

Improvement of Poly(vinyl alcohol) Properties by the Addition of Magnesium Nitrate

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ABSTRACT: Aiming at the improvement of mechanical and dielectric properties of poly(vinyl alcohol) (PVA), we prepared composites of PVA and magnesium nitrate hexahydrate. It was found that the composites were very soft and rubber-like, and the glass transition temperature decreased with increasing the salt concentration. Wide-angle X-ray diffraction and small-angle X-ray

scattering revealed that the crystallites of PVA were destroyed by the additive and it was the cause of the softening. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1647–1652, 2009

Key words: poly(vinyl alcohol); magnesium nitrate hexahydrate; softening; WAXD; SAXS

INTRODUCTION

Poly(vinyl alcohol) (PVA) is an interesting synthetic polymer because it is water-soluble and biocompatible, which are mainly due to hydrogen bonds between hydroxyl groups on the chain and water molecules or biomolecules.¹ Another interesting point is that it can crystallize even if the chain configuration is atactic.² This is caused by strong hydrogen bonds between hydroxyl groups on the same chain as well as other chains. Because of the hydroxyl groups, PVA also crystallizes in some solvents such as water,³ mixture of dimethyl sulfoxide and water,^{4–6} and other solvents,⁷ leading to physical gels. These PVA gels are used in various industrial products such as contact lens, disposable diaper, and sewage treatment. It is also well known that PVA reacts and/or interacts with other organic and inorganic compounds because of the hydroxyl groups.^{8–10} For example, PVA chemical gels can be obtained through chemical reactions with glutaraldehyde⁷ and borax.¹¹ Color reaction with iodine is also a famous reaction because of the charge transfer.^{12–14} Recently, Yamaura and Naito¹⁵ reported that it was possible to prepare high-modulus fiber spun from a PVA solution including sodium chloride. Thus, we

can modify or improve the properties of PVA using reactions/interactions of hydroxyl groups with other chemical compounds.

In this work, we prepared composites of PVA and an inorganic salt, magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$, to improve the bulk mechanical and dielectric properties. The composites studied in this work include relatively large amount of $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$. As far as we know, no other works are reported for PVA/salt bulk composites with such high salt concentration. This is a distinct feature of this study. We also investigated the structural changes of PVA because of the addition of $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ using wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) to reveal the origin of the property change.

EXPERIMENTAL

Materials

PVA used in this experiment has a number-average molecular weight M_n of 74,800, corresponding to a degree of polymerization of 1700, and the molecular weight distribution of $M_n/M_w = 2.02$, where M_w is weight-average molecular weight. The PVA was mixed with $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ as follows. PVA was dissolved in water at 100°C to give a 25 wt % solution, and then the given amount of $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ was added to the aqueous solution during stirring.

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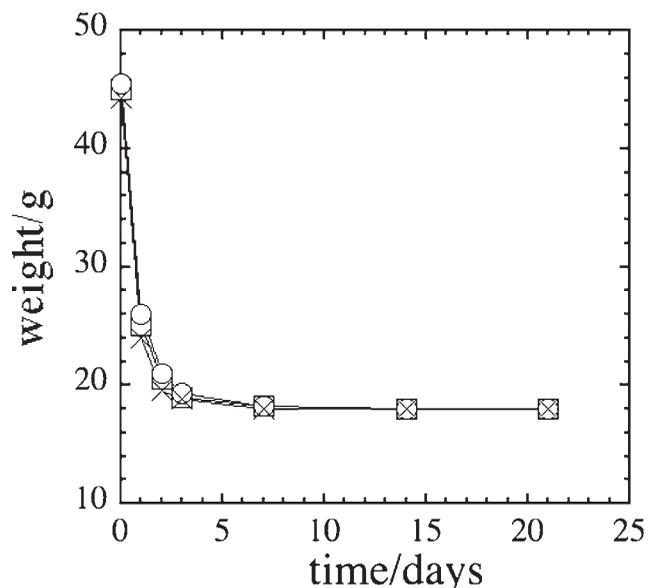


Figure 1 Weight change of the 100/100 composite after the preparation for three different runs. RH = 40%, $T = 23^{\circ}\text{C}$.

The homogeneous solution was kept in a relative humidity (RH) of 40% at 23°C for 3 weeks to evaporate the water. In these experiments, we prepared PVA/ $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ composites with weight ratios of 100/20, 100/60, 100/150, and 100/200. Hereafter, these composites are called, for example, the 100/100 composites, and the concentration of $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ is described as weight per 100 g of PVA, C_{MN} (g/100 g).

Measurements

Tensile storage modulus E' and loss modulus E'' were measured at a frequency of 1 Hz in a temperature range of -50 to 120°C using a Rheometric RSA-2. Differential scanning calorimeter (DSC) measurements were done using Perkin-Elmer Diamond DSC. The DSC scans were performed under nitrogen environment. Storage dielectric constant ϵ' and loss dielectric constant ϵ'' were measured at 25°C in a frequency range from 10^2 to 10^7 Hz using a Multi Frequency LCRMeter 4274A/4275A, Hewlett-Packard. WAXD measurements were carried out using X-ray diffractometer RINT-2000, RIGAKU. Wavelength, λ , of the incident X-ray was 1.54 \AA . SAXS measurements were performed using an apparatus installed at a beam line BL-10C in the synchrotron radiation facility, Photon Factory, KEK, Tsukuba, Japan. Wavelength (λ) of the incident X-ray was 1.54 \AA . The range of length of scattering vector q in the SAXS measurements was 0.008 to 0.15 \AA^{-1} , where q is given by $q = 4\pi\sin(\theta)/\lambda$ (2θ being the scattering angle).

RESULTS AND DISCUSSION

Stability and appearance

First of all, we examined the stability of the composites. After preparing the aqueous solution of PVA and $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$, we measured the weight as a function of time in a RH of 40% at 23°C . The change of weight of the 100/100 composite is shown in Figure 1 for three different runs. For the first 3 days, large weight loss due to the evaporation of water was observed, but the sample weight was very stable for 3 weeks after the first water loss, showing the stability of the composite. The obtained composites are transparent and very soft (or rubber-like) when compared with the original PVA without magnesium nitrate, which is demonstrated in Figure 2 for the 100/100 composite.

Mechanical measurements

We performed mechanical measurements on the 100/0, 100/60, and 100/100 composites at a frequency of 1 Hz in a temperature range of -50 to

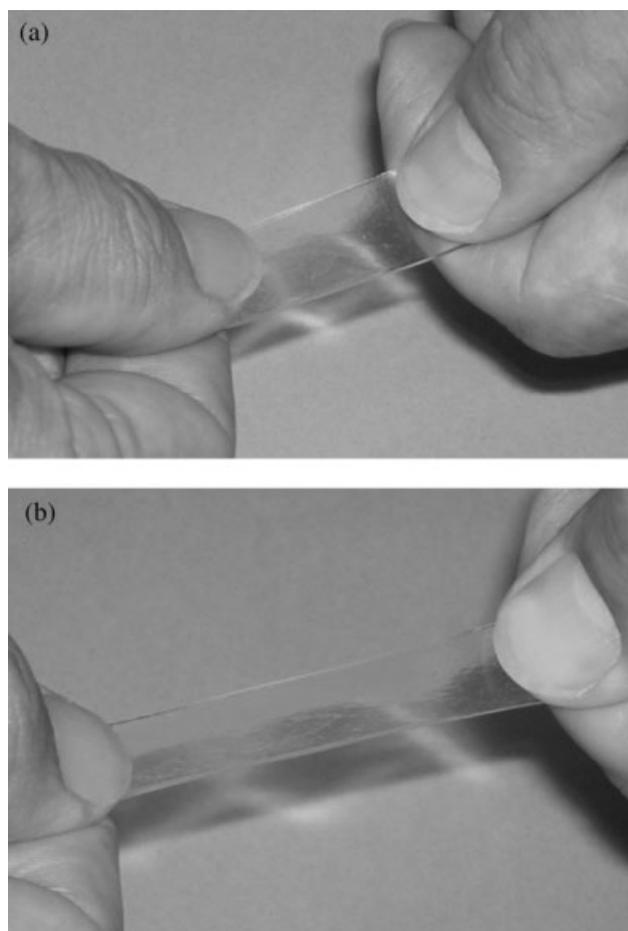


Figure 2 Photographs of the 100/100 composite before (a) and after (b) elongation by hand.

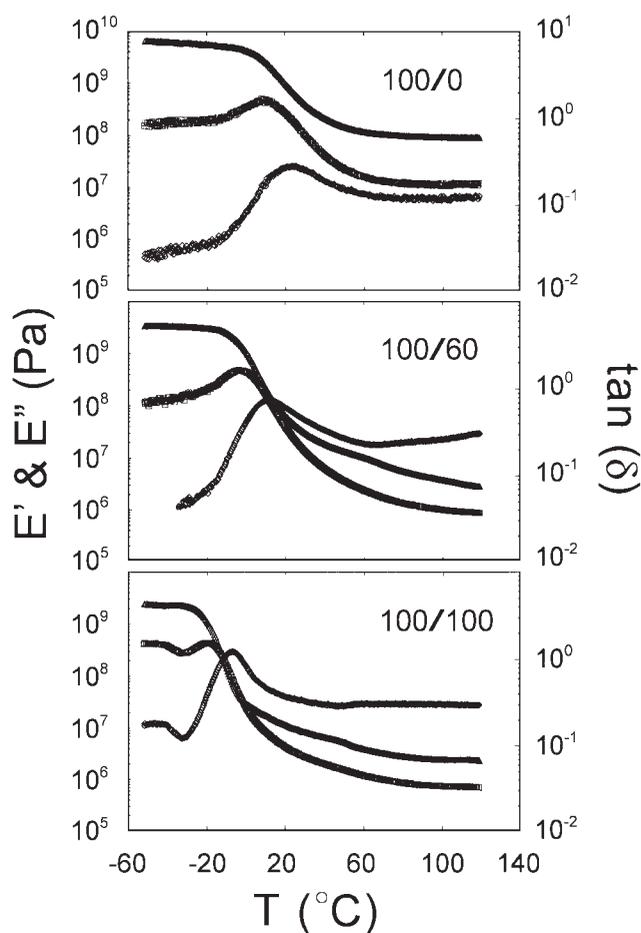


Figure 3 Tensile storage modulus E' (triangle), loss modulus E'' (square), and loss $\tan(\delta)$ (diamond) for the 100/0, 100/60, and 100/100 composites at a frequency of 1 Hz.

120°C. The observed tensile storage modulus E' , loss modulus E'' , and $\tan(\delta)$ are plotted in Figure 3 against temperature. The tensile storage modulus E' at 25 and 60°C and the peak temperature of $\tan(\delta)$ are plotted against the salt concentration C_{MN} in Figure 4. As the concentration, C_{MN} , of $Mg(NO_3)_2 \cdot 6H_2O$ increases, the peak temperature decreases, suggesting that the glass transition temperature T_g decreases. It is very clear that the storage modulus E' decreases with increasing the salt concentration, and the salt concentration dependence is almost identical between 25 and 60°C. In other words, the addition of $Mg(NO_3)_2 \cdot 6H_2O$ makes PVA very soft. It is noted that the tensile loss modulus E'' also decreases with increasing the salt concentration while the dependence of the loss modulus E'' is weaker than that of the storage modulus E' .

Thermal measurements

To evaluate the thermal properties of the composites, we carried out DSC measurements on the composites in a temperature range of -70 to 100°C

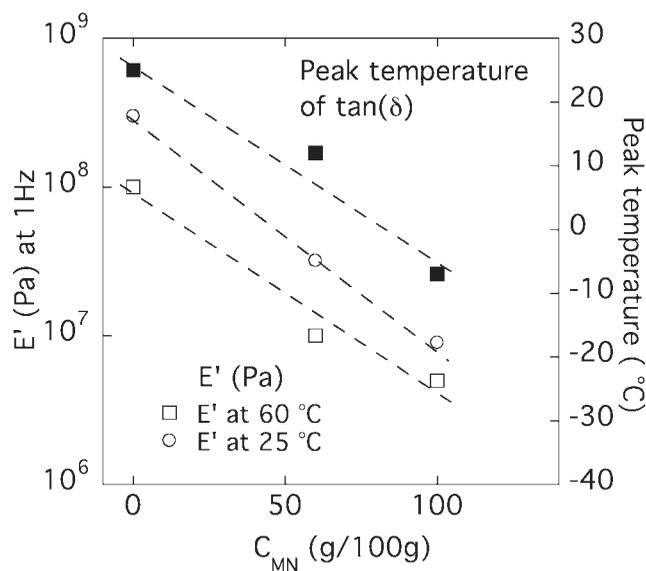


Figure 4 Tensile storage modulus E' at 60°C and peak temperature of $\tan(\delta)$ for the 100/0, 100/60, and 100/100 composites as a function of the salt concentration C_{MN} .

under nitrogen atmosphere. The heating rate was 10°C/min for all the measurements. An example of heat flow is shown for the 100/100 composite in a heating run in Figure 5. We observed the glass transition at around $T_{g1} = -40^\circ\text{C}$ while a small hump was also observed at $T_{g2} = 68^\circ\text{C}$. The latter is rather close to the glass transition temperature of pure PVA without salt (75°C). This can be understood as follows. The lower glass transition temperature T_{g1} must be caused due to some interactions with the salt and located at -40°C , which is lower than the peak temperature of $\tan(\delta)$ because of the frequency of 1 Hz. On the other hand, the higher glass transition temperature of PVA must be originated from amorphous PVA chains without interactions with the salt, and the value of $T_{g2} = 68^\circ\text{C}$ is close to T_g of pure PVA while it slightly shifts to lower temperature. These two glass transition temperatures are plotted in Figure 6 as a function of the salt

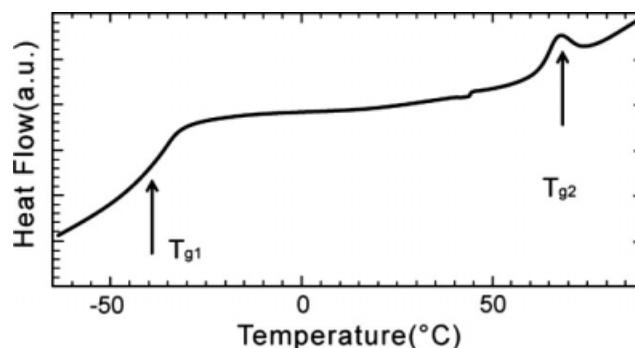


Figure 5 DSC curve of the 100/100 composite during heating process from -70 to 120°C . Heating rate was 10°C/min.

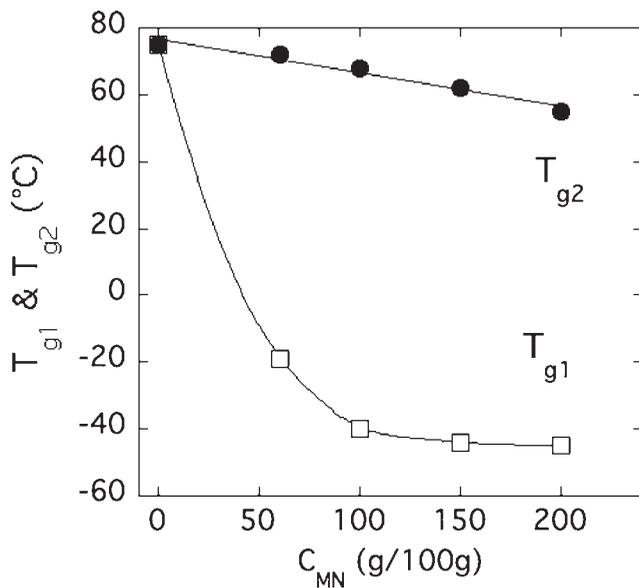


Figure 6 Glass transition temperatures T_{g1} and T_{g2} as a function of $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ concentration C_{MN} .

concentration C_{MN} . It is clear that the lower glass transition temperature T_{g1} decreases with increasing the salt concentration. This is one of the causes for the softening of the composites with the salt concentration. The higher T_{g2} also decreases with increasing the salt concentration, but the extent of the decrease is very small when compared with T_{g1} .

Dielectric dispersion measurements

It is expected that the dielectric properties of the PVA are modified by the addition of $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$. Hence, we carried out dielectric dispersion measurements on the 100/0, 100/20, 100/60, 100/100, and 100/150 composites to examine the dielectric properties. In Figure 7, the observed dielectric loss $\tan(\delta)$ is plotted as a function of the frequency. The peak of $\tan(\delta)$ of PVA without salt is not observed in the present frequency range, suggesting that it is below 1×10^2 Hz. For the composites, however, the peaks are observed in the present frequency range. The peak frequency f_p and the peak intensity of $\tan(\delta)$ are plotted as a function of the salt concentration C_{MN} in Figure 8. As the salt concentration C_{MN} increases, the peak frequency gradually increases and the value of $\tan(\delta)$ decreases, whereas the $\tan(\delta)$ begins to increase above the 100/100 composite ($C_{\text{MN}} = 100$ g/100 g). Note that the peak frequency increases very sharply above $C_{\text{MN}} = 100$ g/100 g following the increase of $\tan(\delta)$. As the salt concentration increases in the low salt concentration region (roughly below the 100/100 composite), the mobility of the salt in PVA may increase because the PVA crystallites are destroyed as will be shown below, resulting in the high frequency shift in the

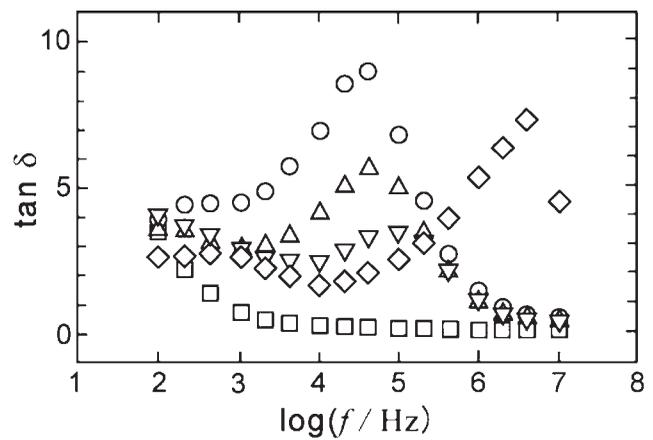


Figure 7 Frequency dependence of dielectric $\tan(\delta)$ for the 100/0 (\square), 100/20 (\circ), 100/60 (\triangle), 100/100 (∇), and 100/150 (\diamond) composites.

peak of $\tan(\delta)$. The value of $\tan(\delta)$ decreases with increasing the salt concentration below the 100/100 composite as mentioned earlier. This result is hard to understand at the moment. One possibility is that there are two binding sites of the salt in the composite, but we have no final conclusions on it. Further increase in the salt concentration produces free salts, which are not bound to PVA, leading to the steep increase in the peak frequency. As expected, the results show that the composites have high-frequency dielectric properties.

Wide-angle X-ray diffraction measurements

To investigate what structure changes occur in the PVA/ $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ composites as the salt

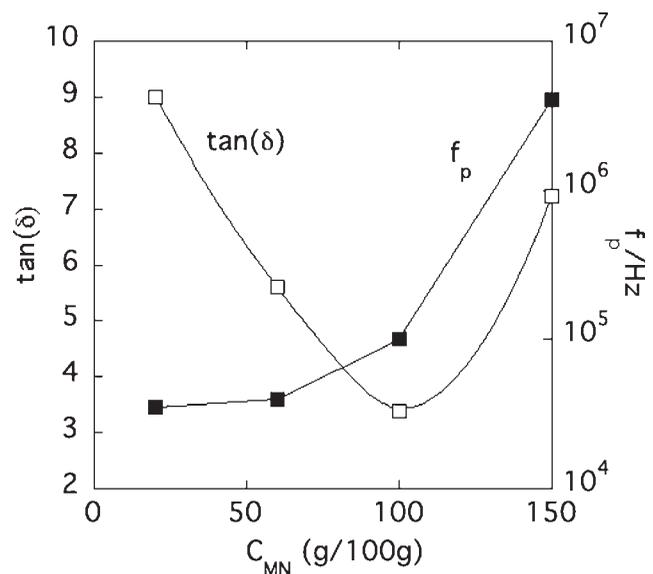


Figure 8 Peak frequency f_p and peak intensity of dielectric $\tan(\delta)$ as a function of salt concentration C_{MN} .

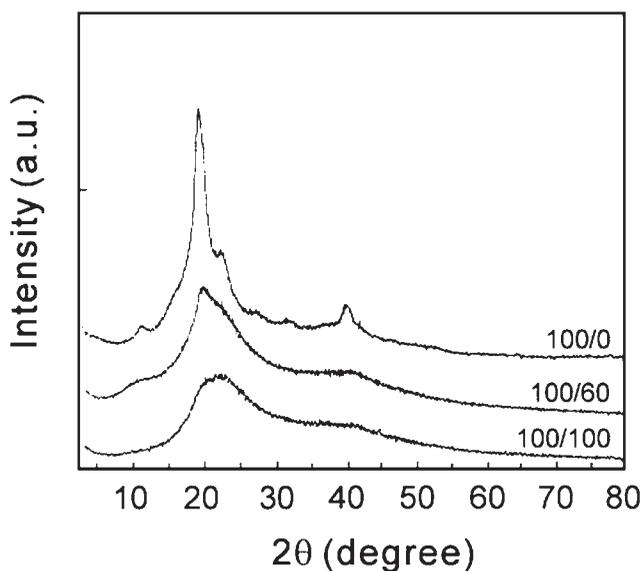


Figure 9 WAXD curves for the 100/0, 100/60, and 100/100 composites.

concentration increases, we performed WAXD measurements. The WAXD curves are shown in Figure 9 for the 100/0, 100/60, and 100/100 composites. In PVA (100/0), we clearly observed (101) and (10 $\bar{1}$) diffraction peaks at $2\theta = 19.5^\circ$, and other weak diffraction peaks from (200), (002), and (111) planes were observed at 22.7° , 32.4° , and 39.5° , respectively. With increasing the salt concentration, the diffraction peaks decrease in intensity and are slightly observed in the 100/100 composite. It is clear that the addition of the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into PVA destroys the crystallites of PVA. It is noted that we did not see any Bragg peaks from the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt in the measurements, suggesting that the salt molecules are dispersed in PVA at molecular level because the interactions between $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and hydroxyl groups in PVA are very strong. Magnesium salt is hexaquomagnesium nitrate¹⁶ and it is assumed to be nearly six dentate hydrogen bond, that is, a hexaquomagnesium forms about hydrogen bonds with six hydroxyl groups of PVA chains and breaks the intermolecular hydrogen bond of PVA chains. In other words, the interaction between hexaquohydratemagnesium with PVA chains reduces the degree of crystallinity of PVA, resulting in an amorphous structure. This destruction may cause the decrease in the glass transition temperature as shown earlier. Using the WAXD curve of amorphous PVA,¹⁷ we have separated the crystalline contribution and the amorphous contributions in the WAXD curve of the composites and evaluated the degree of crystallinity and the crystallite size for the (101) direction using Sherrer's equation¹⁸ as a function of the salt concentration C_{MN} . The results are shown in Figure 10. In the 100/100 composite, the degree of crystallinity is

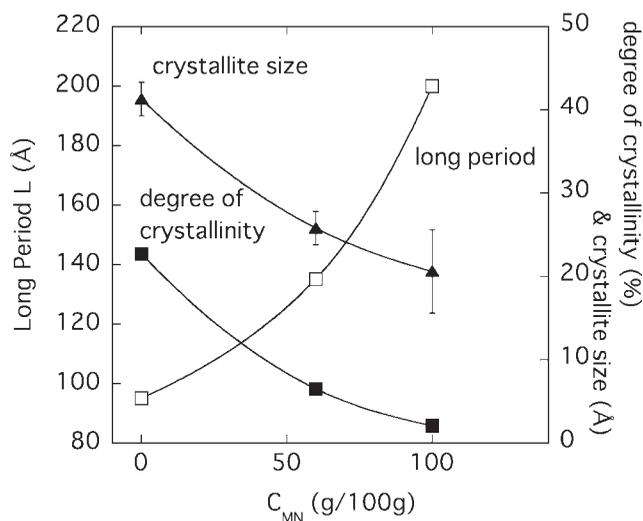


Figure 10 Crystallite size along (101) direction, degree of crystallinity, and long period L as a function of salt concentration C_{MN} .

very small ($2 \pm 1\%$) and the size is only $20 \pm 5 \text{ \AA}$. The crystallite size as well as the degree of crystallinity decrease with increasing the salt concentration, confirming that the addition of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ destroys the PVA crystallites.

Small-angle X-ray scattering measurements

We performed SAXS measurements on the 100/0, 100/60, 100/100, and 100/200 composites. The observed SAXS curves are shown in Figure 11. In the SAXS curves of pure PVA (100/0), we clearly observed a broad peak at around $q_m = 0.067 \text{ \AA}^{-1}$, which is the so-called long period peak. The long

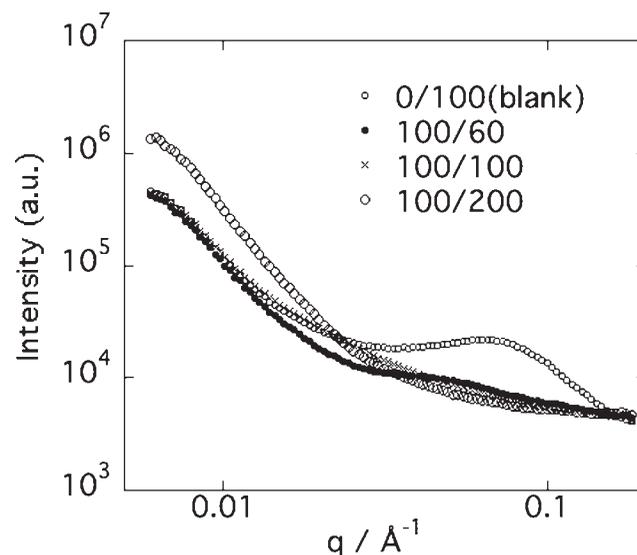


Figure 11 SAXS curves for the 100/0 (circle), 100/60 (filled circle), 100/100 (cross), and 100/200 (diamond) composites.

period L can be calculated from an equation $L = 2\pi/q_m$, which is the spacing between the stacked lamella crystals. In Figure 10, we plotted the long period L as a function of the salt concentration. The long period L increases with the salt concentration, corresponding to the decrease in the number of crystallites.

All the data presented here in this article suggests that $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ is dispersed in PVA at molecular level and destroys the PVA crystallites because of the strong interaction between the salt and hydroxyl groups in PVA. In addition, it is expected that the salt acts as the crosslinking point between the PVA chains, resulting in a network of amorphous PVA chains. This is likely to be an origin of the rubber-like properties of the composites.

CONCLUSION

In this work, we prepared composites of PVA and $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ with various ratios and examined the mechanical, thermal, and dielectric properties. The mechanical measurements showed that the addition of the salt made the composite very soft and rubber-like, and the DSC measurements suggested that the softening must be due to the decrease in the glass transition temperature, T_g . The dielectric $\tan(\delta)$ shifted to higher frequency with increasing the salt concentration. The structure studies by means of WAXD and SAXS revealed that the crystallites in the composites were destroyed by the

addition of salt because of the strong interactions between $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ and hydroxyl groups in PVA, and it must be the structural origin of the softening and the decrease of the glass transition temperature in the composites.

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