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# A Colorimetric Indicator Based on Methylene Blue-Dyed Pullulan Thin Films for the Detection of Hydroxyl Radicals

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**Abstract**

Methylene blue (hereinafter MB)-dyed pullulan thin films are applied as hydroxyl radical (OH*) indicators. In the present study, the chemical reaction and decolorization mechanism of MB-dyed pullulan thin films upon exposure to active oxygen species (hereinafter AOS) were elucidated under low and high humidity conditions. Importantly, decolorization was observed only under high humidity. The $^{1}$H-nuclear magnetic resonance (NMR) and $^{13}$C-NMR analyses revealed the presence of the interaction between MB and pullulan. It was also determined that the decolorization of the film was caused by the decomposition of MB upon exposure to OH*.

*Keywords: Methylene blue dye, Hydroxyl radicals (OH*), Pullulan film*

## 1. Introduction

Owing to their remarkably strong oxidative ability, AOS generated in the atmosphere can be applied in various industrial processes. It is well known that excited singlet oxygen atoms [O ($^{1}$D)], ozone ($O_3$), and OH* are valuable in the field of surface modification. AOS can also be generated by ultraviolet (UV) lamps with wavelengths of 185 and 254 nm [1]. Although numerous different AOS are known, which have long lifetimes, or high oxidization abilities, such as O($^{1}$D), $O_3$, OH*, and hydrogen peroxide ($H_2O_2$), O($^{1}$D) and OH* are of particular interest [2-10]. We previously reported that MB can be decomposed by $O_3$. MB is the convenient indicator for the detection of AOS, as following exposure to AOS, decomposing the dye, and decolorization [11]. Notably, $O_3$ has a lower oxidative ability compared with other AOS. To detect AOS with higher oxidative ability, it is necessary to stabilize MB by mixing it with pullulan, which has a high affinity for the dye, in order to form MB/pullulan composite films. Pullulan is a natural and water-soluble polysaccharide having excellent film-forming ability.

Humidity affects the type of the generated AOS. Under low humidity conditions, O ($^{1}$D) and $O_3$ are typically produced, while under high humidity conditions, the most oxidative species "OH*" is generated. Based on this observation, the decolorization mechanism of the composite film has been previously investigated, and it was found that decolorization occurred only at high humidity, presumably caused by the presence of the OH* species [12]. Moreover, the mechanism of the specific decolorization of the MB-dyed Nafion® films was reported [11]. However, the described indicator film was not a uniform thin film.

Consequently, we aimed to elucidate their chemical reactions as well as the decolorization mechanism upon exposure to OH* by using the uniform thin film indicator based on MB and pullulan.

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