

Title	塩の添加がポリビニルアルコールの特性に及ぼす影響
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Effect of Salt Addition on the Properties of Poly(vinyl alcohol)

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Poly(vinyl alcohol) (PVA) is known as one of the most important biodegradable plastics and have the potential to solve the current problem related to marine pollution from conventional plastics. The excellent mechanical properties of PVA originated from intermolecular hydrogen bonds, such as high modulus and high yield strength, are sufficient to fulfill the requirements to replace from rigid non-biodegradable plastics. However, in commercially available products, strong hydrogen bonding could lead to poor mechanical properties of the fibers and films because it prohibits a high level of molecular orientation. Incorporation of specific salts, such as lithium bromide (LiBr), lithium chloride (LiCl), and magnesium chloride ($MgCl_2$) can reduced the hydrogen bonding between polymer chains. From the previous studies, the addition of the salts could retard the PVA crystallization rate greatly. This phenomenon is caused by the interaction between hydroxyl groups and cations which attributed to the restricted segmental motion. However, there is no specific studies about the effects of ion species on the mechanical and thermal properties of PVA.

The present study focused on the effects of the addition of potassium, sodium, magnesium, and lithium salts on the rheological properties of PVA aqueous solutions, solid state of PVA films and also fibers. A plateau modulus can be detected in the low frequency region of shear storage modulus for PVA aqueous solution. This phenomenon demonstrates that hydrogen bonding of the PVA have developed a network structure. The addition of lithium salts evidently decreased the value of the plateau modulus with temperature. The anion species in the salt plays an important role in determining the rheological properties, including the magnitude of the plateau modulus as demonstrated by the experimental results. In the Hofmeister series (HS), the iodide anion was classified as a “water-structure-breaker” ion, it can decrease both plateau modulus including the oscillatory shear moduli effectively. Besides, at high temperatures, the modulus decreased with the LiI addition owing to the reduced extent of hydrogen bonding. The data obtained in this study demonstrated that the strong ion-dipole interactions between anions and PVA chains also have a significant impact on glass transition temperature and crystallinity. This study is the first to reveal that the impact of the salts addition follows the Hofmeister series. The study using different type of bromine salts revealed that Li^+ is more effective at disrupting the water structure than other salts such as Na^+ , K^+ , or Mg^{2+} . Furthermore, further experiments using lithium salts with various anion species verified that lithium salts are responsible in determining the hydrogen bonding within aqueous PVA and crystallinity, and therefore affect the mechanical properties of films. This phenomenon clearly follows the HS in order of $LiClO_4 > LiI > LiBr > LiNO_3 > LiCl$. Besides, magnesium salts also show an interesting result as the glass transition temperature T_g of the PVA films was enhanced and this result was attributed to the strong ion-dipole interactions between magnesium salts and PVA chains.

In case of PVA fiber, the addition of LiBr in spinning solution reduced the inter- and intramolecular hydrogen bonding in the PVA chains greatly and which results in the higher level of molecular orientation. It was evident from the results obtained in these studies, that the addition of metal salts gives significant impact on the properties of PVA aqueous solutions, films, and fibers, which corresponds to the HS.

Keywords: Poly(vinyl alcohol), Metal salt, Hofmeister Series, Crystallization, Hydrogen Bonding

