



## Investigation of abiotic degradation of tire cryogrinds

Jomin Thomas<sup>a</sup>, Seyed Kasra Moosaviani<sup>b</sup>, Teresa Cutright<sup>b,\*</sup>, Coleen Pugh<sup>c</sup>, Mark D. Soucek<sup>a</sup><sup>a</sup> School of Polymer Science and Polymer Engineering, University of Akron, Akron, OH 44325, United States<sup>b</sup> Department of Civil Engineering, College of Engineering and Polymer Science, University of Akron, Akron, OH 44325, United States<sup>c</sup> Department of Chemistry and Biochemistry, Wichita State University, Wichita, KS 67260, United States

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## ABSTRACT

The abundance of microplastics found in the environment is a major cause of concern. Tire tread particles containing additives such as curing accelerators and antioxidants, can be a major source of elastomer pollution in the environment. Such tire particles combined with road pavement particles are referred to as tire and road wear particles, TRWP. The environmental availability from parent elastomers and the release of additives in the process of abiotic degradation were evaluated using freeze-thaw, wet-dry and accelerated UV-weathering experiments. Acceleration factor determination tests were conducted to correlate UV-exposure to the natural aging in the environment. Freeze-thaw testing showed many additives such as diphenyl guanidine (DPG), benzothiazole sulfenamide (BTS) and para-phenylene diamine (6 PPD) as tetrahydrofuran leachates and BTS transformation products. Further, UV exposure equivalent to 1.5 yr., 3 yr. and 5 yr. aging resulted in the formation a combination of ketones and carboxylic acids for styrene butadiene rubber (SBR), natural rubber (NR), and butadiene rubber-based tire cryogrinds. Attenuated total reflectance- Fourier- transform infrared spectroscopy (ATR-FTIR) was used to detect the degradation of the elastomers on UV-exposure while gas chromatography-mass spectroscopy (GC-MS) was used as a nontargeted, suspect screening analysis technique. The degradation intermediates and leachates identified using GC-MS represents useful data for the life cycle analysis of the functional polymers and additives and their possibility of environmental release.

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## 1. Introduction

The study of microplastics have been an emerging area of research in the field of sustainability [1]. Risks associated with microplastics such as neurotoxicity, toxicity through oxidative stress, metabolic disturbances, inflammatory lesions and increased cancer risk have been widely studied [2,3]. In addition to the common plastics, rubber or elastomers are also part of the set of constituents causing negative environmental impact. Although rubber does not fall under the technical definition of a plastic, many researchers have erroneously reported rubber or elastomer based degradation and leachate components as microplastics [4]. Tire and road wear particles (TRWP) are an understudied elastomer component and is gaining huge momentum for research from several tire companies and environmental agencies [5]. The tire formulations have elastomers as the major components combined with many

additives and vulcanizing agents [6]. The additives primarily include curing accelerators and antioxidants among several others. Tire tread wears off with time due to friction with the road and the following tire debris subsequently combine with the road pavement particles to form the tire and road wear particles [7]. The effect of TRWP on air and water have been reported in many studies [8–13]. For instance, Maceira et al. [14] reported a 0.003% health risk (negative effect on the liver and kidneys and respiratory irritation) from derivatives of benzothiazole in atmospheric samples. Studies have also shown that TRWP can reach estuary and water bodies and cause toxicological problems on aquatic life [11,15]. Using elastomer-specific pyrolysis markers and other sensitive analytical capabilities, TRWP quantification has also been reported [12,13]. In soils, TRWP has been detected as the parent compound, as hydrolysis or transformation products or as leachates of tire constituents [15,16]. Quantification of TRWP in soil systems often requires the use of pyrolysis-based analytical techniques. Standardized analytical techniques and generalized protocols are needed to establish reliable TRWP related research outcomes across the globe

\* Corresponding author.

E-mail address: [tcutrig@uakron.edu](mailto:tcutrig@uakron.edu) (T. Cutright).

[4,17]. ISO technical specifications relevant to TRWP, in terms of mass concentration determination using pyrolysis-GC/MS [18], environmental fate [19], and the physical and chemical characterization [20], has been developed recently. These specifications serve as a great foundation to the relevant and upcoming TRWP research which has gained huge attention in the tire industry and the academia.

We aim to study the abiotic degradation of tire particles to serve as a major precursor and novel database in the TRWP research. Grinding materials at liquid nitrogen temperature (i.e., cryogrind) has been recognized as an efficient particle size reduction method [21] and was used in this research for obtaining the tire tread cryogrinds of different formulations. Tire cryogrinds were used for obtaining chemical specific data on the availability of susceptible additive-related chemical constituents found in TRWP combined with their potential environment release. Several previous studies concentrated on assessing the environmental impact potential using accelerated weathering tests, column leaching tests, extractions, and aerobic incubators [7,22]. For instance, Unice et al. [16] studied the fate of additives like benzothiazole, diphenyl guanidine and para phenylene diamine using column leaching experiments and provided a database for possible transformation products. Further, Eisentraut et al. [23] reported the effective use of thermal extraction desorption gas chromatography (TED-GC-MS) for identifying and quantifying TRWP. They were able to disseminate a list of possible degradation products of elastomers and tire specific marker compounds. There is also report of use of Pyrolysis-GC/MS marker analysis for TRWP quantification by Unice et al. [24]. Numerous research has been published on the effects of UV, ozone, temperature etc. in regards to the basic elastomer components [25–28]. Free radical mediated reactions which are initiated by solar irradiation were the prevalent photo-degradation pathway for elastomers [29]. The most commonly reported photooxidation degradation intermediates of elastomers were carboxylic acids, ketones and epoxides [25]. Even with well-established rubber degradation pathways, the abiotic degradation of “real-life” tire particles and elucidation of specific intermediates is limited. As per our knowledge, there is no reported literature on the study of assessment of the effects of abiotic degradation on the tire cryogrinds. Further, this study proposes methodology to characterize and integrate the environmental accessibility of the tire particles with the help of laboratory-scale data. Our objective was to elucidate the degradation intermediates formed due to the abiotic degradation of tire cryogrind. We hypothesized that UV-weathering impacts the TRWP degradation more significantly than freeze-thaw and wet-dry cycles. There is plethora of research ongoing and reported separation of tire wear particles from environmental samples [30–33]. The results reported in this paper will be essential to better identify the TRWP concentration and tire-based degradation intermediates in the soil, and to develop kinetic degradation rates for evaluating the fate of TRWP in soil systems.

## 2. Methods and materials

### 2.1. Test tire preparation and TRWP collection

Using the common constituents in a tire formulation (elastomer, vulcanizing agent, accelerating agents, antioxidants, fillers), five industry standard test tire samples were used for the research. The specific formulation of the passenger car with silica filler (PC-Si), passenger tire with carbon black filler (PC-CB), natural rubber truck tire (T-NR) and styrene butadiene truck tire (T-SBR) cryogrind is given in Supplemental Table S.1. Baseline tires cryogrind samples analogous to TRWP were processed in the industry in the presence of nitrogen at freezing temperatures. One g subsamples were subjected to sequential sieving, using stainless steel sieves (sieve

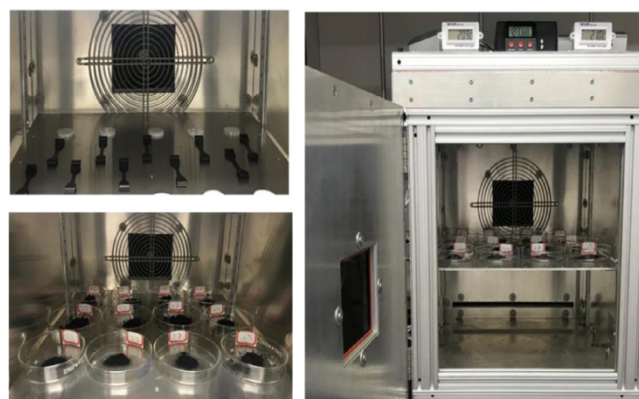


Fig. 1. Pictures of the artificial aging UV chamber.

no. 4, 10, 16, 20, 40, 50, 60, 70, 100 and 200), to separate the tire cryogrind into appropriate size fraction range and to estimate the particle size distribution.

### 2.2. Artificial weathering

Artificial weathering mainly involved the abiotic degradation experiments to expose the tire cryogrind to similar environmental conditions. Less aggressive abiotic weathering processes included freeze-thaw (F-T) and wet-dry (W-D) cyclic experiments according to the principles of ASTM D7792 [34] and ASTM D4843 [35], respectively. F-T tests involved 25 cycles where one cycle constituted of cryogrind (1 g) kept in sealed vials for 24 h at  $-15^{\circ}\text{C}$ , followed by thaw of 24 h at room temperature. Similarly, W-D tests involved 25 cycles where one cycle constituted of Cryogrind (1 g) kept in sealed vials for 24 h at  $60^{\circ}\text{C}$ , followed by thaw of 24 h at room temperature. The major abiotic weathering processes (ultra-violet (UV) light, ambient heat, and moisture) were simulated in a UV test chamber fabricated at the University of Akron according to the principles of ASTM G151-16, D4329-13 and ISO 4892-1, 4892-3 [36–40]. One g of each tire cryogrind in triplicates were placed in glass petri dishes (90 mm diameter and 15 mm depth) transparent to UV light, supplied by UVB-313 nm with an irradiance of  $0.425\text{ W/m}^2$ . The cryogrind samples were spread manually by a spatula and evenly distributed. The V test chamber is as shown in Fig. 1.

A single weathering cycle included 8 h of UV exposure followed by 4 h of condensation period with the target particle temperature at  $25^{\circ}\text{C}$  at 22% relative humidity. Tensile properties (100% modulus and elongation at break) of a reference rubber sample (a representative natural rubber-based tire formulation, refer to the supporting Fig. S.2) were evaluated to determine the acceleration factor of the UV-chamber. The tensile properties data were evaluated and compared against the tire data obtained from Phoenix, Arizona which were subjected to natural aging. Tire cryogrinds were aged for 700, 1000 and 2100 h. After 2100 h of UV exposure, cryogrinds were subjected to another cycle of F-T and W-D.

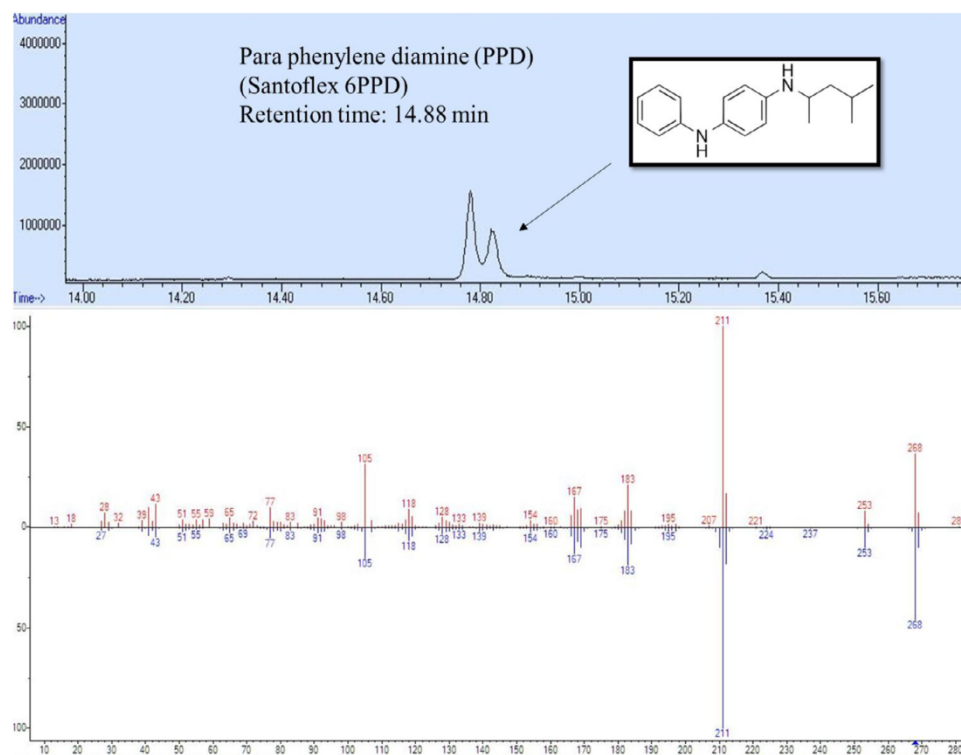
### 2.3. TRWP and tire cryogrind extraction

Fresh tire cryogrinds samples and aged samples of the cryogrind were extracted and subsequently subjected to GC-MS testing. Approximately 1 g of tire cryogrind were Soxhlet extracted for 48 h using analytical grade tetrahydrofuran (THF) solvent. The extract was later evaporated to dryness, and the residuals were dissolved in THF to a concentration of 3 mg/mL. THF selected as it was judged to solubilize a relatively broad range of polar and non-

**Table 1**

Mass loss of cryogrind samples after F-T and W-D tests. Averages based on triplicate samples.

Sample	F-T Average Mass loss (%)	W-T Average Mass loss%
Passenger Car with Silica filler (PC-Si)	-0.1	2.62
Passenger Car with Carbon black filler (PC-CB)	-0.1	2.53
Truck Tire with Natural rubber (T-NR)	-0.1	1.19
Truck Tire with Styrene Butadiene rubber (T-SBR)	-0.17	1.38

**Fig. 2.** GC-MS spectra and NIST database comparison of PPD observed in Passenger car cryogrind with silica filler (PC-Si): Post F-T Tests.

polar compounds while also adequately swelling the cured cryogrind to enhance recovery. For instance, Dierkes et al. [17] used THF for extracting low concentrations of polyethylene, polypropylene, and polystyrene for their method development of analyzing microplastics. An earlier study by Avagyan et al. [41] found that THF yielded higher extraction efficiencies of BT than methyl tert butyl ether. Recoveries of 72–102% was also observed for microextraction of BT and benzotriazole when used with ultrasound [42]. It should be noted that the extractions were carried out in THF solvent, and therefore do not translate to what would occur during environmental leaching in water.

#### 2.4. Identification and quantification of tire compounds and transformation products

FTIR spectroscopy was performed on a Thermo Scientific Nicolet i50 with Attenuated total reflector attachment (ATR-IR). Data spacing is  $4\text{ cm}^{-1}$ , resolution is 32. GC-MS analysis of the tread and roadside soil samples extracts was performed by the GC-MS system (Thermo ISQ™ QD Single Quadrupole) equipped with a TG-5MS column ( $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ). The conditions were set at electron ionization mode with MS transfer line and ion source temperatures of  $300\text{ }^{\circ}\text{C}$ , mass range ( $35\text{--}450\text{ amu}$ ), oven temperature range and initial temperature of  $15\text{ }^{\circ}\text{C min}^{-1}$  and  $60\text{ }^{\circ}\text{C}$ , inlet temperature  $300\text{ }^{\circ}\text{C}$ , split flow  $30\text{ ml min}^{-1}$ , and sample injection volume  $1\text{ }\mu\text{l}$ . All the chemicals used were of analytical grades and used as received.

### 3. Results

#### 3.1. Tire cryogrind particle size

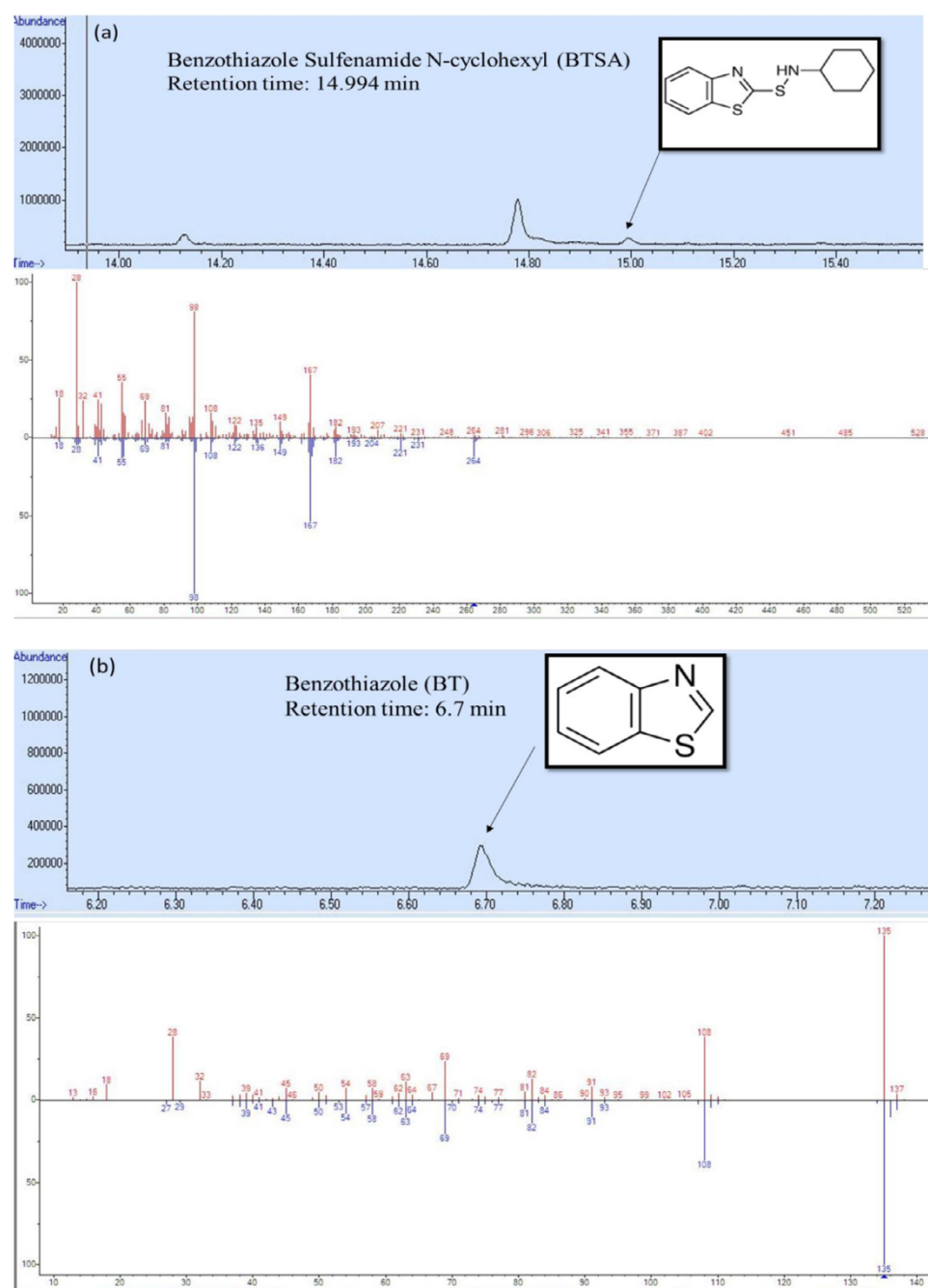
Over 98% of the cryogrind passed through the 2 mm opening. The passenger carbon black tire tread had the smallest cryogrind size with only 57% of the sample passing through the 0.425 mm sieve opening; whereas 38% and 3% of the passenger silica and SBR truck cryogrinds, respectively passed through the same opening. Supplemental Fig. S.3 shows the particle size distribution of the cryogrind with the cumulative percent passing. The smallest particle sizes were exhibited with the passenger silica treads. One percent of the passenger silica cryogrind was retained by a 0.74 mm sieve. Natural rubber truck tire tread was too sticky to yield reliable particle size results. The results were comparable to the TRWP size reported in the literature, which varies from 1 to 5 mm [12,43,44]. However, the results were higher than the 100–400  $\mu\text{m}$  that was reported in studies of tire wear particles obtained from road simulators [7,12].

#### 3.2. Aged tire cryogrinds and TRWP content analysis

##### 3.2.1. Freeze thaw (F-T) and wet-dry (W-D) experiments

Initially, the cryogrind were subjected to the less aggressive environmental weathering experiments of F-T and W-D. Although less aggressive, the F-T and W-D tests did evaluate the effect of temperature ranging from  $-15\text{ }^{\circ}\text{C}$  to  $60\text{ }^{\circ}\text{C}$  on the tire cryogrind.





**Fig. 3.** GC-MS spectra and NIST database comparison of observed Benzothiazole Sulfenamide leachates and intermediates (a) Benzothiazole Sulfenamide N-cyclohexyl, (b) Benzothiazole and (c) Benzothiazole Amine, N-phenyl.

As shown in Table 1, most of the samples lost mass; a negative mass loss value corresponds to mass gained. Table 2 summarizes the leachates and intermediates identified by GC-MS (Figs. 2–4) for the F-T and W-D experiments. Several leachates were present in a few of the cryogrinds. Luongo et al. [45] also previously found that benzothiazole tends to leach out easily. Diphenyl Guanidine (DPG) and *p*-phenylenediamine (PPD) leached from passenger car treads with silica filler after freeze-thaw cycles. Similarly, unreacted benzothiazole (BT) and various transformation products from VANAX NS leached from truck tire cryogrinds, especially after freeze-thaw. The leachates and intermediates are summarized in the Table 2 with the respective GC-MS spectra and database comparison in Figs. 2–4. Butylated hydroxytoluene (BHT), which was present in all the GC-MS results (retention time 9.7 min), is an im-

purity that was present as a stabilizer in the THF used for extractions.

Leachates from antioxidants and curing accelerators in the tire formulation were the major compounds observed during the F-T and W-D testing. This includes para-phenylene diamine, diphenyl guanidine and benzothiazole sulfonamide constituents. Several studies report such leachates found in water bodies [14,43,44]. The environmental release of these compounds are thus a cause of concern and sustainable intermediates with appropriate functional properties need to be formulated to overcome this challenge.

### 3.2.2. Accelerated UV-weathering experiments

The average UV-chamber acceleration factor was found to be 13 times the natural age (Fig. 5). Thus, the UV-exposure testing that

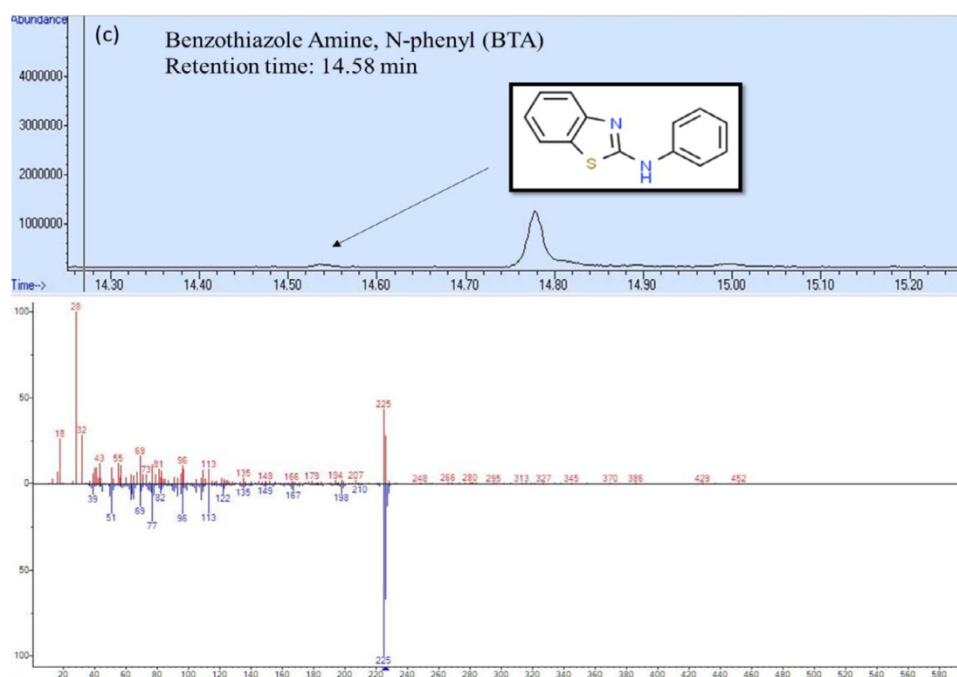


Fig. 3. Continued

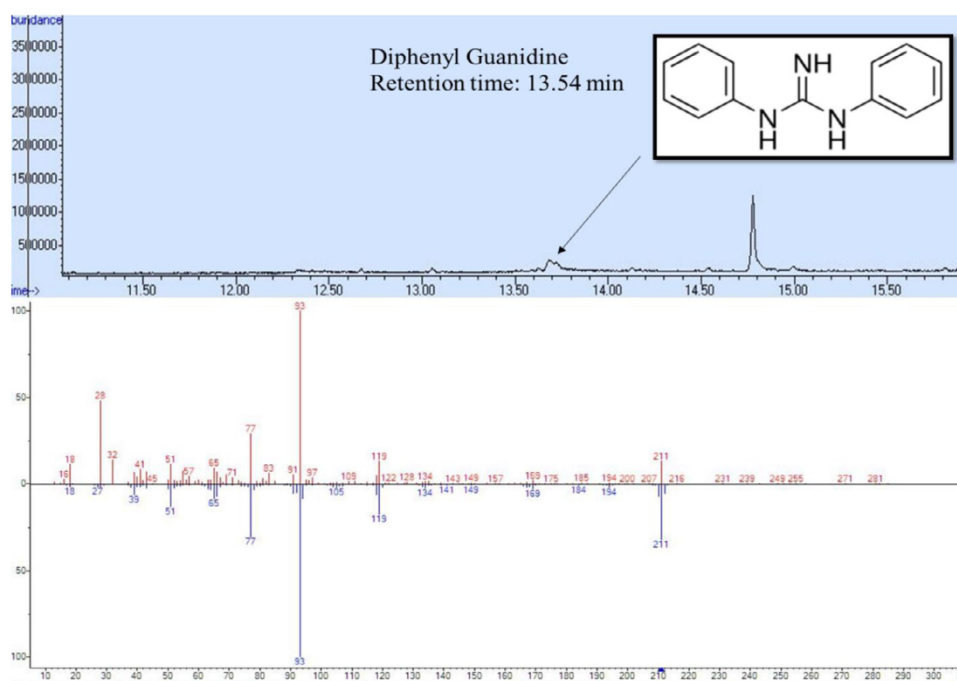


Fig. 4. GC-MS spectra and NIST database comparison of DPG observed in Truck tire-SBR Post F-T Tests.

Table 2

Leachates and transformation products identified in the GC-MS results after Freeze-thaw(F-T) and Wet-dry(W-D) tests.

Possible Transformation product/Leachate and Retention times	Degradation Mechanism	Samples/ Experiment	Components and Possible source
Diphenyl Guanidine (13.54)	Leachate	PC-Si and T-SBR: F-T PC-CB: W-D	Diphenyl Guanidine (DPG)
Para Phenylene diamine (14.88)	Leachate	PC-Si: F-T	Para phenylene diamine (PPD) (Santoflex 6PPD)
Benzothiazole Sulfenamide N-cyclohexyl (BTSA) (14.994)	Thermal	T-NR: F-T	Benzothiazole Sulfenamide (VANAX NS)
Benzothiazole (BT) (6.7)	Thermal	T-NR and T-SBR: F-T	Benzothiazole Sulfenamide (VANAX NS)
Benzothiazole Amine, N-phenyl (BTA) (14.58)	Thermal	T-SBR: F-T	Benzothiazole Sulfenamide (VANAX NS)

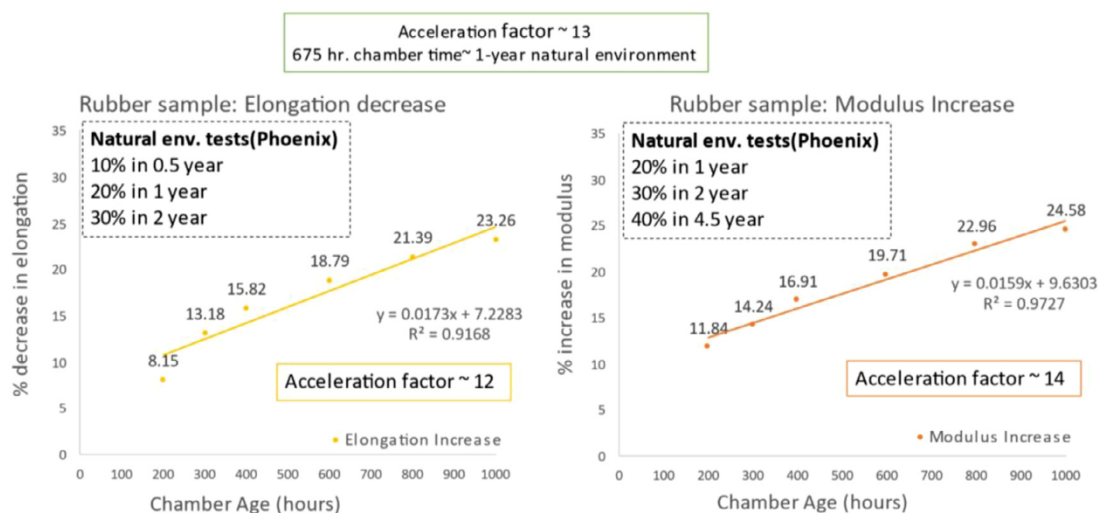


Fig. 5. Acceleration factor measurement for rubber dumbbell reference material.

was conducted for 700, 1000 and 2100 h, which was equivalent to 1, 1.5 and 3 years in natural environment, respectively. The acceleration factor yielded slightly longer exposure times than Unice et al. [16] who achieved 3 years aging after 1191 h, in a chamber equipped with 340 nm UVA UV light.

Critical analysis of the infra-red spectral peak changes was evaluated as a sign of probable degradation of the tire cryogrind. We evaluated the following peaks as an indicator of the photo oxidation of the tire cryogrind; New peaks of carboxylic acids at  $1710\text{ cm}^{-1}$  and disappearance of peaks of double bonds of  $\text{CH}=\text{CH}_2$   $1050\text{--}1090\text{ cm}^{-1}$  and  $890\text{ cm}^{-1}$  [46]. As shown in Fig. 6, PC-Si and T-NR showed signs of degradation at a 700 h. exposure which is equivalent to one-year natural aging. However, T-SBR and PC-CB did not show any degradation until 1000 h. as shown in the Fig. 7. Even at 1000 h. and 2100 h. there is only a minor presence of peak that appears at  $1710\text{ cm}^{-1}$ . It can be attributed to the highest percentage of styrene butadiene rubber in the respective tire formulations which are less susceptible to UV-weathering compared to natural rubber. Osswald et al. [26] reported that the higher double bond content and the aromaticity in SBR made it more resistant to weathering than natural rubber. However, the presence of fillers like carbon black in the tire cryogrind interfered with the analysis due to the near complete IR light absorption as previously reported [43]. Carbon black also decreases the impact of UV exposure. For instance, Sahu et al. [47] reported that carbon black in high density polyethylene decreased UV weathering of solar photovoltaic structures. Although effective at mitigating some of the impact from UV exposure, Kim et al. [27] recently reported that carbon black might also be released through continuous abrasion of tire particles.

After the accelerated weathering tests, GC-MS results showed the presence of several degradation intermediates in all the cryogrinds. Sufficient heating helps long polymer chains break and generate radicals [48], which react with oxygen to form peroxy radicals and then hydroxy peroxides upon hydrogen abstraction. Further, they dissociate into alkoxy, hydroxy radicals and several intermediates are formed [25] as shown in Fig. 8. Ketones and chain scission products like acids are also produced [25], and epoxides are also formed by decomposition of the peroxy alkyl radicals [49]. Aldehydes, carboxylic acids, and ketones are the most prominent and possible tire degradation intermediate due to the photo-oxidation of the elastomers after the two exposure times corresponding to 1-year and 3-year natural age. The 3-year natural age results also provided a way to access the impact of weathering time on the tire cryogrind. As expected, more carboxylic

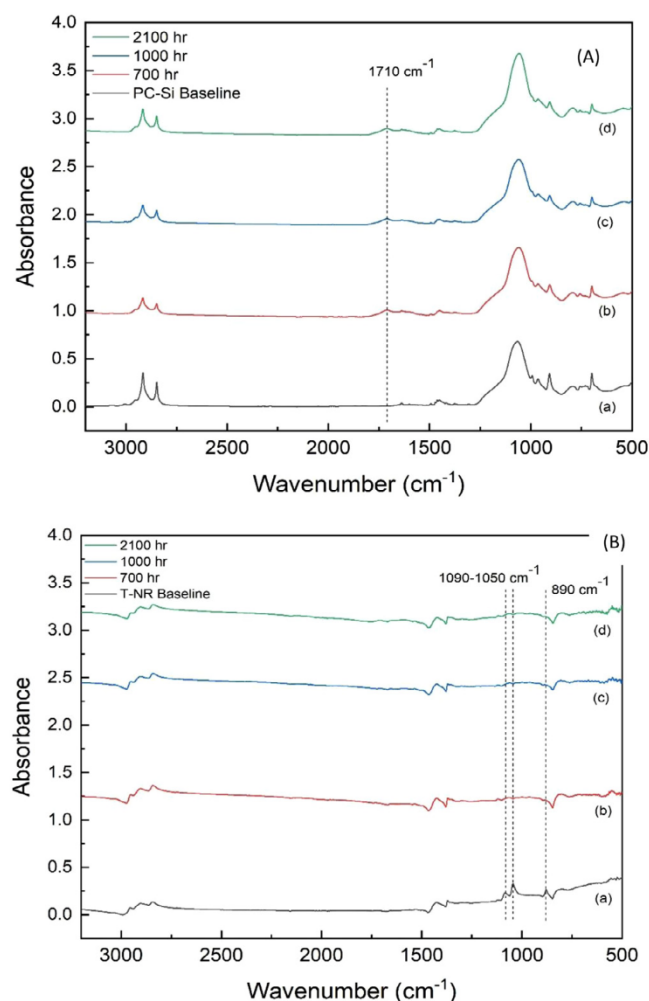


Fig. 6. Infra-red Spectra of (A) PC-Si cryogrind and (B) T-NR cryogrind samples after UV weathering at (a) 0 h. (b) 700 and 1000 h. and (c) 1000 h. and (d) 2100 h.

acid degradation intermediates were formed after extended UV-weathering times. This observation can be attributed to the fact that under prolonged photo-oxidation, ketone groups can be converted to carboxylic acid groups by Norrish type 1 reactions [25].



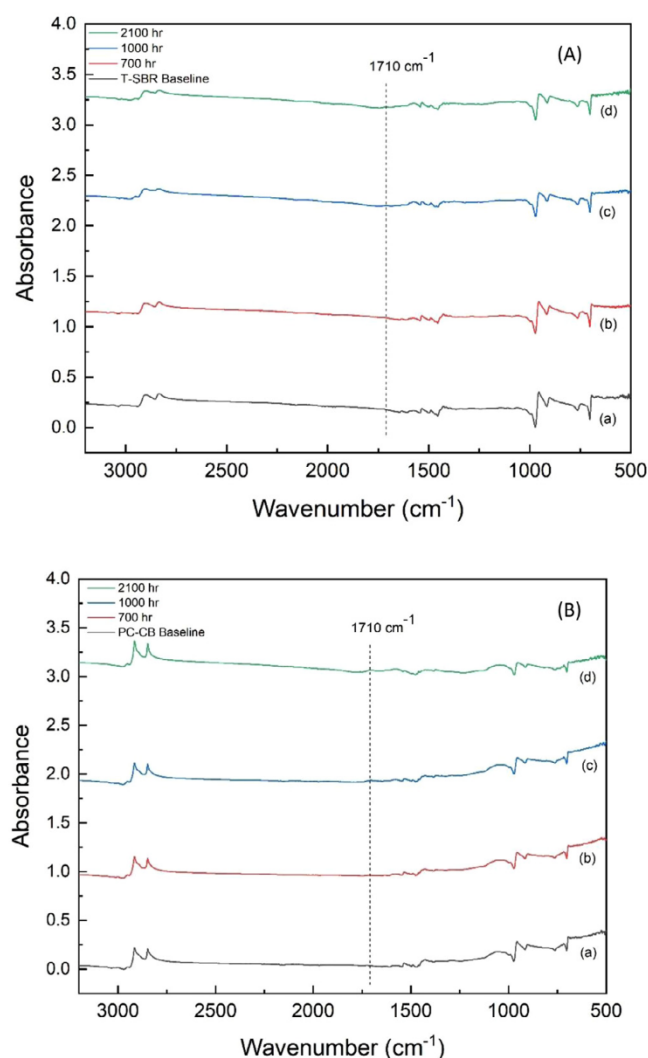


Fig. 7. Infra-red Spectra of (A) T-SBR cryogrind and (B) PC-CB cryogrind samples after UV weathering at (a) 0 h, (b) 700 and 1000 h, and (c) 1000 h. and (d) 2100 h.

The pertinent photo-oxidation degradation mechanisms of elastomers in tire particles are shown in Fig. 8.

The leachates (DPG, BT and PPD) found in the Soxhlet extracted samples of cryogrinds after F-T and W-D tests, were not present after UV-exposure. Further, the carboxylic acids, ketones and epoxides were not observed in the baseline/non-aged tire cryogrind samples, demonstrating the effect of thermal and photo oxidation on the tire particles. All the distinguishable peaks detected in the GC-MS results were analyzed and the compounds with more than 60% confidence in NIST database prediction were tabulated. All peaks, excluding those corresponding to THF impurities, are summarized in the Table 3.

Carboxylic acids, ketones and epoxides were observed as the degradation intermediate after the accelerated UV-exposure tests. This was expected based on the established photooxidation mechanism and reaction pathways of elastomers discussed earlier. The impact of temperature on the weathering of cryogrind was assessed by subjecting the UV-weathered cryogrind to another cycle of wet-dry and freeze-thaw tests. It was observed that the wet-dry testing after UV-exposure resulted in further degradation of the cryogrind (Table 4). This was expected as it was subjected to a temperature of 60 °C, which was higher than the temperature of the UV-chamber testing (25 °C). Even though natural conditions do not reach such a high temperature frequently, it is analogous

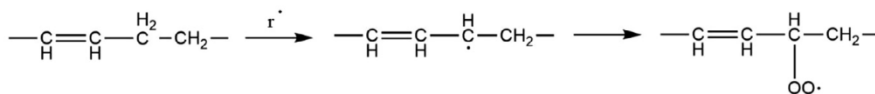
to summer temperatures in conjunction with temperature exhibited during friction that generated TRWP [50]. Ketones, epoxides, and carboxylic acids were again identified as the degradation intermediates from the elastomers and are shown in Table 4. The truck tire natural cryogrind was the most susceptible to degradation followed by the consumer car with silica as filler. However, none of the UV-weathered cryogrind yielded any degradation intermediates or previously found leachates (BT, PPD and DPG) after F-T and W-D.

Among all the cryogrind tested in this research, the formulation with natural rubber showed the most susceptibility to photo-degradation by UV-weathering. This was first observed in the IR spectra changes and later corroborated by the higher number of degradation intermediates observed in all the GC-MS results. It was followed by the consumer car cryogrind with silica as the filler. The truck tire SBR cryogrind showed the least degradation susceptibility. This tendency can be attributed to the presence of styrene content and the rigid benzene rings in the SBR tire system coupled with the usage of functionalized SBR used in the tire formation [51]. However, the quantification of the degradation intermediates with possible kinetic rates are in progress in our lab and will be reported later in the future. Although PPD was observed as a leachate in the PC-Si cryogrind, 6 PPD-Quinone, an oxidation transformation product from 6-PPD (*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine), was not detected in any of the UV-weathered samples. This could be attributed to the lesser sensitivity of GC-MS used in our study, compared to the UPLC-HRMS. 6-PPD has become of significant interest to researchers and the tire manufacturing industry due to its aquatic toxicity as demonstrated by acute mortality in Coho salmon species [52]. We are currently evaluating the possible presence of 6 PPD-Quinone as a degradation product.

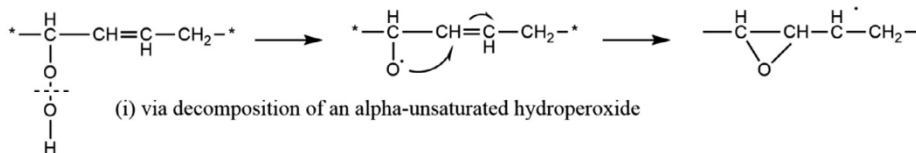
Our aim was to understand the degradation intermediate and leachates arising from tire particles in virtue of exposure to the natural conditions. Nevertheless, there were few limitations and simplifications in our analyses. One of the limitations of this research is the temperature range (25–30 °C) in the accelerated UV-weathering tests. Although it mimics the real scenario in the environment lesser, running the tests at higher temperature would help us get more transformation products, especially in terms of the degradation intermediates and transformation products of the leachates observed. Unice et al. [15] studied the accelerated UV-weathering at higher temperature and different UV light source (340 nm), but their research was concentrated on only three of the common additives used in the tire formulation and their degradation intermediates. Further, the weathered and characterized target analytes were of very low concentrations which made the detections difficult. The high temperature requirement makes exothermic oxidation unlikely under natural conditions. With pavements that are directly exposed to sunlight, slow thermal oxidation in concert with photo-degradation is a more probable situation. THF was used as the solvent for Soxhlet extractions based on literature showing its ability to extract even low concentrations of microplastics and tire related additive intermediates. However, THF extracts may not translate to “naturally occurring” leachates. The aging process implemented in this research was evidently effective considering that many THF leachates and degradation intermediates were identified in both baseline and freeze-thaw weathered cryogrind. The UV-weathered degradation intermediates showed that the dumbbell used for the acceleration factor determinations tests were a good representative of aging.

Overall, the study was able to identify the main leachates and degradation products of abiotic degradation of tire particles. Method improvement for artificial aging of laboratory surrogate tire wear debris and better reliability of field extractions to laboratory extractions are possible using the disseminated results. There is a technical data gap on artificial aging protocols of the

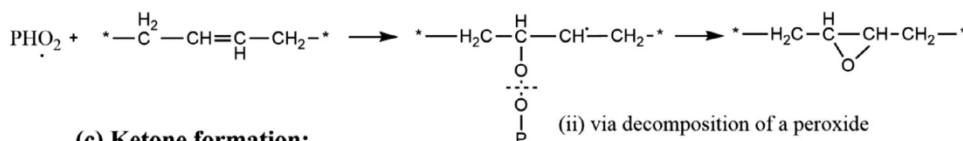
### (a) Peroxy radical formation from elastomers



**(b) Epoxide formation:**

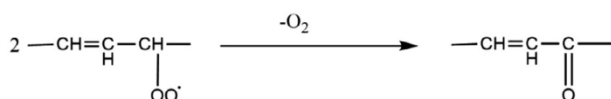


(i) via decomposition of an alpha-unsaturated hydroperoxide

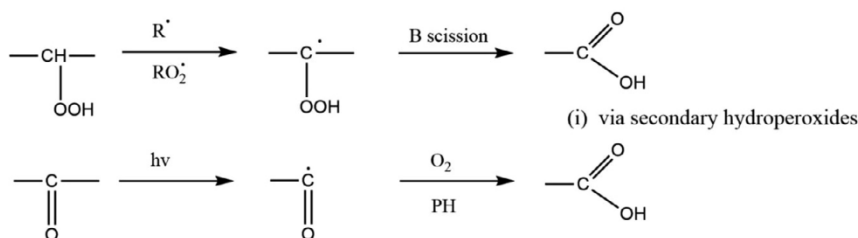


(ii) via decomposition of a peroxide

**(c) Ketone formation:**



**(d) Acidic groups/ chain scission products formation:**



(i) via secondary hydroperoxides

(ii) via Norris type I reactions on the ketonic groups

**Fig. 8.** Possible degradation pathway and mechanisms of elastomers post weathering tests.

Table 3

Intermediates identified in the GC-MS after accelerated UV-Weathering experiments.

Possible Transformation product/Leachate and Retention times	Degradation Mechanism	Cryogrind and exposure times.	Components and Possible source
1-hydroxy-2 pentanone (3.818)	Thermal photo-oxidation: Ketones	<b>1.5-Year Natural age</b> PC-Si, T-NR, T-SBR	Elastomers
Hexanoic acid, 3-oxo-ethyl ester (5.014)	Thermal photo-oxidation: Carboxylic acids	PC-Si	Elastomers
Ethane dioic acid, bis(3-methylbutyl) ester (5.938)	Thermal photo-oxidation: Carboxylic acids	T-NR	Elastomers
Butanoic acid, 2-propenyl ester (5.939)	Thermal photo-oxidation: Carboxylic acids	PC-Si and PC-CB	Elastomers
Benzothiazole 2-Butyl (6.7)	Thermal	T-NR and T-SBR	Benzothiazole Sulfenamide (VANAX NS)
Propanoic acid, 2-methyl, anhydride (4.325)	Thermal oxidation: Carboxylic acids	<b>3-Year Natural age</b> NR Truck tire and PC CB	Elastomers
Propanoic acid, 2-methyl, methyl ester (4.352)	Thermal oxidation: Carboxylic acids	CG UV	Elastomers
Propanoic acid, anhydride (4.375)	Thermal oxidation: Carboxylic acids	PC CB CG UV	Elastomers
Butanoic acid, 2, dihydroxyl propyl ester (6.993)	Thermal oxidation: Carboxylic acids	PC Si CG UV	Elastomers



**Table 4**  
Intermediates identified in GC-MS after the wet-dry tests on the UV-weathered cryogrind.

Possible Transformation product/Leachate and Retention times	Degradation Mechanism	Cryogrind and exposure times.	Components and Possible source
Propanoic acid, anhydride (4.375)	Thermal oxidation: Carboxylic acids	NR, PC Si CG UV (1.5-year Natural age + W/D)	Elastomers
Propanoic acid, 2-methyl, methyl ester (4.352)	Thermal oxidation: Carboxylic acids	NR, PC Si CG UV (1.5-year Natural age + W/D)	Elastomers
1,4-Butanediol diglycidyl ether (6.653)	Thermal oxidation: Epoxides	NR, PC Si CG UV (1.5-year Natural age + W/D)	Elastomers
Butanoic acid, anhydride (7.809)	Carboxylic acids	PC Si CG 1.5-year Natural age + W/D	Elastomers
4-Heptanone-3-ethyl (8.002)	Ketones	NR (1.5-year Natural age + W/D)	NR

tire wear particles and TRWP. Our aim was to fill this specific gap by identifying prospective degradation intermediates associated with aging of “real-life” tire particles materials. This is critical for the TRWP research involving environmental samples and could be helpful in establishing validated artificial aging protocols, especially of aged tires, for which very limited information is known on the intermediates. The major strength of our approach involves the high possibility of leveraging the tabulated degradation intermediates in the future tire wear degradation and TRWP studies. For any research involving separation of tire particles from environmental samples, the results discussed can be used as a tire-related specific marker compounds in GC-MS or HPLC. Future investigation in our lab following this work would be concentrating on the quantification and finding a kinetic rate for the degradation of the tire cryogrind and the TRWP.

#### 4. Conclusion

The results of cryogrind tested for evaluating their abiotic degradation helps increase the knowledge database of the possible degradation expected in TRWP in roadside samples. This information, coupled with advanced soil sample collection and separation techniques can be used to identify and quantify tire intermediates in soil samples. Further, the availability of functional chemical with their degradation intermediates, and the respective leachates from additives that might occur in the nature from tire particles were elucidated. The formulators in tire industry can adapt to sustainable alternatives of these compounds and a toxicology study of the found intermediates would be beneficial.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

**Jomin Thomas:** Formal analysis, Investigation. **Teresa Cutright:** Funding acquisition, Conceptualization, Project administration. **Coleen Pugh:** Funding acquisition, Conceptualization, Methodology.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.polymdegradstab.2021.109814](https://doi.org/10.1016/j.polymdegradstab.2021.109814).

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