EB2020-MDS-022

Practical Measurement of Fiber Particle Content in Titanate by Dynamic Image Analysis

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https://doi.org/10.46720/EB2020-MDS-022

ABSTRACT: To obtain a sufficiently accurate fiber particle content in some titanate products with an industrially practical method, issues and attentions in the measurement by Dynamic Image Analysis (DIA) were investigated. Small particles which cannot be clearly investigated by an optical method are all non-WHO fibers with high aspect ratio, and DIA using light is enough for evaluating WHO fiber content in the titanate products investigated in this study (TOFIX SNR series and TOFIX NTO). By using the special shape factor defined as the ratio of envelope peripheral length / peripheral length, some data for irregular particles such as overlapped ones and aggregates / agglomerates can be effectively excluded for the estimation of WHO fiber content. It is confirmed that all three materials investigated have WHO fiber contents fully lower than 0.1 mass %.

KEY WORDS: titanate, fiber content, dynamic image analysis, aspect ratio, brake pad

1. Introduction

K₂Ti₆O₁₃ (potassium hexatitanate) has been widely used as a brake pad additive for a long time. However, each particle of K₂Ti₆O₁₃ has fiber-like configuration in many cases and there has been strong requirement recently to reduce fiber particle content in the commercial products of this material. The movement is based on some reports that some forms of fiber particles may increase the risk of cancer when they enter human bodies. In Europe, content of what is called “WHO fiber”, which is defined as a particle having major axis of 5μm or longer, minor axis of 3μm or shorter and aspect ratio (ratio of lengths of long and short axes) of 3 or larger, is required to be 0.1 mass % or less in the commercial products [1] including titanate. To clear the restriction, a lot of studies have been conducted so far and new K₂Ti₆O₁₃ based products with smaller amount of fiber particles have been developed. TOFIX SNR series manufactured by Toho Material Co., Ltd. are the examples [2]. They are the K₂Ti₆O₁₃ based materials composed of shape-controlled particles, resulting in low contents of WHO fiber. TOFIX NTO which is a Na₂Ti₆O₁₃ (sodium hexatitanate) based material developed as a substitute for K₂Ti₆O₁₃ [3] is another example. It has the same crystallographic structure as that of K₂Ti₆O₁₃ [4] and quite similar physical properties to those of K₂Ti₆O₁₃ but is not filed in H351 category and WHO fiber content is extremely low [3]. Meanwhile, it is not easy for us manufacturers to ensure low fiber particle contents in the actual commercial products because the conventional direct observation and measurement using an optical microscope or SEM [5][6] is not practical since it takes quite a long time and very costly. It would be impossible to measure WHO fiber content for each commercial lot with this method. To obtain a sufficiently accurate fiber particle content in titanate for a short time of period, we are recommending what is called “Dynamic Image Analysis” (DIA) as a measurement method from viewpoints of accuracy and simplicity [3]. As sown in the last EuroBrake conference in 2019 [3], DIA is quite effective to obtain sufficiently accurate content of the fibers in titanate products with industrially affordable burden for examination. For example, around 70,000 particles in one product lot can be analyzed only in 10 min and a fiber content value with very low data scatter can be obtained simultaneously. Analytical results for fine particles smaller than 20μm well agreed with the results by direct SEM observation.

In the present study, some issues and attentions in the measurement of fiber particle contents by DIA were investigated and discussed.

2. Methodology

2.1. Materials Investigated

Materials used in the study were K₂Ti₆O₁₃ based TOFIX SNR Large type and small type and Na₂Ti₆O₁₃ based TOFIX NTO. All of them were the products of Toho Material and had powder characteristics shown in Table 1.

Table 1 Major powder characteristics of the materials used.

<table>
<thead>
<tr>
<th>Material</th>
<th>TOFIX SNR (Large type)</th>
<th>TOFIX SNR (Small type)</th>
<th>TOFIX NTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area [m²/g]</td>
<td>1.65</td>
<td>2.65</td>
<td>1.70</td>
</tr>
<tr>
<td>D50(V) [µm] (Volume distribution)</td>
<td>80.8</td>
<td>42.7</td>
<td>73.3</td>
</tr>
<tr>
<td>D50(N) [µm] (Number distribution)</td>
<td>2.61</td>
<td>2.69</td>
<td>2.78</td>
</tr>
</tbody>
</table>

*1 Measured with BET method
*2 Measured with dynamic image analysis method using PITA-3 [7]
2.2. Observation using Dynamic Image Analysis (DIA) method

Powder shape and size analyses were conducted by a particle analyzer “PITA-3” (manufactured by Seishin Enterprise Co., Ltd.) [7], which is one of the commonly used DIA method based machine, and the measurement procedure is based on International Standard (ISO) [8] and the Japan Industrial Standard (JIS) [9]. Outline of the procedure is available in reference [3].

A lot of DIA based analyzers are using an optical observation method and the following two issues should be accessed to obtain more accurate values of WHO fiber content:

1. How to deal with very fine powders which cannot be recognized by an optical method
2. How to exclude the overlapped images of two or more particles and aggregates or agglomerates formed by two or more particles, both of which may be recognized as non-WHO fiber particles even if they are WHO fibers.

For the subject 1., investigation using an objective lens with higher magnification (20 times) and a high resolution CCD camera (28,590,000 pixel / inch²) was conducted and the results were compared with the investigation obtained using a 10-times magnification lens and a commonly used CCD camera (15,510,000 pixel / inch²).

For the subject 2., the shape factor (SF) defined as the ratio of envelope peripheral length and peripheral length was used for identification of particles which should be involved or excluded for estimating WHO fiber content, where “peripheral length” is the length of the particle periphery which PITA-3 measured on the photo image of the particle as shown in Figure 1(b), and “envelope peripheral length” is the length of the periphery of the polygon created by the lines connected with convex points of the particle as shown in Figure 1(c), which was also taught by PITA-3. When SF is 1, it means that the particle observed on the photo image has a simple shape and are not overlapped particles or aggregates generally having a complicated irregular shape.

3. Results and Discussion

3.1. Observation with High Magnification and Resolution

As indicated in the previous study [3] for TOFIX NTO, particles of 0.6 μm or larger in width (length of short axis) can be detected using an objective lens with 10-times magnification and a CCD camera with 15,510,000 pixel / inch² of resolution. Meanwhile, particles of 0.45 μm or larger in width were detected using an objective lens with 20-times magnification and a CCD camera with 28,590,000 pixel / inch² of resolution when the adjustment of the suspension flow in the flow cell and the parameters for the numerical data processing were correctly conducted. Although the resolution may be further improved by the use of light with short wavelength including X-ray in place of visible light, the device would be costly and it would be opposed to the initial target of “simple and industrially practical” method.

However, as indicated in Figure 2, which is the distribution of lengths of long and short axes of 600 TOFIX NTO particles measured by SEM method and reported in the previous study [3], SEM observation revealed that all particles of 0.6 μm or smaller in length of short axes in this product were non-WHO fibers. It means that very small and light weight particles smaller than 0.6 μm did not significantly affect WHO fiber content value expressed with “mass %” even if the number of such particles was large. The situation was the same in other titanate investigated in this study. It does mean that by using SEM observation supplementarily, DIA method can be fully used as a simple and accurate measurement method for fiber particle content in titanate products.

![Figure 1](image1.png)  
(a) Photo image of a particle taken by PITA-3 [7],  
(b) peripheral length and (c) envelope peripheral length measured by PITA-3.

![Figure 2](image2.png)  
Distribution of lengths of long and short axes of TOFIX NTO particles measured with SEM method [5]. The data for particles smaller than 12μm or smaller only are depicted. WHO fiber range is also shown.
3.2. Exclusion of Overlapped Particles and Aggregates of Fiber Particles

In Figure 3, 10 images of TOFIX SNR Large type particles randomly extracted from the obtained data sets for SF=0.85 (Figure 3(a)) and 0.90 (Figure 3(b)) are shown. Particle images for SF=0.85 contained some overlapped particles or aggregates. In some cases, fiber particles having high aspect ratio formed those particle images. Meanwhile, those for SF=0.90 did not contain such irregular images. Further investigations suggested that the images of particles for SF=0.90 or higher seldom contain such complex irregular ones. The number of particles having SF=0.90 or more was still around 70,000 for the three materials investigated in this study, as shown in Table 2, resulting in that the exclusion of particles for SF < 0.90 increases accuracy of WHO fiber content without keeping the large population.

![Particle Images](image)

Figure 3 Images of particles of TOFIX SNR Large type taken by PITA-3[7]. Shape factor defined as the ratio of envelope peripheral length and peripheral length as explained in Figure 1 was (a) 0.85 and (b) 0.90.

Based on this criterion, WHO fiber content was evaluated for the three materials. Results are shown in Table 2.

As shown in Table 2, WHO fiber contents of all three materials were less than 0.1 mass % in the overall products which include some large sized particles. However, as pointed out in the previous study [3], large particles are basically heavy and they make WHO fiber content decrease. By taking the large-sized particle affection on WHO fiber content into account, WHO fiber contents for the particles smaller than 100 μm were also evaluated although the number of such particles was small, and it was confirmed that WHO fiber contents were sufficiently less than 0.1 mass % as shown in Table 2. WHO fiber content for the particles having SF=0.90 or more were a little bit higher than the values evaluated for other conditions as shown in Table 2. However, they were still lower than 0.1 mass %. The values may be overestimated, i.e. some non-WHO fibers may be excluded for the estimation. However, the errors are considered to be on the side of prudence.

Table 2 WHO fiber content and the number of evaluated particles measured with PITA-3 for three titanate products. Shape factor was defined as the ratio of envelope peripheral length and peripheral length as explained in Figure 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Overall Products</th>
<th>Particles smaller than 100μm</th>
<th>Particles smaller than 100μm and with shape factor of 0.90 or larger</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOFIX SNR Large type</td>
<td>WHO fiber content (mass %)</td>
<td>0.023</td>
<td>0.041</td>
</tr>
<tr>
<td>Number of particles</td>
<td>70,022</td>
<td>69,815</td>
<td>68,878</td>
</tr>
<tr>
<td>TOFIX SNR Small type</td>
<td>WHO fiber content (mass %)</td>
<td>0.076</td>
<td>0.076</td>
</tr>
<tr>
<td>Number of particles</td>
<td>70,005</td>
<td>70,005</td>
<td>69,773</td>
</tr>
<tr>
<td>TOFIX NTO</td>
<td>WHO fiber content (mass %)</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Number of particles</td>
<td>70,020</td>
<td>69,922</td>
<td>69,688</td>
</tr>
</tbody>
</table>

In Figure 4, size distribution of all particles smaller than 100μm and with shape factor of 0.90 or larger for each titanate products investigated in this study was shown. As shown in Table 2, almost 70,000 particles were evaluated for each material. However, it took only 10 min for observation and several minutes for analysis. It does indicate that Dynamic Image Analysis is quite efficient and practical method for evaluating WHO fiber content in titanate.

There were some plots in WHO fiber range, which means there are some WHO fiber particles in each products. However, as shown in Table 2, WHO fiber content was less than 0.1 mass %.
Issues and attentions in the measurement of contents of WHO fiber particles having high aspect ratio in titanate by Dynamic Image Analysis (DIA) are investigated and discussed. Obtained results are as follows:

1. Resolution of the optical method can be improved by the use of an objective lens with higher magnification and higher resolution CCD camera. However, small particles which cannot be clearly recognized by an optical method are all non-WHO fibers, which can be demonstrated by SEM observation, and DIA using visible light is enough for evaluating WHO fiber content in the titanate products investigated in this study (TOFIX SNR series and TOFIX NTO).

2. By using the shape factor defined as the ratio of envelope peripheral length and peripheral length, some irregular particles such as overlapped ones in the photo images and agglomerates can be effectively excluded for the estimation of WHO fiber content.

3. By fully utilizing the results in the current and previous studies, it is confirmed that all three materials investigated have WHO fiber contents fully lower than 0.1 mass %.

References


Acknowledgement

The authors express their special thanks for Mr. M. Osumi and Mr. N. Hayakawa, Seishin Enterprise Co., Ltd. for their kind support and fruitful discussion.

4. Conclusion

Issues and attentions in the measurement of contents of WHO fiber particles having high aspect ratio in titanate by Dynamic Image Analysis (DIA) are investigated and discussed. Obtained results are as follows:

1. Resolution of the optical method can be improved by the use of an objective lens with higher magnification and higher resolution CCD camera. However, small particles which cannot be clearly recognized by an optical method are all non-WHO fibers, which can be demonstrated by SEM observation, and DIA using visible light is enough for evaluating WHO fiber content in the titanate products investigated in this study (TOFIX SNR series and TOFIX NTO).