Optical scattering (*TAOS*) by tire debris particles: preliminary results

Giovanni F Crosta[1], Marina C Camatini, Simeone Zomer
University of Milan - Bicocca, Department of Environmental Sciences,1, Piazza della Scienza, I - 20126 Milan, IT
[1] and University of Massachusetts - Lowell,Center for Electromagnetic Materials and Optical Systems
One, University Avenue, Lowell, MA 01854 - 2881
giovanni@disat.unimib.it

Stephen Holler[2], Yongle Pan
Yale University, Department of Applied Physics,New Haven, CT 06520
[2] Currently at Los Gatos Research, 67 E. Evelyn Ave. Suite 3, Mountain View, CA 94041

Praveena Bhaskara, Pongphisanu Muangchareon, Changmo Sung
University of Massachusetts - Lowell, Center for Advanced Materials,
One, University Avenue, Lowell, MA 01854 - 2881

Simone Cencetti, Claudia Regazzoni
Pirelli Pneumatici, Viale Sarca 222, I - 20126 Milan, IT

Abstract: Tire debris particles from low severity laboratory wear tests have been investigated by the *TAOS* optical scattering facility at Yale University. The incident wavelength is 532 nm. After the *TAOS* event some particle samples have been imaged by a scanning electron microscope and microanalyzed. The *TAOS* intensity patterns recorded within a solid angle in the backward sector have been processed by cluster analysis and compared with the patterns computed by a ***T***-matrix code. Preliminary agreement has been found between *TAOS* data and the particle models (size, shape, refractive index). The purpose of the investigation is to obtain signatures of the material, based on its *TAOS* pattern.

OCIS codes: (290.5820) Scattering measurements; (160.4760) Optical Properties

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1. Introduction

Airborne particulate matter (*PM*) in urban areas affected by heavy traffic has many sources, among which the combustion of hydrocarbons and the wear of tires, brakes and the road surface. In particular, the amount of debris produced by the normal wear of tires ranges from 40×10^6 kg per year for Italy [1] to more than 5×10^8 for the US [2]. *PM* generally has to be characterized by its morphological, physical and chemical properties, which then make identification and source apportionment possible. Some types of particles can be characterized and identified by optical means: see e.g., [3, 4]. The purpose of this investigation is to find out whether and to what extent tire debris particles can be characterized in a non destructive way by optical scattering implemented e.g., by the *TAOS* (two dimensional angular optical scattering) setup [5]. The problem is of interest to at least two types of applications: the monitoring of tire wear in the laboratory and the estimation of the impact tire debris may have on the environment and on human health.

2. Materials, Specimen Preparation

The selected materials are the following.

a) Polystyrene (*PS*) spheres having an average diameter of 10 μm;

b) debris from low severity laboratory tests, which simulate the normal wear of a tire.

The latter material consists of a mixture of starch ellipsoids and tire tread particles.

Purified water, microfiltered by a 2 stage (0.8 + 0.2 μm pore size) cartridge was used to prepare all suspensions. *PS* spheres, the reference material, were suspended and sonicated. Material ***b***, instead, underwent several preparation stages aimed at breaking down the starch - rubber clusters, removing starch and selecting sufficiently small rubber particles. Namely, dispersion in water was followed by sonication, settling in a 10 cm high vertical column at 23 C for 30 min and drawing of the supernatant fraction. The latter was filtered through a 5 μm *Pall Gelman PVC* membrane. Both suspensions, *a*) and *b*), were finally diluted to attain an approximate concentration of 75 particles per mm^3, equivalent to 1 particle every ≅ 120 drops of 50 μm diameter. Particle concentrations were estimated by passing a known volume of suspension through a 0.45 μm *Millipore PVC* membrane and visually counting the retained particles inside a given membrane area under an optical microscope.

3. Instrumentation

The *TAOS* instrumentation at the *Department of Applied Physics*, Yale University [5], has four components: an Ink Jet Aerosol Generator (*IJAG*), coherent light sources, collection optics, triggering and imaging electronics.

The particulate suspensions were loaded into empty inkjet cartridges, which were then mounted atop the *IJAG*. Liquid droplets of the suspension (50 μm diameter) were ejected at a selectable rate from the cartridge into a vertical drying column, heated to ≈105 C. The particle of either material, *a*) or *b*), emerged from the *IJAG* and fell into the sample volume. Namely, the relatively low particle concentration excluded the formation of aggregates. Upon crossing a diode-laser (λ = 635 nm) trigger-beam, the particle was illuminated by the horizontally polarized second harmonic (λ = 532 nm) beam of a Q-switched (70 ns pulse) *Nd*:*YAG* laser (FIGURE 1.*a*). The scattered light was collected inside a two dimensional angular domain by either a lens or a concave mirror, both of which satisfied the ABBE sine condition (FIGURE 1.*c*), and relayed to a CCD camera. The angular domain Ω resulting from the concave mirror - CCD camera combination was $\Omega = \{ 86 \leq \theta \leq 94$ deg x $142 \leq \varphi \leq 168$ deg $\}$ in the laboratory coordinate frame, where φ = 180 deg corresponds to backscattering (FIGURE 1.*b*). The size of each acquired image was 1024 x 256 pixels. Particles leaving the sampling volume fell onto a specimen holder, a 1/4" *Al* stud covered by adhesive carbon tape. These specimens were stored for further analysis.

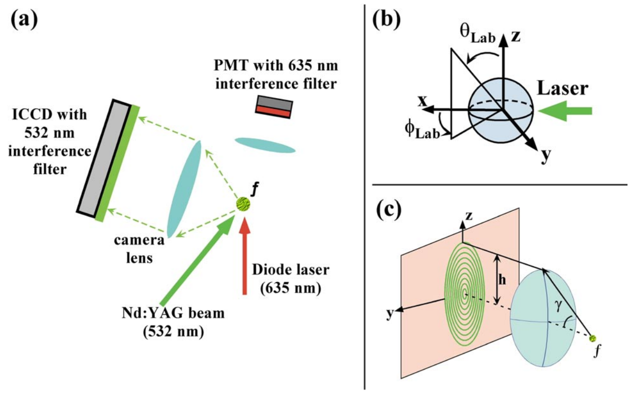

Fig. 1. (a) Triggering and *TAOS* optics; (b) the reference frame; (c) the ABBE sine condition.

Analytical scanning electron (*SE*) microscopy was carried out by an *Amray 1400 SEM* operated at 20 kV, equipped with a *Tracor Northern TN 3205 1000V* energy dispersive X-ray (*EDX*) spectrometer, located at the *Center for Advanced Materials*, University of Massachusetts - Lowell, MA.

4. Preprocessing of *TAOS* data

Raw *TAOS* data were interpolated by *Surfer™* of *Golden Software*, which yielded the images displayed below.

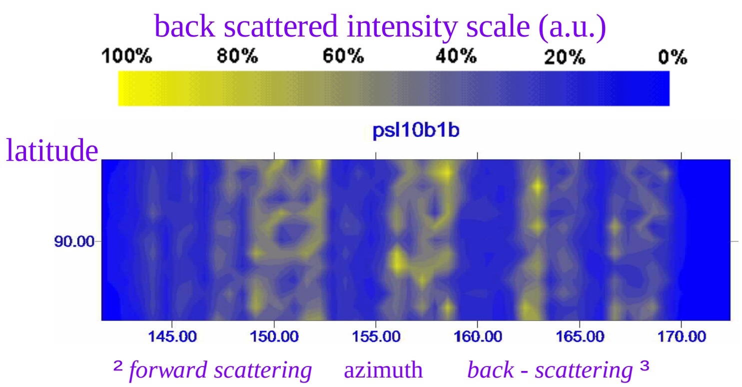

FIGURE 2. *TAOS* pattern produced by a *PS* sphere of nominal radius = 5 µm (psl10b1b). The intensity scale, in arbitrary units, is the same for all *TAOS* images.

A typical scattered intensity pattern produced by *PS* spheres is shown by FIGURE 2. In the domain of observation the local maxima form vertical bands. Patterns are symmetrical with respect to the equator (θ = 90 deg). The detected bands are approximately centered at φ = 150, 157, 163 and 167 deg, respectively.

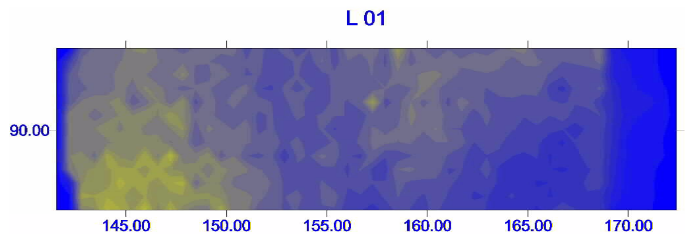

FIGURE 3. *TAOS* pattern produced by particle *LS01* of material *b*.

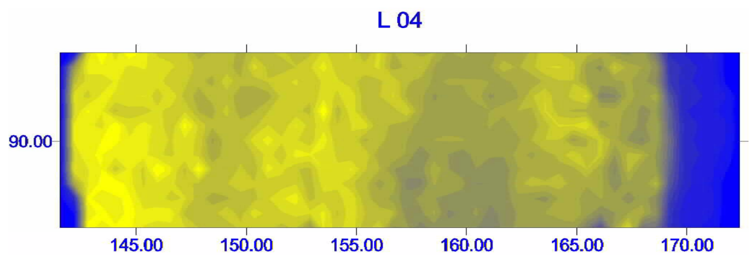

FIGURE 4. *TAOS* pattern produced by particle *LS04* of material *b*.

The *TAOS* patterns produced by material *b*, on the other hand, appear heterogeneous, as shown e.g., by *LS01* (FIGURE 3) and *LS04* (FIGURE 4).

5. *SEM* imaging and microanalysis

Samples of material *b* particles collected after the *TAOS* event were imaged and microanalyzed.

Some particles of a given size e.g., 3 µm diameter, exhibit sharp contours with corner points (FIGURE 5, *yf-a2*), other look like ellipsoids with rippled contours (FIGURE 6, *yf-a6*).

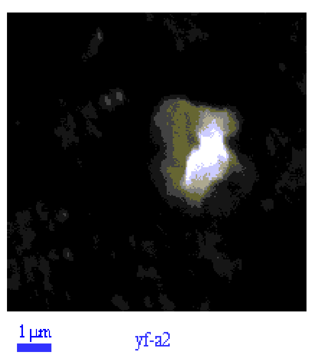

FIGURE 5. SE micrograph of particle *yfa2*, material *b*.

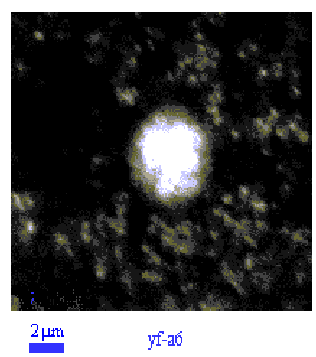

FIGURE 6. SE micrograph of particle *yfa6*.

Elemental microanalysis is summarized in TABLE 1. An X-ray detector having a 1 keV lower threshold, like the above mentioned *TN 3205 1000V*, can characterize tire debris by *Si*, *S* and *Zn*. Namely, precipitated SiO_2 is a reinforcing filler of rubber, whereas *S* and *Zn* are related to vulcanization.

Table 1. Normalized peak intensities above background of the elements detected in material *b*
Values normalized separately, for each particle, with respect to that K_α peak, which exhibits the highest intensity.
Neither *Ca* nor *Fe* could be detected in any particle. ND = not detectable.

Particle	*Size*	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*K*	*Mn*	*Cu*	*Zn*	I_{Zn} / I_S
yfa1	4μm	3	<1	1	9	36	10	46	100	2	<2	3	.2
yfa2	3μm	4	<1	4	8	33	18	59	100	2	1	2	.13
yfa3	2.5μm	6	<1	7	7	29	22	55	100	1.5	<1	2	.1
yfa4	3.5μm	2.5	ND	3	12	61	10	20	100	1.6	1.6	2.4	.25
yfa5	2μm	5	ND	8	15	61	15	23	100	2.3	1.5	3	.2
yfa6	4.5μm	8	ND	4	4	13	27	81	100	<1	<1	3	.11
yfa7	4μm	3	ND	4	11	38	9	38	100	2.3	<1	3	.33

All other detected elements in TABLE 1 are ascribed to contamination of the original debris supplied by the industrial laboratory, where the wear tests were carried out.

Let I_{Zn} and I_S respectively denote the peak K_α X-ray intensities of *Zn* and *S* above background. Microanalysis of uncontaminated tire tread particles [6] yields $0.1 < I_{Zn} / I_S < 0.35$, where the spread is due to topography effects [e.g., Ch. 10 of 7]. Since material *b* yields $0.1 < I_{Zn} / I_S < 0.33$, then all imaged particles containing *S* and *Zn* can be ascribed to tire debris, in spite of the relatively high contamination.

6. Cluster analysis of *TAOS* images

The *TAOS* patterns were classified by means of cluster analysis as follows.

1) Intensity was averaged over a square of 2 x 2 degrees; hence, each *TAOS* image reduced to 70 pixels.

2) From pixel intensities a vector in the non negative orthant of R^{70} was formed.

3) An affine transformation was applied such that, the smallest component of each vector became 0 and the largest one became 100; all other components were transformed accordingly; this removed background and enhanced contrast.

4) The EUCLIDean distances between pairs of vectors were computed and the vectors grouped (clustered) according to increasing distances.

A total of 15 images were processed by the Statistical Package for the Social Sciences (*SPSS*™). The maximum computed distance was $d_{\max} = 0.313$ in units of $\sqrt{(2)}$. The threshold distance $d_T = 0.167$ was chosen to define a cluster. As a result, the following four clusters were obtained.

Cluster #1: particle *LS01* (FIGURE 3). Cluster #2: *LS02*, *LS04* (FIGURE 4) to *LS12*, *LS15*.
Cluster # 3: *LS03* and *LS14*. Cluster # 4: *LS13*.

7. Numerical simulation of forward electromagnetic obstacle scattering

The numerical solution of the direct obstacle scattering problem was carried out by means of M I MISHCHENKO' s **amplq.new.f** extended precision code [9], which is based on the ***T***-matrix method [e.g., 10, 8]. The code can deal with axially symmetric, penetrable obstacles, the boundary of which, $r[\theta] \in C^2(0,\pi)$, is a linear combination of trigonometric functions. The same incident wavelength and polarization (H) were used as in the experiments. The incidence angles were $\theta_0 = 90$ deg, $\varphi_0 = 0$ deg. The symmetry axis was the vertical one i.e., the EULER angles were both 0. Computation was performed by *IBM RS/6000/3ct* (*Department of Environmental Sciences*, *University of Milan - Bicocca*) and *-42t* (first author' s own) machines. The code performed in a satisfactory way in the resonance region.

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8. Interpretation of *TAOS* data

TAOS data are a set of intensity values from a limited aperture. No result is known about the unique reconstruction of a non spherical, penetrable obstacle from such data at a single incident wavevector [11]. On the experimental side, no attempt was made to collect single material particles after the *TAOS* event; therefore *SEM* images provide at most hints on particle size and shape classes e.g., spheroids and rounded tip cones. Microanalysis suggested a range for the refractive index values. As a consequence, a relationship between measurements and obstacle properties had to be sought for on a heuristic basis.

The refractive index, m, was such that, Re[m] = 1.59 (the value of styrene - butadiene rubber and carbon black) and the imaginary part varied stepwise in $0.0 \leq \mathrm{Im}[m] \leq 0.66$.

Sequences of numerical simulations were run for a given shape class by letting the radius of the circumscribed sphere also vary stepwise between 1 and 2 μm.

Cluster analysis of the scattering patterns was applied to select the fittest particle models. The shape of e.g., the rounded cone **Th14Sj** (height = 1.4 μm, Im[m] = 0.1, FIGURE 7) was suggested by the *SEM* image of FIGURE 5, the refractive index by the microanalysis of TABLE 1. The scattering pattern of **Th14Sj** was found to fit in cluster # 1 at a distance d = 0.168 i.e., to interpret the *LS01* pattern of FIGURE 3. **Th15Sj** (a rounded cone of height = 1.4 μm, Im[m] = 0.1) was in qualitative agreement (d = 0.288) with pattern *LS04* (FIGURE 4) because the local maxima occurred near φ = 145, 154 and 166 deg and the pattern was asymmetric; it did not fit cluster # 2, since d is too large.

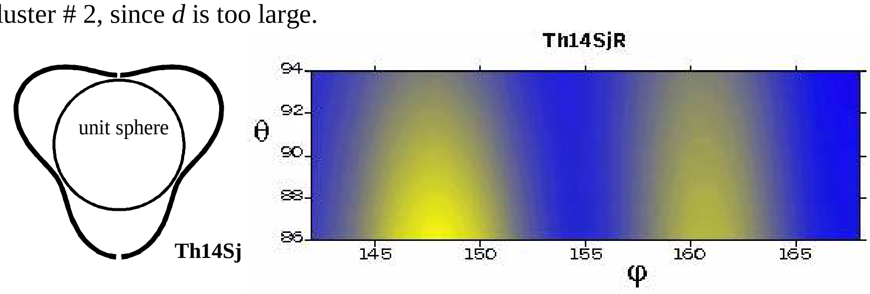

FIGURE 7. Rounded cone **Th14Sj** (height 1.4 μm, Im[m] = 0.1) and its scattering pattern in Ω. . The pattern fits in cluster # 1. From G.F. Crosta, S. Zomer, *Numerical Simulation of Forward Obstacle Scattering*, http://web.tiscalinet.it/_TAOS/index.html

9. Discussion

The question, which prompted this investigation is: *do tire debris particles have a TAOS signature ?*

In other words, *do intensity data measured in Ω. provide information about the shape, orientation and refractive index of the particles ?*

The underlying assumptions are that specimen preparation, experiment geometry, set of incident wavevectors and polarization(s) are all adequate. If exact obstacle reconstruction were the objective, the limitations posed by the above described experimental setup would imply a negative answer and preempt any further effort aimed at improving the technique. If additional information about shape classes and refractive index ranges is made available by different experimental techniques (*SEM*, microanalysis), even a heuristic method e.g., cluster analysis, leads to consistency (measured by the distance between vectors) between experimental results and numerical simulations and therefore to an estimate of the particle properties, in spite of the limited range of simulations carried out so far.

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