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# Advances in Manufacturing a New Cable Coating Resistant to Thermal Aging and γ Rays by Cobalt-60 up to 50 KGy

Nabila Boutouchent-Guerfi, Sabrina Berkani, Inas Al-Qadsy, Nesrine Seddiki, Waseem Sharaf Saeed,* and Taieb Aouak

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**ABSTRACT:** Poly(vinyl chloride) (PVC) is widely used for covering electrical cables, but a decrease in its physicochemical, thermal, and mechanical properties has been observed over time. Poly(nitrile butadiene) rubber (NBR), due to its certain properties, was chosen to be blended with PVC to improve its specific properties, when used as insulation for electrical cables installed in nuclear power plants. Thus, this work focuses on the effect of γ radiation at doses ranging from 10 to 50 KGy on the physicochemical, thermal, morphological, and mechanical properties of PVC, as well as on the improvement of its properties by the incorporation of NBR in the PVC matrix as a blend. A series of PVC/NBR blends containing 10, 20, 30, 40, and 50 wt % NBR was prepared and subjected to thermal aging at 80 °C after adding appropriate additives. The results obtained reveal that thermal aging at 80 °C and exposure of the PVC/NBR blend to γ radiation up to 50 KGy do not practically affect the properties of this material.
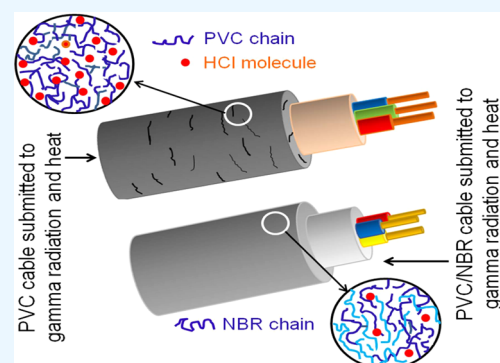
## 1. INTRODUCTION

PVC stands for poly(vinyl chloride) and is today among the most used thermoplastic polymers in the world for its superior mechanical and physical properties. This polymer is mainly synthesized by free radical polymerization of vinyl chloride, in which about 80% of the production involves suspension polymerization.[1] On the production side, this polymer occupies the third place after polyethylene and polypropylene. According to the data reported by the Statista Research Department, the global PVC production in 2018 was 44.3 million metric tons.[2] On the other hand, its thermal and radiological stability is however inferior to that of other common polymeric materials such as polyethylene and polystyrene, for example.[3] Among the application of PVC, this thermoplastic polymer is often used as the insulating sheath on electrical cables due to its good electrical insulation, ease of extrusion, and resistance to burn.[4]

The lifetime of an electrical cable is mainly related to that of its sheath. Indeed, the sheath is, on the one hand, the element in direct contact with the external environment, and as a result, the sheath is the first victim of chemical and mechanical aggressions. On the other hand, it is the first barrier to water penetration. In fact, if water penetrates through the sheath, it can corrode the aluminum screen and subsequently create damp trees in the electrical insulation, causing breakdown of the cable.[3,5,6] The constituent material of this outer sheath is generally the PVC. During the use of such cables with the PVC sheath, a decline in physicochemical and mechanical properties

suggests that the aging of the cable would result from a dehydrochlorination mechanism.[7−9] On the other hand, polyethylene (PE) with its excellent mechanical and electrical properties is used on a large scale as insulating medium and high-voltage cables, but its high-temperature behavior and its thermoplastic character limit its use, especially with the development of the new technology of 500 kV cables.[10−12]

Recent studies have focused on the use of another material obtained from ethylene vinyl acetate (EVA), used as a sheath, which is better resistant to temperature with improved mechanical, thermal, and electrical properties for cable application; however, this cable is not resistant to weather and γ-radiation,[13−15] since most polymers subjected to γ radiation undergo changes in their molecular structure by chain scission and cross-linking, which entail the degradation of the mechanical properties.[16] In the literature, some work related to the effect of γ radiation on the dielectric properties of PVC can be found.[17,18] These studies reported that the dielectric constant increased with increasing γ radiation assay and evidenced a change in dielectric properties under the effect of γ radiation and an increase in the crystallinity rate. Recently,

CampiI et al.[19] studied the possibility of using PVC in nuclear applications, and Castaneda et al.[20] studied the thermal stability of the latter under the effect of $\gamma$ radiation. The polar chloro groups enhance the options in blending this polymer with other polymers or compounds (plasticizers).[21]

Nitrile butadiene rubber (NBR) belongs to the family of unsaturated copolymers and is one of the most used elastomers in the world. According to The International Institute of Synthetic Rubber Producers (IISRP) Worldwide Rubber Statistics (2022), the global rubber production decreases to 27.4 million metric tons before recovering in 2021 and 2022 to reach a global production value of 29.6 million metric tons in 2022.[22] This yellow- or orange-colored copolymer, depending on its microstructure, is obtained mainly by copolymerization of acrylonitrile (ACN) and 1, 3-butadiene (BD) through free radical copolymerization in an aqueous emulsion.[23] The NBR material has excellent properties including high gas impermeability, resistance to wear and tear, thermal resistance, low-temperature flexibility, high resistance to petroleum products such as gasoline, diesel oil, and other fuels over a wide range of temperature, high strength, excellent resistance to abrasion, water, alcohols, and heat.[24−26] Because of these desirable properties, NBR find application in hoses, belting, cables, o-rings, seals, latex applications, molded, extruded products, adhesives, and sealants. Other uses of NBR include the use of this copolymer as powder for an impact modifier for PVC.

An important factor in the properties of NBR is the ratio of acrylonitrile groups to butadiene groups, referred to as the ACN content.[27] The lower the ACN content, the lower the glass transition temperature; however, the higher the ACN content, the better resistance the polymer will have to nonpolar solvents, as mentioned above. Most applications requiring both solvent resistance and low-temperature flexibility require an ACN content of 33%.

Materials based on the NBR/PVC blend are widely used in the industry.[28] The main applications of the resulting materials are conveyor belt coatings, cable jackets, pipe coatings, gaskets, shoes, and cellular products.[29] It should be noted that the NBR in these blends acts as a permanent plasticizer of PVC in applications such as wire and cable insulation, in which PVC improves the chemical resistance, thermal aging, and abrasion resistance of NBR.[30,31] Adding NBR to PVC improves the inferior properties of PVC. Indeed, NBR offers more elasticity to PVC, increased resistance to compression, and good flexibility at low temperatures. In addition, the elongation at break of PVC increases with increasing the amount of NBR in the resulted blend, while the tensile strength decreases in this direction.[32] Recently, Thoral et al.[33] investigated the photo- and thermal aging of nitrile butadiene rubber (NBR)/ poly(vinyl chloride) (PVC) blends cured with sulfur and a vulcanization agent to understand the formation of cracks upon aging and to put in evidence correlations between the different scales, from the chemical structure to functional properties, and the results were that the radical chain oxidation mechanism of the polymer leads to the formation of oxidation products, such as carboxylic acids, and a decrease of unsaturation.

To improve the thermal and radiological properties and the durability of PVC, when used as an electrical cable sheath, several studies were carried out.[34−36] Flexible PVC was loaded with different levels of tantalum carbides (TaCs) and exposed to two doses of $\gamma$ radiation.[34] The resulting materials were examined for the impact of these radiations in terms of their cross-linking, thermal stability, and mechanical properties. The protective properties of PVC loaded with different TaCs and exposed to two doses of $\gamma$ radiation were the aim of the gel characterizing the formation of a relatively stable interchain and intrachain bridge (cross-linkage), after irradiation, although thermal stability observed by TGA was maintained. TaC particles were properly dispersed within the PVC material; Paum et al.[35] studied the effects of thermal aging on a low-voltage PVC cable subjected to a thermal cycle ranging from −20 to +140 °C in a climate chamber at controlled temperature. The results obtained revealed that the thermal cycles of accelerated aging caused diffusion of the plasticizer in the sheath and then its release into the environment. These data also showed that thermal shock produced microcracks in the cable sheath, thus accelerating the removal of the plasticizer. NBR/PVC blends, depending on the PVC and plasticizer content, provide elasticity, increased compressive strength, and good flexibility at low temperatures. The elongation at break increases with the percentage of NBR in the blend, while the tensile strength, impact strength, and swelling resistance increase with the PVC content in the NBR/ PVC system.[36] Flexible PVC plasticized with conventional plasticizers can lose the plasticizer under certain conditions and become more rigid and brittle. In contact with fuel, NBR reduces the plasticizer extraction. Soft PVC modified with NBR loses less weight on contact with oils.[37] On the other hand, maintaining flexibility and a longer lifespan are ensured.

The aim of this work concerns the preparation and the study of the physicochemical, mechanical, thermal, and morphological properties of the miscible blend[20] involving PVC and NBR at different compositions and exposed to thermal aging at 80 °C after the addition of the appropriate additives and being subjected to $\gamma$ radiation; the choice of NBR was based on its specific properties.[38,39]

The dioctyl phthalate (DOP) plasticizer was chosen for its resistance to heat and radiation as approved by Ikhuoria et al.[40] In 2011, Ca/Zn stearate was incorporated to provide a heat and weather-resistant coating for low- and medium-voltage electrical cables and communication cables by improving their physicochemical, mechanical, morphological, and $\gamma$ radiation-resistant properties as well as their implementation.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Methods.** *2.1.1. Materials.* PVC powder SHENTECH SE 1200 was purchased from American company Inc. (Texas). Nitrile butadiene rubber (NBR) paste (6240) containing 34% acrylonitrile was supplied from LG CHEM (Seoul, South Korea). Dioctyl phthalate (DOP) was provided by SGP (Rades, Tunisia), and chalk (OMYACARB 2XT-KA) was purchased from OMYA (Izmir, Turkey). Zn/Ca stearate (REAPAK B-CV/3037) was obtained from IACN (Milan, Italy), and carbon black (BK 30) was provided from Wilson.

*2.1.2. Preparation.* The preparation of the samples was carried out in accordance with the international standard IEC 60811-1-1 (1985). Two devices were necessary for the preparation of these samples: a LESCUYER ML 150-type cylinder mixer (France) and a FONTIJNE brand press (Holland). In the first step, the PVC samples were prepared according to the IEC 60227 standard in the first apparatus, using DOP, Zn/Ca stearate, chalk, and carbon black. In the second step, the PVC thus prepared is blended with NBR at different compositions in a two-roller mixer heated to 140 °C

**Table 1. Preparation Conditions of NBR/PVC Blends**

| blend | NBR/PVC-10 | NBR/PVC-20 | NMR/PVC-30 | NBR/PVC-40 | NBR/PVC-50 |
|---|---|---|---|---|---|
| NBR (wt %) | 10 | 20 | 30 | 40 | 50 |
| PVC (wt %) | 90 | 80 | 70 | 60 | 50 |

and rotating at a speed of 20 rpm for about 5 min, and the preparation conditions are gathered in Table 1. In order to obtain samples in the form of thin plates of uniform thickness, when the blend reached a complete homogeneity, the latter was then placed between two metal plates under a table press under the action of a load of 300 kN maintained at 170 °C for 2 min. The samples obtained with a thickness of 2.0 ± 0.1 mm are then removed from the press system and left to cool on a metal plate at room temperature (∼25 °C). Note that these samples are then left to rest for at least 16 h before being cut into test pieces intended for characterization.

*2.1.3. γ Radiation Source.* The radiation source used in this work is the γ 60 Co type. The pilot irradiator used is composed of three COP 4 cylindrical sources of 60 Co manufactured by ORIS (France). These sources are arranged vertically in a stainless-steel source holder. The initial activity on 10.08.2002, the date of installation of the source, was 13.32.1014 Bq or 35990 Ci.

**2.2. Characterization.** *2.2.1. Determination of the Density.* The density of the film samples was measured using a graduated balance, which allows the specimens to be successively weighed in air and then in water. This test is carried out according to the NF T 51-561 (1990) standards.

*2.2.2. Determination of the Mass Loss.* The tests of the mass loss of the film samples are carried out at 80 °C during 7 days on dumbbell samples according to the ISO 227:2011 standard.

*2.2.3. Determination of the Water Uptake.* The water uptake measurements allowed the evaluation of a possible variation in mass when the polymer material is in contact with water or exposed to humidity. The absorption is then determined by immersing a known mass of the copolymer sample in water maintained at room temperature (∼25 °C).[41]

*2.2.4. Determination of the Mechanical Properties in Traction.* The tensile tests have been carried out using a ZWICK/ROELL-type tensile machine trademark (Germany, Ulm). This machine is controlled by computer software PC/ Test Xpert V10.11. The test consists of subjection of the sample to tension at a constant controlled speed (300 mm· $min^{-1}$ in our case) up to rupture. The test was performed according to ISO 527-1/-2 and CEI 811.1 (1993). The result was taken from the arithmetic average obtained on five specimens.

*2.2.5. Determination of Hardness.* The determination of the Shore D hardness was carried out using a BAREISS brand Shore D durometer (Germany, Upper Swabia). The hardness value was read directly on the durometer dial 5 s after application of the weight, in accordance with ISO 868 (1991). The Shore D hardness result is averaged over 5 tests.

*2.2.6. Determination of Breakdown Voltage.* In this part, the specimen underwent a transformer test voltage powered by a low-voltage sinusoidal source and increased from zero at a uniform rate to breakdown in accordance with the international standard IEC 60243-1 (2013). High-voltage direct current (HVDC) is applied to the electrodes and increased with voltage rates of 2 kV·$s^{-1}$ until breakdown occurs at the electrode and dielectric barrier.

*2.2.7. Morphology.* The morphology of the film samples was characterized by an optical microscope of the type OXION EUROMEX (Germany, Munich).

*2.2.8. Thermogravimetric Analysis.* The thermogravimetric analysis was performed on a TGA 2 Star system from Mettler Toledo (USA, Ohio). Samples were packed in aluminum pans and then scanned from 25 to 600 °C with a heating rate of 10 °C·$min^{-1}$.

## 3. RESULTS AND DISCUSSION

**3.1. Density.** As shown from the profile of the curve indicating the variation of the density of the PVC/NBR blend
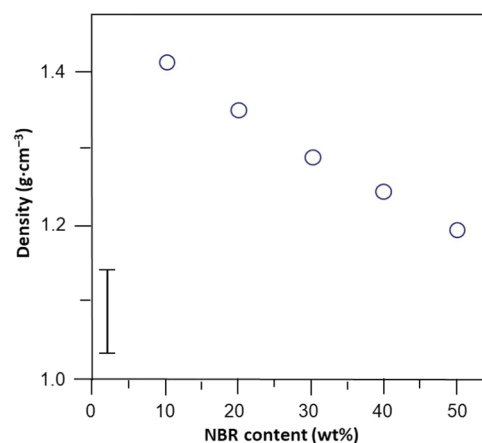


**Figure 1.** Variation of the density of PVC/NBR vs the NBR content in the blend.
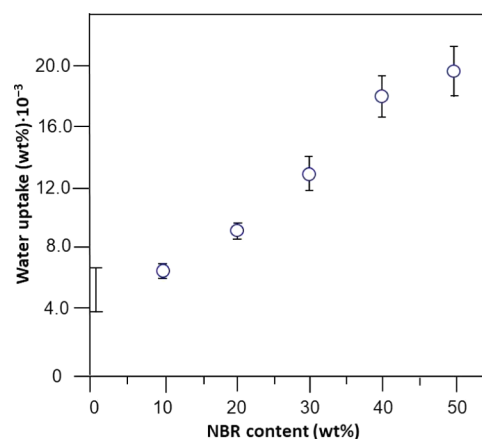


**Figure 2.** Variation of the water uptake of the PVC/NBR blend vs the NBR content.

vs the NBR content in Figure 1, the average density of the prepared material decreased when the NBR content in the PVC/NBR blend increased from 10 to 50 wt %. In addition, these values also reveal that the average value of the density of NBR was found to be greater than that of the PVC. The free volume created in the interfacial adhesion between both the polymers PVC and NBR decreased linearly when the elastomer
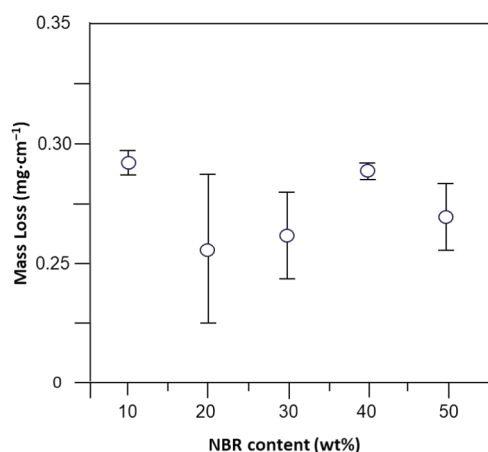
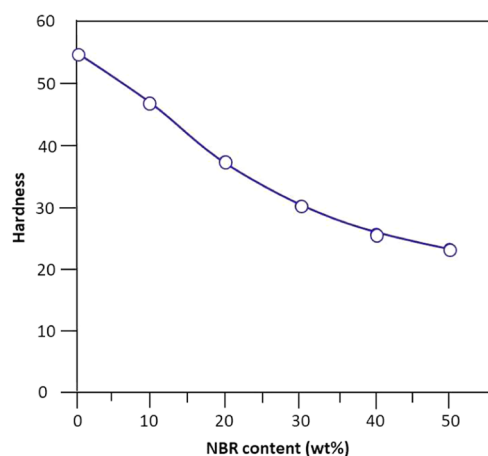**Figure 3.** Change in the mass loss as a function of the NBR content.



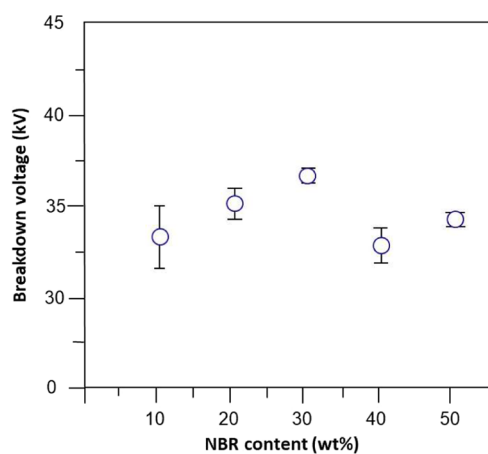**Figure 4.** Variation of the hardness versus NBR content in the PVC/NMR blend.



**Figure 5.** Variation of the breakdown voltage as a function of NBR incorporated in the PVC matrix.



**Figure 6.** Comparison of the tensile strength as a function of NBR in the blend before and after aging.



**Figure 7.** Comparison of elongation at break of the PVC/NBR blend vs the NBR content before and after aging at 80 °C.



**Figure 8.** Comparison of Young's modulus of the PVC/NBR blend vs NBR content before and after aging.

increased in the blend, suggesting the absence or presence of a low concentration of defects and a good interfacial adhesion between both principal polymer matrixes, in agreement with those reported by several authors.[42−44]

**3.2. Water Uptake.** The change in the water uptake of the PVC/NBR blend as a function of the NBR content is shown in Figure 2. The curve profile obtained reveals that the water
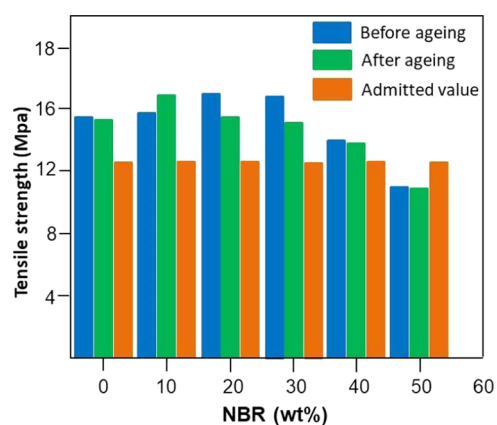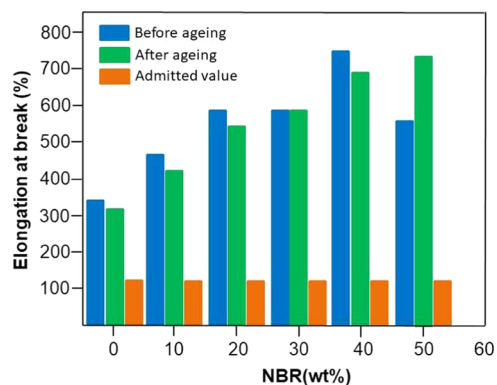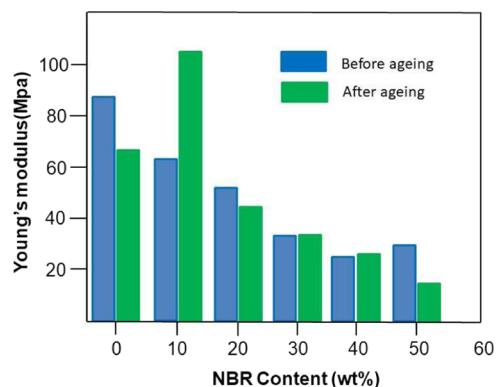
uptake of the PVC/NBR blend with different compositions is higher than that of the pure PVC, suggesting the presence of microcavities in the prepared materials. These results also indicate that the water uptake rate increases as a function of the NBR content in the blend. This means that the free volume occupied by water molecules is relatively higher, indicating that microvoids increase with the NBR content in the blend. These results also indirectly confirm the density results (Section 3.1).

**3.3. Mass Loss.** Polymers often contain residual organic substances of low molecular weight during their preparation such as traces of solvents, precipitants, and unreacted monomers in addition to plasticizers. These substances can,
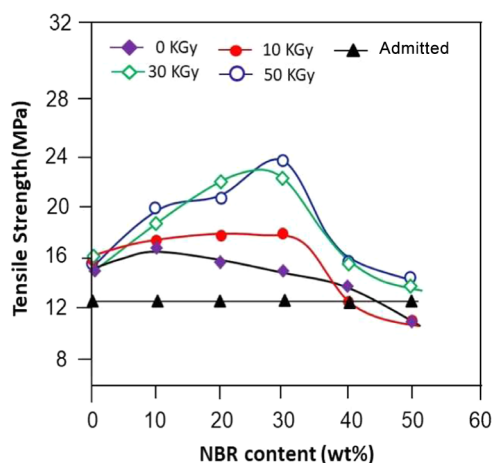
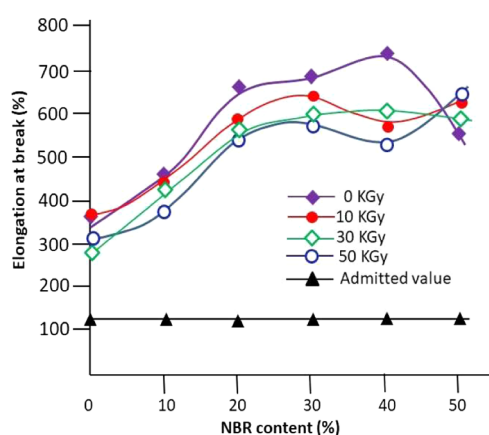**Figure 9.** Variation of the tensile strength of the PVC/NBR blend vs the NBR content under the effect of $\gamma$ radiation.
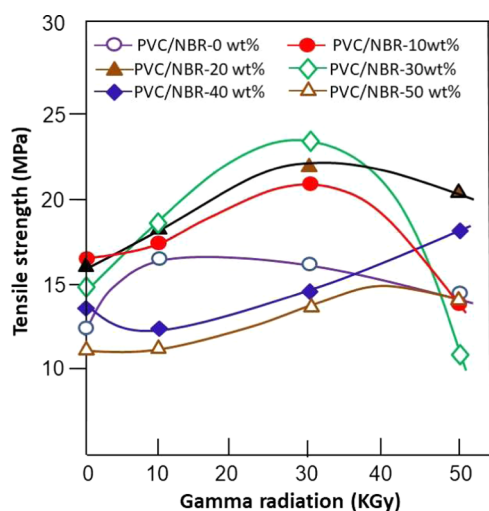


**Figure 10.** Variation of the tensile strength of the PVC/NBR system vs the NBR content measured after radiation at different doses.



**Figure 11.** Variation of the elongation at break of the PVC/NBR blend vs NBR content under the effect of the $\gamma$ radiation.

under the effect of temperature, migrate more or less slowly out of the polymer material. The loss of these substances by migration can concern relatively large amounts and thus have a significant impact on the properties of the material, in particular mechanical and thermal properties. The migration
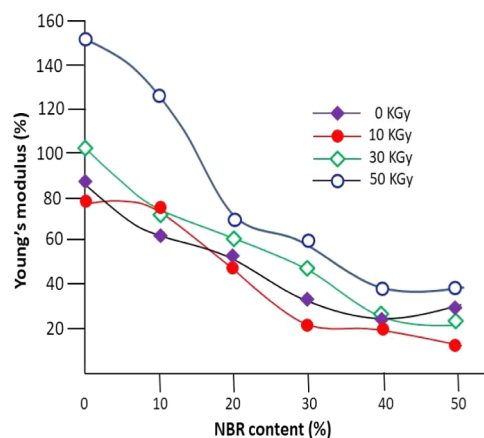


**Figure 12.** Change in Young's modulus of the PVC/NBR blend, under the effect of $\gamma$ radiation, versus the NBR content.
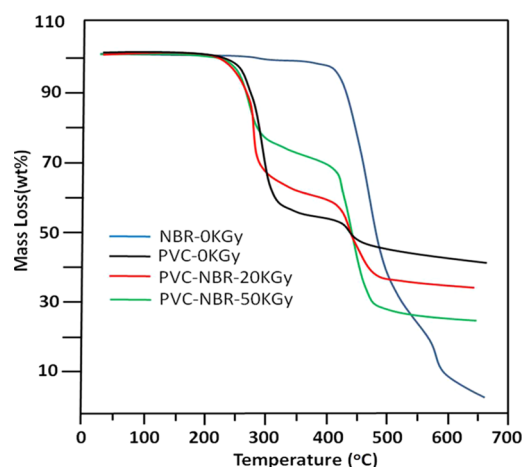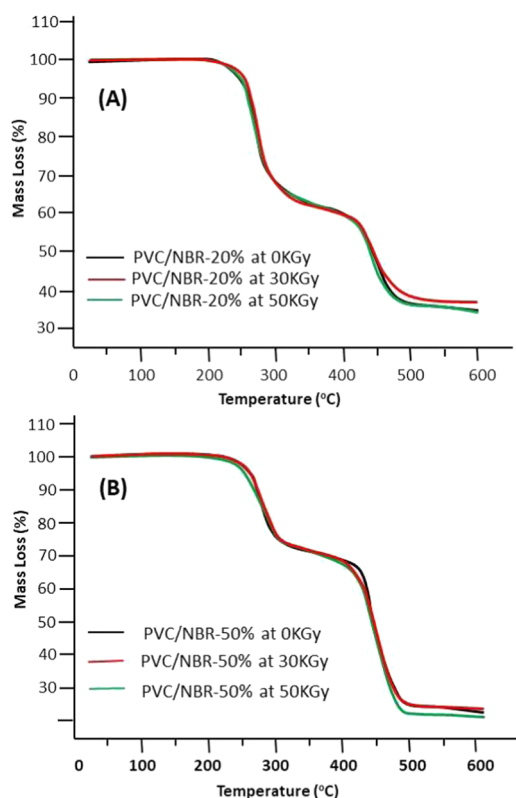


**Figure 13.** TGA thermograms of nonirradiated pure PVC and pure NBR and their blend containing 20 wt % NBR exposed at 30 and 50 KGy irradiation doses.

speed of a plasticizer is inversely proportional to its vapor pressure, which is itself linked to a certain extent to the molecular weight at chain breakage at low NBR concentrations. Chain breaks greatly affect the mechanical properties of the material.[45] The results plotted in Figure 3 indicate that the mass loss varies slightly as the NBR content increased in the PVC/NBR blend. The variation in mass loss is 3.5 wt % for the blend containing between 10 and 50 wt % NBR content. Furthermore, it can also be noted that the high mass loss (29 wt %) was observed at low NBR content (10 wt %).

**3.4. Hardness.** Figure 4 depicts the variation of the hardness as a function of the NBR content. As can be seen from the curve profile obtained, the hardness decreased quickly from 56 to 30 for the PVC/NBR blend containing from 0 to 30 wt % NBR and then tends to stabilize for larger NBR contents. This behavior indicates that the blend system quickly loses its rigidity under the effect of the NBR incorporated in the PVC matrix.

**3.5. Breakdown Voltage.** According to the results presented in Figure 5, indicating the change in the voltage breakdown versus the NBR content, the breakdown voltage of PVC/NBR blends with different compositions is fairly stabilized at an average value of 35 kV. This means that electric current at this voltage value did not weaken these

**Figure 14.** TGA thermograms of PVC/NBR containing (A) 20 wt % NBR and (B) 50 wt % NBR nonirradiated and irradiated at 30 and 50 KGy.

blend systems by creating permanent changes, either molecular or physical, thus indicating that these mixtures are qualified for use as electrical insulators in accordance with IEC 60243 (2013).

**3.6. Influence of Thermal Aging on Mechanical Properties.** *3.6.1. Tensile Strength.* PVC/NBR blends containing different NBR contents were subjected to tensile tests before and after exposure to a temperature of 80 °C for 7 days. Figure 6 illustrates the appearance of the tensile strength curve as a function of the rate of NBR incorporation into the PVC matrix. It should be noted that the breaking properties are widely used to evaluate the state of mechanical degradation of a material and particularly that of the elongation at break, which is very sensitive even to minute changes.[46]

According to the data of Figure 6, aging of the PVC/NBR blend at 80 °C did not have a great effect on the tensile strength when the material contained between 0 and 40 wt % NBR, where the tensile strength values obtained are above the threshold of 12.5 MPa in accordance with the requirements of the standard IEC 60811-501. This indicates a good interfacial adhesion between the two different polymer matrices and also a good conservation of the PVC/NBR elasticity under stress after aging. However, for the blend with 50 wt % NBR content, the tensile strengths before and after aging are found to be lower than the accepted value. This indicates immiscibility between the two polymers, leading to the reduction of the tensile strength property of the blend. The partial miscibility of such a blend was also proved by Komori et al.[47] using the dynamic mechanical analysis (DMA). According to the literature, the miscibility of the PVC/NBR blend system is controversial and depends on the acrylonitrile content in the

NBR copolymer.[48−51] The results reported by Zakrzewsky,[49] Perera et al.,[50] and Pena et al.[51] using NBR containing between 23 and 45% acrylonitrile in the PVC/NBR blend reveal that this system is considered miscible in a wide range of compositions. This was proven on the basis of the appearance of a single glass transition temperature of the blend on the thermogram, obtained by the differential scanning calorimetry (DSC) analysis, and confirmed by the negative sign of the Flory interaction parameter ($\chi$) between PVC and NBR chains estimated by the inverse gas chromatography method.[29,52] On the other hand, for the same NBR compositions, two different phases have also been observed for the NBR/PVC blends by a transmission electron microscope (TEM).[53−55] The state of miscibility of this pair of polymers may depend on the preparation method of the sample and the composition of the blend, and this can be rigorously explained by a phase diagram of this system. Note that the composition of a polymer blend can be estimated from the compositional dependence of the glass transition.[56,57] Indeed, an ultimate glass transition temperature can be observed between those of the two pure polymer components of the blend, concerning the miscibility of the system. This is due to the cooperative segmental movement of the component polymers.[58] On the other hand, when the mixture is biphasic (immiscible), the DSC thermogram shows the appearance of two glass transition temperatures around those of the pure components.

*3.6.2. Elongation at Break.* The elongations at break of the PVC/NBR material with different NBR contents are presented in the form of histograms in Figure 7. These data reveal that the elongation at break before and after aging increased as a function of the NBR loading rate in the blend; a maximum of 40% is reached. This is attributed to the rubbery nature of NBR inducing an increase in the elasticity rate of the PVC/NBR blend by inserting polar bonds between the macromolecular chains.[59] These data reveal that the elongation at break before and after aging increases as a function of the NBR content in the blend to reach a maximum of 750% when the rubber content was 40 wt % (before aging) and 50 wt % (after aging). This is attributed to the rubbery nature of NBR inducing an increase in the elasticity rate of the PVC/NBR material by inserting polar bonds between the macromolecular chains of different natures.[59] In addition, the histogram also indicates that the aging of the PVC/NBR material as a function of the NBR content taken at 80 °C has practically no great effect on the tensile strength for blends containing between 0 and 40 wt % NBR. However, when the blend material reached 50 wt % NBR, the elongation at break after aging is improved compared to the nonaged blend system. Finally, note that the elongation at break for blends containing between 10 and 50% by weight of NBR is greater than 125%, according to the standard IEC 60811-501 before aging and IEC 60811-401 after aging.

*3.6.3. Young's Modulus.* The evolution of Young's modulus of the PVC/NBR blend as a function of the NBR content before and after aging is plotted in Figure 8. As shown by the profile of the curve obtained, Young's modulus of the blend after aging decreases for NBR contents of 20, 30, and 50 wt %, which means that these prepared materials gain flexibility. This is because the samples undergo some degree of degradation. It can be noted that this phenomenon is not observed in the PVC/NBR blend containing 10 wt % NBR, thus confirming its tensile behavior observed for this material.
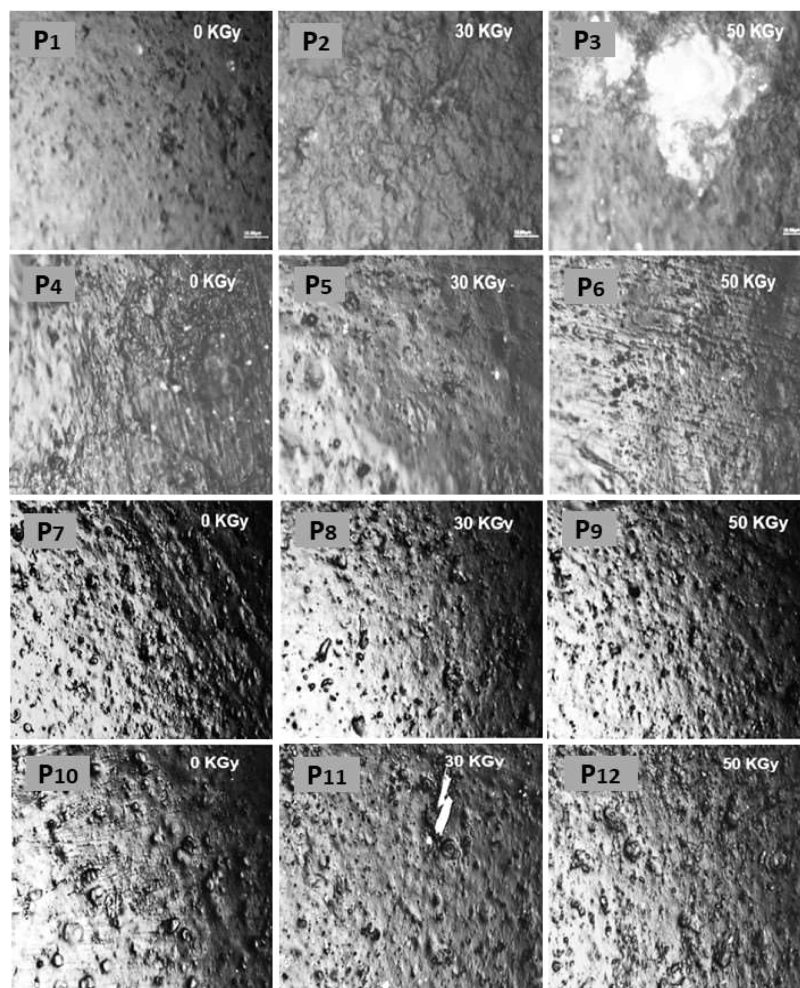
**Figure 15.** Optical images taken at 1000 x magnification of PVC ($P_1$, $P_2$, $P_3$); NBR ($P_4$, $P_5$, $P_6$); PVC/NBR-20% ($P_7$, $P_8$, $P_9$); and PVC/NBR-50% ($P_{10}$, $P_{11}$, $P_{12}$) nonirradiated and irradiated with 30 and 50 KGy.

**3.7. Influence of $\gamma$ Radiation on the Mechanical Properties.** *3.7.1. Tensile of Strength.* The change in the tensile strength as a function of the NBR content in the PVC/NBR blend taken at different $\gamma$ radiation doses is plotted in Figure 9. As can be observed from the profile of the curves obtained, at a given $\gamma$ radiation dose, the tensile strength of the PVC/NBR blend increased with the NBR content to reach a maximum when the NBR content is 30 wt % by weight in this material and then decreased beyond. In addition, at this composition, the tensile strength of the PVC/NBR system regularly increased with the $\gamma$ radiation dose. This means that radiation has an effect on the properties of the PVC/NBR material. This may be due to the formation of radicals on the PVC and NBR chains under the effect of $\gamma$ radiation, thus causing radical cross-linking reactions but also chain breakages caused by oxidation reactions. Indeed, according to Cota et al.,[60] in their work, the decrease in tensile strength under $\gamma$ radiation was closely linked to the cross-linking of the polymers involved. However, certain researchers[61,62] have explained the degradation of these polymers under the effect of $\gamma$ radiation, first by the oxidation in the air of the samples with the formation of radicals. These authors linked the rate of oxidation to the thickness of the film sample and showed that the oxidation reactions will be complete for a thickness varied between 0.5 and 2 mm. These results were confirmed by

Premnath et al.,[63] who adjusted the thickness of the sample so that the oxidation was complete under the effect of $\gamma$ radiation. These authors found that the thickness should not exceed 1.6 mm. However, in this present work, the thickness of the prepared film samples is 2 mm; in this case, this means that the degradation is justified by oxidation, which creates free radicals followed by cross-linking.

The variation of the tensile strength of the PVC/NBR blend with the $\gamma$ radiation dose was measured at different NBR contents, and the data obtained are plotted in Figure 10. As can be seen from the profile of the curves obtained, the tensile strength of the blend containing an NBR content less than or equal to 30% by weight goes through a maximum when the $\gamma$ radiation was 30 KGy. For the blend containing 50% NBR, this maximum shifts toward the higher dose (40 KGy). On the other hand, when the NBR content in the prepared material is 40% by weight, the tensile strength reached a minimum at an irradiation dose of 10 KGy. It should also be noted that for all the compositions of the blend studied, the variation of the tensile strength with the irradiation dose behaves practically in the same way as that of pure PVC with only a shift of the maximum toward the higher doses, except that of the blend containing 40 wt % NBR, in which this property behaves differently; it increases when that of other systems decreases and vice versa.

*3.7.2. Elongation at Break.* The change in the elongation at break of the PVC/NBR blend versus the NBR content measured at different KGy values is shown in Figure 11. These results reveal that the elongation at break of the prepared PVC/NBR material with different compositions subjected to the γ radiation dose varied between 10 and 50 KGy significantly increased, reaching a threshold of 12.5 MPa. This means that the elasticity of this new material has also increased. As a result, the blend materials become flexible through the breaking of the chains and the formation of double bonds under the effect of radiation as suggested by the work reported in the literature.[64,65] These results confirm those obtained previously (Section 3.6.3). Indeed, the microstructure of the sequences of conjugated double bonds in a zigzag shape (hybridization of $sp^2$ of the central carbon and valence angle of 120°) on parts of the main chains of the degraded PVC provides an increase in the flexibility of the material and a change in color varying from white to beige or brown depending on the conjugated sequence number on the chains that resulted after degradation.

*3.7.3. Young's Modulus.* Figure 12 shows the variation of Young's modulus of the PVC/NBR blend as a function of the NBR content. As can be seen from the profile of the curves obtained, at a given γ radiation dose, Young's modulus of these prepared materials decreased rapidly with the NBR content. This result seems interesting because it indicates that these systems acquire rigidity when exposed to a certain dose of γ radiation. To be more rigorous, it will be more interesting to carry out other characterizations at the macromolecular scale using FTIR analysis employed in the ATR mode and ATG mode followed by SEM observation.

*3.7.4. TGA Analysis.* To complete this study, a thermogravimetric investigation on the thermal behavior of PVC/NBR materials subjected to different doses of γ radiation was also carried out in this work, and the TGA thermograms obtained for the blend containing 20% by weight of NBR, chosen as a typical blend in this series, are gathered in Figure 13 with its pure components. As shown from the profile of the thermal curve of virgin PVC, the decomposition of this polymer passes through two stages in which the first one begins at 200 °C and generates the release of HCl molecules, which turn the litmus paper from blue to red. The HCl molecules released are yielded by the combination of two radicals, which are Cl* and H* intra- and interchains. During this stage, the formation of double and single bonds, sometimes conjugated, was also revealed and proven by the change in color from white to yellow. The second stage starts at 400 °C and generates fragments of aliphatic and aromatic compounds. Similar results are also obtained by different authors and reported that the PVC loses nearly 55% of its mass, which approximately corresponds to the percentage of HCl initially contained in PVC (57%).[66−68] Thus, at least 10 wt % of the evaporated mass of this polymer during the heat treatment corresponds to other volatile products coming from the hydrocarbon skeleton of PVC and additives. The thermogram of pure NBR reveals only a single decomposition stage, which begins at 420 °C. Thus, the NBR sample can be considered thermally stable up to this temperature. Above this temperature, the volatilization of the products generated through this decomposition reaction becomes very rapid up to 520 °C. The thermogram of nonirradiated pure NBR reveals only a single decomposition stage, which begins at 420 °C. Thus, the nonirradiated NBR sample can be considered thermally stable up to this

temperature. Above 420 °C, the volatilization of the products generated by the thermal decomposition reaction of this polymer becomes very fast up to 520 °C. During this period, NBR loses approximately 70% of its initial mass. The volatile fragments produced by chain scission are mainly cyclic and aromatic compounds that are homogeneous or contain nitrogen in their chemical structures. Above this temperature, a significant amount of char (∼30% by weight) is produced at the end of the decomposition process. The two thermal curves belonging to the PVC/NBR blends, subjected to the γ radiation doses of 20 and 50 KGy, reveal that these polymer materials behave thermally like pure PVC by presenting two stages of decomposition. The first stage starts around 220 °C for both samples, where around 32% of its weight will be lost during this stage when this blend was subjected to irradiation of 50 KGy and 42% will be lost when this same material was subjected to 20 KGy. The second stage begins at 410 °C, where the compounds generated by the decomposition reaction of the NBR will be mainly released.

Figure 14 shows the TGA thermograms of the PVC/NBR blend containing 20 wt % (A) and 50 wt % NBR (B) nonirradiated and subjected to irradiation of 30 and 50 KGy. As shown from the profile of the thermal curves obtained, in this range of the γ radiation dose, practically no change in the shape of the PVC/NBR curves is observed. This means that the PVC/NBR blends, in these two compositions, resist the γ radiation and that the incorporation of NBR in the PVC matrix improves the thermal properties of this vinylic polymer. These results are interesting since under these conditions, the PVC/NBR material can be a candidate for its application in γ radiation environments as a covering for electrical cables in nuclear power plants.

**3.8. Study of the Morphological Aspect.** In order to follow the evolution of the surface morphology of the two irradiated PVC/NBR film samples containing 20 and 50% by weight of NBR, optical microscopy photos were taken from the surface of these specimens and compared to those of these same materials nonirradiated as well as those of their pure components. Figure 15 shows the optical photos of the surface morphology of the NBR/PVC film containing 20 wt % NBR, deliberately chosen to be presented in this article, taken before and after the exposition to the irradiation at 30 and 50 KGy. The optical images of pure nonirradiated and irradiated PVC under 30 KGy show almost no apparent change in the surface morphology of this material; a clear surface with nonregular pits and microcracks is observed. This relief is probably due to a weakening of the material during sample preparation when the metal plates became detached from the press used for this purpose. However, these defects which are distributed randomly throughout the sample extend for a dose of 50 KGy. This indicates that certain properties of PVC weaken at this bombardment dose, which means that this material has undergone a phenomenon of degradation and a loss of mass. Figure 15 (P$_4$, P$_5$, and P$_6$) shows the surface morphology of NBR film samples nonsubjected (P$_4$) and subjected to γ radiation of 30 and 50 KGy (P$_5$ and P$_6$). The photo of the NBR film (P$_4$) shows the presence of ridges and cracking damages on the surface of this material. This relief disappears under a γ radiation dose of 30 KGy (P$_5$), leaving a relatively smooth surface. However, at a dose of 50 KGy (P$_6$), these streaks reappear again. Figure 15 (P$_7$, P$_8$, and P$_9$) shows the images of the surface morphology of the nonirradiated PVC/NBR-20% film sample (P$_7$) and subjected to γ radiation of 30

KGy ($P_8$) and 50 KGy ($P_9$). These photos show virtually no significant change in the relief of the corresponding films when subjected to both of these irradiation doses, except perhaps few streaks as those on the top right side of the image ($P_7$), which are probably formed during the preparation of the specimen. The same remarks are also valid for the PVC/NBR-50% system when it is subjected to the same irradiations ($P_{11}$ and $P_{12}$). In general, regardless of the irradiation dose employed, no notable change in the surface morphology of the two film samples is observed. According to Waqas et al.,[33] the phenomenon of degradation of the PVC cable sheath when exposed to accelerated thermal aging at a temperature of 100 °C for 4 days and then irradiated under n's flux of $1.5 \times 10^{11}$ n's/cm$^2$.sec for 1 h revealed that the hydrogen and chlorine ions were ejected toward the outside of the sample.

The molecular chains of PVC recombine to form, through the phenomenon of dehydrochlorination, hydrogen chloride, which induces porosity by creating pits and microcracks produced by scission of the PVC chains. These facts result from the synergistic effects of temperature and radiation aging. These cracks were observed on the exterior surface of the cable sheath in a time equivalent to 2 years, indicating that cables covered with PVC insulation are not suitable for long-term exposure (i.e., a few decades) in a thermoirradiation environment.

## 4. CONCLUSIONS

In this work, a series of PVC/NBR blends of different compositions was prepared, and the physicochemical, mechanical, thermal, and morphological properties of these materials were successfully characterized before and after thermal aging at 80 °C and subjected to $\gamma$ radiation. The results obtained revealed that in the case of PVC, a reduction in the stress at break and an increase in the elongation at break were revealed. These facts correlate with the chemical stability of this polymer. This degradation is less observed in the case of the PVC/NBR-10% blend, which means that adding 10 wt % NBR to PVC improves the properties of the PVC. Furthermore, it has also been demonstrated that thermal aging at 80 °C of this material and its exposure to $\gamma$ radiations at doses up to 50 KGy do not affect the properties of the PVC/NBR material. Finally, the results obtained have always complied with the standard, indicating that this blend can be applied in the field of low-voltage electrical cables working in environments at temperatures less than or equal to 80 °C and under $\gamma$ radiation with doses of up to 50 KGy.

## ■ AUTHOR INFORMATION

### Corresponding Author

Waseem Sharaf Saeed − *Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia;* ⊙ orcid.org/0000-0002-5254-5665; Email: wsaeed@ksu.edu.sa

### Authors

Nabila Boutouchent-Guerfi − *Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique (CRTSE), Algiers 16038, Algeria*

Sabrina Berkani − *Centre de Recherche Nucléaire de Draria, Algiers 16050, Algéria*

Inas Al-Qadsy − *Chemistry Department, Maulana Azad College of Arts, Science and Commerce, Aurangabad 431001, India*

Nesrine Seddiki − *Laboratory of Polymers Treatment and Forming, F.S.I., M'Hamed Bougara University, Boumerdes 35000, Algeria*

Taieb Aouak − *Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c06241

### Author Contributions

Data curation, S.B. and N.S.; formal analysis, N.B.-G., S.B., and N.S.; funding acquisition, T.A.; investigation, T.A.; methodology, N.B.-G., S.B., and N.S.; resources, N.B.-G. and S.B.; supervision, N.S.; validation, N.B.-G. and I.A.; writing— original draft, N.B.-G. and N.S.; and writing—review and editing, I.A., W.S.S., and T.A.

### Notes

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