

Sulfonyl-containing polymer and its alumina nanocomposite with high Abbe number and high refractive index

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Abstract: In this study, we focus on refractive-index and Abbe-number improvements to optical polyesters. First, we modify polymers by introducing sulfonyl groups and removing phenyl groups in the monomer structure. In this manner, new polymers with Abbe numbers higher than 40 are synthesized. To further increase the refractive index and Abbe number, the polymers are hybridized with well-dispersed alumina nanoparticles (NPs). The prepared polymer/alumina nanocomposites have a high refractive index and Abbe number; ($n_D = 1.580$ and $V_D = 55$) and ($n_D = 1.631$ and $V_D = 53$), which easily exceeds the empirical “limiting line” of conventional optical polymers.

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1. Introduction

High-refractive-index (n_D) as well as low-chromatic-dispersion optical materials are particularly vital in optic and optoelectronic applications such as lenses, prisms, optical waveguides, diffractive gratings, etc. The Abbe number (V_D), which is an indicator of chromatic dispersion, is defined by the following equation:

$$V_D = (n_D - 1) / (n_F - n_C) \quad (1)$$

where n_D , n_F , and n_C are the refractive indices of the material at the wavelengths of the sodium D (589.3 nm), hydrogen F (486.1 nm), and hydrogen C (656.3 nm) lines, respectively [1]. Highly refractive materials generally exhibit small Abbe numbers and high-Abbe-number materials always correspond to lower dispersions [2,3]. Polymeric materials, for example allyl diglycol carbonate [4,5] (known as CR-39, $V_D = 59.3$, $n_D = 1.498$), with high Abbe numbers and easy processability, were designed and fabricated for use in eyeglass lenses 50 years ago. For these traditional optical polymers, however, it is difficult to push both the refractive index and Abbe number beyond the empirical "limiting line" [6]. Recently, numerous optical polymers with very high refractive index and high Abbe number have been reported [6–8]; however, these still suffer from many problems such as low glass-transition temperatures, high toxicity during fabrication, etc. Furthermore, there remains a large performance gap when we compare the optical properties of these polymers with those of inorganic optical materials.

On the other hand, nanocomposites are seen as a new class of advanced optical materials, not only because of their versatile means of fabrication but also because the performance of polymers can be enhanced by inorganic nano-fillers. Therefore, the hybridization of optical polymers with high-performance inorganic NPs is a viable method for further improvement of the optical properties of polymers [9–13]. In this paper, to achieve high refractive index and high Abbe number, polyesters containing sulfonyl groups are designed and prepared. Then, these new polyesters are hybridized with surface-modified alumina NPs to further increase their refractive indices and Abbe numbers. Using this dualistic approach, we successfully produce nanocomposites with $n_D = 1.58$ and $V_D = 55$ and with $n_D = 1.63$ and $V_D = 53$.

2. Methods and results

From the molecular point of view, the Abbe number can be predicted by Eq. (2) [14], where R and ΔR represent molecular refraction and molecular dispersion, respectively.

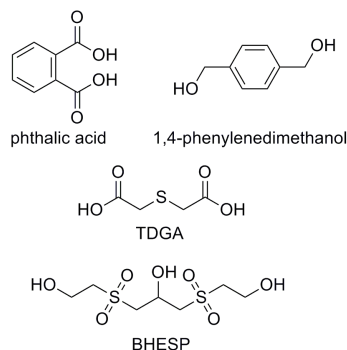
$$V_D = \frac{6n_D}{(n_D + 2)(n_D + 1)} \frac{R}{\Delta R} \quad (2)$$

From Eq. (2), we can see that the Abbe number is inversely proportional to the refractive index; this means that a high n_D always results in a low Abbe number and vice versa. However, from this equation we also can predict that the Abbe number is also strongly influenced by R and ΔR . Thus, in obtaining a polymer with high refractive index and high Abbe number, the $R/\Delta R$ ratio becomes a vital factor.

Table 1. Molecular Refraction and Molecular Dispersion

Atomic groups	R	ΔR	$R/\Delta R$
-S-	7.80	0.22	35.45
-SO ₂ -	9.76	0.09	108.44
phenyl	25.46	0.71	35.86

Table 1 lists a few atomic groups' molecular refraction and dispersion [15]. We can see that aromatic groups, for example benzene rings, etc. have high molecular refraction despite their low dispersion. Therefore, aromatic groups are suitable for pairing with high-refractive-index polymers but not for increasing the Abbe number of polymers. In contrast, a sulfonyl group has a moderately high refraction and very low dispersion, resulting in a large $R/\Delta R$ value that allows for molecular design with high Abbe numbers. In terms of spectroscopy, the introduction of a sulfonyl group can effectively displace the absorption edge of a polymer to a shorter wavelength [6]. This low chromatic dispersion leads to an increase in V_D , though sulfonyl is not especially effective in increasing n_D . In this study, to obtain a polymer with high refractive index and high Abbe number, we systematically select various kinds of polyols and polyacids for polyester synthesis. These structures are shown in Fig. 1, where phthalic acid (PA) and 1,4-phenyldimethanol (PDM) are used for per-aromatic polyester synthesis; the triol 1,3-bis(2-hydroxyethylsulfonyl)-2-propanol (BHESP), which contains two sulfonyl groups, is used for substituting PDM to increase the Abbe number of the polymer; and 2,2'-thiodiglycolic acid (TDGA) is used for substituting PA in non-aromatic polymer synthesis.

**Fig. 1. Monomers structures used in polyesters synthesis.**

The synthesis processes are very simple and almost non-toxic. First, PA/PDM, PA/BHESP, and TDGA/BHESP combinations are dissolved into dimethyl sulfoxide (1 M) respectively, and heated at 160 °C for 1 h for pre-polymerization. Then, the pre-polymerized combinations are cast on quartz-glass plates and baked in a vacuum oven at 180 °C for 6 h for final polymerization.

The refractive indices of these samples are subsequently measured using a prism coupler (Meticon 2010/M) at wavelengths of 407 nm, 589 nm, and 780 nm, respectively; the results are shown in Fig. 2. To calculate the Abbe numbers of the polymers using Eq. (1), the refractive indices are fit by Cauchy's formula to obtain n_D , n_F , and n_C values. From Fig. 2, we can see that although per-aromatic polyester has a large refractive index ($n_D = 1.571$), its large molecular dispersion leads to a low Abbe number ($V_D = 31.7$). By substituting PDM with BHESP, the two sulfonyl groups improve the dispersion, and a relatively high V_D of 43.9 (BHESP/PA) is obtained. For the non-phenyl polymer, BHESP/TDGA, the V_D increases to 46.4, meanwhile the n_D decreases from 1.571 to 1.556. These results are consistent with our design predictions. All the refractive indices and Abbe numbers are plotted in Fig. 3 for comparison with the empirical limiting line [6, 16]. Although there are substantial improvements to the value of the combined index/Abbe number versus that of the per-

aromatic polymer (BDM/PA), none our newly synthesized polymers breach the limiting line of conventional optical polymers.

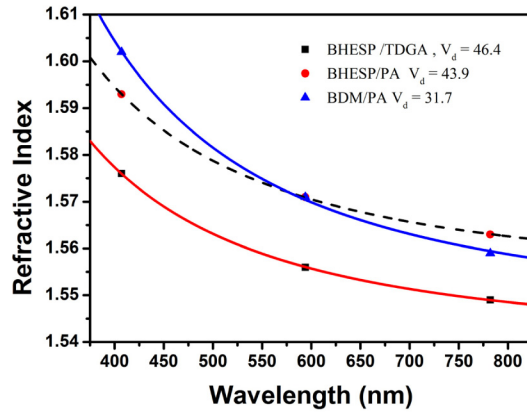


Fig. 2. Wavelength dispersions of the experimental refractive.

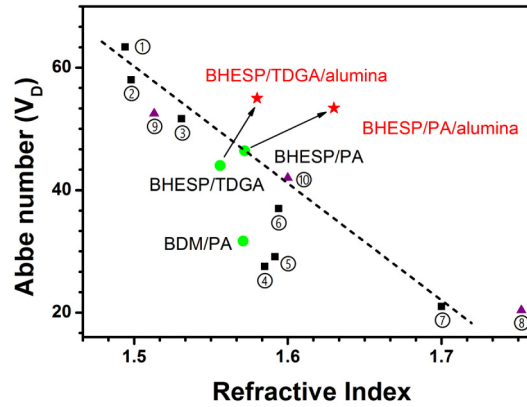


Fig. 3. An n_D - V_D diagram of conventional optical polymers and the materials fabricated in this work. The empirical limiting region is demarcated by the dashed line. The conventional polymers (■) from 1 to 7 are: 1, polyacrylate; 2, CR-39; 3, Zeonex E48R; 4, polycarbonate; 5, polystyrene; 6, MR-6; and 7, PEN polymer. Triangles (▲) indicate the nanocomposites of 8, ZnS-poly(vinylpyrrolidone) [17]; 9, TiO₂-polyacrylate [18]; 10, TiO₂-epoxy [19]. Circles (●) indicate the polymers synthesized in this study; while (★) indicates BHESP/TDGA/alumina ($n_D = 1.580$, $V_D = 55$) and BHESP/PA/alumina ($n_D = 1.63$, $V_D = 53$) nanocomposites.

In order to further increase our samples' refractive index and Abbe number, we attempted to hybridize our synthesized polymers with inorganic NPs. Alumina has a relatively high refractive index ($n_D = 1.768$) and very low dispersion ($V_D = 70$), therefore it is a strong candidate for increasing Abbe numbers and refractive indices. Compared with the widely used zirconia NPs, alumina NPs have several advantages. By Rayleigh-scattering theory [20] and effective-index theory, we calculated the transmittances and Abbe numbers of the composites blended with alumina or zirconia NPs; these results are shown in Fig. 4. For the transmittance calculation, the diameter of the NPs was set to 20 nm, and the refractive indices at 589.1 nm of bulk alumina, zirconia, and BHESP/PA polymer were used. From the results, we can see that for equal refractive index values, the polymer/alumina hybridized nanocomposite always

exhibits higher transmittance, as well as a higher Abbe number, than the polymer/zirconia nanocomposite. Thus, we chose Al_2O_3 NPs for nanocomposite fabrication.

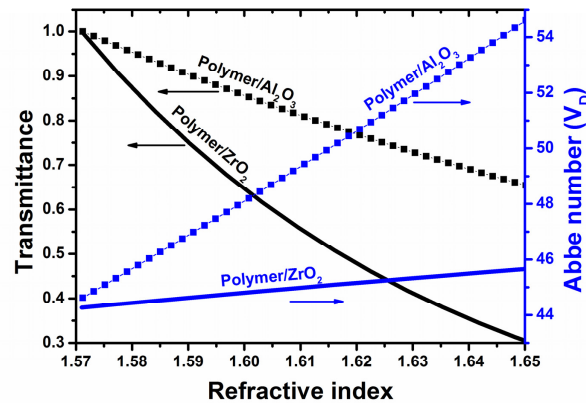


Fig. 4. Transmittance and Abbe number comparison of polymer/alumina and polymer/zirconia nanocomposites by Rayleigh-scattering theory and effective-refractive-index theory.

From the Rayleigh-scattering theory, we also know that the level of scattering is proportional to the 4th power of the NP diameter. Therefore, the transparency of a nanocomposite is very sensitive to the size of the NPs. The relationship between the transparency of the nanocomposite and the NPs' volume ratio, as well as diameter of the NPs, is illustrated in Fig. 5(a). For this calculation, the refractive indices of polymer and alumina NPs are taken as 1.571 and 1.768, respectively, and the thickness of the composite is set to 100 μm . From the Fig. 5(a), we can see that to obtain a transparency of 90% for a high-volume-ratio polymer/ Al_2O_3 nanocomposite (say, 30%), the average size of the NPs must be smaller than 40 nm. Therefore, alumina NPs of an average size of roughly 20–30 nm were chosen for the final tests in this study. A transmission electron microscope (TEM) image of the NPs is shown in Fig. 5(b).

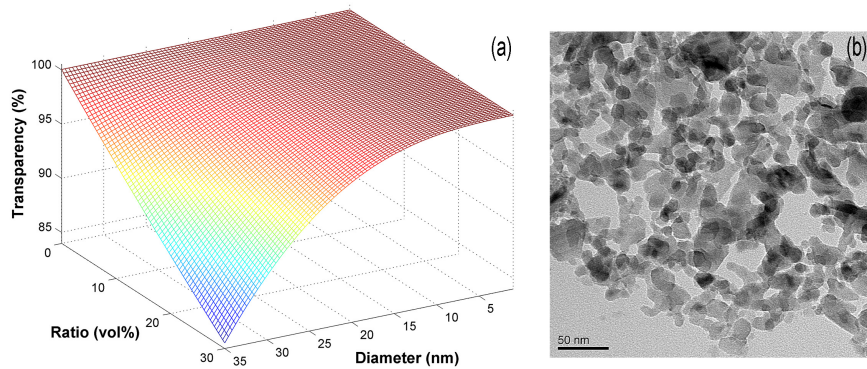


Fig. 5. (a) Calculated transmittance of a polymer/alumina nanocomposite as a function of nanoparticle diameter and volume percentage, based on Rayleigh-scattering theory. (b) Transmission electron microscope (TEM) image of alumina NPs used in this study.

It is well known that, owing to the attraction of the van der Waals force, free NPs can easily agglomerate and form larger 2nd-order particles. To suppress this agglomeration, surface modification of the free NPs is required. We thus used an in situ mechano-chemical surface modification method, the so-called bead-milling method, to prepare Al_2O_3 NP

suspensions. These details of the dispersion process are described in a previous study [11]. Fatty acids are commonly used as coupling reagents to modify NP surfaces. However, in this study, we chose toluenesulfonic acid for this task. Since the tosylate group has a high-molar-refraction benzene group and a low-dispersion sulfonyl group, its use as a coupling agent is appropriate for high- V_D and $-n_D$ nanocomposite fabrication. Thus, for the Al_2O_3 NP surface modification, 10–20 wt% toluenesulfonic acid was used.

To hybridize polymers with alumina NPs, the surface-modified Al_2O_3 NP suspension (5 wt%, 5 ml) is mixed with polymer precursors (1 M, 0.8 ml) and the mixed solution is heated by a hotplate at 165 °C, for 30 min for pre-polymerization. Then, the solution is cast on a glass substrate and baked in a vacuum oven at 180 °C, -0.1 MPa, for 8 h for the final polymerization. The refractive indices and the Abbe numbers of the nanocomposites are measured with a prism coupler and the experimental results are shown in Fig. 3 by solid red stars. From the Fig. 3, it is clear that the Abbe numbers of both the BHESP/TDGA/alumina ($n_D = 1.580$, $V_D = 55$) and BHESP/PA/alumina ($n_D = 1.631$, $V_D = 53$) nanocomposites increase significantly with increasing refractive indices, and can easily exceed the limiting line of conventional optical polymers.

The refractive indices of the nanocomposites can be predicted by the Drude model of effective media theory [21], which is given as

$$n_{\text{eff}}^2 = V_{\text{poly}} n_{\text{poly}}^2 + V_{\text{NPs}} n_{\text{NPs}}^2 \quad (3)$$

where n_{eff} , n_{poly} , and n_{NPs} are the refractive indices of nanocomposite, polymer matrix, and NPs, and V_{poly} and V_{NPs} are the volume fractions of polymer matrix and NPs, respectively. However, we find that the experimental results are lower than those from the calculated model. Moreover, the deviations tend to become larger when increasing the volume ratio of NPs. For example, in the BHESP/TDGA/alumina nanocomposite, for 10 vol% alumina NPs the n_D is approximately 1.573, while the calculated result is 1.578; for 20 vol% the n_D is 1.580, while the calculated result is 1.601. This could be caused by several factors: it may be due to the presence of impurities in the alumina particles or the addition of coupling agents; it also could represent the appearance of nano-voids, particularly at high NP concentration, which corresponds with observations from our previous work [11].

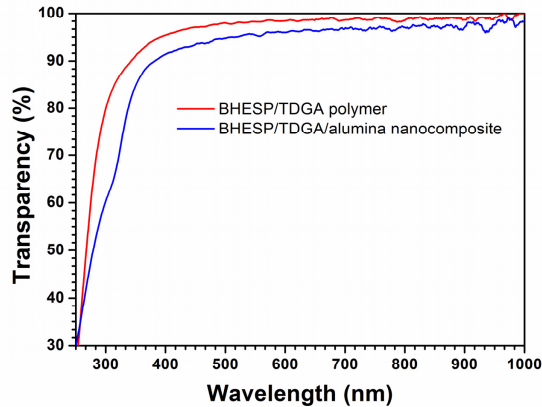


Fig. 6. UV-Vis transmittance spectra of the BHESP/TDGA polymer and its 20 vol% alumina nanocomposite.

The transparency spectra (without Fresnel reflection compensation) of the BHESP/TDGA polymer, as well as its alumina nanocomposite, are shown in Fig. 6. The nanocomposite maintains ~95% transparency despite a high concentration (20 vol%) of alumina NPs. Because of the low index difference between the polymer matrix and the surface-modified

NPs, the scattering loss is reduced in our nanocomposite material. However, in the blue and violet region, the transparency of the nanocomposite drops quickly compared with that of the pure polymer. This may be due to the Rayleigh scattering of the alumina NPs, which is inversely proportional to the 4th power of the incident-light's wavelength.

3. Conclusions

In summary, by systematic polyester design and hybridization with NPs, we successfully developed high-refractive-index and high-Abbe-number nanocomposites with high transparency. Alumina NPs are more suitable for highly transparent and high-Abbe-number nanocomposite preparation than zirconia NPs. With this approach, we can easily surpass the empirical limiting line of conventional optical polymers. The nanocomposite material used is free from rare-earth elements and its synthesis is simple. Thus, we are confident that such a combination of molecular design and nanotechnology comprises a powerful method to achieve our goals of producing high-index low-dispersion optical materials.

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