UNIVERSITY OF THE WITWATERSRAND

MASTER OF SCIENCE IN ENGINEERING

# Breakdown Strength Influences of Titanium Dioxide Nanoparticles on Midel Canola-Based Natural Ester oil: A Comparison Between the Anatase and Rutile Phases of Titanium Dioxide.

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# Abstract

Natural ester oils are an alternative solution for sustainable transformer insulation. They offer good dielectric properties and in addition improve safety of equipment and sustainable environment. They have higher fire resistance than the widely used mineral oil and are less prone to explosions. They are also highly biodegradable and renewable. However, some challenges such as inconsistent breakdown voltage at higher temperatures and higher streamer speeds hinder the wide use of natural esters. Nanotechnology has been found to improve the properties of the oil, including the breakdown voltage. Different nanoparticles have been previously studied, giving varying results. This dissertation presents a study of the use of two phases of $TiO_2$ nanoparticles, namely rutile and anatase, to improve the breakdown voltage of natural ester oil at higher temperatures. The study seeks to find the effects of the nanoparticle phases on the oil under uniform and non-uniform electric fields. Nanofluids of different loading concentrations (0.01 vol%, 0.03 vol%, 0.05, vol%) were created in each nanoparticle phase for the purpose of the study. The findings are that both phases of the nanoparticles improve the breakdown voltage under uniform fields. The anatase portrayed an impressive improvement of 85% at ambient temperature, while the rutile phase enhanced by 61%. At higher temperatures however, the rutile phase had better improvement. Rutile $TiO_2$ nanoparticles consistently outperformed the anatase phase in improving the breakdown voltage at higher temperatures. Under non-uniform electric fields, the rutile $TiO_2$-based nanofluid was found to be superior to the anatase-based fluid. Rutile $TiO_2$ resulted in a significant 10% improvement in the average breakdown voltage and streamer acceleration voltage. An overall decrease in the streamer speeds was observed with the addition of the rutile $TiO_2$ nanoparticles. In contrast, anatase $TiO_2$ resulted in decreased breakdown voltage and increased streamer speeds when compared to both the rutile nanofluid as well as the pure natural ester oil. The rutile phase of $TiO_2$ can be regarded as a feasible solution for breakdown voltage improvement of natural ester oil in both cases of uniform and non-uniform electric field. The effects are attributed to the electron capture phenomenon and the good thermal stability of rutile $TiO_2$. A stable composite is formed between the rutile nanoparticles and the host natural ester. The resultant morphological structure enables stable interfacial regions even at higher temperatures. In conclusion therefore, rutile $TiO_2$ nanocomposite natural fluid is a possible solution to the current limitations in ester oils as power transformer insulation oil alternative.

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# Declaration

I declare that this dissertation is my own unaided work. It is being submitted for a Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination to any other university.

Signature: ………………………………….

Date: 26 September 2024

*To my husband, sister, and the ever-cheerful daughter*

*You gave me strength to wake up and try again…*

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# List of Publications from Dissertation Work

1. M. Miya, C. Nyamupangedengu, K. Nixon and N. Moloto**, "Breakdown Voltage of Natural Ester-Based Nanofluid: A comparison between anatase-TiO2 and rutile-TiO2 nanoparticles,"** *2023 31st Southern African Universities Power Engineering Conference (SAUPEC)*, Johannesburg, South Africa, 2023, pp. 1-5,
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# Chapter 1 Introduction

## 1.1 Transformer Insulation

Transformers have been a critical component in the evolution of electrical technology over the years. They enable voltage and current transformation necessary for transmitting electricity from generation power stations to the consumers. High reliability in power transformers is, therefore, essential. There is heating during the operation of the transformer, usually up to 70 ˚C – 90 ˚C. However, the hottest spots can reach even higher temperatures. It is, therefore, critical that the oil used as insulation is capable of maintaining good dielectric strength even at such high temperatures [1].

Mineral oil has provided insulation and cooling functions in power transformers successfully for over 100 years. It provides cooling of the transformer through convection. Mineral oil does this well due to its low viscosity. Mineral oil is also a good dielectric material, preventing arcing for up to 30 kV/mm under AC tests. There are, however, shortfalls associated with the use of mineral oil in power transformers. These include a high rate of fires and explosions of mineral oil-filled transformers. A transformer explosion leads to catastrophic fires causing damage to infrastructure and the environment. The other problem with mineral oil is that it has a low biodegradability rate. With a low biodegradability rate, spillages from such oil have adverse effects on the environment. The soil and vegetation are polluted and destroyed. Mineral oil is also a fossil fuel-based oil. It is derived from crude fuel. It has been reported that this fossil fuel is on the verge of running out in the future since it is not a renewable resource. This challenges the availability of oil in the future and may also lead to high cost implications [2], [3], [4], [5].

Because of the stated problems, researchers have investigated other alternatives to mineral oil for transformer insulation in recent years. One such alternative is ester oil. Ester oil is a family of vegetable-based oils that are processed through esterification to enhance certain oil properties. In this family, there are synthetic and natural ester oils. Different vegetable oils have been studied and used to form ester oils, including palm, canola, sunflower, and castor oil. Apart from being renewable since they are vegetable-based, these oils have also been found to have good dielectric properties. Hence they are highly regarded as alternatives to mineral oil as electrical insulation. Ester oils are highly biodegradable. While mineral oil has a low biodegradability of 30%, synthetic and natural ester oils have a biodegradability of 80% and 99% respectively [3], [6]. This entails that ester oils are much safer for the environment than mineral oil. Adding to this is the reluctance of ester oils to ignition. Synthetic and natural ester oils have a much higher fire-point than mineral oil. Fig. 1 shows the comparison of the fire point and biodegradability; it is evident from the figure that ester oils have double the fire-point level of mineral oil. Ester oil’s fire-point is also much higher than the typical hottest temperatures in a transformer, which can rise to approximately 150 ˚C. It is for this reason that ester oils have higher fire safety than mineral oil [3], [5], [7], [8], [9], [10].

It is evident from this that natural ester oils are a better alternative to mineral oil when considering their environmental impact. However, natural ester oils also have limitations that are hindering their mass use in power transformers.

## 1.2 Problem Statement

One of the challenges associated with ester fluids include being highly hygroscopic, meaning that they can easily absorb moisture from the air. Moisture is an unwanted entity in transformer insulation as it deteriorates the dielectric strength of the insulation. Moisture accelerates polarization in a transformer which leads to streamer formulation and lower breakdown voltages [11], [12]. Natural esters are also prone to oxidation rate and have a higher acidity [3], [11], [13], [14], [15], [16].

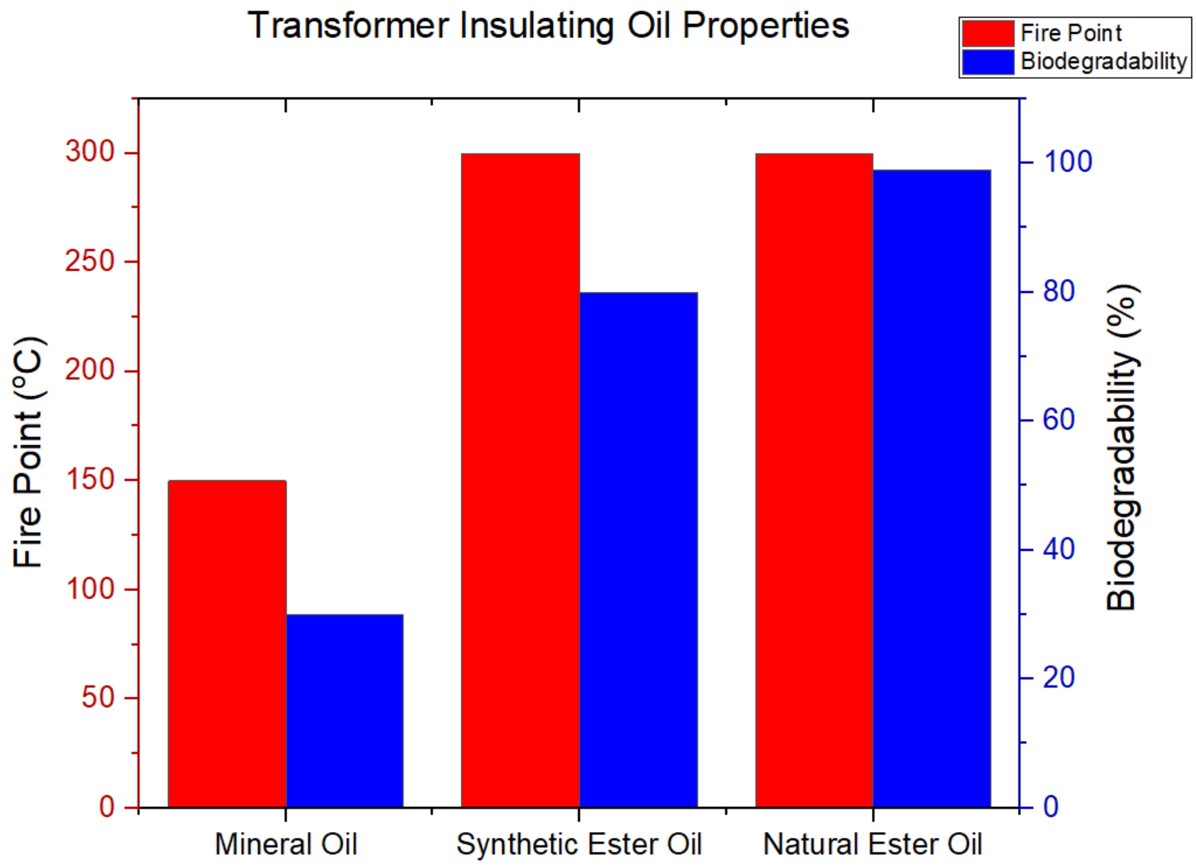


*Fig. 1: Biodegradability and Fire Point of Transformer Insulation Oils [3], [10]*

The attempt to prevent oxidation and moisture factors through extreme sealing conditions on a transformer leads to high production costs. Among the shortfalls of natural ester fluids is the higher streamer breakdown speeds than in mineral oil, as well as higher viscosity. High viscosity leads to challenges with cooling for natural ester-filled transformers. According to Wang et al [9], natural ester oil-filled transformers are found to tolerate higher temperatures at hot spots and top oil as compared to similarly loaded mineral oil-filled counterparts. They found the highest hotspot temperature for mineral oil to be 149 ˚C, while that of natural ester oil was 167.8 ˚C. Smith and Beaster [8], also assessed the temperature rise of a natural ester-filled transformer and found the average top oil and winding temperature rise to be 9 - 16 ˚C hotter than the mineral oil-filled. This confirms the challenge in cooling with natural ester oils. Based on Wang's research [9], natural ester is still preferred in this regard as natural ester has a much higher fire point and thus less risk of fires. However, the higher temperature rise could be very detrimental to the health of transformers as it can facilitate thermal aging of the insulation and hence poor dielectric strength. A concern therefore arises on the dielectric properties of natural ester oil during high-temperature conditions. Research shows reports of inconsistent breakdown voltages in natural ester oil at higher temperatures, especially temperatures higher than 90 ˚C [17], [18]. With such limitations, and natural esters being significantly prone to these higher temperatures, it is thus critical to find a solution for improving the breakdown voltage of natural esters at higher temperatures.

Nanotechnology has been explored as an alternative solution for improving the properties of insulation liquids. Nanoparticles have been found to exhibit qualities that enhance properties such as cooling and breakdown strength, provided that an optimal choice of nanoparticles is selected. Different nanoparticles have been explored over the years and found to improve insulation fluids significantly. The main ones being $TiO_2$, $Fe_3O_4$, $Al_2O_3$, $SiO_2$ and ZnO. $TiO_2$ is considered the optimum solution for better breakdown strength at higher temperatures due to its good thermal properties. It has a high thermal conductivity and is mostly thermally stable in nanocomposites [19], [20]. In some studies where $TiO_2$ nanofluids were compared to other nanofluids, such as the works of Saenkhumwong et al [21], Makmud et al [22] and Mendez et al [23], $TiO_2$ has been found to have superior breakdown voltage improvement. Maneerat et al [24], found that $TiO_2$ nanoparticles improved natural ester breakdown voltage better than $BaTiO_3$ at higher temperatures.

While the breakdown improvement has been widely reported, there is limited research on the effects of the phases of $TiO_2$ on the breakdown voltage of insulation. There is a knowledge gap on the phase of $TiO_2$ that yields the most improvement of breakdown voltage and this leads to the research question of the present work.

## 1.3 Research Question

The following is the research question to be answered and addresses the stated knowledge gap.

***Which phase of $TiO_2$ (anatase or rutile) nanoparticles and to what extent does it give the most improved breakdown strength under uniform and non-uniform electric fields of the resultant natural ester nanofluid with changing temperature?***

In the process of answering the research question, the following sub-questions must be addressed:

1) *What is the optimal concentration of anatase and rutile $TiO_2$ of a specific size and shape, that will result in the most improved breakdown strength compared to the unfilled liquid in a uniform electric field environment?*

2) *Which of the two phases of $TiO_2$ results in the most improved breakdown strength at higher temperatures in a uniform electric field environment?*

3) *How do the streamer breakdown speeds of anatase and rutile $TiO_2$ nanofluids compare with the unfilled natural ester fluid?*

## 1.4 Dissertation Structure

The study has been introduced in this chapter. In Chapter 2, literature review on natural ester insulation oil for transformer use and its breakdown voltage effects are presented. The evolution of nanodielectrics, including nanofluids, as well as the effects of $TiO_2$ nanoparticles in nanofluids are also presented in the literature review. Chapter 3 presents the materials and methods of the experimental study. In the chapter, the nanophases, and their properties, as well as those of natural ester oil, are discussed. The nanofluid synthesis and characterisations are also discussed in Chapter 3. The resultant nanofluids are assessed and investigated in experimental processes. Chapter 4 presents the experimental process and results of the uniform field breakdown voltage tests. The chapter presents a comparison between the effects of rutile and anatase nanoparticles on the breakdown voltage of the natural ester at different temperatures. Chapter 5 gives the comparison of the resultant streamer speeds between the anatase and rutile-based nanofluids under lightning impulse breakdown. Finally, in Chapter 6 is the discussion and conclusion.

# Chapter 2 The Literature Review

*Chapter 1 has briefly described problems associated with natural ester oil which have led to conception of the research question of the present research study. The introductory chapter also highlighted on nanotechnology and benefits to insulation oils. Nanoparticles can improve the shortfalls in natural ester oils, including those of the breakdown voltage. There is a knowledge gap on the type of nanoparticles and their phases, that will give the most improvement in breakdown voltage. Hence, the current study seeks to find the effects of the phases of* $TiO_2$ *on the breakdown voltage of natural ester oil. In this chapter, details of natural ester oil and the use of nanotechnology are presented through a critical literature review. The use of natural esters for transformer insulation is discussed, and the benefits and shortfalls are discussed in detail with reference to existing literature. The focus is on the breakdown voltage challenges at high temperatures. The different nanoparticles studied, as well as the effects as reported in literature are used as a basis for the choice of* $TiO_2$ *nanoparticles for breakdown voltage improvement in the present work.*

## 2.1 Natural Ester oil – An Alternative Transformer Insulation Liquid

Most of transformer failures are attributed to dielectric faults in the core and windings [25], [26]. These faults can have disastrous consequences in large power transformers due to the high levels of fault currents and potential explosions that may occur during faults. To ensure safe transformer use, an insulating medium with good dielectric properties, good thermal properties (high fire resistance), and good cooling properties is essential. Mineral oil has been successful in providing transformer insulation in the past, with its good dielectric strength and cooling properties. However, its fire resistance has challenges during high loading conditions as the transformer tends to reach temperatures beyond its fire point of about 150 ˚C [9]. Transformer faults also lead to massive fires in mineral oil. Natural ester oils are suitable alternatives to mineral oil as they have much higher fire point and hence are more resistive to fires than mineral oil. The safety of natural ester oils extends to their environmental safety as previously discussed. There are other benefits to using natural ester oils, as well as downfalls that are hindering their use in large power transformers. These are discussed further in this section.

**Benefits of Natural Ester Oil in Transformers**

Natural esters are deemed fire safety class K, and have a minimum fire point of 300˚C [2], [4]. This is double that of mineral oil and much higher than the typical temperature rise of large power transformers at full load. They are thus much safer for the people, equipment, and environment. Their biodegradability and renewability make them a better choice for an environmentally sustainable footprint. What is mostly critical is the benefits associated with their dielectric strength.

It has been reported in the literature that natural esters can prolong the lifespan of transformers due their reaction to moisture. Natural esters are highly hygroscopic, meaning that they can easily absorb moisture. While moisture is a known threat to the dielectric strength of insulation medium, its effect to natural ester oil is different to that of the common mineral oil. Natural esters have a higher water saturation limit, and can withstand much higher voltages with the presence of water [12], [27]. Due to their hygroscopicity, natural esters can absorb moisture from transformer insulation paper and pressboard. According to Suwarno [28] and Chao et al [29], water in a transformer usually originates from heating of the insulation paper, and eventually migrates to the oil and deteriorates the dielectric strength. This accelerates aging of a transformer. Since natural ester oils can absorb moisture from the paper, this thus delays the degradation process of the paper and hence increases the transformer lifespan. This was proven in the studies by Martins and Gomes [30], Adelmalik et al [31], and Suwarno [32], who studied the thermal aging of natural ester-impregnated paper and compared it to other oils. They found a reduced aging rate with natural ester oil. Martins and Gomes also showed a reduction in moisture on kraft paper with synthetic and natural ester oil, but the reduction was pronounced in natural ester oil-impregnated paper.

The breakdown strength is another property in which natural ester oil has shown good results. The AC breakdown voltage is significantly higher than that of mineral oil. Beroual et al [33], and Kamal et al [13], followed the IEC 60156 for AC breakdown voltage in insulating liquids. The presented breakdown voltage differences of 69% and 57%, respectively, between mineral and natural ester oil.

While the AC uniform field breakdown voltage has shown these positive results, there are shortfalls particularly at higher temperatures as well as in non-uniform electric fields.

### Challenges with Natural Ester Oil in Transformers

Among the challenges associated with natural ester oil under non-uniform electric fields is in their pre-breakdown criteria. When natural ester is tested under streamer impulse breakdown, it is found that the velocity of the streamer is faster than that of mineral oil. Research shows that even though the inception of breakdown is similar to mineral oil, the propagation of the streamers through natural ester oil is relatively fast [34], [35]. The propagation speed of streamers is classified into four different modes, that is, the 1st, 2nd, 3rd, and 4th modes. Table 1 presents these modes and the associated average order of propagation speeds. The widely used mineral oil normally propagates between 2nd and 3rd modes.

*Table 1: Classification of Streamer Propagation Modes*

| Mode | Range of Average Speed (mm/μs) | Fast/Slow |
|---|---|---|
| **1st** | 0.1 | Slow |
| **2nd** | 2 | Slow |
| **3rd** | 10 | Fast |
| **4th** | 100 | Fast |

It is worth noting that the speed of a streamer is dependent on the stress voltage. When the oil is stressed at voltages beyond its breakdown voltage, it tends to have fast streamer propagation. There is a voltage at which streamers switch from slow (2nd mode) to fast (3rd mode). This is known as the acceleration voltage. According to Rozga et al [35], natural ester oils normally have a lower acceleration voltage than mineral oil, and hence most streamers in natural ester will be fast. Fig. 2 presents a difference between the streamer speeds in two types of oil from an existing study. A significant difference is denoted between the acceleration voltage of mineral and natural ester oil. While the breakdown voltage of natural ester is much higher, and complete breakdown may not easily occur, the streamer stopping length is usually much longer than in mineral oil under the same impulse stress. This indicates that the oil may suffer more damage in natural ester oil than mineral oil for the same period of breakdown. If a streamer is initiated by a short duration transient overvoltage such as lightning, the probability of the streamer bridging the insulation gap before excitation of the impulse voltage is higher in ester oils than in mineral oil. Therefore, the need to slow down streamer speeds in ester fluids is an ongoing research area and the present work will include this aspect of research.

The impulse breakdown voltage is also challenged in natural ester as there are inconsistencies in the resultant breakdown effects. As reported by Li et al [36], natural ester's positive impulse breakdown voltage is superior to mineral oil for small gaps. Still, it is exceeded by mineral oil for gaps between 25 mm and 50 mm. Large gaps, greater than 50 mm were comparable to mineral oil. This is supported by Huang et al [37], who found positive impulse breakdown voltage between different natural ester oils and a mineral oil to be comparable at a 25 mm gap, but that of mineral oil was significantly higher as the gap increased. Williamson and colleagues [38], found contradicting results in their study. They found the positive impulse breakdown significantly higher for natural ester than mineral and synthetic ester oils, while the negative impulse gave the opposite results. Williamson used a gap of 80 mm. In the latter, they also show significantly higher propagation velocities with natural ester oil than the other oils.

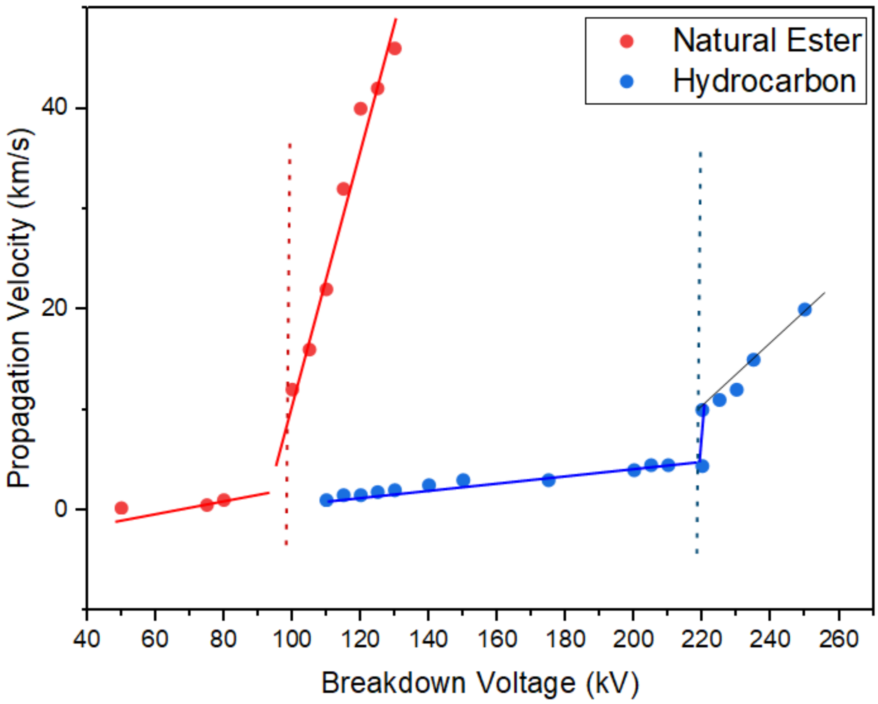


*Fig. 2: Positive impulse breakdown streamer velocity of dielectric liquids at insulation gap 50 mm [37]*

The findings above clearly indicate inconsistencies in the lightning impulse breakdown voltage. It is thus notable that the intrinsic properties of natural ester oil have challenges associated with the breakdown strength of the oil. Another issue with the breakdown strength is found with changes in temperature. The superiority of the breakdown strength of natural ester oil at higher temperatures is challenged. The next section elaborates on the breakdown effects at higher temperatures.

## 2.2 Effects of Temperature on the Breakdown Strength of Natural Ester Oil

Transformers operate nominally between 40˚C-90˚C, but they can reach temperatures beyond 150 ˚C due to overloading. A good transformer insulation is expected to withstand such thermal conditions while maintaining good dielectric properties [1]. It is thus imperative that temperature effects be one of the key parameters for assessing the insulation properties. However, the effects of temperature on the breakdown strength of transformer insulation are not extensively described in the literature. Most of the existing literature is focused on temperatures up to 90˚C, although the transformer hotspot temperatures are known to reach much higher temperatures. When the common transformer faults are analysed, it is found that most faults are related to the windings and cores [26], which are the hotspots in question. This necessitates the need for good dielectric strength at hotspot temperatures.

Existing studies from Rozga et al [39], Kocatepe et al [40] and Rasaruk et al [41] focus on the effects of temperature on mineral oil. They report an increase in breakdown voltage with the increase in temperature. Rasaruk highlighted that the relationship is more pronounced under highly non-uniform impulse stress. Kocatepe et al [40], studied the breakdown voltage with temperatures up to 110 ˚C, and they found the same increase in AC breakdown voltage for new mineral oil. However, when water content was introduced into the oil, the breakdown voltage increased with temperature only up to 100 ˚C, then decayed beyond that. This effect was attributed to vaporisation at 100 ˚C, the air bubbles accelerated the breakdown process. This coincides with the earlier work of Nossier et al [42], who presented a probability curve of the breakdown voltage of mineral oil with changing temperature. They show a decay of breakdown voltage at temperatures beyond 60 ˚C. Rozga et al [39], did similar work on the lightning impulse breakdown voltage of mineral oil. A similar trend of increase in breakdown voltage with increasing temperature was observed up to 100 ˚C. After which, the breakdown voltage decreased. They attributed the increase in breakdown voltage to a decrease in viscosity, and the change at 100 ˚C to bubble formation due to vaporisation. It is worth noting that lightning impulse is not as dependent on moisture as the AC breakdown voltage for small gaps. Having studies in both AC and impulse breakdown with similar outcomes implies that the presented temperature effects are not only moisture related but are related to the intrinsic properties of the oil.

Based on the above review, it is notable that the breakdown voltage at the hotspot temperatures is of concern as it is not easily predictable. Researchers have noted the insignificance of the breakdown voltages at these temperatures due to transformer normally operating below 90 ˚C. Mineral oil however has good cooling properties and is not subjected to as high temperatures as ester oils during high loading conditions. The dielectric strength at higher temperatures may therefore be of greater concern in ester oils. Wang et al [9], studied the response of transformers filled with mineral and natural ester oil and found that for the same transformer loading, under the same conditions, natural ester-filled transformers have higher temperature hotspots and top oil temperatures. Fig. 3 depicts these changes in temperature for mineral and ester oil. They reported the highest hot spot temperatures to be 149 ˚C and 167.8 ˚C for mineral oil and natural ester oil, respectively [9]. This is supported by Velandy et al [43], where they reported a 15 ˚C - 20 ˚C higher hotspot temperature in natural ester oil compared to mineral oil. While this temperature rise in natural ester oil-filled transformers is environmentally safer due to the higher fire point and closed cup flash point associated with natural ester oil, an optimal operation of the insulation material up to these temperatures is questionable.

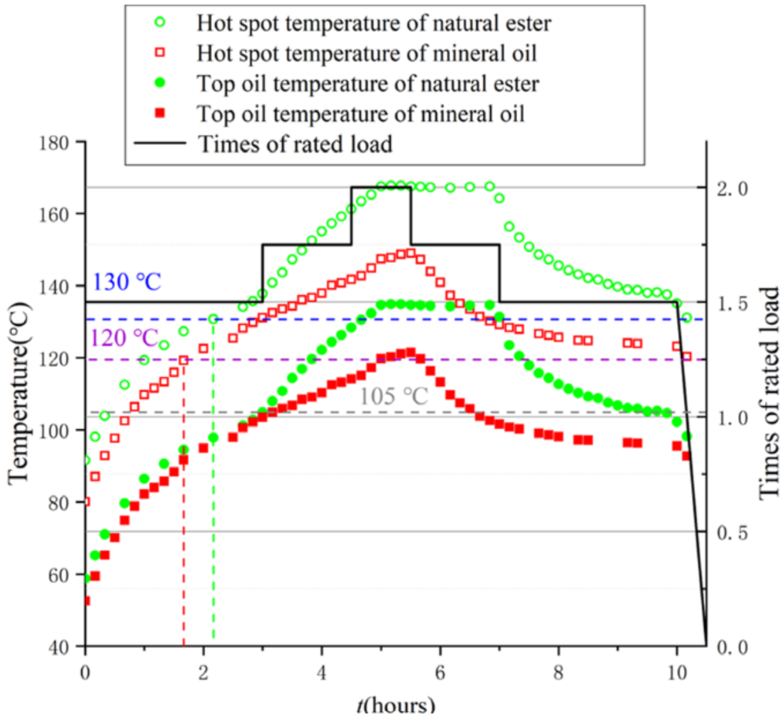


*Fig. 3: Temperature Variations of Ester and Mineral Oil in transformers [9]*

There is limited literature on the temperature effects on the breakdown voltage of natural ester oil. Most of the literature is focused on the aging influence on the breakdown voltage. There is evidence, from this literature, of inconsistencies in the breakdown voltage of natural ester oil at temperatures higher than 90 ˚C. Gockenbach and Borsi [17], indicated a weakness in ester oils at higher temperatures. Their study explored the blending of mineral oil with ester oil to improve mineral oil properties. In the work, they reported the enhancement of properties due to the superior ester oil. However, at higher temperatures, the positive improvements cease due to the lack of influence of ester oil at these temperatures. This correlates to the findings of Suwarno and Marbun [18], where they found that the AC breakdown voltage of pure natural ester oil decreased more abruptly under thermal aging at 120 ˚C, as compared to other blends of mineral oil. They also showed worsened dielectric loss effects for natural ester, the effects were more prevalent with a temperature of 150 ˚C. These effects were reported within the first 20 days of testing. This indicates that the increase in temperature had a negative impact on the dielectric strength. A similar study was conducted by Amalanath et al [1], where the breakdown voltage of unaged natural ester oil was compared to that of the oil aged at different temperatures. They found that the inception voltage and breakdown voltage both decreased significantly with the increase in temperature. Fig. 4 illustrates the changes in breakdown voltage from the study.

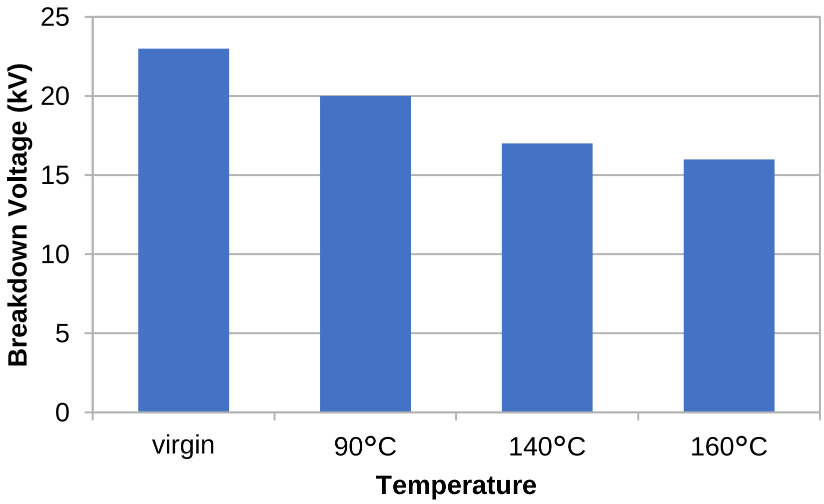


*Fig. 4: Effects of aging temperature on natural ester oil [1]*

Further studies were conducted by Suwarno and Darma [44], where they explored the properties of natural ester, mineral oil and their blends at different temperatures. They found better dielectric constant and hence breakdown voltage on natural ester oil at different temperatures. However, the dielectric loss factor was higher for natural ester oil than mineral oil. A significant rise in the dielectric loss factor was observed at 100 ˚C. The same finding was presented by Jaroszewski et al [45]. Suwarno and Darma attributed these effects to an unbalanced chemical structure and higher water content associated with natural ester as compared to mineral oil. According to Suwarno and Darma, these chemical properties of natural ester oil influence a higher degree of polarisation at 100 ˚C, and as such, resulting in an increase in the dielectric losses. This gives indication of challenges on the breakdown strength at this temperature. This study, however, does not present the breakdown voltage effects at this temperature. Temperature-dependent breakdown voltage is only tested up to 70 ˚C.

Evidently, the changes in temperature affect the breakdown strength of natural ester oil significantly at temperatures higher than 90 ˚C. Considering that transformers may be stressed to maximum capacity due to the growing need for electrical power, these higher temperatures are inevitable in transformers. With natural ester oil being more susceptible to the higher temperatures, the breakdown voltage at these temperatures becomes of greater concern. The use of natural ester oil as an alternative to mineral oil will require improvement of the thermal and dielectric properties at higher temperatures. Possible solutions lie in nanotechnology. Studies have shown that nanoparticles have good thermal properties and can enhance other material's properties. Most nanoparticles also have good dielectric properties, and thus result in improved dielectric material when a nanocomposite is formed. The following section discusses more about nanocomposite dielectrics and how nanoparticles can possibly improve the breakdown strength of natural ester at higher temperatures.

## 2.3 The Evolution of Nanodielectric Technology

### 2.3.1 Solid Nanodielectrics

The adaptation of nanotechnology in dielectric material has been the focus in recent years in order to improve properties of the dielectric material. In the early 2000's, polymer nanocomposites emerged, where researchers used nanoparticles to enhance the thermal and mechanical properties of polymer material. They discovered that polymer nanocomposites can improve partial discharge resistance and increase the electrical treeing time through space charge suppression [46], [47]. Solid nanodielectrics were then discovered. Nanoparticles such $SiO_2$ and $TiO_2$, were studied on XLPE and epoxy material, and gave promising results. The breakdown strength of XLPE was improved by over 50% with the addition of silica nanofillers [46], [48]. Electrical treeing and partial discharge inception were also proven to improve in the research, similar results were found for $TiO_2$ nanofillers on epoxy [46], [49], [50].

The effects of these nanoparticles in dielectrics are directly linked to the physical properties of the particles such as their type, structure, size. Based on the literature, it is the interfacial area between the nanoparticles and the base dielectric material that influences the resultant dielectric performance of the nanocomposite. Because of their size, nanomaterial have a much higher interface area to the surrounding material when well dispersed. This is because the surface area of particles in their nanometre range is larger than when in a bulk form. Equation 1 below gives an expression of the ratio of surface area to volume of a sphere. It is shown from the expression that, assuming a spherical nanoparticle, its surface area is inversely proportional to the radius. Hence nanoparticles will have better physiochemical interactions with the host matrix as compared to their micrometre counterparts [51].

$$\frac{S}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

*Where: S is the surface area of a sphere*
*V is the volume of a sphere*
*r is the radius of a sphere*

According to Lewis [52], and Tanaka [53], it is in this interfacial area that a good bond is formed between the particle and the base material through charge carriers. Tanaka proposed a multi-core model, where a positively charged, spherical nanoparticle exists ideally, as shown in Fig. 5. A tightly bonded layer forms as the first layer around the nanoparticle, known as the stern layer in an electrical double later [53]. A diffuse layer is a layer of free ions, on the outer layer of the model. In this layer, the free ions move and can attract neighbouring charge carriers. This model has been widely used by researchers to explain the improved electrical breakdown effects on nanodielectrics. During breakdown of dielectric material, an electron avalanche develops from the point of highest potential through ionisation, forming a path along the material. When nanoparticles are added to the material, they attract the electrons from the breakdown streamer through the shallow traps in the diffuse layer. This thereby reduces the energy of the streamer and delays the process of complete breakdown. Consequently, a much higher voltage will thus be needed for breakdown compared to breakdown on material without nanoparticles [4], [10], [53], [54], [55], [56]. In Fig. 6 the electron capture theory is graphically illustrated.

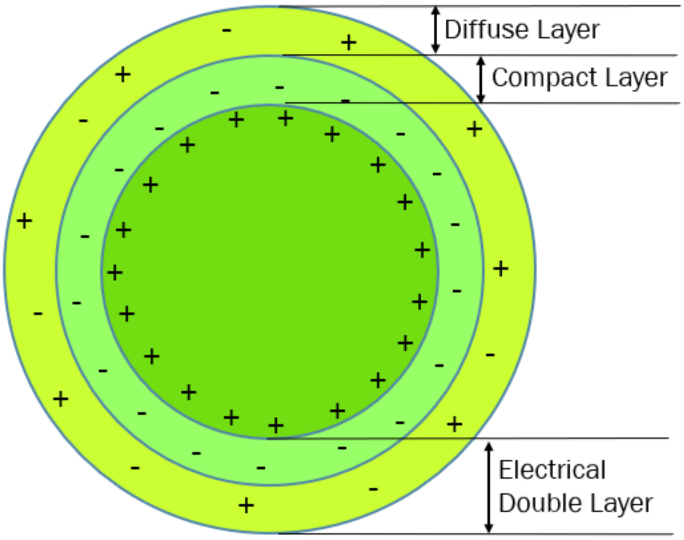


*Fig. 5: Model of a nanoparticle in insulating fluid [53]*

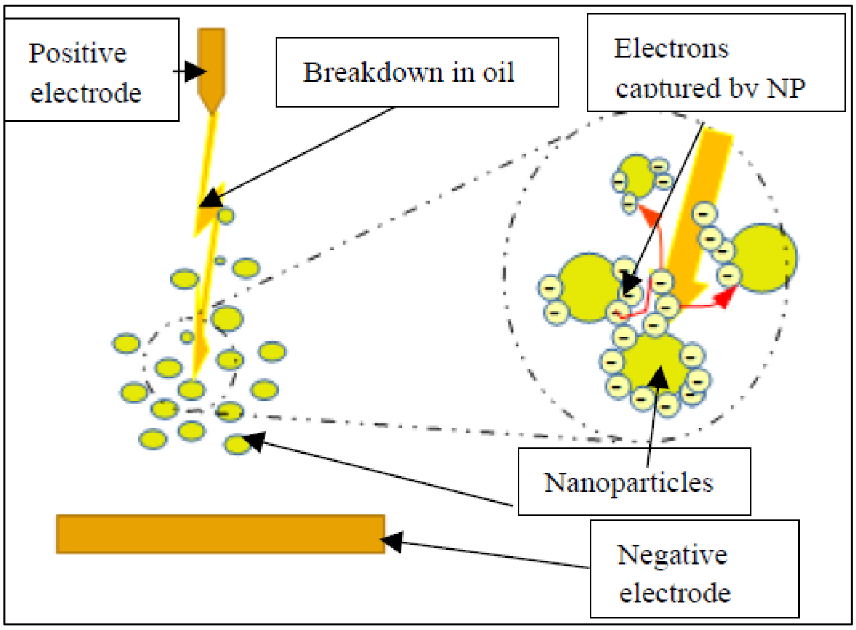


*Fig. 6: Model of electron capture during breakdown of a nanofluid*

### 2.3.2 Liquid Nanodielectrics

The term nanofluid is given to the composite material formed from a base liquid mixed with nanoparticles. Nanofluids have been found to have improvements on both the physiochemical properties and dielectric properties for transformer insulation. Cooling and electrical insulation are critical uses of oil in a transformer. Both of which, nanofluids have shown improved results in studies.

**Nanoparticles as cooling additives**

In the works of Santisteban et al [57], Taheri [58] and Huang[59], the influence of nanoparticles on cooling effects of transformer mineral oil were studied. It is found that nanoparticles enhance the thermal conductivity of fluids, and as such, improving the rate of cooling in a transformer. Metal oxide nanoparticles are mainly used due to their stability in polymer composites [60], [61]. The most common being the iron oxides ($Fe_2O_3$, $Fe_3O_4$), titania ($TiO_2$), others include aluminium and silica oxides. Santisteban et al[57], compared $Fe_3O_4$ and $TiO_2$ and found that at the same concentration of 0.036 vol%, both nanoparticles improve cooling of the base oil at almost the same rate. While at an increased 0.072%, $TiO_2$ decreases the cooling of the oil. Which indicates that the influence of the nanoparticles is dependent on the concentration of the nanoparticles. Lv et al [62], and Jin et al [63], found an increase in the thermal conductivity of $TiO_2$-based nanofluids. Improvement of the thermal conductivity was also reported for $Fe_3O_4$ by Du et al [64], and Nkurikiyimfura et al [65].

Olmo et al [66], studied the cooling effects of $Fe_2O_3$ in natural ester oil and found that it improves the oils cooling effects by up to 11%. Khan et al [67], investigated the effects of $TiO_2$ on thermal conductivity and viscosity of natural ester oil. They found improvement in both properties with the addition of the nanoparticles. They showed increase in thermal conductivity and reduced viscosity with the nanofluid compared to the base fluid for different temperature conditions. Increased thermal conductivity and reduced viscosity lead to improved cooling in transformers.

It is evident from the above findings that the nanoparticles have a positive impact on the thermal properties of the oil. This is an essential trait in transformers given their harsh thermal conditions. Ferrous nanoparticles were mostly superior, followed by $TiO_2$ nanoparticles. It is therefore fitting that these be the focus in the following discussions on the breakdown voltage improvement of nanofluids.

**Nanoparticles as Breakdown Voltage Enhancing Additives in Mineral Oil**

The breakdown voltage effects have also been extensively studied on nanofluids. Hanai et al [68], Muangpratoom et al [69], and Lv et al[70], have found improvements of 25%, 22% and 34% on $TiO_2$ based nanofluids respectively. Studies on $Fe_3O_4$, also show improvement of the AC breakdown voltage by 20-50% [64], [71], [72], [73]. In the studies, it is notable that, in addition to the type of nanoparticle, the size and concentration significantly affects the resultant breakdown voltage enhancement. $TiO_2$ has superior impact on the breakdown voltage in very small size and concentrations. The most improvement was reported to be of concentrations up to 0.05 vol% of $TiO_2$ [54], [60].

**Nanoparticles as Breakdown Voltage Enhancing Additives in Natural Ester Oil**

While the dielectric properties of mineral oil had shown significant improvements with the addition of nanoparticles, the environmental challenges still exist in mineral oil-based nanofluids. Thus, the need for natural ester oil still exists. Natural ester-based nanofluids have also been extensively studied in literature and promising results are reported. Natural ester oils are based of different vegetable oils. The most prominent types being palm oil, rapeseed (canola) oil and sunflower oil. When compared, the oils have similar dielectric properties. Kamal et al [13], studied different properties of vegetable oils, including canola and palm oil. They found that the natural ester oils performed much better than mineral oil, mostly the blend of canola and yellow olive oil. The different oils also showed similar trends in all properties, however, slight differences in values. This is similar to the findings of Hamid et al [74], who found similar trends in different vegetable-based ester oils. They also concluded that canola oil was the better alternative oil for transformer insulation based on its superiority in multiple dielectric properties. It is notable that sunflower oil and palm oil superseded canola oil in some properties in these studies. It is thus sensible that the three oils are the most used in nanofluids and that the effects of nanoparticles would be comparable in all the three.

Charalamapakos et al [75], compared $Fe_2O_3$ and $SiO_2$ nanoparticles in FR3 natural ester oil and found significant changes in the AC breakdown voltage of the nanofluids. They found a maximum improvement of 16% with $Fe_2O_3$, while $SiO_2$ showed a decrement in the resultant breakdown voltage of all tested samples. In both nanofluids, an optimum concentration of nanoparticles was found, at which the breakdown voltage is at the highest, after which it decreases. The optimum $SiO_2$-based fluid was inferior to the pure natural ester fluid in breakdown voltage. The same results for $Fe_2O_3$-based natural ester nanofluid were obtained by Olmo et al [66], when they studied the cooling and insulation properties of the nanofluid at different loading concentrations. Khaled et al [64], assessed the use of $Fe_3O_4$ in mineral, synthetic and natural ester oil and only found a 7% increment of the AC breakdown voltage. Significantly lower than in the other fluids, however, a similar increase in breakdown voltage with increase in loading was observed. These findings show that the significant differences in the influence of each type of nanoparticle, with the two ferrous oxides having distinct influence in a similar base fluid. Mendez et al [23], compared $Fe_2O_3$ to $TiO_2$ in natural ester-based nanofluid. They reported a 15.1% increment of AC breakdown voltage in $Fe_2O_3$, while $TiO_2$ resulted in 33.2% increment. Similarly, Makmud et al [22], compared $TiO_2$ with $Fe_2O_3$ and found the former to have a higher breakdown voltage. This indicating that $TiO_2$ may be a better nanofiller for breakdown improvement in natural ester fluids.

The effects of $TiO_2$ in natural ester-based nanofluids have been further studied in the works of Koutras, Saenkhumwong and Suksri, Fernanedez et al, Sarpataky, and Diego et al [6], [19], [20], [21], [76]. In the literature, they have shown significant improvements in the breakdown strength of the base natural ester fluids. Saenkhumwong [21], compared Palm ester and Soybean ester fluids with $TiO_2$ and ZnO nanoparticles, and in both cases, found that the nanoparticles increased the resultant fluids' breakdown voltages. They also found that $TiO_2$ had the most effect on both nanofluids, although the highest breakdown improvement was on the soybean ester. This was supported by Fernandez [20], who also found greater improvement with $TiO_2$ nanoparticles. Although, Fernandez did not specify the type of vegetable ester used. The findings by Muangpatroom [77], were contrary to the latter, he found ZnO to perform better than $TiO_2$ on a similar palm ester oil. What is denoted from the different studies, is that the concentrations used were similarly between 0.01%-0.05%. The sizes and specific areas were in some literature neglected or not the same between the nanoparticles used. Saenkhumwong did not specify these properties [21], and Fernandez and Muangpratoom used different size particles [20], [77].

Table 2 presents the breakdown voltage enhancements based on the different nanoparticles. It can be deduced from the above and the table that both ferrous and titania nanoparticles have a good influence on the breakdown strength of mineral oil, with the ferrous types being more superior. However, $TiO_2$ had much higher influence on the base natural ester fluid when compared to the iron oxides. This indicating that $TiO_2$ nanoparticles form a better dielectric nanocomposite when blended with natural ester oil. Therefore, in this current study, $TiO_2$ nanoparticles are chosen as a possible solution to the improvement of the breakdown voltage of natural ester oil at higher temperatures as well as the improvement of the streamer speeds. $TiO_2$ nanoparticles exist in different phases, with different properties. It thus follows that this nanoparticle type should be studied further prior to their use in nanofluids.

## 2.4 Titanium dioxide nanofiller

$TiO_2$ nanoparticles have been widely used in nanodielectrics. Mostly because of the benefits that they have with their good thermal stability as well as ability to form stable composites with polymer material. Evidence of this was presented in section 2.3.2 above, with many researchers using it in transformer nanofluids. Their thermal stability is particularly favoured in transformers because of the high nominal temperatures characterized with power transformers. As previously noted, $TiO_2$ nanoparticles have good dielectric and thermal conductivity, and have been found to positively influence a fluids thermal conductivity and hence heat transfer in a nanocomposite. Added to this is the significant improvement of breakdown voltage obtained with $TiO_2$-based nanofluids.

While most literature has shown great results from $TiO_2$ based dielectrics, it is worth noting that there are significant differences in the extent at which these nanoparticles improve the dielectric strength. Besides the size, and loading of nanoparticles, there are distinct differences in the results presented in the literature. Table 2 above presented results of breakdown voltage enhancement in different nanofluids, including $TiO_2$ based fluids. While it is evident that the improvement of the breakdown voltage changes with type of base fluid, size, and concentration of nanoparticle loading, it is concerning that nanoparticles of the same properties still portray differences in breakdown improvement. The studies from Koutras et al, Muangpratroom et al, and Fernandez et al [19], [20], [77], all present results from nanocomposites of natural ester oil and $TiO_2$ of similar size and loading. Nevertheless, the resultant breakdown voltages are significantly different regardless of the similarities in the particles used. Fig. 7 graphically illustrates the differences. This indicates inconsistencies in the effects of $TiO_2$ nanoparticles. In Chapter 2.2 above, the theory of nanodielectrics is discussed, and concludes that the impact of nanoparticles is from the atomic level of the base dielectric material. The intrinsic properties of the nanoparticles are the main contributors to the resultant nanodielectric properties. One of these properties is the crystalline phases. The differences in structure and influences of the crystalline phases may affect the resultant nanofluid properties, including the electron capture ability of the nanofluid. In most literature on nanodielectrics, the effects of particle phases are neglected. It is therefore worth investigating to find out if $TiO_2$ morphological phases have significant influences on the breakdown voltage improvement of nanofluids, and hence find the most effective phase for natural ester oil improvement.

*Table 2: Review of Breakdown Voltage effects of nanoparticles on insulation oils*

| **Base Fluid** | **NP Type** | **Size (nm)** | **Concentration** | **BDV %Improvement** | **Reference** |
|---|---|---|---|---|---|
| **Mineral** | $TiO_{2\text{-rutile}}$<br>$TiO_{2\text{-anatase}}$<br>ZnO | 105<br>46<br>34 | 0.05% | 25%<br>~13%<br>~9% | [68] |
| | $TiO_2$<br><br>$BaTiO_3$ | <100<br><br><100 | 0.01%<br>0.03%<br>0.01%<br>0.03% | 17%<br>22%<br>26%<br>30% | [69] |
| | $Fe_3O_4$ | | 0.04 g/l | 108% | [64] |
| | $SiO_2$<br>$Fe_3O_4$ | 5 - 20<br>10 - 50 | 0.2 g/l | 25%<br>40% | [71] |
| | $TiO_2$ | 10 - 20 | 0.5 ($kg/m^3$) g/l | 33.2% | [60] |
| **Natural Ester** | $Fe_3O_4$ | - | 0.04 g/l | 7% | [64] |
| | $Fe_2O_3$<br>$SiO_2$ | <50<br>12 | 0.008%<br>0.02% | 16%<br>-12% | [75] |
| | $Fe_2O_3$ | 10-20 | 0.2 ($kg/m^3$) g/l | 16% | [66] |
| | $Fe_2O_3$<br>$TiO_2$ | 10-20 | 0.2 ($kg/m^3$) g/l<br>0.5 ($kg/m^3$) g/l | 15.1%<br>33.2% | [23] |
| | $Fe_2O_3$<br>$TiO_2$ | - | 0.01 g/l<br>1.0 g/l | 19%<br>71% | [22] |
| | $TiO_2$ | 21 | 0.02 % | 17% | [19] |
| | $TiO_2$ | - | 0.02 g/l | 35% (Palm)<br>65% (Soybean) | [21] |
| | ZnO<br>$TiO_2$ | 60<br>45 | 0.04% | 27%<br>33% | [20] |
| | TiO<br>ZnO<br>BaTiO | 40<br>30<br>50 | 0.03% | 24%<br>29%<br>16% | [77] |

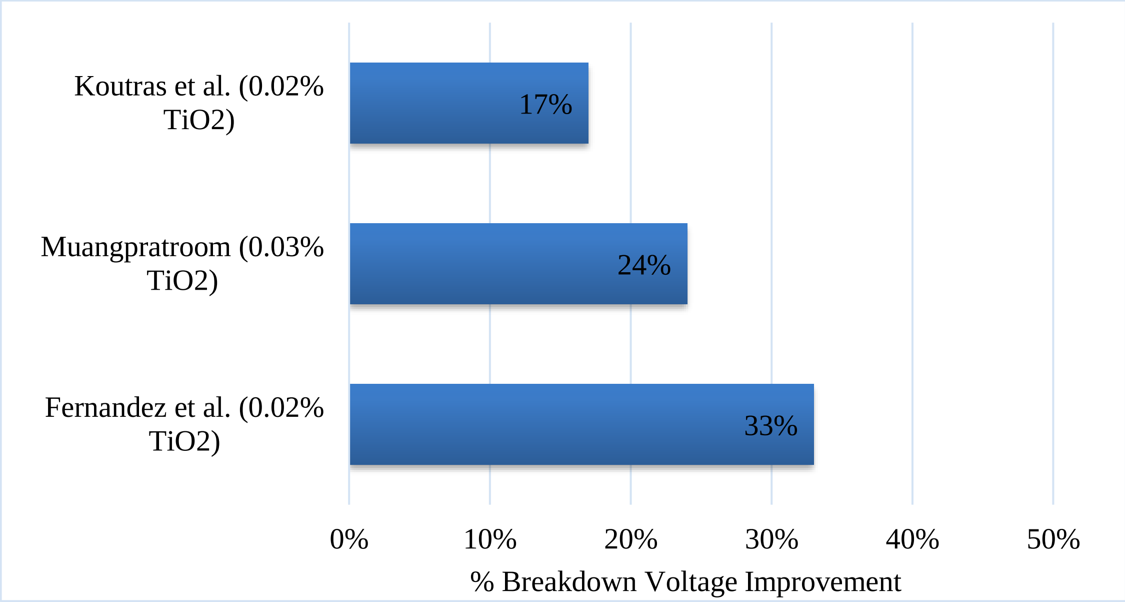


*Fig. 7: Literature Review - Influence of TiO2 on % improvements of Breakdown Voltage*

$TiO_2$ has three natural phases, namely, rutile, anatase and brookite. The crystalline phases have distinct structures, with different atomic bond structures. These structures greatly affect the surface area and hence the interaction between the nanoparticles and base material that they are integrated with. Fig. 8 shows schematics of the structural images of the three phases. It is notable from Fig. 8 that the atomic structures of these phases are different, with anatase appearing to have a larger surface area. Thermal stability is one property that is critical for the application of these nanoparticles in transformers. Rutile $TiO_2$ is deemed more thermally stable of the 3, followed by anatase. The brookite phase is the least used phase of $TiO_2$ due to its thermal instability. Synthesis of pure brookite phase is technically difficult as it can easily transform to anatase or rutile phase in the process [78]. Anatase and rutile $TiO_2$ will thus be investigated further for the purpose of this study.

Both anatase and rutile phase are tetragonal in shape, and they are more stable and are thus the most used forms of $TiO_2$. However, even their common industrial use indicate that they are distinctively different. One of the main applications of $TiO_2$ is in pigmentation, it is widely used in paints and sometimes in food colouring. But the rutile phase is said to have more resistance to UV light than anatase and is mostly used for exterior applications. The rutile phase also has a higher solar absorption rate than anatase. Making the rutile phase the more commonly used for solar energy absorption application of $TiO_2$. The anatase phase is superior to the rutile in photocatalysis applications due to its higher energy band gap [78], [79], [80]. It can thus be deduced that these phases have slightly different chemical reactivity to their surroundings. The composite of each phase with natural ester oil may also have unique resultant properties, including breakdown voltage. The present study compares the effects of these phases on the breakdown voltage of natural ester oil and possibly give the optimal choice for natural ester oil enhancement for transformer insulation.

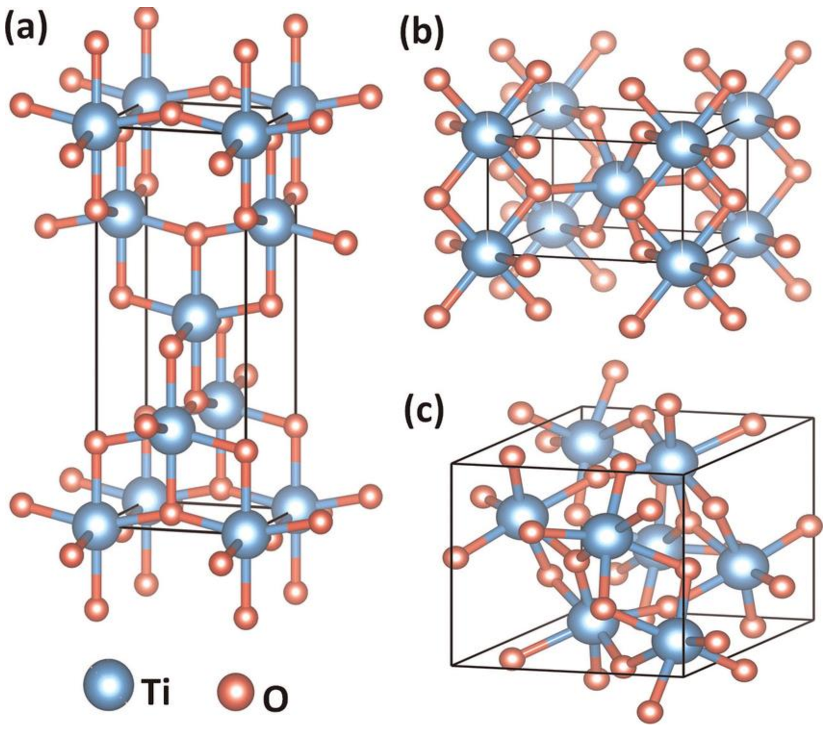


*Fig. 8: Crystal structures of $TiO_2$ phases; (a) anatase, (b) rutile, and (c) brookite [81]*

## 2.5 Conclusion

This chapter has presented detailed literature on the current problem of transformer oil limitations. It is evident from the literature that the use of natural ester oil for transformer insulation presents challenges with the breakdown strength at higher hotspot temperatures as well as speed of streamers. With the ever-growing demand for electrical power, it is inevitable that transformers operate at full capacity. In such conditions a consistently sustainable dielectric strength is necessary for the insulation oil. The presented studies have confirmed that the use of $TiO_2$ nanoparticles can provide positive results to the enhancement of the breakdown voltage of natural ester oil. Specific interest is on the good thermal properties associated with $TiO_2$. With natural ester oils having an increased risk of much higher hotspot temperatures, a nanomaterial that can withstand the temperature changes while improving the breakdown voltage is a critical need. $TiO_2$ is a promising solution, however, there is a need to find the best phase and the concentration loading with the most impact on the natural ester oil.

The presented literature review gave extensive studies and results on $TiO_2$ nanofluids based on both the uniform and non-uniform electric field experiments. However, the present work is focused on the developmental study of nanofluids for transformer insulation. Therefore, the uniform electric field test is used for breakdown strength testing following the IEC60156 standard for new insulating liquids. All analysis and conclusions on breakdown strength throughout the rest of the dissertation will therefore be based on the uniform electric field. The non-uniform electric field is later used to investigate the impulse breakdown streamer velocities of the two nanofluid phases in questions.

The next chapter presents the characterisation and preparation of the materials and the resultant nanofluids to ensure improvement of the breakdown voltage streamer velocities.

# Chapter 3 Materials and Methods

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*The previous chapter presented literature review on the use of natural ester oils in power transformers, highlighting the strengths and shortfalls. The benefits of using $TiO_2$ nanofillers to enhance properties of the natural ester oil was discussed. A research gap was identified on the crystalline phase of $TiO_2$ nanoparticles that results in improved dielectric strength of the base insulation oil. In this chapter, the method of synthesizing anatase and rutile $TiO_2$ nanofluids, is formulated. The nanoparticles in the two phases, anatase and rutile $TiO_{2,}$ as well as the natural ester oil, are firstly characterised physically and chemically, to identify and confirm their properties to the manufacturer specifications. All material conformed to specifications and the two phases were deemed comparable and adequate for the experimental study. Six nanofluids were synthesized, three per nanophase, loaded at 0.01%, 0.03% and 0.05% volume of the base oil. The nanofluids were further characterised to confirm even dispersion of nanoparticles. A UV-Vis spectra confirmed the uniform dispersion of the resultant nanofluids as required.*

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## 3.1 Introduction

The work carried out is based on developing an insulation product with improved dielectric properties. Preparation of the materials and the resultant nanofluid is thus the most critical part of the work. In this chapter, the properties of the nanoparticles used as well as the ester oil are presented and discussed. Section 3.2 presents characterization of the materials, the section presents analysis of the different materials as per factory delivery specifications. In section 3.3, the process of synthesizing the nanofluid is presented, with preliminary results of the fluid characterisation.

## 3.2 Material Characterization

The materials used for nanofluid synthesis were both sourced off-the-shelf. Verification and characterisation of the properties is therefore necessary to ascertain the base materials and ensure the desired nanofluid is indeed synthesised.

### 3.2.1 Host Oil Characterization

The base oil used in the current work is a canola ester oil. The oil is chosen based on the good dielectric properties that it has already shown in existing studies, and as discussed in chapter 2. The Midel 1204 canola natural ester oil was used. Table 3 presents the factory specifications of the oil against the IEC standard limits for transformer oil. Next to be characterised was the nanoparticles.

*Table 3: Midel canola-based ester oil properties*

| Midel 1204 Properties | | |
|---|---|---|
| **Property** | IEC 62770 Limit | Measured |
| **Dielectric Breakdown (kV) (2.5 mm gap)** | ≥ 35 | 66.3 |
| **Moisture Content** | ≤ 200 | 15.09 |
| **Dissipation Factor @90°C** | ≤ 0.05 | 0.004 |
| **Density @20°C (g/cm3)** | ≤ 1.0 | 0.92 |
| **Viscosity @40°C (mm2/sec)** | ≤ 50 | 37 |

### 3.2.2 Nanoparticles Characterization

The $TiO_2$ nanoparticles used to create the nanofluids were commercially sourced from SkySpring Nanomaterials Inc. For optimal comparability, the two polymorphs sourced were of similar physical properties, that is, anatase and rutile $TiO_2$ at 5-30 nm diameter and 95% purity. Table 4 shows these properties. It is notable that the specific surface area is slightly different for the two items. This is consistent with their distinctively different structures as discussed in Chapter 2.4.

*Table 4: $TiO_2$ nanoparticles' supplier specifications*

| $TiO_2$ Nanoparticles Properties | | |
|---|---|---|
| **Property** | **Rutile-$TiO_2$** | **Anatase-$TiO_2$** |
| Purity (%) | 99.5 | 99.5 |
| Average diameter (nm) | 10 - 30 | 10 - 30 |
| Specific surface area (m2/g) | ~50 | > 50 |

The nanoparticles were microscopically characterized in order to identify their size, morphology and purity. X-Ray Diffraction (XRD) and Raman Spectra were used to confirm the purity and morphology of the nanoparticles. XRD additionally gives the size and particle distribution. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were both used to produce imaging of the nano powders. This confirms the structures, size, as well as dispersion of particles. In this section the results obtained from these instruments is presented and discussed.

#### 3.2.2.1 Raman Spectra

Raman spectroscopy uses laser light to direct rays of light onto a molecule which is then scattered at different wavelengths, depending on the nature of the tested molecule. The technique results in a spectrum that consists of several peaks indicating the light intensity at the different wavelengths. These wavelengths are dependent on the different vibrations caused by corresponding molecular bonds. These are known as Raman shifts. Different particles therefore have distinct Raman Spectra. The shape and intensity of the Raman peaks is dependent on the size and purity. Increased intensity is consistent with increased particle size [82].

The Raman spectra for pure rutile $TiO_2$ and anatase $TiO_2$ are given in Fig. 9 and Fig. 10, respectively. It is notable that the two nanoparticles have different characteristic peaks. Anatase $TiO_2$ has a sharp peak at 142±1 $cm^{-1}$, followed by gentler ones at 193±1 $cm^{-1}$,395±1 $cm^{-1}$, 518±2 $cm^{-1}$, and 635±1 $cm^{-1}$. Rutile $TiO_2$ has Raman shifts at 235±5 $cm^{-1}$, 448±2 $cm^{-1}$, and 609±2 $cm^{-1,}$ with the latter two being the most prominent [83].

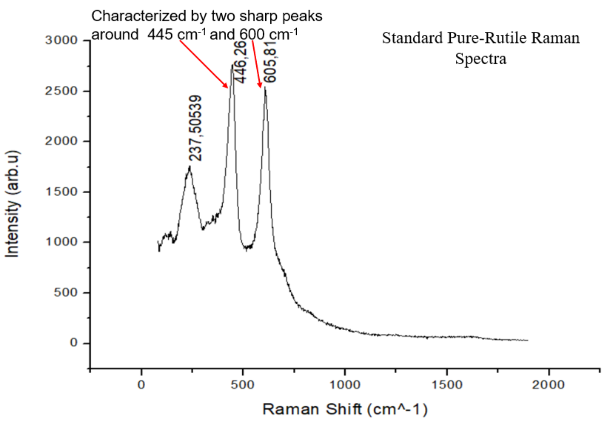



*Fig. 9: Rutile $TiO_2$ standard Raman spectra*

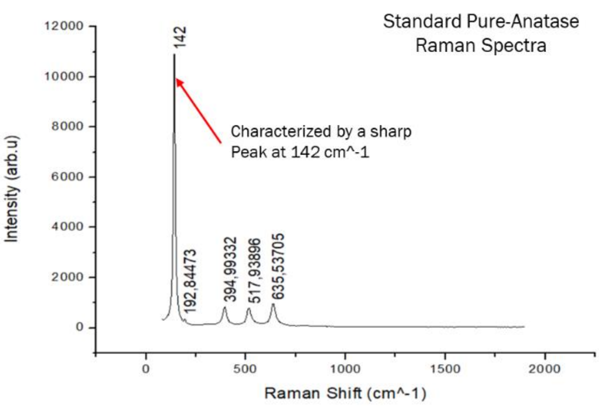



*Fig. 10: Anatase $TiO_2$ standard Raman spectra*

These spectra are used to validate with the sourced $TiO_2$ nanoparticles, with the expectation that they match to confirm the particle morphology and purity. In Fig. 11, The obtained rutile spectrum is presented and superimposed on the standard pure rutile Raman spectra from Fig. 9. Multiple samples of data were taken at different spots of a grid, laced with the nanoparticles, in order to ascertain the repeatability of the results. It can be denoted in the figure that the resultant peak positions coincide with those of the pure anatase spectra fully, confirming that the morphology is rutile. This is consistent with the 99.5% purity indicated in Table 3. There exists a slight difference in the intensities of the peaks, although the profile is identical to that of the standard profile. The reduced intensity on the tested particles can be attributed to possible size differences given that the nanoparticles in question are very small.

The anatase $TiO_2$ Raman spectra is given in Fig. 12. The results also show clear correlation to the phase pure anatase $TiO_2$. Only a slight deflection from the phase pure spectra, also consistent with the purity and size as per specifications in Table 4. It is worth noting that the scales differ for the two phases' spectra due to the intense spike on anatase results. Therefore, the deflection between the standard pure spectra and the tested samples are in fact comparable between rutile and anatase $TiO_2$. While the Raman has validated the nanoparticles in question, it is necessary to characterise nanoparticles with different forms of microscopy to eliminate possible errors and confirm validity. X-Ray Diffraction another technique useful in nanoparticle characterisation which is presented in the next section.

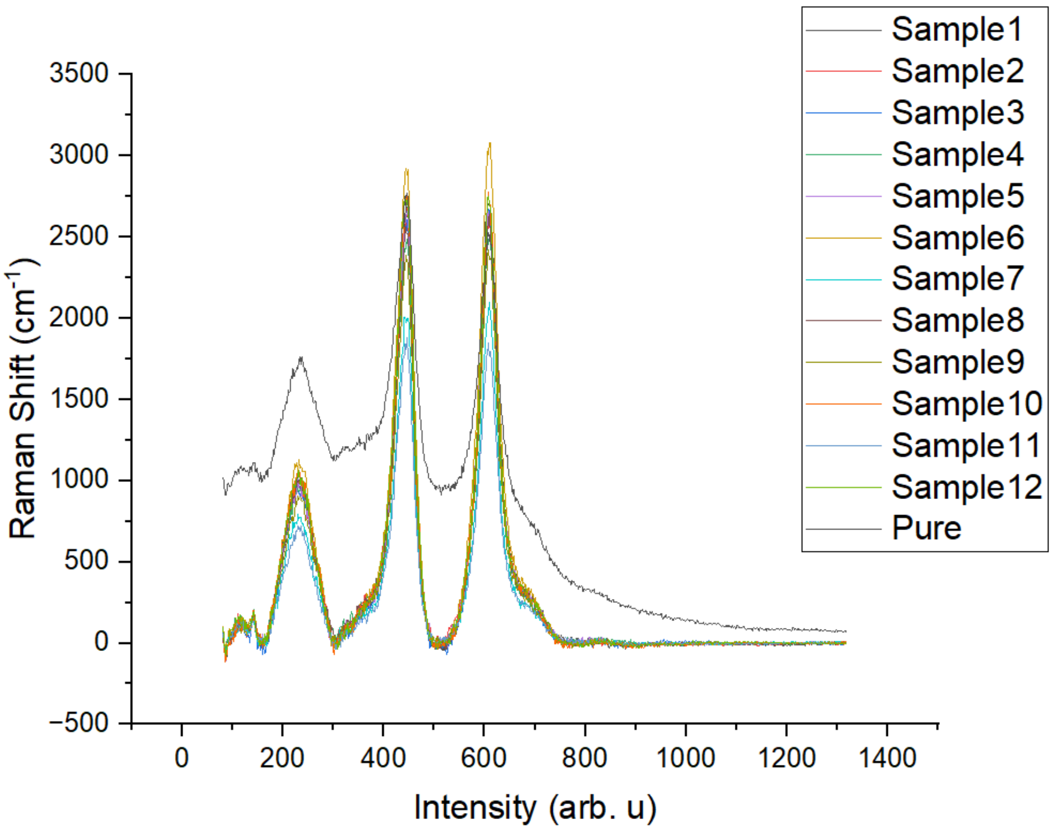



*Fig. 11: Raman spectra for rutile $TiO_2$*

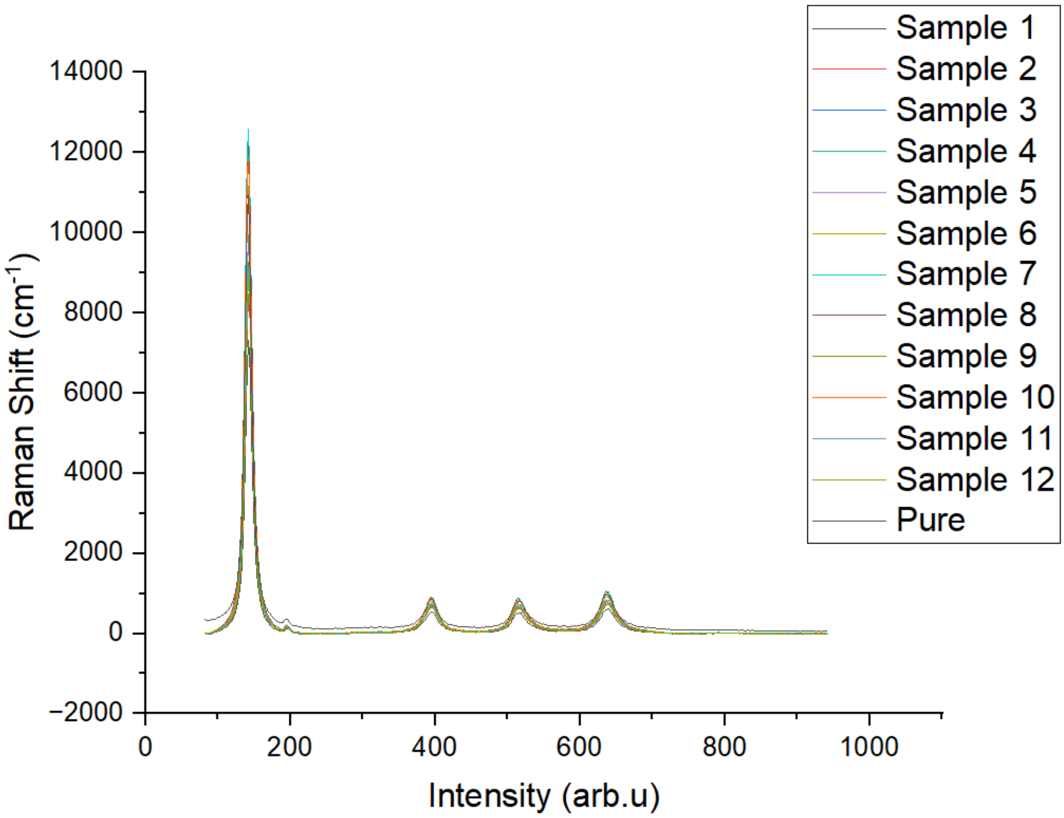



*Fig. 12: Raman spectra for anatase $TiO_2$*

### *3.2.2.2 X-Ray Diffraction*

X-Ray diffraction (XRD) is another technique that is widely used for chemical characterisations. From an XRD profile, the details of a particle's type and morphology can be determined. Additionally, the average size and the weight percentage of phases (in the case of mixed phase particles) can be determined. In XRD, a beam of X-rays is directed to the tested specimen. They are diffracted from the particle at the same angle as the incident angle.

Fig. 13 depicts the typical characteristic spectra for $TiO_2$ nanoparticles in their pure and mixed phases, with R and A denoting rutile and anatase phase respectively. Evidently, the off-the-shelf rutile and anatase nanoparticles XRD profiles in Fig. 14 and Fig. 15 confirm that the nanoparticles are mostly phase pure. This is consistent with the 99.5% purity in the product specifications as well as the corresponding Raman spectra. The rutile profile, however, shows a slight difference, which indicates a slight presence of anatase. This is not uncommon for rutile phase to have traits of anatase because the synthesis of rutile phase involves transforming $TiO_2$ past the anatase phase, to a finally stable rutile phase. The crucial thing is to ensure that the nanoparticles are in their purest form and are comparable to each other for the purpose of the research. With the aid of the Eqn 2 below, the weight percentage of anatase present in the rutile phase is calculated. It is found to be 1.91%, which is negligible. The off-the-shelf rutile $TiO_2$ nanoparticles can thus be used to identify the properties of the phase as required.

$$XA\ (\%) = 100/\ (1 + 1.265 I_R/I_A) \ \ldots\ldots\ldots\ldots\ (2)$$

*where;*
*$X_A$ is the weight percentage of Anatase*
*$I_A$ is the intensity of anatase peak at $2\theta = 25.25^\circ$ (0,52738)*
*$I_R$ is the intensity of rutile peak at $2\theta = 27.42^\circ$ (15,97835)*
*Therefore, $X_A = 1.913\%$*

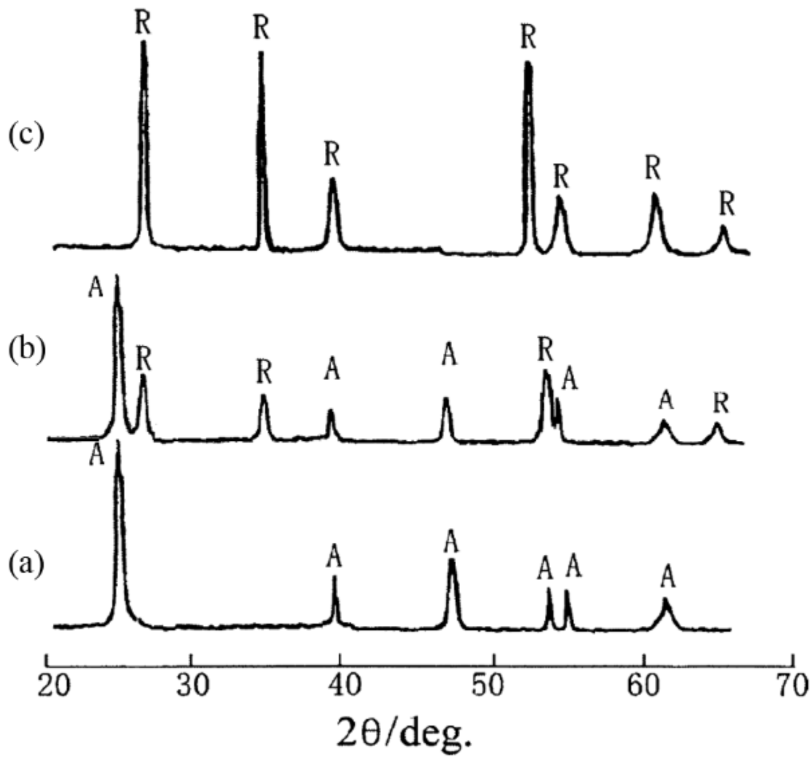



*Fig. 13: Typical characteristic X-Ray Diffraction patterns of $TiO_2$ phases; (a)anatase, (b) anatase-rutile and (c) rutile [79]*

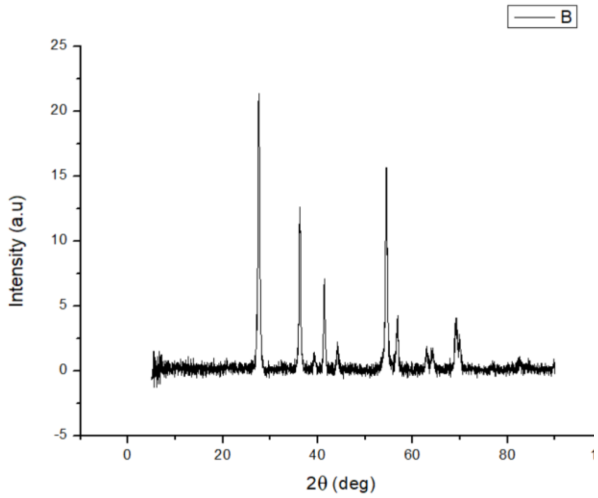



*Fig. 14: Rutile $TiO_2$ measured X-Ray Diffraction pattern*

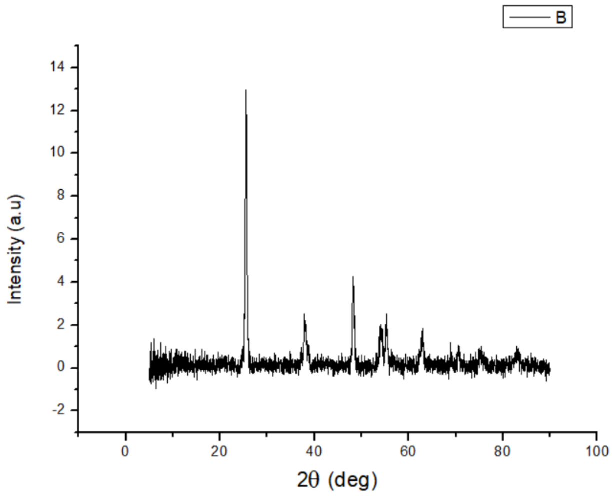



*Fig. 15: Anatase $TiO_2$ measured X-Ray diffraction pattern*

### 3.2.2.3 Transmission Electron Microscopy

Further characterisation of the nanoparticles was conducted through Transmission Electron Microscopy (TEM). TEM is a technique in which a beam of electrons is accelerated through a film with the specimen under observation. Some of these electrons, based on the transparency of the analysed specimen, will then be transmitted through to a screen below the specimen. This forms an image of the specimen which is captured by a camera underneath.

The TEM technique can be used to provide details about a particle's morphology, size and structure which are useful in identifying the phase and confirming comparability of the nanoparticles.

The TEM images of rutile $TiO_2$ and anatase $TiO_2$ are presented in Fig. 16 and 17 respectively. On the images, it is evident that both nanoparticles are semi-spherical, and their size is distributed between 5-30 nm as per specifications above. This confirms the comparability of the particles used, the intent is to have nanoparticles of similar physical properties with only the crystalline phases being the difference. It is however notable that the rutile phase appears to agglomerate more than the anatase from the figures. This is attributed to the intrinsic nature of the phases. The synthesis process of the nanofluids involves deagglomerating nanoparticles, hence this detail does not affect the comparability of nanoparticles.

With the aid of the below TEM images and the use of the *Image J* image processing software, the size distributions for the nanoparticles were obtained as in Fig. 18 below. From both distributions it is notable that the nanoparticles were mostly between 25 – 30nm in diameter with mean of 28.8 nm for rutile and 27. 2 nm for anatase. There is evidence of sizes larger than 30 nm, mostly for rutile. This may be attributed to the agglomeration which causes some particles to appear larger in diameter.

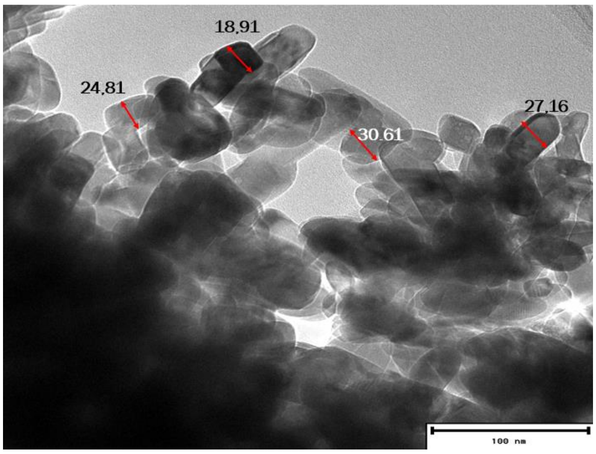



*Fig. 16:TEM Image of rutile $TiO_2$ nanoparticles*

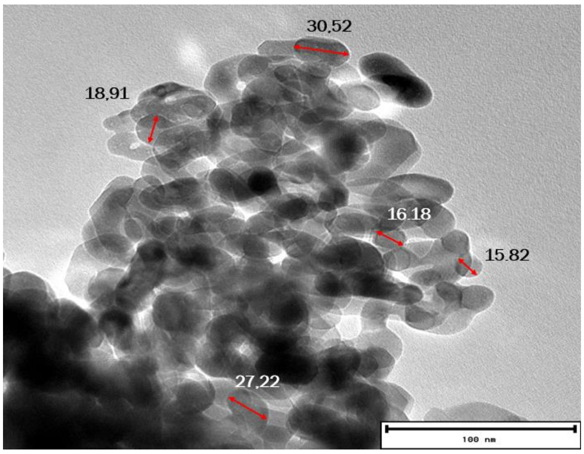



*Fig. 17:TEM image of anatase $TiO_2$ nanoparticles*

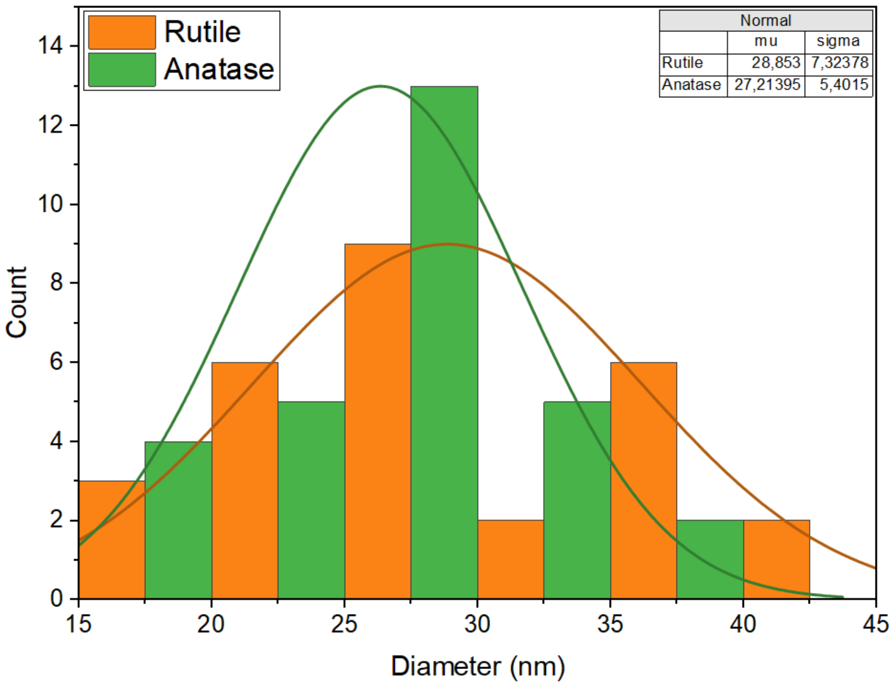



*Fig. 18: Rutile and Anatase $TiO_2$ Sample Particle Size Distribution as determined using the Image J software.*

It can be concluded from the above discussed particle characterisation techniques that the nanoparticles as sourced were pure rutile and anatase as per specifications. Additionally, the comparability of the two phases was assessed. Based on the size, appearance, and level of purity of the nanoparticles, the two types of $TiO_2$ nanoparticles have similar properties except for differences in crystalline phases. Comparability of the nanoparticles is essential in ensuring that the resultant nanofluid effects are associated with only the differences in the nanoparticles' phase influences on the base dielectric fluid. The next section discusses the process of synthesizing nanofluids and the characterisation thereof.

## 3.3 Nanofluid Synthesis

The influence of nanoparticles on dielectric material differs and is dependent on different properties of the nanoparticles. The effects of nanoparticles on the base fluids, as previously discussed, is mainly due to the physiochemical interaction between the particle and the fluid. The important aspect is the active surface area, which is directly linked to the size of the nanoparticle. Secondly, the amount of nanoparticle loading is a significant factor. The more particles there are in a volume of oil, the more prone to agglomeration are the nanoparticles. This is because nanoparticles normally move around and may be attracted to each other and attach due to the Van der Waals forces. Having a high concentration of nanoparticles will lead to collision of nanoparticles and hence more agglomeration [4], [61], [84]. Agglomeration of nanoparticles is undesired because, when the size of the particle is increased, it may exceed the density of the base oil, and sediment easily. The breakdown voltage is also negatively impacted by agglomeration, some studies also show a decrement of breakdown voltage beyond the base fluid's value due to agglomeration [4], [73], [85]. This is essentially because agglomerated nanoparticles get to micrometres in size, which is then a significant size of a suspended particle that acts as contamination in the oil. It is known from the principles of breakdown theory, that for polarisation and hence initiation of breakdown, the force experienced by the suspended particle is given by Equation 3 below. Where $r$ denotes the radius of the particle, $\varepsilon$ the permittivity of the particle and $\varepsilon_{oil}$ the permittivity of the oil. With $r$ cubed, a nanoparticle will result in very small and negligible forces. However, agglomeration of nanoparticles increases the diameter and hence the force becomes significant enough for polarisation [61].

$$F = r^3 \varepsilon_{oil} \frac{\varepsilon - \varepsilon_{oil}}{\varepsilon + 2\varepsilon_{oil}} \frac{dE}{dx} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. (3)$$

Thus, very small sizes and concentration of nanoparticles is desired. This is supported further in the studies Fal et al [54], wang et al [73] and Koutras et al [86], who confirm the requirements for a good nanofluid alternative for transformer use as that with small size, concentration as well as uniformly distributed and deagglomerated nanoparticles. They also show that high concentrations of nanoparticles lead to agglomeration and hence a possible conductive path is formed between electrodes, which leads to reduced breakdown voltage.

Good distribution and dispersion of nanoparticles is achieved with a good synthesis process. The section discusses the synthesis process of nanofluids used to ensure deagglomeration and uniform dispersion of nanoparticles.

### 3.3.1 Nanofluid Synthesis Techniques

There are two methods that are employed for the synthesis of nanofluids. Namely, one-step and two-step methods. In both methods the intention is to produce fluids with well dispersed and deagglomerated nanoparticles. What separates the two methods are the process and equipment used in the techniques.

In the one-step method, the nanofluid is formed by simultaneously making and dispersing the nanoparticles within the oil. It eliminates unwanted transportation and contamination of particles during process. The one step method employs sophisticated equipment and techniques to perform direct evaporation and condensation of nanoparticles within the base fluid. The process usually occurs in a vacuum chamber where, the nanoparticles and the base fluid are evaporated and evenly dispersed in the gaseous state. The even mixture of the nanoparticles and base fluid then undergoes condensation and forms a uniformly dispersed nanofluid. This method avoids agglomeration, and the vacuum chamber ensures no impurities or contamination during the process. This method is illustrated in Fig. 19. Although the method has proven to be the ideal method, with fewer risks, it is unfavoured due to the high costs implicated by the required equipment and therefore not used in the present work.

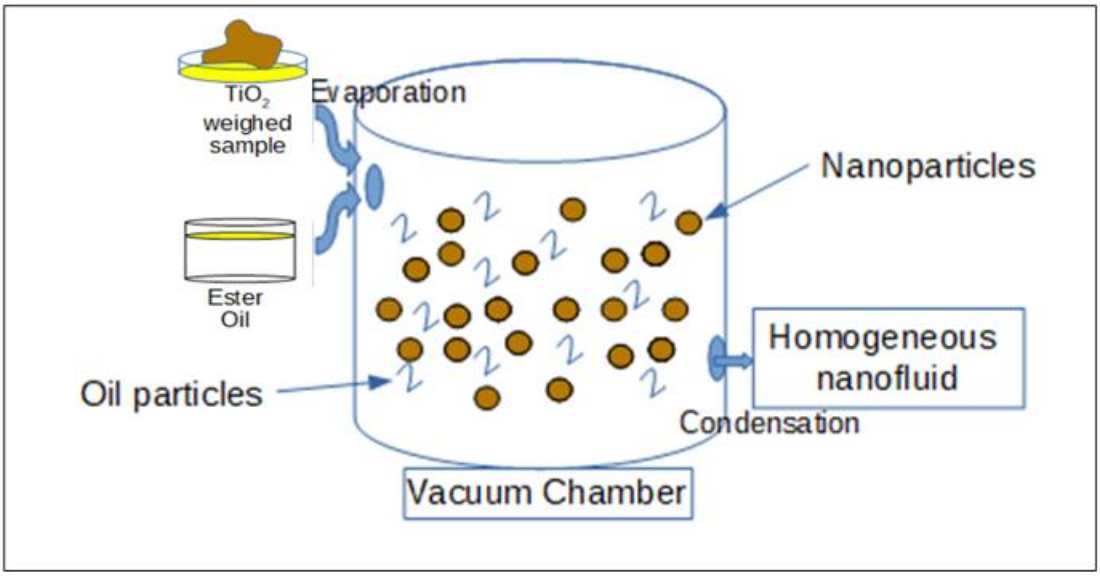



*Fig. 19: 1-Step Nanofluid Synthesis Method*

The Two-Step method is an economical choice since it requires simple techniques with affordable and common equipment. Similarly, there is a trade-off with the risk of contamination. Thus, care has to be taken to minimize the risks by sealing apparatus as much as possible. The method entails producing the nanofluid in 2 stages, the first being creating of the nanopowders and directly mixing the nanopowder with the fluid, the second is dispersing the nanopowders within the fluid to finally form a uniformly dispersed nanofluids. Fig. 20 illustrates the process. The dispersion part is the most critical to ensure deagglomeration of particles and avoid sedimentation of nanopowders. To uniformly disperse the nanoparticles, a magnetic stirrer, ultrasonicator or high-pressure homogenizer are used. An ultrasonicator has been found to be both economical and effective in forming uniform composites of nanopowder and liquids. The ultrasonicator uses high frequency vibrations in water to force particles to separate. Most literature recommend the use of both the stirrer and the ultrasonicator to distribute and deagglomerate nanoparticles fully within the oil. Lv et al [62], studied the effects of the use of a magnetic stirrer, ultrasonic bath, and an ultrasonic probeand they found favourable results. The 2-step method with both magnetic stirrer and ultrasonicator is therefore used in the present work.

There is no standardised specifics in the 2-step procedure, however literature has suggested the optimal times for magnetic stirring particles to be between 15min – 30 min [60], [66], [69], [77], [86]. For Ultrasonication, the times ranging from 15min-2hrs are reported in literature [69], [71], [75], [77]. An optimal time of 75 min was reported by Ma et al [87], after which the particles start to agglomerate again due to the Van Der Wal's forces and the fact that the particles started colliding with each other. Based on the presented literature, the synthesis process for the current study was formulated and is discussed in the next subsection.

### 3.3.2 Synthesis Process

To compare the characteristics of anatase and rutile $TiO_2$ nanofluids, different amounts of nanoparticles were added to the natural ester oil and analysed further to find the optimal concentration based on breakdown voltage. Three concentrations were used per nanofluid, that is 0.01%, 0.03%, and 0.05% of $TiO_2$ in rutile and anatase polymorph. The 2-step nanofluid synthesis method was employed as illustrated in Fig. 20.

The process begins with weighing the oil samples according to the above concentrations. 500 ml of the natural ester oil samples were weighed and heated with a magnetic stirrer up to 60 ˚C, then the weighed nanoparticles are added to the oil samples and stirred for a period of 30 minutes. Following this is an ultrasonication process of up to 1 hour, where the nanoparticles are further deagglomerated and dispersed evenly within the oil. Lastly the oil samples are oven dried for 24 hours to eliminate excess moisture that could have been accumulated during the synthesis process.

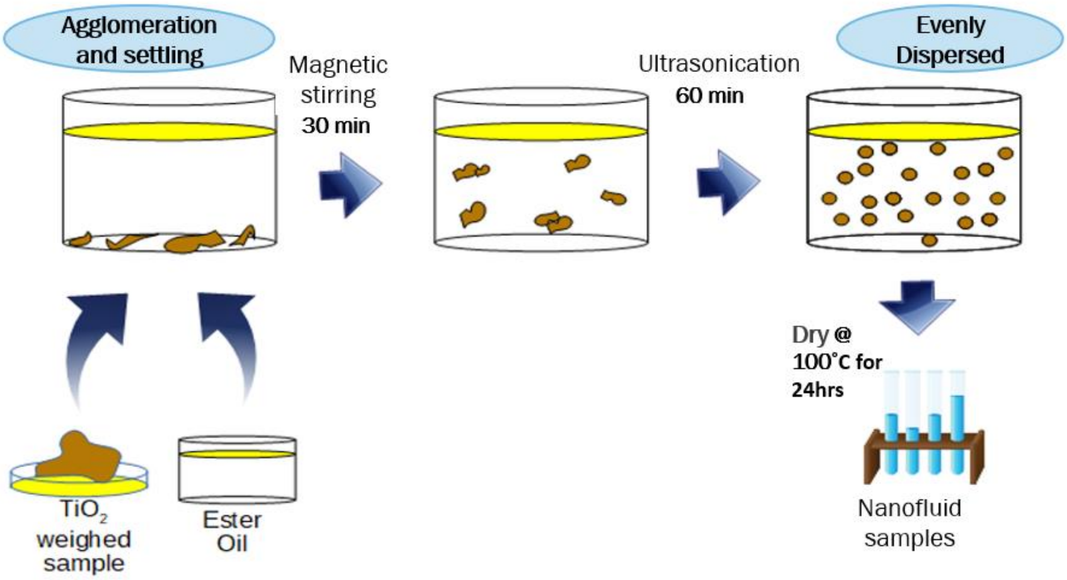



*Fig. 20: 2-Step Synthesis Method of Nanofluids*

At the end of the synthesis process, 7 different samples were prepared, comprising of $TiO_2$-rutile in 0.01%, 0.03%and 0,05%, as well as $TiO_2$-anatase in 0,01%, 0,03% and 0,05%. The seventh sample was control being that of the pure natural ester oil. The nanofluids are renamed from here-on as per Table 5 below.

*Table 5: Prepared nanofluid samples*

| Name | Nanofluid concentration |
|---|---|
| **Pure NE** | Pure Natural Ester |
| **Nano R1** | 0,01% $TiO_2$-rutile |
| **Nano R2** | 0,03% $TiO_2$-rutile |
| **Nano R3** | 0,05% $TiO_2$-rutile |
| **Nano A1** | 0,01% $TiO_2$-anatase |
| **Nano A2** | 0,03% $TiO_2$-anatase |
| **Nano A3** | 0,05% $TiO_2$-anatase |

### 3.3.3 Nanofluid Characterization

The resultant nanofluid specimen are depicted in Fig. 21. Notably both rutile and anatase nanoparticles turn the base Pure NE into whitish colour which gets denser with more concentration of $TiO_2$. The anatase samples are slightly lighter than the rutile counterparts.

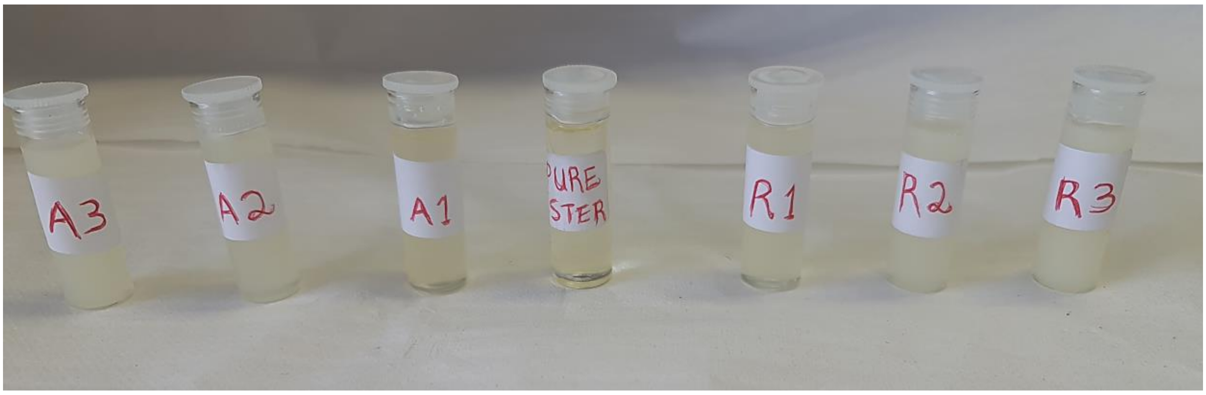
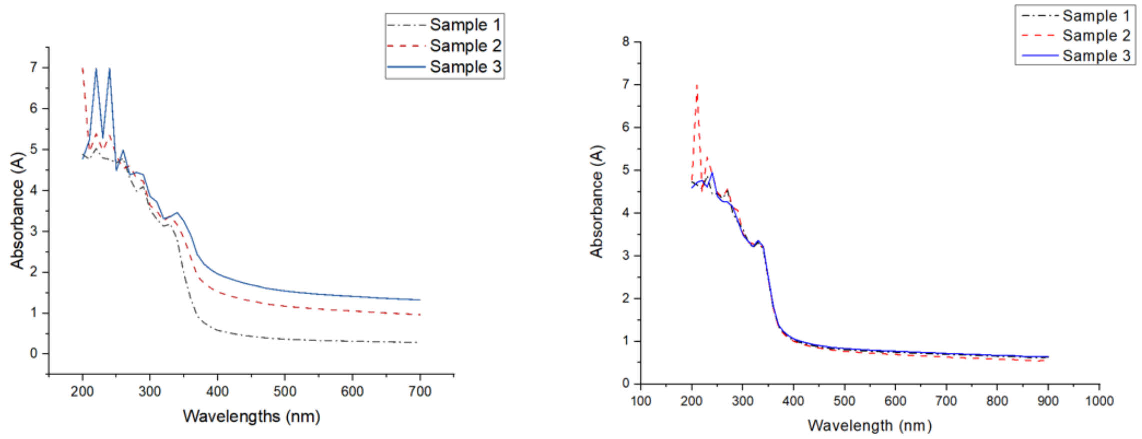



*Fig. 21: Experimental Samples for Pure Ester and Nanofluids*

Uniformity of nanoparticle distribution is essential in the synthesis. To confirm this, and stability of the resultant synthesized nanofluid, a UV-Vis spectroscopy analysis was used. This technique was also employed by Sadeghi et al [88], and Ma et al [87], to analyse stability of nanofluids. The UV-Vis instrument measures the absorption of UV and visible light rays shown through a tested specimen. When the absorption spectrum of Pure NE is referenced, the changes to the absorbance on resultant nanofluid will be due to the added nanoparticles. When multiple samples are assessed from the same fluid, the resultant UV spectrum is expected to be identical for uniformly distributed particles.

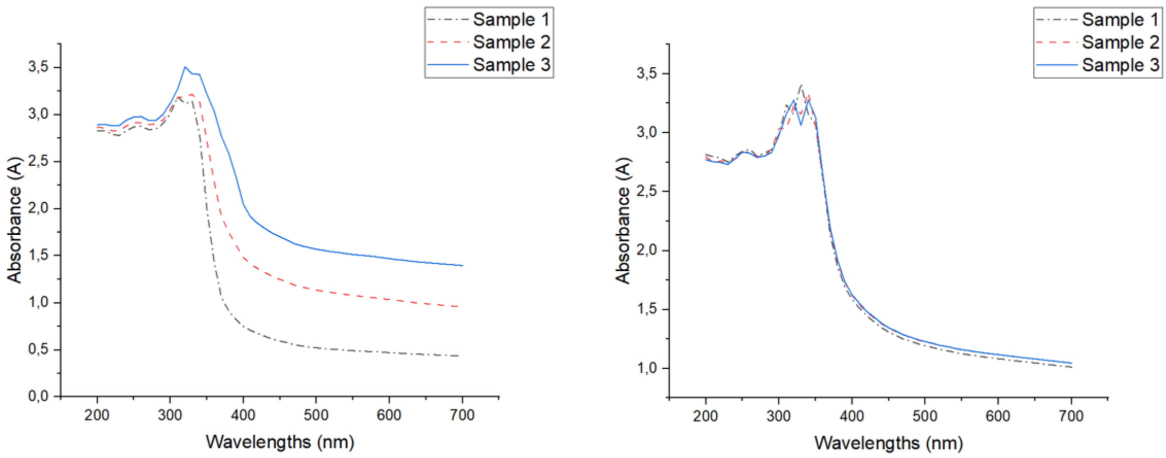
Fig. 22 and Fig. 23 present absorbance spectra of anatase and rutile nanofluids respectively. Each figure shows the spectra of three samples from the same nanofluid sampled before and after the sonication process. It is notable that the two nanophases have distinct absorbance spectra, this supports the fact that the nanophases have significant differences. It is also worth noting that the samples on Fig. 22 (a) and Fig. 23 (a), have similar trends however the absorbance rates differ. This is because the amount of absorbance increases with the increase in particle loading. The samples with spikes of absorbance suggests agglomeration and non-uniformity.

The spectra of samples taken post sonication in Fig. 22 (b) and Fig. 23 (b) indicate improved dispersion stability of the samples as presented. Notably, the 3 samples per nanofluid have almost identical spectra with the exception an error at around 250 nm for anatase and at 350 nm for the rutile nanofluid. This means for the prepared nanofluids, when tested 3 times, they exhibited the same absorbance rates. This indicates that indeed the nanoparticles were mostly uniformly dispersed within the oil, as expected for an optimal nanofluid. What remains is to ascertain the optimal nanoparticle loading for transformer use, which is done through breakdown voltage testing. The next chapter presents the test and findings.




(a) Before sonication (b) After sonication

*Fig. 22: UV-Vis absorbance spectra for anatase nanofluid (a) before sonication, (b) after sonication*




(a) Before sonication (b) After sonication

*Fig. 23: UV-Vis absorbance spectra for rutile nanofluid (a) before sonication, (b) after sonication*

## 3.4 Conclusion

This chapter has presented the details and characteristics of the two $TiO_2$ nanoparticle phases and the resultant nanofluids to be experimented on in this study. The preparation processes have been presented. It is noted that the comparability of the tested nanofluids is essential for finding effects of the nanophases as per the research question. Upon particle and nanofluid characterisation discussed in this chapter, it can be concluded that the nanofluids created are comparable. The synthesis process has also been tested to ascertain that evenly dispersed nanofluids were created. The following experiments on the fluids will therefore provide necessary results for the comparison of the effects of the nanophases.

# Chapter 4 Breakdown Voltage Under Uniform Electric Fields

*The background of the need for the comparison of the anatase and rutile phases of $TiO_2$ for breakdown voltage improvement have been discussed in the previous chapters. In Chapter 3 the preparation of the nanofluids of the two phases has been presented. The chapter presented the characterisation of the two nanophases prior to nanofluid synthesis. The use of different microscopies and the literature confirmed the purity and comparability of the nanoparticles. The synthesis of six different nanofluids, of 0.01%, 0.03% and 0.05% concentration of anatase and rutile $TiO_2$ was presented as well as the validation thereof. In the present chapter, the nanofluids are tested as insulation and compared further through the uniform field breakdown voltage experiments. Each of the nanofluids' breakdown voltages were compared at ambient temperature to determine the optimal concentration for breakdown voltage improvement. The concentration of 0.03% was found as the optimal percentage loading and used for temperature dependent breakdown voltage tests. The anatase nanofluid emerged superior to the rutile nanofluid at ambient temperature. However, the rutile phase was determined to be the overall better phase of $TiO_2$ for uniform field breakdown voltage improvement of natural ester oil, having a more consistent effect on the temperature-dependent test.*

## 4.1 Introduction

The uniform electric field breakdown voltage test is one of the main tests done to characterise transformer insulation oil. The intent of the test is to check for impurities such as moisture or solid particles in the oil through quantifying the average breakdown voltage of the oil. When a new oil is tested, the resultant breakdown voltage is expected to be at its maximum and will decrease as the oil ages or impurities are added. The IEC 62770 standard: *"Fluids for electrotechnical applications — Unused natural esters for transformers and similar electrical equipment"* [89], specifies the minimum breakdown voltage for natural esters as 35 kV per 2.5 mm electrode gap for large power transformers. The test method specified for breakdown voltage is the IEC60156 standard. This test method is used in the nanofluids' experiments. The resultant breakdown voltage is used to compare between the nanofluids and the pure natural ester oil. In this chapter, the uniform field experiment and results are presented. The test cell design and experimental set-up are presented, followed by the experimental process and then the results. The comparison of the breakdown voltage of the nanofluids is presented, as well as the temperature dependent breakdown voltage results for the pure natural ester oil and the two $TiO_2$ nanofluids.

## 4.2 Experimental Method

The experimental process for uniform field breakdown voltage tests was 2-fold. The aim was to answer the following questions as outlined in Chapter 1:

1) *What is the optimal concentration of anatase and rutile $TiO_2$ of a specific size and shape, that will result in the most improved breakdown strength compared to the unfilled liquid in a uniform electric field environment?*

2) *Which of the two phases of $TiO_2$ results in the most improved breakdown strength at higher temperatures in a uniform electric field environment?*

The first part entails testing each of the samples (A1, A2, A3, R1, R2, R3, Pure Ester) at ambient temperature, and determine the optimal nanoparticle loading per phase for the most improved breakdown voltage. In the second part of the experiment, the optimal sample per phase of $TiO_2$ is then used to perform temperature dependent breakdown voltage tests. In Chapter 2 it was noted that the hotspot temperature of natural ester-filled transformer can reach as high as 160 ˚C and is the concern in this study. However, due to safety and practicality of performing the tests on heated oil, the experimental temperature was capped at 140 ˚C. The following sections detail the experimental methodology.

### 4.2.1 The Test Cell

The test cell used was designed to allow continuous heating of the oil for temperatures up to 140 ˚C. A transparent Pyrex glass was used to form the test cell. This type of glass can withstand temperatures as high as 500 ˚C. Thus, the test cell could be directly heated at higher temperatures. In addition to the temperature requirements, the cell was also designed to withstand voltages up to 100 kV without having external flashover. This voltage was used for the design because most literature shows the breakdown voltage of 2.5 mm uniform field electrode gap of ester-based nanofluids at voltages between 50 kV – 80 kV. Therefore 100 kV is used as the maximum possible voltage. Since the IEC 60156 standard requires small electrode gaps in a small volume (350 ml - 500 ml), the cell size is normally small. With the higher breakdown voltages associated with natural esters, a surface flashover is possible. To prevent this, the surface creepage distance was increased through appropriate cell geometry design. The test cell was equipped with a side-by-side geometry of sphere-sphere electrodes. The glass was shaped to extend out to the sides of the electrodes, creating an increased creepage distance along the surface as shown in the image in Fig. 24.

The electrodes used were of sphere-sphere brass material, as per standard specifications. The spheres were of 12.5 mm diameter, spaced 2.5 mm apart. The lid was made from nylon material with a 5mm diameter opening for insertion of a temperature probe.

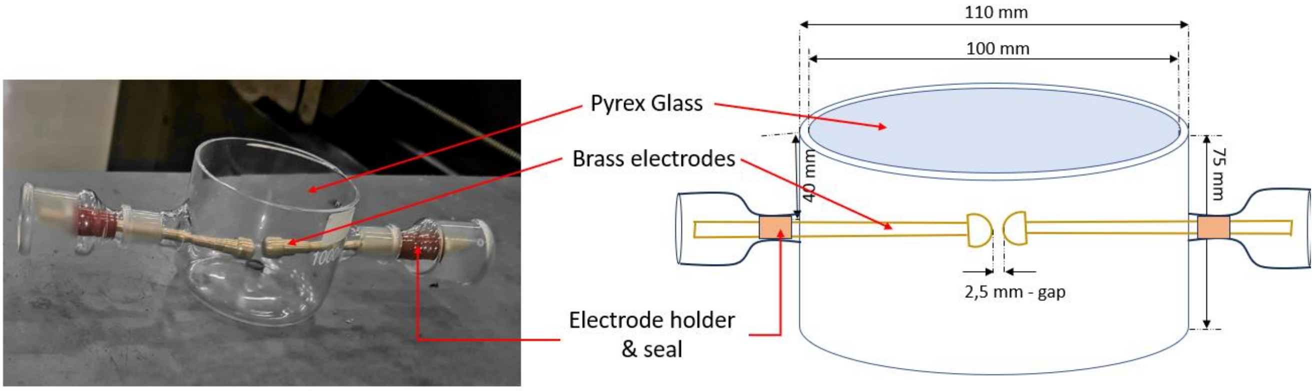



*Fig. 24: Uniform Field Breakdown Voltage Test Cell*

### 4.2.2 The Test Circuit

The circuit used for experiments consists of a variable AC source with 220:140 000 V step-up transformer, a current limiting resistor (water resistor) and the test cell. A voltage divider is connected before the test cell in order to measure the supplied voltage to the test cell safely. The circuit is presented in Fig. 25.

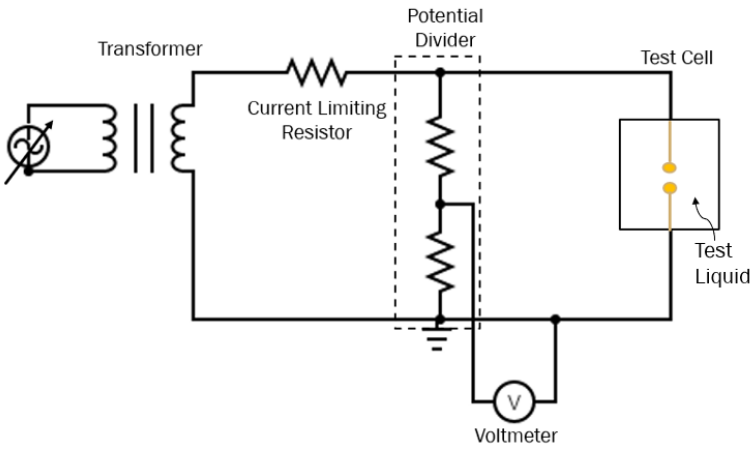



*Fig. 25: Uniform Field Breakdown Voltage Experimental Test Circuit*

### 4.2.3 Experimental process flow and procedure

The overall test procedure comprised of multiple iterations of heating of the insulation fluids and then performing the breakdown tests. Fig. 26 below illustrates the process flow of the experiments.

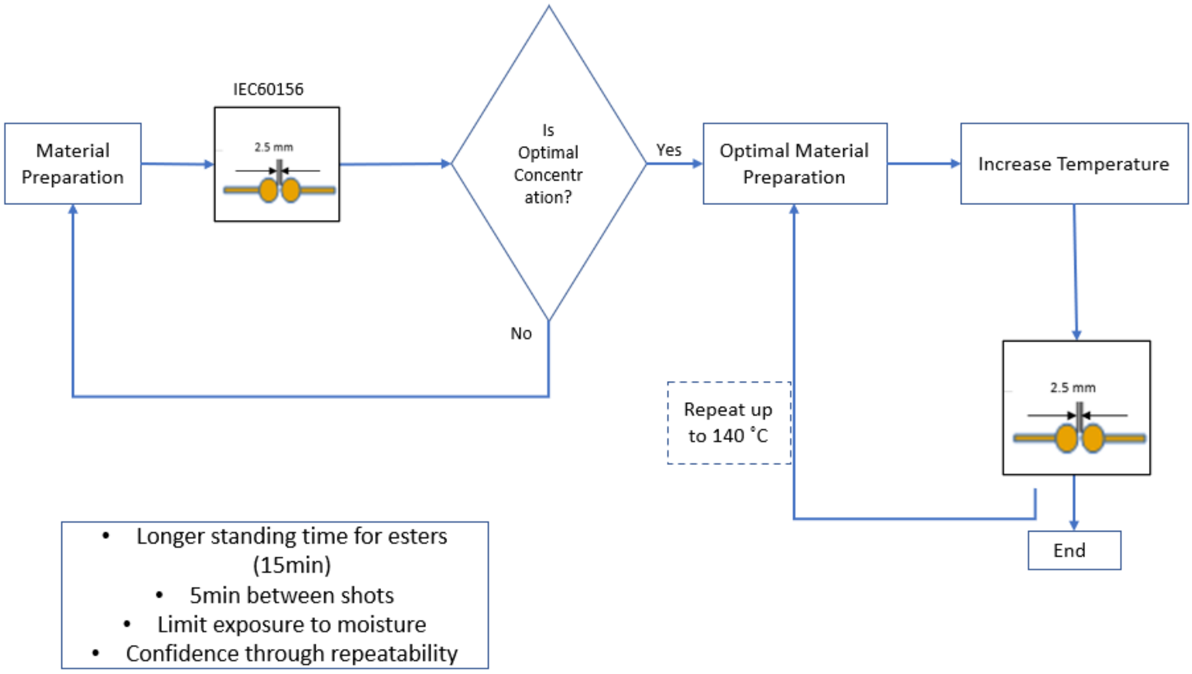



*Fig. 26: Experimental Process Flow*

Preparation of nanofluids was first done as discussed in the previous chapter to create the different fluids for tests. The samples were then heated to specific temperatures and then breakdown voltage tests were done on each sample. To change the temperature of the fluids, a hotplate magnetic stirrer, equipped with a PT1000 temperature sensor was used employed. Each sample was heated continuously to a specific temperature and maintained within ±3˚C throughout the duration of the test.

For breakdown tests, the supply voltage was increased from 0V in steps of 2 kV per second up to the point of breakdown. Six breakdown shots were conducted per oil sample as per standard. A standing time before the first test as well as rest times in-between breakdown shots were added to ensure settling of bubbles before each breakdown is recorded. The IEC60156 standard was under review at the time of testing. However, the posted draft contained increased rest timings specifically for highly viscous oils such as the natural ester oil under experiments. For this experiment the standing time durations were thus adapted. An initial standing time of 15 minutes, and a rest time of 5 min between shots were used. This is also in line with recommendations in the IEC 62770, which states that the standing time before tests should be between 15 - 30 min for natural esters [89].

All tests were repeated at least three times to confirm validity and repeatability of the results. The tests were conducted at temperatures: 20 ˚C, 40 ˚C, 70 ˚C, 100 ˚C, 120 ˚C and 135 ˚C. A total of 18 breakdown shots were therefore performed and recorded per temperature.

## 4.3 Results and Discussion

### 4.3.1 Temperature Effects on the Uniform Field Breakdown Voltage of Pure Natural Ester oil

The results of the uniform field breakdown voltage of pure natural ester are presented in Fig. 27 and Fig. 28. From the results, the average breakdown voltage at ambient temperature (20 ˚C) was found to be 32.9 kV. This is below the manufacturer specified voltage of 66.3 kV as presented in Table 1. This is lightly due to the fact that the oil at the time of use may no longer be at the exact sealed state as per the manufacturer testing. While efforts were made to seal test apparatus, the highly hygroscopic natural ester could gain more moisture during multiple transportation of samples and thus affecting the breakdown voltage. The sample nanofluids in each phase were synthesised from the same oil to be used as a control for every iteration of the tests. This is to ensure comparability of results and minimise the error due to moisture differences. The tests were also repeated at least three times for every tested temperature for repeatability and validation of results. Fig. 28 presents results of the repeated average breakdown voltages of the pure natural ester.

A temperature-dependent study of the breakdown voltage of the tested natural ester oil shows there is significant impact on the breakdown voltage as temperature is increased. The breakdown voltage at ambient temperature averaged at about 32.9 kV and increased to 70 kV at 70 ± 3˚C. The direct proportion between breakdown voltage and temperature is attributed to changes in viscosity that arise as temperature increases and thus pressure also increases. What is interesting however, is that this effect is changed when the temperature increases beyond 70 ± 3˚C. A drop in breakdown voltage is observed at 90 ± 3˚C, followed by an increase in breakdown voltage thereafter. Fig. 28 also shows wider whisker boxes on the box and whisker as temperature increases, indicating increased standard deviation in the breakdown voltage data. This attests to the presented problem of natural ester oil having inconsistencies in breakdown voltage at elevated temperatures.

The trend is also significant to the natural ester oil, as with mineral oil, the breakdown voltage tends to increase as temperature increases up to 80 ˚C, then begins to decay from this point [39], [40], [42]. However, only a consistent drop is reported for mineral oil. The main difference between natural ester and mineral oils is the high hygroscopicity of ester oils. The differences in the breakdown voltage at the higher temperatures could be linked to the changes in the water content present in the oil as the temperature increases. According to P. Rozga et al [39], the turning point of the breakdown voltage rise at 80 ˚C is due to evaporation that initiates as temperatures approach the boiling point of water. This leads to a formation of bubbles, and hence a reduced breakdown voltage. Following this argument, natural ester oil would understandably have a significant impact due to a generally high existence of water content as compared to mineral oil. Of course, ester oils have been found to have the ability to maintain high breakdown strength with the presence of water content. This may explain the sudden increase in breakdown voltage beyond 120 ˚C. A study into the influences of moisture at these high temperatures would best clarify this matter. However, it is not in the scope of the current work.

The current work proposes use of $TiO_2$ to enhance the breakdown voltage of natural ester oil. It is desired that the nanoparticles not only improve the breakdown voltage of the tested natural ester, but also improve the thermodynamics of the oil at these problematic temperatures such that a consistent breakdown voltage is maintained even at such temperatures. In the next sections of this chapter, the nanofluids' breakdown voltages are analysed and the influences of anatase and rutile phases are compared.

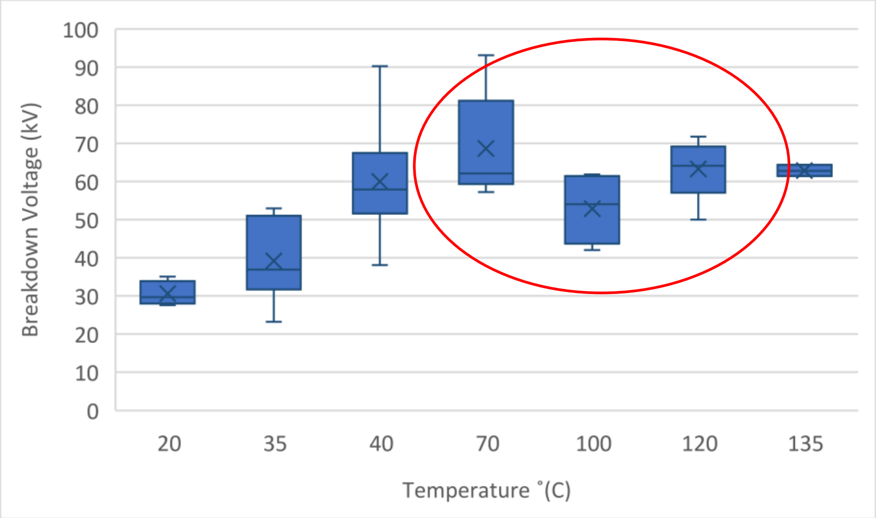



*Fig. 27: Box and whisker plots of temperature-dependent breakdown voltage for pure natural ester oil*

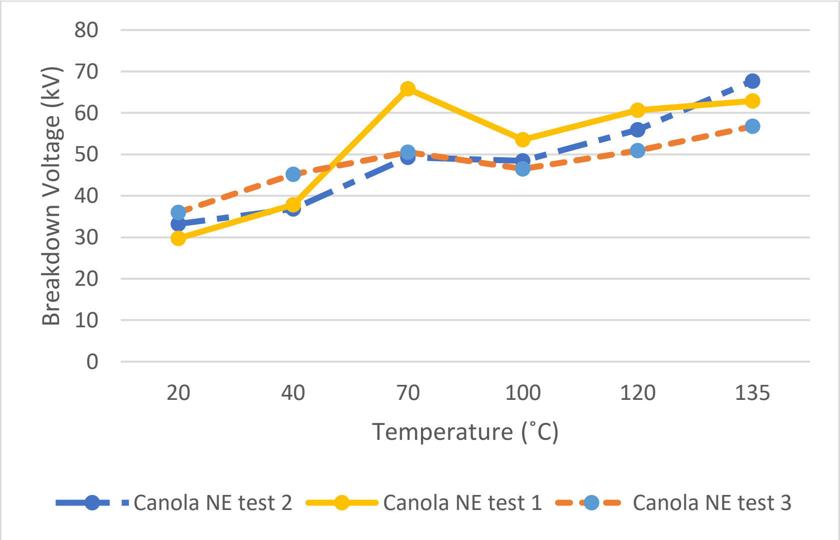



*Fig. 28: Line plots of temperature-dependent breakdown voltage for pure natural ester oil*

### 4.3.2 Effects of $TiO_2$ nanoparticles' loading on the Breakdown Voltage of Pure Natural Ester oil

The AC breakdown voltages of the six nanofluids (A1-3 and R1-3) are presented and compared to those of pure natural ester in Fig. 29 and Fig. 30. The tests were conducted at room temperature, 20 ± 3 ˚C. It is evident from the data that the addition of $TiO_2$ nanoparticles, both in rutile and anatase phases yields a significant improvement in breakdown voltage. From the minimum addition of 0.01vol% in R1 and A1, an improvement of over 50% is achieved. It is also notable that the enhancement increases with the increase in concentration for both phases. The anatase phase yields better improvement on fluids A2 and A3 than the rutile counterparts. This indicates that anatase phase is superior in breakdown strength improvement, the influence increases with increase in concentration. This result is contrary to the general notion that rutile $TiO_2$ performs better and forms better composites with polymer material due to its higher thermal stability. According to Stamate et al [90], rutile $TiO_2$ has a higher dielectric constant than the anatase phase. Which would also suggest that a higher breakdown voltage is expected for rutile $TiO_2$.

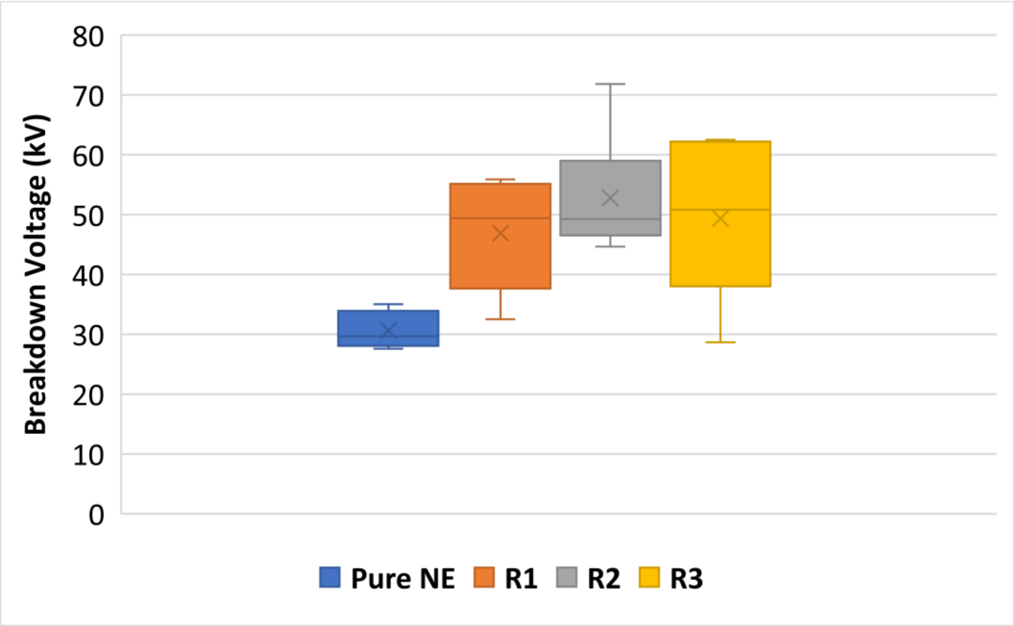



*Fig. 29: Rutile $TiO_2$ nanofluids' breakdown voltage*

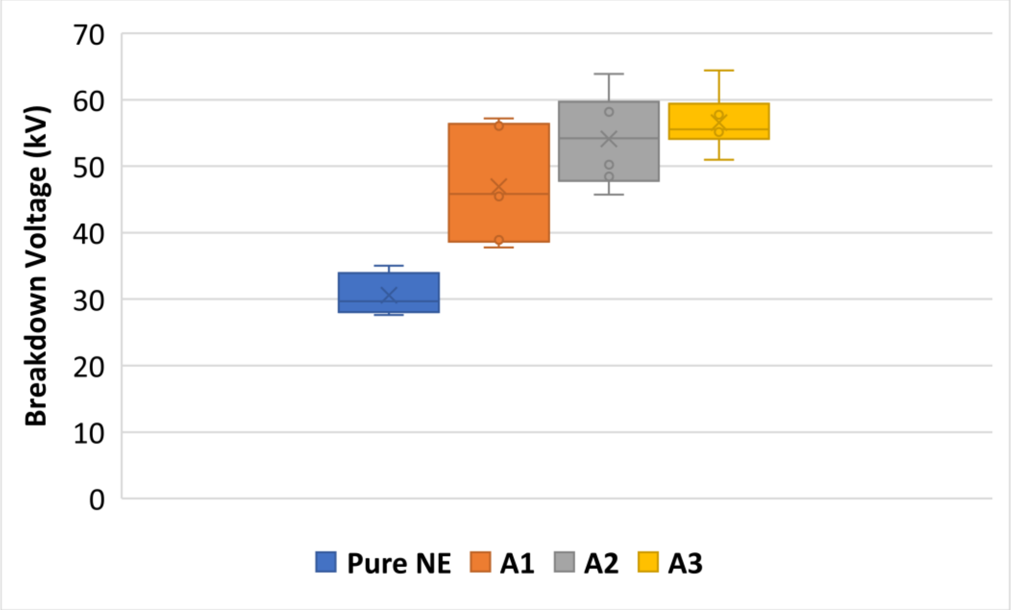



*Fig. 30: Anatase $TiO_2$ Nanofluids' Breakdown Voltage*

Following the contradictory results, the resultant nanofluids were further assessed for moisture content and compared to the unfilled natural ester. It is known that uniform field breakdown is highly influenced by the presence of moisture in a liquid. According to Williamson et al [38], the AC uniform field breakdown voltage is highly sensitive to moisture content. Yu et al [91], also relate AC breakdown voltage to moisture. They say that the initiation of breakdown in a uniform field is dominated by the presence of moisture and contaminants, once initiated a direct propagation from positive to negative electrode occurs, hence breakdown voltage in oil significantly decreases in the presence of moisture. It is thus imperative that the moisture content of the nanofluids and pure ester be compared. The moisture analysis was conducted by Zest Weg Group, a power transformer manufacturing company in Johannesburg, using the Karl Fischer Volumetry titration in accordance with the ASTM1533 standard. To eliminate external factors affecting moisture, the tested samples were sealed as much as practically possible, and all the samples, including the pure NE, underwent the same synthesis process as set out in chapter 3.3.2. Fig. 31 presents this comparison in a chart. Based on these results, the effect of moisture can be associated to the significant differences in the breakdown voltages between pure ester oil and the nanofluids. The moisture content is reduced drastically with the addition of both nanoparticles. The anatase fluid had the least moisture content of 114 ppm, a reduction of about 62% from 301ppm on the pure oil. The rutile nanofluid had 154.5 ppm of moisture, which is 49% less than pure ester. This correlates to the average breakdown voltage of the tested fluids where the anatase based fluid enhances the breakdown voltage more than the rutile nanofluid. The resultant moisture content of the nanofluids suggests that the added nanoparticles absorb moisture, thereby reducing the overall moisture content in the fluid. $TiO_2$ has been reported to be highly hydrophilic [92], [93], thus can easily absorb water from the natural ester. V. Bolis et al [93], studied the influence of the morphology on the hydrophilicity of $TiO_2$ phases and found that anatase $TiO_2$ dominates in the rate of water uptake, indicating higher hydrophilicity in anatase $TiO_2$. This supports the results of the moisture content and breakdown voltage in Fig. 32. It can thus be concluded that the hydrophilic nature of $TiO_2$ nanoparticles is the main contributor to the uniform field breakdown voltage improvement of the host natural ester oil. The anatase nanoparticles are the better nanofiller due to the higher moisture reduction as compared to the rutile.

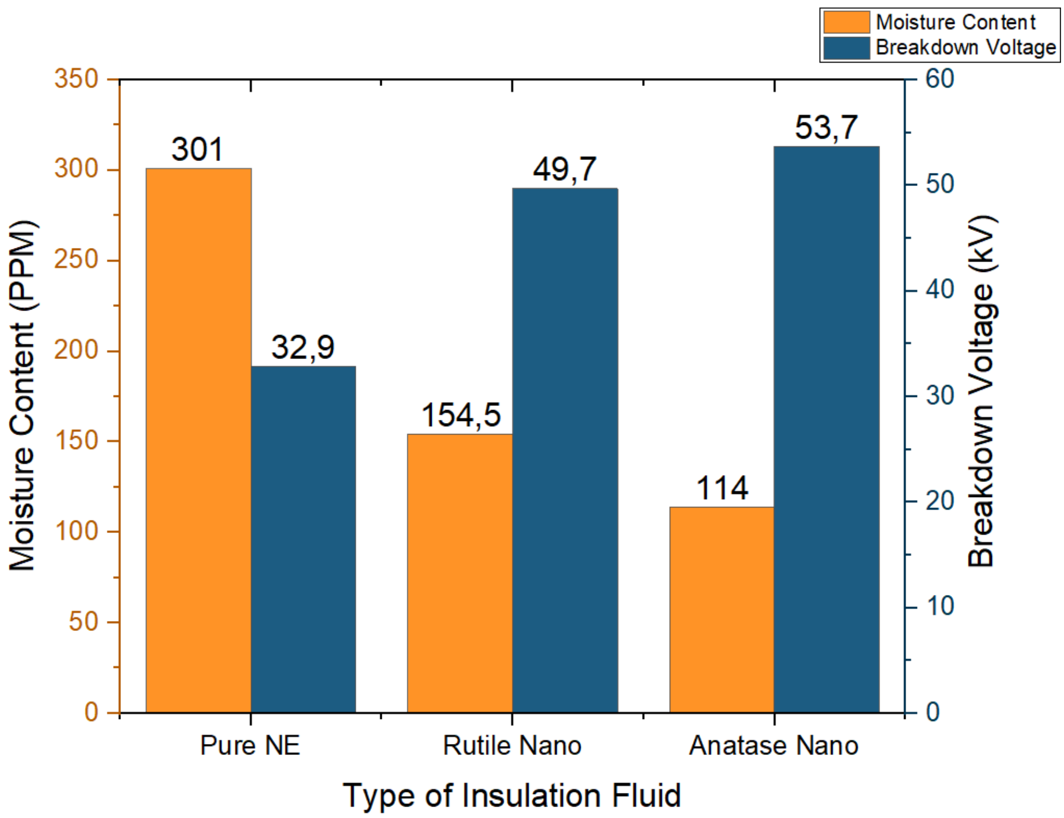



*Fig. 31: Fluids' moisture content and Breakdown Voltage*

However, the results of this study indicate the effects of $TiO_2$ nanoparticles in natural ester oil only at ambient temperatures. Recalling the present work's problem statement, the concern is on the inconsistencies in the breakdown voltage of natural esters at higher temperatures. Thus, the effect of the two nanophases under the usual transformer operating environment of higher temperature remains of concern.

### 4.3.3 Temperature-Dependent Breakdown Voltage of $TiO_2$-based Nanofluids.

The presented results and theories thus far are only of fluids tested and compared at ambient temperature. Further assessments and analysis are necessary at elevated temperatures, where the problem in natural esters lies.

One of the major contributors to the influence of nanoparticles in nanofluids is the concentration of nanoparticles. As reported in many studies, there is an optimum amount in every material where the best breakdown voltage improvement is achieved. An excessive amount leads to agglomeration of the nanoparticles and a reduction in breakdown voltage. Too little concentration of the nanoparticles also results in properties inferior to those of optimal loading [54], [75], [94].

For this study, the optimal concentration is assessed from both the degree of breakdown voltage improvement as well as repeatability of the results. In Fig. 29 it is notable that R2 is the optimal concentration for rutile nanofluids given that it has the highest average breakdown voltage improvement and minimum standard deviation. In Fig. 30, for anatase phase, the best sample was A3. However, for comparability, samples R2 and A2 were chosen as optimal samples. The concentration of 0.03 vol% for both nanofluids was thus used for the temperature-dependent analysis.

Fig. 32 presents the breakdown voltage results for pure NE, and rutile and anatase nanofluids concurrently. All three graphs show differences throughout the tested temperatures. This adds to the conclusion that the two phases differ in their influences on the base fluid in a nanocomposite. The following sections detail the results per fluid.

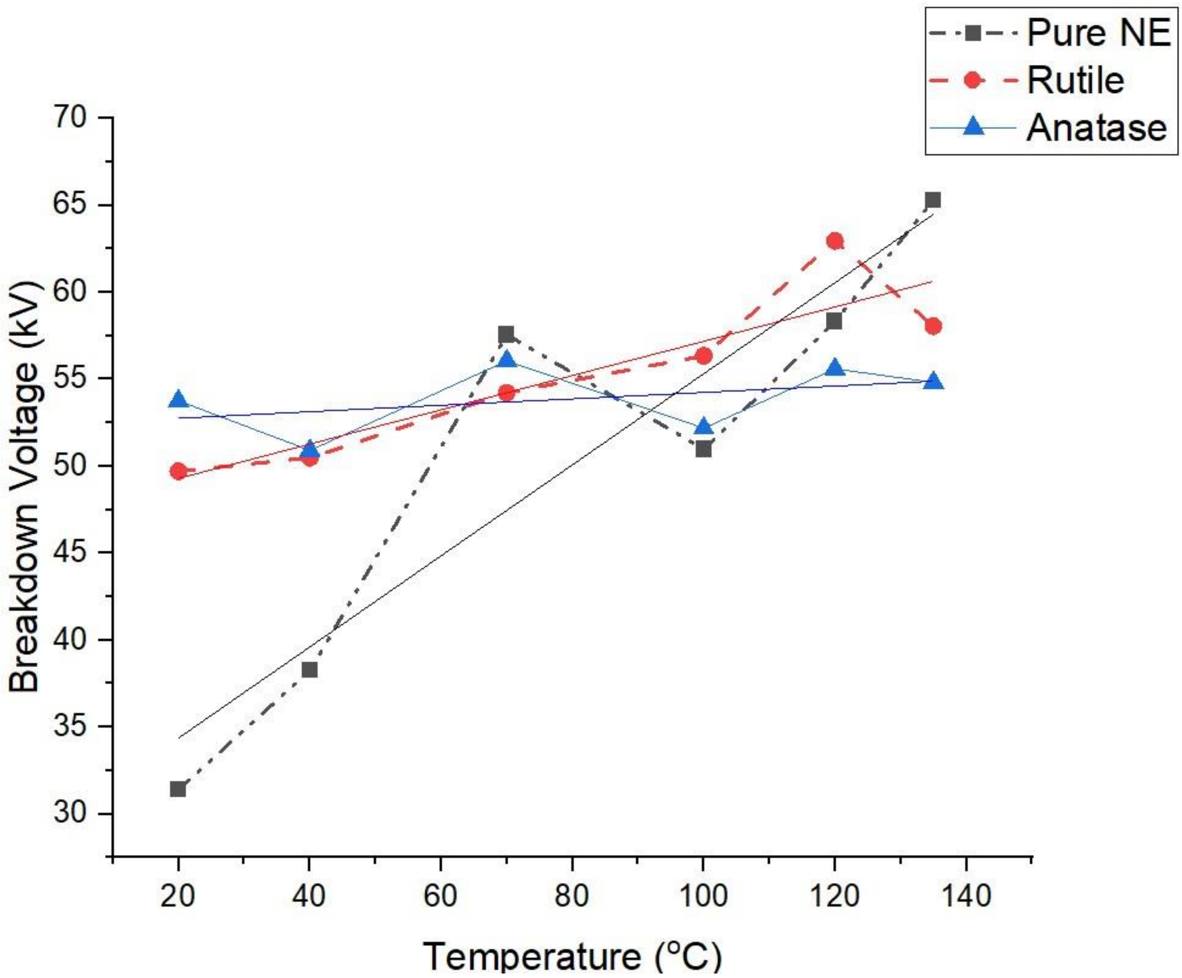



*Fig. 32: Temperature-Dependent Breakdown Voltage of Nanofluids with associated best-fit lines*

### Rutile ester nanofluid

It is notable from the figure that the average voltage of the rutile nanofluid increases with the increase in temperature up to 70 ˚C, similarly to the pure NE. There is still evidence of enhancement of the breakdown voltage, as the average breakdown voltage is consistently well above that of pure NE. In addition, rutile also successfully improves the breakdown voltage of pure NE at higher temperatures. This is evident from the consistently increasing trend of breakdown voltage between 70 ˚C and 135 ˚C, where pure NE is highly inconsistent. Based on the best-fit lines, the rutile nanoparticles supersede the anatase nanoparticles on breakdown voltage enhancement effects at 70 ˚C and higher temperatures.

### Anatase ester nanofluid

A different trend is given by the anatase nanofluid, whereby the breakdown voltage did not show significant changes with changing temperature. The resulting best-fit curve has a gradient that is close to zero. This result indicates that the changing temperature environment does not influence the anatase nanofluid's breakdown voltage. This is a positive finding for the anatase nanofluid as it implies a consistent breakdowon voltage of over 50kV can be expected anatase nanofluid-filled transformer regardless of the adverse temperature changes. However, it is undesired in the context of this work considering that the base natural ester has higher breakdown voltage at temperatures beyond 100 ˚C. With transformers normally operating at higher than 70 ˚C, a breakdown would have a higher probability in anatase nanofluid than in pure NE-filled transformers. The effect of the anatase nanoparticles at temperatures between 100 ˚C and 135 ˚C opposes that of the rutile nanoparticles which are found to maintain breakdown voltage enhancement of the base fluid. In fact, the anatase nanoparticles were deteriorating the breakdown voltage of natural ester oil, which is contrary to the ambient temperature comparison between anatase and rutile nanofluids. The sudden change in the influence that the anatase $TiO_2$ nanoparticles portrayed is associated with the thermal instability of anatase in comparison with rutile nanoparticles. The superior characteristics in moisture adsorption, which is key to their superior breakdown voltage enhancement as discussed, is hindered at elevated temperatures.

It is therefore concluded that the anatase nanofluid composite is not the ideal choice of $TiO_2$ nanofiller for transformer use. The constantly changing temperature in a transformer will compromise the breakdown voltage enhancing effects. Looking at the main problem in this study, which is inconsistent breakdown voltage at hotspot temperatures in natural ester oil, the anatase nanofluid is thus not the solution. Conversely, the rutile nanofluid is the better solution, regardless of its inferior influence at ambient temperature. Future work would be on improving the dielectric strength of rutile $TiO_2$-based ester nanofluid at lower temperatures.

The findings on anatase and rutile nanofluids concludes the first part of the current work, that is, to find the crystalline phase of $TiO_2$ that gives the most improved breakdown voltage of the Midel1204 natural ester oil under uniform electric field. Two questions were investigated to reach the findings. Recapping these questions:

1) ***What is the optimal concentration of anatase and rutile $TiO_2$ of a specific size and shape, that will result in the most improved breakdown strength compared to the unfilled liquid in a uniform electric field environment?***

Both crystalline phases of $TiO_2$ give a resultant increase in breakdown voltage as the nanoparticle loading is increased. This was shown in this chapter. However, it was a loading of 0.03 vol% of the rutile nanofluid that resulted in the highest breakdown voltage improvement, while the anatase nanofluid had its highest improvement at 0.05 vol%. The improvement of anatase $TiO_2$ was significantly higher than that of rutile in all concentrations. This attests to the notion that the crystalline phases of the nanoparticles have distinct effects on the host oil.

2) ***Which of the two phases of $TiO_2$ results in the most improved breakdown strength at higher temperatures in a uniform electric field environment?***

The main problem in the present work is the inconsistent breakdown voltage of natural ester oil experienced at higher temperatures. With question 1 proving that indeed, $TiO_2$ nanoparticles improve the uniform electric field breakdown voltage of the host oil in a nanocomposite. It is worth finding out if these effects are consistent at the higher temperatures, particularly the typical transformer hotspot temperatures.

Evidently, the rutile nanofluid had more promising results at higher temperatures, having improved the breakdown voltage of the host oil consistently throughout the temperature range of 20 - 120 ˚C. While the rutile nanofluid exceeded the anatase nanofluid improvement at lower temperatures, the higher temperatures challenged their improvement effects. This making the rutile nanoparticles the favoured solution for transformer use.

Having concluded on this, the correlation of the uniform field breakdown voltage to moisture effects have also been highlighted in this chapter. Indicating how the superior effects of anatase nanoparticles at ambient temperature are linked to their superior moisture adsorption capabilities at ambient temperatures. Also, their inferior effects at higher temperatures are also due to their thermal instability which is the result of their inconsistent moisture adsorption rate at higher temperatures and hence the deteriorating breakdown voltage effects. It is evident that moisture content plays a critical role in the uniform field breakdown voltage. It is however significant in transformers, especially for transformer design and insulation coordination purposes, to know the intrinsic properties of the insulation liquid and hence its effects under non-uniform electric fields [12], [39], [95]. The present work is thus extended to non-uniform field breakdown voltage, where the acceleration voltage and streamer speeds of the unfilled natural ester oil and the two nanofluids are investigated. This will conclude the last part of the work.

## 4.4 Conclusion

This chapter has presented the uniform field breakdown voltage experiments on natural ester oil and the nanofluids. The resultant temperature-dependent breakdown voltage of pure NE has confirmed the inconsistencies associated with natural ester oil at higher temperatures as reported in the literature. This is observed at temperatures higher than 70 ˚C. In the nanofluid experiments, it is found that both phases of $TiO_2$ (anatase and rutile) successfully improve the breakdown voltage at ambient temperature. The anatase nanofluid resulted in much higher improvement than the rutile. However, rutile nanofluid portrayed better breakdown voltage improvement on the natural ester fluid at higher temperatures. A consistent breakdown voltage improvement was obtained on the tested temperatures, while the anatase nano deteriorates the breakdown voltage at some of the higher temperatures. It can thus be concluded that the rutile phase of $TiO_2$ enhances the uniform electric field breakdown voltage better than the anatase nanofluid. The rutile nanofluid's superiority is more pronounced at higher temperatures. This concludes the one part of the present work. Investigation of the effects of nanoparticles on the host oil under non-uniform electric fields, particularly on the streamer speeds, remains of interest.

# Chapter 5 Streamer Speed under Lightning Impulse Voltage in Rutile and Anatase Ester Nanofluids

*The presented study so far has provided a comparative analysis of anatase and rutile-based nanofluids based on the breakdown voltage in uniform electric fields. The previous chapter provided a detailed experiment of the uniform field breakdown voltage. The results obtained have provided more insights on the effects of rutile and anatase phases of $TiO_2$. Rutile $TiO_2$ proved to be the phase that yields the highest breakdown voltage improvement in a uniform field environment. In this chapter, the effects of the two phases on natural ester oil are further investigated under non-uniform field. The influences of the nanoparticles on the streamer breakdown voltage as well as on the streamer speed are presented. An increased acceleration voltage is found in rutile $TiO_2$-based nanofluid, indicating improved streamer speeds compared to that of pure NE. The Anatase $TiO_2$-based nanofluid exhibited decreased acceleration voltage. The breakdown voltage increased by 11 % with rutile $TiO_2$ nanofillers, while the anatase $TiO_2$ nanofillers resulted in a 4 % decrease in breakdown voltage.*

## 5.1 Introduction

Uniform field breakdown tests are a widely used measure of insulation oil dielectric strength. The theory of uniform field breakdown in liquid insulation lies on the initiation of breakdown due to bubble formation and existence of contaminants between the electrodes [38]. While this method effectively shows the moisture-dependent dielectric strength of the insulation, it does not give the full information about the intrinsic properties of the fluids. On the contrary, the impulse streamer breakdown is independent of impurities in the liquid insulation, but measures the probability of the development and propagation of a streamer under high electric field stresses. The streamer breakdown thus provides data about the intrinsic properties of the oil. Furthermore, in equipment design, breakdown voltage and streamer speeds are more important than uniform field breakdown. The common breakdown propagations in transformers are of an impulsive nature [96]. The insulation could breakdown due to an internal fault, presence of suspended solid particles or lightning impulse, all which having a divergent electric field. A non-uniform streamer breakdown test is thus necessary in confirming an insulating liquid's breakdown strength and hence its applicability in a transformer environment.

Moreover, the non-uniform field streamer breakdown is more dependent on the streamer propagation time than initiation. Meaning a streamer inception does not typically lead to complete breakdown, however, its properties of the propagation govern complete breakdown [91]. The attributes of the streamer propagation such as the shape, structure and velocity have an influence on the resultant complete breakdown. The velocity of the streamer is a particularly important property in analysing the insulation strength as it directly influences the probability of a complete breakdown in the liquid. Streamers with very high speeds are reported to have the ability to propagate for longer distances within the duration of the impulse stress, and hence, they have a higher probability of a complete breakdown whenever inception occurs [34]. This is detrimental to the health of a transformer. As previously discussed in Chapter 2, natural ester oil is known to have high streamer speeds compared to mineral oil. This means even with their benefits, use of ester oils in transformers could lead to added problems during overvoltage conditions. The current work is thus extended to the investigation of streamer speeds in $TiO_2$-based nanofluids under lightning impulse conditions. The investigation is conducted in ambient temperature only as the streamer speed is the only parameter in question.

A standard Lightning Impulse (LI) wave is characterised by a steep rise time of 1.2 µs and a time to fall to 50% of peak voltage of 50 µs as illustrated in Fig. 34. The fast streamers tend to propagate faster than the impulse rise time, where the impulse voltage is stronger, hence complete breakdown is likely to occur. With slow streamers, the impulse voltage decays while the streamer still propagates and may dissipate before complete breakdown due to reduced voltage and hence electric field. It is thus desired that the streamer propagation be delayed longer than the impulse rise time to prevent fast streamers and reduce the probability of complete breakdown.

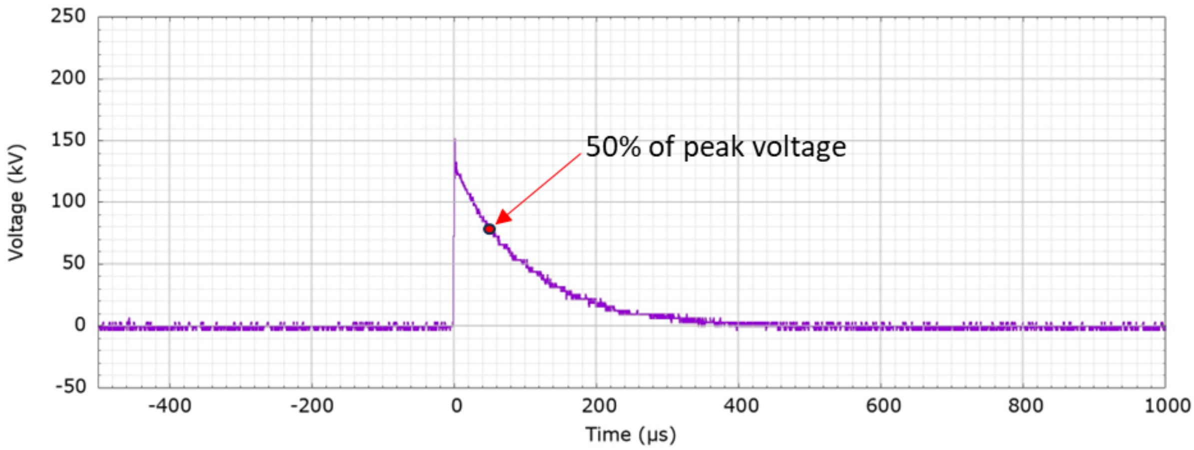



*Fig. 33: Measured Lightning Impulse (1.2/50 µs) Waveform*

If the nanoparticles' influence on natural ester oil is due to electron capture as discussed, then it is believed that they will reduce the energy and hence delay streamer propagation. It is thus desirable to compare the streamer speeds of the rutile $TiO_2$ and anatase $TiO_2$-based nanofluids to that of the natural ester oil, and confirm if the nanoparticles have any influence on the propagation of the streamer.

A measure of the acceleration voltage is used to determine the speeds of streamers. An acceleration voltage is the voltage at which the streamer propagation significantly changes from the slow ($1^{st}$ and $2^{nd}$) modes to fast ($3^{rd}$ and $4^{th}$) modes. A lower acceleration voltage entails that the insulation oil will transition much quicker to fast modes. The acceleration voltage has been widely used as a parameter for determining the general speeds associated with insulation liquids. According to Rao et al [97], the acceleration voltage of natural ester oil tends to be equal to the breakdown voltage in large gaps. However, in mineral oil the acceleration voltage is much higher than the breakdown voltage. This means that streamer propagations are almost always fast for every breakdown initiated in natural esters. Which has been confirmed by the works of Duy et al [34], and Rozga et al [35], who reported mostly $3^{rd}$ and $4^{th}$ propagation modes in natural esters, while mineral oil had mostly $2^{nd}$ and $3^{rd}$ modes for the same breakdown voltages. Rozga et al [35], also concluded that ester-filled transformers should have overvoltage limiting protection as the last resort to preventing breakdown voltages that lead to $3^{rd}$ mode propagation, the reason being that streamers in ester oil are usually fast and once initiated there is no influence on velocity to prevent them from transitioning to $3^{rd}$ or $4^{th}$ mode propagation. However, with the studies on nanocomposites proving to improve breakdown voltage through an electron capture theory, it is hypothesised in the current work that the addition of $TiO_2$ nanoparticles can have an influence on the streamer propagation speeds in natural esters. The acceleration voltage should be increased in natural ester oils in order to improve their streamer speeds. If the $TiO_2$ nanoparticles succeed in capturing electrons from an already initiated streamer, the streamer energy will decrease and hence the transition to 3rd modes will be hindered, leading to a much higher acceleration voltage.

This chapter assesses the effects of the two morphological phases of $TiO_2$, anatase and rutile, on the acceleration voltage of natural ester oil. The samples of the optimal nanofluids found in Chapter 4, with 0.03% rutile and anatase $TiO_2$ nanoparticles, as well as that of pure NE are assessed under lightning impulse voltage to compare their streamer speeds.

## 5.2 Methodology

The experiment follows a lightning impulse breakdown test protocol with a point plane electrode geometry. A standard lightning impulse wave of 1.2/50 µs was used to create a highly non-uniform electric field within the insulation liquid under test and measure the resultant streamer speed. A measure of the time-to-breakdown (TTB) of the streamer is used as the method of determining the speed for a pre-determined electrode gap length [95]. The time-to-breakdown (TTB) is known as the time it takes a streamer to propagate from inception until complete breakdown is reached. It is notable that most studies on streamer velocity, such as those of Huang et al [37], Yao et al [7] and Duy et al [34], have been based on modern approaches of making use of highspeed cameras to record the streamer lengths and propagation times. However, in this study the cameras were not employed as the use on the non-transparent nanofluids would not be effective. As previously indicated in Chapter 3.3, the nanofluids are of a milky colour, which hinders the appearance of the electrodes and possible streamers. The approach for measuring the streamer velocity was therefore done through measurement of TTB from the waveform captured during breakdown. This approach has been previously used and affirmed in the literature as an accurate method of determination of streamer velocity. The method is based on the knowledge that during impulse breakdown, the voltage measured at the gap is increased as the electric field increases, and from the moment the streamer starts developing in the gap the voltage starts dropping. At the moment the streamer completely bridges the gap, the voltage collapses to zero. The waveform is chopped at the instance of breakdown, as the gap is breached by the streamer and a voltage discharge occurs. On the waveform, this is denoted by a sharp sudden drop of the voltage to zero [38], [95]. The time taken from the initial rise of the voltage up to the point where voltage starts dropping, as illustrated in Fig. 35, is thus the time-to-breakdown of the streamer.

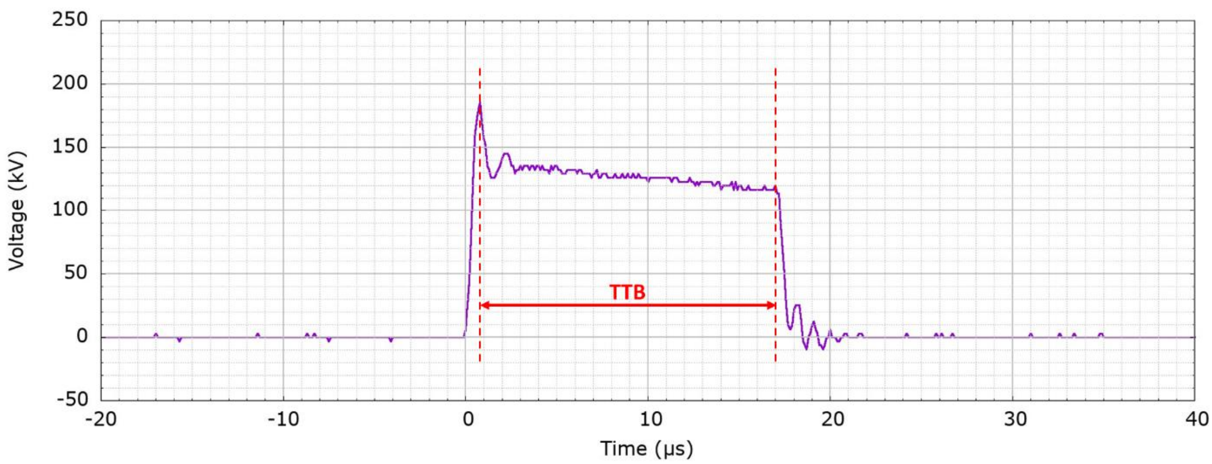



*Fig. 34: Breakdown Waveform Measured on an Oscilloscope to indicate Time-To-Breakdown (TTB)*

In their study, C. P. Wolmarans et al [95], compared and proved the correlation between the TTB measured through a highspeed camera and through the breakdown waveform. The method showed clear consistency with the camera images for slow streamers. For very fast streamers, with <1.2 μs TTB, the time cannot be adequately measured from the waveform as breakdown occurs before the peak voltage is reached. The resulting waveform generally looks like the one in Fig. 36. The exact point of breakdown cannot be ascertained. A time of 0.75 μs is kept as TTB of such fast streamers as per the study in [95].

Since the latter method is followed, the experimental method is also adapted from the study to better compare results and increase confidence on the velocity measurements without use of a camera.

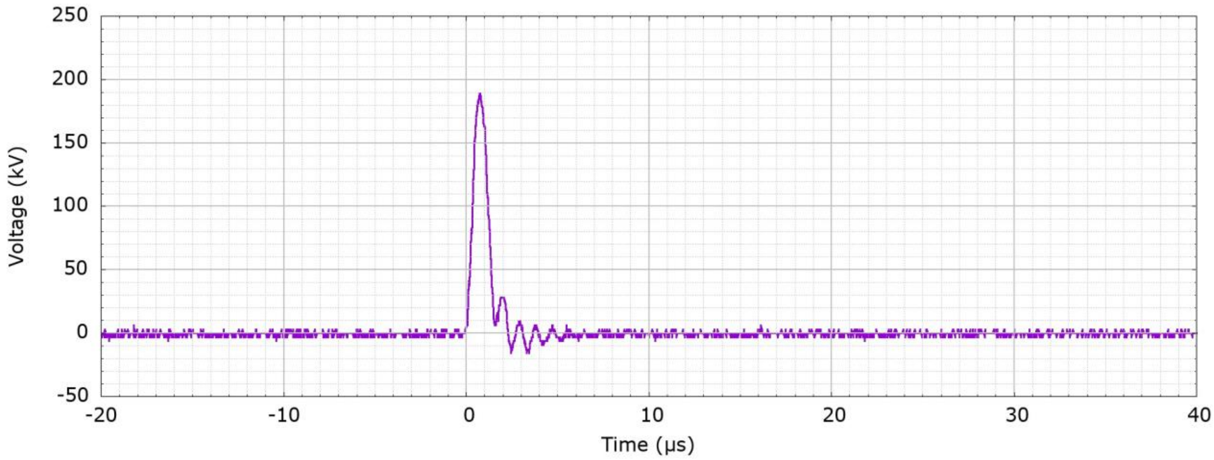



*Fig. 35: Fast Streamer Breakdown voltage Waveform*

### 5.2.1 The Test Cell

It is known that impulse breakdown is influenced by the electrode geometry, electrode tip radius and gap length. It is important to use the same test cell and set-up for all tests in order to obtain better comparability. The test cell design is therefore adopted from the study, which is made of a Perspex tube with height of 280 mm. The height of the tube ensured no surface breakdown outside the test cell for up to 270 kV [95], The tube housed an Ogura needle with a 5 ± 1μm tip radius as the positive electrode, and brass plane electrode with a diameter of 70 mm. The plane electrode had smooth, curved edges, to avoid additional sharp points and hence interference in the electric field profile. Fig. 37 shows a diagram of the test cell with dimensions. The cell design is found to be adequate for the experiments because the expected impulse breakdown voltages of the natural ester liquid and nanofluids are in the range of about 100 - 200 kV for gaps of ~5 - 10 mm, according to most literature [7], [34], [35], [38], [94].

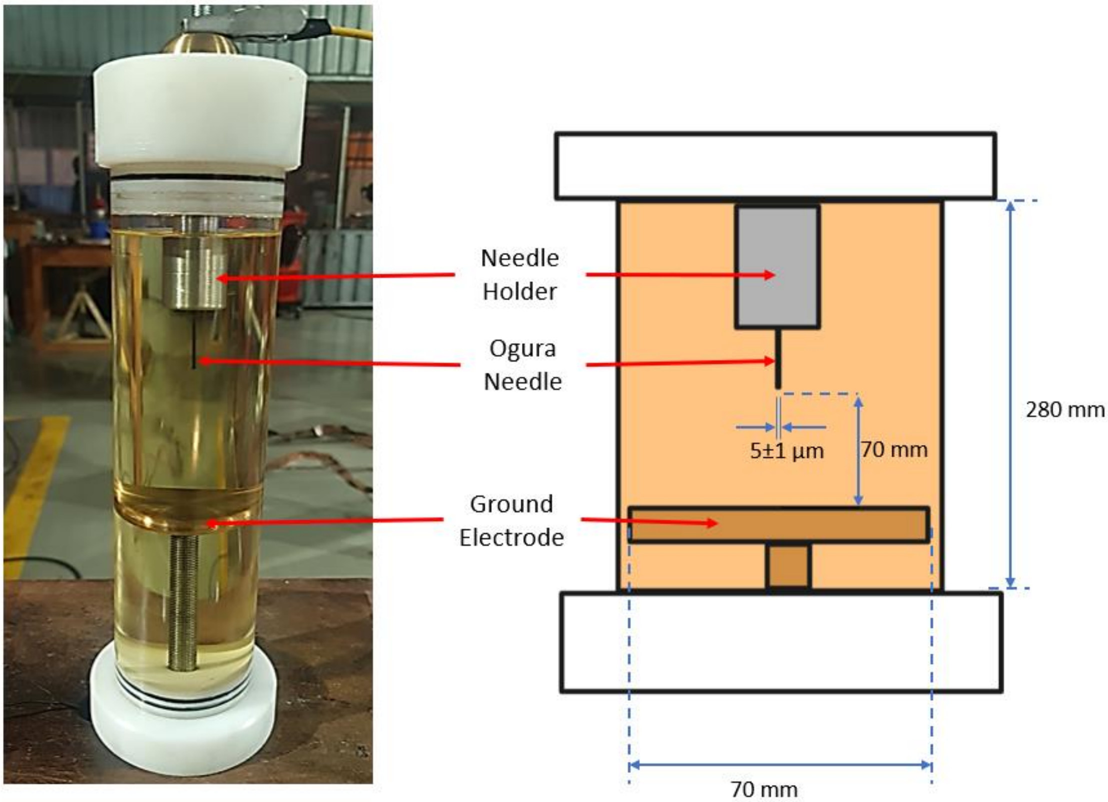



*Fig. 36: Non-uniform field breakdown voltage test cell*

### 5.2.2 Test Set-Up

Á 5-stage Marx Generator with accompanying front and tail resistors and capacitors from the High Voltage Lab at the University of the Witwatersrand, Johannesburg was used to create the required 1.2/50 µs impulse wave shape. The Marx generator was powered by a variable AC supply with a 220 – 140 000 V step-up transformer. The set-up was calibrated and preset for the lightning waveform as per the IEC 60060-1 standard. A schematic of the circuit is given by Fig. 38 below, which also shows the connection of an oscilloscope for recording the waveforms. The measured lightning impulse waveform given by the test set-up is illustrated in Fig. 38.

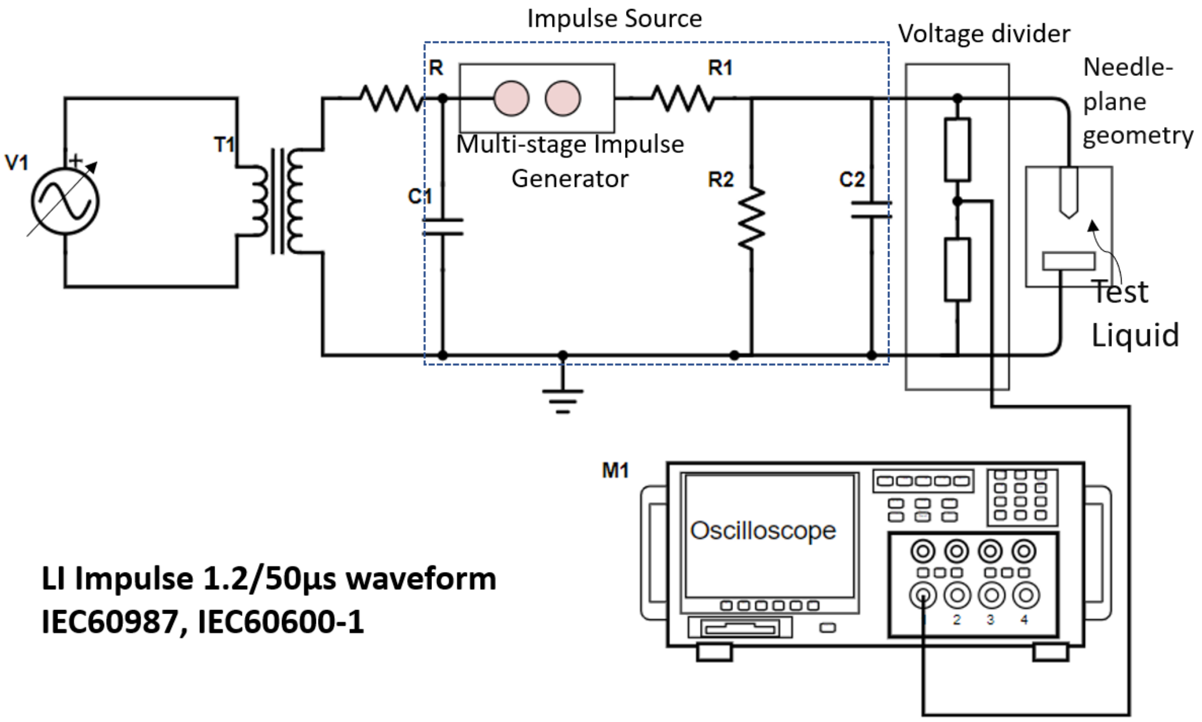



*Fig. 37: Non-Uniform Field Breakdown Voltage and Streamer Speed Test Circuit*

### 5.2.3 Test Method

The experimental procedure was conducted in accordance with the IEC 60897 standard for *"Methods for the Determination of the Lightning Impulse Breakdown Voltage of Insulating Liquids"*, and the SANS 60060-1 for *"High-voltage test techniques"* [98]. The step method was used to determine breakdown voltage and record all impulse waveforms for further analysis. A total of ten (10) breakdown shots were recorded per test sample and three samples were tested per insulation fluid type to ensure repeatability. Thus, a total of thirty (30) breakdown shots were conducted per fluid specimen. Between consecutive shots, a /.-minute break was provided to allow the oil to settle after each breakdown. All tests were conducted at ambient temperatures only for the scope of the experiment.

## 5.3 Results

### 5.3.1 Lightning Impulse Breakdown Voltage

The Weibull probability distribution of the impulse breakdown voltages of pure natural ester oil as well as the two $TiO_2$-based nanofluids are given in Fig. 39. It is notable that the breakdown voltage of the Midel canola is comparable to the mineral oils at an average 211 kV for positive impulse. This is contrary to the conclusion by Huang et al [37], that natural ester oils have a lower impulse breakdown voltage than general hydrocarbons. They reported positive impulse breakdown voltages less than 150 kV for three natural esters, including Rapeseed (Canola) oil.

As expected, the addition of the nanoparticles had a significant impact on the impulse breakdown voltage. The anatase $TiO_2$-based fluid resulted in a 4 % decrease in breakdown voltage of the pure oil, from 211 kV to 203 kV. Rutile $TiO_2$, on the other hand, resulted in an improvement of 11 % of the breakdown voltage to an average of 234 kV. The results from all fluids conform to the Weibull distribution with minor outliers. However, it is worth noting that the rutile distribution showed the most consistency towards the impulse breakdown voltage of 234 kV. The anatase had higher scattering with a skewer reference line. Indicating less consistency than the other two fluids. Similarly to the uniform field, the higher stability of the rutile nanoparticles appear to facilitate higher and more stable breakdown voltages.

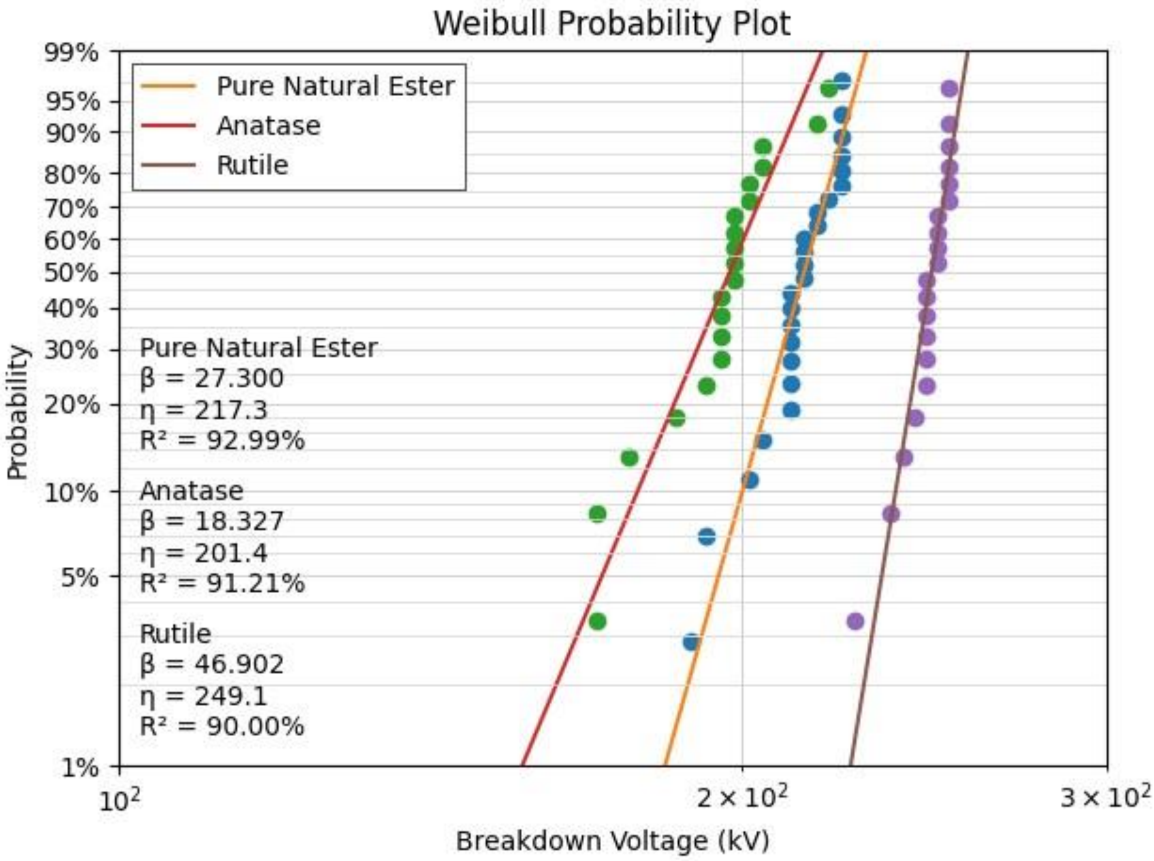



*Fig. 38: Weibull Probability Plots of Lightning Impulse Breakdown Voltage of (a) Pure NE; (b) Anatase Nanofluid; and (c) Rutile Nanofluid*

These obtained results are contradictory to those of the uniform field breakdown tests in Chapter 4 for ambient temperatures, where the anatase phase resulted in much higher breakdown improvement than the rutile. This is attributed to the fact that the impulse breakdown is independent of moisture, hence the anatase-based nanofluid showed a reduction in breakdown voltage regardless of its reduced moisture content as discussed in Chapter 4.3.

The superior stability of the rutile phase is evidently the main contributor to the resultant breakdown voltage improvement. According to the theory on the electron scavenger nature of nanoparticles, better breakdown voltage improvement relies on the interface between the nanoparticles and the base oil. When a stable composite is formed between the nanoparticles and the natural ester oil, the electrical double layer is more effective, and hence more electrons are captured by the particles.

The effect of the stability of the rutile phase of $TiO_2$ is also evident in the consistency and repeatability of the breakdown voltage results obtained in the tests. As discussed previously, the Weibull representation of the breakdown tests showed more scattered plots for the anatase nanofluid than the rutile-nanofluid. This shows the consistency of the rutile-$TiO_2$ influence on the natural ester oil.

### 5.3.2 Streamer speeds in rutile and anatase nano ester fluid composites

Fig. 40 presents the measured streamer velocity in pure NE, anatase $TiO_2$ and rutile $TiO_2$ nano-ester fluids. It is notable from the figure that the pure NE plots are predominantly in the 3rd and 4th modes with few plots in 2nd mode. The graph indicates that the acceleration voltage is around 210 kV, almost the same as the average breakdown voltage of 211 kV. This confirms the findings of Rao et al [97]. It is also notable that the distribution of the speeds is skewed towards the fast modes. The results confirm the high probability of fast streamer propagations in natural ester oils, as reported in the literature [5], [35], [37], [97].

When the nanofluids were tested for streamer velocity, they were found to behave differently to pure natural ester as hypothesised. Like the breakdown voltage effects, it is evident from Fig. 40 that anatase and rutile phases of $TiO_2$ nanoparticles have significantly different influences on the speeds of the streamer in the nanofluid. The speeds in anatase nanofluids exhibit more random scatter, where some streamers with lower voltages propagate in 3rd modes and others in 2nd mode. This is shown as outliers to the general trend of insulation oils' streamer velocities, indicating inconsistency in the effects of anatase phase on the natural ester. The distribution curves on the far right of the graph also indicate this scattering of data, with the anatase curve being relaxed across a wider span on the velocity axis. Due to the highly scattered data, determining the exact acceleration voltage for the anatase nanofluid is not trivial. However, it can be deduced that the acceleration voltage has decreased compared to the pure natural ester given that the plots are consistently in the 3rd and 4th modes of propagation from 190 kV, which is below the acceleration voltage of natural ester above. Notably, streamers at breakdown voltages of about 200 kV are predominantly in the 3rd propagation modes for anatase, whereas they are slow streamers in pure NE for similar voltages. It can thus be deduced that the steamer speeds worsen with the addition of anatase $TiO_2$. It is also worth noting from the chart that the anatase nanofluid tends to reach complete breakdown at voltages below those of the average breakdown voltage of the unfilled pure NE of 210 kV. This implies that the anatase weakens the breakdown strength of the base natural ester oil.

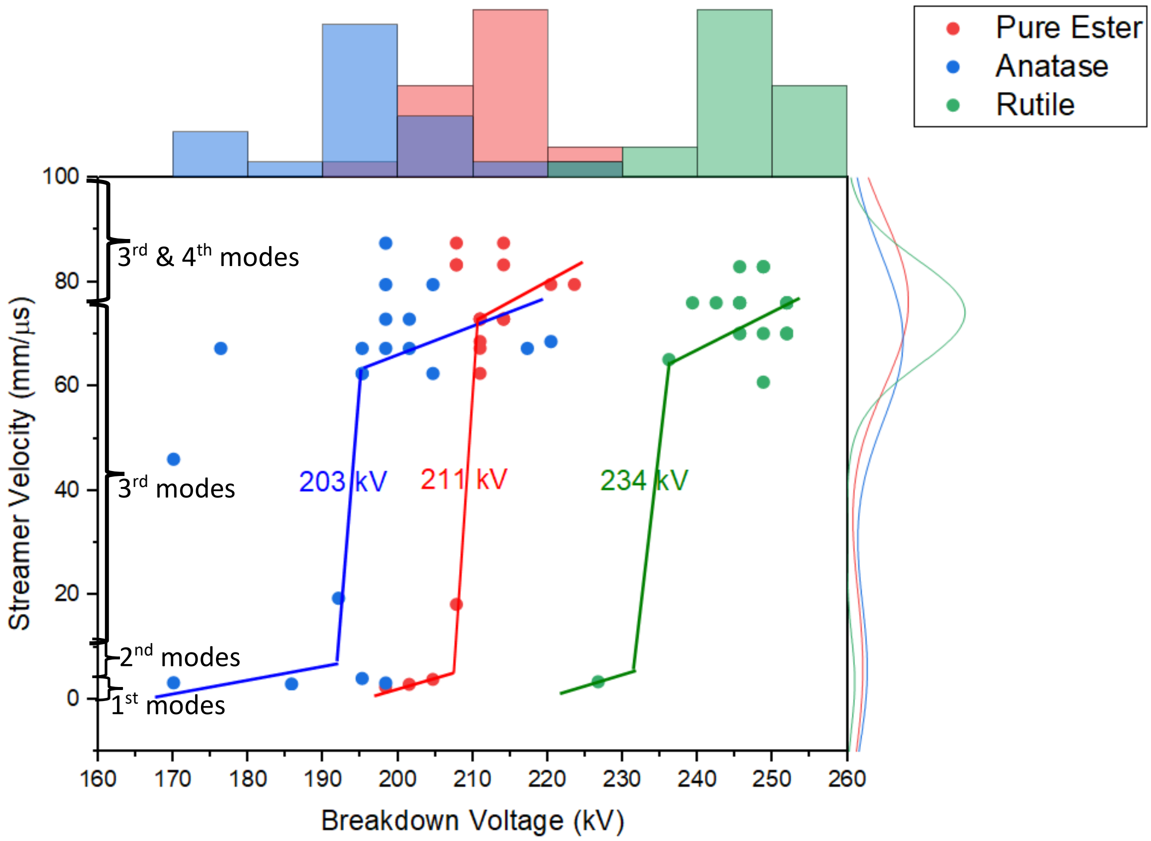



*Fig. 39: Streamer breakdown and velocities probability plots for Pure NE, Anatase Nano and Rutile Nano fluids*

The rutile nanofluid's streamers are predominantly in the 3rd propagation mode with the highest probability at around 70 mm/µs. While this indicates a predominantly fast propagation in rutile nanofluids, the resultant speeds are mostly below the maximum velocity of the natural ester fluid which was above 75 mm/µs. The rutile $TiO_2$-based nanofluids exhibit complete breakdown only at voltages higher than the acceleration voltage of the pure natural ester. This suggests that the rutile nanoparticles succeeded in delaying breakdown in natural ester oil, and only resulted in complete breakdown at much higher voltages. The rutile nanofluid resulted in an acceleration voltage that is 11 % higher than that of the pure NE, while the anatase nanofluid resulted in an acceleration voltage that is 4 % less than the pure NE. Furthermore, Fig. 41 shows the waveforms captured for the three fluids at distinct breakdown voltages. Fig. 41 (a) and (b) show the pure NE and anatase nanofluid respectively, both at the same breakdown voltage of 200 kV. Notably, a much faster propagation prevails in the anatase nanofluid, with a speed greater than 75 mm/µs while that of pure NE was ~4.1 mm/µs. Comparing these with the speed of the rutile nanofluid at a higher breakdown voltage of about 220 kV, the streamer propagation of the rutile nanofluid was even slower than that of pure nanofluid, having a speed of ~3.4 mm/µs. It can be clearly deduced that the rutile nanofluid will have a longer streamer propagation time for the same breakdown voltage stress as both the anatase nanofluid and the pure natural ester oil. This indicates a general reduction in speed with the addition of the rutile $TiO_2$ nanoparticles.

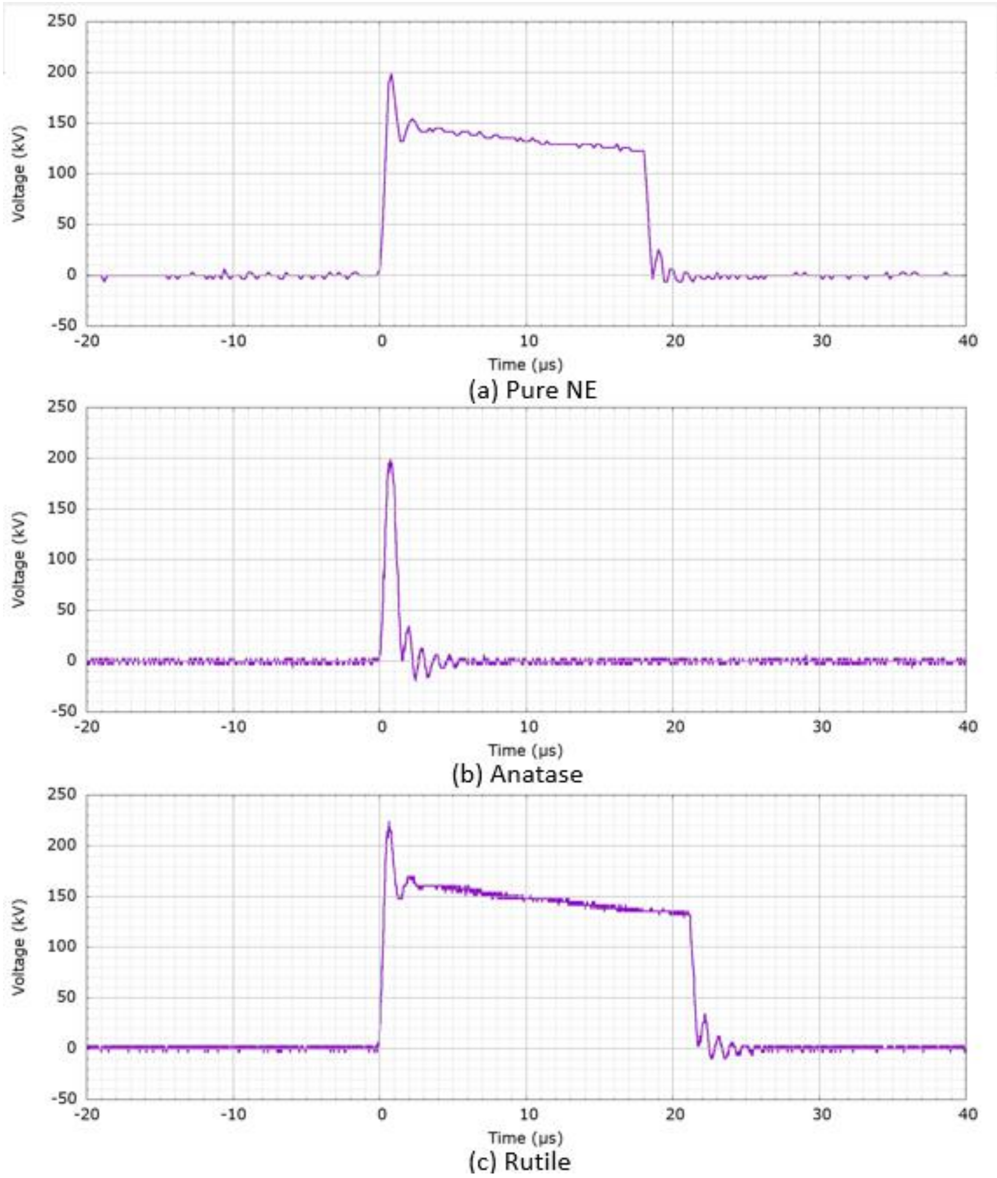



*Fig. 40: Oscilloscope measured streamer voltage profiles for the different fluids; (a) Pure NE, (b) Anatase, (c) Rutile*

## 5.4 Discussion

The aforementioned results show that the addition of both the anatase and rutile $TiO_2$ nanoparticles in ester oil has a significant effect on the dielectric strength of the oil. As previously mentioned, the impulse breakdown voltage test is governed by streamer propagation and gives information about the intrinsic properties of a fluid. The negative results obtained in the anatase nanofluid confirm the analysis in Chapter 4, that the uniform electric field breakdown is dependent on moisture content. The superiority of the anatase nanoparticles in the uniform field breakdown voltage improvement was associated with their higher moisture absorption ability over rutile nanoparticles in Chapter 4. In the current chapter, however, the anatase nanoparticles prove to deteriorate the breakdown voltage. This is partly attributed to the inferior dielectric properties of anatase nanoparticles when compared to the rutile. The dielectric constant of anatase nanoparticles is reportedly less than that of rutile [90], [99], [100], and hence results in reduced breakdown effects in the nanofluid. While the dielectric constant differences between the rutile and anatase explain the opposing effects of the two $TiO_2$ nanophases, the significant deterioration both in the average breakdown voltage as well as the streamer speeds remains of concern. It is evident that composite fluids from the two nanophases have distinct dielectric properties. Based on the literature, these resultant properties are affected by the interfacial zone between the nanoparticles and host fluid in a nanocomposite. Recalling the electrical double layer and electron capture theory illustrated in Chapter 2, the interfacial zone between the nanoparticle and the host fluid creates increased deep traps that can capture nearby electrons during breakdown. If the resultant composite material does not form this good interfacial zone, the electron capture fails and hence breakdown voltage improvement is not achieved. The significant differences between the anatase and rutile nanophases thus lies in the interfacial zones. Ijadpadah et al [79], and Hanaor et al [101], compared the atomic band charge carrier processes between anatase and rutile $TiO_2$, and in both studies, it was concluded that anatase has more shallow traps in the conduction band while rutile has more deep traps. According to Vequizo et al [78], the energy level correlates to the distance between the valency band and the conduction band (where reactions occur) of a particle. The energy band gap in the anatase nanoparticles is higher than that of the rutile as shown in Fig. 41 below. This thus makes it easier for deep traps in the rutile nanoparticles to move to the conduction band. When electrons are captured by the deep traps, their mobility is reduced, making them less reactive [78], [102]. The anatase nanoparticles have more shallow traps which keep electrons reactive in the conduction band. While the higher shallow traps in anatase are associated with higher reactivity and facilitating electron transfer, electron de-trapping is also possible in such traps [56]. The shallow traps added with the instability of the anatase nanophase suggest that electrons captured by the anatase nanoparticles could be easily de-trapped and re-create paths for streamer propagation. In contrast, the deep traps in the rutile nanophase consistently capture electrons and delay streamer propagation. This is consistent with the breakdown voltage results in Fig. 38 showing consistent voltage plots in rutile nanofluid and scattered plots in the anatase nanofluid, owing to the instability of the electron capture with anatase nanoparticles. The rutile $TiO_2$ is thus the better nanophase for breakdown voltage improvement of the host ester fluid.

Future work is necessary to study and confirm the electron trapping mechanism in the two nanofluids through possible charge trapping density and the comparison of the streamer shapes in the two nanofluids.

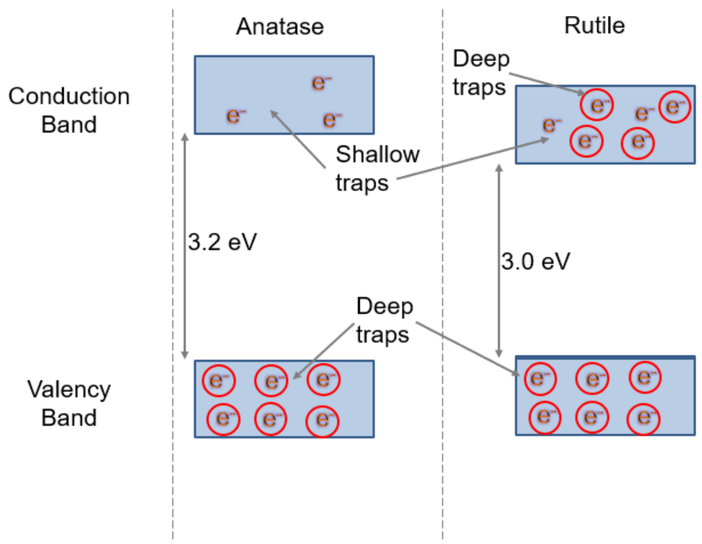



*Fig. 41: Representation of $TiO_2$ anatase and rutile phase solid state band gap*

## 5.5 Conclusion

In this chapter, the dielectric strength of the tested canola-based natural ester oil has been assessed through lightning impulse breakdown voltage and found comparable to the popular mineral oil. While this is true, it is also noted from this study that the streamer propagation velocity for natural ester oil is mostly in the fast, 3$^{rd}$ and 4$^{th}$ modes of propagation. Fast streamers are more detrimental to the transformer's health as they travel further, resulting in complete breakdown at lower voltages. It is thus desired to have high breakdown voltage and slower propagation.

The use of $TiO_2$ in natural ester oil to improve the streamer propagation velocity was assessed in the attempt to answer the last question of the current work which is:

***3) How do the streamer breakdown speeds of anatase and rutile $TiO_2$ nanofluids compare with the unfilled natural ester fluid?***

The addition of $TiO_2$ rutile and anatase phase nanoparticles has resulted in opposing results for both impulse breakdown voltage and velocity. The anatase phase significantly reduced the breakdown voltage and had inconsistencies in the velocity of the streamers with changing breakdown voltage. The rutile phase gave an improved breakdown voltage with an overall reduction in velocity when compared to the pure natural ester oil. The behaviour of the rutile nanofluid is consistent with the notion that the existence of nanoparticles in a nanofluid hinders propagation of streamers by attracting and capturing the electrons within the streamer. When the fluid is stressed with voltages up to the breakdown voltage of the base fluid, a streamer may initiate and start propagating through the fluid. As the electrons are captured from this streamer, the energy is lost and hence the speed with which it propagates is reduced. The rutile nanofluid recorded breakdown voltages that are 11% higher than the pure NE, but with reduced propagation velocity than the pure NE. This indicates an improvement due to the rutile $TiO_2$ nanoparticles. This influence of rutile $TiO_2$ is attributed to the higher stability of the rutile phase as compared to anatase, resulting in a stable nanocomposite fluid with better electron activity. It is believed that the anatase phase does not form stable nanocomposite with the base pure NE, hence the electron capture theory was ineffective. This may lead to the nanoparticles behaving as suspended semiconductive particles that facilitate ionisation and hence breakdown. It is thus concluded that the rutile phase of $TiO_2$ is the optimal solution for improving the breakdown strength of natural ester oil.

# Chapter 6 Conclusion

*The last two chapters presented the experimental study in detail. The procedure as well as the results were discussed with reference to appropriate literature. This conclusion chapter re-emphasises the research study and aim. The results and analysis from the experiments are discussed in relation to the study research question, and concluding remarks are added.*

Insulation liquids are an integral part of oil-filled transformers. Their sustainability and the integrity of their dielectric strength are crucial for the continuous use in large power transformers. Natural ester oils have gained research attention in recent years as sustainable liquids with good dielectric properties for transformer use. However, there are challenges associated with the use of these ester oils in large power transformers. One of which is inconsistencies in breakdown voltages at higher temperatures, coupled with high streamer velocities. With large power transformers operating at temperatures as high as 90 ˚C and up to 160 ˚C at hotspot temperatures for natural ester-filled transformers, there is a need to improve the breakdown strength of natural esters at such high temperatures. Nanotechnology is one possible solution that has been studied and found to have both positive and negative results based on different properties of the base material and nanoparticles used. The phase of nanoparticles used is one of the significant properties for breakdown voltage enhancement but is seldom studied in the literature.

The present work explored the use of $TiO_2$ nanoparticles with the aim of improving the breakdown voltage and ultimately the speed at which the streamers propagate in a natural ester oil. $TiO_2$ nanoparticles are used as they are found to be among the popular nanoparticles with evidence of forming stable nanocomposites with good dielectric and thermal properties. However, there are inconsistencies in the extent of breakdown voltage enhancement due to these $TiO_2$ nanoparticles in existing literature. This study aimed to investigate the effects of different phases of $TiO_2$ on the breakdown voltage of natural ester oil. Particularly focusing on the improvement of the highlighted shortfalls associated with natural ester oil, which are the inconsistent breakdown voltage at higher temperatures as well as high streamer speeds.

The influence of nanoparticles on insulation oil is highly dependent on the preparation method and physical properties (i.e., type, size, shape) of the nanoparticles used. A highly uniform dispersion of nanoparticles is necessary for better breakdown voltage improvement. Chapter 1 and 2 laid the associated background and literature in nanofluids, showing the smallest sizes of nanoparticles as the most favourable for highest enhancement. In Chapter 3, extensive physical and chemical characterisation of the nanoparticles was presented to confirm the properties and comparability of the nanophases. The study's major aspect was the synthesis process and creating an optimal fluid to ascertain a stable nanofluid. The 2-Step Method for synthesis was used with optimal stirring and sonication timings to ensure a well dispersed solution for breakdown voltage improvement. The use of UV-Vis spectroscopy showed results of well dispersed solutions for the resultant nanofluids. This ascertaining that the synthesis process on both nanofluid phases were equally successful and that the comparative experimental results would be influenced only by the intrinsic properties of the nanoparticles.

The comparative study was three-fold, having three main questions to investigate. The first question focused on identifying the concentration of the nanoparticles in either anatase or rutile, which would improve the natural ester oil's breakdown voltage the most. The question reads:

1) ***What is the optimal concentration of anatase and rutile $TiO_2$ of a specific size and shape, that will result in the most improved breakdown strength compared to the unfilled liquid in a uniform electric field environment?***

The two phases of $TiO_2$ were of similar size and shape as confirmed through characterisation methods, thus direct comparison was used. The concentrations tested were between 0.01% vol and 0.05% vol. The uniform field breakdown voltage experiment was conducted under ambient temperature conditions. Both phases resulted in significant improvements of the breakdown voltage while having the smallest concentration of 0.01% of the nanoparticles. The anatase based nanofluid resulted in a higher improvement of 85% compared to the unfilled natural ester fluid, while rutile nanofluid a 61% improvement. This significant difference confirms the possible influence of the two phases of $TiO_2$ on inconsistent breakdown voltage effects of $TiO_2$ as highlighted in the literature review.

The optimal concentration was deemed to be the concentration of nanoparticles that would result in the highest breakdown voltage improvement while maintaining consistency and low standard deviation. The two nanofluid types, anatase and rutile, both showed the least scattering of results and good improvement of breakdown voltage at a concentration of 0.03%. It is thus concluded that a concentration of 0.03% vol of $TiO_2$ nanoparticles is optimal for breakdown enhancement for both the anatase and rutile nanophases.

The optimal concentration of 0.03% of anatase and rutile $TiO_2$ were used to form nanofluids to address the problems in question, that is, the inconsistent breakdown voltage at high temperatures as well as high streamer speeds. A uniform field temperature-dependent breakdown voltage experiment for temperature between 0 ˚C to 135 ˚C was conducted to address the following question:

2) ***Which of the two phases of $TiO_2$ results in the most improved breakdown strength at higher temperatures in a uniform electric field environment?***

The findings from the experiment further prove the significant differences between the influences of the two phases of $TiO_2$ on natural ester oil. At ambient temperatures, the anatase-based nanofluid showed the highest improvement, with a breakdown voltage of 53.7 kV compared to 49.7 kV for rutile-based nanofluid. Both voltages were much higher than the 32.9 kV of the pure natural ester oil. These results are attributed to the relationship between moisture and breakdown voltage under uniform fields. Both nanoparticles absorb moisture, hence a reduced moisture content is found in the 2 nanofluid solutions as compared to that of the initial base oil. The anatase nanofluid absorbs the most moisture, resulting in the highest breakdown voltage improvement. Another contributing factor is the electron energy band coupled with electron capture capability, whereby the anatase phase is characterised with a wider energy gap that allows for more shallow traps in the outermost layer. Thus, more electron capture is evident on the anatase nanofluid than the rutile.

However, this is only true at ambient temperatures. The anatase nanofluid had insignificant change in breakdown voltage with the changing temperature and resulted in reduced breakdown voltage at higher temperatures compared to the unfilled natural ester. Meanwhile, the rutile phase consistently improved breakdown voltage of the natural ester throughout the higher temperatures. The thermal stability of the rutile $TiO_2$ nanoparticles is the main contributing factor to the superior influence of this phase. As temperature increases, the moisture content and the electron capture mechanisms are affected. But, since the rutile nanoparticles are thermally stable, they are believed to maintain the breakdown voltage enhancement as at ambient temperatures, while the anatase nanofluid fails. It can thus be concluded that the rutile phase of $TiO_2$ gives the highest improvement of breakdown voltage at higher temperatures.

There is room for possible future work in this area, to unpack further and model the effects of moisture on the two nanophases as well as modelling the breakdown improvement mechanisms under the influence of moisture and high temperatures (100 ˚C to 135 ˚C), where natural ester oil has challenges.

The last question address by the study is on the streamer speeds in natural ester oil and reads as follows:

3) ***How do the streamer breakdown speeds of anatase and rutile $TiO_2$ nanofluids compare with the unfilled natural ester fluid?***

There is a significant difference to the influence of anatase and rutile phases of $TiO_2$ on the streamer speeds. While natural ester oils are characterised with fast streamers, the anatase nanofluid had faster streamers. This is denoted by the significantly reduced acceleration voltage compared to the pure ester. Contrary to that, the rutile nanoparticles successfully reduced the speed of the streamers. The rutile nanofluid had a 10% higher acceleration voltage compared to pure natural ester, while that of the anatase nanofluid was 4% lower. This implying that under the same conditions and voltage, streamers in an anatase nanofluid will tend to be faster than those in unfilled natural ester oil. Similarly, the streamers in unfilled natural ester oil will tend to be faster than those in a rutile based nanofluid. It is thus concluded that the rutile $TiO_2$ nanoparticles reduce the streamer speeds in natural ester oil, and ultimately delay complete breakdown. Anatase $TiO_2$ nanoparticles lead to faster streamer propagation, which is undesired as it accelerates complete breakdown and hence is detrimental to transformer operation.

This correlates to the findings under uniform electric fields where the anatase nanoparticles appear to deteriorate the breakdown strength of the base natural ester at higher temperatures. Conversely, the rutile nanoparticles continued to improve the breakdown voltage even at elevated temperatures.

These findings attest to the nanodielectrics breakdown mechanism theories by Tanaka [53] and Lewis [52], of the electron capture capability of nanoparticles. Due to the higher stability of the rutile phase, the rutile nanoparticles have a more effective atomic reactivity. Thus, they successfully attract nearby streamers, reducing the energy and hence the propagation speed. The deterioration of the streamer breakdown strength on the anatase nanofluid is attributed to their instability and hence the lack of interfacial reactivity within the base oil. When nanoparticles do not form a stable nanocomposite, they tend to behave like suspended particles that facilitate ionisation and ultimately breakdown as discussed in section 3.3.

It can be concluded from the study that the rutile phase of $TiO_2$ is the ultimate solution for the most improved breakdown voltage under both the uniform and non-uniform fields.

The integration of nanotechnology in transformer insulation is still a topic of research. Further study on the performance of the nanofluids in a transformer lifespan is a need. However, the topic is beyond the scope of the current research topic. Future work is thus proposed to assess the stability of the rutile-based nanofluid for industry use through accelerated thermal aging.

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# Appendix: Related Publication

# Breakdown Voltage of Natural Ester-Based Nanofluid: A comparison between anatase-$TiO_2$ and rutile-$TiO_2$ nanoparticles

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***Abstract*—Nanoparticles have been found to improve the dielectric properties of insulation fluids. Existing literature has shown that the improvement given by these nanoparticles is dependent on the different properties of the nanoparticles, including the type and the amount of nanoparticles used. This work presents a study on the effects of $TiO_2$ nanoparticles on the breakdown strength of natural ester oil. A uniform field AC breakdown voltage test was used to compare anatase and rutile $TiO_2$ polymorphs' effects on a natural ester liquid. The nanofluid containing anatase-$TiO_2$ was found to provide the highest breakdown voltage for different concentrations. A maximum improvement of 85% was obtained with a sample containing 0.05 vol% of anatase-$TiO_2$. Rutile-$TiO_2$ had a 61% improvement at the same volume concentration. The improvement is attributed to the electron-trapping ability of the nanoparticles. The possible related electron transfer mechanisms are discussed.**

***Keywords—Nanofluids, $TiO_2$, anatase, rutile, natural ester, AC breakdown voltage***

## I. Introduction

Transformer oil is an integral part of the electrical network. Its health is critical to the efficiency of the entire network. Insulation oil provides the dielectric and cooling functions of the transformers. Over the years, mineral oil has successfully provided this. However, it is prone to explosions during fault and high load conditions due to its lower fire point. The oil is also harmful to the environment given that it has a very low biodegradability rate. Additionally, mineral oil has a risk of running out due to the scarcity of petroleum fuel on which mineral oil is based [1]–[6].

In recent years, many researchers have focused on natural ester oils as alternative insulating liquids for large power transformers due to better sustainability. Natural ester oils have a higher fire point of 300 ˚C, which is double that of mineral oil [6]. They are also biodegradable as they are vegetable based, and are therefore renewable.

Although natural ester oil possesses superior properties, its application has limitations due to the characteristics of having higher viscosity and therefore lower cooling effects, higher oxidation rate, and inconsistent breakdown voltage behaviour especially at higher temperatures [1], [6].

Nanoparticles have been employed by researchers to address the shortfalls associated with natural esters. The integration of nanoparticles in insulation oils forms a nanofluid with improved dielectric properties. Rafiq *et al.* [2], and Suhaimi *et al.* [4], conducted reviews on nanofluids for power transformer applications, confirming the improvement of the resultant nanofluids' dielectric properties. They also concluded that the resultant properties of nanofluids depend on the type of particles, size, and percentage loading. Among the nanoparticles commonly used in nanofluids are $Fe_3O_4$, ZnO, $Al_2O_3$, $SiO_2$, and $TiO_2$. However, $TiO_2$-based nanofluids exhibit better dielectric properties as compared to other nanofluids. In the literature, Olmo *et al.* [7] modified natural ester oil with $TiO_2$ nanoparticles. The breakdown voltage of the resultant nanofluid was reported to have improved by 33%. Muangpratoom [5], compared nanofluids modified with $TiO_2$, ZnO, and $BaTiO_3$. It was concluded that at 0.01 vol%, $TiO_2$ had the most breakdown voltage improvement. Koutras *et al.* [8], also studied an ester-based nanofluid with $TiO_2$ nanoparticles and found a 22% improvement in the breakdown voltage with the nanofluid containing 0.02% of $TiO_2$.

It is notable from the literature that $TiO_2$ nanoparticles in natural ester oil enhance the breakdown strength of the resultant nanofluid. However, $TiO_2$ exists in two common stable polymorphs, namely, rutile and anatase [9], [10]. The phases have different properties and industrial uses. According to Stamate *et al.* [11], the electrical properties of anatase and rutile $TiO_2$ differ significantly. Their study on $TiO_2$ film suggests that the rutile dielectric constant is higher than that of anatase. This indicates that the polymorphs may have significantly different effects on the dielectric strength of nanofluids.

Currently, there is limited literature that specifies the phase of $TiO_2$ that results in the most improved nanofluid. In this regard, this work compares the effects of rutile-$TiO_2$ and anatase-$TiO_2$ nanoparticles on the uniform breakdown voltage of natural ester oil. The following sections present the materials, experimental methods, and the breakdown voltage test results.

## II. Materials and Methods

### A. Material Characterisation

Midel eN 1204 canola-based ester oil and the SkySpring nanomaterials Inc. sourced $TiO_2$ nanoparticles were used in the preparation of the nanofluids. Table I and Table II present the supplier specifications of the oil and nanoparticles respectively. Similar nanoparticles were used to ensure optimal comparability.

TABLE I: NATURAL ESTER OIL SUPPLIER SPECIFICATIONS

| Midel 1204 Properties | | |
|---|---|---|
| ***Property*** | ***IEC 62770 Limit*** | ***Actual*** |
| Dielectric Breakdown (kV) | ≥ 35 | 66.3 |
| Moisture Content | ≤ 200 | 15.09 |
| Dissipation Factor @90°C | ≤ 0.05 | 0.004 |
| Density @20°C (g/cm$^3$) | ≤ 1.0 | 0.92 |
| Viscosity @40°C (mm$^2$/sec) | ≤ 50 | 37 |

TABLE II: $TiO_2$ NANOPARTICLES SUPPLIER SPECIFICATIONS

| $TiO_2$ Nanoparticles Properties | | |
|---|---|---|
| **Property** | **Rutile-$TiO_2$** | **Anatase-$TiO_2$** |
| Purity (%) | 99.5 | 99.5 |
| Average diameter (nm) | 10 - 30 | 10 - 30 |
| Specific Surface area (m$^2$/g) | ~50 | > 50 |

Midel eN 1204 canola-based ester oil and the SkySpring nanomaterials Inc. sourced $TiO_2$ nanoparticles were used in the preparation of the nanofluids. Table I and Table II present the supplier specifications of the oil and nanoparticles respectively. Similar nanoparticles were used to ensure optimal comparability.

The physical properties of the nanoparticles were further confirmed with the use of Raman spectroscopy and Transmission Electron Microscopy (TEM).

A pure rutile-$TiO_2$ phase is characterized by four Raman shifts at 143±1 cm$^{-1}$, 235±5 cm$^{-1}$, 448±2 cm$^{-1}$, and 609±2 cm$^{-1}$. While pure anatase-$TiO_2$ has a sharp peak at 144±1 cm$^{-1}$, followed by four more at 196±1 cm$^{-1}$,395±1 cm$^{-1}$, 518±2 cm$^{-1}$, and 639±1 cm$^{-1}$ [10]. Fig. 1 shows the standard Raman Spectra signatures of the pure nanoparticles' phases, while Fig. 2 and Fig. 3 show the experimented rutile and anatase nanoparticles, respectively. Eleven samples of data were taken at different spots of a grid spread with each of the nanoparticles. It is notable from the figures that the spectra are almost identical for all sample iterations of the Raman. This coincides with a purity of 99.5% as per specifications.

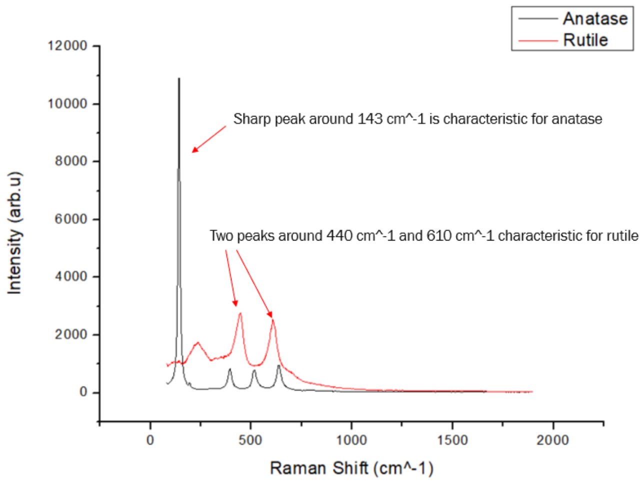


Fig. 1: Standard Raman Spectra of Phase-Pure $TiO_2$ Polymorphs

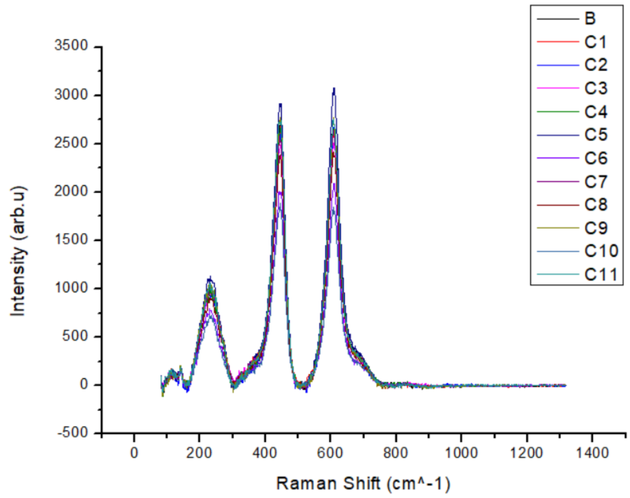


Fig. 2: Raman Spectra for Rutile $TiO_2$

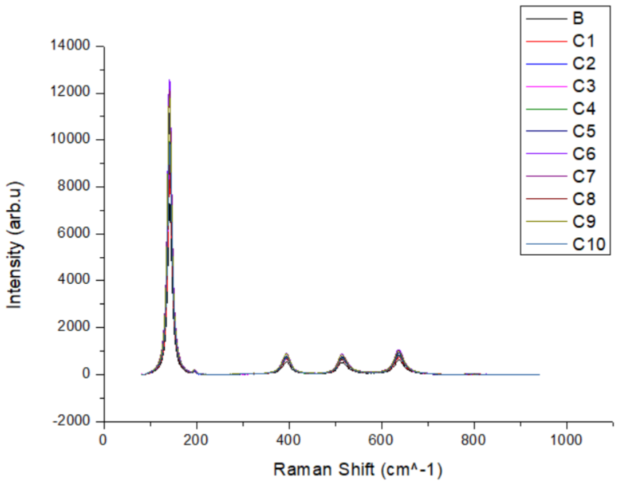


Fig. 3: Raman Spectra for Anatase $TiO_2$

TEM analysis also confirmed the sizes and morphology of the nanoparticles. Fig. 4 and Fig. 5 show the TEM images of the rutile and anatase $TiO_2$ respectively, confirming the particles' diameter range of 10-30 nm with quasi-spherical shapes as per the materials' specifications in Table I. In addition, the rutile sample is more agglomerated compared to the anatase $TiO_2$.

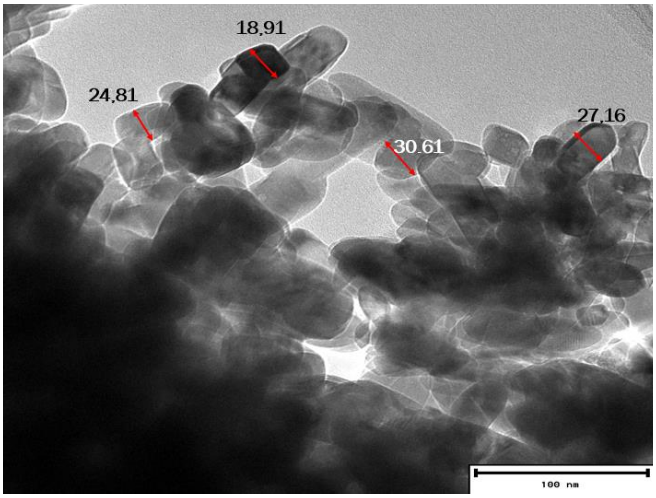


Fig 4: TEM Image of rutile $TiO_2$ nanoparticles

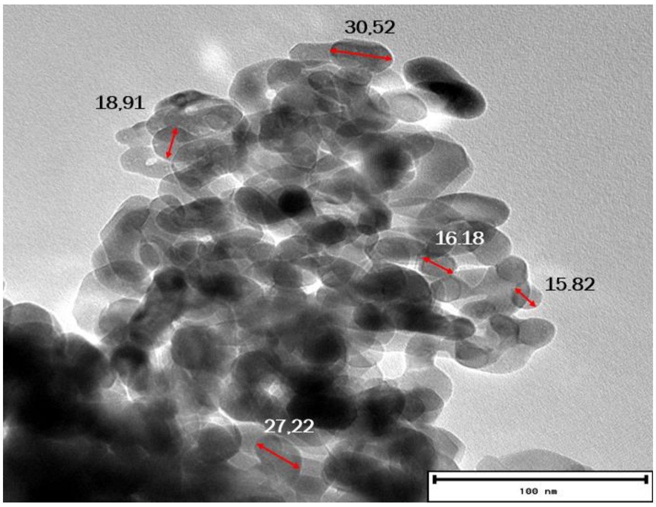


Fig 5: TEM image of anatase $TiO_2$ nanoparticles

## B. *Nanofluid Synthesis*

Uniform dispersion of nanoparticles is critical for an optimal enhancement of the base oil's properties. To ascertain this, a two-step method of synthesis was adopted for the preparation of the nanofluids. Three samples of each polymorph nanoparticles in different concentrations were added to the natural ester to form the nanofluids. The composite was stirred with a magnetic stirrer at 60˚C for 30 minutes, followed by ultrasonication for 1 hour to form a homogeneously dispersed nanofluid. Lastly, the samples were oven dried for 24 hours to eliminate excess moisture. Fig. 6 illustrates the synthesis process.

A total of 6 nanofluid samples were conducted at 0.01 vol%, 0.03 vol%, and 0.05 vol% for each phase of the nanoparticles. The rutile-$TiO_2$ nanofluids will be referred to as R1, R2, and R3 for concentrations 0.01%, 0.03%, and 0.05% respectively. The anatase-TiO2 nanofluids will be referred to as A1, A2, and A3 for concentrations 0.01%, 0.03%, and 0.05% respectively.

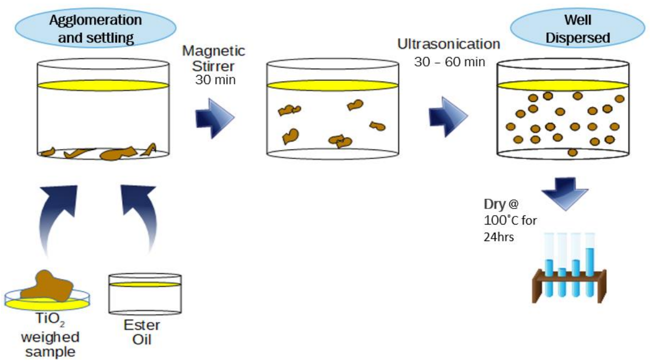


Fig. 6: 2-Step Nanofluid Synthesis Process

## C. *Breakdown Voltage Experimental Procedure*

Uniform electric field breakdown tests were conducted following the IEC60156 standard. Due to the higher viscosity of ester fluids, the rest time before experiments and in-between shots was extended to 15 min and 5 min respectively to ensure bubbles are depleted in the oil. The test cell used comprised of sphere-sphere brass electrodes spaced 2.5 mm apart. The experimental set-up was as per Fig. 7, comprising of a variable AC supply, a Step-up transformer, a current limiting resistor, a voltage divider, and the test cell. A voltmeter was used to record the breakdown voltages. As per the standard, 6 breakdown shots were recorded per sample.

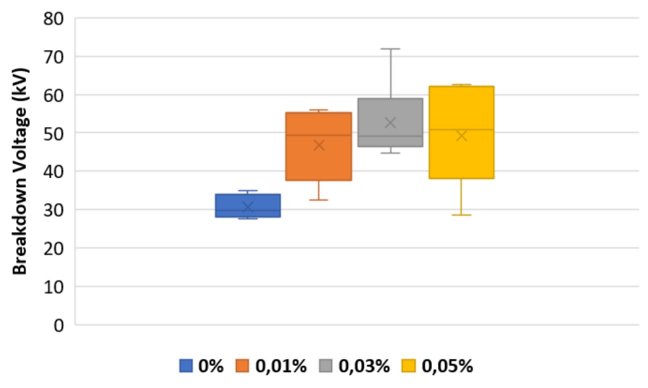


Fig. 7: Effects of rutile-$TiO_2$ loading on the breakdown voltage of an ester-based nanofluid

# III. Results and Discussion

Fig. 8 and Fig. 9 present the breakdown results of rutile-$TiO_2$ and anatase-$TiO_2$ nanofluids, respectively.

It is evident from the figures that the use of $TiO_2$ nanoparticles in both polymorphs yields an improved breakdown voltage. The trend increases with the increase in nanoparticle concentration. It is notable in both graphs that the results of the nanofluids lie well above the distribution of the pure ester fluid breakdown voltage. This shows a clear enhancement of the breakdown voltage in the nanofluids.

## A. *Rutile-$TiO_2$ Nanofluid Breakdown Voltage*

Rutile-$TiO_2$ had the highest average breakdown voltage of 49.3 kV from sample R3, which is over 60% enhancement compared to the 30.6 kV recorded for pure oil. It is however notable that sample R2 exhibited the most optimal results based on the repeatability of results. A narrow interquartile range is observed, indicating less scattering of plots compared to those of R1 and R3.

## B. *Anatase-$TiO_2$ Nanofluid Breakdown Voltage*

Similar to the rutile-based nanofluid, the anatase-based nanofluid exhibited an increase in the breakdown voltage as the concentration of anatase-$TiO_2$ nanoparticles was increased. 56.6 kV was recorded as the highest average breakdown voltage from sample A3. Based on the compact distribution of the results, this sample gave the most optimal resultant nanofluid.

## C. *Rutile vs Anatase $TiO_2$ Breakdown Voltage Enhancement*

A further comparison of the influence of the two morphologies on natural ester oil gives distinct differences in the amount of the resultant breakdown voltage enhancement. The anatase polymorph is found to have the most prominent effect on the breakdown strength of the oil. In Fig. 10, a clear comparison of the percentage improvement of breakdown voltage is presented. The two profiles follow a similar trend of enhancement, although the anatase-based nanofluids resulted in a much higher enhancement, a maximum of 85% improvement. However, samples R1 and A1 resulted in the same extent of improvement. This indicates that the superiority of the anatase polymorph is more evident at higher concentrations.

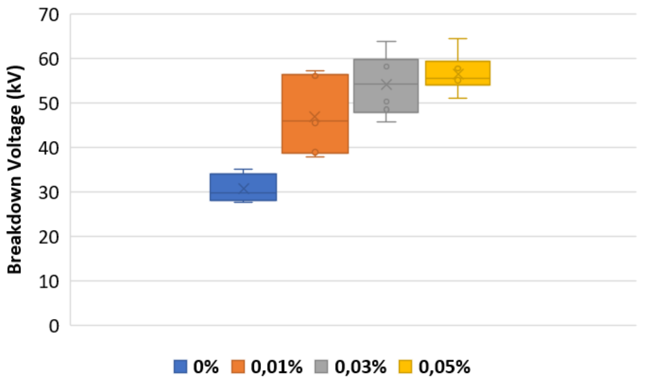


Fig. 8: Effects of anatase-$TiO_2$ loading on the breakdown voltage of an ester-based nanofluid

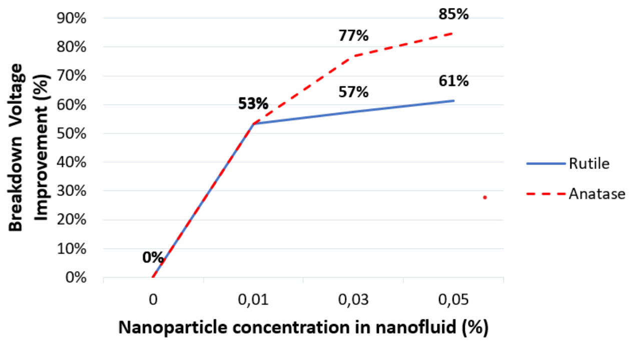


Fig. 9: Improvement of the Breakdown Voltage of Natural Ester oil based on rutile and anatase $TiO_2$ nanoparticles loading

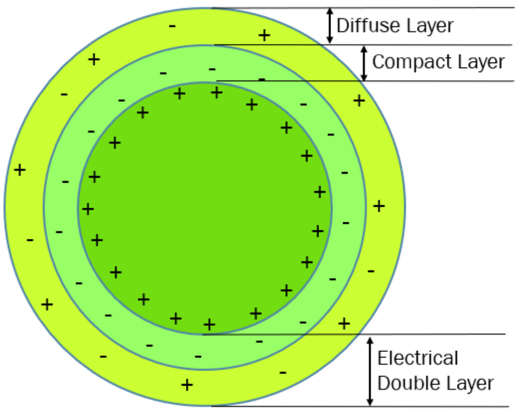


Fig. 10: Model of a nanoparticle in insulating fluid

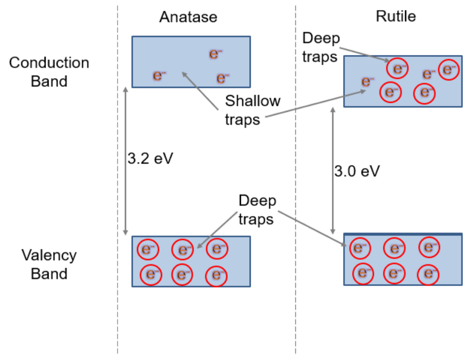


Fig 11: $TiO_2$ rutile and anatase solid state band gap

### *D. Possible Mechanisms*

The results obtained are contrary to the common belief that rutile $TiO_2$ has better dielectric properties due to its higher thermal stability as compared to anatase [11], [12]. However, anatase nanoparticles have been reported to have superior effects over rutile in other applications, particularly in photocatalysis processes. These are relatable to nanodielectrics because of the electron activity attributed to the polymorphs' effects.

According to most literature, the enhancement of the breakdown voltage in nanofluids is attributed to the electron scavenger nature of nanoparticles. In a nanofluid, the interface between the nanoparticles and the oil forms an electrical double layer around the nanoparticles. In this layer are free ions on the outer-most diffuse layer, which have the ability to attract and trap free electrons. Fig. 11 shows a representation of the interface. During breakdown, the nanoparticles tend to attract and trap the electrons from the streamer [13]–[15]. This phenomenon results in a reduction in the electric field strength, and the energy of the streamer. Hence, a much higher voltage is required for a complete breakdown.

In photocatalysis studies, researchers have studied the electron trapping of $TiO_2$ polymorphs. It was reported that anatase has a larger band gap than rutile. According to the electron band theory, semiconductive solid particles have a narrow gap between the valency band and conduction band as seen in Fig. 12, which electrons may cross given the right energy. The conduction band has shallow traps and free reactive electrons, while the valency band is occupied by deeper trapped electrons which may move to the conduction and reduce the shallow trap holes. Thus, reducing the shallow trapping ability. When a smaller band gap exists, trapped electrons can easily move to the conduction band, causing the conduction band to repel electrons [16]–[18]. It is evident from the literature that anatase-$TiO_2$ has a larger electron band gap than rutile. The band gap is 3.2 eV and 3.0 eV for anatase and rutile respectively [17], [18]. This entails that, for the same size and concentration of nanoparticles, anatase crystals will require higher energy to facilitate electron transfer. It follows that the shallow-trap mechanism associated with nanofluids may be having a much higher effect on anatase nanoparticles, hence the resultant breakdown voltage is higher than that of the rutile nanoparticles.

## IV. Conclusion

The integration of nanoparticles into ester oil results in a nanofluid with enhanced dielectric properties. The use of $TiO_2$ nanoparticles in natural ester oil has proven to significantly improve the breakdown voltage of the resultant nanofluid. Both the anatase and rutile $TiO_2$ polymorphs exhibit this enhancement. The composite containing 0,05 vol% of anatase-$TiO_2$ resulted in the highest improvement at 85% of the base fluid's breakdown voltage. The rutile-$TiO_2$ nanofluid also had a maximum improvement at 0.05 vol% of the base fluid. The breakdown voltage improved by 61%, which is significantly lower than that of anatase-$TiO_2$.

The improvement of the breakdown voltage is attributed to the electron-trapping ability of nanoparticles. The electron band theory and the differences in anatase and rutile band gaps are likely responsible for the differences in rutile and anatase breakdown voltage enhancements.

The experimental results from this work indicate that the anatase polymorph of $TiO_2$ nanoparticles is more prominent in providing improved dielectric properties to natural ester oil. This is inconsistent with the literature that suggests that rutile-$TiO_2$ has better dielectric properties than anatase. Rutile-$TiO_2$ is also more stable than anatase, which gives rise to an inquisition about the extent of improvement that anatase-$TiO_2$ has under different conditions. It is thus, prudent to pursue more studies on the effects of the polymorphs on the dielectric properties of the nanofluids.

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