

SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED CARBON BLACK/POLY(VINYL ALCOHOL) HIGH REFRACTIVE INDEX NANOCOMPOSITES*

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Abstract Carbon black (CB)/polymer composites with high refractive index (RI) were fabricated from poly(vinyl alcohol) (PVA) and covalently functionalized nano-CB (PVA-es-CB) by simple esterification reaction. Transmission electron microscopy showed that uniform aggregates of PVA-es-CB nanoparticles with a size smaller than 100 nm formed in the nanocomposite films. Ellipsometric measurements indicated that the PVA-es-CB/PVA composite films had a RI in the range 1.520–1.598 linearly increased with the PVA-es-CB volume content. Theoretical equation based on Lorentz-Lorenz theory provided reasonably close estimation of the refractive indices to the experimentally observed values. The hybrid films also revealed relatively good surface planarity, thermal stability and optical transparency.

Keywords: High refractive index; Carbon black; Poly(vinyl alcohol); Nanocomposite.

INTRODUCTION

Hybrid organic-inorganic materials have attracted widespread attention due to their special physical (optical, mechanical and magnetic) and chemical (reactivity, catalytic) properties^[1–4]. In particular, the needs for novel optical transparent materials with high refractive index (RI) in fields including optical waveguides, ophthalmic lenses, LED encapsulation materials, antireflection films and adhesives for optical components are increasing with the expansion of applications of optical materials^[5–8].

Initial attempts to design the high RI materials have involved a variety of additives, including common organic materials^[9], metal salts and acids^[10, 11], heavy metal cations stabilized with surfactants^[12] and nanoparticles^[13]. Among these approaches, considerable progress has been made using metal oxide nanoparticles^[14–19]. In recent years, the most prominent strategy for fabricating these hybrid nanocomposites is the incorporation of high RI inorganic building blocks (such as TiO₂, ZrO₂, PbS or ZnS) into organic matrices on the nanoscale^[20].

Carbon black (CB) is a very promising inorganic material among many RI materials due to its relatively high RI ($n = 2.26$)^[21], good thermal and chemical stability. There has been substantial effort to make use of CB as a conductive additive or electrodes in fuel cells^[22, 23]. However, very little attention has been given to using CB nanoparticles in a high RI material because it has not been well known until recently that CB has a high RI. Previously, it has been reported that high RI inorganic materials with low densities appear to be the optimal

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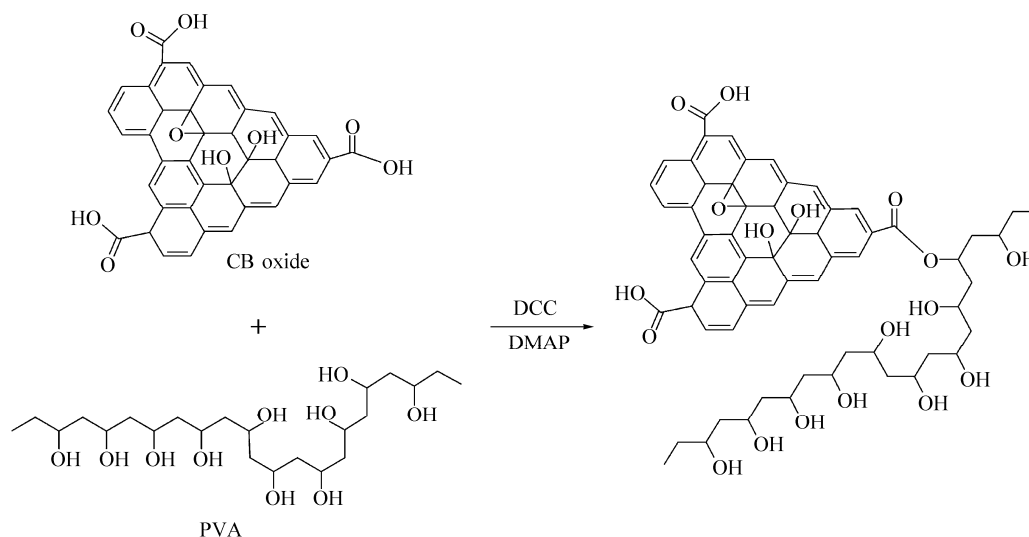
candidates for inorganic building blocks in the design of high RI nanocomposites^[20]. Compared to other inorganic building blocks, CB has a low density of about $1.7\text{--}1.9\text{ g cm}^{-3}$. Therefore, CB has been expected to offer polymer nanocomposites optimal high refractive properties as a new route, which can approach the values of TiO_2 ^[24].

In this study, we selected poly(vinyl alcohol) (PVA), a water-soluble and biodegradable polymer, as a polymer matrix. PVA is the oldest photocrosslinkable polymer used as dichromated resist. PVA is a water-soluble polymer that can be easily spincoated onto a variety of substrates and directly patterned by photolithographic techniques. PVA has a refractive index about 1.5 and is used in a wide range of applications such as color image displays, holographic optical elements, biomedical hydro gels or as a binder polymer^[25–29]. We present a novel route to increase the refractive index of PVA films by mixing of the water-soluble additives (covalent functionalization of CB particles with PVA) directly into a PVA aqueous solution. The morphologies of the prepared hybrid materials were characterized by AFM and TEM. The thermal properties, optical transmittance and refractive index dispersion of the prepared hybrid films were also investigated and described herein.

EXPERIMENTAL

Materials

PVA was purchased from Sinopharm Chemical Co., Ltd., the degree of polymerization is 1800, and the degree of saponification is more than 99%. *N,N'*-dicyclohexylcarbodiimide (DCC, 99%) and 4-(dimethylamino)pyridine (DMAP, 99%) were obtained from Acros, and 1-hydroxybenzotriazole (HOBT, containing less than 5% H_2O) was from Aldrich. Dimethyl sulfoxide (DMSO, 99.5%) was also purchased from Sinopharm Chemical Reagent and dried over 0.4 nm molecular sieves before use. Carbon blacks (CB, Mogul[®]L) were purchased from Cabot and were dried in vacuum at 110°C .



Scheme 1 Schematic illustration of the esterification of CB oxide with PVA

Functionalization of CB

CB (1.5 g) was suspended in an aqueous HNO_3 solution (2.6 mol/L) and refluxed for 4 h while stirring. The oxidation product was obtained by centrifugation and washed with deionized water several times till the wash was neutral, and the residual was vacuum-dried at 80°C . Conductimetric titration of the oxidized product can quantitatively provide carboxylic group concentration on the CB's surface. The reported content of carboxylic groups in OCBs is in the range of $5.1\text{--}6.7\text{ mmol g}^{-1}$ ^[30]. CBs were functionalized with PVA in carbodiimide-

activated esterification reactions (Scheme 1). In a typical reaction, DCC (520 mg, 1.56 mmol), DMAP (86 mg, 0.39 mmol) and HOBT (169 mg, 0.78 mmol) were dissolved in DMSO (20 mL). A CB oxide sample (216 mg) was added to the solution, followed by sonication for 1 h. Then, a solution of PVA in DMSO (166 mg mL⁻¹, 10 mL) was added, and the mixture was sonicated for another 1 h by an ultrasonic processor (JY-92 IID, 22 kHz, 300 W) under N₂ purge at approximately 25°C. The solid nanocomposite (named as PVA-es-CB) was filtered, washed with methanol and dried at 50°C under vacuum. In order to eliminate rest of non-reacted CB, the nanocomposites were redissolved in hot deionized water (85°C), centrifuged at a high speed (12000 r/min) and the supernatant dark-colored solution coagulated with methanol. The procedure was repeated twice. Then a black glassy sample of PVA functionalized CBs (360 mg) was obtained.

Preparation of PVA/PVA-es-CB Nanocomposite Films

A typical procedure for the wet-casting of a PVA/PVA-es-CB composite thin film is to mix an aqueous solution of PVA-es-CBs with a 10 wt% aqueous solution of PVA (15 mL). The mixture was first sonicated for a short period of time and then stirred for 4–12 h until homogeneous and visually without any air bubbles. The viscous but homogeneous solution was spin-coated at 3000 r/min on a silicon wafer for 40 s. The finally hybrid films were cast in a closed oven at 40°C for 2 days and the PVA/PVA-es-CB nanocomposites with different contents of PVA-es-CB particles were obtained.

Characterization

Fourier transform infrared spectra (FTIR) were obtained by using a Nicolet Avatar 360 model FTIR Spectrometer. UV-Vis/NIR absorption spectra were recorded on a Cary 500 spectrometer. NMR measurements were performed on a Bruker Avance 500 NMR spectrometer at room temperature with dimethyl sulfoxide-d₆ (10 wt% solutions) as a solvent. Thermal gravimetric analysis (TGA) was performed with a Netzsch TG at a heating rate of 10 K min⁻¹ from room temperature to 800°C in a nitrogen atmosphere. Morphology of the PVA and hybrid membranes was studied using a Rigaku D/max 2500 v/pc X-ray diffractometer in the range of 5°–50° at the speed of 4 (°)/min (Cu KR 40 kV/200 mA). Differential scanning calorimetry (DSC) of samples was investigated under nitrogen atmosphere by a Netzsch PC200 at a heating rate of 10 K min⁻¹. An atomic force microscope (NanoScope IIIa MultiMode AFM) was used to probe the surface morphology of the coated films in tapping mode. Transmission electron microscopy (TEM) analyses were conducted on JEOL JEM-2100 TEM systems equipped with a Gatan CCD camera. Ultrathin cross-sectional slices of the nanocomposite films for TEM imaging were obtained using a Ultracut-E microtomy system equipped with a diamond knife. An ellipsometer (W-VASE32TM) was used to measure the refractive index (*n*) and the extinction coefficient (*k*) of the prepared films in the wavelength range of 300–1300 nm. The thickness (*h*) of the prepared film was also determined simultaneously.

RESULTS AND DISCUSSION

Functionalized CB

The PVA functionalized CBs are soluble in water and DMSO with the aid of moderate heating, similar to the parent PVA. The dark-colored solutions from the soluble samples are stable, without any precipitations over time.

The FTIR spectrum of PVA-es-CB retained most of the bands of PVA, although some of them changed in intensity or even disappeared due to the modification, and showed some new bands (Fig. 1). The band at 1714 cm⁻¹ suggests the presence of new carbonyl species. This band is most often related to the C=O stretching motions of COOH groups situated at the edges of the graphite lamellar structure of CB oxide^[31]. Similarly, in this case the band at 1714 cm⁻¹ can be attributed to C=O stretching of ester groups. In fact, this band was also observed in the esterification reaction of PVA and glycerol^[32], suggesting that esterification is also taking place in our system. This is confirmed by the significant increase in the band around 1640 cm⁻¹, which appears weakly in PVA and has been assigned to adsorbed water^[33]. However, this is a strong band centered at 1628 cm⁻¹ in the spectrum of the CB oxide, and although may also be due to adsorbed water, it contains a significant contribution

from the skeletal vibration of graphitic domains^[31]. In addition, some interesting changes in the relative intensities of the characteristic bands of PVA in the 1200–1000 cm^{-1} region can be observed. These bands are attributed to the C—O of doubly H-bonded OH in crystalline regions (1143 cm^{-1}) and C—O unbonded in amorphous zones (1095 cm^{-1})^[34]. The intensity ratio of these bands (I_{1143}/I_{1095}) diminishes markedly for the esterified products, suggesting a large decrease in the degree of crystallinity of the modified polymer.

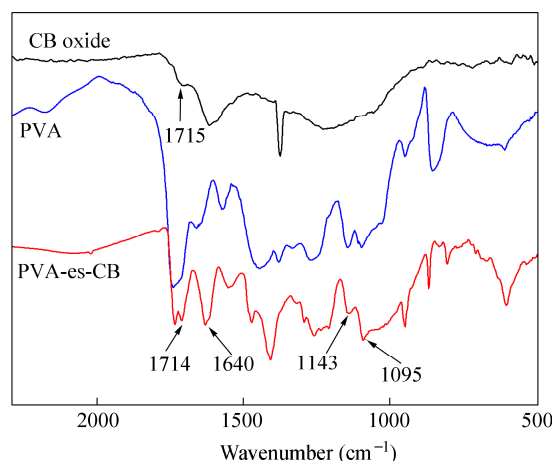


Fig. 1 FTIR spectra of CB oxide, PVA and PVA-es-CB

The solubility of the PVA-es-CBs allowed solution-phase NMR characterization. Figure 2 shows that the ^1H -NMR spectrum of the soluble PVA-es-CB sample in DMSO-d_6 is comparable with that of neat PVA. The latter exhibits the polymer backbone signals at $\delta = 3.95\text{--}3.75$ (methine) and $\delta = 1.6\text{--}1.2$ (methylene) and the

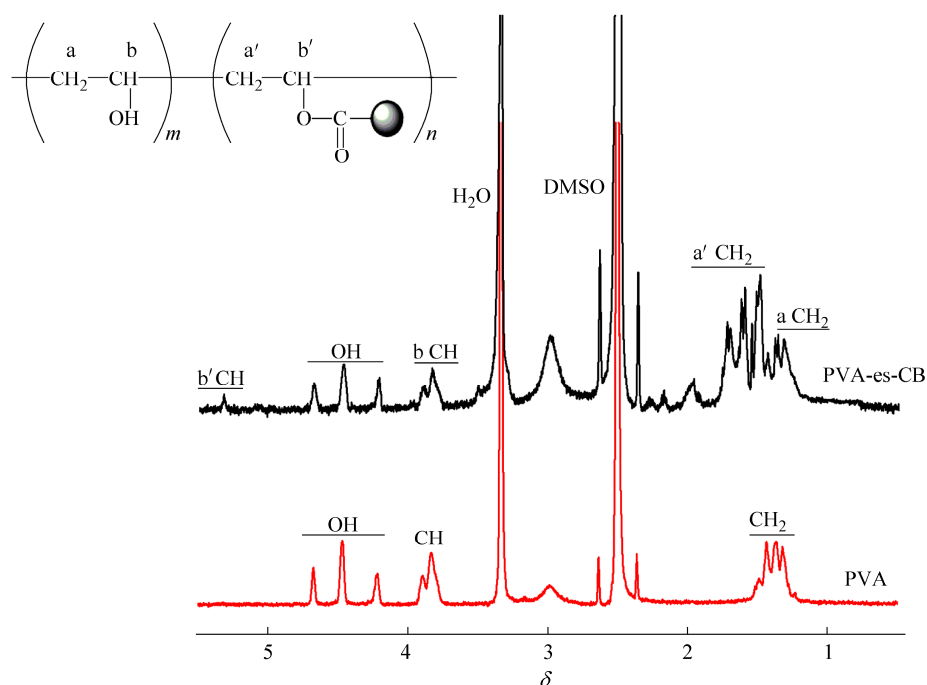


Fig. 2 ^1H -NMR spectra of neat PVA (bottom) and PVA-es-CB (top) at room temperature in DMSO-d_6

hydroxyl signals at $\delta = 5\text{--}4$, from which the stereoregularity of PVA is estimated as isotactic (mm): heterotactic (mr): syndiotactic (rr) of roughly 2:5:3^[35, 36]. Upon the attachment to CB the PVA proton signals become a little different. As shown in Fig. 2, new signals at $\delta = 5.3$ and $\delta = 1.8\text{--}1.5$ are clearly observed. These signals can be related to methine and methylene protons next to acetate groups as have been reported for esterification of PVA^[37, 38]. It is necessary to pay attention to the hydroxyl proton resonances which are resolvable in terms of configurational sequences (Fig. 2). Wu *et al.* have concluded that the hydrogen bonding tendency is dominant for hydroxyl units in a meso configuration, predominantly determines the hydroxyl proton shielding^[39, 40]. As hydrogen bonding leads to downfield shifts, the chemical shifts of hydroxyl sequences resonances increase when passing from iso ($\delta = 4.7$) to hetero ($\delta = 4.5$) and from hetero to syndio ($\delta = 4.2$) triad. On the other hand, it has been confirmed that the reactivity of substituent groups along the polymer chain can be influenced by tactic sequence^[41], where the substituents at mm sequence exhibited higher reactivity than those at the rr counterpart. By an inspection of the evolution of the ^1H spectrum, it is easy to observe an increase in the rr signal in detriment of the mm one for PVA-es-CB which suggests that esterification reaction occur at isotactic configuration.

Preparation and Characterization of PVA/PVA-es-CB Nanocomposites

To examine the particle dispersion in the polymer matrix at the nanoscale, PVA/CB thin films were sliced into specimens of *ca.* 100 nm in thickness by microtomy and then analyzed by TEM. As shown in Fig. 3, there are obviously abundant PVA-es-CBs randomly dispersed in the polymer matrix. Figure 3(a) shows that the particle size of PVA-es-CB in PVA matrix is about 30–70 nm, similar particle size was obtained for the cases of the PVA/2.5PVA-es-CB (Fig. 3b). However, the coagulation of PVA-es-CB particles was observed and resulted in a large particle size of 80–120 nm for the case of the PVA/5PVA-es-CB (Fig. 3c). In addition, the TEM image of PVA/CB (Fig. 3d) shows a large aggregated domain of CB. These results demonstrate that the esterification functionalization on CB played important roles for not only enhancing the solubility and providing bonding sites with CB but also effectively improving the resultant dispersity and morphology stability of these hybrid materials.

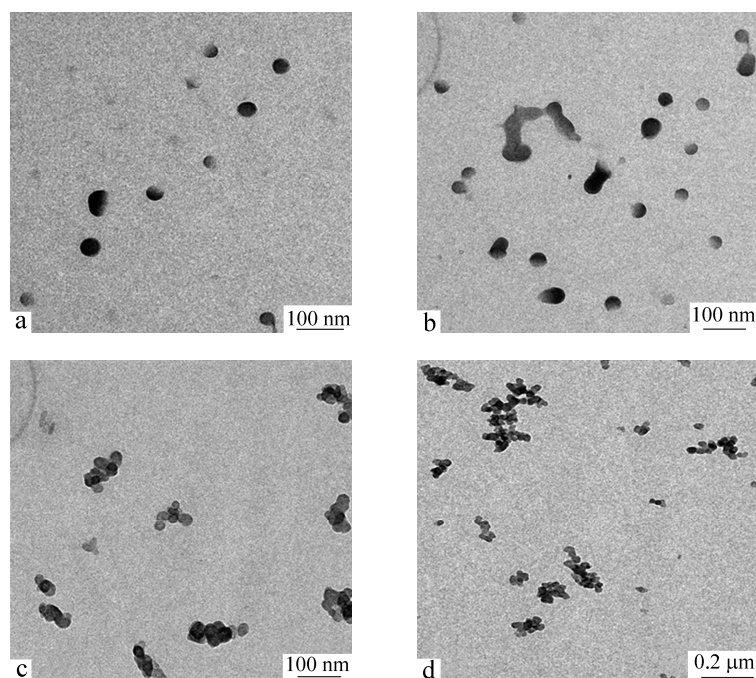


Fig. 3 TEM micrographs of the PVA/CB nanocomposite films: (a) PVA/1PVA-es-CB, (b) PVA/2.5PVA-es-CB, (c) PVA/5PVA-es-CB and (d) PVA/2.5CB

The structures of these films are studied by XRD. The characteristic XRD diffraction peaks of CB appear at $2\theta = 25^\circ$ and 44° . XRD patterns of PVA/PVA-es-CB nanocomposites with different PVA-es-CB contents are shown in Fig. 4. Due to the semicrystalline character of pure PVA, the pure PVA membrane exhibits typical peaks that appears at $2\theta = 21^\circ$ and 40° corresponding to the crystalline phase of the polymer^[42, 43]. In the nanocomposites, the main peak at 21° decreased and became broader, showing a decrease in crystallinity and indicating that some interactions between polymer chains and the filler may take place.

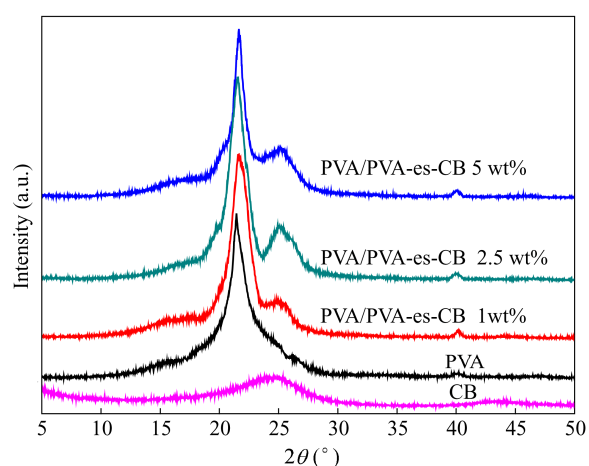
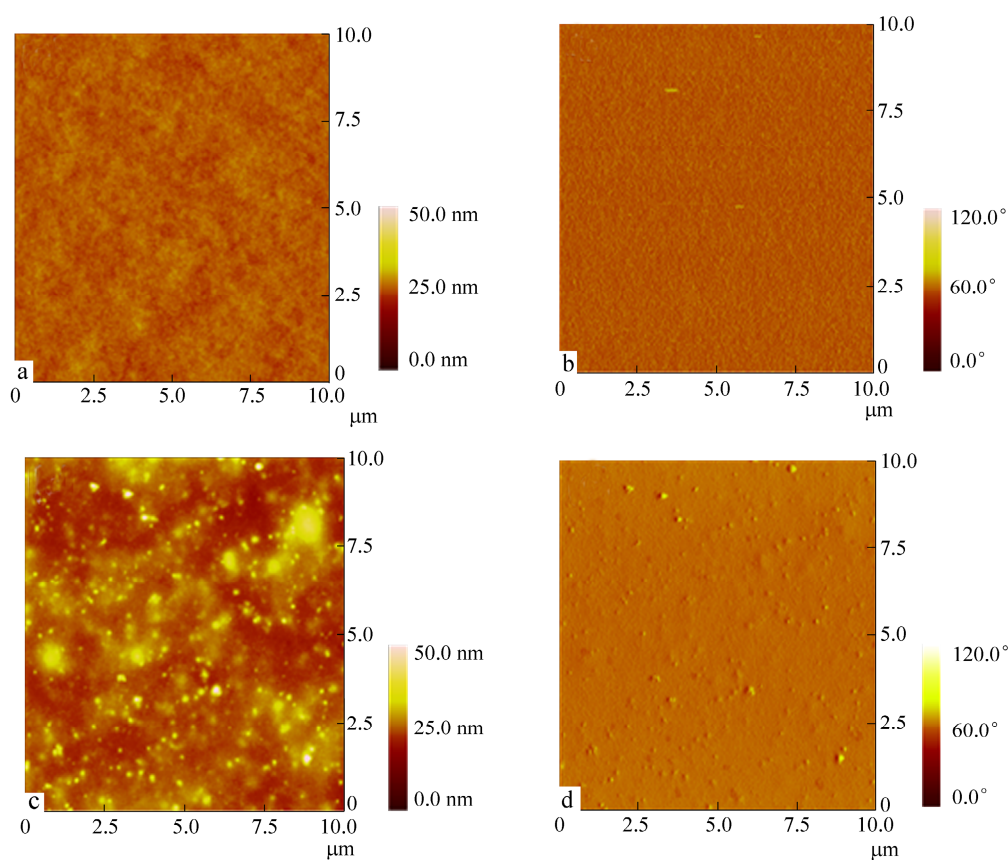


Fig. 4 XRD profiles of CB, neat PVA and PVA/PVA-es-CB hybrid films



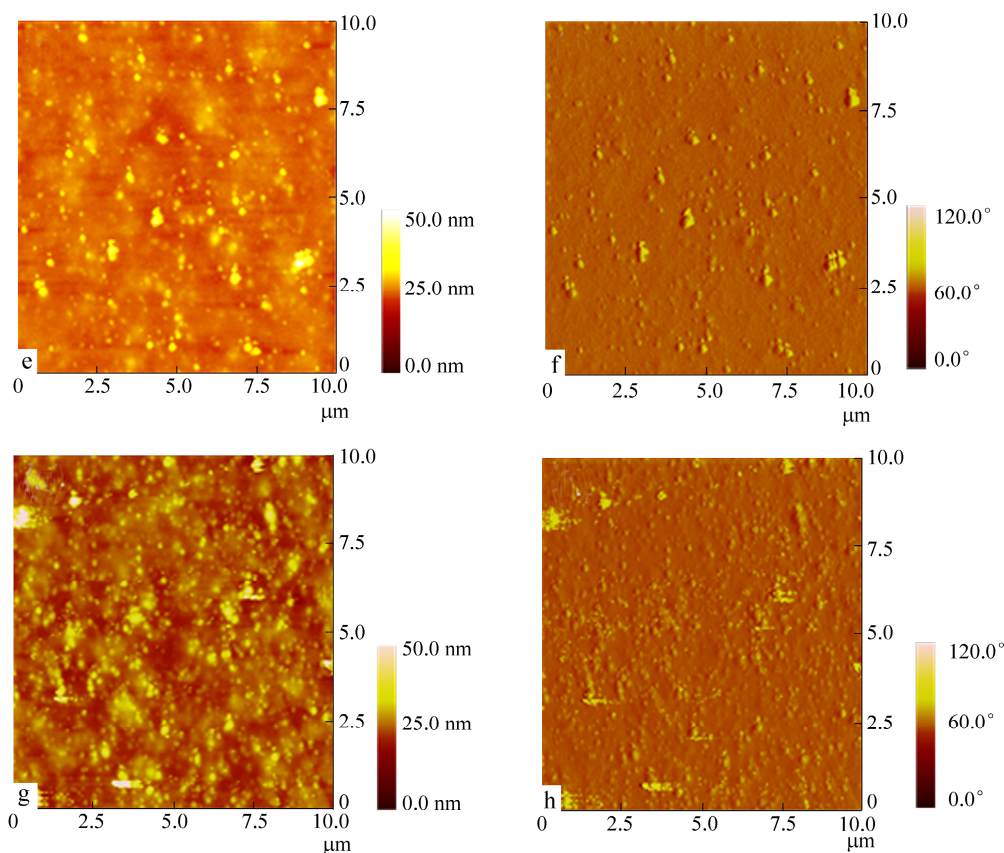


Fig. 5 AFM of the neat PVA films (a) height image, (b) phase image; PVA/1PVA-es-CB hybrid films (c) height image, (d) phase image; PVA/2.5PVA-es-CB hybrid films (e) height image, (f) phase image; PVA/5PVA-es-CB hybrid films (g) height image, (h) phase image

The AFM images of the PVA/PVA-es-CB hybrid thin films are shown in Fig. 5, and the film thickness (h), average roughness (R_a), mean square roughness (R_q) for the hybrid films are listed in Table 1. The ratio of surface roughness to film thickness (R_q/h) was less than 0.5%, implying the great surface planarity of the hybrid films could be obtained. As shown in Table 1, the surface roughness increases with the PVA-es-CB content due to the growing particle size at high PVA-es-CB content. The film thicknesses of the prepared hybrid films depend on the spin speed, solid content and viscosity of the coating solution. The solid content of the concentrated solution for the case of films is varied for the studied samples as shown in Table 1. Hence, it might affect the film thickness of the prepared hybrid films. Therefore, it is difficult to explain the trend of the film thickness with the PVA-es-CB content. However, Yu and Chen reported that the surface roughness increases with the film thicknesses at the same solid particles contents^[44].

Table 1. Properties of the PVA/PVA-es-CB hybrid films

Sample	PVA-es-CB content of hybrids		T_g (°C)	h (nm) ^b	R_a (nm) ^c	R_q (nm) ^d
	(wt%) ^a	(vol%)				
PVA	0	0	62	464.0	0.725	0.963
PVA/1PVA-es-CB	1.2	0.7	65	568.9	1.102	1.657
PVA/2.5PVA-es-CB	2.6	1.9	68	496.2	1.816	2.123
PVA/5PVA-es-CB	5.7	4.2	69	434.8	2.649	3.200

^a Experimental CB content estimated from TGA curves; ^b h : film thickness; ^c R_a : the average roughness;

^d R_q : the root mean square roughness

Figure 6(a) illustrates the TGA curves of the hybrids at a heating rate of 10 K min^{-1} under nitrogen flow. The CB contents in the hybrid materials were in good agreement with the theoretical contents and ensured the successful incorporation of the PVA-es-CB. TGA curves suggest that PVA-es-CBs improve the thermal stability of the nanocomposites. Despite a weight loss is observed around 200°C common in these systems, the onset of decomposition for PVA/CB-es-PVA is retarded. This noticeable effect in the thermal properties can be attributed to the high aspect ratio of the CBs linked to PVA. Addition of CB at low concentrations somewhat improved the thermal stability of the nanocomposite, which could be reasonably explained by the covalent bonds and the hydrogen-bonding interactions between the residual oxygen-containing groups of the CBs and the hydroxyl groups grafted onto the PVA backbone. Because the mobility of the polymer chains is strongly affected by the covalent linkage of CB species and because T_g is strongly dependent on the mobility of the polymer chains^[45], DSC analysis was used to compare the T_g of PVA with that of the PVA/PVA-es-CB nanocomposites. As shown in Fig. 6(b), the pure PVA material has a T_g of around 62°C , and the T_g of PVA/PVA-es-CB nanocomposites increased with increasing CB loading.

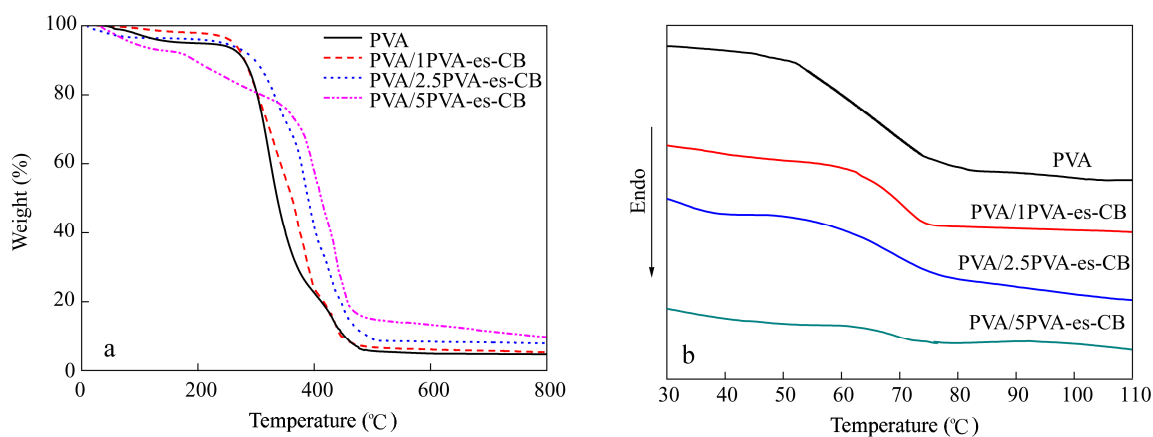


Fig. 6 (a) TGA curves of PVA, PVA/PVA-es-CB nanocomposites in N_2 ; (b) DSC curves of pure PVA and the PVA/PVA-es-CB nanocomposites

To this T_g increase, we suppose that the covalent bonds and hydrogen bonding between oxygenated groups in CB and PVA are both involved. This T_g shift is similar to the best available data obtained for polymer composites using individual functionalized graphene sheets as filler^[46]. In that system, the surface oxygen and hydroxyl groups of graphene sheets gave rise to intimate filler-polymer interactions. In our system the effect can be ascribed to the effective covalent attachment of the polymer to the CBs that prevents the segmental motions of the polymer chains. Obviously, the presence of CBs restricts the movement of the polymer chains. In addition, the CBs in a chain can interact with nearby chains by hydrogen bonding, limiting even more the mobility. Moreover, the hydrogen bonding represents an additional factor that contributes to the polymer dynamics. Salavagione *et al.* reported a similar case of functionalization of graphene sheets with PVA^[47].

Optical transparency of the PVA/PVA-es-CB nanocomposite thin films was characterized by UV-Vis spectra. As shown in Fig. 7, the results indicate that the pure polymer matrix (PVA) has high transmittance ($> 92\%$) at 400–800 nm and the nanocomposite films containing CB particles below 2.5 wt% exhibit good transparency ($> 81\%$) above 600 nm, although the PVA-es-CB particles have strong absorption below 400 nm in the UV-Vis region. Usually, the transparency of nanocomposite films with PVA-es-CB nanoparticles is mainly dependent on the size and content of PVA-es-CB particles. When the content of PVA-es-CB increases, the transparency of the nanocomposite decreases because of the aggregation of nanoparticles. Transmission electron microscopy studies support this result (Fig. 3c). The particle aggregates reach 100 nm in size and can result in severe optical scattering and reduced transmittance of the nanocomposites^[48].

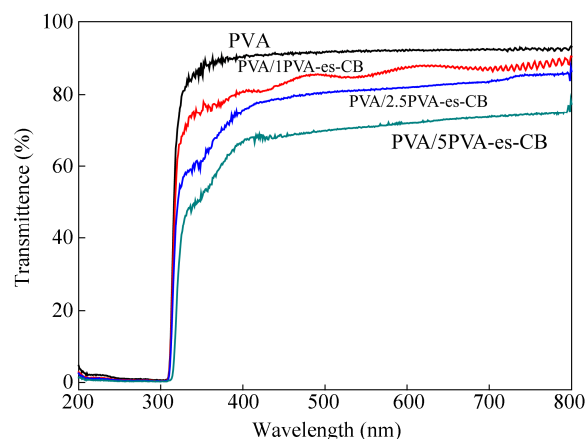


Fig. 7 Transmittance UV-Vis spectra of PVA and PVA/PVA-es-CB nanocomposites

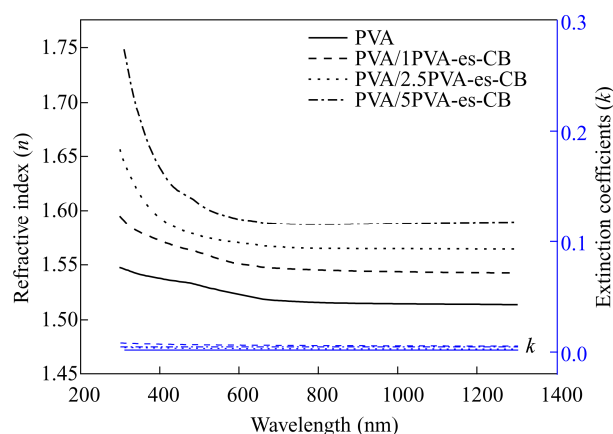


Fig. 8 Variation of refractive index (n) and extinction coefficient (k) of the hybrid films

Figure 8 shows the dispersion of the refractive index (n) and extinction coefficient (k) of the hybrid films. The extinction coefficients (k) of the films are almost zero in the wavelength range of 300–1300 nm, as shown in Fig. 8. The result also suggests that the prepared hybrid thin films have an excellent optical transparency in the visible region. The refractive index (n) of the prepared hybrid thin films is listed in Table 2. As shown in Table 2, the n at 633 nm increases from 1.520 of PVA to 1.598 of PVA/5PVA-es-CB. It is obvious that the CBs have a great contribution to the increase of refractive index for polymer composites.

Table 2. Optical properties of the PVA/PVA-es-CB hybrid films

Sample	Refractive index			T_{600}^a (%)	v_D^b
	550 nm	633 nm	800 nm		
PVA	1.516	1.520	1.527	91.2	38.2
PVA/1PVA-es-CB	1.535	1.544	1.550	87.3	36.4
PVA/2.5PVA-es-CB	1.560	1.568	1.570	82.0	32.1
PVA/5PVA-es-CB	1.591	1.598	1.604	71.9	27.3

^a n : transmittance at 600 nm; ^b Abbe's number is given by $v_D = (n_{589} - 1)/(n_{486} - n_{656})$

Figure 9(a) demonstrates that the refractive index at different wavelengths of the PVA hybrid films increases linearly from 1.516–1.527 to 1.591–1.604 depending on the volume percent of PVA-es-CB. Here, the refractive index of polymer is between 1.516 and 1.527 depending on the wavelength, and the hybrid PVA/PVA-es-CB shows an increase in the refractive index of the nanocomposites films. This refractive index of PVA hybrid films can be controlled by adjusting the content of PVA-es-CB. The higher the volume percent of PVA-es-CB, the larger the refractive index value of PVA hybrid films. A linear dependence of the refractive index on the volume content of the incorporated particles has also been found in many systems^[49–51]. In particular, compared with the PVA-TiO₂ hybrid materials^[24], for the same refractive index value, the needed content of PVA-es-CB particles is much lower than that of TiO₂. The density of inorganic phases should also be considered in the design of high RI nanocomposites due to the linear dependency of nanocomposite RI on the volume fraction of inorganic phases. In order to achieve a high RI nanocomposite, it is necessary to incorporate a high content of inorganic particles with high RI into a polymer matrix. In view of this fact, high RI inorganic particles (such as CBs) with low densities would be an optimal candidate for high RI nanocomposites.

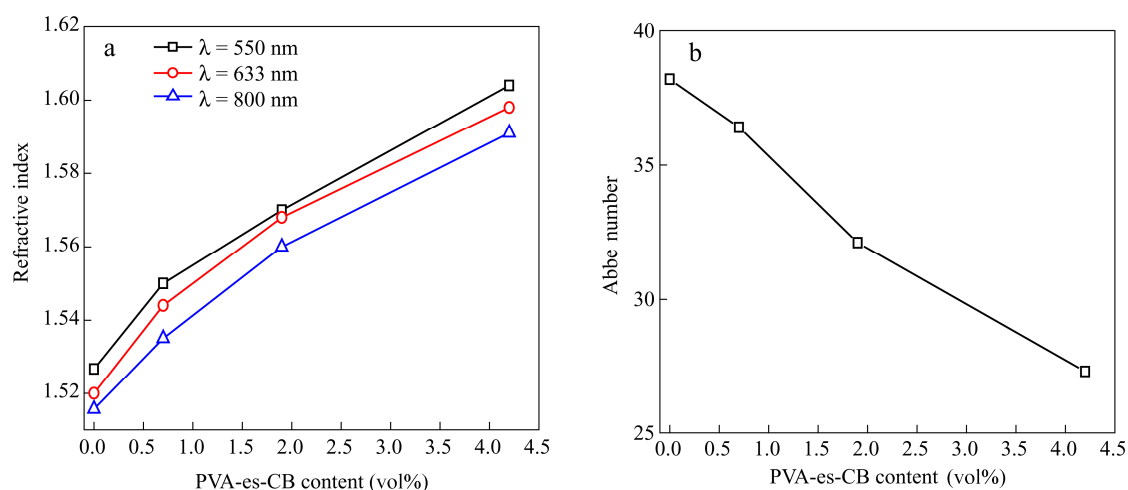


Fig. 9 (a) Refractive index as a function of volume percent of PVA-es-CB in nanocomposites measured with different wavelengths and (b) Abbe number of nanocomposites at different volume fractions of PVA-es-CB

Figure 9(b) illustrates the variations of Abbe number of the hybrid polymer films with the PVA-es-CB content. The refractive index increases with an increase of PVA-es-CB content. However, the Abbe number decreases from 38.2 for PVA to 27.3 for PVA/5PVA-es-CB for the hybrid materials, as shown in Table 2. The relationship between the refractive index and the PVA-es-CB content is the reverse of the trend for the Abbe number. This suggests that the optical properties of the prepared hybrid films can be tuned through their compositions. The Abbe number suggests the optical dispersion of the prepared films. The absorption edges of the hybrid materials increase with the size of the PVA-es-CB segment, and therefore the Abbe number decreases.

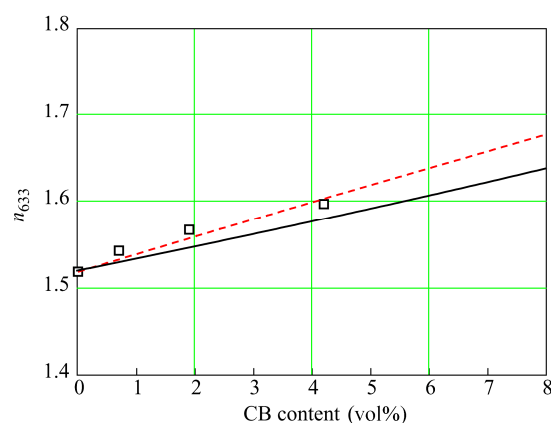


Fig. 10 Refractive indices of the PVA-es-CB/PVA nanocomposites at 633 nm. Solid and dotted lines are theoretical predictions based on Maxwell-Garnett and Lorentz-Lorenz theories, respectively.

The refractive indices of the nanocomposites at 633 nm are plotted in Fig. 10 as a function of the volume ratio. Two theoretical curves are also given in the figure. The solid lines are calculated based on Maxwell-Garnett effective medium theory^[52, 53]. According to this theory, the bulk dielectric constant of the composite can be described from the dielectric constants of the host and the inclusion as

$$\frac{\epsilon_c - \epsilon_h}{\epsilon_c + 2\epsilon_h} = \phi \left(\frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} \right) \quad (1)$$

where ϵ_c , ϵ_h , and ϵ_i are the dielectric constants of the composite, host and inclusion, respectively, and ϕ is the volume fraction of the inclusion. The refractive index n of the composite was calculated using Eq. (1) and the Maxwell relation $n^2 = \epsilon$. In this system, the densities of $\rho_{\text{PVA}} = 1.3 \text{ g cm}^{-3}$ for the PVA component and $\rho_{\text{CB}} = 1.8 \text{ g cm}^{-3}$ for CB particles, and the refractive index $n_{\text{CB}} = 2.26$ was used for the calculation. The dashed lines in Fig. 10 are based on the Lorentz-Lorenz effective medium expression^[53], given by

$$\frac{n_c^2 - 1}{n_c^2 + 2} = \phi_{\text{CB}} \cdot \frac{n_{\text{CB}}^2 - 1}{n_{\text{CB}}^2 + 2} + \phi_{\text{PVA}} \cdot \frac{n_{\text{PVA}}^2 - 1}{n_{\text{PVA}}^2 + 2} \quad (2)$$

where n_c , n_{CB} and n_{PVA} are the refractive indices of the composite, CB and PVA, respectively, and ϕ_{CB} , and ϕ_{PVA} are the volume fractions of CB, and PVA, respectively. The Maxwell-Garnett theory gave a slightly lower estimation than that determined using the Lorentz-Lorenz calculation. And the Lorentz-Lorenz calculation gave better estimation for most of the observed refractive indices. Due to the many assumptions included in the calculation, it seems difficult to make a more precise prediction of the refractive indices of these composites. However, a rough estimation could be made.

CONCLUSIONS

In summary, we have prepared a high refractive index organic/inorganic hybrid nanocomposite. CB can be functionalized by PVA in carbodiimide-activated esterification reactions. The morphology studies suggest that the formed PVA-es-CB nanoparticles in polymer networks display homogeneous dispersion. The hybrid films also revealed good surface planarity, high thermal stability, tunable refractive index and optical transparency in the visible range. The refractive indices of the obtained nanocomposites increased with the amount of nanoparticles. The increase could be roughly estimated using the Lorentz-Lorenz theory. Especially to deserve to be mentioned, the present paper provides a novel high RI nanoparticle, the commonly used nanoparticles for high refractive index nanocomposites (such as TiO_2 , ZrO_2 , PbS and ZnS) are expensive, high densities and generally require large amounts in composites. CB, being a cheap, widespread material consisting of relatively small particles with a low density, is a possible alternative. The doped PVA solutions can be easily spin-coated, and the coatings combine the optical transmittance of polymer with the high refractive index of PVA-es-CBs. If inorganic salt was mixed into this doped PVA solution, this doped PVA seems to be a possible material for use in the channel waveguides fabrication^[48].

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