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AC Conductivity Analysis and Chemical Changes of Thermally Aged PVC/B Insulation for Medium Voltage Cables

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Abstract: This work aims to study the correlation between the chemical changes and the variation of the electrical conductivity of thermally aged Polyvinyl chloride class B (PVC/B) material intended for medium voltage cables. For this purpose, thermal aging experiments were carried out on PVC/B samples at 80, 100 and 120 °C for a maximum total duration of 5040 hours (210 days). Chemical changes were assessed by Fourier Transform Infrared Spectrum (FTIR). Besides, Frequency domain dielectric spectroscopy was used to analyze the electrical conductivity of PVC/B samples before and after aging. The results have shown that aging has a significant influence only at 100 and 120 °C. It has been found that the main chemical aging mechanism of PVC/B is dehydrochlorination which leads to a noticeable change in the color of the material. Additionally, more polar molecules are being released which enhance the electrical conductivity mainly at low frequencies.

Keywords; polyvinyl chloride, dielectric, thermal aging, FTIR, conductivity.

Introduction

With the advent of synthetic insulation materials in the middle of the 20th century, polymers continue to be extensively used in cable manufacturing [1]. In Algeria, Polyvinyl chloride (PVC) is widely used as an insulation in medium voltage cables. In practice, PVC presents a dielectric constant of about 5 to 9, and a dissipation factor of 4 to 12 % at 20 °C and a maximum operating temperature of 70 °C [1].

Furthermore, power cables are exposed to thermal stresses during their operating conditions in which the insulation may suffer degradation and structural changes. In extreme cases, failure may occur, which could result in not only the deterioration of the power cable, but also environmental and financial damages [2]. The chemical and physical changes during aging may affect the dielectric properties of the insulation and lead to increase the electrical conductivity [3, 4].

In reality, the AC conductivity (σ'_{AC}) may include dipole orientation as well as charge carrier migrations (by space charge polarization). According to the theory of dielectric physics, a typical dielectric response implies that, at low frequencies, σ'_{AC} is independent of frequency. However, at higher frequencies, conductivity increases with an empirical power law as expressed in Equation (1) [5]:

$$\sigma_{AC}(\omega) = \omega \varepsilon_0 \varepsilon''(\omega) = \sigma_{DC} + A\omega^n \quad (1)$$

where ω is the angular frequency, ε_0 is the vacuum permittivity, ε'' is the imaginary part of the complex dielectric permittivity, A is a temperature-dependent parameter and n is the exponent of the universal power-law.

On the other hand, since thermal degradation is due to the acceleration of chemical reactions, it is very important to assess the evolution of the main chemical groups in the material. For this, Fourier Transform Infrared Spectroscopy (FTIR) is commonly used in order to determine the chemical composition of a material [5].

The work presented here aims to study the effect of thermal aging on the chemical and dielectric behavior of PVC/B samples. These samples were subjected to artificial thermal aging for 5040 hours at 80 and 100 °C and for 1008 hours at 120 °C. After that, FTIR characterization is used to study the chemical structure changes of samples. Additionally, the evolution of the AC conductivity with aging is proposed as a diagnostic parameter to reflect the degradation level of the insulation. Therefore, frequency domain dielectric spectroscopy has been performed. Moreover, comparing the properties of virgin and aged PVC/B samples allows the effect of thermal aging to be assessed. Besides, we aim to study the correlation between the chemical processes and electric conductivity, which leads to a better understanding of aging and degradation mechanisms.

Experimental

Material and thermal aging experiments: According to IEC 60502-2 standard [6], PVC class B compound (or PVC/B) is intended for cables with rated voltages $U_0/U = 3.6/6$ kV. In fact, PVC/B is used as electrical insulation in medium voltage cables manufactured by CABEL factory located in Algiers, Algeria.

Polyvinyl chloride resins (SE-1200) manufactured by the company SHINTECH (USA) were blended with di-isodecyl phthalate (DIDP) plasticizer and calcium-zinc Stabilizer (Ca-Zn). Additionally, aluminosilicate anhydrous (Whitetex N^o2) were used as fillers to obtain calendaring and extrusion that perfectly lined. PVC resins and additives were mixed at 140 °C for 20 min and melt compressed at 170 °C for 5 min under a pressure of 300 MPa in order to obtain square plates of

about 25 cm x 25 cm and thickness of (2 ± 0.3) mm. In order to perform electrical and chemical analysis, PVC/B plates were cut into circular shaped samples with a thickness of (2 ± 0.3) mm and a diameter of (46 ± 0.2) mm.

Accelerated thermal aging was performed according to the IEC 60216 standard [7]. The circular samples were vertically arranged inside air-circulating ovens for a total duration of 5040 hours (210 days) at 80 and 100 °C. Moreover, since the degradation process of PVC/B is very fast at 120 °C, samples have been aged for a maximum duration of 1008 hours (42 days). Note that the samples that were aged for longer periods at 120 °C can be easily broken.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR characterizations were carried out in Attenuated Total Reflection (ATR) mode since our samples present relatively high thickness of about 2 mm. Samples were analyzed and starting with a background spectrum acquisition without the sample. Then, 24 scans were recorded in the wavenumber range of 430 – 5000 cm^{-1} with a resolution of 2 cm^{-1} for each sample. The obtained ATR-FTIR spectrum present the average of three spectra recorded from three different samples that have been aged in the same conditions (temperature and time).

Frequency Domain Dielectric Spectroscopy: AC conductivity σ'_{AC} measurements were performed using Novocontrol Alfa-A High Performance Analyzer dielectric spectrometer with a ZGS active sample cell. The system can control the temperature under N_2 atmosphere by a Quatro cryosystem within ± 0.1 °C. Prior to the dielectric measurements, gold electrodes were deposited onto both surfaces of the PVC/B circular samples by sputtering. The diameter and the thickness of the sputtered electrodes are respectively 35 mm and 30 nm. The AC conductivity was measured in the frequency range 10^{-2} to 10^5 Hz at 20 and 70 °C.

Results and Discussions

Color Changes: Figure 1 shows the change in color of PVC/B. It has been clearly observed that the color changes significantly for aging temperatures of 100 and 120 °C and the color has become very dark brown. This change is attributed to the dehydrochlorination mechanism and the formation of the C=C bond, as will be discussed latterly.

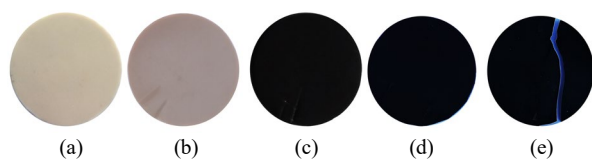


Figure 1: Color change of PVC/B samples: (a) before aging, (b) aged at 80°C for 5040 h, (c) aged at 100 °C for 5040 h, (d) aged at 120 °C for 1008 h, (e) aged at 120 °C for 1512 h.

Also, we notice that aging at 120 °C engenders shrinking of the samples (Figure 1d and e).

ATR-FTIR Spectroscopy Results: We present in Figure 2 the FTIR spectra results of the virgin PVC/B sample and of those aged at 80 and 100 °C for 5040 h and at 120 °C for 1008 h. Also, the main characteristic peaks of pure PVC (without additives) are summarized in Table I.

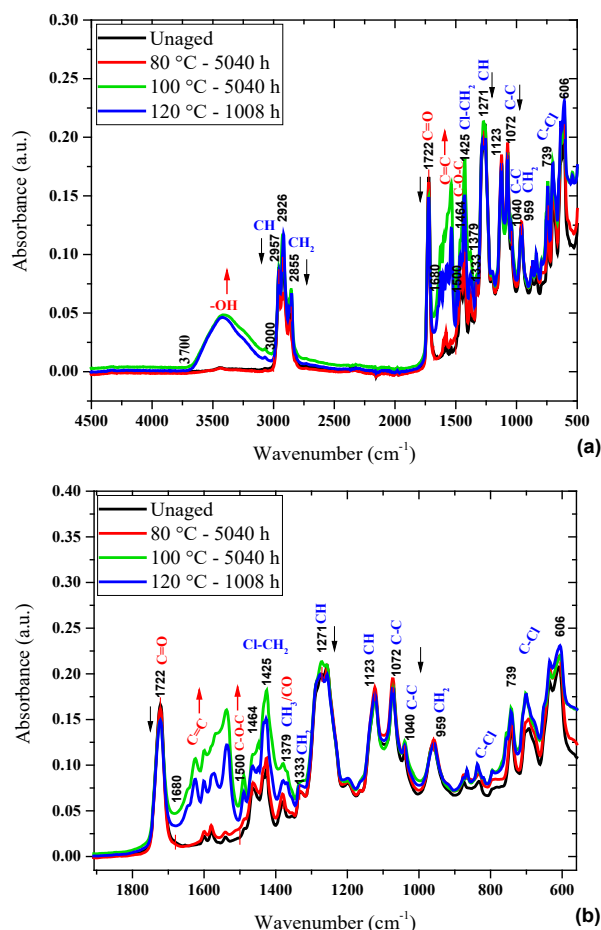


Figure 2: Evolution of the FTIR spectra of PVC/B with thermal aging: (a) complete spectra, (b) zooming on the absorption bands between 600 and 1800 cm^{-1} .

Table 1: Characteristic peaks of pure PVC by FTIR.

Wavenumber (cm^{-1})	Functional group and vibration	Reference
600 – 700	C-Cl Stretching	[8]
1040, 1072	C-C Stretching	[9]
1123	-CH Stretching	[8]
1271	-CH angular deformation	[10]
1425	Cl-CH ₂ angular deformation	[11]
1464	-CH Scissoring	[12]
2855, 2926	-CH ₂ Stretching	[12]
2870, 2957	-CH Stretching	[12]

The degradation of PVC/B includes three main mechanisms: dehydrochlorination, oxidation and loss of plasticizer. From Figure 1b, a significant increase of the absorbance intensity from 1500 to 1680 cm^{-1} was found.

This band is attributed to the $-C=C-$ double bond of unsaturated groups vinylidene and trans-vinyl. In addition, a new band corresponding to vinyl groups appears after aging at 1624 cm^{-1} . These observed bands are due to the dehydrochlorination which also leads, under the effect of the high temperature, to the release of hydrochloric acid HCl [10, 13]. Besides, after consumption of the stabilizer, the HCl molecules accumulate which results in a drastic increase of the dehydrochlorination rate with aging time [14].

The second mechanism of chemical degradation is oxidation, which leads to the scission of macromolecular chains and to the formation of oxidation by-products [14]. When the antioxidant is consumed, hydroperoxides (ROOH) will be formed which subsequently generate free radicals. As a result, we observe an absorption zone between 3000 and 3700 cm^{-1} relative to the $-OH$ function of the hydroxyl groups (Figure 2a) [13]. In addition, the oxidation can be characterized by the peaks at 1464 and 1539 cm^{-1} which present respectively $-C-O-C$ stretching and COO -vibration. Moreover, the characteristic peaks of $C-O$ function could be found at 1127 and 1288 cm^{-1} . Also, the carbonyl group $C=O$ is related to the absorbances at 1624 and 1722 cm^{-1} [11, 15].

The third degradation mechanism in PVC/B consists of the loss of plasticizer. In fact, the peaks at 1127 , 1288 and 1722 cm^{-1} could also indicate the presence of phthalate plasticizers (DIDP). Therefore, it appears difficult to distinguish between the physical loss of the plasticizer and oxidation reactions by FTIR method. We can also assume that the decrease at 1127 , 1288 and 1722 cm^{-1} (Figure 2b) is related to the diffusion of plasticizer molecules from the core of the material to the surface.

Therefore, it can be concluded from FTIR spectra that thermal aging at $80\text{ }^\circ\text{C}$ has a weak effect on the chemical structure of PVC/B. In the contrast, at aging temperatures 100 and $120\text{ }^\circ\text{C}$, a significant increase of vinylidene and trans-vinyl groups has been observed which reflect the increase of hydrochloric acid in the material. Besides, hydroxyl groups are released rapidly. Also, 1008 hours of aging at $120\text{ }^\circ\text{C}$ were enough to observe a significant chemical degradation against 5040 hours at $100\text{ }^\circ\text{C}$. Meaning that the higher the aging temperature is, the faster is the degradation process in the PVC/B material.

AC Conductivity Results: Figures 3 and 4 show the variation of AC conductivity σ'_{AC} at 20 and $70\text{ }^\circ\text{C}$ respectively, for different PVC/B samples before and after thermal aging.

From the obtained results, and at aging temperature of $80\text{ }^\circ\text{C}$, the conductivity remains unchanged at $20\text{ }^\circ\text{C}$ where a slight decrease observed at $70\text{ }^\circ\text{C}$ for frequencies lower than about 1 Hz . This decrease is probably due to thermal agitation which disturbs the interfacial polarization and decreases the mobility of dipoles at the electrodes over macroscopic distances.

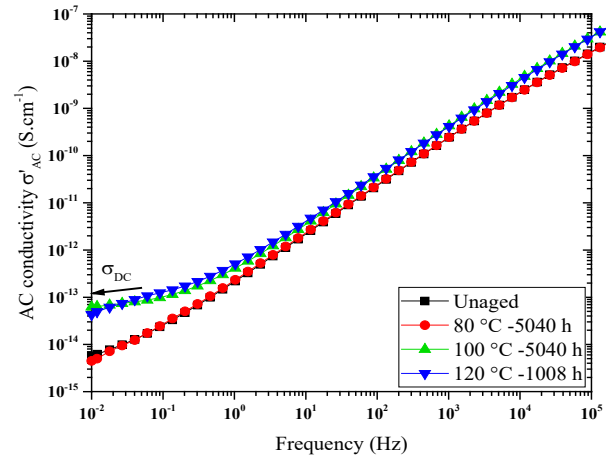


Figure 3: Frequency dependence of the AC conductivity at $20\text{ }^\circ\text{C}$ in PVC/B samples before and after aging.

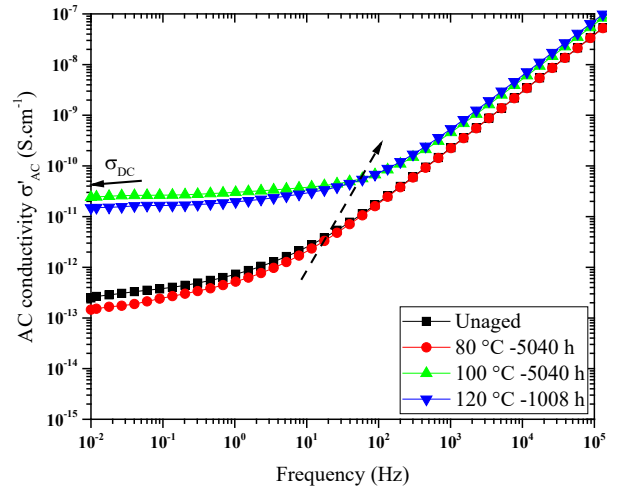


Figure 4: Frequency dependence of the AC conductivity at $70\text{ }^\circ\text{C}$ in PVC/B samples before and after aging.

Moreover, σ'_{AC} changes linearly for frequencies higher than 0.1 Hz at $20\text{ }^\circ\text{C}$ and 1 Hz at $70\text{ }^\circ\text{C}$, exhibiting a slope close to unity [16]. However, a noticeable deviation could be observed for samples aged at 100 and $120\text{ }^\circ\text{C}$, as illustrated in Figure 3 and 4. In fact, σ'_{AC} becomes progressively independent of the frequency and tends towards a higher constant value as the degradation of the material is more accentuated. This constant value presents the DC conductivity σ_{DC} of the material which is in agreement with Equation 1 [5]. Furthermore, the frequency range corresponding to the horizontal conduction plateau extends towards the high frequency when the temperature increases. Such a behavior demonstrates the thermally activated character of the DC bulk conductivity [16].

In fact, the dehydrochlorination mechanism in PVC/B leads to the creation of conjugated double bonds. The electrons then become mobile over the length of these conjugations. Hence, the mobility of electrons participates in the overall conduction of the material [10]. On the other hand, at high temperatures,

dehydrochlorination leads to the creation of ions and then the conductivity will depend strongly on the mobility of the ions and their concentration.

When the material temperature is low, the mobility of the ions is low and therefore the electronic conduction assumes the leading role. As the material temperature increases, the ions become more and more mobile and the ionic conduction may play the most important role in conduction [5, 10].

Moreover, the interfacial polarization (Maxwell-Wagner-Sillars) is established after a relatively long time. Hence, the AC conductivity will show a significant change at very low frequencies due to interfacial polarization and to the accumulation of mobile charge carriers in the insulation bulk. After the stabilizer was consumed after aging at 100 and 120 °C, dehydrochlorination process will be accelerated and as a result, more ions (e.g. Cl⁻ and H⁺) will be released which drastically enhance the conductivity σ_{DC} .

Conclusion

This paper highlights the evolution of the AC conductivity in PVC/B samples with thermal aging. Also, the chemical structure of the material was investigated. The main conclusions of this study can be summarized as follows:

- 1) The color change of PVC/B to dark brown reflect the deterioration of the material. This change is attributed to the formation of vinylidene and vinyl groups.
- 2) The degradation of PVC/B is caused mainly by the dehydrochlorination mechanism which is accompanied with the accumulation of molecules of hydrochloric acid HCl.
- 3) During thermal aging, thermo-oxidative reactions and loss or migration of the plasticizer occur, leading to accelerate the decomposition of PVC/B and facilitate the release of more polar groups such as hydroxyl OH.
- 4) The formation of polar groups implies a significant increase in the AC conductivity. The origin of this latter in the virgin PVC/B sample is the interfacial polarization (Maxwell-Wagner-Sillars).
- 5) When the thermal stress is high (100 and 120 °C), the conductivity increases with aging mainly at low frequencies. Meaning that σ_{DC} conductivity is strongly correlated with the material degradation.
- 6) If the mobile charges are of ionic origin, the ionic conduction may play an important role in the conduction behavior of PVC/B.

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