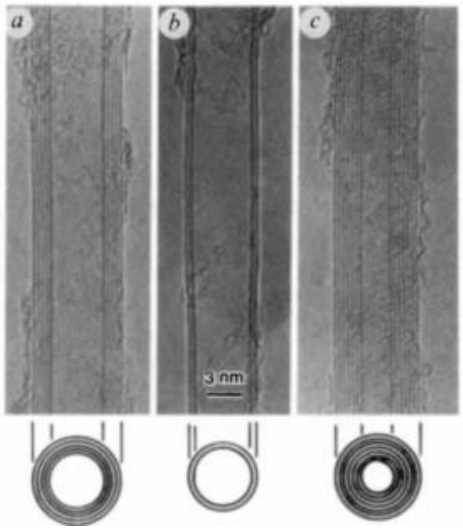
Comment on the CLH Report

Multi-Walled Carbon Tubes (synthetic graphite in tubular shape) with a geometric tube diameter range ≥ 30 nm to < 3 µm and a length ≥ 5 µm and aspect ratio ≥ 3:1, including Multi-Walled Carbon Nanotubes, MWC(N)T

Zeon Corporation, 3rd September 2021

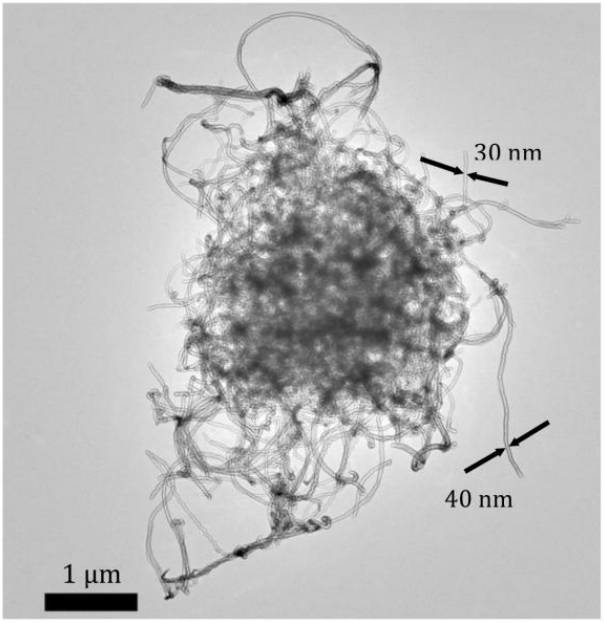
1. In the CLH report, multi-walled carbon nanotubes (MWCNT) were divided into two groups, that is "high diameter MWCNT" (> 30 nm) and ” low diameter MWCNT” (≤ 30 nm). The low diameter MWCNT (< 30 nm) are not subject to the proposed classification, as they are assumed to have a more tangled morphology. There is uncertainty regarding on the assumption. To our understanding, there has been no such distinction of MWCNT so far. Not every low diameter MWCNT type is entangled and not every high diameter MWCNT type is straight. The outer morphology of MWCNT depend on the production methodologies as arc discharge method, laser ablation method, and chemical vapor deposition(CVD) method. For instance, the MWCNT first reported by S. Iijima in 1991 were prepared by DC arc discharge of carbon electrodes. The MWCN are straight, and those diameters are lower than 10 nm [1]. The temperature of arc plasma is 3000 ~ 6000 C. Such high temperature proceeds the ordering of graphitic structure in inert gaseous condition, and the MWCNT become straighter.



MWCNT prepared by DC arc discharge method [1]

Contrary, MWCNT production by CDV method is carried out at the temperature range 600 ~1000 C. In general, entangled MWCNT is produced at relatively low temperature, and the MWCNT become straighter with increasing temperature of CVD process. As shown in Fig. 1 of Reference [2], all MWCNT having 10 – 50 nm outer diameter are entangled. There is no intercorrelation between the diameter and morphology of MWCNT.

Therefore, there is no scientifically rational reason to divide MWCNT into two groups at 30 nm in diameter.



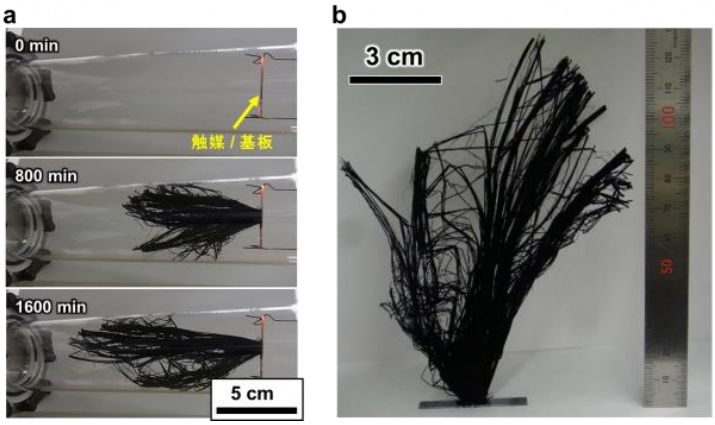
Tangled MWCNT having MWCNT 10 – 50 nm outer diameter[2]

2. The proposal is based on the observation that fibers of high diameter MWCT (≥ 30 nm) have potential like asbestos and asbestiform fibers and thus is consistent with the "fiber pathogenicity paradigm". In the proposal, the higher diameter MWCNT and multi-walled carbon tubes (MWCT) of less than 3 μm diameter are classified in the same group of substances, and the same measures are proposed. However, the fiber pathogenicity paradigm is not universally applicable for MWCNT, as demonstrated in the assessment of carcinogenicity of MWCNT in the International Agency for Research on Cancer (IARC). As mentioned above, morphology of MWCNT depends on methodology of production. Also, the morphology and physicochemical properties of the MWCNT depend on the process parameter as temperature, pressure, type and size of catalyst transition metals, carbon source materials, atmospheric gas, and so on [3]. So, we cannot approve of the requirement to put all these materials together in one group and to ban them together. There is no toxicological reason to do so.

3. We agree to list in the CLP annex as carcinogen all of those types of MWCT and MWCNT that potentially cause cancer. As an example, the well-assessed MWNT-7 type should be listed as carcinogen in the class 2 in the CLP annex to keep the harmonization with the categorization as "possibly carcinogenic to humans (Group 2B)" by IARC. We disagree to list all of high diameter MWCT and MWCNT with less than 3 μm diameter as carc.1B in the CLP annex. Some low diameter MWCNT types appear to be carcinogenic and some high diameter MWCNT types appear to be not carcinogenic. It would become clear by accumulating more data as long-term inhalation toxicity test and/or its alternatives.

4. Also, there is no scientifically reasonable ground in length. One of research trend on production of MWCNT is "long MWCNT". Recently a research group reported an ultra-

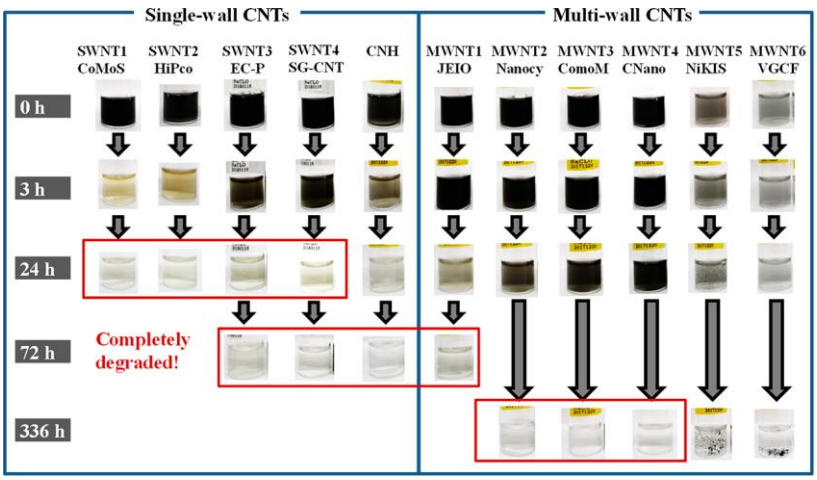
long MWCNT bundle even longer than 10 cm [4]. Question is if this extra-long MWCNT bundle show pathological behavior like those having μm length. Subjecting all high diameter MWCT including such extra-long MWCNT is too hasty.



Vertically aligned carbon nanotube forest having a length of 14 cm [4]

5. We therefore call for an immediate stop of the current CLH process about MWCT. We also propose to introduce scientifically based toxicological distinctions of material types. It would be useful to draw out the potential of MWCT even safely.

6. Finally, we propose all of MWCNT manufacturers and users to refer a paper reporting the degradation of MWCNT using commercial chlorine bleach[5]. As is well known, MWCNT are highly durable and bio persistent materials. Therefore, a process of degrading MWCNT is necessary for the lifecycle management in production, use and disposal of MWCNT. For instance, the paper suggests safe and cost-effective management of working clothes contaminated by MWCNT and of wastewater containing MWCNT with chlorine bleach. In addition, the mentioned oxidization of MWCNT to CO_2 using ClO^- shows a clear difference from asbestos.



Estimation of the quantity of SWCNT and MWCNT in aqueous dispersions following treatment with commercial chlorine bleach [5]

References;

[1] “Helical microtubules of graphitic carbon” by Sumio Iijima, Nature Vol. 354, 56-58(1991)

[2] “Characterization and Control of Airborne Particles Emitted During Production of Epoxy/Carbon Nanotube Nanocomposites” by Lorenzo G. Cena and Thomas M. Peters, Journal of Occupational and Environmental Hygiene, 8: 86–92(2011）

[3] “Self-Assembly of Graphene on Carbon Nanotube Surfaces” Kaiyuan Li, et al., Scientific Reports volume 3, Article number: 2353 (2013)

[4] “Ultra-long carbon nanotube forest via in situ supplements of iron and aluminum vapor sources” By H. Sugime, et al., Carbon, Volume 172, February 2021, Pages 772-780.

[5] “Diameter-Dependent Degradation of 11 Types of Carbon Nanotubes: Safety Implications” by M. Zhang, M. Yang, H. Nakajima, M. Yudasaka, S. Iijima and T. Okazaki, ACS Appl. Nano Mater. 2019, 2,7, 4293-4301