FORMATION AND PROPERTIES OF POLY(VINYL BUTYRAL)-ZIRCONIA HYBRIDS

Koji Nakane, Kosuke Mizutani, Ruonan Zhang and Nobuo Ogata
Department of Materials Science and Engineering, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan.

Introduction

Poly(vinyl butyral) (PVB) is sturdy and flexible. Especially, it is known for its high impact strength at low temperatures. Furthermore, PVB has excellent adhesive properties with many materials such as glass, metal, plastics and wood. Thus, PVB is widely used as a paint, an adhesive agent, a printing paste and a film sandwiched in a laminated safety glass for automobiles [1]. Laminated glass consists of two glass plates bonded together by a PVB interlayer. PVB material keeps the shards of broken glass plates in the frame of the glass unit after the failure and makes them safety. However, heat-resistance of PVB is not so outstanding, which could be the main reason leading to PVB mechanical weakness in higher temperature range, because of the low glass transition temperature (T_g) of PVB. Thus, the anti-penetrability of laminated glass decreases at higher temperature range, and it should be improved.

The author considered that a hybrid of PVB and glass could be prepared by means of the sol-gel process due to the high adhesive property of PVB. By mixing glass with PVB, the properties of PVB would be expected to change and its functions to develop. Fu et al. prepared silica/PVB hybrid material and used as a support of ternary europium complexes and phenanthroline [2]. But, the properties of the hybrid have not been reported. In a previous paper, we reported the formation and the properties of PVB-titanium dioxide hybrids [3]. While the reactivity of zirconium alkoxide is higher than that of titanium alkoxide, thus in this study, we tried to form PVB-zirconium dioxide (zirconia) hybrids instead through sol-gel process. We considered that the thermal/mechanical properties of PVB can be improved effectively, and transparent PVB-inorganic hybrids can be formed by using zirconium alkoxide as a staring reagent to prepare a zirconia sol.

Experimental

Materials

PVB (Mowital B60H, degree of polymerization = 1000, degree of acetalisation = 70%) was a kind gift from Kuraray Co., Ltd., Japan. Zirconium (IV) butoxide 1-butanol solution (85 wt.%) was obtained from Wako Pure Chemical Ind., Ltd, Japan, and used without any purification.

Specimen preparation

Zirconium (IV) butoxide ($Zr(OC_4H_9)_4$, 0.1mol) was diluted by ethanol (100ml). Hydrochloric acid (HCl) (2N, 2.7ml) was poured and stirred into this solution, resulting in a transparent zirconia (ZrO_2) sol. The general sol-gel reaction of the zirconium butoxide is shown by the following scheme:

$$Zr(OC_4H_9)_4 + 4H_2O \rightarrow Zr(OH)_4 + 4C_4H_9OH$$

$$nZr(OH)_4 \rightarrow nZrO_2 + 2nH_2O$$

A fixed amount of zirconia sol was added to PVB 5 wt% ethanol solution. This mixed solution was then aged at room temperature in sealed dish for 48 h, and the transparent PVB-zirconia hybrid films (thickness, ca. 50 μm) were obtained by drying wet gel at 40℃ in air and further in vacuo.

Apparatus and procedures

The dynamic mechanical analysis (DMA) was performed with E4000-Type-DVE viscoelastic analyzer (UBM Co., Ltd., Japan). Temperature scans at 100 Hz frequency were carried out with a heating rate of 2˚C/min.

Results and discussion

Figure 1 shows the relationship between the composition of PVB/zirconia and the gelation time (the time until gel is formed) in a sealed dish. In the case of pure zirconia sol without PVB, the gelation was not observed even after 3 months. Whereas the

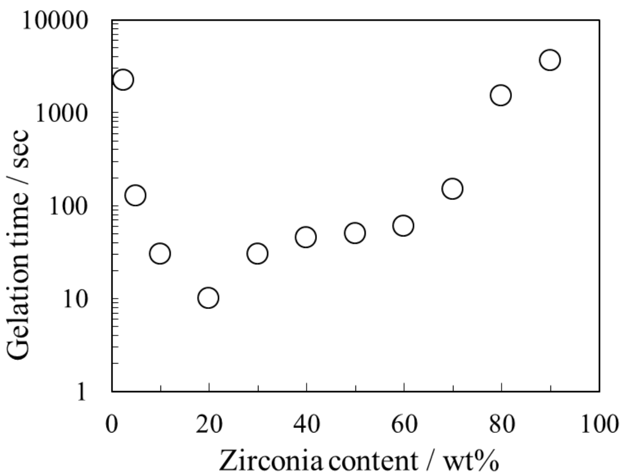

Figure 1 Effect of zirconia content in PVB/zirconia mixed solution on gelation time.

gelation time showed the minimum value (ca. 15 sec) as zirconia content rose up to 20 wt%, however, the gelation was retarded by the existence of excess zirconia. It is likely that zirconia acts as a crosslinking agent of PVB, but redundant zirconia would impede the reaction bonding between PVB and zirconia.

Figure 2 shows the relationship between the degree of acetalisation of PVB in PVB/zirconia (90/10 wt.%) mixed solution and the gelation time. The increase in the degree of acetalisation prolongs the gelation, accordingly indicates that the gelation will occur due to the interaction between remaining hydroxyl (OH) group of PVB and zirconia. All hybrids obtained after gelation and drying were colorless and transparent.

Figure 3 shows the TEM image of PVB-zirconia (80/20 wt.%) hybrid. The few dark spots corresponding to zirconia consequently demonstrates that zirconium particles below several dozen nanometers can be dispersed in PVB matrix.

Figure 4 shows the results of the DMA measurements. The *tan*δ decreases with increasing the zirconia content, and peak [corresponding to the glass transition temperature (T_g) of PVB] becomes broader and shifted to a high temperature gradually. In addition, when the zirconia content increased, the decrease of the storage modulus near the T_g became gentle, and high values were maintained at high temperature ranges. From these results it is likely that zirconia is dispersed homogeneously in PVB matrix, and thermal motion of the PVB molecular chain can be prevented by the interaction between them.

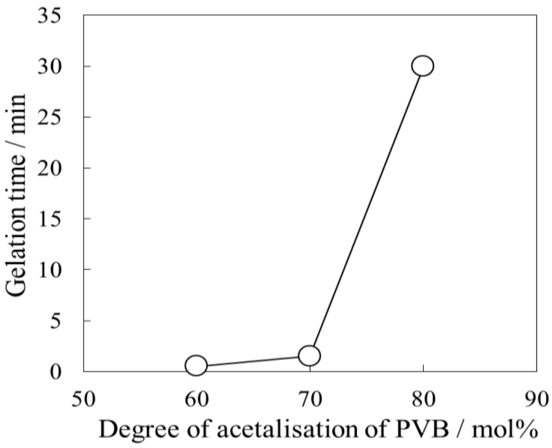

Figure 2 Effect of degree of acetalisation of PVB in PVB/zirconia (90/10 wt.%) mixed solution on gelation time.

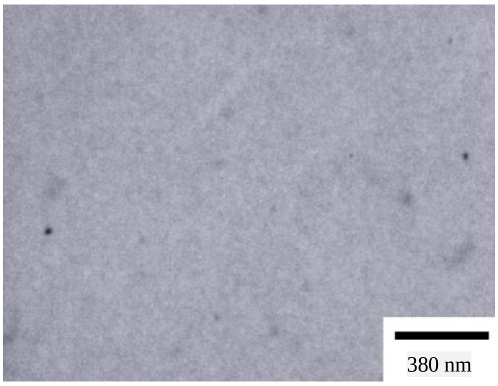

Figure 3 TEM image of PVB-zirconia (80/20 wt.%) hybrids.

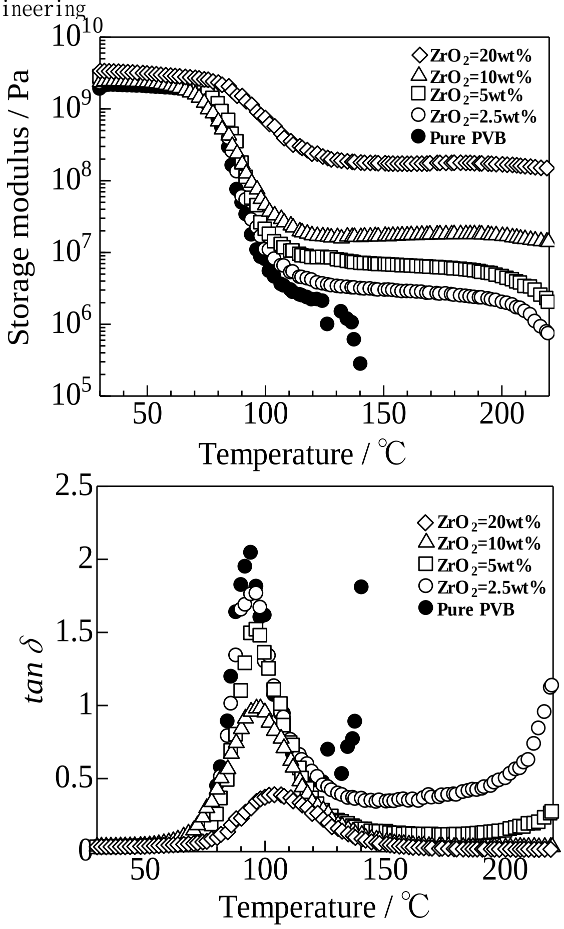

Figure 4 Thermo mechanical spectra of PVB-zirconia hybrids.

Conclusion

The PVB-zirconia hybrids formed by means of the sol-gel process showed good compatibility and a strong interaction between them. The thermal/mechanical properties of PVB were effectively improved by hybridization of PVB and zirconia.

References

1. Blomstrom, T. P. "*Concise Encyclopedia of Polymer Science and Engineering*", Edited by Kroschwitz, J. I. John Wiley & Sons, Inc., N.Y. (1990).
2. Fu, L., Zhang, H., Wang, S., Meng, Q., Yang, K. and Ni, J. Preparation and luminescence properties of the ternary europium complex incorporated into an inorganic/polymer matrix by a sol-gel method. *J. Sol-Gel Sci. Tech.*, **15** (1999) 49-55.
3. Nakane, K., Kurita, T., Ogihara, T., Ogata, N., Properties of Poly(vinyl butyral)/TiO_2 Nanocomposites Formed by Sol-Gel Process, *Composites: Part B*, **35** (2004) 219-222.