Dehydrogenative Condensation via Plasma: Impacts on Sugar Alcohol Crystals

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Abstract: This study analyzes the crystal and molecular structure of mannitol treated with dielectric barrier discharge (DBD) plasma. The plasma-treated mannitol predominantly exhibited the metastable δ form. Additionally, several dehydrogenated condensation compounds were formed, which likely disrupted and reformed hydrogen bonding between mannitol molecules, facilitating the formation of the δ form.

1. Introduction

Plasma treatment is widely used in biology, medicine, and agriculture as a method to modify the physicochemical properties of target substances [1]. Plasma has also attracted attention for its usefulness in organic chemistry [2]. Here, we investigate the potential of plasma as a new crystal manipulation technique based on the analysis of the crystallization properties and molecular structure of a sugar alcohol with polymorphism that was treated with plasma.

2. Methods

D(-)-mannitol (MAN) was used to examine the crystal structure modification by plasma treatment. MAN has three crystalline polymorphs: the stable α and β forms and the metastable δ form [3]. An aqueous solution of MAN was treated with DBD plasma, generated by an alternating current (AC) pulse voltage of 10.5 kV at 10 kHz. This plasma-treated solution is designated as MAN(PT). For comparison, a solution of MAN dissolved in plasma-treated ultrapure water (UPW) was also prepared (MAN + UPW(PT)). The crystal structures of MAN(PT) and MAN + UPW(PT) were characterized using X-ray powder diffraction (XRPD), and their micro-scale morphologies were observed via scanning electron microscopy (SEM). Additionally, molecular structures were examined using mass spectrometry (MS) and nuclear magnetic resonance (NMR).

3. Results and Discussion

Untreated MAN and MAN + UPW(PT) crystals exhibited a needle-like morphology, whereas MAN(PT) crystals formed agglomerates with fine plate-like structures (**Fig. 1(a)**). XRPD pattern analysis revealed that untreated MAN and MAN + UPW(PT) were closely similar, while MAN(PT) displayed a distinctly different pattern (**Fig. 1(b)**). Quantitative analysis of the polymorphic composition, calculated from the intensity ratios of the XRPD patterns, indicated that untreated MAN consisted entirely of the α form, and MAN + UPW(PT) contained more than 90% of the α form. In contrast, MAN(PT) was predominantly composed of more than 95% of the δ form (**Fig. 1(c)**). MS and NMR analyses showed dimer-like compounds of dehydrogenated MAN molecules in MAN(PT). The δ-type polymorph, which is known for its extended hydrogen bond distances [4], may be affected by these dimer-like compounds. Based on their relatively large molecular size, these compounds are likely to disrupt the molecular arrangement of the MAN molecules, reducing the likelihood of hydrogen bond formation. This disruption may facilitate the stabilization of the δ form.

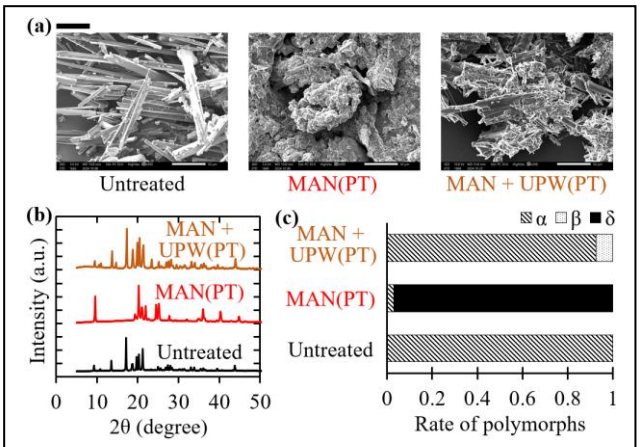

Fig. 1. Plasma-induced structural modifications in MAN crystals. **(a)** SEM images (scale bar: 50 μm), **(b)** XRPD patterns, and **(c)** rate of polymorphs of the untreated MAN, MAN(PT), and MAN + UPW(PT).

Acknowledgement

This study was supported in part by Grants from the JST FOREST Program (Grant No. JPMJFR222S to DY), the JSPS KAKENHI (Grant Nos. 18K19894 and 21K19893 to DY; Grants No. 24KJ1028 to RW), and the Sasakawa Scientific Research Grant, Japan Science Society (Grant No. 2023-2027 to RW).

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