

STUDIES ABOUT GAMMA-RAY IRRADIATION OF PVC PLATES USED IN ELECTRIC CABLE INSULATION

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Abstract. *In this paper, studies concerning the changes brought by gamma radiation on some PVC plates were made. The respective samples were exposed to gamma irradiation, at room temperature and different doses, such as (10, 20, 40, 80) kGy. The changes in the irradiated PVC plates' properties were studied by UV-Vis, electrical measurements, and SEM analysis on non-irradiated and irradiated samples. The results show that gamma irradiation affects the properties of PVC plates. This degradation leads to the appearance of free radicals, the interruption of polymer chains, reticulation, and the decrease of molecular weight.*

Keywords: PVC, gamma rays, SEM analysis, electrical measurements.

1. INTRODUCTION

Studies on the action of radiation on polymers that describe and quantify the changes they undergo are a recent field of research. Applications involving radiation in the technology field are getting great attention and are constantly expanding. As a general observation, the action of radiation on polymers leads to the improvement of many of their properties [1-3]. Exposure of polymers to gamma radiation results in cross-linking of polymer chains, followed by an increase in molecular weight. The changes brought to polymers by radiation can be: recombination without changing the properties, cross-linking, which determines the strengthening of the mechanical resistance, the reduction of the elongation, the breaking of the polymer chains that cause the decrease of the mechanical resistance, and combinations of the previously exposed changes. Crystalline polymers show a higher resistance to radiation compared to amorphous ones. Under radiation, the polymers release hydrogen, leading to modification of the polymer chains, the appearance of smaller areas by chain cleavage, and many double bonds and radicals appear. Due to the electrostatic attraction, the small units that appear and contain carbon are grouped into electrically conductive clusters [4]. Polyvinyl chloride (PVC) features polyhalogenated chains with carbon atoms bonded to chlorine atoms, leading to many points of dipolar action that increase the chain interaction, resulting in

considerable stiffness. Plasticizer additives break the dipole interaction between the chains, thus creating flexibility for the polymer structure. There have been numerous studies of the action of gamma radiation on plasticized PVC [5-7], but many phenomena related to this aspect still need to be fully clarified. In this work, the changes made by gamma irradiation on some PVC plates are studied to find new applications in current technologies.

2. MATERIALS AND METHODS

Commercially available PVC samples from SIMONA® PVC-GLAS (Germany) are used. The samples have a thickness of 2 mm and are cut in a square shape with a side of 30 mm.

The exposure of the PVC samples was carried out in an irradiation machine (Ob-Servo Sanguis, Hungary) with a ⁶⁰Co source. The irradiation rate of the PVC samples was 0.6 kGy/h, corresponding to the doses set for the study: 10 kGy, 20 kGy, 40 kGy, and 80 kGy. Both non-irradiated and irradiated samples were analyzed.

2.1. UV-Vis Spectrophotometric Analysis

In this analysis, the electromagnetic radiation is in the near UV range with wavelengths between 200 ÷ 400 nm or in the visible spectrum with wavelengths in the 400 ÷ 800 nm range. The measurement result is a graphic representation of the absorption intensity according to the wavelength of the electromagnetic radiation used to irradiate the studied material. The component organic molecules of the studied material are located on certain energy levels due to their electronic states, which correspond to the order of magnitude of UV or visible radiation. In resonance conditions, the component molecules of the irradiated material absorb energy quanta from the electromagnetic radiation. The final effect consists of the promotion of low-energy electrons (ground state) into high-energy electrons (excited state) [8].

Cary 5000 UV-Vis-NIR (Agilent Technologies, USA) was used for the optical absorption measurements performed at room temperature in the range 350 ÷ 800 nm. The absorbance of each sample was measured after irradiation.

2.2. SEM Measurement

The scanning electron microscopy (SEM) technique is based on the analysis of surfaces with a beam of electrons down to a nanometer scale. The electrons interact with the atoms in the studied material, resulting in signals containing data on the material's composition and topography. Scanning electron microscopes produce high-resolution images with great accuracy representing ideal tools for various scientific applications [9].

SEM analysis was performed to evaluate the morphological change related to the effect of gamma radiation using a field emission scanning electron microscope Nova NanoSEM 630 (FEI Company, USA). A gold layer of 4 ÷ 5 nm was deposited on the surface of the samples, to eliminate the effect of the dielectric properties of PVC.

2.3. Electric Measurement

Volume resistivity is defined as the electrical resistance between the opposite faces of an insulating material cube with a side of 1 cm. For applications that require superior insulation characteristics, the volume resistivity must be as high as possible. The volume resistivity decreases rapidly with the plasticizer content. In the present work, the volume resistivity was measured in accordance with the ASTM 257 standard. The 4339B High-Resistance Meter (Agilent Technologies, USA) with a measuring range of up to $4 \times 10^{18} \Omega \text{cm}$ and the measuring cell 16008B were used.

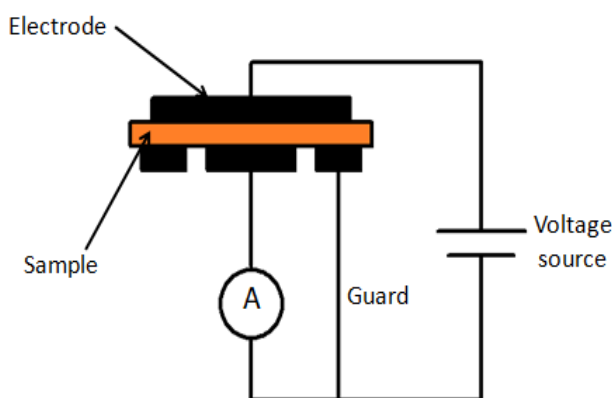


Figure 1. Schematic diagram of volume resistivity measurement.

Figure 1 describes the principle of volume resistivity measurement. A voltage is applied to the opposite surfaces of the sample, then the current passing through the circuit is measured.

$$\rho = R \frac{S}{l} \quad (1)$$

$$R = \frac{U}{I} \quad (2)$$

Equations (1) and (2) show the method of calculating the volume resistivity ρ , where U is the applied potential difference, I is the current passing through the measuring cell, and R is the resistance of the sample. The geometrical parameters are S as the surface area on which the potential difference is applied, while l is the length of the sample [10-13].

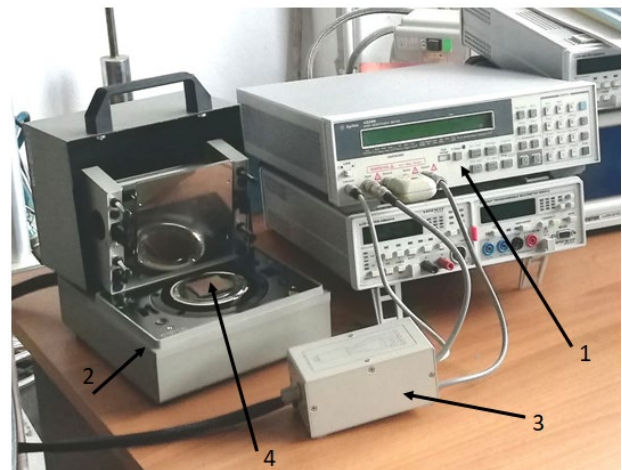


Figure 2. Experimental setup for volume resistivity measurement: Agilent 4339B High-Resistance Meter (1), measuring cell 16008B (2), adapter (3), sample (4).

Figure 2 shows the setup components and connections for measuring the volume resistivity.

The dielectric constant is defined as the ratio between the electric charge stored in an insulating material positioned between two metal plates and the electric charge held between the same metal plates but which has a vacuum instead of an insulator. The dielectric constant indicates the electrical energy storage capacity that an insulating material may have. Very low dielectric constant materials exhibit a low capacitance and, therefore, improved insulation.

The ratio between the resistive current and the capacitive current represents the dissipation factor of the insulator. In electrical applications, it is required that the dissipation factor be as low as possible. The dissipation factor is equivalent to electrical inefficiency and indicates the amount of energy exchanged with the exterior. PVC is not indicated in high-frequency applications due to high losses [14-17].

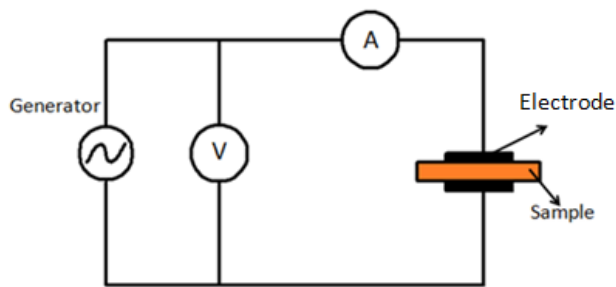


Figure 3. Schematic diagram of dielectric spectroscopy.

The dielectric properties of a sample dependent on the working frequency are measured with the help of dielectric spectroscopy. The measurement principle consists of the interaction of the electric dipole of the sample with the applied electric field. Dielectric spectroscopy measures the impedance of a sample within a frequency range and its energy storage and dissipation properties.

The sample for the measurements is located between two electrodes with a well-defined geometry and placed in a fixing device with parallel plates, according to Figure 3. Impedance Z represents the resistance to the flow of an alternating current and is calculated from the passing current I through the sample and the voltage V at its terminals. Impedance Z , being expressed as a vector in a complex plane, measures both the ratio between current and voltage values, but also the phase difference between current and voltage [18-21].

In the present work, the dielectric permittivity and dissipation factor were measured according to ASTM D150 standard using an Agilent 4294A impedance analyzer (Agilent Technologies, USA) and a 16451B measuring cell.



Figure 4. Experimental configuration of the dielectric measurement: Agilent 4294A impedance analyzer (1), measuring cell 16451B (2), sample (3).

Figure 4 shows the setup components and connections for the dielectric property measurements.

3. RESULTS AND DISCUSSIONS

3.1. Color Differences Analysis

Figure 5 shows the digital photographs of the studied PVC samples. The non-irradiated PVC sample (a) is compared with that of the irradiated ones (b), (c), (d), and (e). There are color changes from yellow to orange with the degradation of the samples by gamma irradiation, corresponding to the radiation level.

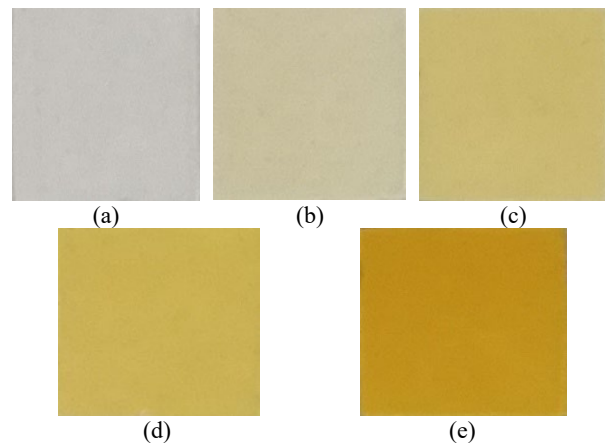


Figure 5. Digital photos of non-irradiated and gamma-irradiated PVC samples at different doses: non-irradiated (a), 10 kGy (b), 20 kGy (c), 40 kGy (d) and 80 kGy (e).

PVC irradiated with gamma radiation changes its color (darkens) in proportion to the level of radiation. The change in the color of the irradiated samples is due to the modifications in the polymer structure through the appearance of double bonds along the polymer chain (Zipper effect) [22-24].

3.2. UV-Vis Results

Figure 6 presents the absorbance spectra in the ultraviolet-visible region depending on the wavelength.

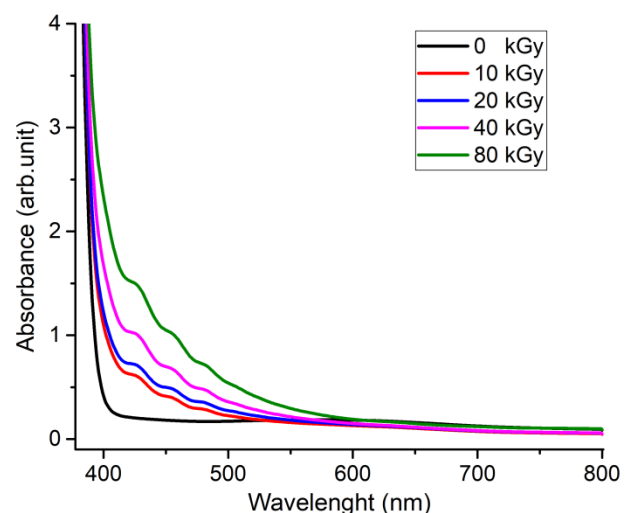


Figure 6. Absorbance of the UV-Vis vs. wavelength.

According to Figure 6, the displacement of the absorption edge of the UV-Vis spectra, corresponding to the samples irradiated with increasing dose towards the zone of increasing wavelength, is due to the increase in the molecular weight of the polymer following the cross-linking of the polymer chains.

3.3. SEM Results

According to Figure 7, after irradiation, the fracture morphology of the PVC plates presents a different architecture than the non-irradiated plates.

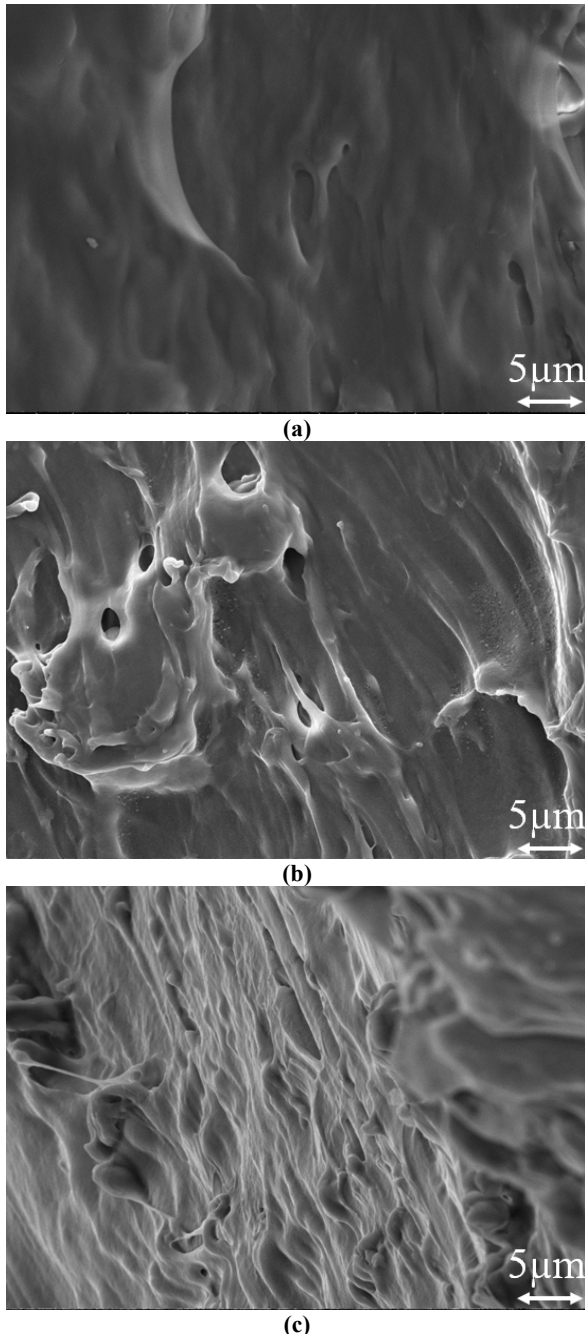


Figure 7. SEM images of the fractured PVC sample: (a) non-irradiated, (b) irradiated at 40 kGy, (c) irradiated at 80 kGy with 5000 $\times$ magnification.

The SEM images with a magnification of 5000 $\times$ show a change in the relief of the fracture after irradiation at 40 kGy and 80 kGy, compared to the non-irradiated sample. After gamma irradiation, the breaking of the molecular chain takes place, the appearance of free radicals, and cross-linking phenomena occur, which leads to the morphology modification.

3.4. Electric Results

In Figure 8, the variation of the dielectric constant spectra vs. the radiation dose frequency is presented.

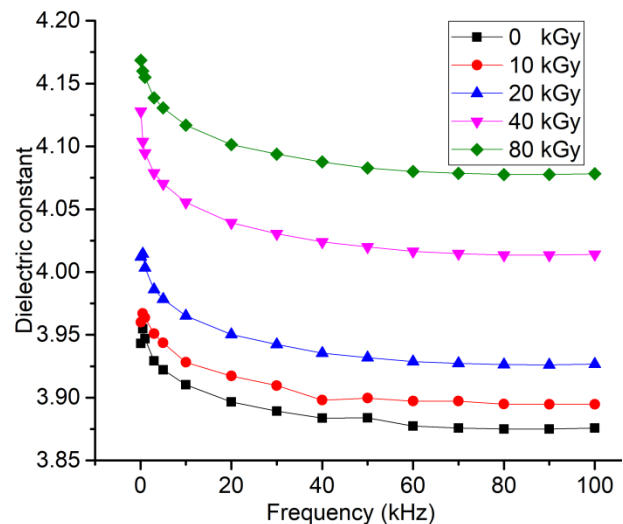


Figure 8. Dielectric constant versus frequency for different radiation doses.

The dielectric constant has higher values in proportion to the irradiation speed. This increase is due to radicals that form in the polymer structure as a consequence of irradiation. The dielectric constant decreases as the frequency increases, but at high frequencies, it remains almost constant due to the rotational movement of the polymer molecules that do not keep up with the very rapid variation of the electric field.

The dissipation factor spectra vs. the radiation dose frequency are presented in Figure 9.

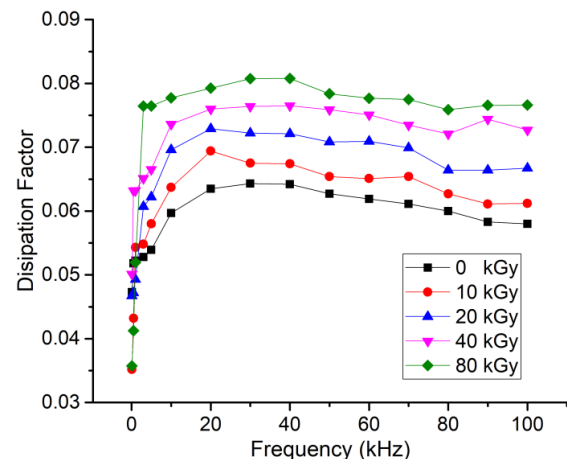


Figure 9. Dissipation factor versus frequency for different radiation doses.

The dissipation factor increases proportionally with the radiation dose rate, with a high rate at low frequencies (up to 10 kHz), but after 29 kHz, it shows a slight decrease towards higher ranges.

Table 1 displays measured electrical volume resistivity values and calculated volume electrical conductivity values versus radiation dose.

Table 1. Volume electrical resistivity and volume electrical conductivity values versus the radiation dose.

Radiation [kGy]	Resistivity [Ωm]	Conductivity [S/m]
0	8.2×10^7	1.21×10^{-8}
10	7.3×10^7	1.36×10^{-8}
20	6.3×10^7	1.58×10^{-8}
40	4.1×10^6	2.43×10^{-7}
80	9.1×10^5	1.09×10^{-6}

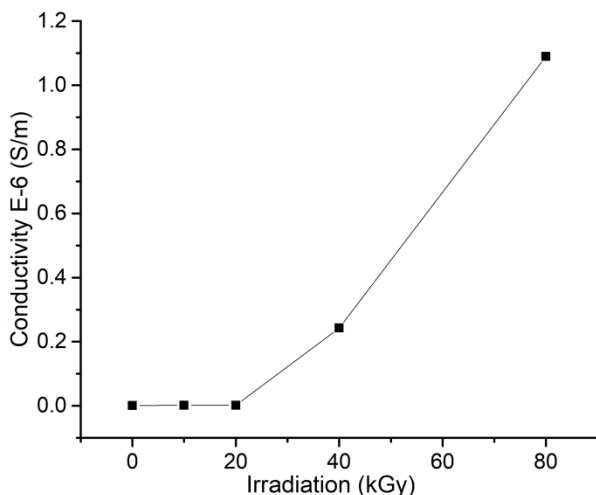


Figure 10. Volume electrical conductivity versus the radiation dose.

Figure 10 shows the volume electrical conductivity values measured at different radiation doses at room temperature. The conductivity value slightly increases up to the radiation dose of 29 kGy. After this value, the conductivity ascends steeply due to the more pronounced radiation effect on the polymer, exponentially increasing the number of free radicals [25-27].

4. CONCLUSIONS

According to the results obtained in the current research, the PVC material undergoes physical and chemical changes when it is gamma irradiated at different doses. There are changes in the dielectric constant and the loss factor, which is the effect of cross-linking phenomena and polymer chain scission. According to the electrical conductivity analysis, depending on the radiation dose, the phenomenon of breaking the polymer chains occurs, which leads to the appearance of free radicals. The SEM images show a change in the morphology in the fracture

of the gamma-irradiated PVC samples, due to a modification of the polymer chains, with the appearance of smaller areas through chain cleavage and the formation of many double bonds and radicals. The value of the radiation absorption rate in the case of UV-Vis measurement increases above 400 nm due to the cross-linking of the polymer chains. There is also a change in the color of the samples depending on the radiation dose. So, modifying the properties of PVC with gamma radiation may have numerous applications in current and future technologies.

5. ACKNOWLEDGEMENTS

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