Pérez-Rosa, D., García, B., Burgos, J.C. et al. Morphological analysis of transformer Kraft paper impregnated with dielectric nanofluids. Cellulose (2020)

DOI: https://doi.org/10.1007/s10570-020-03386-1

Cellulose manuscript No.
(will be inserted by the editor)

Morphological analysis of transformer Kraft paper impregnated with dielectric nanofluids

Daniel Pérez-Rosa · Belén García · Juan Carlos Burgos · Adrian Febrero

Received: date / Accepted: date

Abstract The use of dielectric nanofluids has been recently proposed as a method to improve the insulation system of transformers. It has been widely reported that these liquids present superior dielectric properties than conventional dielectric liquids and have a better behavior as cooling agents. Nevertheless some aspects need to be addressed before these materials are applicable to real equipment. This paper analyzes the interaction between dielectric nanofluids and the cellulose materials that constitute the solid insulation of transformers. The impregnation process of a transformer has been emulated in order to obtain samples of solid insulation impregnated with a Fe_3O_4 based nanofluid. The samples have been subjected to ICP testing and Cryo-SEM observation, complemented with the determination of the EDX sprectrum. The interaction between the nanoparticles and the cellulose fibers has been investigated finding that bonds are established between them when cellulose is impregnated with nanofluids.

Keywords Power transformers · Kraft paper · Nanofluids · Cryo-SEM · Mineral oil · Fe_3O_4 Nanoparticles

1 Introduction

Power transformers are one of the most important components of an electrical system. They are responsible for raising the voltage level of the energy in order to transport it with low power losses and to reduce the voltage level near to consumption points. The reliability of these elements is vital for the adequate operation of the electrical network and in some cases, transformer faults have led to power outages and severe accidents which result in high economic losses (Martin et al., 2019; Marks et al., 2016; Martin et al., 2017).

One of the main elements that makes possible the safe operation of transformers is the insulation system, which is divided into liquid and solid insulation. Transformer solid insulation is composed of different types of cellulose based materials such as Kraft paper and pressboard (Heathcote, 2007). The liquid insulation is commonly mineral oil, which is a petroleum derivative, although other fluids are starting to be used such as natural and synthetic esters.

In the last decade, the addition of nanoparticles (NPs) to transformer liquid insulation has been proposed as an attempt to improve the electrical and thermal properties of conventional insulating liquids (Segal and Raj, 1998; Wang and Xu, 1999; Özerinç et al., 2010). The development of liquids with superior dielectric and thermal properties could lead to the manufacturing of transformers with smaller sizes and higher reliability.

A number of authors have demonstrated that the addition of small concentrations of NPs can significantly improve the dielectric (Du et al., 2012b; Dai et al., 2016) and thermal (Shukla and Aiyer, 2015) properties of the oils. Experimental work has been published reporting large improvements in the AC and DC breakdown voltage, the partial discharge inception voltage and the impulse breakdown voltage of these liquids compared with those of the base fluids (Peppas et al., 2016; O'Sullivan, 2007; Kudelcik et al., 2010; Du et al., 2012b).The potential application of the improved properties observed

Universidad Carlos III de Madrid
Universidad Carlos III de Madrid, Avda de la Universidad nº30, 28911 Leganés, Madrid, Spain
Tel.: +34 916 24 8851

Fax: +123-45-678910
E-mail: daperezr@ing.uc3m.es

in nanofluids (NFs) to real transformers, could lead to the construction of more compact and efficient equipment; this idea has been studied by Weijun Yin (2013). However, although the properties of the insulating oils are improved by the addition of NPs, one of the main issues is to guarantee that the stability of this colloids is good enough to make possible their use in real transformers. The topic of the stability of the NFs is right now one of the main issues that needs to be addressed in the field of NFs for use in transformers; Several authors have published research about this topic (Primo et al., 2019; Mansour and Atiya, 2016; Ma et al., 2019), obtaining in some cases promising results of stability in NFs prepared with mineral oils or natural esters.

Another aspect that has not been investigated in depth up to the date is the relationship between NFs and other components of the transformer is an aspect that has not been investigated in depth up to date. Understanding how NPs interact with the main insulating components, as the Kraft paper or the pressboard, inside a transformer, is one of the key aspects that should be studied in order to make these fluids applicable to real units.

Very few authors have studied the influence of the NPs dispersed in the oil in the cellulose performance. Zhou et al. (2012) compared the AC and DC breakdown voltage of pressboard samples impregnated with a TiO_2 based NF and mineral oil-impregnated pressboard. In another work of the same authors (Du et al., 2012a) performed a comparison between the space charge distribution of the aforementioned samples, concluding that the increase in the AC and DC breakdown voltage observed on the pressboard with TiO_2 NPs is due to a change in the electric field distribution in the material caused by the presence of TiO_2 NPs.

Another aspect that has been studied by only a few authors is how the NPs influence the paper and pressboard ageing processes. Transformers are quite long life devices, so is important to understand how cellulose behaves in the long term when it is impregnated with a nanofluid. Cimbala et al. (2017) investigated the thermal degradation of ferrite NF-paper insulation, concluding that NF-impregnated paper insulation offers better long term moisture resistance than normal paper improving its life expectancy. In a further work (Bucko et al., 2018) the authors analyzed how the abrasive properties of NFs can affect the cellulose ageing process; the authors found that the presence of magnetic NPs might alter the cellulose structure, creating conductive channels during the ageing process that can worsen the paper insulating properties.

An aspect that has not been studied in depth up to date is how the NPs dispersed in oil chemically interact with the cellulose fibres. That is an important point to understand, since it might anticipate the influence of the NPs on the cellulosic components of the transformer. Only one study (Zhou et al., 2012) was carried out focused on the relationship between cellulose and NPs. The work was mainly devoted to analyze the change of the space charge transport process produced by the presence of NPs in NF-impregnated pressboard, but the authors include a morphological characterization, performed with Scanning Electron Microscopy (SEM), to compare the NF-impregnated pressboard and the mineral oil-impregnated pressboard. That study can be completed using more powerful techniques that make possible a clearer identification of the NPs in NF impregnated cellulose.

The main aim of the present paper is to investigate the physical and chemical interaction of the NPs and the Kraft paper when a NF is used to impregnate the cellulose material. Mineral oil and Fe_3O_4 based NFs have been prepared in the lab and have been used to impregnate Kraft paper samples following a similar procedure to the one used in transformer factories. The prepared samples were tested using Cryogenic Electron Scanning Microscopy (Cryo-SEM) and analytical techniques, to investigate how the NPs dispersed in the oil penetrate in the cellulosic insulation. Additionally, samples in which the NF had been removed, were analyzed to study whether the NPs remain in the cellulose once the samples had been cleaned, what would indicate that a bond is formed between the cellulose fibers and the NPs.

2 Materials and methods

2.1 Materials

Transformer dielectric mineral oil Nynas Nytro 4000x was used in the present work as base fluid to prepare the NF used to impregnate the cellulose insulation studied in the paper. Nynas Nytro 4000x is manufactured by the company Nynas AB (Nynas AB, Stockholm, Sweden), and it is composed of 70–90% hydrotreated light naphthenic acid, and 10–30% lubricating oils (C20-50, hydrotreated neutral oil-based) and less than 0.4% 2, 6-di-tert-butyl-p-cresol.

Fe_3O_4 NPs were provided in form of a custom-made NP suspension by the company Magnacol (United Kingdom). The Fe_3O_4 NPs in the dispersion are about 10 nm of diameter, and its concentration is 60% in weight. The solvent for the dispersion was the mineral oil Nynas Nytro 4000x. As will be explained below, small amounts of that suspension were added to samples of the mineral oil to obtain the NF used in this work.

The cellulose insulation was provided by a transformer manufacturer and was standard Kraft paper for electric insulating purpose. The specifications of the paper are grammage 0.75 g/cm^3 and thermal class 105 ^{o}C. The typical composition of this type of Kraft paper insulation is 75-85 % alpha cellulose 10-20 % hemicellulose and 2-6 % lignin (Franchek and Levin, 2016)

2.2 Experimental procedure

The NFs used in this work were prepared by mixing the base mineral oil Nynas Nytro 4000x with the Fe_3O_4 dispersion to three different concentrations 0.2, 0.3 and 0.4 g/L, no additional surfactant has been added to the mixture, the one present in the original commercial dispersion was the only used. The mixture was performed using a sonicator Sonics& Materials, Inc model VC 750 Watt. The sonicator is an ultrasonic liquid processor, which generates ultrasounds that are capable to disperse NPs within the base fluid to obtain a uniform colloid. The mixture was homogenized with the sonicator, at 40% of the rated power (i.e., power 300 W and ultrasound wave intensity 268 W/cm^2), for two hours in intervals of 30 seconds of agitation and 30 s of pause to avoid overheating of the mixture. The NF stability of the obtained colloids was evaluated in a previous work (Primo et al., 2019) using two different methods; to assess the short-term stability daily visual inspection was used, and for the long term-stability particle-size was evaluated by dynamic light scattering. It was observed that the prepared NF remained stable at ambient temperature for more than one year and had a typical distribution of NP diameter between 10 and 16 nm.

2.3 Preparation of the Kraft paper samples

The Kraft paper samples were rolled on an aluminium core (Fig. 1) using to this aim a winding machine to wrap the paper layers around the core to a thickness of 1 mm thick (14 turns). The arrangement emulates the solid insulation system of a transformer winding.

The solid insulation test specimens and the NFs were subjected to drying process at temperature 60^{o} C and vacuum 1 mbar for 24 hours in a Binder VD 53 vacuum oven before starting the impregnation process. The moisture content of the solid insulation specimens at the end of the drying process was evaluated using Karl Fischer titration, obtaining values of relative humidity (HR) ranging between 0.5 and 0.9 % relative humidity in all cases.

As explained before, the main objective of this paper is to analyze the interaction between the Fe_3O_4 NPs

Fig. 1 Solid insulation test specimen

that are suspended in the prepared NFs and the cellulose insulation during the manufacturing process of the equipment when a dielectric NF is used as an insulating liquid for the transformer. Aiming at analysing that interaction, three different types of solid insulation samples are investigated in the work: solid insulation samples impregnated with mineral oil, solid insulation samples impregnated with Fe_3O_4 based NF, and samples that had been initially impregnated with NF and subsequently treated with chloroform to remove the impregnating NF.

The solid insulation test specimens were subjected to an impregnation process that emulates what is typically done to impregnate the solid insulation of the transformer active part in factory. The process is generally done under vacuum and applying a hot-oil-spray to impregnate the solid insulation. The impregnation process was carried out in an impregnation device that is composed of two chambers connected by a hosepipe (Fig. 2). Chamber 1 has a heating resistor inside it and a thermometer to control the temperature. Chamber 2 is provided with a vacuum pump and a manometer.

In the first step the fluid is placed in Chamber 1, where it is preheated at 40^{o} C until the temperature is homogeneous. A solid insulation test specimen is placed in Chamber 2 and vacuum is applied in order to keep the Kraft paper as dry as possible. When the temperature of the fluid in Chamber 1 is stable, the hosepipe is filled with fluid. Finally, in the last step the fluid goes from the hosepipe to chamber 2, while applying vacuum in order to obtain a spray effect. The oil and the solid insulation test specimens remain under vacuum for 30 minutes. Finally the oil in Chamber 2 is drained by means of a valve located at the bottom of the chamber and the solid insulation test specimen, already impregnated, is kept in a closed container in absence of NF. The containers are sealed and maintained in this way

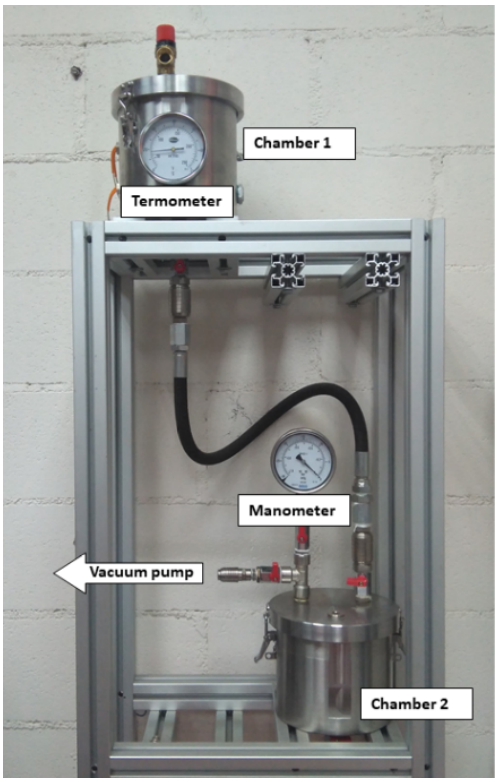

Fig. 2 Oil impregnation plant

to preserve the conditions achieved at the end of the impregnation process.

The impregnation process was evaluated by weighing samples taken from the 14 layers of paper of several solid insulation test specimens. No significant differences in weight were observed between the evaluated samples which suggests that the impregnation degree of the paper at the different layers was similar and that the impregnation process was repetitive.

To analyse the different scenarios described before, identical solid insulation test specimens were impregnated with mineral oil and with Fe_3O_4 based NFs with NP concentrations 0.2 g/L, 0.3 g/L and 0.4 g/L.

Finally, smaller samples of paper were taken from the solid insulation test specimens to be tested with the analytic techniques described next. For that purpose, a hollow drill bit of 7 mm of diameter was used. The samples used for testing were taken in all cases from the central layers of the solid insulation test specimens (i.e. layers 7 and 8)

2.4 Characterization of the paper samples

The samples were evaluated using three different techniques: Inductively Coupled Plasma mass spectrometry (ICP), Scanning Electron Cryomicroscopy (Cryo-SEM) and Energy Dispersive X-ray Spectrometry (EDX). Additionally the FTIR spectra of the samples was obtained to get insight on the types of bonds that are formed between the cellulose and the NPs.

An important objective of the characterization process is being capable to observe the presence NPs within the paper while it is impregnated with mineral oil or NF. This aspect is one of the main difficulties of the present work, since a small quantity of mineral oil could be quite corrosive to the components of the Scanning Electron Microscopy (SEM) classic equipment, due to the high vacuum conditions required to observe the samples.

ICP is an element identification technique that is suitable to identify the presence of Fe or other elements in solid samples. It was used in this work to identify the presence of Fe_3O_4 NPs in Kraft paper that had been impregnated with NF of different NP concentrations after the oil had been chemically removed from the Kraft paper. The ICP measuring process starts by cleaning the NF from the impregnated paper using chloroform as solvent; after that the samples are crushed and dried. In order to obtain a solution for the ICP determination a 24 hours digestion is carried out in acid medium (HCl 50%).

To observe the interaction between NPs and the cellulose fibres, Cryo-SEM was used. This technique enables the observation of cellulose samples in presence of oil or dielectric NF.

Transmission electron microscopy (TEM) has been widely used by some authors (Smiechowicz et al., 2018; Alsalhi et al., 2012; Lay-Ekuakille et al., 2018) for morphological characterization of solid samples and observation of NPs within solid materials. However, the application of TEM is not possible in this work, since it would require the transference of the NPs to a hydrophilic solution, what would lead to remove of the oil that supports the NP dispersion.

For the Cryo-SEM characterization, the samples are set on carbon film in a Cryo-holder and transferred in a Cryo-SEM preparation system PPT2000 with Cryo-transfer (Quorum Technologies), to be analyzed in a cryogenic dual beam microscope, NOVA Nanolab 200 (FEI). The Kraft paper samples are treated at low temperature using liquid nitrogen and vacuum. Samples are fast frozen in liquid nitrogen in order to preserve the natural state of the sample and then transferred, under vacuum, into a preconditioning chamber. Surface frost is removed by subliming the sample at -90º C for 5 min. The samples are then platinum-coated using plasma sputtering and subsequently inserted in the microscope chamber and kept at temperature -130º C and vacuum. As explained before, samples impregnated with nanodi-

electric oil and cleaned with chloroform were also observed by Cryo-SEM.

The microscope NOVA Nanolab 200 deployed in this work is also equipped with an Energy Dispersive X-ray Spectrometer (EDX) (Oxford INCA). An EDX analysis of the samples was carried out to complete the study, for that purpose the surface and the cross section of the cellulose samples was analyzed at several regions. An accelerating voltage of 30 kV was applied to determine the Fe presence with the peak intensity of the Fe K-α X-ray line (6.398 keV).

3 Results and discussion

3.1 ICP Analysis

The results of the ICP analysis are shown in table 3.1. As can be seen, all the samples showed measurable quantities of Fe, even those samples that had been treated in an acid medium and digested, which is a chemical process capable of eliminating most of the Fe in the samples. The presence of Fe in those samples seems to indicate that the NPs dispersed in the NF tend to migrate towards the Kraft paper and bind to cellulose fibres.

Table 1 Table 1. ICP analysis results

Sample	Paper weight (g)	Fe (ppm)	Mean
0.2 g/L	0.5095	115	220
	0.5055	325	
0.3 g/L	0.5009	270	170
	0.4640	70	
0.4 g/L	0.5099	135	440
	0.5030	672	

It must be noted that there are important differences between the ppm of Fe obtained on twin samples prepared at identical conditions (i.e. using a NF with the same NP concentration). Additionally, the results do not show a clear relation between the presence of Fe and the concentration of NPs in the NF as the ppm of Fe determined from the different samples do not keep a monotonous relation with the NP concentration in the oil.

Although ICP measures provide a clear evidence of the presence of NPs in the cellulose samples, they are insufficient to clearly report a direct relationship between the NP concentration in the oil and the concentration of Fe in the Kraft paper. The lack of consistency observed in the Fe concentrations might be caused by the chemical digestion process and the use of HCl as acid medium which can eliminate a non constant amount of Fe_3O_4 NPs.

3.2 Cryo-SEM and EDX

Circular samples of 7 mm paper of diameter extracted from the solid insulation test specimens displayed in Fig. 1, were characterized using Cryo-SEM as explained in Section 2.

Three different types of samples were evaluated in order to understand the interaction between NPs and Kraft paper:

1. NF-impregnated Kraft paper samples. Further referred to as NFS.
2. Mineral-oil-impregnated Kraft paper samples. Further referred to as MOS.
3. NF impregnated Kraft paper samples that had been treated with chloroform to remove the oil. Further referred to as NFScl.

The main objective of the study is to compare the morphology of the three types of samples (NF, MOS and NFScl) and to identify the NPs attached to the cellulose fibres in those cases where NFs were used to impregnate the paper. The samples were analyzed from two different points of view: On a first step, a cross section of the Kraft paper was observed; then the surface of the Kraft paper was observed using in both cases Cryo-SEM microscopy.

The NF-impregnated samples (NFS and NFScl) characterized with Cryo-SEM were extracted from the solid-insulation test specimen impregnated with the NF with highest NP concentration (i.e. 0.4 g/L). The reason to choose the samples with the highest content of NF is to facilitate the observation of the NPs.

Initially the samples were observed using the Back Scattered Electrons (BSE) mode, to distinguish the Fe_3O_4 NPs from the cellulose fibres in brightness, due to the different atomic numbers of the elements. After some attempts we found that it was not possible to detect a significant difference of brightness and we moved to use Secondary Electrons (SE) mode, which gave us information about the morphology and made it possible to obtain clearer images of the samples.

Fig. 3 shows the cross section image of the NF-impregnated Kraft paper sample (NFS). The image is quite clear and it is possible to identify the cellulose nanofibres on the right bottom part of the image and on the centre of the image. It is also possible to observe

a large number of bright spherical forms that were identified in a first moment as Fe_3O_4 NPs; some of them are highlighted with yellow circles.

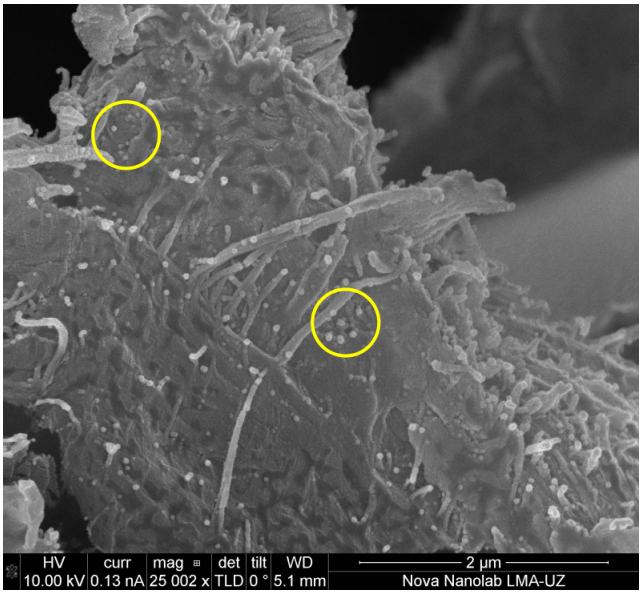

Fig. 3 Cryo-SEM image of the cross section of a NF impregnated Kraft paper sample (NFS)

Fig. 4 compares two images of the cross section of a mineral-oil-impregnated Kraft paper sample (MOS) (b), and a NF-impregnated Kraft paper (NFS) (a). Both images clearly show the cellulose nanofibres, which are part of the cellulose macrofibres. It can be observed how, depending on the orientation of the nanofibres, they are visible as spheres or cylinders.

The comparison of the two images in Fig. 4, in which one of the samples was impregnated with mineral oil (i.e. without presence of NPs) and the other one was impregnated with NF (i.e. with presence of NPs), lead us to infer that, because of the shape and the size of the cellulose nanofibres, these can be confused with NPs. Thus, it must be concluded that although presumably some of the circular shining forms are observed in Fig. 3 and 4 (b) are Fe_3O_4 NPs, it is not possible to assert it with total confidence.

To complete the study, a Cryo-SEM evaluation of the surface of three additional samples of types NFS, MOS and NFScl was carried out. Those analysis were complemented with the obtaining of the EDX spectra of the three samples, aimed at providing an accurate evidence on the presence of Fe_3O_4 NPs in paper, and to make possible a quantification of the NP content in the different samples.

Fig. 5, 6 and 7 show the images of the three samples observed with Cryo-SEM and the spectra measured by EDX.

Fig. 5 shows the surface of a Kraft paper sample impregnated with mineral oil (MOS); that sample is used as blank sample to be compared with the ones impregnated using NFs (NFS and NFScl). In Fig. 5 (a) the cellulose structure can be clearly seen as a randomly crossing fibres structure. A detail of the same section of Kraft paper surface is shown in Fig. 5 (b). Finally, in Fig. 5 (c) an EDX spectra is shown, which was taken on the surface of the Kraft paper. As can be observed in the EDX spectra, the composition of the sample corresponds mainly to the cellulose element components (C and O); the platinum coating used to improve the resolution of the technique is also present in the EDX spectra.

Fig. 6 (a) and (b) shows the surface of a Kraft paper sample impregnated with NF (NFS). As can be seen the Fe_3O_4 NPs are not easily visible on the cellulose surface shown in (a). In Fig. 6 (b), which is a detail of the cellulose fibres, some regions might be identified as NP agglomerates, although, as in the case of the cross section sample, it is not possible to make it completely certain from the image. Fig. 6 (c) shows the results of the EDX spectra of the sample surface. The presence of Fe in it confirms the presence of the NPs on the surface of Kraft paper.

Fig. 7 shows the surface of a Kraft paper sample NFScl type, which was first impregnated with NF and then cleaned with chloroform to remove the NF. As in Fig 6, the NPs on the surface of the sample can not be made certain, although it seems highly probable that some of the bright regions in the figure are NPs and NP agglomerates. In this case the images are more clear than in the previous ones and the cellulose fibre structure can be very clearly appreciated. It must be noted that the presence of oil in the cellulose samples reduces the resolution of the Cryo-SEM method; in NFScl samples the oil that impregnated the cellulose has been removed what allows to distinguish the presence of NP agglomerates on the paper surface surface and even to measure them.

Fig. 7 (c) shows the EDX spectra of the sample. One of the important things that can be noticed in it is that, although the NF has been removed from the cellulose in this case, a remarkable amount of the Fe stays bounded to the cellulose fibres. Bonding between cellulose fibres and NPs was also reported by Klapiszewski et al. (2017) who proposed an interaction mechanism between both elements, according to which the interaction occurs by the formation of bridges from an organic carbon molecule to the inorganic Fe_3O_4 NPs.

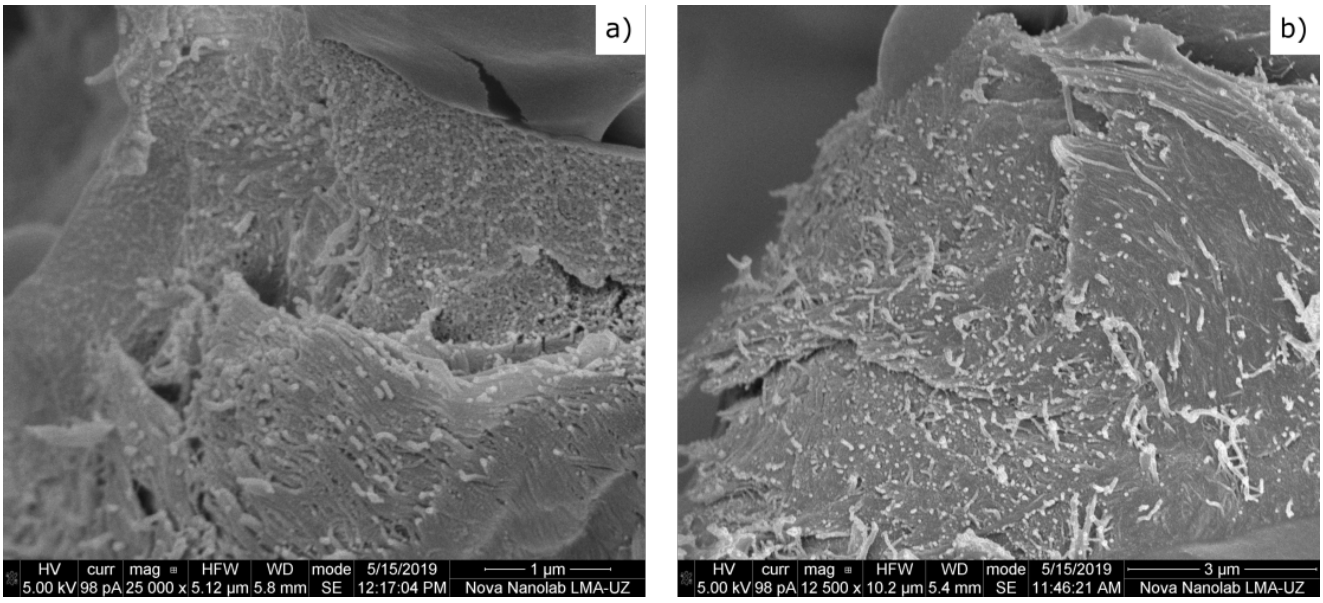

Fig. 4 (a) Cryo-SEM image of a cross section of mineral oil impregnated Kraft paper (MOS).(b) Cryo-SEM image of cross section of NF impregnated Kraft paper (NFS)

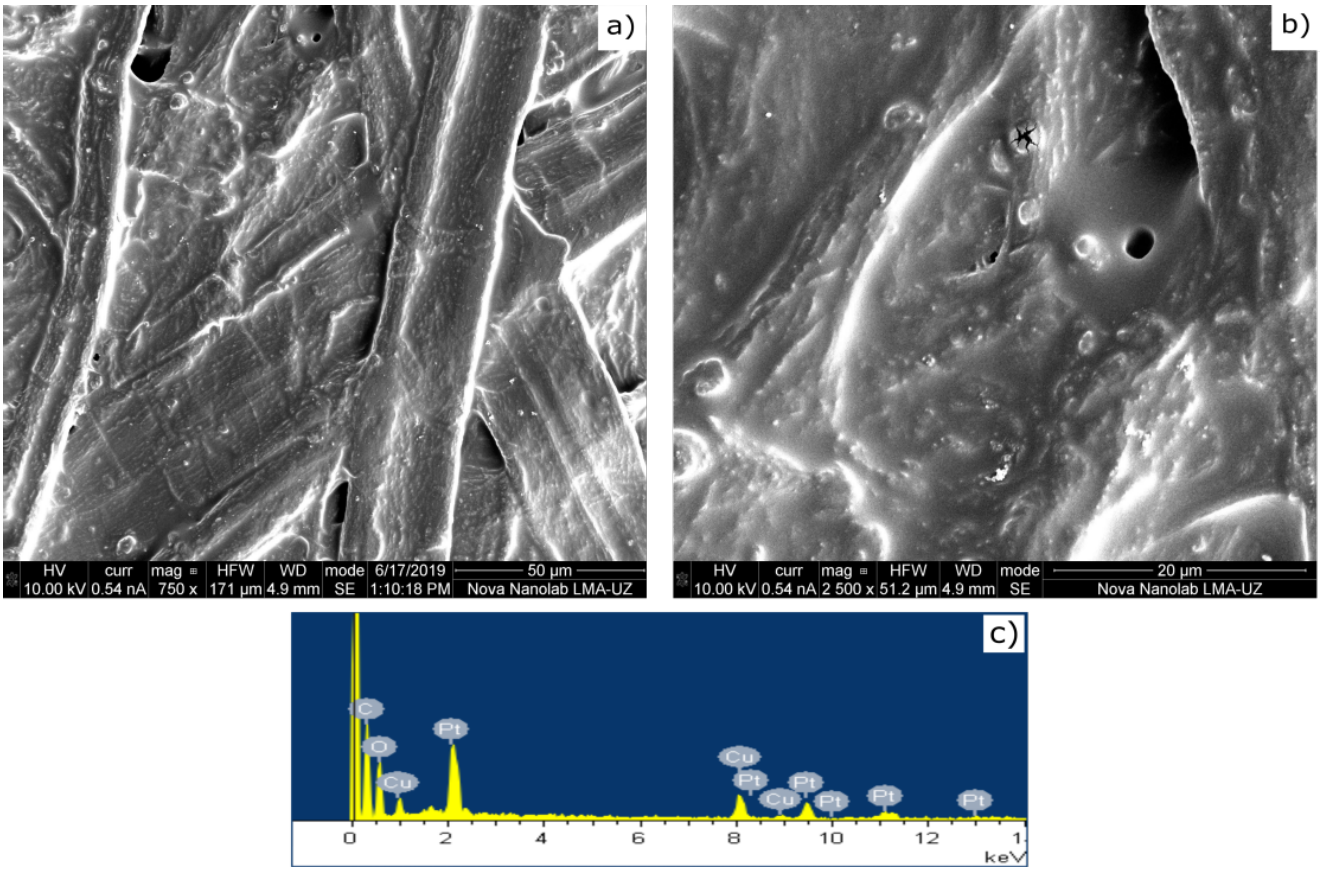

Fig. 5 (a)(b) Cryo-SEM images of the mineral oil impregnated Kraft paper (MOS). (c) EDX analysis of oil impregnated Kraft paper (MOS)

Fig. 8 shows the image of a NP agglomerate that remained in the cellulose surface when the oil was removed,; the figure also shows the EDX spectra of the agglomerate. The results of the spectra are quite clear; the visualized agglomerate is composed of Fe and the rest of elements appearing in the spectra are the same

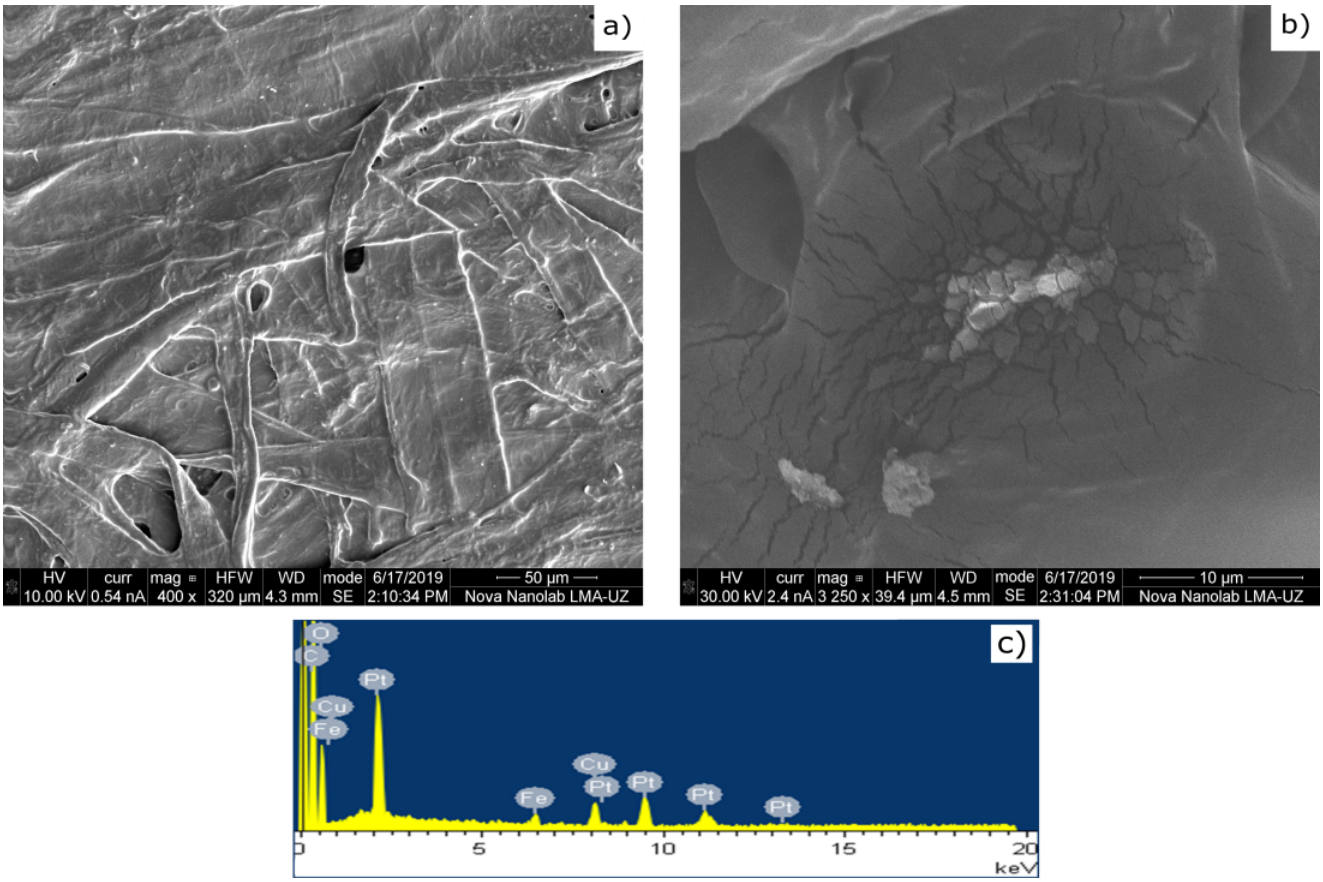

Fig. 6 a)b) Cryo-SEM images of the NF impregnated Kraft paper (NFS). c) EDX analysis of NF impregnated Kraft (NFS)

that in the previous before: carbon, oxygen, platinum and copper (these last elements belong to the cellulose structure or the coating).

Fig. 9 shows an impurity macroparticle that was found on the surface of the Kraft paper sample treated with chloroform (NFScl). It can be observed how a number of NPs are attached on the paper. Those NPs were measured with the Cryo-SEM equipment to obtain a relation of sizes. The measured NP sizes are within 19 and 40 nm, what is in agreement with the sizes of NPs measured in the NF by the authors in a previous work (Primo et al., 2019).

According to the images and the EDX spectra shown in Fig. 7, 8 and 9, we can conclude that the NPs can behave in three different ways when removing the oil: they can remain bounded to cellulose, they can form agglomerates that deposit on the cellulose surface or they can deposit on impurities. The presence of agglomerates or a non uniform distribution of NPs on the surface of the cellulose could affect to the insulation properties such as partial discharges. Since the agglomerates appear on our samples when removing the oil, and regarding the Cryo-SEM images we have observed an uniform distribution of NPs on the cellulosic insulation, nevertheless the NPs could affect to the insulation properties as reported by Liu et al. (2019) who observed improvements in partial discharges in TiO_2 NPs impregnated cellulose.

Table 2 summarizes the results of the EDX spectra on all the analyzed samples and on the NP agglomerate.

Table 2 Comparison of the results of EDX spectra

Element	Samples			
% Weight	MOS	NFS	NFScl	NP agglomerate
C	47.53	52.98	50.44	51.34
O	35.09	30.03	37.08	36.12
Fe	-	0.78	0.26	0.23
Pt	12.72	13.53	11.30	10.52
Cu	4.66	2.68	0.92	1.79

It is possible to observe how Fe does not appear in the sample impregnated with mineral oil. This sample is used as blank to be compared with the others. The amount of the main elements of cellulose (C and O) present in all the samples is similar; the same happens with Pt, which is the metal that is used to coat

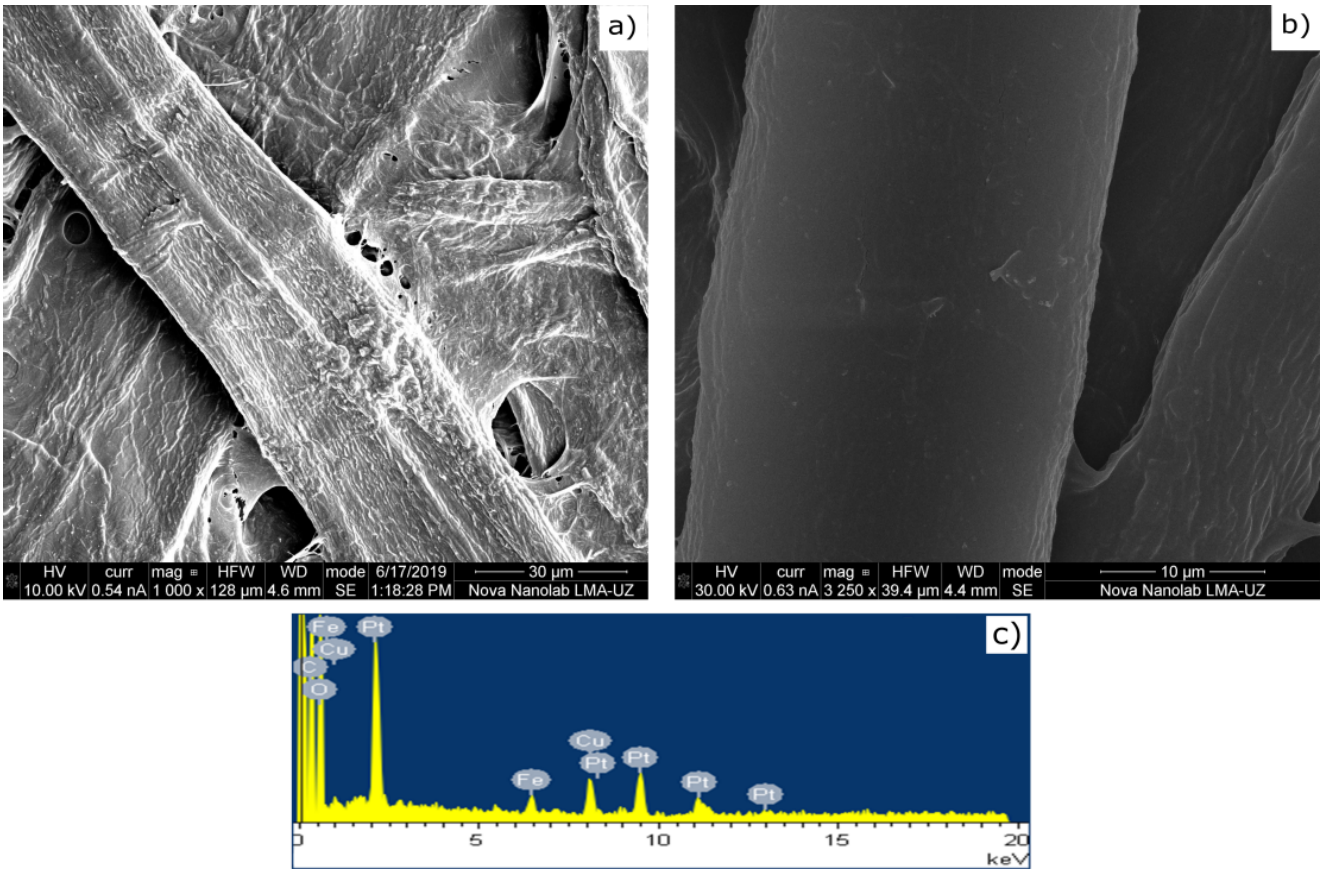

Fig. 7 (a)(b) Cryo-SEM images of the NF impregnated Kraft paper (NFScl). (c) EDX analysis of NF impregnated Kraft (NFScl)

all the samples. The presence of Cu in all samples, can be explained as the Cu is present in an important amount, in the commercial aluminium alloys (Hildeman and Koczak, 1989), used in this case as core for the solid insulation test specimens.

On the other hand, the presence of Fe in the samples that are impregnated with NF or in those that were impregnated with it and subsequently cleaned is clear. The sample containing NPs and oil presents the higher weight percentage of Fe, but it is remarkable how Fe is also detected in the sample cleaned with chloroform (NFScl). Additionally, it was possible to detect the NPs aggregates formed when the NF was removed from the samples.

3.3 FTIR analysis

In order to complete the analysis of the mentioned Fe_3O_4-lignin structures circular samples of paper of diameter 7 mm extracted from the solid insulation test specimens, were characterized using FTIR. Fig. 10 shows the results of the analysis. Fig. 10 (a) correspond to a sample taken from a test-specimen impregnated with mineral oil, Fig. 10 (b) to a sample impregnated with NF and NP concentration 0.4 g/L and subsequently washed with chloroform, and Fig. 10 (c) to a sample impregnated with NF and NP concentration 0.4 g/L.

As can be seen in Fig. 10 small changes appear in the Fe-O stretching vibration at 569 cm^{-1} comparing Fig. 10 (b) and (c) with reference Fig. 10 (a). It can be also seen how the the multiple C-O vibrations signals at 1370, 1208, 1025 cm^{-1} changes from 10 (a) to (c). The small changes on the FTIR spectra correspond to the vibration of C-O bonds (1370, 1208, 1025 cm^{-1}) and Fe-O stretching vibration (569 cm^{-1}) might be explained as changes on the chemical environment when ferrite-lignin bridges are formed. Despite the changes in the spectra are quite small it can be noted that the chemical environment changes, even when the NP concentrations are as small as 0.4 g/L. These variations are in agreement with the results presented by Klapiszewski et al. (2017).

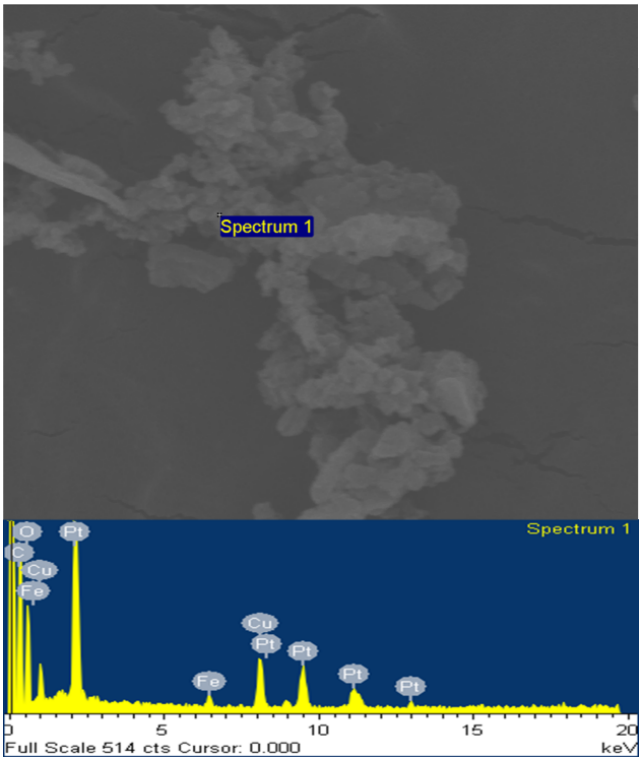

Fig. 8 NP Agglomerate detail

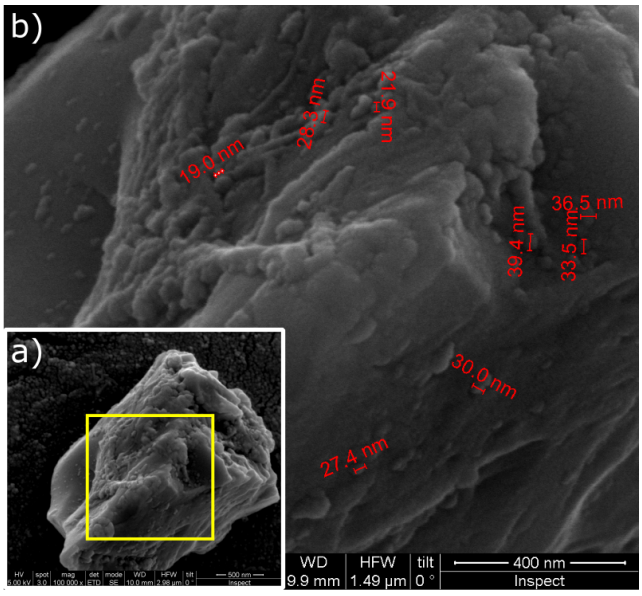

Fig. 9 (a)Macroparticle with NPs attached, (b)NPs detail

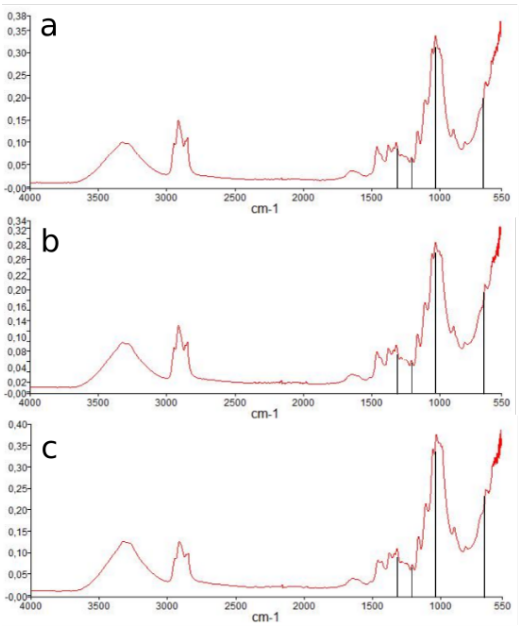

Fig. 10 (a)FTIR spectra of MOS, (b)FTIR spectra of 0.4 g/L NFScl (c)FTIR spectra of 0.4 g/L NFS

4 Conclusions

In the present work the morphological structure of NF-impregnated Kraft paper was evaluated. It was proved that the Cryo-SEM technique combined with EDX spectra is an suitable way to evaluate the structure of the cellulose, even when the samples are impregnated with oil, which can be corrosive to the components of the SEM classic instruments.

As it was shown in this paper, for a clear identification of the presence of NPs in the paper the combination of both characterization techniques (EDX and Cryo-SEM) is required. Although the visual differentiation between NPs and cellulose nanofibres is not easy, a methodology was proposed that made it possible to identify the presence of NPs in NF-impregnated Kraft paper.

From the conducted analysis, it possible to conclude that the NPs dispersed in the mineral oil tend to bound the cellulose molecules. Even when the paper is treated chemically to remove the base oil a remarkable number of NPs remain bounded to the cellulose.

Despite the fact that it was impossible to identify single NPs on the Kraft paper surface, NP agglomerates have been identified on it when the oil is removed by chemical methods. Also, the size of some NPs attached to an impurity were measured obtaining values that match typical NP sizes corresponding to the ones measured in the prepared NF.

An analysis based on the determination and comparison of the FTIR spectra of different samples was carried out, which suggested that a chemical bond is formed between the cellulose and the Fe_3O_4 NPs.

It would be desirable to complete the study using other analytical techniques which can show changes in the elemental state, such as X-ray photoelectron spectroscopy. Additionally, investigation with other types of NPs will be conducted in the future to complete the investigation.

Acknowledgements This research was funded by the Spanish Ministry of Economy and Competitiveness. Grant number DPI2015-71219-C2-2-R and Spanish Ministry of Innovation. Grant number PID2019-107126RB-C21.

5 Bibliography

References

Alsalhi MS, Aldwayyan AS, Jasas AH, Atif M, Aslam Farooq W (2012) Study of the Structural Analysis of Dye-Silica Core-Shell Nanoparticles (DSC-SNPs). 9th Int Conf High Capacity Optical Networks and Enabling Technologies pp 175–178, DOI 10.1109/HONET.2012.6421458

Bucko S, Martin K, Cimbala R, Kruželák L, Zbojovský J (2018) Abrasive Properties of Transformer Oil-based Magnetic Nanofluid. Int Sci C Pow Eng pp 1–4

Cimbala R, Bucko S, Kruželák L, Kosterec M (2017) Thermal Degradation of Transformer Pressboard Impregnated with Magnetic Nanofluid Based on Transformer Oil. Int Sci C Pow Eng (26220120055):1–5

Dai J, Dong M, Li Y, Zhou J (2016) Influence of Nanoparticle Concentration on the Frequency Domain Spectroscopy Properties of Transformer Oil-based Nanofluids. IEEE Conf on Electrical Insulation and Dielectric Phenomena pp 587–590

Du Y, Lv Y, Li C, Chen M, Zhong Y, Zhang S, Zhou Y (2012a) Effect of Nanoparticles on Charge Transport in Nanofluid-impregnated Pressboard. J Appl Phys 111(12), DOI 10.1063/1.4730778

Du Y, Lv Y, Li C, Chen M, Zhong Y, Zhou J, Li X, Zhou Y (2012b) Effect of Semiconductive Nanoparticles on Insulating Performances of Transformer Oil. IEEE T Dielect El In 19(3):770–776, DOI 10.1109/TDEI.2012.6215079

Franchek M, Levin A (2016) Insulations ® DPE. Transformers Magazine 3

Heathcote MJ (2007) Basic materials. In: J & P Transformer Book, Elsevier, DOI 10.1016/b978-075068164-3/50005-3

Hildeman GJ, Koczak MJ (1989) Powder-metallurgy Aluminum Alloys. Treatise on Materials Science & Technology, vol 31, Elsevier, pp 323–364, DOI 10.1016/B978-0-12-341831-9.50016-4

Klapiszewski Ł, Zdarta J, Antecka K, Synoradzki K, Siwińska-Stefańska K, Moszyński D, Jesionowski T (2017) Magnetite Nanoparticles Conjugated with Lignin: A Physicochemical and Magnetic Study. Appl Surf Sci 422:94–103, DOI 10.1016/j.apsusc.2017.05.255

Kudelcik J, Bury P, Kopcansky P, Timko M (2010) Dielectric Breakdown in Mineral Oil ITO 100 Based Magnetic Fluid. vol 9, pp 78–81, DOI 10.1016/j.phpro.2010.11.019

Lay-Ekuakille A, Di Paola M, Conversano F, Casciaro S, Sommella P, Liguori C, Bhateja V (2018) Determining Shapes and Sizes Using TEM Images: Functionalized Nanoparticles. Nanotechnology for Instrumentation and Measurement pp 5–16, DOI 10.1109/NANOFIM.2016.8521426

Liu D, Wu Y, Xu X, Ye J, Li J, Yu S, Li X (2019) Suppression Mechanism of TiO2 for the Partial Discharge of Oil-paper Insulation in Intensive Electric Field. I C Dielect Liquids pp 1–4, DOI 10.1109/ICDL.2019.8796771

Ma X, Dong M, Li Y, Xie J, Zhang C (2019) Suspension Stability of Transformer Oil-based Nanofluids. I C Dielect Liquids pp 1–4, DOI 10.1109/ICDL.2019.8796826

Mansour DeA, Atiya EG (2016) Application of UV / Vis Spectroscopy to Assess the Stability of Oil-based Nanofluids. IEEE Conf on Electrical Insulation and Dielectric Phenomena pp 671–674

Marks J, Martin D, Saha T, Krause O, Alibegovic-Memisevic A, Russell G, Buckley G, Chinnarajan S, Gibson M, MacArthur T (2016) An Analysis of Australian Power Transformer Failure Modes, and Comparison with International Surveys. Austr Univ Pow Eng pp 1–6, DOI 10.1109/aupec.2016.7749314

Martin D, Marks J, Saha T (2017) Survey of Australian Power Transformer Failures and Retirements. IEEE Electr Insul M 33(5):16–22, DOI 10.1109/MEI.2017.8014387

Martin D, Beckett C, Brown J, Nielsen S (2019) Analysis and Mitigation of Australian and New Zealand Power Transformer Failures Resulting in Fires and Explosions. IEEE Electr Insul M 35(6):7–14, DOI 10.1109/MEI.2019.8878255

O'Sullivan FM (2007) A Model for the Initiation and Propagation of Electrical Streamers in Transformer Oil and Transformer Oil Based Nanofluids. Thesis (Ph D)–Massachusetts Institute of Technology, Dept of Electrical Engineering and Computer Sci-

ence, 2007
Özerinç S, Kakaç S, Yazıcıoğlu AG (2010) Enhanced Thermal Conductivity of Nanofluids: A State-of-the-art Review. Microfluid Nanofluid 8(2):145–170, DOI 10.1007/s10404-009-0524-4
Peppas GD, Bakandritsos A, Charalampakos VP, Pyrgioti EC, Tucek J, Zboril R, Gonos IF (2016) Ultrastable Natural Ester-Based Nanofluids for High Voltage Insulation Applications. Acs Appl Mater Inter 8(38):25202–25209, DOI 10.1021/acsami.6b06084
Primo VA, Pérez-Rosa D, García B, Cabanelas JC (2019) Evaluation of the Stability of Dielectric Nanofluids for Use in Transformers under Real Operating Conditions. Nanomaterial-Basel 9(2), DOI 10.3390/nano9020143
Segal V, Raj K (1998) An Investigation of Power Transformer Cooling with Magnetic Fluids. Indian J Eng Mater S 5(6):416–422
Shukla G, Aiyer H (2015) Thermal Conductivity Enhancement of Transformer Oil Using Functionalized Nanodiamonds. IEEE T Dielect El In 22(4):2185–2190, DOI 10.1109/TDEI.2015.004678
Smiechowicz E, Niekraszewicz B, Kulpinski P, Dzitko K (2018) Antibacterial Composite Cellulose Fibers Modified with Silver Nanoparticles and Nanosilica. Cellulose 25(6):3499–3517, DOI 10.1007/s10570-018-1796-1
Wang X, Xu X (1999) Thermal Conductivity of Nanoparticle–fluid Mixture. J Thermophys Heat Tr 13(4)
Weijun Yin N (2013) Patent No; US 2013/0285781
Zhou Y, Zhong YX, Chen MT, Zhang SN, Du YF, Lv YZ, Li C, Liu T (2012) Effect of Nanoparticles on Electrical Characteristics of Transformer Oil-based Nanofluids Impregnated Pressboard. IEEE Int Sym Elec In pp 650–653, DOI 10.1109/ELINSL.2012.6251552