Methods for CMTT Generation

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1 Tire Types

In November 2019, Cardno ChemRisk supported the generation of cryogenically milled tire tread (CMTT) particles on behalf of the Tire Industry Project (TIP). This report describes the methods utilized to generate CMTT particles. To generate CMTT, similar tire types were used as compared to the tires that were utilized for tire and road wear particles (TRWP) at the road simulator laboratory at Karlsruhe Institute for Technology (KIT). The selection of the three different tires types was intended to represent the basic characteristics of passenger car tires of different types, including winter and summer tires, as well as tires containing carbon black or amorphous silica as primary fillers (Table 1).

Table 1: Tires used for CMTT Generation.

Tire Name	Size	Season	Primary Filler
Pirelli Sottozero 3	205/55 R16	Winter	Silica
Michelin Primacy 3	225/55 R16	Summer	Silica
Saetta Touring 2 (Bridgestone)	235/60 R16	Summer	Carbon Black

Tread/sub-tread, color indicators (for tire production purposes), and conductive tread all exist on typical passenger tires. During TRWP generation, all of these portions are potentially released. For analytical purposes, it should be noted that the color indicators and conductive tread will typically have slightly different chemical compositions from tread.

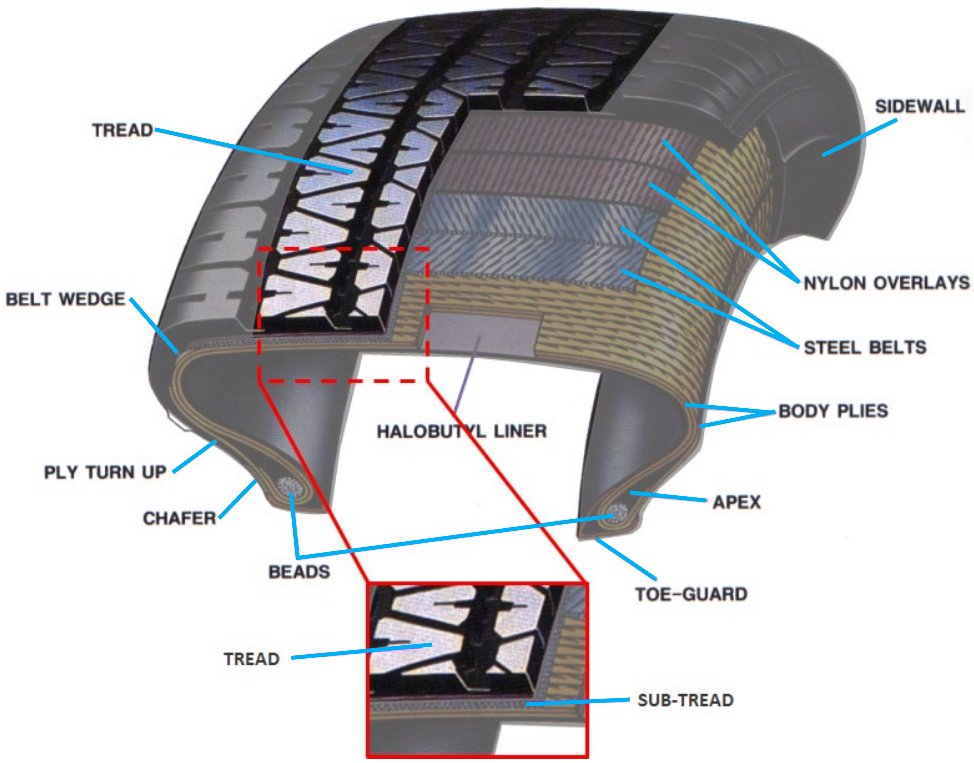
2 CMTT Generation

2.1 Tread Removal and Processing

The purpose of this report was to communicate methods that were utilized to generate cryogenically ground tread materials. In no way does this report represent an overview of safety protocols necessary to perform this work in a safe manner. It is the obligation of any person or entity to institute safety and health practices and to ensure compliance with any national regulatory conditions.

Figure 1 provides an overview of the different components of a tire. It should be noted that the compounds used for different parts of a tire (i.e. tread vs. sub-tread) can vary, so it is important to keep the tread portion separate during the removal process and prevent contamination from other sections of the tire. Under normal driving conditions, only the tread compound should be in contact with the road surface, therefore only the tread compound is needed for the CMTT generation.

Figure 1: Overview of tire components and location of tread.



The tread was removed from each tire according to Step 1 of Section 3 under Annex B of ISO 21461 with minor modifications. The surface of the tire can first be cleaned with compressed air or a cloth. Tread was removed from the top of the upper belt or top of the overlay from intact tires using an applicable cutting tool. The cross-section of the removed piece was inspected to ensure the absence of any materials that may contaminate the tread sample (i.e. portions of the tire from other components such as the sub tread or side wall). The serial side and non-serial side tread ribs were not removed with the tread to eliminate contamination from any other tire components that can be present at tread edges. Tread external surface was not removed. The underside of the tread was removed if tread base and/or overlay/belt components were observed. This was accomplished using the sectioning machine as noted in ISO 21461.

Strips of tread were then cut into 1 cm^3 pieces using a water jet machine (Jet-Edge) at Ilene Industries[1] (Shelbyville, TN). Any remaining tread material was cut using industrial scissors capable of sectioning rubber material to produce 1 cm^3 pieces (Figure 2). Each tire was processed separately so that the amount of mass from each tire type could be controlled for during CMTT generation.

Figure 2: Tire Tread was cut into small pieces (~1 cm^3).

[1] Ilene Industries contact – Jay Wilkerson: 1-800-251-1602

2.2 CMTT Generation and Mass Distribution

The 1 cm^3 pieces of tread were then sent to Pulva Corporation[2] (Valencia, PA) for CMTT generation in the ratio of 2:1:1 for Bridgestone:Pirelli:Michelin. This ratio is consistent with what was previously used for TRWP and was initially intended to represent the approximated market average of major passenger tire types. Five hundred grams of Pirelli tread, 500 grams of Michelin tread, and 1000 grams of Bridgestone tread were combined at Pulva and cryogenically ground using a Model A Hammer Mill in accordance with the operational conditions outlined in Table 2. The Model A Hammer Mill was run for approximately 7 minutes. This was then repeated for a second run for 5 minutes. Therefore, in total the sample was run through the mill twice for a total time of 12 minutes. Figure 3 displays CMTT particles after cryogenic milling.

[2] Pulva Corporation contact – Brad Gray: 1-800-878-5828

Table 2: Overview of Pulva methods for CMTT generation using a Model A Hammer Mill.

SET-UP	TEST #1
Model	A
Type Hammer	LFS
No. Hammers	6
Rotor RPM	9600
Direction	STD
F.S. Type	Cryo
F.S. RPM	Cryo
Feed Trough	Cryo
Screen Perf.	.250
Bridge Ga.	
Clearance	STD
Cover Liner	MDL
Clearance	STD
Cover Inlet	Closed
Loops	Yes-1
Relief Req.	Yes
HP-AMPS	4.5
Pounds	4
Min.	7
#/ Hr.	
Suction	-
Blow Back	-
Accumulation	-
Screen Clog	-
Outlet Press.	Slight
Temp. – MILL	-100^{0}F
Temp. –Tunnel	-250^{0}F

Figure 3: CMTT particles after cryogenic milling.

Approximately 2 kg of total tread material was milled, which yielded approximately 1480 grams of CMTT for further use. Pulva used an aliquot of 50 grams of CMTT for mass analysis (note: 5 grams of calcium stearate was added to 50 grams of CMTT for sieve analysis only at Pulva). The mass used in the sieve analysis was disposed after measurement. Table 3 displays the mass distribution data after sieving. It should be noted that the size distribution presented below is for one specific generation period of CMTT at Pulva. Subsequent CMTT generation periods from Pulva or other labs may produce different ranges in size distribution.

Table 3: Example mass distribution of CMTT particles

Size fraction (standard sieve)	Mass %
> 595 micron	0
420 - 595 micron	2.4
250 - 420 micron	16.8
177 - 250 micron	16.6
149 - 177 micron	15.2
< 149 micron	49

As indicated in Table 3, approximately 49% of the mass of CMTT were less than 149 µm according to sieve analysis. CMTT particles were then placed in amber glass jars for long-term storage. CMTT are stored at RJ Lee Group in Monroeville, PA. While this report describes work to generate large quantities of CMTT particles, other benchtop machines are capable of generating CMTT particles on a smaller scale (e.g., single gram quantities).

3 Discussion/Uncertainties

3.1 Rubber composition

The method described above was utilized to generate CMTT particles with similar rubber composition as TRWP generated on the road simulator at the BASt in Germany and the Karlsruhe Institute of Technology (KIT), including the use of a similar ratio for CB and silica tires. The selection of the three different tires types for the TIP studies was intended to represent the basic characteristics of passenger car tires of different types, including winter and summer tires, as well as tires containing carbon black or amorphous silica as primary fillers. It should be noted that the three tires selected for the TIP studies were intended to give a mix of tire types for analysis; this selection is not inclusive of all available tire types currently on the market. This methodology can produce CMTT for any selected tire type, however researchers should consider the limitation of representative particles based on the selection of tires used in their studies.

The intent of this CMTT generation method is to minimize potential external variables (i.e. other tire compounds found in the tire, environmental contamination, etc.) and study only the tread component of the tires. This will allow for researchers to understand the tires contribution to any potential human health and environmental impacts associated with TRWP. However, it should be noted that CMTT is not a direct replacement for the study of pure TRWP due to the lack of the road component of the particles.

3.2 Particle size

Additionally, methods were employed to generate particles with the smallest possible size in order to replicate the size range of TRWP (1 – 350 µm) (Kreider et el., 2009). However, the size distribution of CMTT may differ from TRWP. While the run time for CMTT generation at Pulva was approximately 12 minutes total, it is unknown whether longer or shorter run times would generate different size distributions. It was noted by the engineer at Pulva that a longer run time using a Model A Hammer Mill would likely not generate smaller particle sizes based on extensive previous experience with the instrument. A detailed analysis of the size distribution for CMTT and TRWP is beyond the scope of this report, however, in general, CMTT particles are likely larger than TRWP.

For future studies conducted by TIP or others using this methodology, it is important that characterization of size distribution be performed (e.g., by sieve analysis and/or laser diffraction) so that comparison of results can be made with other batches of particles generated on separate days and to TRWP. Though CMTT is not completely representative of TRWP as explained above in Section 3.1, having characterization of particles, including the size distribution of the CMTT being used for studies is important for interpretation of study results. This will enable conclusions and comparisons to be made for selected studies. While no formal quantitative acceptable mass distribution range can be provided at this time, it is important to note that techniques such as sieving of larger particles (e.g., >595 µm) could be employed to generate a more acceptable size distribution of CMTT particles. However, sieving of tread rubber without the use of calcium stearate or some other dispersing agent may cause a larger number of particles to agglomerate, limiting the use of a sieving technique. Taken together, proper physical characterization of the size distribution of CMTT particles is essential in order to compare different batches of CMTT with TRWP particles.

An example of a size distribution for CMTT that is comparable to TRWP was provided by TIP as a guideline to understand if the particle size distribution remains representative of other studies conducted using TRWP. In instances when CMTT size distribution varies from these size distribution bounds, careful consideration of the results of any CMTT analyses and influence of particle size on conclusions of studies and extrapolation to TRWP is necessary. As appropriate, researchers should acknowledge potential differences between TRWP and CMTT in particle size and account for or understand whether there may be influence of those differences on the results and conclusions.

3.3 Additional Considerations

The availability of pure TRWP particles for use in studies is limited, with the ability to produce CMTT in greater quantities, typically helpful for preliminary studies. However, physical and chemical differences between the two different materials should be considered as noted above. Other potential differences between CMTT and TRWP include (1) morphology, (2) the aggregation of rubber with material from the road surface, and (3) degradation of the TRWP by environmental weathering or frictional forces not present in the generation of CMTT (4) density of CMTT may be less than TRWP due to the exclusion of road material.

The appropriateness for use of CMTT or TRWP for different experimental conditions is beyond the scope of this report and should be assessed on a weight of evidence. For example, the paper from Kreider et. al. 2010[3] “Physical and chemical characterization of tire-related particles: comparison of particles generated using different methodologies”, has made a useful comparison between CMTT (TP in that manuscript), particles collected on the road (RP in the manuscript) and TRWP produced on drum test (TWP in the manuscript). It gives a few general considerations regarding the representativeness of CMTT: “[f]rom a physical and chemical standpoint, both RP and TWP differ from TP and from one another such that toxicity data derived from the use of one should not be used interchangeably or extrapolated to represent the toxicity of another”. Additionally, the manuscript from Cadle and Williams 1980[4] “Environmental degradation of tire wear particle”, compares the degradation of TRWPs produced on drum compared with tread rubber. It concludes: “[m]ost importantly, we have shown that tread-wear particles degrade at a faster rate than tread rubber itself”. So again, careful consideration should be given when comparing aging data derived from the use of CMTTs compared to aging of TRWPs.

[3] Kreider ML, Panko JM, McAtee BL, Sweet LI, Finley BL. Physical and chemical characterization of tire-related particles: comparison of particles generated using different methodologies. *Sci Total Environ*. 2010;408(3):652-659.

[4] S. H. Cadle, R. L. Williams; Environmental Degradation of Tire-Wear Particles. Rubber Chemistry and Technology 1 September 1980; 53 (4): 903–914. doi: https://doi.org/10.5254/1.3535066