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Effect of addition of lithium salts on properties of poly(methyl methacrylate)

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Heat resistance and optical properties of amorphous polymers are important for engineering applications such as automobile parts, electrical devices, and displays. In general, a single plastic material often possesses poor physical properties for engineering application, so that the improvement of properties has been tried in decades. In particular, one of the promising processes to modify a polymer is mixing with low-molecular-weight compounds. Recently, it was found that the addition of a specific lithium salt enhances glass transition temperature (T_g) of poly(methyl methacrylate) (PMMA), which is a typical amorphous polymer. T_g is an index for heat resistance for amorphous polymers. Thus, the improvement of heat resistance of PMMA was achieved by the addition of the lithium salt as a simple way. However, it was not revealed that what kind of anion species of the salts powerfully affects T_g enhancement. In this study, I focused on the improvement of heat resistance of PMMA using this method. I found a lithium salt with the most effective anion for T_g increase of PMMA. Another salt that enhanced T_g and suppressed water absorbency of the blend film was also found. It was also attempted to investigate the mechanism of T_g enhancement of PMMA by adding such lithium salts. In the case of optical properties of polymers, orientation birefringence occurs during molding process of plastics. Furthermore, photoelastic birefringence is caused by elastic deformation of final products. It is required to suppress the birefringences for optical films. Therefore, orientation birefringence and photoelastic birefringence of the blend films were investigated.

In Chapter 2, the T_g enhancement of PMMA by the addition of various lithium salts was investigated using $LiNO_3$, $LiClO_4$, $LiCF_3SO_3$, $LiCOOCF_3$, and $LiN(CF_3SO_3)_2$ with 0.07 molar ratio of lithium cations per 1 molar of carbonyl groups in PMMA. As a result, $LiCF_3SO_3$ was the most effective on T_g enhancement for PMMA, which is due to ion–dipole interactions between the lithium cations and the carbonyl groups in PMMA molecules. However, at the same time, the addition of $LiCF_3SO_3$ also increased moisture absorption. Because water acted as a plasticizer in the case of $LiCF_3SO_3$, the T_g decreased with low modulus, even in the glassy region of PMMA/$LiCF_3SO_3$. In contrast, plasticization due to moisture absorption was not detected in the case of LiBr.

In Chapter 3, the mechanism of T_g enhancement by the addition of LiBr was investigated. It was found that a strong physical crosslinking occurs in PMMA/LiBr, leading to a prolonged relaxation mode. Furthermore, it was revealed that the prolonged relaxation mode is dominant to increase T_g in PMMA/LiBr. This phenomenon had not been reported that such strong crosslinking occurs only by the addition of a specific lithium salt. This technique could be applicable to provide strong physical crosslinking in various functional materials composed of PMMA.

In Chapter 4, the optical properties and thermal expansion of the blend films of PMMA with $LiCF_3SO_3$ were investigated. The orientation birefringence of films was decreased by addition of $LiCF_3SO_3$ when the film was stretched with same level of stress. The orientation birefringence of the blend was small since pure PMMA has a small intrinsic birefringence. Moreover, the addition of $LiCF_3SO_3$ reduced the photoelastic birefringence in the glassy state and the stress-optical coefficient. This may be attributed to the strong ion–dipole interactions between the lithium cations and the carbonyl groups of PMMA. The small thermal expansion was caused by such strong interactions. The modification of properties of PMMA by blending with salts is an attractive choice for optical applications including liquid crystal displays.

Keywords: Poly(methyl methacrylate), Salt, Glass transition temperature, Birefringence