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Polymer-free Organic–Inorganic Hybrid Materials with High Refractive Indices and Thermoplastic Properties

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We prepared a new class of organic–inorganic hybrid materials with high refractive indices and thermoplasticity. Titanium and zirconium alkoxides were hydrolyzed in the presence of β-diketones of high melting and boiling points, followed by concentration and heating over 100 °C. Transparent, glass-like solid materials were obtained, exhibiting softening or melting behavior on heating in spite of the absence of organic polymers. The refractive indices of the thermoplastic hybrid materials were as high as 1.7.

Organic–inorganic hybrids of high refractive indices are attracting much attention because of their applications as antireflective coatings, optical waveguides, holographic materials, coatings for plastic lenses, and encapsulants for light-emitting diodes.[1,2] Such materials can easily be fabricated into thin films by dip- or spin-coating, while high bulk formability and hopefully melt-castable properties are desirable when they are to be used in the form of bulk or monoliths.

Hybrid or nanocomposite materials of high refractive indices reported so far are classified into (1) nanocomposites comprising high-refractive-index metal oxide nanoparticles dispersed in organic polymer matrices, and (2) hybrids composed of metalloxane polymers of high refractive indices and organic polymers.[1] Their thermoplasticity, if any, arises from the flexibility of organic polymer components, which results in the loss of thermoplasticity in high fractions of high-refractive-index components, indicating the difficulty in compatibility between thermoplasticity and high refractive indices. Here we propose a new type of hybrid materials where high refractive indices and thermoplasticity or melt-castable properties are concurrently achieved by employing chemically modified metalloxane polymers without using organic polymers.

$Ti(On\text{-}C_4H_9)_4$ and $n\text{-}C_3H_7OH$ solution of $Zr(On\text{-}C_3H_7)_4$ (70 wt %, TPZR) were used as titania and zirconia sources, respectively.[3] Acetone was employed as solvent.[3] β-Diketones of different melting and boiling points listed in Table 1 with their abbreviations were used as chelating agents, including pentane-2,4-dione (acetylacetone), heptane-3,5-dione, 1-phenylbutane-1,3-dione, 1-(morpholin-4-yl)butane-1,3-dione, and 1,3-diphenylpropane-1,3-dione.[3] Starting solutions were prepared by adding β-diketones, $Ti(On\text{-}C_4H_9)_4$ or TPZR, and deionized water in this sequence, where the mole ratios, alkoxide:β-diketones:water:acetone, were fixed at 1:2:1:20, where two kinds of equimolar β-diketones were employed in one solution (In some cases, only one kind of β-diketone was used at its mole ratio to alkoxide of 1 or 2). The solutions thus prepared were mixed under stirring at room temperature for 1 h. All the starting solutions thus prepared were homogeneous and transparent.

The experimental procedure following the solution preparation is illustrated in Figure 1. The starting solutions were concentrated at 80 °C in uncovered glass containers for the periods of time shown in the fourth column of Table 2 to obtain viscous, resin-like solutions. A drop of the viscous solutions thus obtained was placed on an Si(100) substrate and heated at 100–200 °C for 10 min in an oven, where the specified heat-treatment temperature is shown in

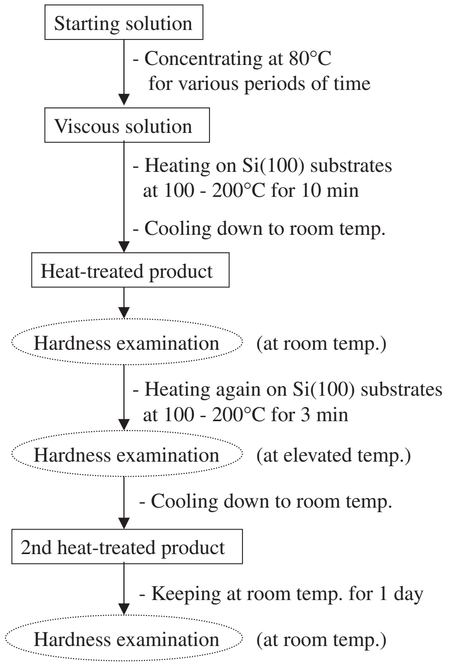

Figure 1. Experimental procedure for examining the thermoplasticity of hybrid materials.

Table 1. Abbreviations and properties of the β-diketones used as the chelating agents

β-Diketone	Abbreviation	State at room temperature	Melting point/°C	Boiling point/°C
Pentane-2,4-dione	Pen24	Liquid	−23	140
Heptane-3,5-dione	Hep35	Liquid	—	175 at 754 mmHg
1-Phenylbutane-1,3-dione	PhBu13	Solid	57	262
1-(Morpholin-4-yl)butane-1,3-dione	MphBu13	Solid	68	140 at 2 mmHg
1,3-Diphenylpropane-1,3-dione	DPhPr13	Solid	78	221

Table 2. States of the products after cooling down, on second heating, and after one day at room temperature

Sample	β-Diketone 1	β-Diketone 2	Duration at 80 °C for concentration /min	Heating temp./°C	State			Thermo-plasticity	Remarks
					After cooling	On 2nd heating	After one day at room temp.		
Titania-based hybrids									
a	Pen24	None	70	120	Hard	Hard	Hard	No	Opaque on heating
b	Pen24	Pen24	60	120	Hard	Hard	Hard	No	Opaque on heating
c	Pen24	Hep35	70	120	Hard	Hard	Hard	No	Opaque on heating
d	Pen24	DPhPr13	40	120	Hard	*Soft*	Hard	Yes	Transparent
e	Hep35	Hep35	60	100	Hard	Hard	Hard	No	Opaque on conc.
f	Hep35	DPhPr13	40	120	Hard	*Soft*	Hard	Yes	Transparent
g	PhBu13	None	50	120	Hard	*Soft*	Hard	Yes	Transparent
h	PhBu13	PhBu13	50	120	Hard	*Soft*	Hard	Yes	Transparent
i	PhBu13	MphBu13	40	120	Hard	*Soft*	Hard	Yes	Transparent
j	PhBu13	DPhPr13	50	120	Hard	*Soft*	Hard	Yes	Transparent
k	MphBu13	None	40	120	Hard	*Soft*	*Soft*	Yes	Transparent
l	MphBu13	MphBu13	60	140	Hard	*Soft*	*Soft*	Yes	Transparent
m	MphBu13	DPhPr13	30	120	Hard	*Soft*	Hard	Yes	Transparent
n	DPhPr13	None	50	200	Hard	*Soft*	Hard	Yes	Transparent
o	DPhPr13	DPhPr13	50	120	Hard	*Soft*	Hard	Yes	Transparent
Zirconia-based hybrids									
p	PhBu13	None	30	120	Hard	Hard	Hard	No	Opaque on heating
q	PhBu13	Pen24	30	120	Hard	*Soft*	Hard	Yes	Transparent
r	PhBu13	PhBu13	30	120	Hard	*Soft*	Hard	Yes	Transparent

the fifth column of Table 2. After cooling down to room temperature, whether the product is hard or soft was examined by touching it with forceps. Then the product was heated again for 3 min at the same temperature as that employed in the first heat treatment, and the hardness was checked again with forceps before cooling down in order to examine the thermoplasticity of the product. After cooling down, the product was kept in a sealed polyethylene bag for 1 day, and the hardness was examined again at room temperature. The refractive index of the products was measured by a prism coupler[3] using a prism with a refractive index of 1.9648. The optical absorption spectra were measured on the samples prepared on silica glass substrates using a spectrophotometer[3] where a bare silica glass substrate was used as the reference.

Crack-free, transparent, and glass-like solid products as thick as 700 µm were obtained by the solvent (acetone) vaporization through the first heat treatment at 100–200 °C, except for Samples a–c, e, and p, which turned opaque during the concentration or heat-treatment steps as is denoted in the last column of Table 2. Typical appearance and optical absorption spectra of the products are shown in Figure 2, revealing their optical transparency. The solid products were colored in yellow (deep yellow for titania-based ones) and exhibited rigidness at room temperature as indicated by "Hard" in "After cooling" column of Table 2.

The products were then subjected to the second heat treatment, and the hardness was examined during heating. The samples prepared from solutions containing PhBu13, MphBu13, or DPhPr13 (Samples d, f–o, q, and r in Table 2) exhibited thermoplasticity, being softened during heat treatment as indicated by "*Soft*" in the "On 2nd heating" column and by "Yes" in the "Thermoplasticity" column of Table 2. On the other hand, Samples a–c and e from solutions containing Pen24 and/or Hep35 without PhBu13, MphBu13, or DPhPr13, and Sample p from a solution of $\mathrm{PhBu13/Zr(O}\mathit{n}\mathrm{\text{-}C_3H_7)_4 = 1}$ did not show thermoplasticity, remaining hard during the second heat treatment. It should be noted that PhBu13, MphBu13, and DPhPr13 have high melting and boiling points and are solids at room temperature while Pen24 or Hep35 are liquids (Table 1). Pen24 and Hep35 may be vaporized during the heat treatment, which promotes polycondensation reaction of alkoxides to develop metalloxane bonds, making the samples hardened during heating. On the other hand, PhBu13, MphBu13, and DPhPr13 are not vaporized, remaining in the samples, which provided thermoplasticity. In the case of Sample p prepared from the solution of $\mathrm{PhBu13/Zr(O}\mathit{n}\mathrm{\text{-}C_3H_7)_4 = 1}$, the degree of chelation may not be enough to suppress the hydrolysis and condensation, resulting in the loss of thermoplasticity. The rapid progress of the hydrolysis and condensation due to the lack of chelation may also be the cause of the loss of transparency during concentration and heat-treatment steps for Samples a–c, e, and p.

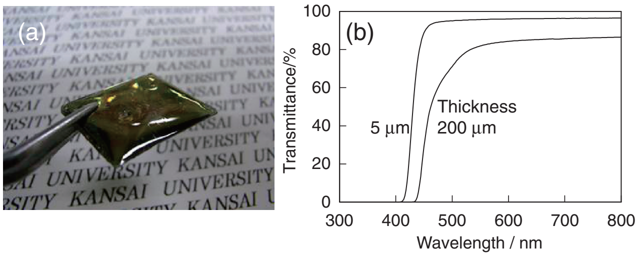

Figure 2. (a) Appearance of a zirconia-based hybrid material (Sample r, 770 µm thick) prepared on an Si(100) substrate, and the optical absorption spectra of 5 µm thick and 200 µm thick titania-based hybrid materials (Sample h) prepared on silica glass substrates.

Sample h exhibited infrared absorption peaks at 1520 and 1595 cm^{-1},[3] which are assigned to the stretching of C–C and C–O

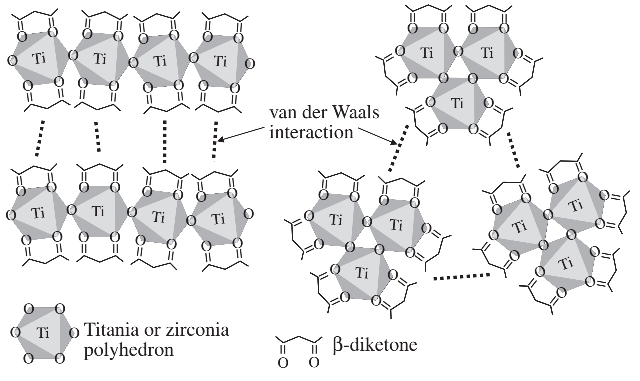

Figure 3. Possible structure of the hybrids having van der Waals interaction between chemically modified metalloxane polymers or metal oxide clusters.

bonds in chelate rings with bidentate PhBu13.[4–6] The yellow color of the hybrids also evidences the chelate rings.[7–9] Pure PhBu13 exhibited an exothermic peak at its melting point, 57 °C, on the differential thermal analysis curve while Sample h did not, which excludes the melting of β-diketones as the origin of the thermoplasticity. Figure 3 shows a possible structure of the hybrids, where metal oxide nanoclusters or metalloxane polymers are surrounded by β-diketones, being weakly bonded with each other via van der Waals interaction. Figure 3 is just a possible model, and more precise structural analyses especially on the coordination number of metal atoms and the linkage between polyhedra are mandatory. However, considering that well-developed three-dimensional metalloxane networks can never exhibit thermoplasticity and that the melting of β-diketones is not the origin of the thermoplasticity, it may be reasonable to attribute the thermoplasticity to van der Waals interaction between β-diketones covering the coordination polyhedra.

Segawa et al. prepared thin titania-based organic–inorganic hybrid films from $Ti(On\text{-}C_4H_9)_4$ solutions containing DPhPr13 and 2-(methacryloyloxy)ethyl acetoacetate, via dip- and spin-coating, followed by drying at 100 and 120 °C.[10,11] The thickness was 0.8 and 1.25 µm for the former and the latter, respectively, which are relatively as large as those achieved by single-step deposition without cracking for oxide-based films. However, the thickness we achieved without cracking was much larger (as large as 700 µm). The absence of cracking in such an extremely thick material can only be achieved via stress relaxation in molten states, not by the suppression of stress evolution by chelating agents[12] during film densification.

Generally organic polymers are responsible for the thermoplasticity of hybrid materials, while the materials we prepared contain no organic polymers. Takahashi et al. proposed a new type of hybrid materials that exhibit thermoplasticity without organic polymers. They prepared organically modified silicate–phosphate alternating copolymers via a nonaqueous acid–base reaction between anhydrous phosphoric acid and organically modified chlorosilane.[13,14] Silica and phosphoric acid tetrahedra were linked by sharing their corners, where one of the corners is not linked due to alkyl- or phenyl-Si groups and P=O groups, which provided thermoplasticity. The hybrid materials we proposed here have different structural features from that of Takahashi et al. in that β-diketones covering the metal coordination polyhedra provides thermoplasticity, which has never been achieved and reported.

Table 3. Refractive index of the thermoplastic hybrids obtained after heating and solidification

Sample	β-Diketone 1	β-Diketone 2	Refractive index of hybrids
Titania-based hybrids			
d	Pen24	DPhPr13	1.72
f	Hep35	DPhPr13	1.71
h	PhBu13	PhBu13	1.70
i	PhBu13	MphBu13	1.66
j	PhBu13	DPhPr13	1.73
m	MphBu13	DPhPr13	1.69
Zirconia-based hybrids			
q	PhBu13	Pen24	1.65
r	PhBu13	PhBu13	1.66

Table 3 shows the refractive indices of the transparent and thermoplastic hybrid materials. The refractive indices were relatively high at 1.65–1.73 where the titania-based hybrids had slightly higher indices than the zirconia-based ones. All of these hybrids (Samples d, f–o, q, and r) were stable at room temperature as shown in "After one day at room temp." column in Table 2, except for those prepared from solutions containing only MphBu13 (Samples k and l in Table 2). Samples k and l showed softness or fluidity after one day, which indicates their chemical instability, but the origin for the instability is unknown.

Thermoplastic hybrid materials have been demonstrated to be prepared without organic polymers by employing chelating agents of high melting and boiling points. The present work opens a way to a new class of hybrid materials that have melt-castable properties combined with metal oxide-based functions or properties such as high refractive indices.

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