Synthesis and Characterization of Anti-flammable Vinyl Ester Resin Nanocomposites with Surface-functionalized Nanotitania

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Abstract

Polymer composites play a significant role in developing flame retardants to prevent fire accidents. The current work aims at investigating the flame retardancy of vinyl ester resins (VER) reinforced with nanotitania (nano-TiO₂) nanofiller. The surface functionality of nano-TiO₂ was modified by adding Si and N₂ to improve its flame retardancy. The chemical structure and thermal stability of nanocomposites were studied using Fourier-transform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA). Peaks of Si and N₂ in the modified TiO₂-VER nanocomposite and weight loss of the modified composite confirmed the addition of Si and N₂. The tensile strength results have shown that modified TiO₂-VER nanocomposites didn't make any significant impact on the tensile strength in comparison with pure VER. The flammability and thermal stability behaviors of these nanocomposites are evaluated using microscale combustion calorimetry (MCC). At high percent loading of nanofiller, the normalized heat release capacity (HRC) of modified TiO₂-VER nanocomposites was decreased by 27.7%, whereas the HRC of unmodified TiO₂-VER nanocomposites was only reduced by 9.8%. Also, the normalized total heat release of modified nanofiller based PNC was found to be 21.4%, whereas the unmodified PNC was 12.4%.

Keywords: Polymer nanocomposite; Vinyl ester resins; Nanofiller; Nanotitania; Anti-flammable material.

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1. Introduction

Owing to the multipurpose use of different anti-flammable materials in industry and household, the studies around flame retardants have become one of the most promising research fields in science and engineering.^[1,2] Halogens, phosphorus, nitrogen, and inorganic compounds are the most commonly used flame retardants.^[3] However, due to the long-term ecological problems associated with the halogen-based materials, these materials are no longer used.^[4,5] After the 20th century, carbon-based materials^[6,7] and nanoclays^[8] have generated considerable interest in fabricating nanocomposites with significantly improved mechanical, thermal, and flame-retardant performance. Researchers have studied the effect of the thermal and mechanical properties

and particle size of the composites on flame-retardant performance. Zhang *et al.* (2014) have shown that the fire retardant properties of Mg(OH)₂ filled rubber nanocomposites was better than microcomposites. Chen *et al.* (2008) investigated the effect of silica loadings on thermal and mechanical properties of the silica/epoxy resin nanocomposites. Mechanical testing demonstrates a 30% enhancement in toughness at lower loadings. However, as the loading increased, the samples continued to increase in modulus but decreased in strength and fracture toughness.

In addition, the epoxy resin nanocomposites reinforced with silica nanoparticles have gained more and more attention due to the high stability of silica at high temperatures and in strong acid/base environments and the strong adhesion between silica and epoxy matrix.^[9,10] As the designing of fire retardants to minimize fire hazards became an urgent issue, polymers have grown increasing interest due to their use in a wide variety of applications, where specific mechanical, thermal, and electrical properties are required.^[11] However, to make a material anti-flammable, it is necessary to either mix the material with a base material

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(additive flame retardants) or chemically bonded to it (reactive flame retardants).^[12] Vinyl ester resins (VERs) are thermosetting resins consisting of a multi-methacrylate oligomer derived from epoxy (typically bisphenol-A based) with styrene as reactive diluents.^[13] The development of vinyl ester resins (VERs) has attracted more interest due to their unique physicochemical properties, which combined the mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins.^[14] VER has superior mechanical properties with high moisture and chemical resistance. In polymer research, it has been used everywhere to fabricate high-quality particulate nanocomposite filled with organic or inorganic nanoparticles.^[15]

On the other hand, titanium dioxide (TiO_2) is one of the most attractive inorganic material with high capability, high safety, and low cost.^[16] Nanocrystalline titanium dioxide (nano- TiO_2) or nanotitania has been presented as an environmentally friendly additive that improved the decomposition temperatures and flame-retardant properties.^[17] Nano- TiO_2 is very attractive in practical applications because of advantages such as its permanent stability under UV exposure and chemical stability at high temperatures. In the current work, the VER nanocomposites reinforced with Si and N_2 surface-modified TiO_2 nanoparticles were successfully prepared. Multi-amino silane was used as a coupling agent to functionalize the surface of nano- TiO_2 . Two types of nanocomposites were prepared; (i) amino-modified TiO_2 -VER nanocomposite, and (ii) unmodified TiO_2 -pure VER nanocomposite. Compared to traditional flame retardant materials,^[18] newly prepared material containing the unique structure to improve both the thermal and mechanical properties. The modified nanoparticle and the as-received nanoparticle-based nanocomposite were named as AMT and UMT, respectively. UMT and pure-VER were used as comparator groups. The chemical structure and thermal stability of nanocomposites were studied using Fourier-transform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA). The mechanical properties, including dynamic mechanical analysis (DMA) and tensile tests of these nanocomposites, were studied. The flame-retardant behaviors of these nanocomposites were investigated using microscale combustion calorimetry (MCC).

2. Materials and Methods

2.1 VER and Nano- TiO_2

The Derakane™ momentum 411–350 epoxy vinyl ester resin (VER) (manufactured by the Ashland Inc.), which is a mixture of 55 wt% epoxy vinyl ester with an average molecular weight of 970 g/mole and 45 wt% styrene monomers was used as a polymeric matrix. Epoxy vinyl ester monomers with two reactive acryl end groups enable the cross-linking for network formation and styrene monomers with only one vinyl group serve as a solvent and provide linear chain extension. The liquid resin has a density of 1.045 g/cm^3 and a viscosity of 350 centipoises (cps) at

room temperature. The curing agent, methyl ethyl ketone peroxide (MEKP), was purchased from Miller-Stephenson Chemical Company. Isopropanol (99.5%) was purchased from Fisher Scientific.

Titanium oxide nanoparticles with an average diameter of 30–40 nm (99% purity, 89 vol% anatase + 11 vol% rutile) were obtained from Nanostructured & Amorphous Materials Inc., USA. Four different silanes were used as coupling agents for nanoparticle surface functionalization. 3-[2-(2-aminoethylamino)ethylamino]propyl-tri methoxysilane, (3-methacryloxy) propyltrimethoxy-silane (98%) and (3Chloropropyl) tri methoxysilane (98+%) were purchased from Fisher Scientific, and (3-Mercaptopropyl) tri methoxysilane was purchased from Sigma Aldrich. All chemicals except nanoparticles were used as received without further treatment.

2.2 Surface Functionalization of Nanoparticles

Isopropanol (80 ml), silane (7 g), and deionized water (0.7 g) were added to a three-necked flask equipped with a condenser and mechanically stirred for 20 min at room temperature. Later, 10 g of nanoparticles diluted in 120 ml of isopropanol was added to the flask under stirring. The mixed suspension was then heated to 80 °C and refluxed under mechanical stirring for 3 h. After the reaction, the mixture was cooled to room temperature, and the modified particles were collected by vacuum filtration, washed with isopropanol to remove any unreacted reactants, dried under vacuum at 50 °C overnight, and then grinded for further application.

2.3 Preparation of VER Nanocomposites

The modified and unmodified TiO_2 nanoparticles of 1, 3, 5, 7, and 10 wt % were added to VER and stored in the ice-water bath under ultrasonication for forced wetting at room temperature overnight without any disturbance. The curing agent MEKP was added to the VER or above prepared TiO_2 nanoparticle-VER nanosuspension with a resin to curing agent weight ratio of 100:1. The mixture was stirred at room temperature for 5 min, and then poured into silicone rubber molds and cured isothermally at 40 °C for 4 h. After that, the temperature was raised to 85 °C for 30 min to accomplish the post-curing process. Finally, the samples were cooled down naturally to room temperature before being trimmed and grinded for further characterization.

2.4 Dynamic Rheological Behaviors of VER Nanocomposites

Dynamic rheological measurements were performed both isothermally and non-isothermally by using an environmental test chamber aluminum parallel-plate geometry (25 mm in diameter). For the isothermal test, shear storage and loss moduli were obtained by operating the measurement isothermally at 20, 40, 60, and 80 °C with a comprehensive time range between 0 and 700 s at a low strain (1%) in a rheometer (AR 2000ex, TA Instrumental Company). For the

non-isothermal test, the shear storage and loss moduli were measured at different temperature ramp rates (0.5, 1, 2, 5 °C/s).

2.5 Mechanical Characterization of VER Nanocomposites

Dynamic mechanical analyses (DMA) measurements were carried out in the rectangular torsion mode using a AR 2000ex (TA Instrumental Company) with a strain of 0.05%, a constant frequency of 1 Hz and a heating rate of 2 °C/min in the temperature range of 30–200 °C. The sample dimensions were 12×3×40 mm³. Tensile tests were carried out following ASTM (Standard D 412-98a, 2002) in a unidirectional tensile testing machine (ADMET tensile strength testing system). The parameters (displacement and load) were controlled by a digital controller (MTEST Quattro) with MTEST Quattro Materials Testing Software. The samples were prepared as described for the nanocomposite fabrication in silicone rubber molds, which were designed according to the standard ASTM requirement. A crosshead speed of 1.0 mm/min was used, and the strain (mm/mm) was calculated by dividing the crosshead displacement by the original gauge length.

2.6 Flame Retardancy Characterization of VER Nanocomposites

Microscale combustion calorimetry (MCC) was conducted on 3 ± 1 mg samples using a Govmark Microscale Combustion Calorimeter (Model: MCC-2) operated at a heating rate of 1°C/s until 750 °C in the pyrolysis zone. The samples were tested according to ASTM guidelines (ASTM D7309–07). The combustion zone was set at 900 °C. The oxygen and nitrogen flow rates were set at 30 and 70 mL/min, respectively. The heat release rate (HRR) in W/g of the sample was calculated from the oxygen depletion measurements. The heat release capacity (HRC) in J/gK was obtained by dividing the sum of peak HRR by the heating rate in K/s. The total heat release (THR) in kJ/g was obtained by integrating the HRR curve. The char yield was obtained by weighing the sample before and after the test.

2.7 FTIR and TGA of polymer nanocomposites

The chemical structures of the modified and unmodified TiO₂-VER nanocomposites were analyzed by Fourier transform infrared spectroscopy (FT-IR, a Bruker Inc. Vector 22 coupled with an ATR accessory) in the range of 500–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The thermal stability was studied in thermogravimetric analysis (TGA, TA Instruments, Q-500) with a heating rate of 10 °C min⁻¹ under an air and nitrogen flow rate of 60 mL min⁻¹ from 25 to 800 °C, respectively.

3. Results and Discussion

3.1 Surface Modification and Characterization

In current work, FTIR was conducted to study the interaction between the organic group and TiO₂ nanoparticles. From the FTIR spectrum in Fig. 1, we see that the amine group

addition to TiO₂ nanoparticles showed a peak. From the curve of pure amino silane and unmodified TiO₂ nanoparticles it has been observed that –CH=CH–(ethylene group) and –NH–(amine) group peaks are present in modified TiO₂ nanoparticles.

Fig. 1 FTIR spectrum of amino silane, modified (AMT) and unmodified (UMT) TiO₂ nanoparticles

TGA analysis was performed to confirm the presence of an amino group in the modified TiO₂ nanoparticles. Fig. 2 shows that the weight loss in the amino-modified TiO₂ nanoparticles was 2.75 %. In contrast, the weight loss in the unmodified TiO₂ nanoparticles was 1.25 %, which is almost half compared to the modified filler. The weight loss in the modified nanoparticles takes place in two stages. The first stage is from 100 to 300 °C, and the second stage is from 300 to 500 °C. In the first stage, the heat loss was due to the water loss from the amino-modified TiO₂ nanoparticles, and the second stage was due to the organic group decomposition.^[19] The reason for the more significant amount of weight loss in amino-modified TiO₂ Nanoparticles was due to the loss of water and decomposition of the organic group upon heating.

Fig. 2 TGA graph of amino-modified (AMT) and unmodified (UMT) fillers.

3.2 Dynamic Mechanical Properties of Titania/VER Nanocomposites

Dynamic mechanical analyses (DMA) gives the information on the storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$) of nanocomposites in the test temperature range. The storage modulus and loss modulus reflect the elastic property and viscosity behavior of nanocomposites, respectively. Fig. 3(a-c) and 4(a-c) show the dynamic mechanical behaviors of VER reinforced with different loadings of unmodified and modified TiO_2 , respectively. At 7% loading in glass plateau (below 75 °C), the G' values of unmodified and modified TiO_2 -VER composites were almost the same but a little bit lower while the loading was 10%. In the glass transition range (6-120 °C), G' curve of nanocomposites at less than 5 % loading shows a shoulder peak, which is attributed to the additional curing of VER because of the increased molecular mobility at high temperatures.^[20] As the loading increases, the shoulder peak decays gradually and vanishes when the loading is 10%. The TiO_2 nanoparticles restrict the molecular mobility of VERs, thus decreasing the additional curing of nanocomposites.^[10]

Fig. 3(b) and 4(b) show G'' curves of VER nanocomposites reinforced by unmodified and modified TiO_2 nanoparticles, respectively. It has been observed that all the G'' curves of pure VER and unmodified TiO_2 -VER nanocomposites show two peaks (or shoulder peaks). The first peak is between the temperature range of 83 °C to 91 °C, which represents the start of the glass transition temperature of samples. The second peaks (or shoulder peak) above 100 °C were due to the friction between enlarged polymer chains caused by the additional curing of VERs.^[21,22] This peak was shifted to the higher temperature as the loading of the TiO_2 nanoparticles increased i.e., 105 °C for pure VER to 120 °C for VER at the samples with 10% loading of TiO_2 nanoparticles. It has been noticed that the G'' curves of modified TiO_2 -VER nanocomposites is similar to unmodified ones except that the two peaks merge into one at higher loadings, and move to a lower temperature. This phenomenon implies that modified TiO_2 nanoparticles have increased stiffness and constriction between the epoxy polymer chains that restrict the mobility at higher loadings.

$\tan \delta$ is the ratio of loss modulus to the storage modulus, and the peak of $\tan \delta$ is often used to determine the glass transition temperature, T_g . $\tan \delta$ curves of unmodified and modified TiO_2 -VER nanocomposites are shown in Fig. 3(c) and 4(c), respectively. Pure VER has two $\tan \delta$ peaks (95 °C and 115 °C), which are due to the additional curing of VERs.^[21] As mentioned earlier, with an increase in temperature, the samples first enter the glass transition range, and with further increase in temperature, the additional curation becomes complete, and the samples enter into the second glass transition again.^[20] When the unmodified TiO_2 nanoparticles are added to VERs, the further curing has been restricted. Therefore, the two peaks of $\tan \delta$ curves merged into one gradually and moved to the

lower temperature at higher loadings. $\tan \delta$ curves of modified TiO_2 -VER nanocomposites show a similar tendency, except that the peak temperature at higher loadings moved to a much lower temperature (75 °C), which also confirms that modified nanofillers have strong influence on the cured structured of VERs.

Fig. 3(a) Storage modulus (G') vs. temperature curves of unmodified TiO_2 -VER nanocomposites.

Fig. 3(b) Loss modulus (G'') vs. temperature curves of unmodified TiO_2 -VER nanocomposites.

Fig. 3(c) $\tan \delta$ vs. Temperature curves of unmodified TiO_2 -VER nanocomposites.

Fig. 4(a) Storage modulus (G') vs. Temperature curves of modified TiO_2 -VER nanocomposites.

Fig. 4(b) Loss modulus (G'') vs. Temperature curves of modified TiO_2 -VER nanocomposites.

Fig. 4(c) $\tan \delta$ vs Temperature curves of modified TiO_2 -VER nanocomposites.

3.3 Tensile Properties of VER nanocomposite

Fig. 5 shows the tensile stress comparison of modified and unmodified TiO_2 -VER nanocomposites. The percent loading

of the unmodified TiO_2 -VER nanocomposites showed no effect on the tensile strength. On the other hand, the tensile strength of the modified TiO_2 -VER nanocomposites slightly decreased at higher loadings. Also, modified TiO_2 -VER nanocomposites didn't make any significant impact on the tensile strength in comparison with pure VER; instead, its tensile strength is 60 MPa at 5% loading that is almost same as that of pure VER.

Fig. 5 Tensile strength of modified (AMT) and unmodified (UMT) TiO_2 -VER nanocomposite.

3.4 Evaluation of the Flame Retardant Property of Nanocomposite

MCC test was performed on the modified and unmodified TiO_2 nanocomposites to evaluate the flame retardancy of the nanocomposites. The main parameters for assessing flame retardancy are the HRR peak, THR, HRC, and char yield.^[23,24]

Fig. 6 shows the heat release rate (W/g) comparison of modified and unmodified TiO_2 -VER nanocomposites. The results have demonstrated that the HRR increased with increasing temperature from 375 °C until the maximum heat release peak was achieved and then started to decrease.

Fig. 6 HRR peak comparison of UMT, AMT, and Pure VER.

The HRR peak (675 W/g) of P-VER was much higher than that of the modified and unmodified TiO₂-VER nanocomposites. The HRR peak of modified and unmodified TiO₂-VER nanocomposites was 450 and 560 W/g, respectively. The results of the current study agree with Kashiwagi *et al.* (2005) findings that increased viscosity of polymer matrix by the introduction of nanoparticles could reduce the flammability of matrix.^[25] Also, the HRR peak of modified TiO₂-VER nanocomposite is much less than the unmodified TiO₂-VER nanocomposite. These results proved that by modifying the nanoparticles by adding Si and N₂ improved the flame retardant capacity of the TiO₂-VER nanocomposites. Heat release capacity is known as a combination of the thermal stability and combustion properties, which can be used to classify the flammability of materials. Fig. 7(a) shows the heat released capacity (HRC) of nanocomposites by nanofiller loading percent. The HRC decreased with the increase in nanofiller loading percent in both modified and unmodified TiO₂-VER nanocomposites. At the highest loading percent of 10, the HRC of modified TiO₂-VER nanocomposite decreased by 29.9%. In contrast, at the same loading percent of 10, the HRC of unmodified TiO₂-VER nanocomposites decreased by 18.8%.

Fig. 7 Heat release capacity of modified (AMT) and unmodified (UMT) TiO₂-VER nanocomposite by loading percent.

HRC of nanocomposite is normalized, Fig. 7(b) shows the normalized heat released capacity (HRC) of nanocomposites by nanofiller loading percent. Although there was a slight change in the percent decrease of HRC, the trend remains the same after normalization. Therefore, from the result, it is found that the normalized HRC of amino \-modified nanofiller based PNC decreased by 27.3%. These findings are further corroborated by the results obtained from the total heat release rate comparisons with loading (Fig. 8) and heat release rate peak comparisons with loading (Fig. 9).

Fig. 8 The total heat release rate of modified (AMT) and unmodified (UMT) TiO₂-VER nanocomposite by loading percent.

Fig. 9 Heat release rate peak of modified (AMT) and unmodified (UMT) TiO₂-VER nanocomposite by loading percent.

Char residue is one of the major parameters like all other parameters of flame retardancy. Fig. 10 shows the percent of char residue with different percent loading of modified and unmodified TiO₂-VER nanocomposites.

Fig. 10 Comparison of the residue of modified (AMT) and unmodified (UMT) TiO₂-VER nanocomposite by loading percent

From the table 1 it is seen that the char residue of modified and unmodified PNC increased with increasing nanofiller loading percent. As the char residue increases, the flame retardancy increases. These results also indicated that the functionalization of TiO₂ nanoparticles by Si and N₂ didn't offer many benefits to the char formation during the combustion process.

Table 1. Char residue comparison of modified (AMT) and unmodified (UMT) TiO₂-VER nanocomposite by loading percent

Loading (%)	Char residue (unmodified) %	Char residue (amino-modified) %
0	4.5	4.5
2	6	4.9
4	8	7
6	8.5	7.5
8	11	9

IR test was used to check the UV reflectance of nanocomposites. Fig. 11 presents the UV reflectance of the pure VER, modified, and unmodified TiO₂-VER nanocomposites. The results have shown the reflectance of unmodified TiO₂-VER nanocomposites was about 95 % compared to the reflectance of pure VER of about 8 %. The results also indicated that the modified TiO₂-VER nanocomposite does not show a significant impact in the reflectance of UV light in comparison with unmodified nanocomposites. TiO₂ nanoparticle-based nanocomposite can be used as a coating which can protect the material from UV radiation.

Fig. 11 UV reflectance comparison of modified (AMT) and unmodified (UMT) TiO₂-VER nanocomposite.

4. Conclusion

In the current study, we synthesized and characterized flame retardant VER nanocomposites, where the VER was reinforced with silicon-containing/nitrogen-containing surface-functionalized nanotitania. We used a multi-amino

silane as a coupling agent to successfully functionalize the surface of nano-TiO₂. We investigated the surface functionalization by FTIR and found Si and N₂ peaks that confirmed the successful addition of new groups on the TiO₂ nanoparticles. DMA tests and tensile tests were carried out on modified and unmodified TiO₂-VER nanocomposites. DMA results indicated that the modified titania has a strong influence on the cured structure of VERs at high loadings. The tensile strength test results have shown that modified TiO₂-VER nanocomposites didn't make any significant impact on the tensile strength in comparison with pure VER; instead, its tensile strength is 60 MPa at 5% loading that is almost same as pure VER. Flame retardancy results from the MCC test have demonstrated that the rate of the decrease of flame retardant parameters such as HRR, HRC was higher in modified TiO₂-VER nanocomposites compared to unmodified TiO₂ based nanocomposites. The char residue was increased with the increased amount of nanofiller for both AMT and UMT TiO₂ based nanocomposite. The flame retardant results show significant improvement in the case of modified TiO₂-VER nanocomposites

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Supporting information

Not applicable

Conflicts of Interest

The authors declare no conflict of interest.

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