PVC nanocomposites for cable insulation with enhanced dielectric properties, partial discharge resistance and mechanical performance

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Abstract: The current study aims to develop polyvinyl chloride (PVC) nanocomposites with enhanced electrical and mechanical properties by incorporating titanium oxide (TiO₂) nanoparticles within PVC chains. Different loading of nanoparticles and different nanoparticle surface states were considered. The surface states are unfunctionalised, functionalised using vinyl silane and functionalised using amino silane. The choice of a most suitable surface state was a critical factor that guarantees a good dispersion of nanoparticles and consequently enhances the compatibility between TiO₂ and PVC matrix. The process followed in the PVC/TiO₂ nanocomposites preparation, loaded with different wt.% of TiO₂ nanoparticles, was the solvent method. The dielectric properties measured here were the relative permittivity (ɛᵣ), dielectric loss (tanδ), breakdown strength (AC and DC under uniform field) and the internal partial discharges (PDs) within insulation cavity. All measurements have been performed under room temperature and at frequency ranged from 20 to 1.0 MHz. Furthermore, the mechanical properties of the samples like elongation, elasticity modulus and tensile strength were also studied. Vinyl silane showed better improvements in both electrical and mechanical performances compared to the amino silane, especially in cases of high weight fractions of TiO₂. This is because of the improvement in the PVC-TiO₂ interfacial region arise from the similarity of polarity and surface tension values of vinyl silane with that of PVC matrix and TiO₂ nanoparticles.

1 Introduction

Recently, the increased demand in polymer industry and applications stimulated the researchers for improving physical, electrical insulation and mechanical properties of these polymers. Many years ago, polymers such as polyethylene, polypropylene, and polyvinyl chloride (PVC) are widely used in electrical grids as the electrical insulating materials for power cables [1]. PVC, rigid or flexible, is one of the most extensively manufactured polymers all over the world. For the power cable industry, flexible PVC is widely used as an electrical insulating material for low and medium voltage cables [2]. It has excellent properties such as its ability in flame retardancy and its great mechanical performance. However, its brittleness, poor processability and poor thermal stability limits its applications. These poor properties may be enhanced by the addition of some heat stabilisers [3]. During normal operation of PVC-based cables, it is subjected to different types of stresses that cause, in turns, some degrees of insulation deterioration and degradation. These problems can be avoided, and the PVC overall properties can be improved by introducing the nanosised materials to form nanocomposites or nanodielectrics [4, 5]. Upon the development in nanotechnology, these nanodielectrics, solid or liquid, have attracted great attention [6–9]. The basic concern behind the obtained enhancements in the properties of those materials was credited to the interfacial zone between the polymer matrix and the imbedded nanoparticles [10].

Considering the nature of polymers, mixing the nanoparticles with polymeric materials faces some challenges. The first challenge is the incompatibility between nanoparticles, that are inorganic materials and polymers, that are organic materials. The second challenge is the trend of nanoparticles to aggregate and form clusters causing a loss of their favourable effects. To overcome these challenges, several studies proposed surface functionalisation of nanoparticles by using proper coupling agents [11, 12]. The functionalisation process plays two important roles. The first role is decreasing the hydrophilicity of the inorganic nanoparticles to be compatible with the hydrophobicity of the organic nature of polymers within which they will be mixed [13, 14]. The second role is steric stabilisation of nanoparticles preventing their aggregation.

In literature, many reported articles showed the role of inserting different nanoparticles within different polymeric matrices in order to enhance their engineering properties such as electrical and mechanical properties. Some of these reported articles focused on studying the role of chemical modification of these nanoparticles in the enhancement of the insulation ability of the electrical insulating cables, and the mechanism behind this enhancement. Through using functionalised silica (SiO₂) nanoparticles, Abdel-Gawad et al. [15] succeeded to decrease ɛᵣ and tanδ of PVC nanocomposites by 25 and 39%, respectively, compared to pure PVC. In addition, the AC and DC breakdown strength enhanced with 16.8 and 16.3%, respectively compared with the pure one. Also, the mechanical properties were enhanced by increasing the elasticity and the durability and decreasing the degree of elongation.

Recently, Mansour et al. [16] have reported the effect of iron oxide (Fe₂O₃) nanocrystals on DC breakdown strength of PVC under room temperature and at different temperatures up to 120°C and they showed a remarkable improvement in DC breakdown strength up to 20.5%. Moreover, the same research group [17]...
enhanced the DC breakdown strength of PVC by adding synthesised zinc oxide (ZnO) nanoparticles by 45% compared to the pure PVC. Regarding partial discharge (PD) enhancement, and compared again to the pure PVC, the PD properties of PVC nanocomposites including PD inception, PD pulse number and PD charge magnitude have been clearly improved [18].

Despite several studies investigated surface functionalisation of nanoparticles, none of these studies considered the effect of coupling agent on the performance of PVC nanocomposites. It is believed that the type of coupling agent is crucial in terms of its surface tension and chain length.

From this viewpoint, in this study, TiO$_2$/PVC nano-composites have been fabricated with chemically functionalised TiO$_2$. Such functionalisation has been performed using two different coupling agents (vinyl-, and amino types), in order to study the effect of coupling agent on improving the dispersion of the selected nanoparticles and consequently on enhancing the electrical and mechanical properties of the resulted nanocomposites. The two coupling agents are distinct in their surface tension and chain length. The chemical modified nanoparticles have been characterised by Fourier transformation infrared spectroscopy (FT-IR). To monitor these properties enhancement, dielectric properties and breakdown strength have been measured. In addition, PD activity of PVC nanocomposites has been investigated using an embedded needle electrode with an intentional air-filled cavity. Furthermore, some of the mechanical parameters such as Young’s modulus, tensile strength, and elongation, have been investigated.

2 Experimental setup

2.1 Raw materials

Commercial PVC pellets were used in this study. They were supplied from EGYPLAST, El-Sewedy Electric Co. Egypt. PVC pellets had the following composition approximately: 44.8% PVC resin, 31.4% coated calcium carbonate, 17.9% diisononyl phthalate as a plasticiser, 4.5% chlorinated paraffin oil, 1.3% lead-free stabiliser and 0.1% stearic acid. TiO$_2$ nanoparticles, received from Sigma Aldrich, were 21 nm in size and with a purity of 99.5%. Other chemicals needed for the nanoparticles functionalisation were obtained with 99% purity, and they include: tris (2-methoxy ethoxy) silane (abbreviated as ‘vinyl silane’) and gamma- amino propyl triethoxy silane (abbreviated as ‘amino silane’), which were purchased from Momentive Inc. and used as coupling agents. Other chemicals were obtained from Fisher Inc. such as methanesulfonic acid, isopropyl alcohol, toluene and cyclohexanone. All chemicals were used without any treatments.

2.2 Nanoparticles modification

In this section, the steps of functionalisation of the nanoparticles and their utilisation in preparing PVC/TiO$_2$ nanocomposites will be described in more details. Chemical functionalisation of nanoparticles targets decreasing the surface energy of nanoparticles, thereby, improving the compatibility of those nanoparticles with filling matrix and enhancing their dispersion within the polymer chains. According to Fig. 1, and as reported previously in [12, 19], the functionalisation process includes two stages: surface activation of TiO$_2$ using 10% methane sulfonic acid, and then the reaction of the activated nanoparticles with vinyl silane or amino silane coupling agent. The solvent used in both steps was toluene, and the final product was isolated and cleaned several times with isopropyl alcohol. The obtained powder was dried overnight under vacuum in an oven at 120°C, and it was kept dry for characterisation and utilisation in nanocomposites synthesis.

2.3 Nanocomposites preparation

Synthesis of polymeric films was performed using the solution-casting technique in which a suitable amount of PVC pellets were dissolved in a suitable volume of cyclohexanone at 130°C and a uniform and thin PVC film was obtained by casting the above viscous mixture on a Pyrex dish and keeping at ambient temperature for two days in order to allow gradual evaporation of the solvent without any formation of air bubbles inside the film. In this study, three groups of PVC/TiO$_2$ nanocomposites were prepared. Each group contain three different loadings: 0.5, 1 and 3%. The first group was the one prepared with unfunctionalised TiO$_2$ nanoparticles. While, the second and third groups were prepared using functionalised TiO$_2$ nanoparticles with vinyl and amino silane, respectively. Prior to mixing the nanoparticles with the dissolved PVC, they were sonicated and dispersed in a suitable quantity of cyclohexanone for 30 min. Then, they were added to a proper amount of molten PVC/cyclohexanone mixture and mixed together with the aid of mechanical stirrer followed by a planetary centrifugal mixer in order to effectively disperse nanoparticles all over the processed volume. A pure PVC sheet was also cast to be used as a blank. All prepared samples were dried under vacuum in an oven at 60°C for 24 h. Hence, the obtained samples became ready for the characterisation and testing.

2.4 Characterisation and measurements

In a wavenumber ranging from 400 to 4000 cm$^{-1}$, the FT-IR was applied on functionalised TiO$_2$ nanoparticles, either with vinyl or amino silane. The experiments were performed using Nicolet 380 FT-IR spectrometer. Also, for reference, the same spectrum was obtained for unfunctionalised one in order to identify the new surface bonds that created due to the functionalisation process.

For more confirmation of the structure and the composition of the functionalised samples, a QUANTA FEG-250 spectroscopy coupled with back-scatter electron diffraction energy-dispersive X-ray spectroscopy, and EDS take-off angle of 34° was employed in order to analyse the main constitution and low-level contaminants in the functionalised and unfunctionalised nanoparticles.

The morphology of the prepared nanocomposite samples was investigated by using scanning electron microscopy (SEM), QUANTA FEG-250, FEI-Inc. that operated at 10–30 kV, and with carbon fibres used to coat the fractured surfaces.

The nanocomposite samples were then tested for dielectric properties, breakdown strength and PD activity. For measuring dielectric properties, a precise LCR meter was used. The sample under consideration is sandwiched between two cylindrical electrodes having a radius of 10 mm. The thickness of the measured samples ranged from 0.17 to 0.25 mm as measured by using the electronic micrometer. All measurements have been done at the ambient temperature for a frequency range between 20.0 Hz and 1.0 MHz. Regarding breakdown strength; it was performed under AC and DC voltage application using sphere-to-sphere electrode system in accordance with ASTM D149-09 standard [20]. The electrodes were immersed in the transformer oil to prevent possible surface flashover with the sample. The voltage ramping rate was adjusted to around 500 V/s.

Regarding PD test, it was done in accordance with IEC standard 60270 [21], and the detailed set-up of the designed circuit was mentioned previously by our group in [18]. To create micro-cavities inside the PVC insulating sample, needle-plane geometry
polymeric specimens were cut with a dimension of 40 × 4 mm, as shown in Fig. 3. The tensile test was monitored. In this test, dumbbell-shaped specimens were used, the mechanical behaviour in the form of mechanical deformation of the prepared samples were: stress, strain, modulus of elasticity, tensile strength and elongation.

3 Results and discussion

3.1 FT-IR spectra of TiO$_2$ nanoparticles

As described in the experimental part, the surface functionalisation of TiO$_2$ nanoparticles have been performed chemically using two different coupling agents; vinyl and amino silane. To validate this chemical reaction, FT-IR transmission spectra for unfunctionalised TiO$_2$, vinyl and amino-functionalised TiO$_2$ nanoparticles were obtained and depicted in Fig. 4. It is seen that the FT-IR for vinyl-functionalised TiO$_2$ nanoparticles as well as unfunctionalised one is observed as presented in Fig. 4 with red and blue colour, respectively.

3.2 EDAX of the nanoparticles

Fig. 5 shows EDAX spectra of the functionalised TiO$_2$ nanoparticles functionalised by both vinyl and amino silane. The pure TiO$_2$ nanoparticles were also detected by the same technique for comparison, as shown in Fig. 5a. The spectra showed the elements have been detected in each sample and their relative distribution. The elemental ratio output of EDAX system for the tested samples is shown in Table 1. The data shown in Fig. 5 and Table 1 confirm the attachment of vinyl and amino silanes to TiO$_2$ since the Si atom appeared in both samples, however N that is present in the amino structure appeared only in the EDAX spectra of amino-TiO$_2$ sample.

3.3 SEM of the TiO$_2$-PVC nanocomposites

Fig. 6a shows the SEM micrograph of pure PVC, which ensures the absence of air bubbles and impurities inside the film and this will be important in measuring the dielectric properties of these samples, especially, with relatively thick sheets. This observation was expected during the preparation stage since prior to the curing process, the polymeric samples were subjected to ultra-sonication with the ‘degas mode’ to remove any air bubbles before curing. However, Figs. 6b and c present SEM micrographs of two PVC nanocomposite samples from which the distribution of nanoparticles within the polymeric chains can be noticed.

Comparing these two micrographs, it is shown that the nanoparticles distribution is better in case of vinyl-functionalised nanoparticles than for amino-functionalised ones. Besides, the ununiform spherical aggregates spread densely on the surface of PVC/3% amino-TiO$_2$ sample that is shown in Fig. 6b might be due to the incompatibility between the amino-functionalised nanoparticles with the PVC as will be discussed later.

3.4 Dielectric data

3.4.1 Permittivity and dielectric loss: In this paper, it is of great importance to show the effect of incorporating TiO$_2$ nanoparticles that functionalised with different coupling agents within a common electrical insulating material such as PVC (with its details composition as described in the materials section) on the electrical properties of that material. This is because enhancing the insulating
materials will prolong their ageing and decrease the chance of energy losses.

Complex dielectric permittivity \( \varepsilon_r \) of any insulating material consists of two components; the real \( \varepsilon' \) and the imaginary \( \varepsilon'' \) parts. They are related to each other as follows:

\[
\varepsilon_r = \varepsilon' - j\varepsilon''
\]

For each cycle of the applied field, these two parts represent, respectively, the energy storage and the energy losses of dielectric materials. Moreover, the ratio of these two parts is given by the dissipation factor or dielectric loss (tan\( \delta \)), and it can be represented by the formula:

\[
tan\delta = \frac{\varepsilon''}{\varepsilon'}
\]

Moreover, the average thickness of the tested samples was about 0.21 mm, and there is no chance for this relatively high thickness to affect the measurement of the dielectric parameters since there is no air bubble defect in the prepared films as shown in their SEM micrographs, Fig. 6.

Here the variation of relative permittivity, \( \varepsilon_r \), with frequencies of all prepared polymeric samples was shown in Figs. 7a and b. As expected, and with increasing the frequency, the relative permittivity decreases due to the shortening of the time needed for the dipoles to orient themselves in the direction of the applied electric field. As a result, there is no chance for the tested material to build up additional polarisability. Furthermore, the same figures show the dependence of permittivity on the presence of nanoparticles, their functionalisation, and the type of coupling agent used in the functionalisation. It is found that all prepared nano-composites have lower permittivity than that of the pure PVC except nanocomposites prepared with 1 and 3% amino-functionalised nanoparticles.

The obtained results prove the role of nanoparticles, either functionalised or unfunctionalised, in restricting the mobility of polymer chains existing in the vicinity of nanoparticles. Also, it can be highlighted that the functionalisation of those nanomaterials with a suitable coupling agent such as vinyl silane reduces the permittivity to values less than that of amino-functionalised

| Sample         | Element | WT.% | Atomic % |
|----------------|---------|------|----------|
| pure TiO\(_2\) | Ti      | 59.99| 33.39    |
|                | O       | 40.01| 66.61    |
| vinyl-TiO\(_2\) | C       | 8.49 | 15.12    |
|                | O       | 48.95| 65.48    |
|                | Si      | 1.21 | 0.92     |
|                | Ti      | 41.35| 18.47    |
| amino-TiO\(_2\) | C       | 17.74| 28.7     |
|                | N       | 3.02 | 4.19     |
|                | O       | 42.64| 51.81    |
|                | Si      | 1.54 | 1.07     |
|                | Ti      | 35.06| 14.23    |
nanoparticles. This can be explained by the low surface energy between the vinyl-functionalised nanoparticles and the PVC chains due to the closer surface tension value of vinyl silane ($\gamma_{\text{vinyl}} = 41.1 \text{ dyn/cm}$) to PVC ($\gamma_{\text{pvc}} = 41.9 \text{ dyn/cm}$) compared to that of amino silane ($\gamma_{\text{amino}} = 38.7 \text{ dyn/cm}$) [24]. Hence, the compatibility and dispersion of nanoparticles within the PVC matrix will be better when using vinyl silane.

At 50 Hz (power frequency), the maximum change in permittivity was 13.9% lower than pure PVC when using unfunctionalised nanoparticles. On the other hand, the maximum decrease was 43 and 22% when using vinyl-functionalised and amino-functionalised nanoparticles, respectively. For unfunctionalised and vinyl-functionalised nanoparticles, the maximum decrease has been observed at the weight fraction of 3 wt.%, while for amino-functionalised nanoparticles, it has been observed at a weight fraction of 0.5 wt.%. However, for higher weight fraction of amino-functionalised TiO$_2$ nanoparticles, the permittivity increases rapidly compared to that of the pure PVC. This increase in permittivity may be due to two reasons: one of them is the presence of unfunctionalised sites on the TiO$_2$ nanoparticle surfaces or unreacted NH sites of the amino coupling agent, i.e. presence of unreacted hydrophilic moieties that might result in an additional kind of polarisation, which act toward increasing the permittivity values [25]. The second reason is the chance of nanoparticles agglomeration (Fig. 6b) resulted from the chance of H-bond formation between each unreacted N–H bond.

Regarding tanδ, it is presented in Fig. 8 for different PVC/TiO$_2$ nanocomposites. The values of tanδ mostly decrease in nanocomposites prepared with amino-functionalised nanoparticles. Moreover, it is inferred from Figs. 8a and b that a maximum reduction of about 41% has been obtained for PVC nanocomposites containing 3 wt.% vinyl-functionalised nanoparticles. Followed by 27% reduction for PVC nanocomposites containing 0.5 wt.% amino-functionalised nanoparticles.

### 3.4.2 AC & DC breakdown strengths:

In this study, the measurement of AC and DC breakdown strengths (AC-BDS, DC-BDS) was performed under a uniform field of sphere-to-sphere electrode considering that the sample thickness is much smaller than the sphere diameter. The measurements were repeated five times for each sample and the average breakdown strengths are shown in Table 2. The AC-BDS values of PVC nanocomposites containing vinyl-functionalised nanoparticles are higher than any other samples, and they increase as the loading of TiO$_2$ increases. The reason behind that is also referred to the low surface energy at polymer/nanoparticles interfacial region making good dispersion of nanoparticles inside the polymeric matrix. For the nanocomposites containing TiO$_2$ amino-functionalised nanoparticles, the values of AC-BDS is just high for the sample with low wt.% of nanoparticles, however, during high loading of nanoparticles, the AC-BDS decreases because of the formation of many aggregates due to the incompatibility between PVC matrix and amino-functionalised TiO$_2$ nanoparticles. The other reason that causes such aggregates formation, and hence lowering in BDS, is the formation of H-bonding between the free amino groups that are being unreacted above the nanoparticle surface. The enhancement...
takes place in samples of PVC containing 3 wt.% unfunctionalised, vinyl-functionalised TiO$_2$ and PVC containing 0.5 wt.% amino-functionalised TiO$_2$ nano-composites with percentages tend to be 2.6, 7.7 and 14%, respectively, compared to pure PVC.

Similar to AC-BDS, it is clear that the highest value of DC-BDS (72.47 kV) was found in the nanocomposite containing 0.5% amino-functionalised nanoparticles. This high value corresponds to an enhancement of 11.6% compared to that of the pure PVC, and it is followed by the sample containing 3% vinyl-functionalised and unfunctionalised nanoparticles that exhibited an enhancement of 9.8 and 4.3%, respectively, compared to the pure one, Table 2.

Generally, the high values of DC-BDS means enhancement in DC-BDS, and from the data obtained, it is recommended to use these kinds of composites as insulating materials for high-voltage direct current cable.

3.4.3 PD activities: PD activity was evaluated under AC voltage application. First, PD inception voltage was measured for various samples. Then, PD characteristics were obtained using phase-resolved PD analysis [26, 27]. Through this analysis, PD generation rate and average PD charge magnitude can be obtained all over the complete cycle of the applied AC voltage.

Considering the dielectric properties and breakdown strengths obtained in previous sections, it was found that the maximum enhancement is observed at a weight fraction of 3 wt.% for vinyl-functionalised nanoparticles and at a weight fraction of 0.5 wt.% for amino-functionalised nanoparticles. So, these samples and corresponding weight fractions of unfunctionalised nanoparticles were used for PD evaluation in comparison to pure PVC.

For statistical analysis of PD pulses, the PD parameters were grouped for every 10 degrees of the phase angle of the applied AC voltage [28]. The PD generation rate expressed in pulse per second (pps) is illustrated in Figs. 9 and 10, while the PD magnitude in (pC) is shown in Figs. 11 and 12.

Besides, Table 3 tabulates PD statistical parameters for various samples.

It is obvious that the PVC nanocomposite sample containing 3% vinyl-functionalised TiO$_2$ exhibited better resistance against PD than the other samples. The PD inception of this sample was the highest indicating a percentage enhancement of 22.2% over pure PVC. Also, this sample and the 0.5% amino-functionalised nanocomposite sample had the smallest numbers of PD pulses either during the positive polarity or negative one.
This enhancement is attributed to the role of nanoparticles in acting as trapping sites for electrons and hindering their movement. The better the dispersion of nanoparticles is, the more the trapping sites are generated. For all samples, the PD pulse number during positive polarity is different from that during negative polarity due to the difference in the initial electron generation mechanism [29].

The average magnitude of PD pulses, as obtained in Figs. 11 and 12, are not aligned with the obtained trend for PD generation rate, where there are other factors affecting PD magnitude [30, 31]. These factors include the electric field strength at the needle tip, the number of charge carriers, the maximum possible travelling distance by electrons, and so on.

3.5 Mechanical performance

To evaluate the mechanical behaviour of the prepared samples, a tensile test has been performed at room temperature (25°C) for different polymeric samples. Data integrated from this test will show the effect of chemical modification of nanoparticles surface, using two different coupling agents, on the mechanical properties of PVC. Moreover, information about the PVC-TiO₂ interfacial adhesion will also be driven from studying the stress–strain profile of the examined samples, as in Fig. 13. The delivered parameters from that figure were recorded in Table 4.

In Fig. 13, all curves begin with a straight line, the elastic region of the samples, and the stress–strain slope of this region refers to Young's modulus. PVC used in this study is not a pure material, it contains plasticisers and other additives, thus, the values of stress and Young's modulus of the examined samples are relatively small [32, 33]. The presence of plasticiser results in additional flexibility to PVC chains which in turn would affect the mechanical properties of the plasticised polymer. Here, TiO₂

![Fig. 11 Average magnitude of discharge pulses in every 10 degree for all samples of PVC and PVC/TiO₂ nanocomposites](image)

(a) Pure PVC, (b) PVC/0.5% unfunctionalised TiO₂, (c) PVC/3% unfunctionalised TiO₂

![Fig. 12 PD magnitude in every 10 degree for PVC/TiO₂ functionalised nanocomposites](image)

(a) PVC/3% vinyl-functionalised TiO₂, (b) PVC/0.5% amino-functionalised TiO₂

| Name of sample | $U_i$, kV | $Q_{IEC}$, pC | $U_e$, kV | Max. pulses in positive cycle, pps | Max. pulses in negative cycle, pps |
|----------------|-----------|---------------|-----------|-----------------------------------|-----------------------------------|
| pure PVC       | 1.35      | 647           | 1         | 149                               | 186                               |
| PVC/0.5% unfunctionalised TiO₂ | 1.35 | 513 | 1.05 | 121 | 168 |
| PVC/3% unfunctionalised TiO₂ | 1.6 | 632 | 1.1 | 108 | 152 |
| PVC/0.5% TiO₂ with vinyl silane | 1.2 | 248 | 0.95 | 139 | 177 |
| PVC/3% TiO₂ with vinyl silane | 1.65 | 612 | 1.15 | 72 | 137 |
| PVC/0.5% TiO₂ with amino silane | 1.5 | 617 | 1.15 | 69 | 94 |
| PVC/3% TiO₂ with amino silane | 1.55 | 716 | 1.1 | 101 | 143 |

![Fig. 13 Stress–strain behaviour of pure PVC and PVC/unfunctionalised, vinyl- and amino-functionalised TiO₂ nanocomposites](image)
nanoparticles have been added to the pure PVC, and this alters its mechanical properties as it decreases the values of strain, taking into consideration the values of stress. This is because the addition of nanoparticles into PVC matrix improves the force strength of the interfacial area, and this in turn would constrain the PVC chains strengthens ductility and elasticity of the sample and reduces its elongation. Generally, the decreasing in elongation of any polymeric materials upon addition of nano- or micro-filler is a common behaviour for polymer nanocomposites, and this is due to the formation of nanoparticles-polymer bonds that causes mobility restriction in the polymer chains [34]. The second part of the stress–strain curve shows that the tension force overcomes the elastic limit, and it involves losing the elasticity of the samples with an increase in the strain due to the breaking of covalent bonds of the chains of the polymer. The data presented in Table 4 show that Young’s modulus of the nanocomposites containing 0.5 and 3% unfunctionalised nanoparticles is much higher than that of the pure PVC sample by 6 and 63%, respectively, however, the maximum value of elasticity and PVC polymer compared to the amino silane as described nanocomposites containing 0.5 and 3% unfunctionalised decreases with 3.5% over the unfilled one. This indicates that the interfacial area, and this in turn would constrain the PVC chains modulus of the PVC/TiO₂ nanocomposites containing 3% vinyl-functionalised TiO₂ is improved by 273 and 128% compared to that of the pure PVC and nanocomposites sample containing 3% unfunctionalised TiO₂, respectively. Otherwise, for the nano composites sample containing 0.5% amino-functionalised TiO₂ there is a limited improvement in elasticity that tends to 17.8% compared with pure PVC, in contrary, the tensile strength decreases with 3.5% over the unfilled one. This indicates that the insertion of vinyl-functionalised TiO₂ nanoparticles improves the mechanical performance of PVC, and this is attributed to the closest value of surface tension of vinyl silane with that of TiO₂ and PVC polymer compared to the amino silane as described above.

4 Conclusions
The following conclusions can be summarised:
(i) PVC/TiO₂ nanocomposites with various wt.% of functionalised and unfunctionalised TiO₂ (0.5, 1, 3 wt. %) were fabricated by the solvent-casting principle. Nanoparticles surface functionalisation was achieved by using vinyl silane and amino silane as coupling agents, and the structure of the obtained materials was confirmed by FT-IR spectroscopy.
(ii) Dielectric properties and mechanical performance of PVC have been enhanced by inserting the functionalised TiO₂ nanoparticles, and the vinyl-functionalised nanoparticles showed the highest enhancement. The decrease in εr and tanδ values for PVC sheets with the incorporation of nanoparticles is due to the restriction of the polymer chains that tied together by the nanoparticles and that might contribute for additional polarisation.
(iii) Thus, the most proper coupling agent in this study was vinyl silane and this can be integrated from the data shown in SEM of vinyl silane-containing nanocomposite as well as the improvement in electrical and mechanical properties. Two reasons are explaining this conclusion: the first one concerns with the closest value of surface tension of vinyl silane with that of TiO₂ and PVC polymer compared to the amino silane. However, the second reason is based on the possibility of agglomeration of amino-functionalised nanoparticles that might arise from the unreacted NH moieties of this silane and which in turn results in the formation of H-bonding between the nanoparticles ending with their agglomeration.
(iv) The measured AC and DC-BDS enhanced with the insertion of vinyl-functionalised TiO₂ into the PVC chain matrix compared to the unfunctionalised and the amino-functionalised nanoparticles. This is because of the role of nanoparticles and their interface in forming barriers and preventing the growth of discharge channels that resulted from the distribution of the nanoparticles, especially, those that were functionalised by vinyl-coupling agent.
(v) PD activity in PVC nanocomposites enhanced the PD inception voltage, delayed the tree initiation and decreased the PD generation rate (pps) and its magnitude.

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