Characteristics of Hybrid Films Composed of Photosensitive PVA and Inorganic Particles

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1. Introduction

In general, composite materials are formed when at least two different types of materials (organic, inorganic, and metallic) are mixed. The combination of organic and inorganic materials is expected to provide remarkable and complementary properties. Organic-inorganic hybrids show highly optical transparency, excellent thermal, mechanical, and solvent-resistant properties. The exploitation of new nanostructure hybrid organic-inorganic composites has recently been expected for their scientific interest and their industrial applications. [1-3]

Poly (vinyl alcohols) with styrylpyridinium groups, PVA-SbQ has good solubility in water. One of the typical applications of water developable photopolymer systems is to produce screen-printing plates. [4] The purpose of this study is to elucidate the water-resistance and the thermal properties of hybrid films composed of PVA-SbQ and inorganic particles.

2. Experimental

Photosensitive polymers were prepared by acetalization with formylstyrylpyridinium according to the known method. [5] The PVAs from Kuraray Co., Ltd. have a polymerization degree of 1700 and a saponification value, 88 mol%. The different contents of tetraethylorthosilicate (TEOS) and HCl were added gradually in 10 wt% PVA-SbQ solutions containing ethanol through constant stirring. The resulting solutions were stirred for a few days under room temperature conditions. In the same manner, titania was incorporated into the PVA-SbQ solution by sol-gel process via tetraisopropylorthotitanate (TPT). The polymer solutions having inorganic particles were casted with a doctor blade and dried in the range of 20 to 150°C under vacuum. The films were irradiated by a high-pressure Hg lamp with a pyrex glass filter.

The films were immersed in water to the equilibrium at 25°C. The weight of swollen films, and then the dried films were measured. Dynamic mechanical analysis (DMA) was performed for film specimens (15 mm long, 5 mm wide, and about 50 μm thick) on a thermo mechanical analyzer at a load frequency of 10 Hz and a heating rate of 5°C min⁻¹ under nitrogen atmosphere. The differential scanning calorimetry (DSC) measurement on films was performed using a thermal analyzer DSC-3100 (Mac Science) at a heating rate of 20°C min⁻¹ under nitrogen flow.

3. Results and Discussion

Figs. 1 and 2 show the relationship between the swelling and the content of inorganic particles in films after immersing in water at the equilibrium state. The weight of the swollen films, W_{eq} , has been normalized with respect to the weight, before immersing in water, W_0 . The value of the water uptake after swelling of films differs from each other, depending of the amount and the kind of

Fig. 1 Water uptake after swelling of PVA-SbQ/TEOS hybrid films in an aqueous water; temperature of preparing film/°C: □ 20, ▒ 110, ▓ 130, ■ 150.

Fig. 2 Water uptake after swelling of PVA-SbQ/TPT hybrid films in an aqueous water; temperature of preparing film/°C: □20, ▨40, ▩60, ▪80, ■100.

Fig. 3 Residual ratio of PVA-SbQ/TPT hybrid films in an aqueous water; Temperature of preparing film/°C: □20, ▨40, ▩60, ▪80, ■100.

inorganic materials. The swelling of the PVA-SbQ films containing dispersed hybrid inorganic particles was also subjected to a temperature of preparing the film from polymer solutions. In hybrid silica films changed from 5 to 100 wt% silica the swelling ratio, W_{eq} / W_0 , was extremely altered by the presence of 10 wt% silica or above at 150°C. This result suggests that the interactions between PVAs and silica proceed in the direction of the most stable form. The extent of swelling of hybrid titania films decreases gradually with the amount of titania and an increase in temperature.

Fig. 3 shows the variation of the residual amount of hybrid titania films after immersing in water. The higher the degree of temperature, the higher is the degree of residual amount of films.

Fig. 4 shows the DMA thermograms of hybrid titania films for various titania contents as mechanical loss tangent, $\tan \delta$, against temperature in the range of 40 to 120°C. The thermogram of

Fig. 4 Temperature dependence of the loss tangent for PVA-SbQ/TPT hybrid films; PVA-SbQ/TPT (wt%); — 100/0, --95/5,85/15, ---80/20.

the PVA-SbQ film exhibits a peak at 76°C, designated as the α_a relaxation, represents the glass transition temperature, T_g of PVA-SbQ. With increasing titania contents, the T_g shifted to the higher temperature. This result suggests that the presence of titania in a film is responsible for an increase of the molecular packing density of amorphous regions. This behavior attributed to the tendency of titania to interact in the PVA. The hybrid titania films exhibited higher value of the maximum tangent δ . This suggests an increase in the volume fraction of the amorphous region.

The DSC thermogram of the PVA-SbQ film exhibited a peak melting temperature, T_m of 167°C. However, the DSC thermograms of hybrid silica films were scarcely influenced by the proportion of silica in films compared with hybrid titania films.

4. Conclusion

The PVA-SbQ-inorganic particles hybrid films have remarkable effects on the water-resistance and the thermal properties. The water-resistance of hybrid titania films is higher than that of hybrid silica films.

References

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