

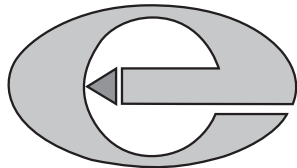
**Poly (vinyl butyral)-zirconia hybrid films
formed by sol-gel process**

by

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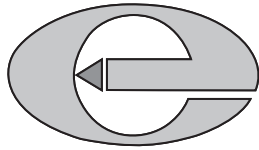
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Poly(vinyl butyral)-zirconia hybrid films formed by sol-gel process

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Abstract

A sol-gel process has been successfully utilized to form hybrid materials of poly(vinyl butyral) (PVB) and zirconium dioxide (zirconia). The gelation occurred due to the interaction between remaining hydroxyl group of PVB and zirconia. The hybrids showed good optical transparency and significant improvement in Young's modulus, dynamic mechanical property, abrasion resistance and impact resistance. The glass transition temperature of PVB shifted to higher temperatures by hybridization of PVB and zirconia.

Key words: *Poly(vinyl butyral), Zirconium butoxide, Zirconia, Sol-gel process, Hybrid*

1. 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 paint, an adhesive agent, a printing paste and a film sandwiched in a laminated safety glass for automobiles (Blomstrom, 1990; Safy and Sabaa, 1995).

Laminated glass consists of two glass plates bonded together by a PVB interlayer (Tuchinda *et al.*, 2006). 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-

penetration of laminated glass decreases at higher temperature range, and it should be improved.

Progress of sol-gel process which synthesizes ceramics at low temperature has made it possible to prepare novel organic-inorganic hybrids (Wen and Wilkes, 1996; Sakka, 2008). They have the possibility to become new materials having both advantages of organic materials such as the light-weight, flexibility, and good moldability, and of inorganic materials such as the high strength, heat-stable, and chemical resistance. 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 PVB/silica hybrid material and used as a support of ternary europium complexes and phenanthroline (Fu *et al.*, 1999). But, the properties of the hybrid have not been reported. Also,

Chen *et al.* formed PVB/silica nanofibers by electrospinning (Chen *et al.*, 2009). Furthermore, Torki *et al.* formed silica or titanium dioxide nanoparticles/PVB nanocomposites and investigated the dynamic mechanical properties of the composites (Torki *et al.*, 2010; Mohallem and Silva, 2010).

In a previous paper, we reported the formation and the properties of PVB-titanium dioxide hybrids (Nakane *et al.*, 2004). 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 starting reagent to prepare a zirconia sol.

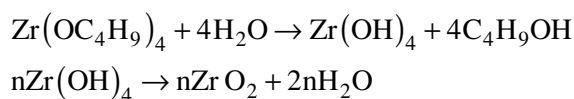
2. Experimental

2.1. 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.

2.2. Specimen preparation

Zirconium (IV) butoxide [$Zr(OC_4H_9)_4$, 0.1 mol] was diluted by ethanol (100 ml). Hydrochloric acid (HCl) (2 N, 2.7 ml) was poured and stirred into this solution, resulting in a transparent zirconia (ZrO_2) sol (Yoko *et al.*, 1987). The general sol-gel reaction of the zirconium butoxide is shown by the following scheme:



A fixed amount of zirconia sol was added to PVB 5 wt% ethanol solution and then poured into sealed dish before forming into wet gel; Later, sealed dish with wet gel was aged at 40°C first in dried air for 48 hours then in vacuum dryer to obtain transparent PVB-zirconia hybrid films (thickness, ca. 50 μm). The hybrid films here are named in shortened form, for instance, hybrid containing 10 wt% zirconia is abbreviated as Zr-10.

2.3. Apparatus and procedures

The light transmittance curves and the haze (turbidity) were measured with U-4100

UV-Visible-NIR spectrophotometer (Hitachi High-Tech Co., Ltd., Japan) and NDH 5000 haze meter (Nippon Denshoku Industries Co., Ltd., Japan), respectively.

The tensile test was carried out at room temperature with an Instron-type tensile testing machine (Tensilon UTM-II-20, Toyo Baldwin Co., Ltd., Japan). The crosshead speed was 10 mm/min and the initial gauge length was 30 mm.

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.

The abrasion test was performed according to JIS L-1096 6-17 A method (CAT-125, Daiei Kagaku Seiki Mfg. Co. Ltd., Japan). The load was 454 g.

The impact resistance was estimated by a weight drop test. The weight is 48 g, and the height from the weight to the surface of the film is 300 mm.

3. Results and discussion

3.1. Formation of PVB-zirconia hybrids by sol-gel process

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 can't be observed even after 3 months. However, the gelation time appears sharp decline as adding zirconia into PVB solution, and reaches a minimum value around 15 sec as zirconia content raised up to 20 wt%; where after, the gelation is retarded by the existence of excess zirconia. It is

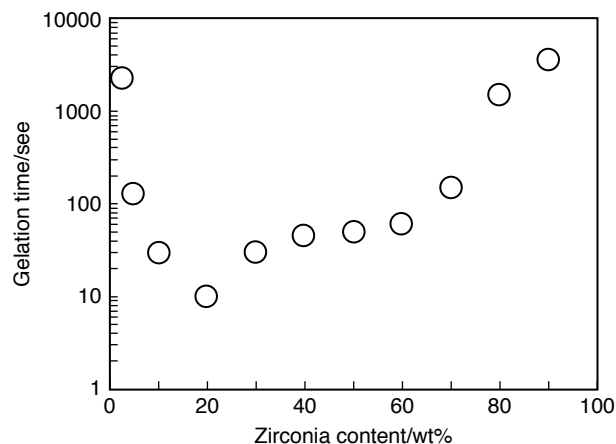


Fig. 1. Effect of zirconia content in PVB/zirconia mixed solution on gelation time.

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 gelation, which accordingly indicates that the gelation will occur due to the interaction between remaining hydroxyl (OH) group of PVB and zirconia.

Figures 3 (a)–(d) show the photographs of pure PVB and PVB-zirconia hybrid films obtained after

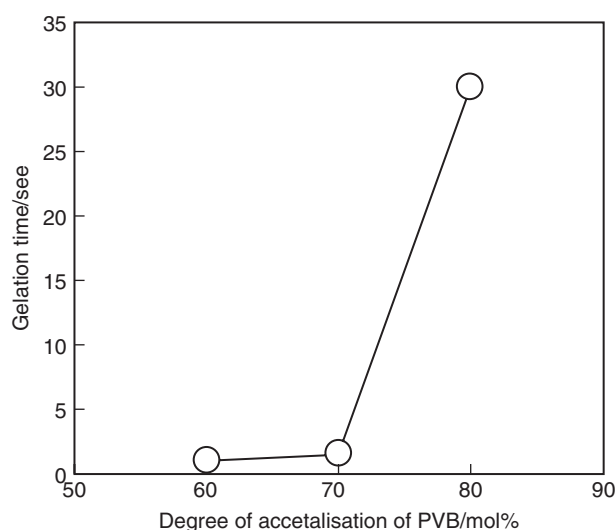


Fig. 2. Effect of degree of acetalisation of PVB in PVB/zirconia (90/10 wt%) mixed solution on gelation time.

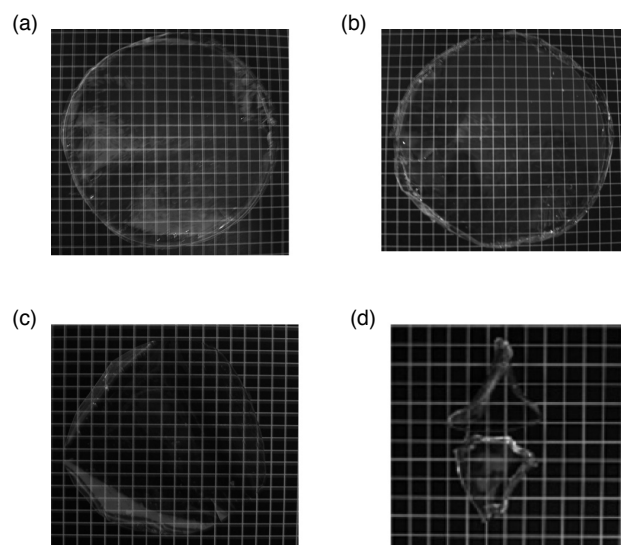


Fig. 3. Photographs of pure PVB and PVB-zirconia hybrid films [(a) pure PVB, (b) PVB/zirconia = 97.5/2.5 wt%, (c) 80/20wt%, (d) 70/30wt%].

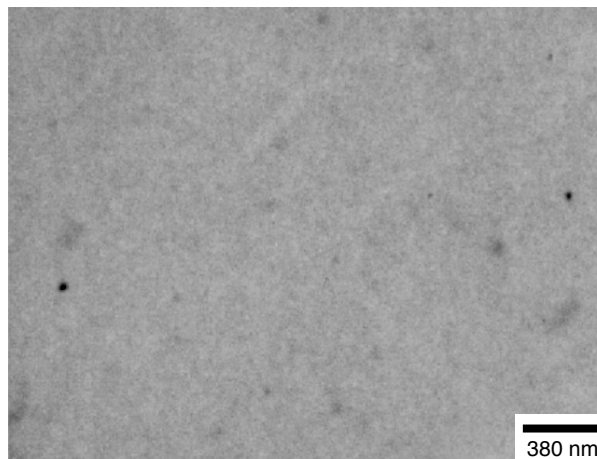


Fig. 4. TEM image of PVB-zirconia (80/20 wt%) hybrids.

gelation and drying. All samples are colorless and transparent, but it becomes difficult to form hybrid films above zirconia 20 wt% because the flexibility of the hybrid significantly decreases [see Figure 3(d)].

Figure 4 shows the TEM image of Zr-20 film. The few dark spots corresponding to zirconia consequently demonstrates that zirconium particles below several dozen nanometers can be dispersed in PVB matrix.

3.2. Optical properties of PVB-zirconia hybrids

Figure 5 shows the light transmittance curves of Zr-9 and Zr-17 films. Both hybrids are obtained with excellent transmittance (all above 90%), over the range of ultraviolet to near infrared rays. Figure 6 shows the haze of each film. The haze of PVB film undergoes subtle change from 0.93% (pure PVB) to 1.12% (Zr-17), which simultaneously indicates that our hybrid films have no turbidity.

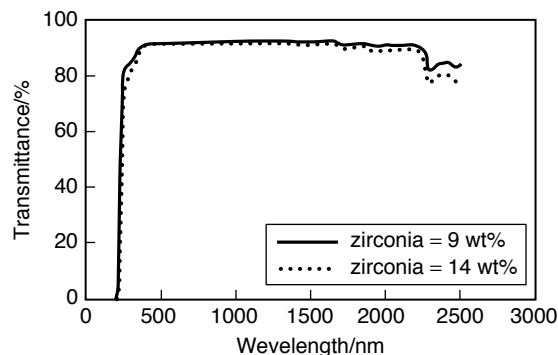


Fig. 5. Light transmittance curves of PVB-zirconia hybrid films.

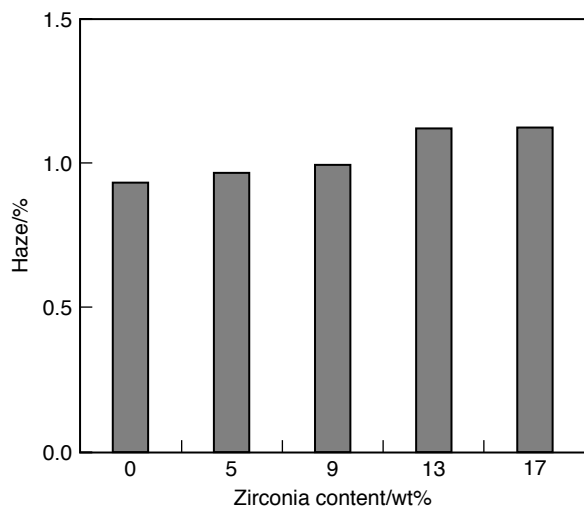


Fig. 6. Haze of pure PVB and PVB-zirconia hybrid films.

From the results listed above, PVB-zirconia hybrid films have the highest level of transparency, similar to that of acrylate resin. High transparency results from good compatibility between PVB and zirconia.

3.3. Thermal/mechanical properties of PVB-zirconia hybrids

Figure 7 shows the stress-strain (s-s) curves of each film. Pure PVB exhibits typical s-s curve with an obvious yield point. The elongation at break decreases as the addition of zirconia in PVB, and Zr-20 converts to exhibit brittle fracture before the yielding behavior taking place. The ductile to brittle fracture transition is observed around Zr-10. Figure 8 and Figure 9 illustrate the

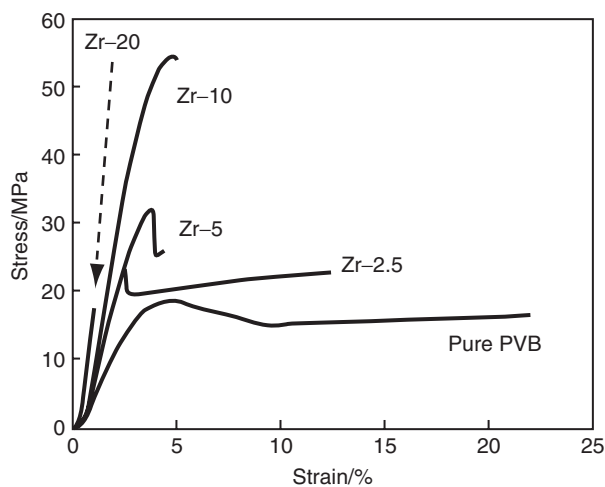


Fig. 7. Stress-strain curves of pure PVB and PVB-zirconia hybrid films.

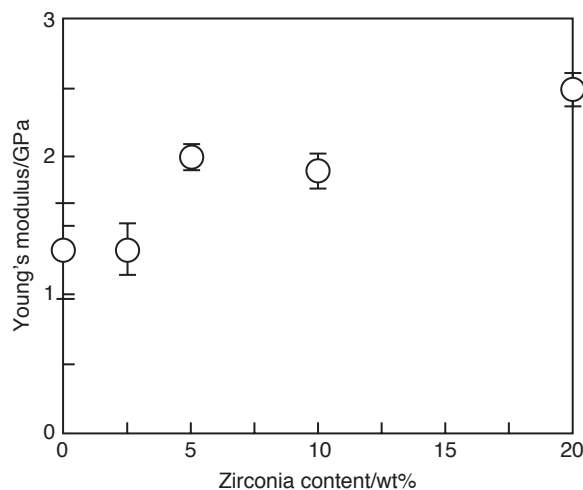


Fig. 8. Effect of zirconia content on Young's modulus of pure PVB and PVB-zirconia hybrid films.

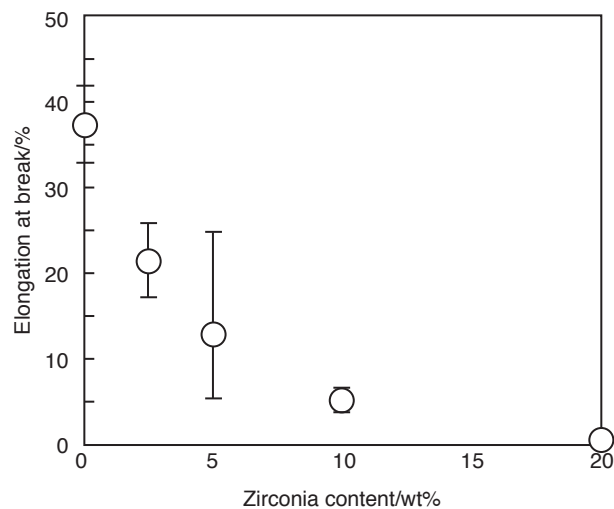


Fig. 9. Effect of zirconia content on elongation at break of pure PVB and PVB-zirconia hybrid films.

plots of the Young's modulus and the elongation at break of the hybrids. The incremental zirconia content gives rise to the linear increasing Young's modulus but simultaneous decline of the elongation at break, which eventually bottoms out as zirconia content up to 20 wt%. Similar tendency was reported in the system of poly(vinyl alcohol)/silica (Nakane *et al.*, 1999).

Figure 10 shows the results of the DMA measurements. The value of $\tan \delta$ decreases along with the accumulative zirconia content, and peak [corresponding to the glass transition temperature (T_g) of PVB] becomes broader and shifts gradually to higher temperature. In addition, the rise of zirconia content significantly alleviates the

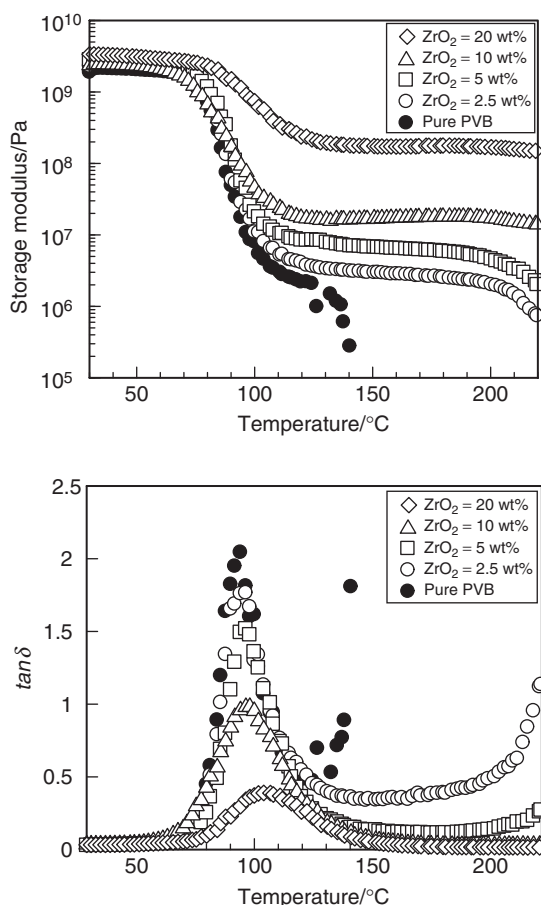


Fig. 10. Thermo-mechanical spectra of PVB-zirconia hybrid films.

reduction in storage modulus near T_g , hence preserving high storage modulus at high temperature range. From these results it is likely that zirconia is dispersed homogeneously in PVB matrix, thus preventing the thermal motion of PVB molecular chain by the interaction between them.

Figure 11 shows the result of abrasion test. The ordinate represents the number friction cycle when the film breaks down. The abrasion resistance of the films can be improved through adding no more than 10 wt% of zirconia, which is probably due to the impaired surface frictional resistance along with enhanced hardness of the hybrid films (e.g. the Young's modulus in Figure 8). On the other hand, the cycles for Zr-20 decrease because of the embrittlement and the stress concentration.

Figure 12 shows the result of impact test. The ordinate stands for the impact cycle number till the film is cracked. The improvement of impact resistance of PVB could be achieved by addition of small amount of zirconia to PVB: The number of

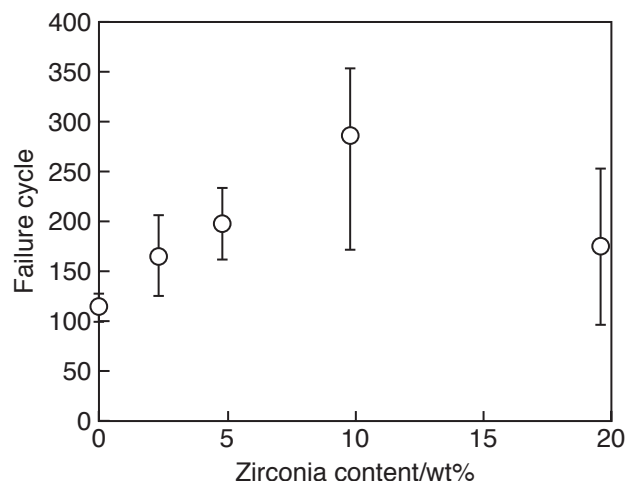


Fig. 11. Effect of zirconia content on abrasion resistance for PVB-zirconia hybrid films.

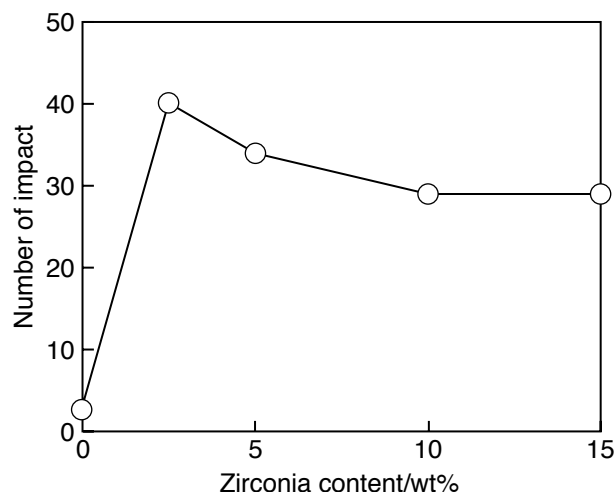


Fig. 12. Effect of zirconia content on impact resistance for PVB-zirconia hybrid films.

impact cycle for pure PVB is 3 times, while, it then drastically increases to 40 times of Zr-2.5. This can be attributed to the crosslinking of PVB molecules with zirconia. Afterwards the number gradually goes down to around 30 times of Zr-15 because of the embrittlement of the hybrid, but Zr-15 film keeps higher impact resistance than pure PVB does.

4. Conclusion

The PVB-zirconia hybrids formed by means of the sol-gel process shows good compatibility and a strong interaction between them. The thermal/mechanical properties of PVB can be effectively improved by hybridization of PVB and zirconia. It is likely that the PVB-zirconia hybrid films would be used as the high

performance interlayer in laminated glass. Furthermore, because the commercially available PVB interlayer used in laminated glasses is normally blended with around 30 wt% of a plasticizer, we might do fully research with that for the purpose of practical application in near future.

Acknowledgement

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