

Novel poly(vinyl chloride) nanocomposite films containing α -Al₂O₃ nanoparticles capped with vitamin B₁: preparation, morphological, and thermal characterization

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Abstract Many studies have been accomplished in the field of nanocomposite (NC) preparation to control the adhesion and spatial dispersion of nano-fillers and effect of these on attributes of the polymer matrix. In this investigation, surface modification of α -Al₂O₃ nanoparticles (NPs) was performed by vitamin B₁ (VB₁) as biodegradable and environmentally friendly modifier agent. Poly(vinyl chloride) (PVC) NCs were prepared with several contents of modified α -Al₂O₃ NPs (3, 5, and 7 wt.%) by ultrasonication method. Then, many standard techniques were used to study the properties of NC films. The results demonstrated that PVC/ α -Al₂O₃-VB₁ NC films had better thermal stability and stress strength properties than pure PVC. Morphology images of PVC/ α -Al₂O₃-VB₁ NCs showed the good dispersion of NPs in the polymer matrix in nanometer scale. They revealed that the α -Al₂O₃ NPs have sphere-like morphology. The mechanical properties of PVC/ α -Al₂O₃-VB₁ NCs were improved by adding different amounts of α -Al₂O₃-VB₁ into the matrix of PVC. Water contact angle analysis showed increase in hydrophilicity of PVC/ α -Al₂O₃-VB₁ NCs.

Keywords α -Al₂O₃ nanoparticles · Biocompatibility · Surface modification · Nanocomposites · Contact angle · Tensile properties

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Introduction

Nanocomposites (NCs) are materials designed for enhanced performance in any number of unique applications: structural, functional or cosmetic. NCs include a matrix, composed of polymer, metal or ceramic combined with nanoparticles (NP)s in suspension [1].

NPs have unparalleled chemical, mechanical, thermal, and electrical properties that make them very noteworthy for application in medicine, biotechnology, and environment-related initiatives.

Metal oxide NPs deputize a new class of substantial materials that are being developed for use in research, as a facility for functional materials of electrical and mechanical parts [2, 3].

Alumina NPs have attracted much interest because alumina is one of the cost-effective NPs that has hardness and high strength. α -Al₂O₃ NPs have supreme dielectric properties, good thermal conductivity [4], wear resistance [5], resistance to intense alkali, and acid attack at high temperatures. They have been used as nano-fillers for polymer NCs to improve the mechanical and conductive attributes [6, 7]. Among different forms of this worthwhile material, the ultrafine α -Al₂O₃ powder has considerable potential for a wide range of requisitions as high-strength materials, catalysts, and electronic ceramics [8, 9]. The wide utilization of ultrafine α -Al₂O₃ makes it a general material and increases the attention [10, 11].

NPs have an extremely high tendency of aggregation [11], due to the fact that they have small particle size and high surface energy [3, 12]. Dispersion of NPs in organic polymers can elevate a wide domain of material properties, such as mechanical and thermal properties as well as fire retardancy and barrier properties [5, 13]. One method to overcome aggregation of NPs is the use of different biocompatible coupling agents such as citric acid and ascorbic acid (vitamin C) [5, 14]. This is an efficacious method due to the strong covalent and hydrogen bonds created between the polymer chains and surface-modified NPs [15–18]. Another method is the use of ultrasound wave energy [19, 20]. Researches showed that the use of ultrasonic waves can improve the distribution of the NPs, control size distribution, morphology and decrease the aggregation in the polymer matrix [21, 22].

In this study, surface modification of α -Al₂O₃ NPs was accomplished by vitamin B₁ (VB₁) as a biocompatible modifier to enhance the dispersibility and prevent agglomeration. VB₁ (also called thiamine), has appeared as an eco-friendly, inexpensive, naturally occurring, and water-soluble compound with the reported toxicity parameter [LD₅₀ (VB₁, oral rat) = 3710 mg/kg]. VB₁ is a pyrimidine derivative with a methylene-bridged thiazole moiety [23, 24]. The use of VB₁ analogs has been reported as powerful catalysts for different organic transformations [25].

Poly(vinyl chloride) (PVC) is one of the polymers with the highest production and applications due to its characteristics such as easy modification and low cost [26].

PVC has been reinforced with various fillers including titanium dioxide (TiO_2) [27], zinc oxide (ZnO) [28], iron oxide (Fe_3O_4) [29], and silver (Ag) [30] NPs for different purposes [31]. In this project, PVC/ α - Al_2O_3 - VB_1 NCs containing α - Al_2O_3 - VB_1 NPs (3, 5, and 7 wt.%) were prepared by ultrasonic irradiation. The PVC/ α - Al_2O_3 - VB_1 NCs were characterized by techniques such as Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and ultraviolet–visible (UV–Vis) spectroscopy. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) analyses were used to determine the morphology of the α - Al_2O_3 - VB_1 and PVC/ α - Al_2O_3 - VB_1 NCs.

Experimental

Materials

α - Al_2O_3 powder (average particle size: 80 nm and purity: 99%) was supplied from Neutrino Co. (Tehran, I. R. Iran). VB_1 ($\text{C}_{12}\text{H}_{17}\text{N}_4\text{OS}$, Mw: 265.35 g/mol) was purchased from Alfa Aesar Co. (Karlsruhe, Germany). Emulsion (E)-PVC grade ($(\text{C}_2\text{H}_3\text{Cl})_n$, Mw: 78.000 g/mol) was obtained from LG Chem Co. (Seoul, Korea). Tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, Mw: 72.11 g/mol) was supplied by JEONG wang Co. (Gyeonggi-do, Korea).

Characterizations

The functionalization of α - Al_2O_3 NPs and fabrication of NCs were accomplished using Topsonics ultrasonic liquid processors (Tehran, I. R. Iran) with a frequency of 25 kHz and power of 100 W. The FT-IR spectra of the samples were recorded in a Jasco-680 (Japan) spectrophotometer in the form of KBr pellets of finely ground samples. It was used to study the characteristic peaks related to the NC films directly. The UV–Vis spectra were investigated by Jasco V-750 UV–Vis–NIR spectrophotometer (Tokyo, Japan), in the wavelength scan range from 200 to 800 nm.

XRD patterns were recorded on a Philips XPert MPDX-ray (Germany) diffractometer by a copper target operating at a voltage of 40 kV, a current of 35 mA, and Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) over Bragg's angles (2θ) ranging from 10° to 80° with a scanning rate of $0.05^\circ/\text{min}$. Field emission scanning electron microscopy (FE-SEM) was performed on Hitachi S-4160 (Japan) instrument at an acceleration voltage of 15 kV. Prior to analysis, the composites were coated with an ultrathin gold layer in sputter coating method. TEM was done with a Philips CM120 microscope (Germany) (accelerating voltage 150 kV). Tensile testing was performed at room temperature on Hounsfield test equipment H25KS (RHI 5DZ, England). Tests were done with the speed of 5 mm/min. Contact angle measurements were done with U-vision MV500 digital camera microscope (China).

Surface modification of α -Al₂O₃ NPs with VB₁

The surface of α -Al₂O₃ NPs was treated with VB₁, 0.1 g of α -Al₂O₃ nanopowder was suspended into deionized (DI) water (8 ml) and ultrasonicated for 30 min. Then, 0.01 g of green modifier VB₁ (10% mass fraction of α -Al₂O₃ content) was dissolved in DI water (5 ml) by ultrasonication for 15 min. In the next step, the mixture of NPs and VB₁ solutions was sonicated for 30 min. Finally, the prepared suspension was dried at room temperature to obtain the powder of modified α -Al₂O₃ NPs with VB₁ (α -Al₂O₃-VB₁ NPs). The reaction sequences are shown in Scheme 1.

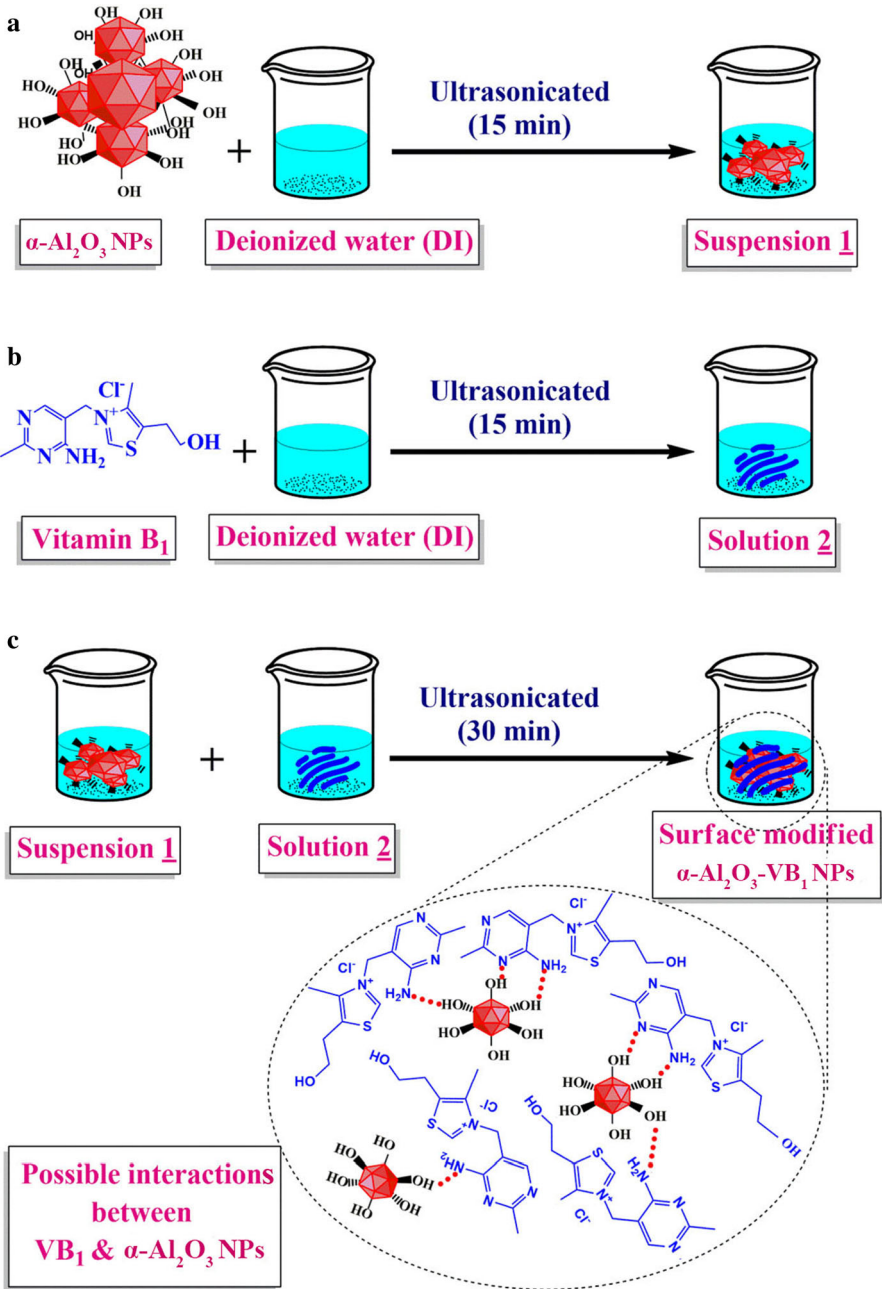
Preparation of PVC/ α -Al₂O₃-VB₁ NC films

The preparation of PVC/ α -Al₂O₃-VB₁ NC films was achieved by the following procedure: 0.10 g of PVC was added to 5 mL of THF by stirring (1 h at 40 °C). After that, different amounts of α -Al₂O₃-VB₁ (3, 5, and 7 wt.% of PVC) were separately added to PVC solution. Prepared mixtures were ultrasonicated for 30 min. Finally, the resulting suspensions were poured into glass Petri dishes and allowed to dry (Scheme 2). After evaporation of THF, NC films with high transparency were obtained that were easily separated from the Petri dishes (Fig. 1). The images of the prepared NC films with different contents of NPs are shown in Fig. 1. As it can be seen, transmission capability of PVC decreased with increasing the α -Al₂O₃-VB₁ NP contents.

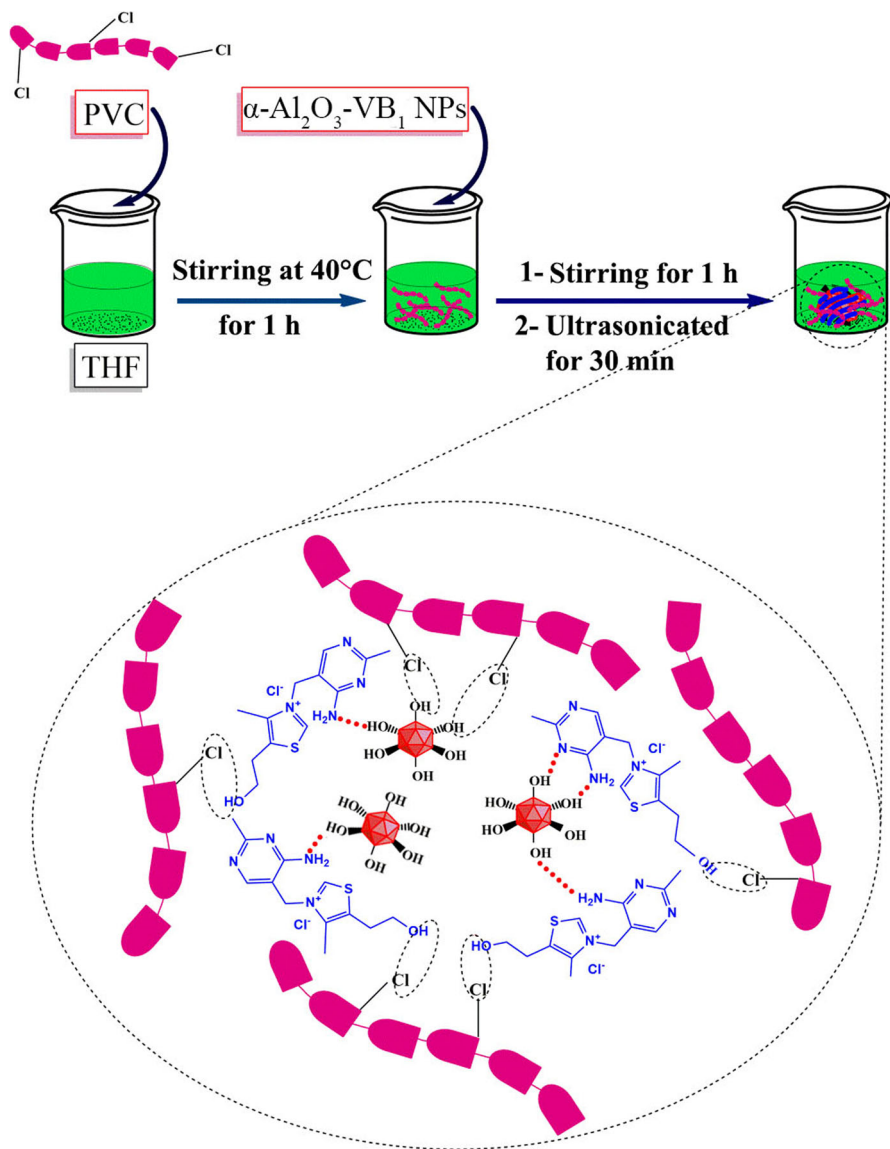
Results and discussion

Modification of α -Al₂O₃ and composites preparation

VB₁ is utilized as a biocompatible modifier for creating more functional groups on the NPs' surface to prevent agglomeration, enhance the dispersibility and good miscibility of NPs in the PVC NCs. Based on performed study and recent investigations, the optimum weight percent of modifier was estimated around 10 wt.% [32]. In the modifying process, the amount of modifier is important because low amount of modifier can cause an inhomogeneous and low miscibility between the α -Al₂O₃ and the PVC matrix while, high amount of modifier can increase agglomeration of the NPs in PVC/ α -Al₂O₃-VB₁ NC. Lone-pair electrons of chlorine atoms made many interactions in PVC. PVC has been used as a polymer matrix for the formation of the NCs [33]. The aim of this research is the manufacture of the NCs without aggregation of NPs in the polymer matrix. To overcome this problem, the environmentally friendly modifier and ultrasonic vibration were used. Ultrasonic power apparatus produces acoustic capitations and thereby affects the reaction. It makes bubble and these bubbles help to distribute the energy. In the modified α -Al₂O₃, the organic structure of VB₁ expands NPs' properties as filler. It gives a good ability to form homogeneous hybrid film with PVC matrix.



Scheme 1 Surface modification of $\alpha\text{-Al}_2\text{O}_3$ with VB₁



Scheme 2 Preparation of PVC/ α -Al₂O₃-VB₁ NC films

FT-IR analysis

Figure 2a presents the FT-IR spectrum of α -Al₂O₃ NPs. The Al–O band is shown at around 400–900 cm⁻¹. The broad peaks at around 3100–3300 and 1600–1700 cm⁻¹ correspond to the stretching and bending bonds of hydroxyl groups of adsorbed water molecules on the α -Al₂O₃ surface [34]. Figure 1c exhibits the absorption bands for VB₁. Two peaks around 1615 and 1592 cm⁻¹ are assigned to the C=C and

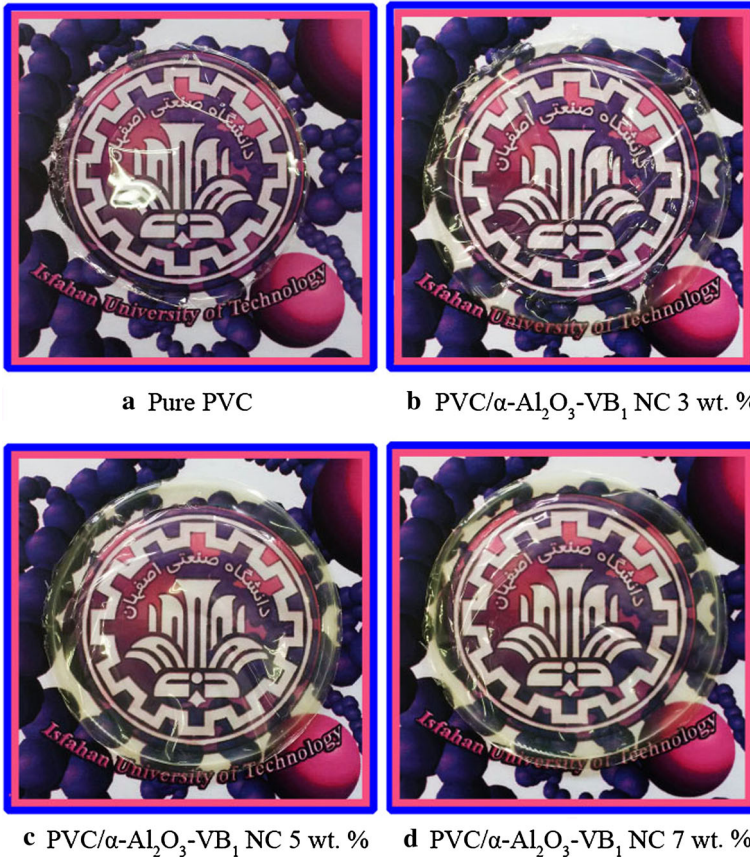
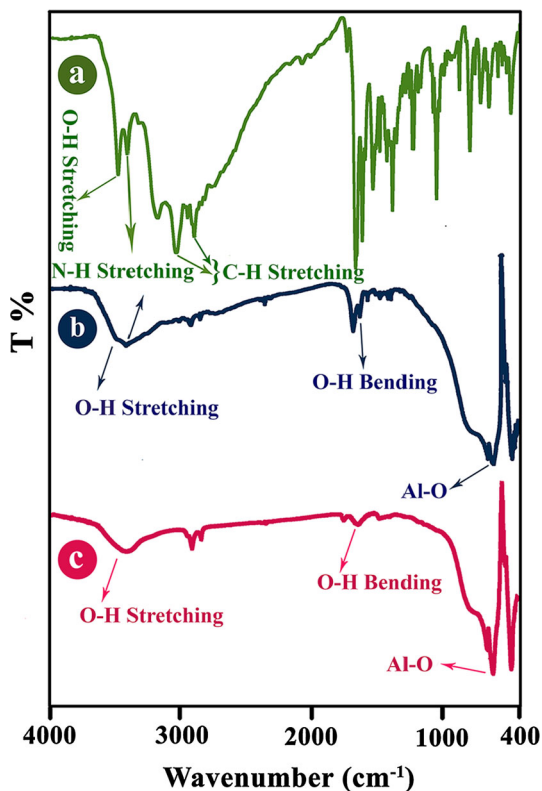


Fig. 1 Photographs of **a** pure PVC, **b** 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, **c** 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film, and **d** 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

C=N stretching modes in the pyrimidine structure for VB₁. The peaks at 3424 and 1666 cm⁻¹ represent the stretching and bending vibrations of -NH (-NH₂), respectively. An absorbance band at 3492 cm⁻¹ corresponded to the O-H stretching. The peak at 3050 cm⁻¹ is assigned to the C-H stretching vibrations of the aromatic rings and at 2910 cm⁻¹ associated with the aliphatic C-H stretching in VB₁ [35].

The FT-IR spectrum of modified α -Al₂O₃ NPs displays new characteristic peaks (Fig. 2b). The absorption band at 1662 cm⁻¹ confirms the existence of VB₁ on the surface of the α -Al₂O₃ NPs; this peak shows that the NH groups of VB₁ appear in α -Al₂O₃-VB₁. The mild shift of absorbance bands toward lower wavenumbers may be ascribed to the interactions between α -Al₂O₃ NPs and VB₁. For instance, the hydrogen bonding between α -Al₂O₃ NPs and VB₁ decreases the frequency of O-H bond from 1637 to 1607 cm⁻¹. The peak at 3431 cm⁻¹ can be ascribed to the N-H stretching vibration and confirmed that VB₁ was tied on the α -Al₂O₃ surface [36].

Fig. 2 FT-IR spectra of *a* VB₁, *b* α -Al₂O₃-VB₁ NPs, and *c* α -Al₂O₃ NPs

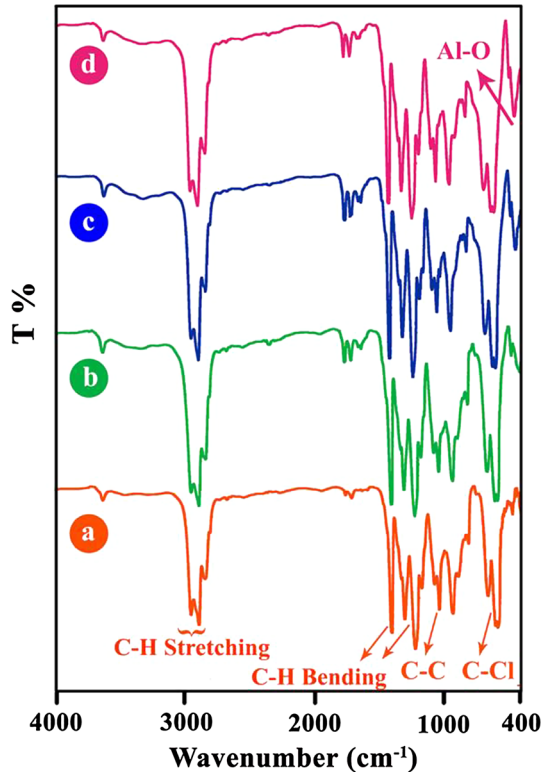


The spectra of the pure PVC and PVC/ α -Al₂O₃-VB₁ NCs are shown in Fig. 3 in absorbance mode. Figure 3a shows the spectrum of pure PVC. The band at 2800–3000 cm⁻¹ is attributed to the C–H stretching bond. The peak at 1250 cm⁻¹ is assigned to the bending bond of C–H near Cl. The absorbance band in a range of 600–650 cm⁻¹ is related to C–Cl gauche bond [37, 38]. In comparison with the pure PVC, new peaks appeared in the spectra of the PVC/ α -Al₂O₃-VB₁ NC films (Fig. 3b–d). In addition, the absorption peak of the O–H group at 1607 cm⁻¹ shifted to a higher frequency which could be attributed to the formation of effective hydrogen bonds between the α -Al₂O₃-VB₁ NPs and the PVC matrix. The presence of α -Al₂O₃-VB₁ makes changes in the infrared spectrum of pure PVC which attributed to NH group of VB₁ at 1772 cm⁻¹. The band at 425–450 cm⁻¹ is in agreement with the Al–O bond. The peak intensity of the α -Al₂O₃ NPs in the PVC/ α -Al₂O₃-VB₁ NCs increased with enhancement of the content of modified NPs.

Crystalline structure

XRD was used for the recognition of the crystalline phases. Figure 4 presents the XRD patterns of α -Al₂O₃ NPs and α -Al₂O₃-VB₁ in the 2θ range. The diffraction peaks of α -Al₂O₃ NPs, namely 021, 104, 110, 024, 116, 211, 122, 124, 030, 208, and

Fig. 3 FT-IR spectra of *a* pure PVC, *b* 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, *c* 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film, and *d* 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

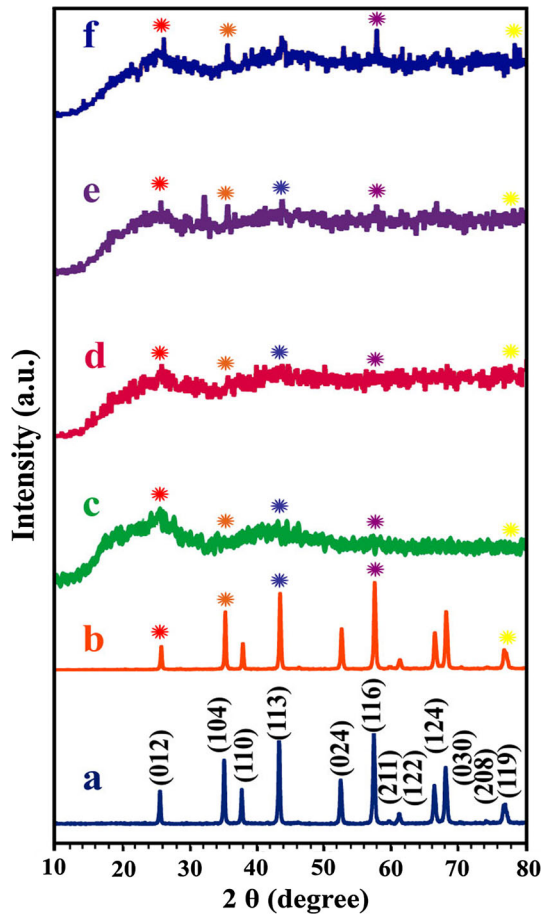


119, related to the hexagonal nature of α -Al₂O₃ NPs [39]. These data have good agreement with reported data in the literature. It is seen from the XRD pattern that pure PVC is an amorphous polymer (Fig. 4c) [40]. The XRD curves of PVC/ α -Al₂O₃-VB₁ NCs (Fig. 4d–f) indicated a broad peak plus certain peaks that are relevant to NPs' crystalline structure. The XRD patterns of the PVC/ α -Al₂O₃-VB₁ NCs demonstrated weak peaks at 2θ , namely 012, 110, 113, 116, and 119 which were slightly raised with increasing the content of the α -Al₂O₃-VB₁ NPs in the PVC matrix. The low intensity of peaks can be attributed to fine dispersion and low percentages of α -Al₂O₃-VB₁ NPs (3, 5, and 7 wt.%) in the polymer matrix [38].

Morphology studies (FE-SEM and TEM)

The morphology of the α -Al₂O₃-VB₁ NPs, pure PVC, and PVC/ α -Al₂O₃-VB₁ NC films was observed by FE-SEM micrographs. The FE-SEM images (Fig. 5a) confirmed that the α -Al₂O₃ NPs after modification were nearly spherical in shape, similar to α -Al₂O₃ NPs [41]. The homogenous surface can be observed from FE-SEM micrograph of NC films (Fig. 5c–e). Actually, the ultrasonication caused a uniform surface morphology which ensures a potent interaction between nano-fillers and the matrix [42]. There was no significant change in FE-SEM images of the

Fig. 4 XRD patterns of *a* α - Al_2O_3 NPs, *b* α - Al_2O_3 -VB₁ NPs, *c* pure PVC, *d* 3 wt.% PVC/ α - Al_2O_3 -VB₁ NC film, *e* 5 wt.% PVC/ α - Al_2O_3 -VB₁ NC film, and *f* 7 wt.% PVC/ α - Al_2O_3 -VB₁ NC film



obtained PVC/ α - Al_2O_3 -VB₁ NCs compared to the pure polymer. For a more detailed observation, TEM analysis was employed.

Clearer morphology and dispersion of NPs into the PVC/ α - Al_2O_3 -VB₁ NCs were scrutinized by TEM micrographs. As shown in Fig. 6a, modified α - Al_2O_3 NPs display individual spherical-like and single crystalline α - Al_2O_3 NPs with a clean surface [43].

TEM images of the 5 wt.% PVC/ α - Al_2O_3 -VB₁ NC film at various magnifications are shown in Fig. 6b. These images confirmed the presence of α - Al_2O_3 -VB₁ NP in the PVC/ α - Al_2O_3 -VB₁ NC films. It can be seen that α - Al_2O_3 -VB₁ NPs distributed uniformly in the polymer matrix and their sizes decreased. On the one hand, successful modification causes steric effect and separates NPs from each other. On the other hand, ultrasonic irradiations during the formation of NC can break the aggregation of α - Al_2O_3 NPs and cause good dispersion of them in the PVC matrix. It is clear that the size of NPs depends on the ultrasonication time [44]. It is possible that sonication for a long time enhances the chance of the lone particle

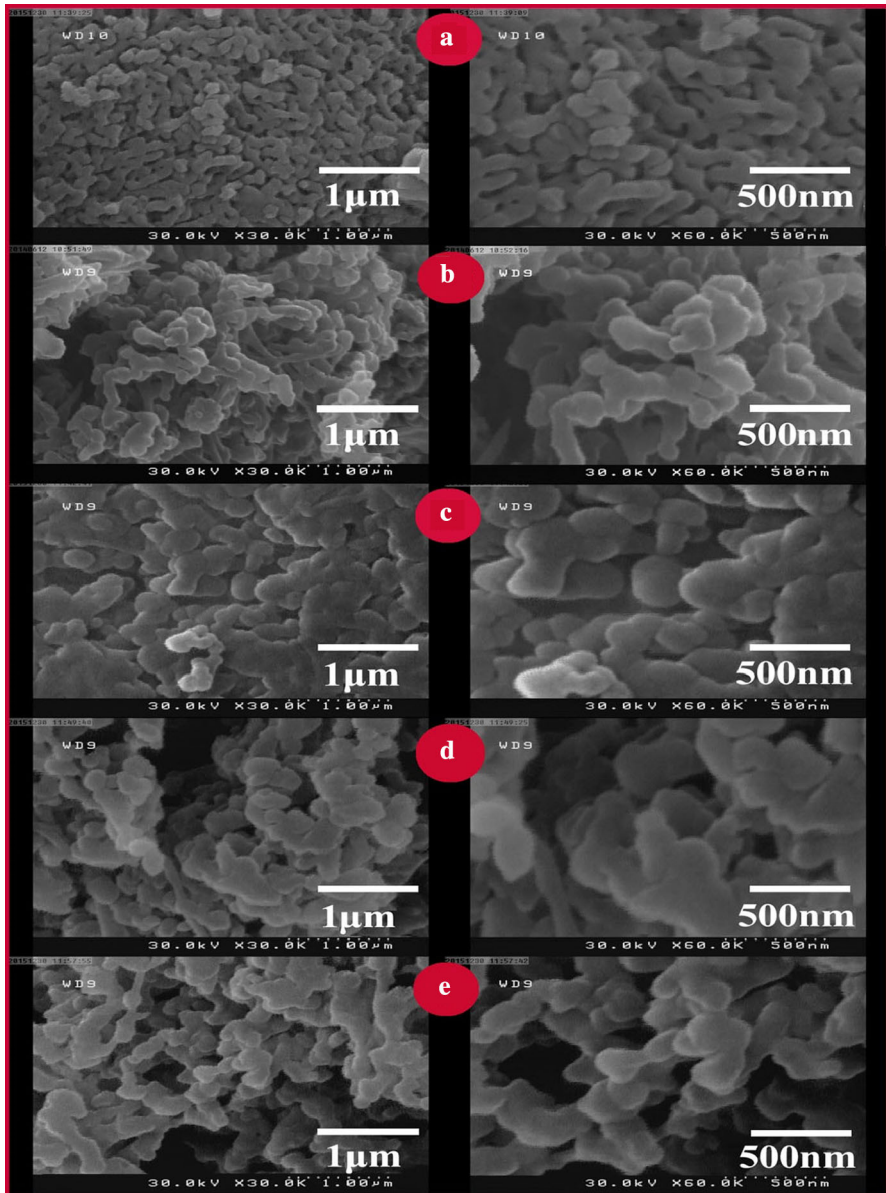


Fig. 5 FE-SEM micrographs of **a** α -Al₂O₃-VB₁ NPs, **b** pure PVC, **c** 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, **d** 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film, and **e** 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

reaction with the micro-bubbles produced by the acoustic cavitation. Consequently, due to successful modification as well as ultrasonic irradiations the size of some α -Al₂O₃-VB₁ NPs embedded in the PVC matrix decreased and was found to be 18–30 nm.

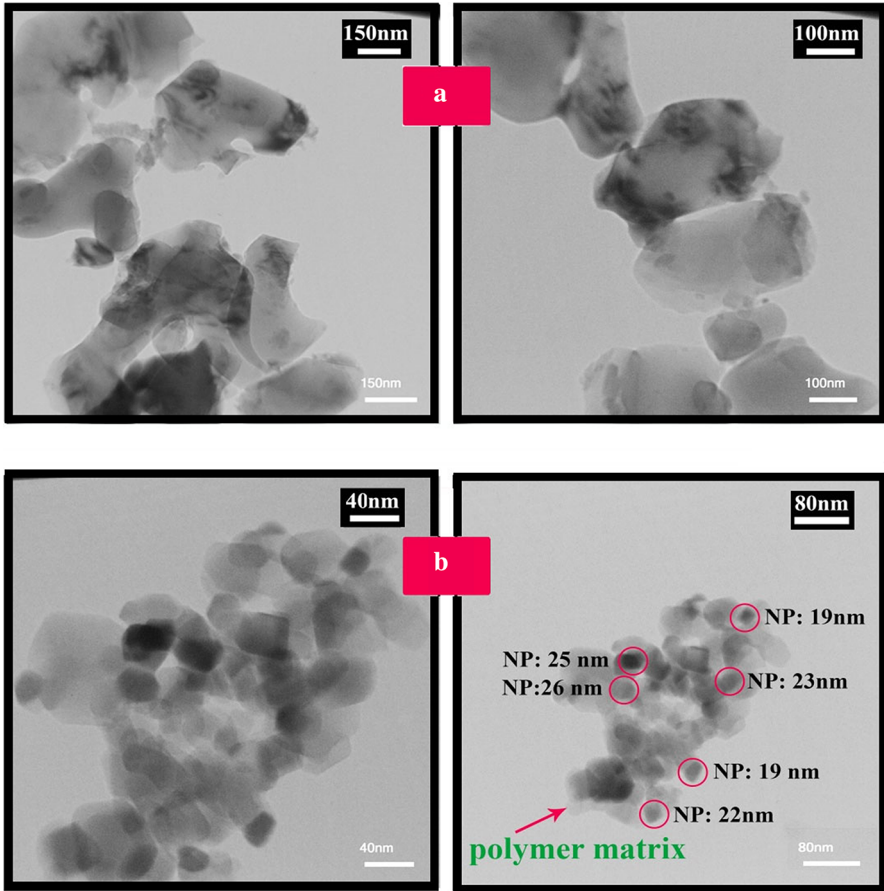


Fig. 6 TEM micrographs of **a** α -Al₂O₃-VB₁ NPs and **b** 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film

Combustion test

To estimate the amount of the α -Al₂O₃-VB₁ NPs in the 5 wt.% PVC/ α -Al₂O₃-VB₁ NC, it was combusted in air. The images of the 5 wt.% PVC/ α -Al₂O₃-VB₁ film before and after combustion from room temperature to 1000 °C and then holding temperature for 4 h at 1000 °C are shown in Fig. 7. It is clear that after combustion, 5 wt.% PVC/ α -Al₂O₃-VB₁ film changed to white powder and shows that the remaining materials are metals, which are approximately 5% of the whole weight. It is well known that PVC is a char-forming polymer during combustion. Under strong heat flux, the PVC macromolecules pyrolyze into various smaller molecules and some of these will combust when their concentration reaches some critical value in air [45]. FT-IR analysis was done on residual white powder and it showed characteristic peaks related to α -Al₂O₃ NPs.

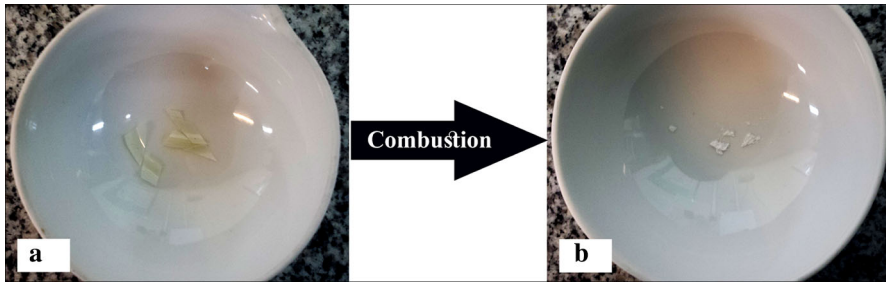


Fig. 7 The digital photographs of 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film before and after combustion in air

Thermal stability

The amount of coupling agent is analyzed by TGA thermograms. From Fig. 8b, it can be estimated that the weight ratio of the VB₁ modifier on the α -Al₂O₃ surface is almost 6 wt.%.

TGA curves of the PVC and PVC/ α -Al₂O₃-VB₁ NC films are recorded in Fig. 9. For the pure PVC and the NCs, two stages of weight loss were detected. The first transition weight loss of pure PVC from 276 to 298 °C corresponded to the dehydrochlorination. During this first decomposition stage, the sample weight loss is about 55%. Under the effect of temperature, chlorine radicals resulting from scission of -C-Cl labile bonds take off a hydrogen radical from adjacent -C-H groups to form a covalent H-Cl bond. This chemical mechanism induces double bonds along the polymer chain and may lead to conjugated polymeric chains [46]. The sample in the region 298–445 °C becomes thermally stable because of the formation of polyacetylene. The second step of weight loss

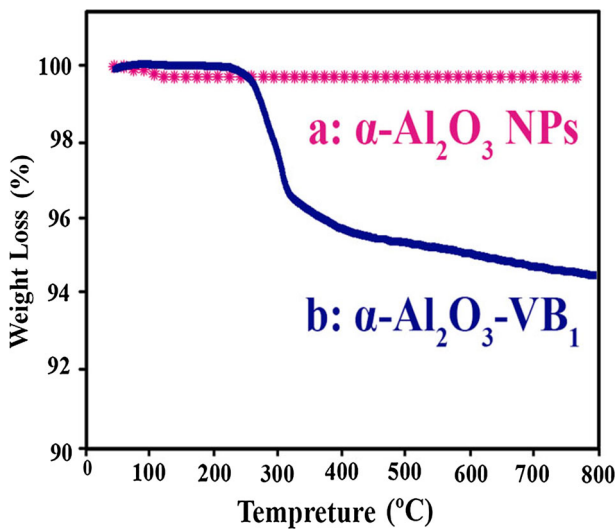


Fig. 8 TGA thermograms of *a* α -Al₂O₃ NPs, *b* α -Al₂O₃-VB₁

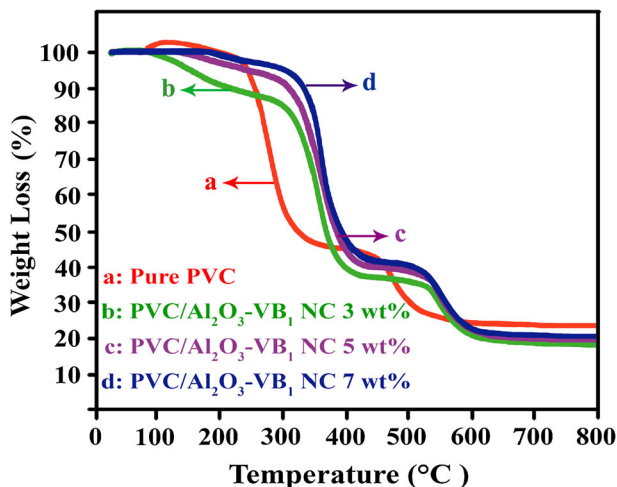


Fig. 9 TGA thermograms of *a* pure PVC, *b* 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, *c* 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film, and *d* 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

Table 1 Thermal properties of the pure PVC, 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film and 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

Samples	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
Pure PVC	240.3	254.8	23.3
PVC/ α -Al ₂ O ₃ -VB ₁ NC film, 3 wt.%	154.5	217.9	18.2
PVC/ α -Al ₂ O ₃ -VB ₁ NC film, 5 wt.%	244.4	308.8	20.0
PVC/ α -Al ₂ O ₃ -VB ₁ NC film, 7 wt.%	304.3	332.9	20.7

^a Temperature at which 5 wt.% weight loss was recognized by TGA at a heating rate of 20 °C min⁻¹ in an argon atmosphere

^b Temperature at which 10 wt.% weight loss was verified by TGA at a heating rate of 20 °C min⁻¹ in an argon atmosphere

^c Percentage weight of the material left undecomposed after TGA analysis at 800 °C in an argon atmosphere

in the range of 445–530 °C is probably a consequence of the polyacetylene cracking [47].

The resulting TGA data including temperatures at 5% (T_5) and 10% (T_{10}) weight loss, and char yield (CY) at 800 °C are summarized in Table 1.

As it can be seen, the TGA curves of the PVC/ α -Al₂O₃-VB₁ NCs shifted to higher temperatures than the pure PVC. After addition of α -Al₂O₃-VB₁, the T_5 and T_{10} values of 5 and 7 wt.% NCs were improved.

UV–Vis absorption

As shown in Fig. 10, pure PVC and PVC NCs display strong absorption in UV region. The spectrum of pure PVC showed absorbance peaks at $\lambda = 210$ and

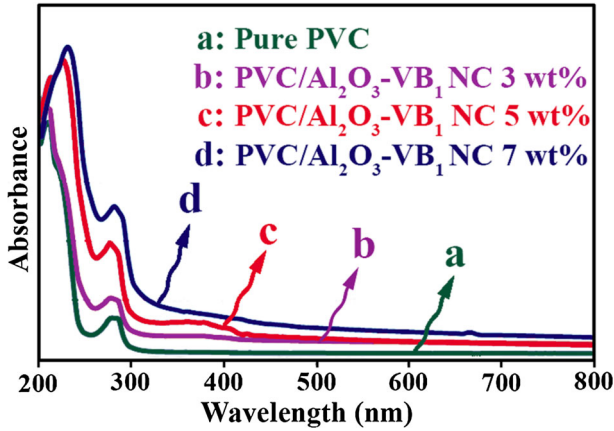


Fig. 10 UV–Vis absorption spectra of *a* pure PVC, *b* 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, *c* 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film, and *d* 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

280 nm, which can be assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively [48]. The α -Al₂O₃ NPs have UV–Vis absorption at $\lambda = 205$ nm [49] which has been covered by adsorption peak related to PVC. Therefore, the absorption intensity of PVC/ α -Al₂O₃-VB₁ NCs increased with increasing the content of the α -Al₂O₃-VB₁ NPs in the PVC matrix.

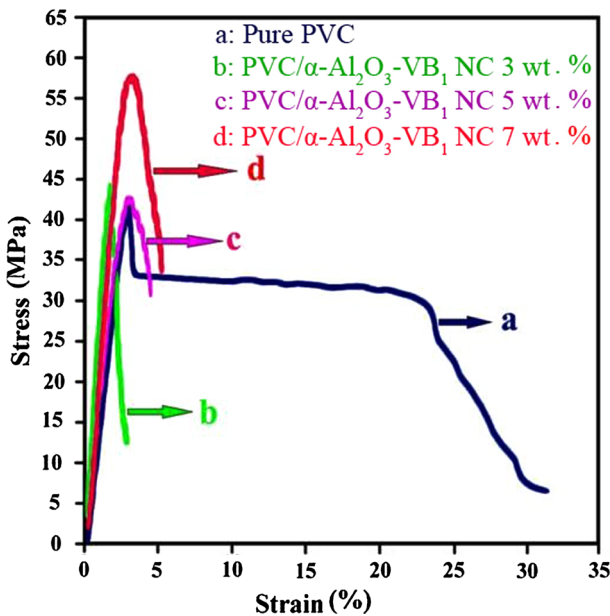


Fig. 11 Mechanical properties of *a* pure PVC, *b* 3 wt.% PVC/ α -Al₂O₃-VB₁ NC film, *c* 5 wt.% PVC/ α -Al₂O₃-VB₁ NC film, and *d* 7 wt.% PVC/ α -Al₂O₃-VB₁ NC film

Mechanical properties

The stress–strain curves of pure PVC film and PVC/ α -Al₂O₃–VB₁ NCs are depicted in Fig. 11 and the corresponding tensile strength, Young's modulus, elongation, and strain are summarized in Table 2. The mechanical properties of PVC/ α -Al₂O₃–VB₁ NCs can be affected by many factors, such as the morphology, size, loading, distribution, and interfacial adhesion of NPs [30, 47].

Table 2 shows that stress, strain, and elongation increased for NCs of 5 and 7 wt.%. This can be explained by the reason that the incorporation of α -Al₂O₃–VB₁ NPs into the PVC matrix effectively enhanced the interfacial interactions between NPs and matrix via the establishment of hydrogen and covalent bonds between them. The interfacial bonding between NPs and matrix can effectively transfer the applied stress to the α -Al₂O₃ NPs and improve the mechanical properties [38].

Water contact angle analysis

Hydrophilicity of a polymer surface is an important property for biomedical application [50]. It is well known that alumina has a hydrophilic surface [51]; therefore, the effect of the presence of α -Al₂O₃–VB₁ NPs on the hydrophilicity of

Table 2 Mechanical properties from tensile testing for pure PVC and PVC/ α -Al₂O₃–VB₁ NC film

Samples	Stress (MPa)	Strain (%)	Young's modulus (GPa)	Elongation at max (mm)
Pure PVC	42.14	2.68	1.87	0.94
PVC/ α -Al ₂ O ₃ –VB ₁ NC film, 3 wt.%	43.82	1.62	2.64	0.57
PVC/ α -Al ₂ O ₃ –VB ₁ NC film, 5 wt.%	42.16	2.71	1.43	0.95
PVC/ α -Al ₂ O ₃ –VB ₁ NC film, 7 wt.%	57.3	2.74	1.98	0.96

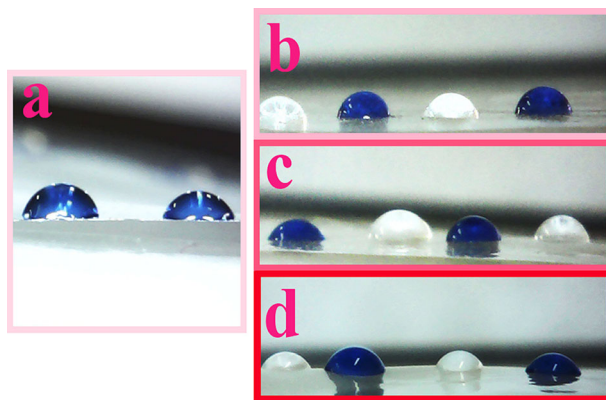


Fig. 12 Images of water droplets on *a* pure PVC, *b* 3 wt.% PVC/ α -Al₂O₃–VB₁ NC film, *c* 5 wt.% PVC/ α -Al₂O₃–VB₁ NC film, and *d* 7 wt.% PVC/ α -Al₂O₃–VB₁ NC film

Table 3 Water static contact angles for pure PVC and PVC/ α -Al₂O₃-VB₁ NC films

Samples	Contact angles
Pure PVC	80.02 ± 1.76
PVC/ α -Al ₂ O ₃ -VB ₁ NC film, 3 wt.%	75.05 ± 1.06
PVC/ α -Al ₂ O ₃ -VB ₁ NC film, 5 wt.%	73.15 ± 1.21
PVC/ α -Al ₂ O ₃ -VB ₁ NC film, 7 wt.%	65.42 ± 1.75

NCs was analyzed in this study. Water droplets on the pure PVC and PVC/ α -Al₂O₃-VB₁ NC films are shown in Fig. 12. In addition, water static contact angles were measured and are summarized in Table 3. The decrease in contact angles of NCs compared to the pure PVC can be ascribed to the presence of abundant hydroxyl groups on the surface of α -Al₂O₃-VB₁ NPs which increases ability of PVC surface to form hydrogen bonds with water molecules (Fig. 12).

Conclusions

In this study we considered a simple and efficient method to obtain the PVC/ α -Al₂O₃-VB₁ NC films with improved thermal and mechanical properties. The ultrasonic technique was used for the synthesis of the NCs in a green and simple way. The α -Al₂O₃ NPs were treated by VB₁ as a biocompatible modifier to enhance homogeneous dispersion and reduce the aggregation in the matrix. Then, the PVC NCs were prepared with different percentages of α -Al₂O₃-VB₁ NPs (3, 5, and 7 wt.%). FE-SEM and TEM images were used to study the distribution of NPs and uniform morphology of the PVC/ α -Al₂O₃-VB₁ NCs. The XRD patterns of PVC/ α -Al₂O₃-VB₁ NCs indicated that the crystalline phase of α -Al₂O₃ NP was not changed. A comparison of T_5 and T_{10} of the PVC/ α -Al₂O₃-VB₁ NCs with pure PVC showed an increase in thermal stability of 5 and 7 wt.% PVC/ α -Al₂O₃-VB₁ NCs. The UV absorbance of PVC/ α -Al₂O₃-VB₁ NCs is raised with increasing the content of the α -Al₂O₃-VB₁ NPs in the PVC matrix. The prepared PVC/ α -Al₂O₃-VB₁ NC films can be used to block the UV radiation (at about 280 nm). Water static contact angles were investigated and showed hydrophilicity enhancement of PVC/ α -Al₂O₃-VB₁ NCs. As a result, it can be mentioned that the presence of VB₁ as modifier agent can prevent the agglomeration of α -Al₂O₃ NPs and cause a positive impact on thermal, mechanical, and optical properties of PVC/ α -Al₂O₃-VB₁ NCs. Due to high mechanical properties and UV absorption ability of the obtained composite films, they may be employed in packaging applications.

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References

1. Mallakpour S, Khadem E (2016). Chapter 16 recent achievements in the synthesis of biosafe poly(vinyl alcohol) nanocomposite. In: Inamuddin (ed) Green polymer composites technology; properties and applications. Taylor & Francis Group, 6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742 CRC Press, pp 261–278. doi:[10.1201/9781315371184-17](https://doi.org/10.1201/9781315371184-17)
2. Stanković A, Dimitrijević S, Uskoković D (2013) Influence of size scale and morphology on antibacterial properties of ZnO powders hydrothermally synthesized using different surface stabilizing agents. *Colloids Surf B* 102:21–28
3. Cava S, Tebcherani S, Souza I, Pianaro S, Paskocimas C, Longo E, Varela JA (2007) Structural characterization of phase transition of Al₂O₃ nanopowders obtained by polymeric precursor method. *Mater Chem Phys* 103(2):394–399
4. Kar KK, Srivastava S, Rahaman A, Nayak S (2008) Acrylonitrile-butadiene-styrene nanocomposites filled with nanosized alumina. *Polym Compos* 29(5):489–499
5. Mallakpour S, Dinari M (2013) Enhancement in thermal properties of poly(vinyl alcohol) nanocomposites reinforced with Al₂O₃ nanoparticles. *J Reinf Plast Compos* 32(4):217–224
6. Mahdavian AR, Sarrafi Y, Shabankareh M (2009) Nanocomposite particles with core-shell morphology III: preparation and characterization of nano Al₂O₃-poly(styrene-methyl methacrylate) particles via miniemulsion polymerization. *Polym Bull* 63(3):329–340
7. Mallakpour S, Javadpour M (2016) Chapter 35 design strategies of green polymer nanocomposites containing amino acid linkages. In: Inamuddin (ed) Green polymer composites technology. Taylor & Francis Group, 6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742 CRC Press, pp 491–512. doi:[10.1201/9781315371184-36](https://doi.org/10.1201/9781315371184-36)
8. Sperling RA, Parak W (2010) Surface modification, functionalization and bioconjugation of colloidal inorganic nanoparticles. *Philos Trans R Soc Lond A Math Phys Eng Sci* 368(1915):1333–1383
9. Smuleac V, Butterfield D, Sikdar S, Varma R, Bhattacharyya D (2005) Polythiol-functionalized alumina membranes for mercury capture. *J Membr Sci* 251(1):169–178
10. Branch M (2011) Preparation of nano-scale α -Al₂O₃ powder by the sol-gel method. *Ceram Silikaty* 55(4):378–383
11. Iijima M, Kamiya H (2009) Surface modification for improving the stability of nanoparticles in liquid media. *KONA Powder Part J* 27:119–129
12. Mallakpour S, Madani M (2015) A review of current coupling agents for modification of metal oxide nanoparticles. *Prog Org Coat* 86:194–207
13. Gaume J, Tavio-Gueho C, Cros S, Rivaton A, Therias S, Gardette J-L (2012) Optimization of PVA clay nanocomposite for ultra-barrier multilayer encapsulation of organic solar cells. *Sol Energy Mater Sol Cells* 99:240–249
14. Mallakpour S, Nezamzadeh Ezhieh A (2015) A simple and environmentally friendly method for surface modification of ZrO₂ nanoparticles by biosafe citric acid as well as ascorbic acid (vitamin C) and its application for the preparation of poly(vinyl chloride) nanocomposite films. *Polym Compos*. doi:[10.1002/pc.23746](https://doi.org/10.1002/pc.23746)
15. Beitollahi A, Hosseini-Bay H, Sarpoolaki H (2010) Synthesis and characterization of Al₂O₃-ZrO₂ nanocomposite powder by sucrose process. *J Mater Sci Mater Electron* 21(2):130–136
16. Zhou Y, Fu S, Zheng L, Zhan H (2012) Effect of nanocellulose isolation techniques on the formation of reinforced poly(vinyl alcohol) nanocomposite films. *Express Polym Lett* 6(10):794–804
17. Khanna P, Singh N, Charan S, Subbarao V, Gokhale R, Mulik U (2005) Synthesis and characterization of Ag/PVA nanocomposite by chemical reduction method. *Mater Chem Phys* 93(1):117–121
18. Sairam M, Patil MB, Veerapur RS, Patil SA, Aminabhavi TM (2006) Novel dense poly(vinyl alcohol)-TiO₂ mixed matrix membranes for pervaporation separation of water-isopropanol mixtures at 30 °C. *J Membr Sci* 281(1):95–102
19. Paranhos CM, Soares BG, Oliveira RN, Pessan LA (2007) Poly(vinyl alcohol)/clay-based nanocomposite hydrogels: swelling behavior and characterization. *Macromol Mater Eng* 292(5):620–626
20. Mallakpour S, Hatami M (2016) Condensation polymer/layered double hydroxide NCs: preparation, characterization, and utilizations. *Eur Polym J* 90:273–300. doi:[10.1016/j.eurpolymj.2017.03.015](https://doi.org/10.1016/j.eurpolymj.2017.03.015)
21. Mallakpour S, Soltanian S (2010) Studies on syntheses and morphology characteristic of chiral novel poly(ester-imide)/TiO₂ bionanocomposites derived from L-phenylalanine based diacid. *Polymer* 51(23):5369–5376

22. Jokar A, Azizi MH, Hamidi Esfehiani Z (2015) Effects of ultrasound time on the properties of poly(vinyl alcohol-based) nanocomposite films. *Nutr Food Sci Res* 2(4):29–38
23. Singh NG, Lily M, Devi SP, Rahman N, Ahmed A, Chandra AK, Nongkhilaw R (2016) Synthetic, mechanistic and kinetic studies on the organo-nanocatalyzed synthesis of oxygen and nitrogen containing spiro compounds under ultrasonic conditions. *Green Chem* 18(15):4216–4227
24. Leopold N, Cîntă-Pînzaru S, Baia M, Antonescu E, Cozar O, Kiefer W, Popp J (2005) Raman and surface-enhanced Raman study of thiamine at different pH values. *Vib Spectrosc* 39(2):169–176
25. Lei M, Ma L, Hu L (2009) Thiamine hydrochloride as a efficient catalyst for the synthesis of amidoalkyl naphthols. *Tetrahedron Lett* 50(46):6393–6397
26. Albeniz S, Vicente M, Trujillano R, Korili S, Gil A (2014) Synthesis and characterization of organosaponites. Thermal behavior of their poly(vinyl chloride) nanocomposites. *Appl Clay Sci* 99:72–82
27. Yang C, Tian L, Ye L, Peng T, Deng K, Zan L (2011) Enhancement of photocatalytic degradation activity of poly(vinyl chloride)-TiO₂ nanocomposite film with polyoxometalate. *J Appl Polym Sci* 120(4):2048–2053
28. Elashmawi I, Hakeem N, Marei L, Hanna F (2010) Structure and performance of ZnO/PVC nanocomposites. *Phys B* 405(19):4163–4169
29. Wang Q, Jang M, Chen YF (2007) Effects of nanosized iron oxide with different morphology on nanomechanical properties of nanocomposite coating. *Key Eng Mater* 336–338:2218–2220
30. Saadatabadi NM, Nateghi MR, Borhanizarandi M (2014) Fabrication and characterization of nanosilver intercalated graphene embedded poly(vinyl chloride) composite thin films. *J Polym Res* 21(8):1–9
31. Mallakpour S, Behranvand V (2016) Grafted nano-ZnO, TiO₂ and CuO by biosafe coupling agents and their applications for the green polymer nanocomposites fabrication. In: Inamuddin (ed) *Green polymer composites technology: properties and applications*, chap 24. CRC Press, Taylor & Francis Group, Boca Raton, pp 381–396
32. Chen J, Zhou Y, Nan Q, Sun Y, Ye X, Wang Z (2007) Synthesis, characterization and infrared emissivity study of polyurethane/TiO₂ nanocomposites. *Appl Surf Sci* 253:9154–9158
33. Abdul Nabi M, Yusop RM, Yousif E, Abdullah BM, Salimon J, Salih N, Zubairi SI (2014) Effect of nano ZnO on the optical properties of poly(vinyl chloride) films. *Int J Polym Sci*. doi:10.1155/2014/697809
34. Ghezelbash Z, Ashouri D, Mousavian S, Ghandi AH, Rahnama Y (2012) Surface modified Al₂O₃ in fluorinated polyimide/Al₂O₃ nanocomposites: synthesis and characterization. *Bull Mater Sci* 35(6):925–931
35. Carraher CE Jr, Roner MR, Lambert RE, Arroyo L, Miller LC (2015) Synthesis of organotin polyamine ethers containing thiamine (vitamin B₁) and preliminary ability to inhibit select cancer cell lines. *J Inorg Organomet Polym Mater* 25(6):1414–1424
36. Azizi K, Heydari A (2014) Vitamin B₁ supported on silica-encapsulated γ -Fe₂O₃ nanoparticles: design, characterization and application as a greener biocatalyst for highly efficient acylation. *RSC Adv* 4(17):8812–8816
37. Dunbai Z, Changgen C, Demin J (2006) Preparation and mechanical properties of solid-phase grafting nanocomposites of PVC/graft copolymers/MMT. *J Wuhan Univ Technol Mater Sci Ed* 21(4):5–8
38. Mallakpour S, Abdolmaleki A, Tabebordbar H (2016) Production of PVC/ α -MnO₂-KH550 nanocomposite films: morphology, thermal, mechanical and Pb(II) adsorption properties. *Eur Polymer J* 78:141–152
39. Mallakpour S, Dinari M (2013) The synergetic effect of chiral organoclay and surface modified-Al₂O₃ nanoparticles on thermal and physical properties of poly(vinyl alcohol) based nanocomposite films. *Prog Org Coat* 76(1):263–268
40. Vasanthkumar M, Bhatia R, Arya VP, Sameera I, Prasad V, Jayanna H (2014) Characterization, charge transport and magnetic properties of multi-walled carbon nanotube-polyvinyl chloride nanocomposites. *Phys E* 56:10–16
41. Kamil F, Hubiter K, Abed T, Al-Amiery A (2015) Synthesis of aluminum and titanium oxides nanoparticles via sol-Gel method: optimization for the minimum size. *J Nanosci Technol* 37–39
42. Mallakpour S, Behranvand V (2016) Manufacture and characterization of nanocomposite materials obtained from incorporation of D-glucose functionalized MWCNTs into the recycled poly(ethylene terephthalate). *Des Monomers Polym* 19(4):283–289

43. Li H, Li Y, Jiao J, Hu H-M (2011) Alpha-alumina nanoparticles induce efficient autophagy-dependent cross-presentation and potent antitumour response. *Nat Nanotechnol* 6(10):645–650
44. Li W, Yue J, Liu S (2012) Preparation of nanocrystalline cellulose via ultrasound and its reinforcement capability for poly (vinyl alcohol) composites. *Ultrason Sonochem* 19(3):479–485
45. Wang Q, Zhang X, Jin Y, Gui H, Dong W, Lai J, Liu Y, Gao J, Huang F, Song Z (2006) Preparation and properties of PVC ternary nanocomposites containing elastomeric nanoscale particles and exfoliated sodium-montmorillonite. *Macromol Mater Eng* 291(6):655–660
46. Bishay I, Abd-El-Messieh S, Mansour S (2011) Electrical, mechanical and thermal properties of poly(vinyl chloride) composites filled with aluminum powder. *Mater Des* 32(1):62–68
47. Yuan W, Cui J, Cai Y, Xu S (2015) A novel surface modification for calcium sulfate whisker used for reinforcement of poly(vinyl chloride). *J Polym Res* 22(9):1–9
48. Hasan M, Kumar R, Barakat M, Lee M (2015) Synthesis of PVC/CNT nanocomposite fibers using a simple deposition technique for the application of Alizarin Red S (ARS) removal. *RSC Advances* 5(19):14393–14399
49. Kortov V, Nikiforov S, Milman I, Moiseykin E (2004) Specific features of luminescence of radiation-colored α -Al₂O₃ single crystals. *Radiat Meas* 38(4):451–454
50. Choinska E, Muroya T, Swieszkowski W, Aoyagi T (2016) Influence of macromolecular structure of novel 2- and 4-armed polylactides on their physicochemical properties and in vitro degradation process. *J Polym Res* 23(7):1–11
51. Deki S, Kajinami A, Kanaji Y, Mizuhata M, Nagata K (1993) Properties of CaCl₂ hydrate with an inorganic powder. Part 2. —Melting behaviour and thermodynamic properties of CaCl₂ nH₂O (n = 6.00–7.35) with α -Al₂O₃ or α -SiC powder. *J Chem Soc Faraday Trans* 89(20):3811–3815