

Study of the Electrical Properties of Flame Retardant Poly(vinylchloride) Using Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: Since the large fire at the Brown Ferry cable plant which occurred at noon on March 22, 1975 in Alabama, attention has been given to the use of flame retardant cable in buildings to meet fire safety requirements. Flame retardants are used in wire and cable applications to prevent the conversion of an electric spark into fire and subsequently to prevent the spread of fire throughout a structure along the wiring. There are many substances used as flame retardants in wires and cables. In Egypt, Multi-Purpose Reactor insulation and jacket cables have been constructed from a flame retardant substance, poly(vinylchloride) (PVC). In the present work, elemental and X-ray fluorescence analyses have been performed to determine the composition of PVC in the jacket cable samples. In addition, the conductivity (σ), permittivity (ϵ'), and dielectric loss (ϵ'') as well as positron

annihilation lifetime (PAL) are measured in the temperature range 30 to 140 °C. It is found that the amount of chlorine in the flame-retardant PVC (FRPVC) jacket cable is significantly higher (5%) than the conventional PVC jacket cable. Inverse relationships between σ and free volume size and fractions (V_f) through the temperature range are obtained. However, a distinct positive relationship between σ and V_f above 100°C is found. The results of PAL and electrical measurements indicate that FRPVC has good electrical insulation properties below 100°C. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 638–644, 2005

Key words: poly(vinylchloride); flame retardant; electrical conductivity; positron annihilation; free volume

INTRODUCTION

In recent years, the world has been greatly interested in using plasticized FRPVC in cable insulation and jackets.¹ By blending various resin grades and plasticizers, PVC cannot easily achieve the high strength, flexibility, or environmental resistance of the synthetic rubbers. For this reason, it is used primarily for small, low-voltage applications such as telecommunications wire or appliance cords.²

From fire hazard analysis of the Multi-Purpose Reactor (MPR), it has been found that the fire load in the electrical board room is due to the large quantity of cables.³ In the MPR, the cable insulation and jackets that are used are made from extinguishing plasticized PVC rated at 1,000 V or less.

Many studies have concentrated on improving the resistance of PVC to ignition and fire spread, as well as comparing it with zero halogenated materials.^{1,4} Some additives such as lead, aluminum, zinc, magnesium,

and iron are used as stabilizers for PVC to shift the temperature of its degradation to higher temperature values and to provide synergistic protection of PVC.⁵ The electrical properties of some FRPVC compositions were studied by Saad et al.⁶ They concluded that the electrical properties of plasticized PVC could be improved by the addition of some adducts, especially at frequencies higher than 10⁴ Hz, making it of interest as a practical wire insulator. On the other hand, the mechanical properties of unplasticized PVC are improved by the introduction of natural, activated, and modified microzoeolite alone or in a combined form with ammonium sulfamate to obtain a fire-retardant material.⁷

Positron annihilation lifetime spectroscopy (PALS) has emerged as an effective method for characterization and investigation of the microstructure of two PVCs, bulk and suspension polymerized as a function of temperature.⁸ Al-Qaradawi and Abdel-Hady⁹ applied the PAL technique to investigate the behavior of the free volume in pure and doped PVC as a function of Pb concentration and temperature. They explained that the shift of the glass transition temperature (T_g) to a lower temperature is due the increase in electrical conductivity. Borek and Osoba¹⁰ investigated the in-

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fluence of the plasticization process on free volume in PVC using PAL measurements. They found that the mean radius (R) of free volume and the relative intensity of the long lived positron lifetime component, I_3 , increase linearly with the plasticizer concentration in PVC.

The aim of the present work is to study the microstructure of a FRPVC cable jacket of the electrical board room in the MPR using the PAL technique, as well as the electrical properties as a function of temperature. Also, a correlation between the macroscopic electrical properties and microstructure free volume properties of the material is established.

THEORETICAL BACKGROUND

Positron annihilation in polymers

In PAL, one employs the antiparticle of the electron, i.e., the positron as a nuclear probe to free volumes in polymers.¹¹ When a positron is injected into polymers, it interacts with molecules by an inelastic collision process leading to their ionization and excitation and thermalization of the positron. During thermalization, the positron may annihilate together with an electron in a free or trapped state with a lifetime in the range of 0.3–0.5 ns. In addition, the positron has the possibility of forming a bound state with an electron called the positronium atom (Ps). Ps has two spin states called the *para*-positronium (*p*-Ps), and the *ortho*-positronium (*o*-Ps) depending upon whether the spins are antiparallel or parallel, respectively. The lifetimes of *p*-Ps and *o*-Ps are 0.125, and 140 ns in a vacuum, respectively. In polymers, the *o*-Ps lifetime is shortened to 1–5 ns due to the pick-off process.¹² It is well known that free volume fractions exist in polymers with the size of a few angstroms; both the thermalized positrons and Ps (size of 1.06 Å) have sufficient chance to sense the existence of such holes. The *o*-Ps in free volumes is approximated by a particle in a spherical potential well of radius R_0 . The assumption is also made that there is an electron layer ΔR between R and R_0 , where $R_0 = R + \Delta R$ and ΔR is an adjustable parameter being ~ 1.06 Å for polymers.

The fractional free volume can be determined from the lifetime measurements. It is assumed that¹³ the free volume consists of spherical cavities with radius R , such that

$$V = \frac{4}{3} \pi R^3 \quad (1)$$

The results of the *o*-Ps lifetime (τ_3) in nanosecond are employed to obtain the average volume V in \AA^3 of the free volume holes by the semiempirical equation:¹³

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right]^{-1} \quad (2)$$

The relative intensity of the *o*-Ps lifetime component, I_3 , is assumed to be proportional to the number of the free volume holes because it gives the information on the *o*-Ps formation probability. Wang et al.¹⁴ proposed a semiempirical equation that may be used to evaluate the fractional free volume such that

$$f = AI_3V \quad (3)$$

where A is the normalization constant. In common polymers, the value of A ranges from 0.001 to 0.002.

Electrical properties

The electrical conductivity of polymers may depend on the presence of low molecular mass impurities, which act as sources of ions. The conduction mechanism of a polymer depends on its physical structure, as well as its chemical nature. There is more than one conduction mechanism in polymeric materials: electronic, ionic, hopping, and tunneling mechanisms.¹⁵ In ac electrical measurements, the frequency and temperature affect the dielectric properties of the polymer. The electrical conductivity σ can be calculated from the equation

$$\sigma = t/AR \quad (4)$$

$$R = 1/2\pi fc \tan \delta$$

where t is the thickness of the sample, A is its area, R is its resistivity, f is the frequency, c is the capacitance, and $\tan \delta$ is the loss tangent.

The permittivity ϵ' , which is the ability of material to establish an electric field is measured as the ratio between the absolute permittivity of material ($\epsilon = tc/A$) and the absolute permittivity of a vacuum ϵ_0 ¹⁶ as

$$\epsilon' = \epsilon/\epsilon_0 \quad (5)$$

where $\epsilon_0 = 8.85 \times 10^{-12}$ f/m

The amount of power lost in a dielectric under the action of the applied voltage is called dielectric loss and is given by:

$$\epsilon'' = \epsilon' \tan \delta \quad (6)$$

EXPERIMENTAL

Materials

FRPVC was obtained from the Egyptian Electrical Cable Company and some of its characteristics are listed in Table I. These properties are tested by the American Standard Technical Measurements (ASTM).

TABLE I
Some Characteristics of FRPVC

Property	Specification
Color	Black
Density (g/cm ³)	1.5
Tensile strength (N/mm ²)	17
Elongation (%)	200
Shore hardness after 3 s	85 ± 3
Volume resistivity at 20°C (Ωcm)	1.5 × 10 ⁹
Volume resistivity at 70°C (Ωcm)	8 × 10 ⁶
Dielectric rigidity at 20°C (KV/mm)	16
Flame retardant	F. H.

The structure of FRPVC is confirmed by organic elemental analysis results using Schoniger's flask. The results in weight percentage are 42.5% for carbon, 5.3% for hydrogen, and 28.3% for chlorine. The accuracy amounts to 0.2%.

X-ray fluorescence

The analysis is performed at the National Center for Technology and Radiological Research, Atomic Energy Authority, Cairo, Egypt. Figure 1 shows the X-ray fluorescence spectrum. The results indicate that the flame-retardant PVC sample has Cl, Ca, Pb, and Sb elements.

Positron annihilation lifetime measurements

The PAL measurements were performed in air at temperatures ranging from 30 to 140°C in 10°C increments at a 1 KHz frequency using a fast-fast coincidence system with a lifetime resolution of 230 ps full width at half maximum (FWHM). A 20 μCi ²²Na positron source was deposited on Kapton foil and then sandwiched between two similar pieces of the sample. PAL spectra containing 10⁶ counts were analyzed with the PATFIT program.¹⁷ Each spectrum consists of three different mean lifetimes, τ_1 , τ_2 , and τ_3 , which have relative intensities (I_1 , I_2 , and I_3). The shortest lifetime component (τ_1 , I_1) is attributed to the annihilation of *p*-Ps, which is characterized by $\tau_1 = 0.125$ ns. The second lifetime component (τ_2 , I_2) is attributed to the positron annihilation with the free electrons at the polymer matrix-additive interface. The longest lifetime (τ_3 , I_3) is due to *o*-Ps annihilation in the free volume. The mean free volume hole size V and its fraction f are calculated from Eq. (1) and (3), respectively.

Conductivity and dielectric measurements

σ , ϵ' , and ϵ'' of the investigated sample were measured at different frequencies ranging from 100 Hz to 20 KHz. An LCR meter-type PM- 6304 Programmable

was used. The sample was in the form of a thin film of diameter 1.5 cm and thickness 2 mm. Calibration of the apparatus was carried out using air as a standard sample of thickness 2 mm. The accuracy for σ , ϵ' , and ϵ'' was ±2%. The measurements were carried out at temperature ranges from 30 to 140°C in 10°C increments at a constant frequency of 1 KHz using ultrathermostate. The capacitance (c) and the loss tangent ($\tan \delta$) were obtained directly from the bridge. σ , ϵ' , and ϵ'' are calculated using Eqs. (4), (5), and (6), respectively.

RESULTS AND DISCUSSION

Effect of fillers and stabilizers on FRPVC

PVC itself may be considered flame retardant due to the presence of chlorine in its structure, but when more flame retardants, fillers, and stabilizers are added to it, the flammable property is more depressed. The flame retardants are additives that are added to the polymer system to prevent or delay ignition and fire.² From the elemental and x-ray fluorescence analysis (Fig. 1), it is obvious that the investigated sample contains two flame-retardant additives, chlorine (Cl) and antimony (Sb), in the form of antimony oxide (Sb₂O₃). From elemental analysis results, Cl is found to be 28.3% in FRPVC, which is higher by 5% than the conventional PVC jacket cable. This percentage of Cl may be present as an additive as well as in the constitution of the polymer itself. With this high percentage we expect a polymer of good mechanical and electrical properties as shown in Table I. On the other hand, the presence of Cl in FRPVC makes it a halogenated flame-retardant polymer and more resistant to the outside influence because the chlorine atoms increase the attraction between chains of the polymer due to the C-Cl dipolar.¹⁸ When FRPVC is exposed to a high heat source, the halogen (HCl) is released, limiting the spread of flame by a free-radical mechanism,² but unfortunately causing a health hazard due to HCl poisonous gases.

Sb₂O₃ is an important synergist when combined with a halogenated flame retardant. At about 250 to 285°C, antimony oxychloride, formed by decomposition of Sb₂O₃ and HCl at the flame front, reacts to form higher oxychlorides and antimony trichloride. In this way antimony oxychloride serves as a reservoir for additional antimony trichloride, extending the time that the halogen can be effective.²

Two fillers are added to the FRPVC, calcium in the form of calcium carbonate (CaCO₃) and carbon black (CB). However, fillers have two main functions, reinforcement and cost reduction. CaCO₃ is the lowest-cost compounding ingredient and gives a smooth surface to a compound.² On the other hand, CaCO₃ does have some disadvantages. Because of its spherical par-

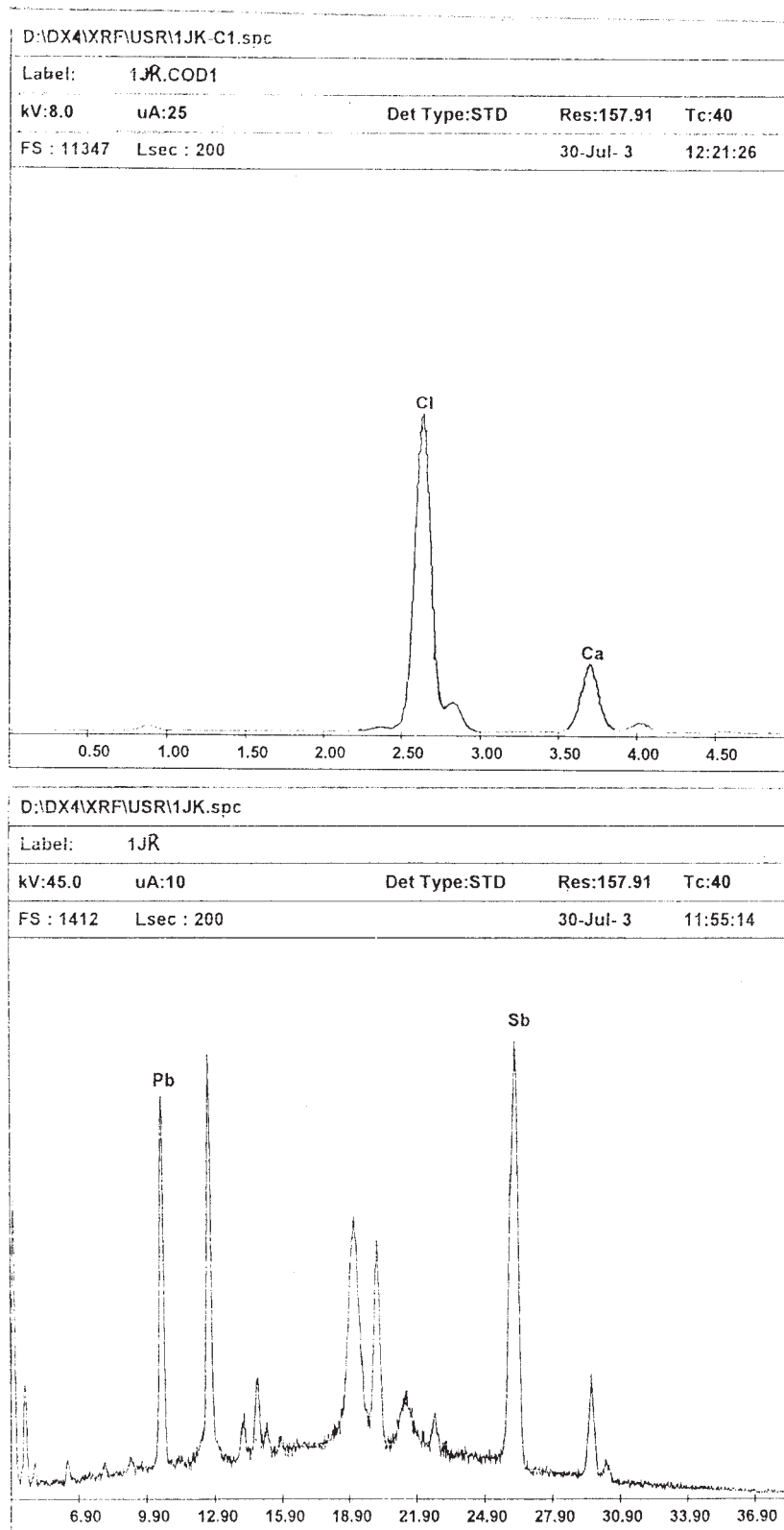


Figure 1 The X-ray fluorescence spectrum of FRPVC.

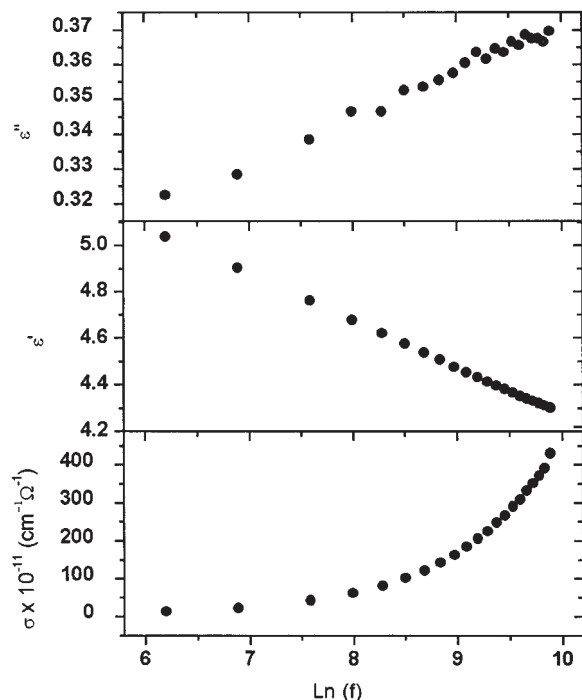


Figure 2 The variation of σ , ϵ' , and ϵ'' with $\text{Ln}(f)$ for FRPVC.

tial geometry, it does not significantly reinforce the compound and, because of its high alkalinity, it can interfere with halogenated flame retardants. CaCO_3 converts HCl, which is released when FRPVC is exposed to a high heat source, into chloride salt.¹ The addition of CB to the polymer introduces an additional physical and chemical crosslinking to PVC, serving as an obstacle against the segmental motion. It is used for reinforcement to give UV resistance as it absorbs UV radiation and inhibit decomposition of the polymer by sunlight.² In addition, CB can dramatically increase the tensile strength of the system, which is obvious from the high value of tensile strength (17 N/mm^2) as listed in Table I, which is close to the value obtained before for improved PVC compounds.¹

A stabilizer such as Pb is added to PVC as an acid scavenger and forms PbO to absorb or inhibit the acid generated by the decomposition of halogenated FRPVC.² The acid must be stabilized or bound in a wire and cable system to prevent corrosion of the metal conductor and to prevent further degradation of the polymer. It is well known⁶ that PVC material free of Pb degrades at 160°C . Addition of Pb stabilizer will shift the degradation temperature up to 210°C .

The electrical conductivity and dielectric results

Figure 2 shows the variation of σ , ϵ' , and ϵ'' at room temperature as a function of frequency (from 100 Hz to 20 KHz) for FRPVC. At the lowest frequency (100

Hz) σ , ϵ' , and ϵ'' have values of $1.78 \times 10^{-11} \text{ cm}^{-1}\Omega^{-1}$, 5.5, and 0.32 respectively. When the frequency is increased, ϵ' decreases continuously to reach 4.2 at 20 KHz. The decrease in ϵ' with frequency was noticed before,⁶ which shows an anomalous dispersion. On the other hand, σ and ϵ'' show a continuous increase with frequency to reach $4.24 \times 10^{-9} \text{ cm}^{-1}\Omega^{-1}$ and 0.37 at 20 KHz respectively. The increase in σ , ϵ'' may be due to the ion mobility. In addition, the ϵ'' increase by the addition of carbon black corresponds to the increase in σ , as carbon black aggregates introduce an additional physical and chemical crosslinking to the matrix, thus the mobility of the polymer molecules diminishes, leading to an increase in σ and ϵ'' .

Figure 3 shows the relation between σ , ϵ' , and ϵ'' as a function of temperature at frequency 1 KHz. At the lowest temperature (30°C), the values of σ and ϵ'' are found to be $18.24 \times 10^{-11} \text{ cm}^{-1}\Omega^{-1}$ and 0.33, respectively, whereas ϵ' has a value of 4.9, which is lower than the data of standard plasticized PVC insulated wire ($\epsilon' = 5-7$ at 1 KHz and 25°C),⁶ as expected because the jacket wire promised less permittivity than the insulated wire.

σ and ϵ'' decrease to $7.69 \times 10^{-11} \text{ cm}^{-1}\Omega^{-1}$ and 0.13, respectively, with an increase in temperature up to 100°C , while ϵ' shows the reverse trend ($\epsilon' = 6.28$). This can be explained by the increase in the mobility of

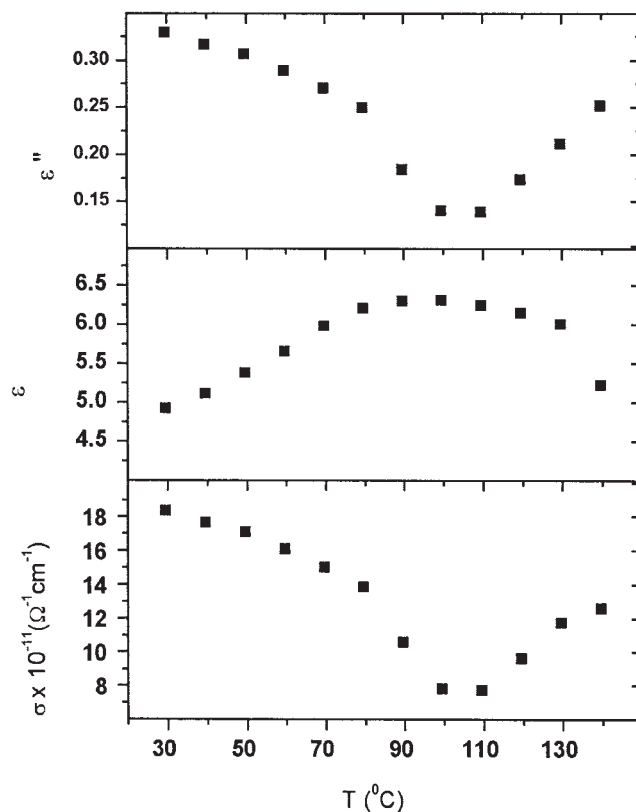


Figure 3 The variation of σ , ϵ' , and ϵ'' with T at 1 KHz for FRPVC.

polar groups and the decrease in density leading to a decrease in the effect of the environment that facilitates the orientation of the mobile groups.⁶ In addition, the presence of large radicals causes some steric hindrance that partially contributes to decreasing the mobility of electric charges. Accordingly, the conductivity of the polymer decreases to some extent. Above 100°C, the slight increase in σ and ε'' and the decrease in ε' is due to the increase in the ions that takes place as a result of the excitation by heat. At high temperatures, it is also probable that the chlorine ions are free to follow the external field.⁶

The PAL results

Figure 4 shows the variation of the intermediate component I_2 with respect to temperature at frequency 1 KHz for FRPVC. I_2 decreases from 66% at 30°C to 60% at 50°C. Since I_2 is attributed to the annihilation of positrons trapped with free electrons at the polymer matrix-additive interface, the intensity I_2 of the intermediate lifetime component can be considered as an indicator of the electric conductivity σ of the material. At this high temperature the additives could perturb the intermolecular forces in their vicinity, leading to a variation in the free electron density, which is reflected by a decrease in the intensity of positron annihilation I_2 . Above 50°C, I_2 shows a slight increase with temperature up to 100°C due to the formation of chlorine ions and creation of local negatively charged regions, which will trap the positrons with a subsequent increase in its annihilation probability. Above 100°C, these ions increase by excitation due to the high temperature, and the positron can annihilate with a higher fraction, leading to a rapid increase in I_2 .

Figure 5 shows the variation of V and f as a function of temperature at 1 KHz for FRPVC. The addition of fillers and stabilizers to PVC make their

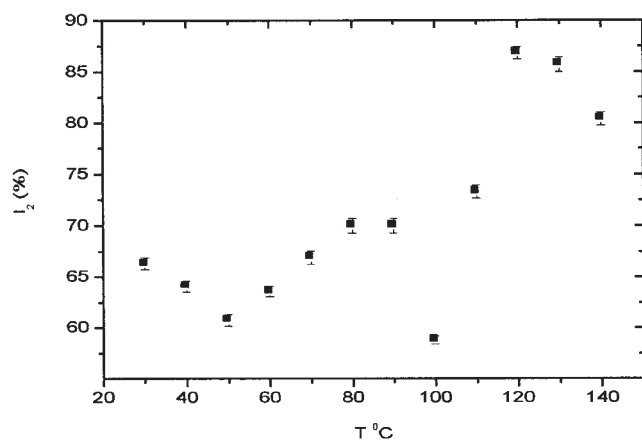


Figure 4 The variation of I_2 with T at 1 KHz for FRPVC.

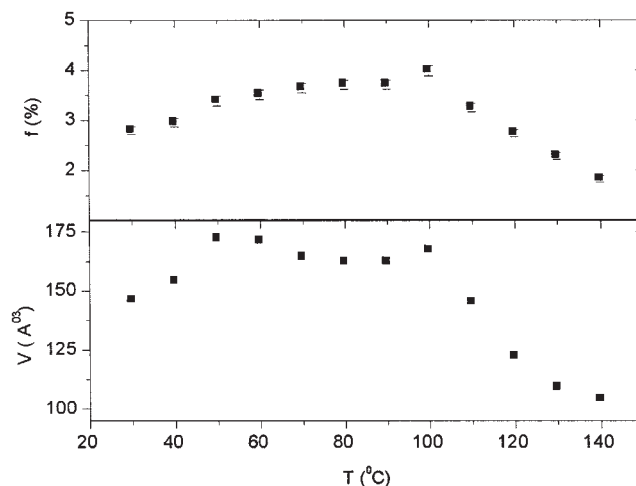


Figure 5 The variation of τ_3 , I_3 , V , and f with T at 1 KHz for FRPVC.

molecules enter between the tightly packed chains of PVC and disperse in the polymer matrix. As a result, there are few free volume fractions ($f = 2.78 \pm 0.07\%$) of small size ($V = 146 \pm 2 \text{ \AA}^3$) at 30 °C. In the temperature range from 30 to 50 °C, a separation of the polymer chains occurs due to the increase in the chain mobility, leading to an increase in free volume size V keeping the fraction f constant. Above 50°C up to 100°C, no considerable variations in V and f can be noticed. Above 100°C, the number of free radicals and ions increases by heat. These tend to fill the free volumes, thus leading to a significant decrease in the free volume size by $\approx 60\%$ and to a reduction in the fraction by 75% at 140 °C.

In conclusion, below 100°C, the variations of the electrical insulation parameters ε' , σ , and ε'' as a function of temperature (Fig. 3) are associated with smooth variations in free volume size and fraction (Fig. 5), as well as in I_2 (Fig. 4). Above 100°C, a decrease in the insulation properties of the FRPVC is observed. This corresponds to an abrupt increase of I_2 as well as a sharp decrease in V and f . Accordingly, the variation in the insulation properties is highly correlated with the decrease in free volume fraction as shown in Figure 6.

CONCLUSION

From organic elemental analysis and X-ray fluorescence spectrum it is found that FRPVC contains some flame retardants, fillers, and stabilizers.

The electrical conductivity and dielectric results show that ε'' has the same variation trend as that of σ , while ε' has the reverse one as a function of frequency and temperature.

The PAL results show that, below 100°C, the chain mobility of FRPVC increases, leading to an increase in

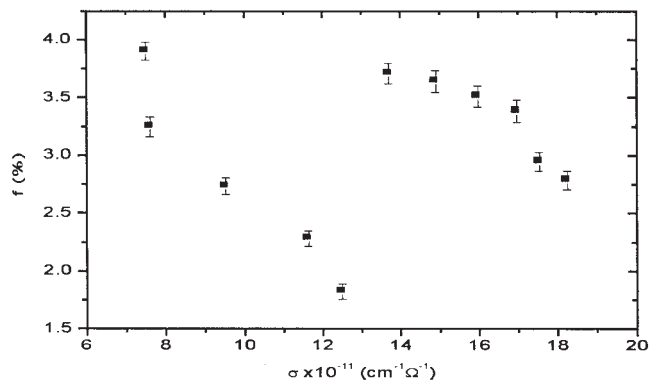


Figure 6 Correlation of microstructure and electrical properties.

free volume size and fraction, while above 100°C, the large numbers of ions and free radicals fill the free volumes, thus decreasing their fractions and therefore inhibiting the *o*-Ps formation.

Comparison between the macroscopic electrical properties and microscopic positron annihilation lifetime measurements shows that FRPVC exhibits good electrical insulating properties below 100°C when large free volume size and high fractions are available. Whereas the less insulating properties above 100°C are highly correlated with small size and fraction.

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