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Communication

# Polymerization of D-Ribose in Dielectric Barrier Discharge Plasma

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**Abstract:** Dielectric barrier discharge (DBD) plasma has been found to uniquely polymerize ribose that is not usually subject to polymerization since molecules that tend to polymerize almost always possess at least a $\pi$-bond. The polymer was analyzed via nuclear magnetic resonance (NMR) spectra, matrix-assisted laser desorption ionization time-of-flight (MALDI TOF) mass spectroscopy and Fourier-Transform inferred spectroscopy (FTIR), and it was found that dehydration occurs during polymerization.

**Keywords:** polymerization; plasma; sugar; ribose

## 1. Introduction

The studies on the applications of discharged plasma are currently very active in the medical, environmental, and agriculture fields [1–10]. Among various plasma techniques, dielectric barrier discharge (DBD) plasma [11,12] is of special interest due to the safety and selectivity in its effects on biological systems [13,14]. The effects of DBD plasma treatments include the promotion of cell proliferation [15], enhancement of cell transfection [16,17], sterilization of root canals [18–20], wound healing [21], and sterilization of skin [13,22], etc. To understand the interactions of plasma with living cells and tissues for the clinical applications of plasma, chemicals species generated from plasma treatments have been under considerable investigation recently [23,24].

Most of these studies for plasma treatments were done for samples in aqueous solutions. The organic chemicals in the studies include sugars, lipids, and amino acids, etc. [25–29] which are the major chemical species in cell culture medium. In all these cases, the organic chemicals decomposed to smaller chemical species. Recently, when we treated sugar powders, such as ribose and glucose, in the solid phase, we found these sugars, especially ribose, underwent polymerization, instead of decomposition. In this short communication, we report our preliminary studies on this new phenomenon. Ribose is the backbone sugar unit in ribonucleic acids (RNA). We are interested in whether ribose can be polymerized. The work will also provide fundamental knowledge for the future study on whether ribonucleotides can be polymerized to RNA when treated with plasma.

## 2. Materials and Methods

DBD plasma was produced by using a previously reported device [29]. The Nano-pulsed DBD plasma was set at 11.2 kV and 690 fHz and the pulse width was 10 ns (FID Technology, Burbach, Germany). The anhydrous ribose powder was placed on a quartz plate on the bottom electrodes. [1]H NMR spectra were recorded on a Varian Gemini 500 MHz spectrometer (Palo Alto, CA, USA). Mass spectrometry (MS) analyses were performed using a Bruker Autoflex III matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF) (Billerica, MA, USA). Fourier-Transform infrared absorbance spectrometers using the universal diamond attenuated total reflectance accessory.

## 3. Results and Discussion

Figure 1a shows the changes of the ribose powder after the plasma treatment for 5, 10 and 20 min. After 5 min treatment, ribose became soft and creamy. After 20 min, the sample appeared to be a mushy gel. It was observed that all samples became gel after leaving the samples in the vials for 5 days (Figure 1d).

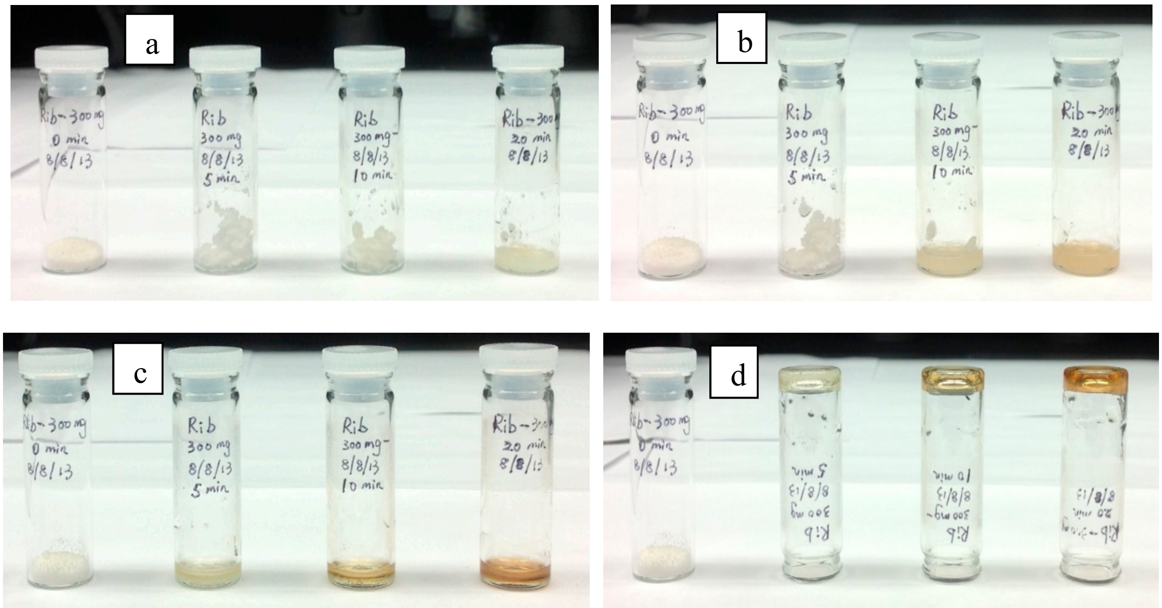


**Figure 1.** The change of the ribose after plasma treatment. (**a**) right after the treatment; (**b**) after the treatment, the vials were left on bench with the cap on for 1 day; (**c**,**d**) After the treatment, the vials were left on bench with the cap on for 5 days.

Figure 2 shows the NMR of the ribose after 10 min exposure to plasma as compared to ribose without the treatment. The NMR is not conclusive on the phase and morphology changes of the ribose powder since no major shifting of NMR peaks was observed except for the peaks between 4 ppm and 4.3 ppm. After 5 days, small peaks between 5 ppm and 5.2 ppm arose. These peaks have a lot of overlaps and are too complex to analyze at this stage.

MALDI-TOF and FTIR, on the contrary, showed significant changes of the ribose powder after the plasma treatments (Figures 3 and 4). The MALDI-TOF mass spectroscopy results showed a unique series of peaks starting at 305 Daltons with an equal difference by a weight of 132 Daltons. The molecular weight of ribose is 150 Daltons, so the 132-Dalton gap suggests the addition of ribose with a loss of water (18 Daltons) to form a mixture of polymers. It is noteworthy that the products are not simple polymers of ribose only, but the addition of the ribose on a moiety that has a molecular weight of 41 Daltons ($305 - 132 \times 2$ Daltons), which is unknown at this stage. FTIR showed the appearance of a significant peak at 1278 $cm^{-1}$ 20 min after the plasma treatment, representing the formation of C-O-C bond, which explains the loss of water when a new ribose was added on the polymer chain.

D-Ribose exists in equilibrium in five different forms: D-(−)-Ribose, α-D-Ribopyranose, β-D-Ribopyranose, α-D-Ribofuranose, and β-D-Ribofuranose. All forms are able to polymerize under the plasma conditions. Plasmas are made of a mixture of active species, such as reactive oxygen and nitrogen species (ROS and RNS), singlet oxygen ($^1O_2$), ·NO, ·OH, ozone ($O_3$), electrons, and ions, etc. Few reports in the past showed reactions of these plasma species with chemicals in the solid form, but it appears any of these species may react with ribose to initiate the polymerization. Because of the complexity, we are unable to determine the reaction mechanism at this stage.

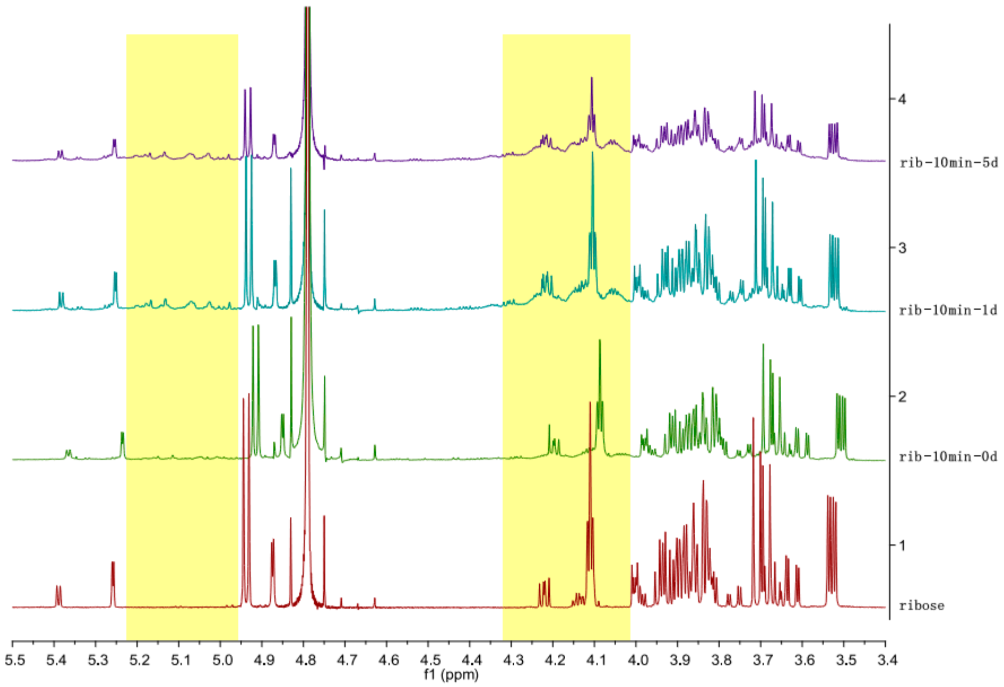


**Figure 2.** $^1$H nuclear magnetic resonance (NMR) spectra of the untreated and air-plasma-treated solid ribose after 0-, 1- and 5-day delay.

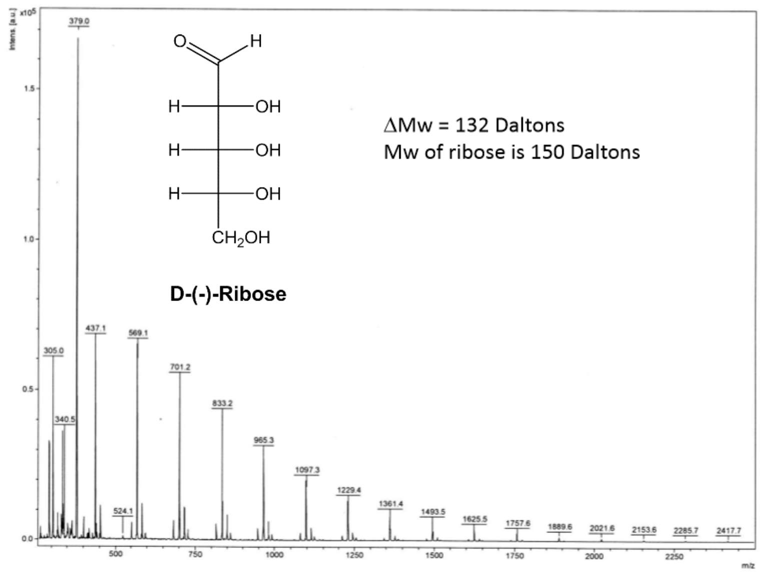


**Figure 3.** Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra of the 10 min treated solid ribose after 5 day delay.

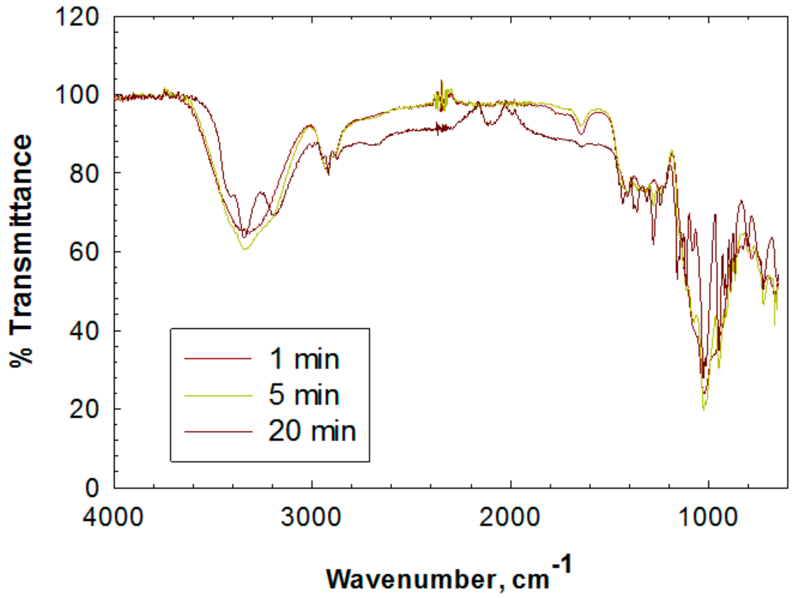


**Figure 4.** Fourier-Transform inferred spectroscopy (FITR) spectra of the untreated and air-plasma-treated solid ribose without delay.

## 4. Conclusions

In summary, as an initial attempt at a study of the reactions of solid powder under plasma, we demonstrate in this work the polymerization of ribose under DBD plasma. Understanding the reaction mechanism to form the polymer is quite challenging because of the existence of many active species in plasma and multiple OH groups in ribose. High-resolution NMR and studies on smaller alcohols are needed to fully understand the mechanism of ribose polymerization. We are also interested in whether plasma can be used to treat other solids, such as plastic, for environmental applications. These are under investigation and will be reported in due course.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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