterogeneity. The intermediate compounds were left to rest for at least 12 hours.

3.4.3. Formulation Design of the softener-promoter-GTR ratio should comply with the surface area of GTR equal 40 m^2 for 100 g. Based on empirical knowledge the formulation design must take into account an optimal ratio of softener to provide an interaction with this area, also a re-curing of a functionalized GTR and unsaturated elastomer matrix. In contrast with the GTR-filled blend where the only elastomer was cured, the functionalized GTR was rated as 50% hydrocarbon content. The addition of elastomer required the subsequent correction of curing group on 100 phr of hydrocarbon.

3.5. Quality analysis and indicators.

The specific methods intended to measure industrial quality for the assessment of GTR- functionalized batch workability. The blend quality can be classified into three major categories: surface defects, building tack, and green strength. Furthermore, the surface roughness caused problems in a post-mixing: extrusion, calendaring, and the loss of building tack because of the lower area of real contact. The GTR dispersion and modification degree of a roll-processed self-supported web were controlled in order to achieve desired regular surface skin and physical properties of the resulting GTR- functionalized batch.

3.5.1. Topography of the macro-composite surface skin. A surface skin quality as an indicator of GTR modification and blend homogeneity has typically been ranged by specific visual methods. The test used a roll mill with temperature 60°C, sheet 3 mm, friction 1:1 allocating a four-point score to each item: the surface skin, the porosity in the cross-section, the sharpness of the edges, continuity with unbroken edges [Kondo, 2014]. Surface skin ranged from 10 (Superior) to 1 (Inferior). Edge sharpness ranged from A (Superior) to E (Inferior). These simple integrity indicators allowed us to find the limit level of GTR content. As a reference, a 100% virgin compound was used, and the samples were sorted according to their visible surface roughness.

3.*5.2. Dispersion qualitative analysis The Phillips Dispersion test of visible particles***.** The heterogeneous blend resulted in visible larger aggregates on the surface and they have an effect on surface skin roughness. Assuming the distance to focus 100 mm the smallest visible size for a naked eye was down to 29 microns. The integrity of discharging stock was expressed in the: slab, big pieces or flakes form, quality of a roll-processed surface skin. For the estimation of the of macro-particles and the size, the GTR macro-composite was blended with a white SBR/BR-clay filled viscous blend, in a ratio 5/95. The sample was prepared in the mold at 105°C for 5 min to remove air. A method used a microscope to examine a sample at 30x magnification and a visual rating of 1 (bad) to 10 (excellent) that based on a comparable Phillips standard dispersion rating chart, thus, provides merely a qualitative analysis of GTR dispersion [Dierkes et al, 2019; Hoek et al, 2021]. This test is a well-known industry method, however, the results are very subjective. Poor dispersion may indicate that some parameters had changed during the mixing cycle - time, temperature or fill factor.

3.5.3. Accelerated oil migration test. For the oil exudation, sheets of size 40 × 40 × 1.5 mm were pressed at 105°C for a contact 10 seconds for uncured and at 150°C for cured materials and then stored under a load of 1 kg for 24 hrs between filter papers at room temperature. The amount of oil taken up by the filter paper, was determined visually from the coloration of the filter paper.

3.5.4. The Mooney test represented the viscosity in the low shear rate range and indicates the physical and chemical interactions within the interphase. MDR determines the duration of the vulcanization step and the degree of crosslinking (MH-ML).

3.5.5. Green strength means the strength of the uncured rubber and its resistance to deformation. It is a key property for all post-mixing steps in which the blend is exposed to a particular elongation rate. Green strength was measured by ASTM D 6746, Part A.

3.5.6. Cured GTR- Functionalized blend integrity indicators.

Tear Nick (or crescent tear) indicated the integrity and fracture process that is initiated at a site of high-stress concentration caused by a localized deformation (ASTM D 624, Method C).
Abrasion Test indicated the integrity of vulcanizate and strength of interactions between polymer matrix with GTR (DIN-53516, method A (non-rotating), 10N.
Oil sorption. Softener dynamic sorption with thermoset GTR was studied by the swelling in static condition according to ASTM D 471 at the longer testing time than mixing cycle, that similarly to timing for static and dynamic conditions. The swelling index (SI), which reflects the process of oil sorption by GTR, was defined as follows:
SI=(Ms-Mi)/Mi where Mi is the mass of original rubber, and Ms is the mass of swollen sheet.
Gel Content. Firstly, the sample was extracted by acetone and subsequently, the residual sample was dried and packaged in a 120-mesh steel pouch in boiling xylene to dissolve the un-vulcanized or devulcanized phase, was dried under vacuum for 24 hours and weighed after being cooled. The obtained result was corrected in terms of comprised in tread formulation and added uncured polymers that are soluble in xylene.

4.Results and discussion.

4.1. Static swelling of thermoset rubber. The effect of aromatic oil and promoter on swelling index and gel content of the NR/BR tread truck blend sheet was shown in Table 1. The swelling was performed with a ratio of oil medium to rubber sheet (100:20) whereas the inverse ratio GTR-softener was used in a blend. Cured tread NR/BR sheet 2 mm as GTR model was tested at temperatures at range 120°C-180°C for 1 hour and 4 hours in RAE oil.

Table 1 - Effect of temperature, aromatic oil RAE, and promoter (3%) on the Swelling Index and gel of cured compounds (medium RAE, promoter 3%) on static swelling

Temperature, °C	RAE oil			RAE oil + promoter		
Test time, hrs	1 hr	4 hrs	Gel 4 hr, %	1 hr	4 hrs	Gel 4 hr, %
120	0,03	0.05	99	0,02	0.06	99
140	0.07	0.14	99	0.08	0.22	98
160	0.14	0.38	98	0.15	0.49	95
180	0.20	0.51	96	0.24	0.63	94

A study indicated a significant influence of the processing temperature on swelling degree. The softener viscosity was reduced with rising temperature, and so could diffuse more easily into rubber. The data showed in Table 1 that oil with rubber-functionalized promoter has easily into rubber. The data in Table 1 showed that oil with rubber-functionalized promoter has a low effect on the swelling in the range up to 140 °C. Swelling due to free molecular movement, made it easier for the softener to penetrate through the rubber and rised faster starting from 160°C. The promoter intensified swelling by more than 30% at 180°C for 4 hr, reduced gel and increased the gel-like volume. It was found that the swollen sample became softer and more viscous, forming a gel-like structure that assisted the disintegration under the mixing shear force.
4.2. Effect of the GTR mixing procedure. Slab compaction was provided by the polymer matrix-softener-GTR-promoter ratio and ram pressure. The expected pattern of polymer matrix fragmentation after GTR loading (GTR-polymer matrix ratio 100/25) and followed batch compaction when torque achieved the maximum as shown on Fig.1.

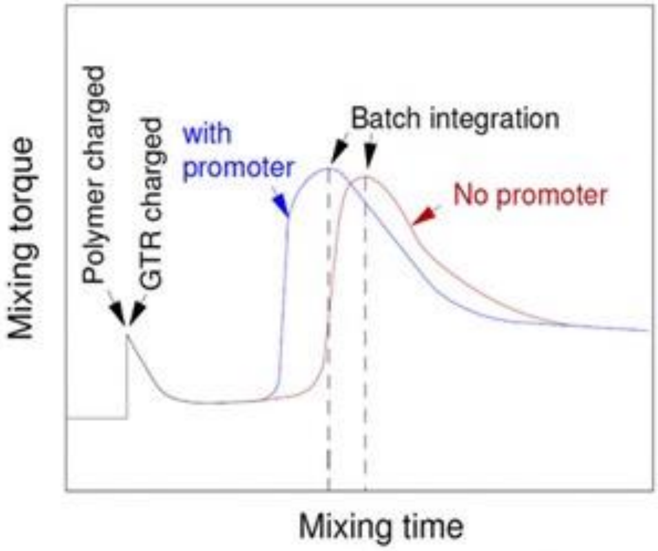

Fig. 1. Mixing torque chart pattern - GTR incorporation/batch compaction process

GTR via surface functionalization and swelling, also via NR scission, became softer and stickier as a result of thermal-oxidative shear degradation, and as a result, the maximum torque, which is a parameter associated with crosslink density, dropped. As the forming mass increased in volume, the torque raised again and presented an integral macro-composite [Kondo 2014].
The molten polymer occluded swollen GTR fragments, after 60-120 sec torque passed through a maximum, and declined slowly until the end of swelling-functionalization forming a dense rubber slab, the volume of polymer + GTR+ softener became equal to the chamber volume, the ram came to the lowest position and the ram pressure on the stock disappeared, the viscous torque dramatically reduced. The viscous effects are more significant with the rise in temperature. Further observation revealed that the promoter action led to a shortening in batch integration time, and increased temperature, that both have a combined effect on dispersion and surface skin. The technical result was expressed in improved workability and mechanical properties.

4.3. *Effect of dynamic swelling on the GTR functionalization.* The softener sorption presented an important indicator of partial GTR network decomposition and determined the re-processing and re-curing properties of the final material. The optimal swelling required a higher temperature below GTR decomposition (TGA >200°C), this finding was important to achieve a performance target for product workability. Effect of oil-insoluble saturated polymer matrix and softener on the blend decomposition and re-curing with an LLDPE, and oil-soluble unsaturated elastic matrix NR were exhibited in Table 2.

Table 2 - Comparison of the re-curing ability of GTR-functionalized preblend with saturated (LLDPE) and unsaturated (NR) polymers (temperature of discharging 180°C). Polymer is 5 phr, promoter 4 phr, softener 24 phr on 100 phr of GTR (migration test after 24 hrs).

Polymer matrix	LLDPE	LLDPE	LLDPE	NR
Promoter, phr	0	0	4	4
Discharging temperature, °C	150	180	180	180
Oil exudation, rating	High	Low	Low	No
Discharged stock – form	Friable	flakes	Big pieces,	Big pieces
Dispersion visual rating*	1	2	2	2
Gel content uncured mix, %	97	93	90	88
Sheet Surface skin rating	1E	1E	2D	3C
Viscosity, ML (1+4),125°C	82	72	63	51
MDR at 150°C				
ML, dNm	4.8	2.5	0.6	1.7
MH - ML, dNm	3.5	4.1	6.6	6.7
TS2, min	2.9	2.2	2.8	2.6
TC90, min	7.8	6.3	7.1	6.4
Tensile, MPa	3.8	7.4.	9.7	8.6
Elongation, %	116	132	213	268

* Phillips Dispersion test - visual rating from 10 (Superior) to 1 (Inferior).

The optimal operational conditions of dynamic GTR swelling were verified by the exudation – in excess of oil migration, gel, and viscosity. Obtained results of oil migration (Table 2) related to GTR swelling, and indicated that the softener adsorption degree of GTR at 150°C and at the absence of promoter was lower. The main cause of GTR exudation was the restricted solubility of an oil level. Dynamic swelling reduced a gel content at 180°C more than at static swelling (Table 1), viscosity also was reduced, that evidenced the dramatic decomposition of the GTR surface. The state of macro-dispersion was governed by the presence or absence of disintegration of GTR aggregates into smaller ones. The saturated polymer in comparison with the NR phase reduced viscosity and improved the flow of testing and molding, but required a higher mill temperature. The swelling effect essentially depended on the softener type. The use 30-40 phr of LLDPE as polymer matrix and softener provided the dissolution of GTR, the thermoplastic TPV-GTR showed good flow properties. NR, on the other hand, enhanced the green strength.

Effect of softener and processing aid Struktol HT-107 were studied (Table 3) at constant sum load (rise of resin decreased the oil content) on blend GTR-TR-40B (100 phr). elastomer 24 phr, total softener 20 phr.

Table 3 - Influence of C9 resin concentration and Struktol HT-107 on the uncured compound. Discharging 160°C.

C9 resin content, phr	Dispersion visual rating*	Viscosity, ML (1+4)125°C	Discharged stock, form
0	1	87	flakes
4	3	77	Flakes, big pieces
8	5	71	big pieces
8 + Struktol (1 phr)	6	68	slab

*Dispersion visual grains rating from 10 (Superior) to 1 (Inferior).

The data in Table 3 showed that a higher resin content resulted in a decreased number of "surface defects", lower viscosity, and more cohesive discharged slab via oligomer-GTR interaction.

4.4. *Effect of promoter on GTR functionalization in the case of the reinforcing carbon black use.* Effect of physical anchorage and chemical attachment of elastomer with functional groups and free radicals of carbon black (CB) results in forming a bound rubber and lower swelling in solvent. Unlike GTR exhibited the very weak elastomer bonding. Therefore, the order of mixing included the separated preparation of GTR-functionalized preblend for the CB step addition. This finding was important to achieve a performance target in product workability. The effect of the GTR functionalization was presented in Table 4.

Table 4 – Effect of promoter on the ambient GTR-functionalized preblend properties (GTR 100 phr, polymer 40 phr, promoter 3 phr, exudation test after 24 hrs).

Composition	GTR-filled Batch - Control	Functionalized GTR	Functionalized GTR re-milled
Promoter	No	Yes	Yes
Discharged stock - form	Flakes	Slab/Big pieces	Coherent Slab
Max torque in mixer, kW	8.9	11.3	9.7
Sheet surface skin rating	2E	5D	8B
Dispersion visual rating*	1	5	7
Oil migration, uncured, rating	Medium	no	no
Green strength, MPa	N/A**	3.6	4.3
Viscosity ML 125°C (1+4)	73	57	48
MDR 143°C, TS2, min	6.5	6.3	6.4
Tear - Type C, N/mm	17	23	27
Modulus 300%, MPa	8.8	10.7	11.2

* Phillips Dispersion test - visual rating from 10 (Superior) to 1 (Inferior).
**N/A -not applicable – easily destructed

The GTR-filled batch (Table 4) was discharged from the mixer in a flake form. After rolling, it formed a sheet with a 'sharkskin' surface, with oil migration on the surface of the uncured sheet. The remaining visible large grains in the GTR-filled blend evidenced that initial aggregates did not broken while mixing. The GTR-functionalized stock was discharged in the form of cohesive slab/big pieces. After re-milling the slab, the size of the remaining visible grains was sharply reduced. As shown in Table 4, this blend and especially re-milled stock demonstrated improved dispersion rating, a lower viscosity, an uncured green strength, and a more regular surface skin. The re-milling step resulted in the improved of dispersion index, surface skin quality, tear, and abrasion resistance. Preblend comprising up to 60-70 phr of GTR can be used "as is" where the addition of curing group and filler were calculated on 100 phr rubber hydrocarbon. The final compound presented a coherent rubber blend.

4.5. Effect of reinforcing CB and processing parameters on properties. Indicative rubber formulation was designed for premium value rubber parts, specifically the tire base/sidewall composition given in Table 5. The compound comprised NR/BR, CB N375 - 50 phr, homogenizing resin 5 phr, processing aid 2 phr, GTR, or GTR-modified preblend, sulfur 1.5 phr, TBBS 1.2 phr.

Table 5 – Effect of GTR-functionalized preblend on the workability of the tire formulation.

Composition	NR/BR-reference	GTR-filled	GTR-functionalized
Virgin Elastomer, phr	100	100	90
Ground rubber TR-40B, phr		24	
GTR Preblend, phr			40
GTR content in blend, phr			24
Surface skin/Edge, rating	10A	4D	9B
Viscosity 125°C ML (1+4)	64	76	68
MDR 143°C, TS2, min	6.3	5.8	6.0
Mixer max torque, kW	11.5	13.9	11.0
Mechanical properties			
Tear - Type C, N/mm	79	55	91
Abrasion loss, mm3	64	76	60

GTR-filled batch (GTR added without promoter) had an irregular surface skin as showed in Table 5. The poor dispersion (remaining visible large grains} and surface skin evidenced that under shear force, large aggregates did not convert into smaller size. It was observed that the addition of active CB suppressed a GTR modification that expressed in rough surface skin, in a lower tear and abrasion resistance that verified worse integrity.

The separated preparation of GTR-functionalized preblend with the following incorporation of base elastomers, reinforcing CB, homogenizer, antidegradants, and other additives into the final batch enhanced the workability. The size of the remaining visible grains was sharply reduced; the technical result was realized in an improved flow, a better scorch resistance, a regular surface skin of roll-processed web, all of which are the key factors in promoting a coherent blend. Functionalization appears to be a more significant factor than GTR size in positive effect on abrasion and tear resistance compared to the control virgin NR/BR batch including improved scorch resistance. This final blend had an unexpected integrity effect because of the compatible and co-cured integral macro-composite.

4.6. *Effect of promoter and soft carbon black simultaneous addition***.** The another compounding tool – simultaneous a GTR functionalization with a promoter, addition of a soft CB and other additives - stock discharging was presented in Fig.2. This feasible option was studied on the rubber compound produced on Banbury 160L. Indicative medium-value rubber formulation and its properties were presented in Table 6.

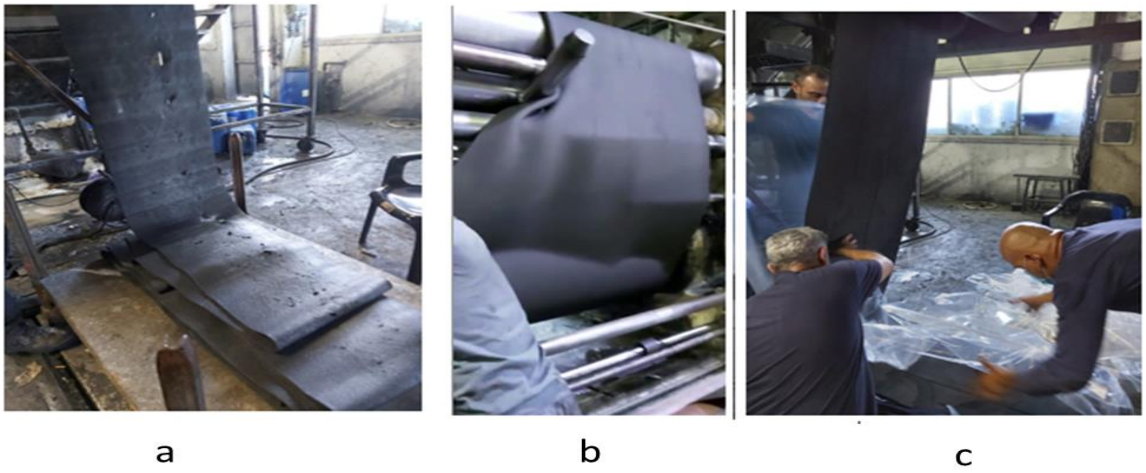

Fig. 2 – Steps of compounding GTR-functionalized compounds with soft carbon black

a) Incorporation of GTR and components, 'defects' on sheeting surface
b) Re-milling process
c) Sheeting after re-mill, regular surface skin.

As shown in Fig 2, the first roll-processed step (a) after incorporation of GTR, softeners evidenced the surface skin defects as result of poor dispersion and low cohesion of web. While re-milling (b) and after re-mill (c) the web had a regular surface skin. The re-milling step eliminated a heterogeneity, enhanced the dispersion index, surface skin quality.

. The indicative GTR-functionalized formulations shown in Table 6 comprised the elastomer 40 phr, GTR-100 phr, promoter 3 phr, soft carbon black SRF N-772 50 phr, also softener, processing aid. Elastomer, GTR, softener, CB and promoter were added together.

Table 6 – Effect of GTR-functionalized blend on the workability of batches with soft CB

Processing properties	NR/BR reference	TR-40TK	TR-40B
GTR type	no	Whole tire	buffing
GTR content in blend, phr	0	100	100
Virgin Elastomer in blend, phr	100	40	40
Max torque in mixer, kW	10	11	12.8
Batch form	Slab	Slab	Slab
Surface skin/Edge/ rating	10A	8C	9B
MDR 150^{o}C, ML dNm	2.7	2.5	2.6
Mechanical properties			
Tensile strength, MPa	15.8	11.9	13.3
Elongation, %	474	325	306
Tear - Type C, N/mm	43	49	54
Abrasion loss, mm3	232	263	222

The GTR-functionalized blends based on the tread TR-40B and whole tire TR-40TK feedstocks with optimal ratio GTR-polymer-softener demonstrated in Table 6 the satisfactory workability and mechanical properties, The technical result realized in the processing viscosity, slab form, regular topography of roll-processed, self-supported web characterized by green strength, also excellent indicators of integrity – tear and abrasion resistance**.**

5. An assumed mechanism for functionalization pattern was based on the steps:

The use of a rubber-functionalized promoter and softener allowed to overcome the heterogeneity and incompatibility of the GTR. Functionalization *in-situ* promoted a reducing the gel content (Tables 1 and 3), disintegration of large size particles and oxidation of network yielded in smaller interconnected phases. The compatibility of the blend components provided a better GTR bonding with the matrix and co-curing with elastomer matrix and an integrity.

The uptake (incorporation) comprised wetting, and distribution of GTR into the polymer matrix.

The softener sorption step – melt-shear swelling (physical route), where GTR was swollen.

The reactive step – thermo-oxidative shear (chemical route) converted the GTR into core/shell configuration. The swelling gradient changed a macro-composite from the intact GTR core phase to the gel-like shell (interphase), and elastomeric matrix phase.

The monolithic encapsulation. The fragments transformed into the macro-gels that were encapsulated into the polymer matrix and yielded smaller interconnected phases in a bulk. The encapsulation was an essential factor that complied with the criteria flow and viscosity.

Dispersive mixing (*re-milling)* intended to the breakdown of the weakened viscous agglomerates under the repeated stretching to eliminate a gross heterogeneity.

Re-curing of functionalized macro-gels retained up to 85% of initial thermoset GTR gel, resulted in rise of tear and wear resistance that explained by hybrid heterogeneous network in terms of sulfidic crosslink including dendrite (macro-gel) spring structure.

It is essential to take into account that the ELT used in a broader framework was defined by the direct incorporation of ambient grinding GTR in the elastomer blend, with retention of processing properties. The use of a rubber-functionalized promoter, softener allowed to overcome the heterogeneity of the GTR by thermo-oxidative mixing to maximize the conversion of a phase-segregated GTR-filled blend into a coherent GTR-functionalized macro-composite. This simple but radical approach opened the door to the ambient GTR with useful processing and mechanical properties through the disintegration of large size GTR. The swelling and oxidative degradation of a network generated the functional groups on the GTR surface and its conversion into compatible and malleable compound.

6. Summary and recommendations

The ambient macro-sized GTR had not typically broken the mixing shear, and the macro-composite bulk heterogeneity caused the ‘sharkskin’, and increased the viscosity of the macro-composite. The GTR incompatibility and absence of co-curing adversely affected the fatigue and wear resistance at loading more than 5 phr.

Thermal GTR shear-induced functionalization resulted in the disintegration of GTR aggregates due to oxidation of the GTR surface network and swelling gradient, assisted in compatibility and co-curing with elastomer matrix. The resulting GTR-functionalized macro-composite comprised an unsaturated elastomer and a co-cured GTR at any ratio, retaining the excellent initial tire properties.

Functionalization appeared to be a more significant factor than GTR amount and particle size, due to reducing of gel content, formation gel-like shell capable of co-curing. It improved the workability, abrasion, and tear resistance compared to the GTR-filled blend and the virgin elastomer based tire indicative compound. The enhanced dispersion and lower grain size, flow criteria, a roll-processed, self-sustained web with regular surface skin verified the integrity of an uncured blend as well as integrity criteria of tear and abrasion resistance. Workability and integrity control indicators were selected.

This cost-efficient process was easily integrated into the rubber compounding on the standard internal mixer, cancelled the reclaiming, decreased operational and compound expenses with a broader framework of their sustainable use. The mild temperature processing eliminated the toxic gases release.

This work conceptualization, methodology, investigation planning, formal analysis, writing, performed by M.Z.R

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