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Preparation of Composite Insulating Paper With Decreased Permittivity, Good Mechanical and Thermal Properties by Kevlar/Nano Cellulose Fibrils/Softwood Pulp Hybrid

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ABSTRACT Kevlar pulp treated with low-temperature plasma and nano cellulose fibrils (NCFs) have been introduced as reinforcements in the preparation for composite insulating paper with low relative permittivity, dielectric loss, good mechanical properties, and thermal stability. More polar groups of Kevlar fibers could be exposed after plasma treatment. Results showed that the relative permittivity of the composite paper containing 20% Kevlar pulp, 10% NCF, and 70% softwood pulp is decreased by 29.6% and the dielectric loss is decreased by 43.2% at 50 Hz, 25°, compared with the conventional paper formed by pure softwood pulp. The change was due to the introduction of Kevlar pulp with intrinsic low dielectric constant and loss, which decreases the whole polarizability of the paper. The mechanical properties of the composite paper became worse after introducing 20% Kevlar pulp. About 10% NCF can work as a mechanical reinforcement to compensate for the tensile and Yang's modulus loss. Scanning electron microscopy results showed that NCF could fill the void defects and improve the interface bonding of the fibers to enhance the paper mechanical properties. The composite paper also had better insulating and thermal properties than the conventional paper. It has been concluded that the Kevlar pulp/NCF/softwood pulp composite paper has the potential to replace the pure softwood paper for the application of high-voltage ac transformer insulation.

INDEX TERMS Kevlar pulp, NCF, composite insulating paper, low permittivity, low dielectric loss, mechanical properties, thermal stability.

I. INTRODUCTION

Lignocellulose material, together with insulating oil, is widely applied in the power transformers due to its low cost, renewability and relatively good insulating performances [1]. The main insulation structure in transformer is mainly formed by oil ducts, pressboards and paper barriers [2]. The oil-impregnated lignocellulosic insulating paper has a permittivity around 4.1–4.8, which is over twice that of insulating oil [3]. As a result, the electrical field strength in the oil ducts is more than two times that in paperboards under AC electrical stress. However, the electrical strength of the oil is far less than that of insulating paper. Thus, insulating oil is easy to initiate discharge and becomes the weakness of the insulation. Reducing the permittivity of the insulating paper can uniform the electrical field distribution in the transformer and further strengthen the transformer insulating ability [4].

The approach of using intrinsic low permittivity synthetic materials hybrid lignocellulose pulp for preparing decreased permittivity composite pressboard has been extensively studied [5]. From the previous researches, blending polymethylpenten fibers, polypropylene fibers, and polytetrafluoroethylene fibers with lignocellulose pulp could prepare composite insulating pressboards with permittivity around 3.0 $\sim$ 3.5 [4]. However, the drawbacks are that, the compatibility of reported synthetic fibers and the cellulosic fibers is extremely poor for the lack of polar groups in synthetic fibers, which causes the mechanical strength of the composite paper far less than that of the conventional cellulose paper [6]. Meanwhile, the introduction of some synthetic fibers leads to a decrease in the thermal stability of the paper and an increase in dielectric loss [7]. In contrast, Kevlar

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pulp, composed by poly-pphenylene ferephthalamide (PPTA) molecular, is widely used in the composites as a reinforcement owing to its low permittivity, high mechanical strength and excellent thermal stability [8], [9]. Moreover, the amide groups in the PPTA molecule are polar groups which can be easily hybridized with polar polymers such as cellulose [10]. Therefore, Kevlar pulp is likely to be a promising material for preparing a composite pressboard with decreased permittivity and dielectric loss. In spite of the amide groups in PPTA, the compatibility of PPTA and cellulose is still unsatisfactory, because of the great difference in chemical composition and structure, resulting in a poor mechanical strength of the composite pressboard [11]. It is reported that increasing the hot pressing temperature and pressure during calendaring could enhance the tensile strength of the composite pressboard [12]. However, the temperature of the metal plate over 150° can degrade the cellulose chains and the high pressure can increase the density of the paper, leading to a higher permittivity and dielectric loss [13]. Researchers carried out abundant investigations to enhance the interfacial bonding between aramid pulp and matrix materials by chemical treatment, coupling agent modification and plasma treatment [14], [15], in which low temperature plasma treatment is an environmentally friendly and efficient method.

The composite insulating pressboards, which have porous structures, are formed by randomly distributed fibers stacked via intermolecular forces [16]. The mechanical strength of the pressboards is determined by the intermolecular hydrogen bond strength and the interfacial bonding strength between fiber clusters [17]. The former can be enhanced by increasing the polar groups of the molecular, while the latter could be improved by decreasing the interface defects between clusters. The Nano Cellulose fibril (NCF) is extensively applied as an adhesive for polymer composites to increase the composites mechanical strength, thanks to its characteristics of nanoscale, large amount of active hydroxyl groups and large specific surface area [18]. It is reported that NCF could reduce ''Micro-pore'' defects in fiber networks, thus increasing the tensile strength of the insulating paper dramatically [19].

This study aims to prepare a kind of composite insulating paper with low permittivity, low dielectric loss and good mechanical properties suitable for insulation of ultra-high voltage transformers, by blending Kevlar pulp, NCF, and lignocellulose pulp. Kevlar pulp was used to reduce the permittivity and loss and increase the thermal stability of the composite pressboard as a reinforcement. The Kevlar pulp was treated with low temperature plasma to expose more polar groups and the hybrid content of Kevlar pulp was from 5% to 20%. NCF was used to enhance the interfacial bonding strength between fiber networks, of which the content was 10%, for it was reported that high content NCF could increase the permittivity and loss of the insulating paper [18]. The electrical properties including permittivity, dielectric loss, resistivity and breakdown strength, thermal properties, and tensile strength of composite insulating papers and conventional softwood paper were tested and compared. The interfaces of the Kevlar pulp, NCF and lignocellulose pulp were characterized by SEM pictures.

II. EXPERIMENTAL

A. MATERIALS

The lignocellulosic unbleached softwood pulp (abbreviated as KWP) used in this study was purchased from Taizhou Xinyuan Electrical Equipment Co., Ltd and degree of polymerization (DP) value of the softwood pulp was 1750. Kevlar pulp (abbreviated as KP) was purchased from DuPont with a size of 0.7–1.6 mm and density of 1.44 g/cm^3 and permittivity of 2.7 at 50 Hz. The NCF was from Guilin Qihong Technology Co., Ltd. It was prepared by mechanical grinding and homogenization. Diameter of the obtained nanofibers was in the 5–60 nm range. Concentration of the NCF suspension was 2.5 wt%. The chemical reagents used in this study including Acetone (AR, 98%) and Ethanol ($\geq$99.5%) were from Shanghai Aladdin Biochemical Technology Co., Ltd. The deionized water (resistivity 18.25 M $\Omega\times$ cm) used in the whole preparing process was generated by Molelement 1805 ultra-pure water system from Chongqing Molecular Water Treatment Equipment Co., Ltd.

B. KEVLAR PULP TREATMENT

The Kevlar pulp was cleaned by acetone at 75° for 24 hours to remove the surface attachments and washed in anhydrous ethanol to remove the impurities such as dust and oil on the surface of the fibers. Then, dried in a vacuum oven at 100° for 3 hours. The cleaned Kevlar pulp was put into low temperature plasma processor in 30 MPa ammonia atmosphere and treated for 15 min with the power of 200 W.

C. CHEMICAL AND MICROMORPHOLOGY CHARACTERIZATION

X-ray photoelectron spectroscopy (XPS, Thermo Fisher, USA) was used to analyze the surface chemical composition of the untreated/treated Kevlar fibers. The XPS spectra was obtained with the use of a monochromatic Al-Kα X-ray radiation source (hν = 1486.6 eV, wattage = 250 W) under a pressure in the analysis chamber of 10^{-9} Torr. Fourier transform infra-red (FTIR) spectroscopy was used to characterize untreated/treated Kevlar pulp fibers and the FTIR spectra were recorded on a Nicolet 6700 Fourier transform spectrometer (Thermo Fisher, USA) ranging from 4000 cm^{-1} to 500 cm^{-1}, with the resolution of 2 cm^{-1}.

To explore the change of the Kevlar fibers before and after low temperature plasma treatment and paper-micromorphology after introducing Kevlar pulp and NCF, the surfaces of Kevlar fibers and composite insulating pressboards with different components were observed and compared using Quanta FEG 450 scanning electron microscope. Prior to the observation, all the samples were sputter coated with 5 nm layer of gold. The voltage rating of 2–10 kV was used for SEM observation, all the samples were sputter coated with 5 nm layer of gold.

D. PREPARATION OF COMPOSITE INSULATING PAPER

The softwood pulp was beaten to 60° SR in the beater. Different content of plasma treated Kevlar pulps and NCF were blending with the corresponding content softwood pulp and dissociated in the disconnector for 75000 r in 2000 mL deionized water. The mix pulp was then filtered on the paper-forming double-layer strainer mesh (800 meshes) by vacuum filtration. Then the obtained wet composite sheets were pressed under 12 MPa pressure to squeeze out excess water. Thereafter, the composite sheets were dried in vacuum (105 °C) for 12 min. The dry composite sheets were pressed under 12 MPa pressure at 120° for 3 min, several times. The conventional insulating paper composed of pure softwood pulp was prepared with the same processing parameters for comparison. Moreover, the basis weight of both the composite pressboards and conventional pressboard were controlled around 125 ± 5 g/m^2 with the thickness of 0.13 ± 0.05 mm by applying corresponding hot pressing times.

E. ELECTRIAL CHARACTERIZATION

Relative permittivity and dielectric loss are important parameters of the insulating materials. The former determines the electrical field strength distribution in the composite material structures and the latter is associated with the heat generation of the material, which further influences its long-term thermal stability [20], [21]. These two parameters of the composite pressboards and conventional pressboard were tested by Novocontrol broadband dielectric spectrometer at 25 °C and humidity of 45% RH, with the applied voltage of 1 V ranging from 10^{-1} Hz to 10^7 Hz.

Insulating paper is a kind of complex material composed by solid fibers and air-pores (oil-pores when impregnated in oil), as shown in Fig. 1. To minimize the effect of the sample density on the value of the relative permittivity, a two-dielectric series model, shown in Fig. 1 and described as (1) and (2), was used to calculate the intrinsic relative permittivity and dielectric loss of the solid part of the composites. In the two-dielectric series model, described as (1) and (2), p is the porosity, d is the thickness of the paper, ε_{solid} is the permittivity of the solid part, ε_1 is the permittivity tested in air, ε_2 is the permittivity tested in oil, $tan\delta_1$ and $tan\delta_2$ are the dielectric loss tested in air and oil respectively. In the process of solving, we set the relative dielectric constant of air to 1 and that of insulating oil to 2.2. The values of $tan\delta_{air}$ and $tan\delta_{oil}$ can be ignored at 50 Hz which is the power frequency of the transformer [20]. Therefore, the specific test operation contains two parts: one is to test the samples in air to obtain the corresponding dielectric results, and the other is to immerse in insulating oil to obtain the second group of results. For each kind of samples, five measurements were taken.

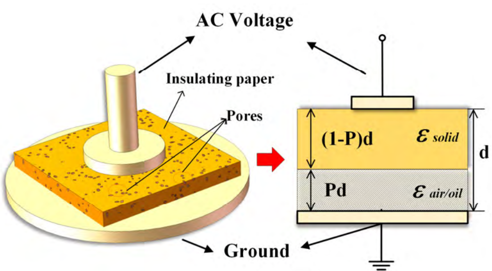

FIGURE 1. Diagram of dielectric response test of insulating paper and equivalent schematic of two-dielectric series model of insulating paper.

$$\begin{aligned} \varepsilon_1 &= \frac{\varepsilon_{solid}}{(1-p)+\varepsilon_{solid}/\varepsilon_{air}p} \\ \varepsilon_2 &= \frac{\varepsilon_{solid}}{(1-p)+\varepsilon_{solid}/\varepsilon_{oil}p} \end{aligned} \tag{1}$$

$$\begin{aligned} \tan\delta_1 &= \frac{\tan\delta_{solid}}{1+p\varepsilon_{solid}/(1-p)\varepsilon_{air}} + \frac{\tan\delta_{air}}{1+(1-p)\varepsilon_{air}/(1-p)\varepsilon_{solid}} \\ \tan\delta_2 &= \frac{\tan\delta_{solid}}{1+p\varepsilon_{solid}/(1-p)\varepsilon_{oil}} + \frac{\tan\delta_{oil}}{1+(1-p)\varepsilon_{oil}/(1-p)\varepsilon_{solid}} \end{aligned} \tag{2}$$

Resistivity is used to characterize the insulating properties of the dielectrics. DC volume resistivity of the samples was measured according to IEC standard 60093, by Keithley 6517B using the three-electrode methods under 100 V. The results were recorded when applying voltage for 60s. Prior to the measurements, all the test samples were immersed in insulating oil and dried in vacuum at 90 °C for 48 h to remove moisture, under the same condition. The test was conducted at 25 °C with humidity of 45% RH.

To obtain the breakdown strength of the samples, AC and DC short-term breakdown tests were conducted according to IEC standard 60243 (part 1 and 2). Diameter of the electrodes was 25 mm. The rise rate of voltage was 500 V/s. Measurements were performed at 25 °C immersed in the insulating oil (Karamay No. 25). For each kind of samples, the effective value of the results were recorded and ten measurements were taken.

F. MECHANICAL AND THERMAL CHARACTERIZATION

To investigate the mechanical properties of the composite paper, tensile tests were carried out according to ISO 1924-2:1994 standard. An AT-L-1 tensile testing machine (Annimat Instrument, China) with ± 0.01% accuracy and 500 N pulling force was used. During the tensile test, the stress-elongation break curves were recorded and the corresponding Yang' modulus was obtained. Eight tensile specimens were tested of each sample. The size of the test specimen was 180 mm × 15 mm × 0.13 mm. The testing speed was 20 mm/min.

To study the thermal ability of the conventional softwood paper and composite paper, the thermal behaviors were observed by thermogravimetric analysis (TGA) technique. Different composites were analyzed using METTLER

TOLEDO Corporation TGA/DSC1/1600LF apparatus with the temperature ranging from 25 °C to 500 °C and a heating rate of 7 °C/min under a constant N_2 gas flow of 50 mL/min.

III. CHEMICAL AND MICROMORPHOLOGY CHARACTERIZATION RESULTS

Kevlar fibers are generally composed of PPTA. To explore the effect of the low temperature plasma treatment to the Kevlar fibers, XPS, was applied to analyze the surface chemical composition of the original and treated Kevlar fibers. The wide-scan spectra results of the untreated and treated Kevlar fibers are shown in Fig. 2a-b. There are three main peaks in the spectra at around 284 eV, 400 eV, and 532 eV, which are attributed to C, N and O atoms, respectively [22]. And they are the main elements of Kevlar fibers. Table 1 shows the changes in the elements on the surface of the Kevlar fiber before and after the treatment.

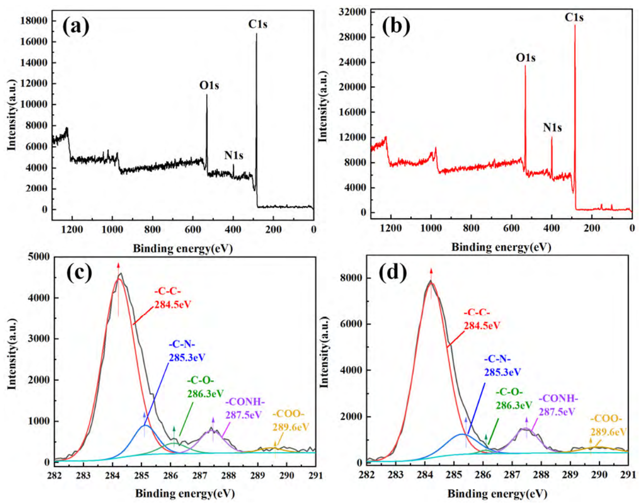

FIGURE 2. XPS spectra of Kevlar fiber surface: (a) untreated, (b) treated and C1s spectra of Kevlar fiber surface: (c) untreated, (d) treated.

TABLE 1. Surface chemical compositions of PPTA before and after plasma treatment.

Sample	Chemical composition (%)			Atom ratio	
	C1s	O1s	N1s	O/C	N/C
Untreated Kevlar fiber	78.51	18.59	2.90	0.227	0.022
Treated Kevlar fiber	74.01	15.43	10.56	0.208	0.143

From the results in Table 1, it can be found that the concentration of C decreased from 78.51% to 74.01% and the concentration of N increased significantly, from 2.90% to 10.56% after low temperature plasma treatment in ammonia atmosphere. Moreover, the ratio of N/C increased evidently from 0.022 to 0.143. In addition, the deconvolution analysis of C1s peaks was performed to further study the changes of distinct functional groups quantitatively. According to the results in Figure 2c and d, C1s spectra contained five peaks with binding energy of 284.5 eV (C–C), 285.3 eV (C–N), 286.3 eV (C–O), 287.5 eV (CO–NH), and 289.6 eV (O–C = O) [23]. There is a remarkable difference in the spectrum intensity and peak areas of the untreated and the plasma treated fibers surfaces in the C1s spectra. Calculating the functional group content of XPS C1s spectra, as shown in Table 2, it can be found that the C–C content decreased from 68.32% for untreated fiber to 59.62%, while the content of the polar groups such as C-N and CO-NH increased form 10.15% and 11.21% to 16.32% and 18.58%, respectively.

TABLE 2. The concentration of the different carbon groups on PPTA surface before and after plasma treatment.

Sample	C-C	C-N	C-O	CO-NH	O-C=O
Untreated Kevlar fiber	68.32	10.15	7.58	11.21	2.74
Treated Kevlar fiber	59.62	16.32	3.13	18.58	2.35

FTIR analysis was also used to investigate the functional groups of the Kevlar pulp before and after the ammonia-plasma treatment and the corresponding curves are shown in Fig. 3. The appearance of main three peaks, attributed to the absorption bands of para-aromatic ring (823 cm^{-1}), N–H (662 cm^{-1}, 3317 cm^{-1}), and C = O (1645 cm^{-1}) groups, respectively [24]. There were many other characteristic peaks for different functional groups. The absorption peak position around 1513 cm^{-1} is produced by the framework vibration of para-aromatic ring. The peak at 1541 cm^{-1} and 1316 cm^{-1} is assigned for C-N groups and its stretching vibration. The absorption peak at 1278 cm^{-1} is caused by the bending vibration of N–H Groups. For the untreated Kevlar pulp, all characteristic peaks were observed at low intensity. After treating with low temperature plasma, the smooth and hard surface of the Kevlar fiber was damaged, thus, more polar groups including –NH–, C = O, and C–N could be exposed, resulting in increased intensity of all functional groups [25].

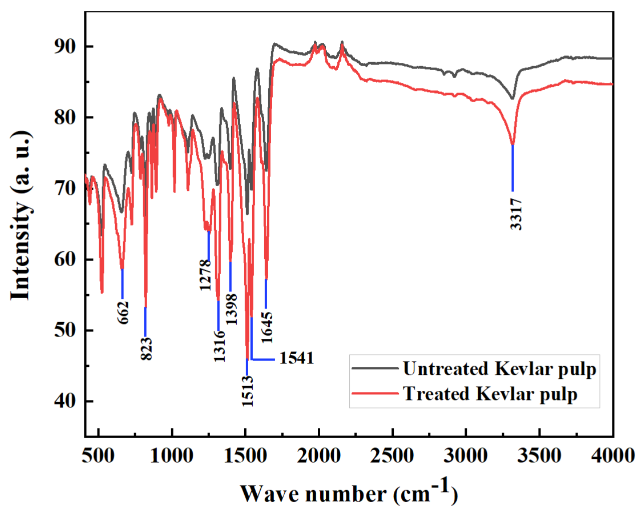

FIGURE 3. The FTIR analysis of untreated and treated Kevlar pulp.

The XPS and FTIR results show that plasma treatment can increase the number of polar groups containing nitrogen on the surface of fibers to a certain extent. Ammonia plasma treatment can not only change the surface chemistry of aramid fibers, but also effectively improve the interfacial bonding strength between Kevlar fibers and cellulosic pulp, which may result in the improvement of thermal and mechanical properties of hybrid composites.

The untreated and low temperature plasma treated Kevlar fibers (abbreviated as KP) were adhered to conductive adhesives and treated by spray-gold for SEM observation. Prior to the test, both of the samples were cleaned by acetone solution and absolute ethanol and dried. Figure 4 shows the micromorphology of the untreated and treated Kevlar fibers. It can be found that the surface of the untreated fibers, shown in Fig. 4a, was relative cleaner and smoother than that of the treated Kevlar fiber, shown in Fig 4b. The surface of the fiber became much rougher with etching pits and lines after being treated with low temperature plasma and numerous grooves, cracks, and fragments were generated on the surface of the fiber. As a result, there could be more effective contact areas between the Kevlar pulp and the matrix material and more polar groups could be exposed (as discussed in XPS and FTIR analysis), leading to an enhanced binding between the Kevlar pulp and the matrix materials.

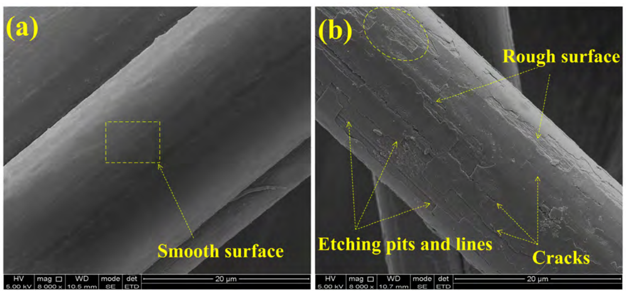

FIGURE 4. SEM images of (a) untreated Kevlar fiber and (b) treated Kevlar fiber.

The surface topographies of the conventional paper and Kevlar/NCF hybrid composite insulating paper are shown in Fig. 5a–f. The micromorphology of the conventional insulating paper made of pure softwood pulp (abbreviated as SWP) is presented in Fig. 5a. The surface of the conventional paper is uneven due to the forming process of the paper which is determined by the random distribution of fiber clusters [26]. It can be seen that the softwood fiber cluster has a diameter about 20–30 μm. Despite that the fine lignocellulosic fibrils can connect the strong fiber cluster and form the compact surface of the paper, there are still numerous tiny holes between the boundaries of the clusters.

Figure. 5b shows the surface of the 10wt% NCF hybrid insulating paper. It can be seen that the surface is much more compact than the conventional paper and the boundaries between the strong lignocellulose clusters are blurred which could decrease the pore amounts. As a result, the bonding strength of the cellulose clusters increased which may lead to an enhanced tensile strength. The surface of 10% Kevlar pulp hybrid 90% softwood pulp composite paper is presented in Fig. 5c. The Kevlar pulp can mixed evenly with the softwood pulp by high speed dissociation. There is an obvious phenomenon of two-phase separation, because of the different chemical composition and physical structure. Thus, there are more pores formed both in the surface and internal parts of the composite paper, compared with the conventional paper. This situation can be improved by hybrid 10% NCF with these two kinds of pulps according to the results in Fig. 5d. Similar to Fig. 5b, the boundary bonding of the fibers has been greatly improved when applying NCF. Figure 5e shows the micromorphology of the 20% Kevlar and 80% softwood pulp composite insulating paper. The surface roughness of the paper increases greatly and more pores formed in the composite paper with the increase of Kevlar pulp concentration, for the lack of associativity of Kevlar fiber and lignocellulose fiber [27]. When adding 10% NCF into the 20% Kevlar pulp hybrid paper, the surface are more compact comparing to the composite paper with no NCF, shown in Fig. 5f. NCF can enhance bonding strength between the fibers, even at relatively high hybrid concentration of two different kinds of pulps, shown in Fig. 6. Kevlar and softwood pulp composite paper combines the advantages of both the natural wood fibers and the synthetic Kevlar fibers. However, the bonding strength between fibers decreases with the increase of mixing concentration. Connection between fibers could be improved by NCF.

IV. ELECTRICAL EXPEIMENT RESULTS

A. ANALYSIS OF RELATIVE PERMITTIVITY AND DIELECTRIC LOSS

The relative permittivity and dielectric loss are very important parameters to determine the electrical field distribution and heat generating in the dielectrics under AC electrical field. These two parameters depends on the frequency of the outer electrical field heavily, for different polarization forms will dominate the whole polarization of the dielectrics at various frequency [28]. In this study, the permittivity and dielectric loss of the samples were tested in air and dried insulating oil environment to calculate the effective permittivity of the composites using the two-dielectric series model. Figures 7a-b show the impact of Kevlar pulp and NCF loading on the dielectric constant values at room temperature as function of frequency of Kevlar pulp/NCF reinforced composite insulating paper. The permittivity values tested in oil, shown in Fig. 7b, are higher than that tested in air, shown in Fig. 7a, because the air has a relative permittivity around 1, whereas the oil has a relative permittivity around 2.2 [29]. The permittivity of all the samples at relatively low frequency are much higher than that at high frequency, for interface polarization and orientation polarization dominate the whole polarization at low frequency and electron polarization is the main factor at high frequency. Either in air or in oil, the permittivity of the composite paper decreases with the increasing concentration of the Kevlar pulp. When the Kevlar concentration

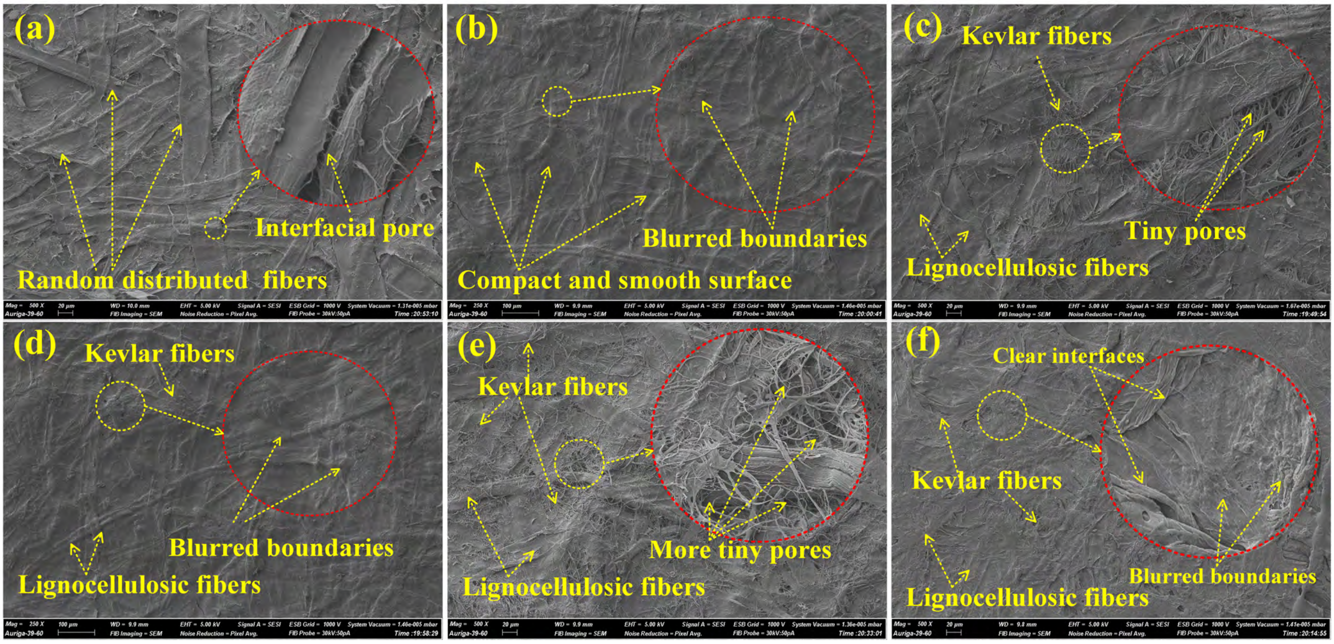

FIGURE 5. SEM images of insulating paper surfaces composed by (a) 100%_SWP, (b) 10%_NCF and 90%_KWP, (c) 10%_KP and 90%_SWP, (d) 10%_KP, 10%_NCF and 80%_SWP, (e) 20%_KP and 80%_SWP, and (f) 20%_KP, 10%_NCF and 70%_SW.

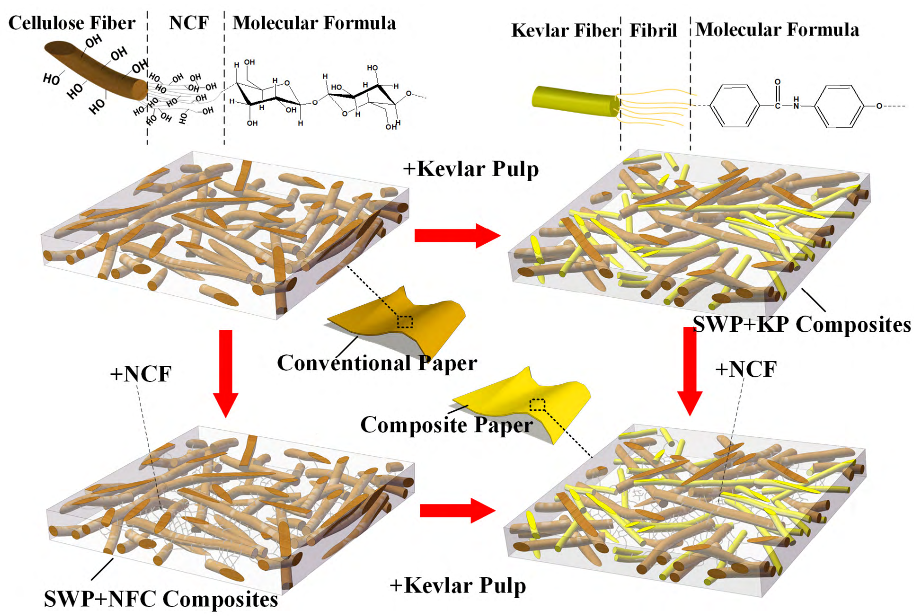

FIGURE 6. The diagram of composite of conventional paper and composite paper with NCF and KP.

is 20%, the permittivity of the composite paper is 3.34 in oil environment and 2.56 in air environment at 50 Hz. The permittivity values of the conventional paper are 4.19 and 2.91, correspondingly. As analyzed above, 10% NCF was used to compensate for the loss of mechanical strength of the Kevlar and softwood pulp composites. Thus, to investigate the influence of NCF to the insulating paper, the permittivity of the modified insulating paper, containing 10% NCF and 90% softwood pulp, has been tested. Results show that 10% NCF blending can increase the permittivity of the paper slightly, from 4.19 to 4.22 in oil and from 2.91 to 2.94 in air at 50 Hz. The relative permittivity of the composite insulating paper composed by 20% Kevlar pulp, 10% NCF and 70% softwood pulp are 3.36 and 2.56 in oil and air, which are 19.8% and 11.3% lower than that of the conventional paper, respectively. Introducing the permittivity values obtained in

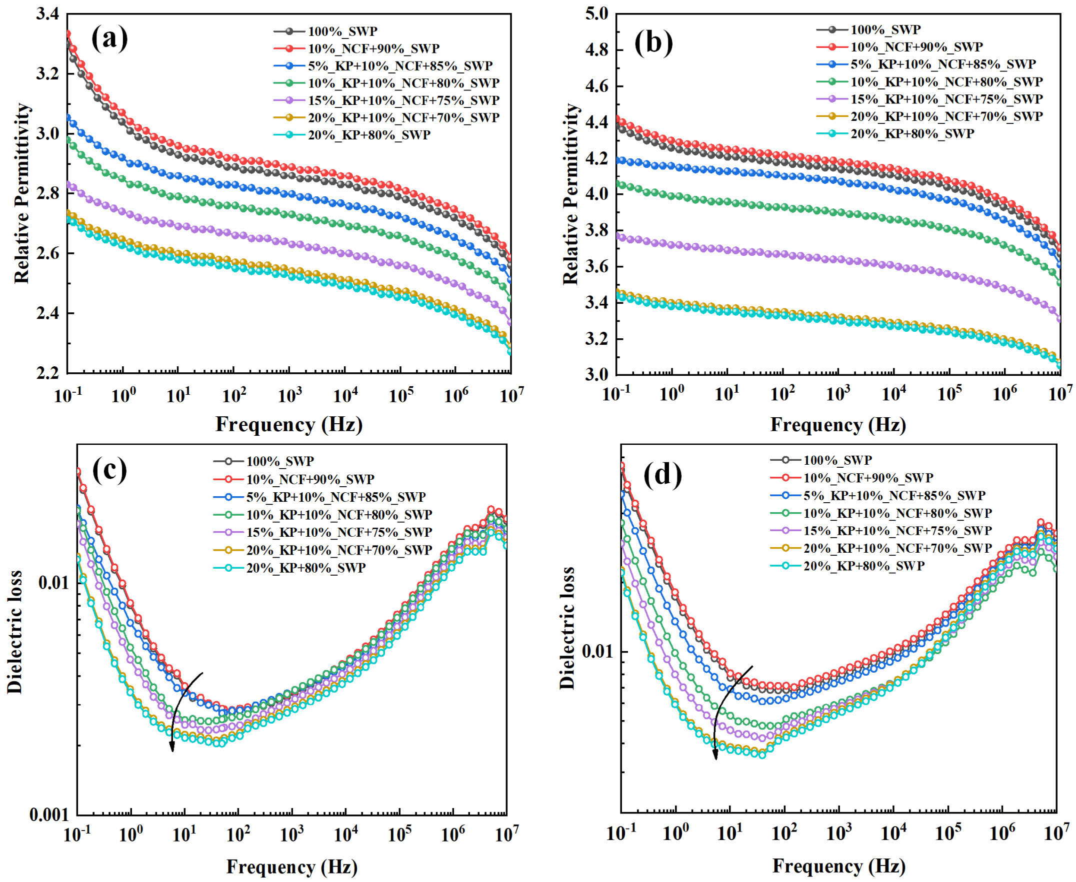

FIGURE 7. Relative permittivity and dielectric loss of the insulating paper (a) permittivity tested in air, (b) permittivity tested in oil, (c) dielectric loss tested in air and (d) dielectric loss tested in oil.

TABLE 3. Relative permittivity and dielectric loss of the samples at 50Hz.

Sample	ε_1	ε_2	$tan\delta_1$	$tan\delta_2$	ε_{solid}	$tan\delta_{solid}$
100%_SWP	2.91	4.19	0.46%	0.61%	5.34	0.81%
10%_NCF+90%_SWP	2.93	4.22	0.58%	0.69%	5.39	0.85%
5%_KP+10%_NCF+85%_SWP	2.83	4.12	0.38%	0.51%	5.28	0.73%
10%_KP+10%_NCF+80%_SWP	2.77	3.94	0.36%	0.48%	4.89	0.65%
15%_KP+10%_NCF+75%_SWP	2.68	3.68	0.34%	0.43%	4.35	0.55%
20%_KP+10%_NCF+70%_SWP	2.58	3.36	0.31%	0.38%	3.76	0.46%
20%_KP +80%_SWP	2.56	3.34	0.30%	0.37%	3.70	0.44%

air and oil into the two-dielectric series model can obtain the intrinsic permittivity of the solid parts of the composite paper, which is shown in Table 3. The permittivity of the solid part in the conventional paper is 5.34 and the permittivity of the solid part of the Kevlar/NCF and softwood pulp composite paper decreases with the increasing of Kevlar pulp. When the Kevlar pulp concentrate is 20%, the permittivity decreases to 3.76 by 29.6% compared with the conventional paper. NCF is cellulose fibrils with much more active hydroxyl groups than the conventional lignocellulosic clusters [18], which contributes the orientation polarization of the paper, as shown in Fig. 6. Thus, the permittivity of the paper containing NCF is higher than that without NCF. Kevlar pulp has an intrinsic permittivity of 2.4 at 50 Hz [30], so the Kevlar pulp and softwood pulp composite paper can contain less electrical energy than the pure softwood pulp paper under AC electric filed. As a result, the effective permittivity of the composites is much less than the conventional paper.

Dielectric loss ($tan\delta$) determines the long term heat generating and is closely related to aging of the dielectrics. Figures 7c and d show the dielectric loss results of the conventional paper and composite insulating paper tested in air and oil. The results of the paper obtained in air is much lower than that in oil, for the dielectric loss of air is lower than that of oil. According to the data in Table 3, the dielectric loss of the solid part of the composite insulating paper formed by 20% Kevlar pulp, 10% NCF and 70% softwood pulp is 0.46% which is decreased by 43.2% compared with the 100% softwood pulp paper. It can be seen that adding NCF into the pulp can increase the dielectric loss of the insulating paper slightly and the dielectric loss decreases sharply when mixing Kevlar pulp with the softwood pulp to form composite paper. The orientation polarization of the molecular chains and polar side groups is the main factor contributing to the dielectric loss of the dielectrics at low frequency [20]. NCF can increase the polar side groups of the cellulose clusters which further increases the polarizability of the paper. The Kevlar pulp has lower orientation polarizability due to the symmetrical rigid molecular structure, shown in Fig. 6. When blending Kevlar pulp with the softwood pulp to form a composite paper, the polarizability of the composite is decreased because the amount of polar molecular has been reduced. As a result, the dielectric loss of the composite paper is lower than the conventional insulating paper.

B. ANALYSIS OF DC AND AC BREAKDOWN STRENGTHS

Figures 8a and b describe the AC and DC breakdown strengths of the Kevlar pulp/NCF and softwood pulp composite papers. It can be seen that both the AC and DC breakdown behaviors are improved by introducing NCF into insulating paper. The AC and DC breakdown strengths of paper loaded with 10% NCF increased by 20.9% and 18.6%, respectively. As a porous structure material, the breakdown of the paper is mainly due to the internal partial discharges [31]. According to the SEM results and Fig. 6, NCF can enhance the

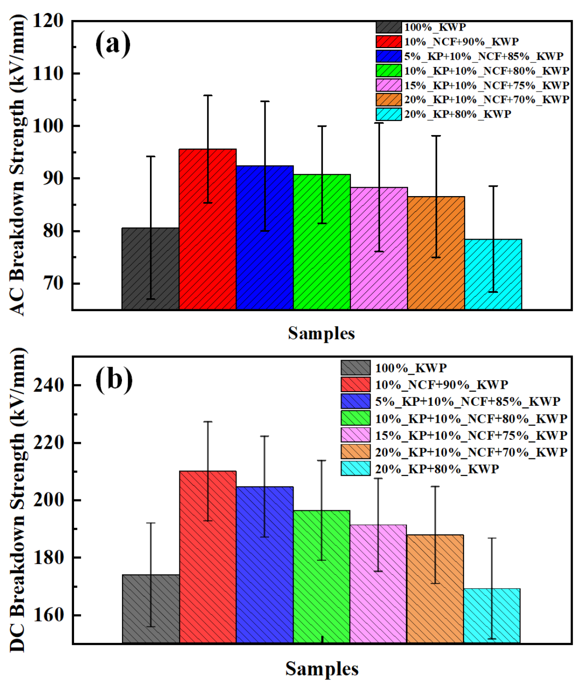

FIGURE 8. Breakdown strengths of the conventional and composite insulating paper, (a) ac breakdown strength and (b) dc breakdown strength.

breakdown strengths of the paper by increasing the connections of the fibers and reducing the void defects between the fiber boundaries. Blending Kevlar pulp with softwood pulp to form composite paper could weaken the AC and DC breakdown strengths of the paper, for more void defects would be produced due to the lack of compatibility between the Kevlar fibers and lignocellulose fibers. And the breakdown strength values decrease with the increasing of the Kevlar concentrate. Therefore, the concentration of Kevlar pulp should be controlled to some limits and NCF is used to compensate for the breakdown strength loss of the composites. It can be noticed that the composite paper containing 10% NCF, 20% Kevlar pulp, and 70% softwood pulp, has an AC breakdown strength of 86.6 kV/mm and DC breakdown strength of 187.6 kV/mm, increased by 7.4% and 8.1% than that of the conventional paper, respectively.

C. ANALYSIS OF VOLUME RESISTIVITY RESULTS

Volume resistivity is one of the vital parameters of the insulating dielectrics. Table 4 shows the volume resistivity results of the conventional and various composed insulating papers.

TABLE 4. Volume resistivity of the paper samples.

Samples	Volume resistivity (Ω×cm)
100%_SWP	4.9(0.12) $\times 10^{15}$
10%_NCF+90%_SWP	6.8(0.14)$\times 10^{15}$
5%_KP+10%_NCF+85%_SWP	6.5(0.15)$\times 10^{15}$
10%_KP+10%_NCF+80%_SWP	6.1(0.13)$\times 10^{15}$
15%_KP+10%_NCF+75%_SWP	5.8(0.12)$\times 10^{15}$
20%_KP+10%_NCF+70%_SWP	5.6(0.10)$\times 10^{15}$
20%_KP+80%_SWP	4.5(0.14)$\times 10^{15}$

It can be seen that the 10% NCF doped insulating paper has a higher volume resistivity than the conventional one. As for the insulating paper, the volume resistivity is mainly determined by the carrier mobility in the molecular and along the molecular chains [32]. From the SEM images, NCF can fill the air gaps between the fibers, which may block carrier transport channels in the paper. As a result, the volume resistivity of the NCF doped paper increased. It can be noticed from Table 4 that, the volume resistivity of the composite paper decreases with the concentration of the Kevlar pulp. Although the carrier mobility in the PPTA is very small due to its chemical elements and structure, much more tiny air-gaps along the fiber surfaces would form with the increase of Kevlar pulp content. Thus, the volume resistivity of insulating paper containing Kevlar pulp is slightly lower than that of the conventional one. Nevertheless, the composite paper containing 20% Kevlar pulp, 10% NCF and 70% softwood pulp has a volume resistivity of $5.6 \times 10^{15} \Omega \times$ cm, increased by 14.3% compared with that of the conventional paper.

V. MECHANICAL AND THERMAL TEST RESULTS

A. ANALYSIS OF MECHANICAL STRENGTHS

The stress-elongation break behaviors of the conventional insulating paper and composite insulating paper composed of 10% NCF, various concentrate Kevlar pulp and corresponding content softwood pulp, are presented in Fig. 9a. It can be noticed that the paper sheets containing 10% NCF have higher Yang's modulus than these without NCF and the Yang's modulus of the insulating paper decreases when loaded with Kevlar pulp. The decreasing of Yang's modulus trends to be more obvious with the increasing of the Kevlar pulp concentration. The conventional paper has a Yang's modulus of 7.3 GPa and it can be increased to 8.3 GPa with the introduction of 10% NCF. The Yang's modulus of the composite paper with 20% Kevlar pulp and 80% softwood pulp decreased by 18% compared with the conventional paper. NCF is applied as a reinforcement phase for the mechanical properties of the composites in this study. The Yang's modulus of the composites with 5% Kevlar pulp and 10% NCF, 10% Kevlar pulp and 10% NCF, 15% Kevlar pulp and 10% NCF, and 20% Kevlar pulp and 10% NCF are 7.9 GPa, 7.6 GPa, 7.2 GPa, and 6.9 GPa, respectively. It can be seen that 10% NCF can compensate for nearly 13% of the loss of Young's modulus caused by the introduction of Kevlar pulp.

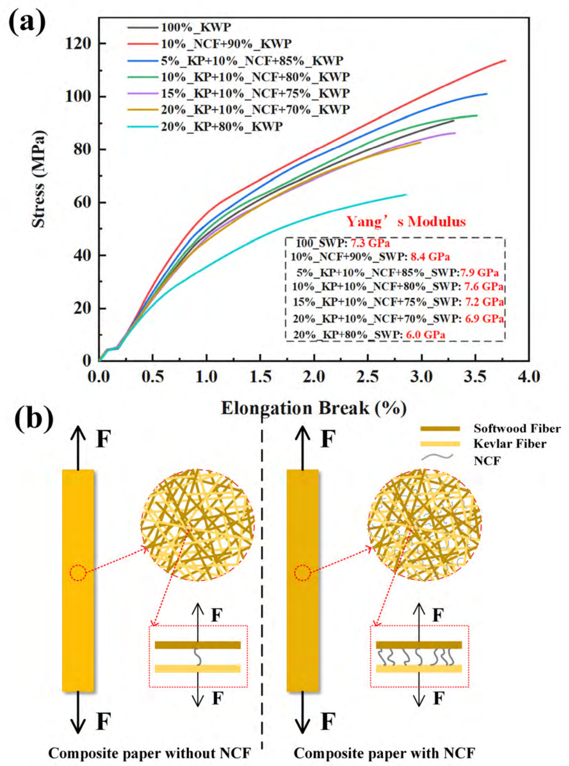

FIGURE 9. (a) Tensile stress-elongation break curves of conventional and composite papers and (b) diagram of Tensile Strength Test.

The tensile strengths and elongation at break results of the conventional and composite papers are shown in Table 5. The tensile strength of the conventional paper is 91.9 MPa and the composite paper containing 20% Kevlar pulp and 80% softwood pulp shows a lower tensile strength, which is 65.3 MPa. The tensile strength of the paper containing 10% NCF and 90% softwood pulp increased by 24.0%, compared with the conventional paper. When applying NCF in the Kevlar pulp and softwood pulp composites, the whole composite paper also show a significant increase in tensile strength, compared with the one without NCF. The composite paper containing 20% Kevlar pulp and 10% NCF has a tensile strength of 84.6 MPa, which is 29.5% higher than that of composite paper only composed of 20% Kevlar pulp and 80% softwood pulp.

TABLE 5. Tensile strength and elongation break of the conventional and composite papers.

Samples	Tensile Strength (MPa)	Elongation Break (%)
100%_SWP	91.9(9.2)	3.3(0.11)
10%_NCF+90%_SWP	114(10.1)	3.8(0.12)
5%_KP+10%_NCF+85%_SWP	101.4(10.2)	3.6(0.13)
10%_KP+10%_NCF+80%_SWP	92.6(9.8)	3.5(0.11)
15%_KP+10%_NCF+75%_SWP	87.2(9.5)	3.3(0.12)
20%_KP+10%_NCF+70%_SWP	84.6(10.1)	3.0(0.14)
20%_KP+80%_SWP	65.3(9.6)	2.9(0.13)

The elongation at break results, presented in Table 5, also show the similar regular, of which NCF can increase the strain value and blending Kevlar pulp into softwood pulp can reduce the strain value of the composite paperboards. The reduction of elongation at break of the Kevlar/softwood pulp composite pressboards is due to the lack of compatibility between the two different kinds of fibers. As mentioned above, NCF can increase the connection points of different fiber boundaries and fill the defects inside the paper. As shown in Fig. 9b, for the composite paper without NCF, the stress is ultimately transmitted to the junction of the fibers and acts at the junction. There are much more junctions between the fibers of the composite paper with NCF. Therefore, the stress can be decomposed into many components, resulting a higher tensile strength of the composite paper. Meanwhile, the more connection points produced by NCF between the fibers of the composite paper bring in a higher elongation at break value. From the tensile response results of the samples, it can be seen that blending Kevlar pulp with softwood pulp will destroy the mechanical properties of the paper and it can be improved, to some extent, by doping NCF into the composites.

B. ANALYSIS OF THERMAL CHARACTERIZATION RESULTS

TGA is used to investigate the thermal stability of the conventional and Kevlar/NCF/softwood pulp composite insulating paper. Figure 10 presents the TGA curves of 100% softwood pulp, softwood paper with 10% NCF, and composite paper containing various contents of Kevlar pulp and softwood pulp. From the results, it can be seen that there are two main weight loss of the conventional and NCF doped insulating paper. The first one is the 6% loss of water within 100° and the rest is the loss of the cellulose. It can be noticed that NCF can increase the loss temperature of the paper slightly by fulfill the pore defects in the paper. When adding Kevlar pulp into

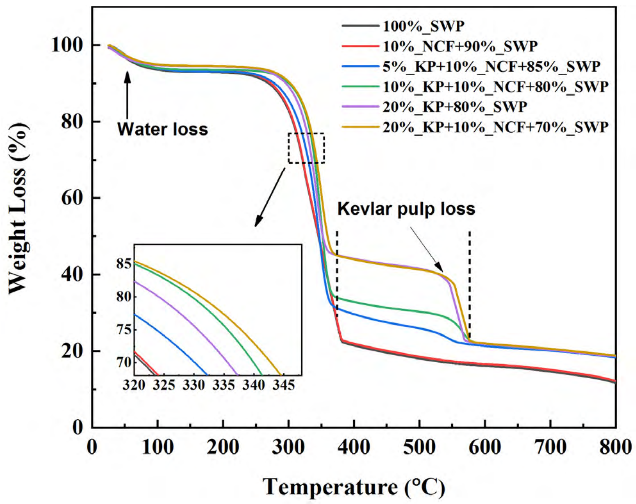

FIGURE 10. TGA thermograms of the conventional and composite insulating papers.

the composite paper, another weight loss process during 550° and 600° occurs. There is an obvious difference in the weight content during 380° and 600° between the curves of various Kevlar pulp concentrate composites, for the higher Kevlar concentration composites, the remaining weight is higher, correspondingly. It is clearly seen that the thermal ability of the composite paper containing Kevlar pulp is higher than that of the conventional paper only composed with natural cellulose. There are many fine Kevlar fibrils exposed after treated with low temperature plasma and the Kevlar fibers and lignocellulosic fibers cross-linked as composite networks by the two kinds of fibrils. Therefore, the cellulosic fibers proportion is always lower than that of the composites during the whole thermal process. Although the mechanical properties of Kevlar/softwood pulp composite paper are worse than the paper made of pure softwood paper due to the lack of compatibility of the two kinds of molecular, the thermal stabilities of the composites are better than the conventional paper because the Kevlar fiber forms the skeleton structure as the thermal reinforcement. To summarize, the thermal ability of the Kevlar/NCF/softwood pulp composite insulating paper is enhanced, compared with the conventional paper.

VI. CONCLUSION

In this study, Kevlar pulp treated with low temperature plasma, NCF and softwood pulp were applied to prepare a novel composite insulating paper with low relative permittivity, low dielectric loss, and good mechanical and thermal properties. The dielectric constant and loss of the composite paper with 20% Kevlar pulp, 10% NCF and 70% softwood pulp were 29.6% and 43.2% lower than that of the conventional paper composed by pure softwood pulp. The introduction of Kevlar paper reduced the polarizability of the whole paper, resulting in a lower dielectric constant and loss. The Yang's modulus and tensile strength of the composite paper were much lower than those composed by pure softwood pulp, due to the lacking of compatibility of the fibers. Low temperature plasma treatment could increase the polarity of the Kevlar fibers which may be good to the associativity with cellulosic fibers. NCF can work as mechanical reinforcement of the composite paper for it can repair the defects and increase the connections between fibers. SEM images showed that composite paper with 10% NCF had more smooth and compact surfaces than the one without any NCF. Therefore, the tensile strength of the composite paper with 10% NCF increased by 29.5% compared with the composites without NCF. Less defects and stronger fiber networks also enhanced the insulating properties including breakdown strength and volume resistivity and thermal stability of the composite insulating paper. As these results demonstrate, Kevlar pulp/NCF/softwood pulp composite paper has the potential to replace the pure softwood paper for the application of high voltage AC transformer insulation.

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