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Notes

New High Refractive Index Organic/Inorganic Hybrid Materials from Sol–Gel Processing

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Introduction

Novel organic/inorganic hybrid materials known as ceramers have been developed within our laboratory in the last few years.[1-5] In general, silicon, aluminum, titanium, or zirconium metal alkoxides have been used as the starting materials and processed by the sol–gel method to obtain a clear metal alkoxide-based sol. Triethoxysilane-capped oligomers have been used to react with these metal alkoxide-based sols to form transparent hybrid network materials. These hybrid materials with different ratios of organic/inorganic content display interesting structure–property behavior. For example, at higher inorganic composition, they show a higher refractive index and a higher modulus while for higher organic oligomer compositions, they show a higher flexibility.

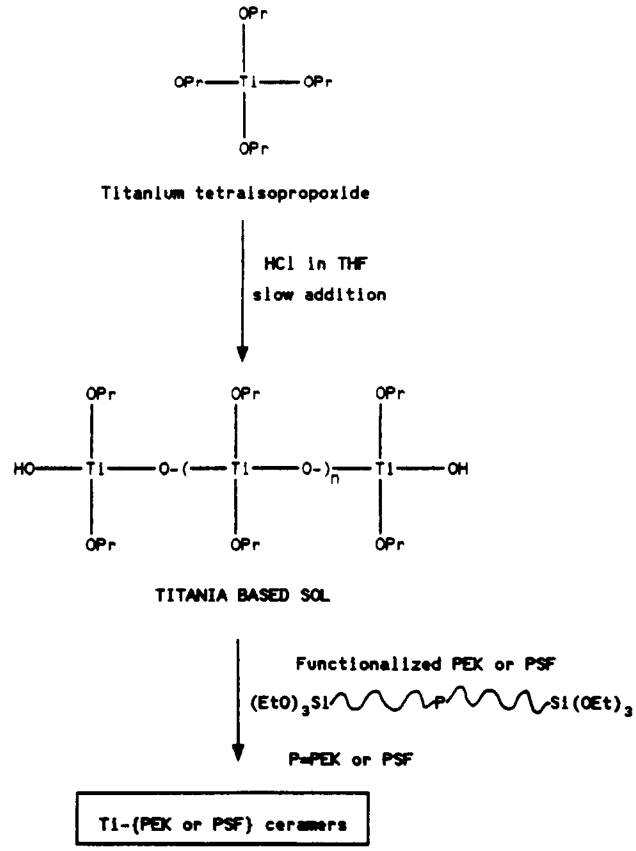
In this study, two series of novel hybrid materials have been prepared by using titanium tetraisopropoxide as the inorganic component to react with triethoxysilane-capped organic oligomers being either poly(arylene ether ketone) (PEK) or poly(arylene ether sulfone) (PSF). The titanium alkoxide was chosen due to its higher refractive index. PEK and PSF were used as the organic component due to their high refractive index relative to most other organic polymers. The refractive index values and their Abbe number,[6] υ_D, which describes the wavelength dependence of the optical dispersion of these hybrid materials, will be discussed.

Experimental Section

Materials. Titanium tetraisopropoxide ($Ti(OPr)_4$) from the Akzo Corp. was used without further purification. Amine-end-capped PSF with number-average molecular weight 7200 and PEK with number-average molecular weight 6000 were prepared as previously described.[7] (3-Isocyanatopropyl)triethoxysilane from Petrarch Systems was used to end cap the PSF and PEK. HPLC-grade *N,N*-dimethylacetamide and tetrahydrofuran were purchased from Aldrich Chemical Co. and used without further purification. Optical monochromatic filters for wavelengths of 589, 486, and 656 nm obtained from MicroCoatings, Inc. (Westford, MA), and refractive index liquids from R. P. Cargille Labs, Inc. (Cedar Grove, NJ), were used as standards to measure the refractive index.

Procedure. (i) Preparation of triethoxysilane-capped PSF and PEK: First, 0.001 mol of PSF (7.2 g) or PEK (6 g) was dissolved in about 1 mol (81.3 mL) of THF under nitrogen and stirred. Next, 0.0025 mol of (3-isocyanatopropyl)triethoxysilane

Scheme I
Preparation of Ti-PEK or Ti-PSF Ceramers



was slowly added to the solution. The solution was then stirred under nitrogen at room temperature for 3 h after which about 3 mol (175.8 mL) of absolute ethanol were added to the solution to precipitate the triethoxysilane-capped PSF or PEK from solution. After filtering, the final solid product was dried under vacuum at room temperature.

(ii) Preparation of Ti-PSF or Ti-PEK hybrid materials: In a typical example, 5 g of tetrahydrofuran (THF) was first mixed with 0.1 mL of HCl (10 N), and then this solution was slowly added to 5 g of $Ti(OPr)_4$ with fast stirring. A clear titania sol was formed. Next, a 10 wt % solution of triethoxysilane-capped PSF or PEK in THF was mixed with the titania sol and stirred for 5 min to obtain a homogeneous system. The final solution was then cast into poly(4-methyl-1-pentene) Petri dishes and covered for further drying and curing at 60 °C for 24 h. For the higher titanium tetraisopropoxide contents (more than a 50/50 weight ratio of $Ti(OPr)_4$ to PSF or PEK), *N,N*-dimethylacetamide was used as the solvent for PSF or PEK instead of THF, and the final solution was cast at 60 °C for the initial stage of curing for 24 h. Films were then removed from the dishes and annealed at 200 °C for 15 min to complete the hydrolysis and condensation (curing) reaction.

Optical Measurements. The immersion method[8] was used to determine the refractive index.

Results and Discussion

All the final cast materials were transparent, which indicated that the titanium alkoxide was well incorporated with the triethoxysilane-capped PSF and PEK, thereby

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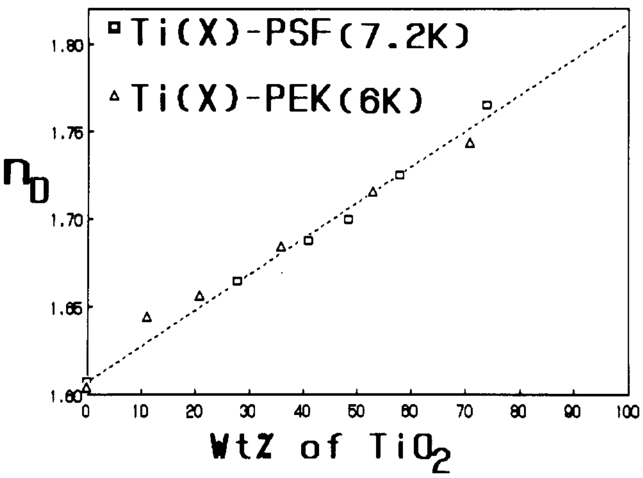

Figure 1. Refractive index of Ti-PSF and Ti-PEK systems with different titanium oxide content where it has been assumed that the titanium tetraisopropoxide is converted to TiO_2.

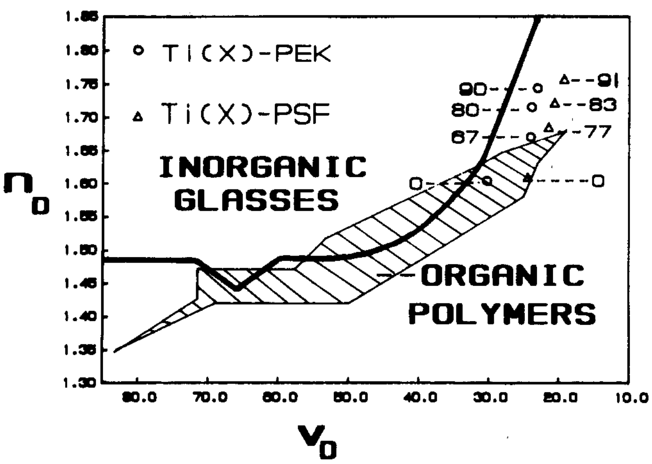

Figure 2. Optical dispersion of Ti-PSF and Ti-PEK systems of the sodium line refractive index (n_D) vs υ_D (Abbe number). The slanted line region represents the organic polymers while the heavy black line represents the typical response range for inorganic glass after Dislich.[12]

giving no macrophase separation. However, there are related ceramer systems that do show microphase separation by small-angle X-ray scattering, as has been described elsewhere.[9-11] The preparation methods of the Ti-PEK and Ti-PSF hybrid materials as shown in Scheme I are similar to those used for Ti-PTMO and Zr-PTMO ceramer systems discussed in a previous publication.[5] In the systems discussed here, THF has been used instead of isopropyl alcohol because the PSF and PEK components are not soluble in the isopropyl alcohol. Since PEK and PSF each have a much higher glass transition temperature (163 and 170 °C, respectively) compared with PTMO (−76 °C), it was necessary to anneal these samples to 200 °C to promote high network density formation. In these organic/inorganic hybrid systems, the higher glass transition temperature limits the extent of cure due to vitrification as gelation and network density buildup occurs, as has been described elsewhere.[11] However, after annealing above the T_g, the final samples show little significant extractable content (less than 2% of weight loss) with THF or methylene chloride, indicating very good incorporation of the functionalized oligomers.

Addressing the optical properties, the refractive index, n_D, at the sodium line (589 nm) of these Ti-PEK and Ti-PSF hybrid materials was found to increase with titanium tetraisopropoxide content. Assuming that hydrolysis and condensation is complete for the titanium tetraisopropoxide reactant, thereby leading to formation of titanium oxide, a linear relationship is noted between weight percent of TiO_2 and n_D for these systems as shown in Figure 1. To illustrate the optical dispersion of all of these hybrid materials, a diagram of the Abbe number (υ_D) vs n_D is shown in Figure 2. The Abbe number is defined as $\upsilon_D = (n_D - 1)/(n_F - n_C)$, where n_F and n_C are the refractive index values of the materials at the wavelengths of spectral lines of F (486 nm) and C (656 nm), respectively. (The reader will note that, in general, as the wavelength dependence of the refractive index increases the smaller the Abbe number will be.) It is well-known that high refractive index materials with high optical dispersion are typically inorganic glasses.[12,13] Transparent polymers with higher n_D values usually have low υ_D values and vice versa. In these Ti-PEK and Ti-PSF systems, the values of n_D and υ_D for PEK and PSF fall within the organic polymers region as expected. By increasing the inorganic content, the values of n_D and υ_D rise above this region as shown in Figure 2.

Conclusion

New hybrid Ti-PEK and Ti-PSF materials can be prepared by reacting titanium alkoxides with functionalized PEK and PSF by the sol–gel method. By using titanium tetraisopropoxide, a considerable increase in the refractive index can be systematically induced. Also, these new materials have an optical dispersion behavior between that of organic polymers and inorganic glasses. It would therefore appear that these new ceramer systems may leave potential applicability for high refractive index optical coatings.

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