NOTE

Preparation and Properties of a Composite of Poly(vinyl butyral) and Titania

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Received 16 March 1998; accepted 13 July 1998

INTRODUCTION

The sol-gel process has been used since the early 1980s to study organic/inorganic hybrid materials.¹ It is possible to design composite materials which have the advantages of organic and inorganic materials by mixing them at a molecular or a nanometer level. We have also prepared composites of silica and organic polymer [poly(vinyl alcohol),^{2,3} poly(ethylene glycol),⁴ and poloxamer]⁵ using the sol-gel process and examined their properties and structures.

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 used as a paint, an adhesive agent, a printing paste, and a film sandwiched in a safety glass for automobiles.⁶ We considered that a compatible composite of PVB and glass could be prepared by means of the sol-gel process due to the high adhesive properties of PVB. By mixing glass and PVB, the properties of PVB would be expected to change and its functions to develop.

In this article, we tried to prepare a PVB/titania (TiO_2) composite by mixing PVB solution and titania sol, which have a common solvent (ethanol), then gelating the mixture. Hybrids of organic polymer and titania were investigated by Wilkes et al.^{1,7,8} [poly(tetramethylene oxide)/titania etc.], Kurokawa et al.^{9,10} (cellulose acetate/ titania), and Mauritz and Jones¹¹ [Poly(*n*-butyl methacrylate)/titania]. However, there are fewer reports for them than for hybrids with silica and organic polymer because titanium alkoxide, which is the starting reagent to prepare titania by the sol-gel process, reacts rapidly with water and is thus hard to use. In this article we will report the results of the preparation of a PVB/titania composite and the properties of this composite.

EXPERIMENTAL

Materials

Titanium tetraisopropoxide (0.1 mol, Wako Pure Chemical Ind., Ltd., Japan) was diluted by ethanol (100 mL). Hydrochloric acid (HCl) (2N, 2.7 mL) was poured and stirred into this solution, resulting in a transparent titania sol.¹²

To obtain PVB, the following reagents were dissolved in ethanol/water (95 : 5 vol %) mixed solution, and the solution was heated at 60°C for 5 h: poly(vinyl alcohol) 5 wt % [PVA: degree of polymerization (\bar{P}) = 1200 and 1700, Kuraray Co., Ltd., Japan]; HCl 1 wt %, butylaldehyde/PVA = 0.6 (molar ratio). Then, PVB was obtained by reprecipitation in water. The PVB of \bar{P} = 700 was obtained from Wako Pure Chemical Ind., Ltd. and used without any purification.

A fixed amount of titania sol was added to PVB 5 wt % ethanol solution. This mixed solution was

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Journal of Applied Polymer Science, Vol. 71, 185–188 (1999)

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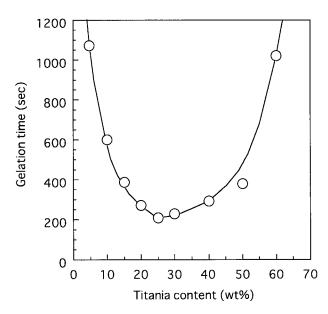


Figure 1 Effect of titania content in PVB/titania mixed solution upon gelation time.

cast in a glass Petri dish, and the PVB/titania composite film (thickness, 100 μ m) was obtained by drying slowly on a mercury bath in a desiccator at room temperature.

Apparatus and Procedures

Stress–strain curves were obtained by an Instrontype tensile testing machine (Toyo Baldwin Co., Ltd., Japan, TENSILON/UTM-III-500) with a load speed of 5 mm/min, the sample length between the jaws being 30 mm. The measurement was performed at 20°C.

The dynamic mechanical properties were measured by RHEOVIBRON DDV-II-C (Toyo Baldwin Co., Ltd.) with a heating speed of 5°C/min, the frequency being 110 Hz.

The solubility and the degree of swelling of each sample were determined by a gravimetric method: the test piece $(10 \times 10 \text{ mm})$ was impregnated in water, alcohol, or acetone at 20°C for 120 h (equilibrium swelling time).

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the composition of PVB ($\bar{P} = 700$)/titania and the gelation time (the time until gel is formed) in a sealed dish. The gelation time showed the minimum value of titania at ~ 30 wt %. In the case of titania sol without PVB, gelation was not observed even after one month. It is considered that titania acts as a crosslinking agent of PVB, but gelation was retarded by the existence of excess titania. The gelation times of the mixture containing titania 30 wt % were 750, 500, 120, and 30 s at -10, 0, 25, and 50°C, respectively. All composites obtained after gelation and drying were colorless and transparent.

| Sa | mple | | | | | | |
|-----------------------|-------------------|---------------------------------|--------------------------|-----------------------|-------------------------------|-------------------------------|--|
| P ^a | Titania (wt %) | Type of Stress– Strain Curve | Young's Modulus (GPa) | Yield Stress (MPa) | Elongation at Break (%) | Ultimate Strength (MPa) | |
| 700 | 0 | Ι | 2.87 | 41.3 | 43.5 | 51.3 | |
| | 5 | Ι | 2.90 | 41.3 | 26.1 | 44.8 | |
| | 10 | II | 3.00 | 49.2 | 15.6 | 41.6 | |
| | 15 | III | 3.05 | _ | 1.5 | 32.1 | |
| 1200 | 0 | Ι | 2.99 | 42.0 | 82.2 | 62.3 | |
| | 5 | Ι | 3.11 | 47.0 | 63.1 | 59.5 | |
| | 10 | I, II | 3.49 | 52.4 | 36.5 | 32.9 | |
| | 15 | III | 3.53 | | 2.3 | 24.3 | |
| 1700 | 0 | Ι | 3.12 | 45.1 | 152.0 | 115.0 | |
| | 5 | Ι | 3.34 | 49.1 | 120.3 | 96.2 | |
| | 10 | Ι | 3.49 | 53.2 | 94.7 | 90.2 | |
| | 15 | II | 3.76 | 57.2 | 49.2 | 87.0 | |
| | 20 | III | 3.98 | _ | 3.6 | 47.9 | |

 Table I
 Mechanical Properties of Each Sample

^a Degree of polymerization of PVB.

Table I shows Young's modulus, the yield stress, the elongation at break, and the ultimate strength obtained from the stress-strain (s-s) curve for each sample. PVB and the composites containing titania 5 wt % (10 wt % for only PVB of P = 1700) showed the typical s-s curve (type I) which has the yield point and the strain after the point. Alternatively, an s-s curve (type II) in which the break occurred immediately after the yield point was observed for the composites of titania 10 wt % (for PVB of $\overline{P} = 700$ and 1200) through 15 wt % (for $\overline{P} = 1700$). After adding more titania, the composites became brittle, and breaking occurred before yield point (type III). All properties in Table I, except elongation at break, increased with increasing the P of PVB or the titania content in the composites. The elongation at break decreased with increasing the titania content because the composite became fragile.

Figure 2(a,b) show the results of the dynamic mechanical property measurements. The tan δ decreased with increasing the titania content, and the peak [corresponding to the glass transition temperature (T_g) of PVB] became broader

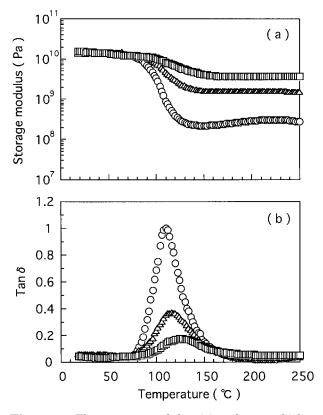


Figure 2 The storage modulus (a) and tan δ (b) behavior of PVB ($\bar{P} = 1200$)/titania composites: titania 5 wt % (\bigcirc), 10 wt % (\triangle), 15 wt % (\square).

| Table II | Solubility | of Each | Sample | in | Ethanol |
|----------|------------|---------|--------|----|---------|
|----------|------------|---------|--------|----|---------|

| | Sample | | | | |
|-------------------|----------------|-------------------|--|--|--|
| $\bar{P}^{\rm a}$ | Titania (wt %) | Solubility (wt %) | | | |
| 700 | 0 | 100 | | | |
| | 5 | 5.32 | | | |
| | 10 | 0.61 | | | |
| | 15 | 0 | | | |
| 1200 | 0 | 100 | | | |
| | 5 | 3.41 | | | |
| | 10 | 0 | | | |
| 1700 | 0 | 100 | | | |
| | 5 | 1.20 | | | |
| | 10 | 0 | | | |

^a Degree of polymerization of PVB.

and shifted to a high temperature gradually. In addition, when the titania 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 considered that titania was dispersed homogeneously in PVB, and the thermal motion of the PVB molecular chain was prevented by the interaction between them. These properties were not affected by the \bar{P} of PVB.

Table II shows the solubility of each sample in ethanol. PVB dissolved completely, but solubility promptly decreased with the mixing of titania. The composites of titania 5 wt % slightly dissolved ($\sim 5 \text{ wt } \%$ or below), turning cloudy. However, they became insoluble by the mixing of titania 10 wt % ($\bar{P} = 1200$ and 1700) through 15 wt % (P = 700). As a whole, solubility became lower when increasing the P of PVB. Table III shows the solubility and the degree of swelling for each sample in alcohol, acetone, and water. PVB alone dissolved completely in alcohol and acetone, but both the solubility and the degree of swelling decreased when mixing titania. However, the swelling of 28.8% was observed in ethanol even when the composite contained titania 30 wt %. The composite became insoluble in acetone by mixing only 5 wt % titania. All samples were insoluble in water, and did not swell.

From the above results, we considered that the PVB/titania composites prepared by means of the sol-gel process showed good compatibility and a strong interaction between them. These composites did not dissolve or swell in water, but they

| Sample | | Solubility (wt %) | | | Degree of Swelling (%) | | | | |
|-------------------|----------------|-------------------|---------|---------|------------------------|----------|---------|---------|-------|
| $\bar{P}^{\rm a}$ | Titania (wt %) | Methanol | Ethanol | Acetone | Water | Methanol | Ethanol | Acetone | Water |
| 700 | 0 | 100 | 100 | 100 | 0 | _ | _ | _ | 0 |
| | 5 | 6.90 | 5.32 | 0 | 0 | 54.11 | 60.17 | 35.19 | 0 |
| | 10 | 1.53 | 0.61 | 0 | 0 | 48.02 | 55.83 | 23.98 | 0 |

Table III Solubility and Degree of Swelling for Samples in Each Liquid

^a Degree of polymerization of PVB.

swelled well in alcohol and became insoluble by mixing titania 10-15 wt %. Moreover, their mechanical properties were excellent. Therefore, we consider that these composites could be used as alcohol-enriching materials, for instance permseparable or sorbseparable materials.

The authors thank Nikko Vics Co., Ltd. for partial financial support, and Kenji Onozato for his cooperation.

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