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Article

Enhanced Hydrophobicity, Thermal Stability, and X-Ray Shielding Efficiency of BaSO₄/P(VDF-HFP) Nanocomposites for Advanced Lead-Free Radiation Protection

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Abstract: In this research, polymer composite sheets were developed by blending poly (vinylidene fluoride-co-hexafluoropropylene) or P(VDF-HFP) with varying concentrations of barium sulfate (BaSO₄) for X-ray shielding applications. The photon counting technique was used to evaluate the composite shielding characteristics through the linear attenuation coefficient. Surface properties, including surface morphology, hydrophobicity, and surface energy, were analyzed using an atomic force microscope (AFM) and a water contact angle machine. Scanning electron microscopy (SEM) was employed to investigate the microstructural distribution and dispersion of BaSO₄ particles within the polymer matrix, providing insights into the composite's uniformity and structural integrity. Additionally, the bulk properties of the composite polymer sheets, such as crystal structures, tensile strength, and thermal stability, were examined. The results demonstrate that increasing the concentration of BaSO₄ in BaSO₄/P(VDF-HFP) composite sheets significantly improves their X-ray attenuation capabilities. Moreover, higher BaSO₄ concentrations enhance the material's hydrophobicity, flexibility, and thermal stability, highlighting the potential of these composites for advanced radiation-shielding applications.

Keywords: P(VDF-HFP) nanocomposites; barium sulfate nanoparticles; X-Ray Shielding

1. Introduction

X-rays, a form of ionizing radiation, pose a risk of causing damage to living tissue, particularly for patients and radiation workers [1]. It is necessary to protect against the danger posed by the radiation. The safety design aims to minimize damage caused by ionizing radiation by adhering to the ALARA principle, which emphasizes achieving the lowest reasonable level of exposure [2]. This principle involves considering factors such as time, distance, and shielding to ensure the safety of individuals and equipment. Traditional shielding material, lead, was favoured due to its high density, atomic number, and low cost. However, it faced numerous drawbacks, including toxicity, weight, environmental disease, poor flexibility, and low chemical stability [3]. Lead-free materials

emerge as alternative options, attracting numerous research groups to address the drawbacks associated with lead [4–6]. Polymer composite shielding has emerged as a promising lead-free material with significant potential for practical applications. Its advantages include lightweight design, excellent flexibility, and ease of processing [7]. Various polymers, such as polymethylmethacrylate (PMMA), polyethylene terephthalate (PET), thermoplastic polyurethane (TPU), polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG), have been employed as matrices for composite shielding materials [8–12]. Among these, poly(vinylidene fluoride) (PVDF) stands out as a fluorine-containing polymer known for its exceptional chemical and thermal resistance, mechanical strength, durability, and biocompatibility. PVDF's high crystallinity significantly enhances its mechanical and thermal performance, making it a preferred choice for demanding applications [13]. However, this crystallinity also imposes limitations, such as reduced flexibility and processability, which restrict its use in adaptable applications. To address these challenges, poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) was developed as an advanced alternative. By incorporating hexafluoropropylene (HFP) into its polymer chain, P(VDF-HFP) reduces crystallinity compared to PVDF, resulting in improved flexibility and processability while retaining good mechanical strength [14]. These properties make P(VDF-HFP) a suitable candidate for applications that demand a balance between mechanical performance and adaptability, such as radiation shielding composites. Furthermore, P(VDF-HFP) exhibits greater hydrophobicity than PVDF due to the presence of trifluoromethyl ($-\text{CF}_3$) groups in its molecular structure. These $-\text{CF}_3$ groups not only increase the fluorine content but also lower the material's surface energy, thereby enhancing its hydrophobic properties. This improved hydrophobicity provides greater resistance to moisture and minimizes the risk of microorganism colonization, a common issue in fluorine-containing polymers [15,16]. These combined features position P(VDF-HFP) as a versatile and advanced material for developing lead-free radiation shielding solutions that offer flexibility, moisture resistance, and high performance.

Barium sulfate (BaSO_4) is a non-toxic, environmentally friendly material with a high atomic number, making it highly effective for X-ray attenuation [17]. Commonly used in radiation shielding applications such as medical imaging and industrial settings, BaSO_4 enhances polymer composites by improving impact resistance, chemical stability, heat resistance, dimensional stability, and mechanical strength. Its chemical stability and compatibility with polymers make it an excellent filler for composite development [18,19]. Although BaSO_4 's incorporation into PVDF has been extensively studied [20,21], limited research has explored its integration into P(VDF-HFP) polymer matrices. To address this, lightweight, flexible, and water-resistant composite sheets made from BaSO_4 and P(VDF-HFP) were developed in this study to provide efficient X-ray shielding. The linear attenuation coefficient was used to evaluate their shielding performance through photon counting techniques, while comprehensive analyses of surface morphology, hydrophobicity, crystal structure, mechanical properties, and thermal stability demonstrated their potential as advanced lead-free X-ray shielding materials.

2. Method

2.1. Materials and Film Preparation

In this study, the polymer matrix used was composed of 10 wt% P(VDF-HFP) (4.5 mol%) (Solef® 11010/1001, Solvay). N,N-dimethylformamide (DMF), a highly polar solvent ($\text{C}_3\text{H}_7\text{NO}$, D158550, Sigma-Aldrich), served as the solvent. Barium sulfate (BaSO_4), a white powder with a molecular weight of 233.39 g/mol (KA264, Kemaus, Australia), was incorporated as the filler material.

To prepare the P(VDF-HFP) solution, 20 g of P(VDF-HFP) powder was dissolved in 100 mL of DMF at room temperature under constant stirring, resulting in a transparent solution (P(VDF-HFP)-DMF mixture) after complete dissolution. Various concentrations of BaSO_4 (5, 10, 20, 30, and 40 %w/v) were then dispersed into the P(VDF-HFP) solution. The mixtures were magnetically stirred until homogenous. The resulting solutions were cast onto clean glass substrates and dried at 60 °C in a hot air oven (FD 115, Binder, Germany) for 4 hours. Once dried, the pure P(VDF-HFP) and BaSO_4 /P(VDF-

HFP) composite films were carefully peeled from the glass substrates. The final film thickness ranged between 100-150 μm , suitable for subsequent characterization. The schematic illustration of the film fabrication process is presented in Figure 1(a).

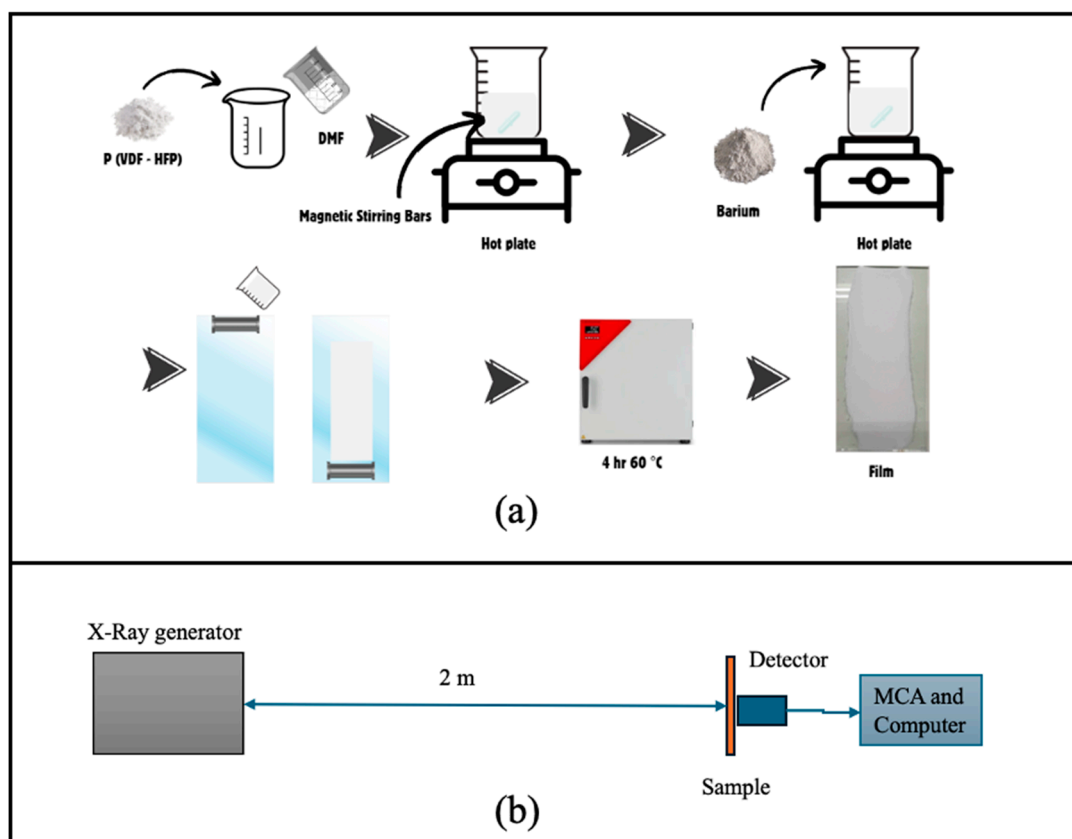


Figure 1. Schematic illustration of (a) the film preparation process and (b) the X-ray absorption experimental setup for BaSO₄/P(VDF-HFP) composites.

A. Sample characterization

1. Surface Morphology

The 2D surface morphology of all P(VDF-HFP) samples was analyzed using a scanning electron microscope (SEM; Quanta 400, FEI, Czech Republic) to visualize detailed surface features. Before imaging, the P(VDF-HFP) samples were carefully mounted onto SEM stubs using carbon tape to ensure stability and prevent charging under the electron beam. The surface microstructure was observed under high vacuum conditions, which allowed for clearer imaging by minimizing interference from air molecules. A 20 kV accelerating voltage was applied, providing sufficient beam energy to interact with the sample surface, while a magnification of 5,000x was used to capture fine details such as surface roughness, porosity, and any structural patterns. Porosity analysis of the surface morphology was conducted using ImageJ, a robust image analysis software. SEM images of the sample surface were processed in ImageJ to distinguish between porous and solid regions. The images were converted to grayscale and thresholded to generate a binary image, with pores represented in black color and solid areas in white color. By applying the "Analyze Particles" function, ImageJ calculated the percentage of the surface area occupied by pores, providing a quantitative measure of porosity. This value reflects the distribution and size of pores across the sample surface, which is essential for understanding the material's structural characteristics.

Atomic Force Microscopy (AFM) was used to examine the surface morphology and topography of P(VDF-HFP) films. The AFM images showed a smooth surface with nanoscale features. A 1x1 cm² film was mounted on a stub and placed on the sample stage. The Nanosurf easyScan2 Flex AFM system (Easyscan2, Switzerland) was used in dynamic force mode, employing an ACL-A probe,

suitable for non-contact or tapping mode. The analysis parameters were set at 50 μm for image size, 1 second per line, and 256 points per line. Surface roughness was analyzed using the Nanosurf software, with the roughness calculated through the root mean square roughness (R_q), representing the standard deviation of surface height.

2. Hydrophobicity

The contact angle and surface energy are important indicators of the wettability of the P(VDF-HFP) surface. In this study, the contact angle was measured using a Dataphysics contact angle goniometer (OCA-15EC, Germany) with SCA20_U software in sessile drop mode. A 2 μL water droplet was used. A 1x3 cm^2 film was placed on the sample holder, and a liquid droplet was deposited on the film's surface. The contact angle formed by the droplet was captured in an image for analysis. To minimize the experimental errors, the contact angles were measured at three random locations for each sample and then the average was reported. The water contact angle (WCA) on a rough surface can be calculated using the following equation [22]:

$$\cos\theta_{CB} = f_1(\cos\theta_1 + 1) - 1, \quad (1)$$

where: $\cos\theta_{CB}$ is the Cassie-Baxter contact angle, f_1 is the fraction of the solid-liquid contact area, and θ_1 is the contact angle of the droplet on the surface. Additionally, the surface energy (SE) of the membrane was analyzed using the Owens-Wendt model [23], based on the contact angles of water, formamide, and ethylene glycol.

3. Crystal Structures

The crystal structures of the samples were examined using Fourier Transform Infrared Spectroscopy (FTIR; Vertex70, Bruker, Germany) and X-ray Diffraction (XRD; Empyrean, PANalytical, Netherlands). FTIR measurements were performed at room temperature in attenuated total reflectance (ATR) mode, with a spectral range from 4,000 to 400 cm^{-1} and a resolution of 2 cm^{-1} . The obtained spectra were analyzed following the methodology described in reference [24]. The XRD measurement was conducted using a Cu X-ray tube with an X-ray generator set to 40 kV and 0.3 mA, producing a wavelength of 0.154 nm (Cu $K\alpha$). The scan range was set from 5° to 90° (2 θ) with a step size of 0.026° and a time per step of 70.125 seconds. The degree of crystallinity (X_c) value was calculated from the peak areas in the obtained XRD patterns using the equation [25]:

$$X_c = \frac{\Sigma A_{cr}}{\Sigma A_{cr} + \Sigma A_{amr}} \times 100, \quad (2)$$

where ΣA_{cr} and ΣA_{amr} are the total integrated areas of the crystalline diffraction peaks and the amorphous halo, respectively.

4. Mechanical Property

To evaluate the mechanical properties of the P(VDF-HFP) copolymer, tensile tests were conducted using a Zwick Roell Germany testing machine (model z010) in accordance with the ISO 37-020 standard. Five samples were tested per composition, with each sample clamped at both ends and subjected to a 100 N load at a deformation rate of 5 mm/min at room temperature. The machine automatically measured stress, based on the applied force over the film's cross-sectional area, as a function of elongation. Key mechanical properties such as tensile strength, elongation at break, and Young's modulus were determined. Young's modulus was calculated from the slope of the stress-strain curve in the elastic region, following Hooke's law [26].

$$\text{Young's modulus} = \frac{\text{Stress}}{\text{Strain}} \quad (3)$$

5. Thermal Stability

The thermal stability of P(VDF-HFP) was investigated through thermogravimetric analysis (TGA) using the Perkin Elmer TGA 8000 instrument. In this process, the sample was subjected to controlled heating, starting at 50°C and gradually increasing to 700°C, with a consistent heating rate

of 10°C per minute. The analysis was performed in an inert nitrogen atmosphere to prevent oxidation or combustion during heating. A constant nitrogen flow of 20 ml/min was maintained, ensuring that any evolved gases or decomposition products were carried away efficiently. This setup allowed for precise monitoring of the sample's weight loss, which provided insights into the thermal decomposition behavior and overall thermal stability of the P(VDF-HFP) samples over a broad temperature range.

6. Absorption performance

The equipment used to study X-ray absorption includes an X-ray generator (G.E. Titan E 320), semi-conductor detector CdTe (AMPTEx XR-100T) and multi-channel analyzer (MCA; AMPTEx PX5). The composite film was set at 2 m from the X-ray source, as shown in Figure 1(b). After generating an X-ray beam, the X-ray photon that transmits through the sample is detected by a detector and sends an electrical signal to be analysed by MCA and the computer system. This process was repeated three times under each condition of each sample. The counts for each condition were averaged, and the total count was obtained by summing these averages. The properties of composite BaSO₄/P(VDF-HFP) sheets on the attenuation performance were investigated from the linear attenuation coefficient (μ) that was calculated from the Beer-Lambert law as an equation [17]:

$$I = I_0 e^{-\mu x}. \quad (4)$$

Rewrite this equation, getting equation:

$$\mu = \frac{1}{x} \ln \frac{I_0}{I}, \quad (5)$$

where I_0 and I were the incidents and transmitted intensity of X-ray, and x was the thickness of the sample. From equation (5), the linear attenuation coefficient (μ) was calculated from the slope of the linear equation, which $\ln \frac{I_0}{I}$ and x , where $\ln \frac{I_0}{I}$ was on the vertical axis and x on the horizontal axis.

To investigate the effect of BaSO₄ concentration in the BaSO₄/P(VDF-HFP) composite sheet on the attenuation performance, the X-ray beam's energy was generated at 60 keV and 0.1 mA. The transmitted intensities were collected from the intensity of X-rays that passed through the composite film with a thickness of 0.2 mm, 0.4 mm, 0.6 mm, 0.8 mm, 1.0 mm and 1.2 mm. In contrast, the incident intensity was collected from the detector without any shielding. The thickness of 0.4 mm was made of 2 sheets of 0.2 mm films, and so on.

In addition, this research also investigates the effect of X-ray energy on the linear attenuation coefficient of composite shielding comprised of BaSO₄ at different concentrations in P(VDF-HFP) polymer. The energy of the X-ray source was 60, 80, and 100 keV. The samples were 2 mm thickness of composite BaSO₄/ P(VDF-HFP) at concentrations of 0, 5, 10, 20, 30, and 40 %.

3. Results and Discussion

3.1. Surface Morphology

SEM analysis

Figure 2 illustrates SEM micrographs showing the surface morphology of both pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films. The micrograph of pure P(VDF-HFP) reveals a relatively smooth and uniform surface, with no visible filler particles or significant texture at the micro-scale. This smooth and dense morphology can be attributed to the solution casting method used during film fabrication, where the evaporation of DMF solvent leaves behind a uniform polymer layer [27]. As BaSO₄ was incorporated into the P(VDF-HFP) polymer matrix, the surface morphology becomes progressively rougher and more granular. At lower concentrations (5% BaSO₄ to 10% BaSO₄), the gradual addition of BaSO₄ introduces small, scattered clusters of particles. The BaSO₄ particles are generally more evenly dispersed and embedded within the polymer, allowing the matrix to maintain a relatively smooth surface, though some aggregation begins to appear at 10% BaSO₄. This initial level of aggregation does not significantly disrupt the overall smoothness of the polymer. For

20%BaSO₄ and higher, the surface becomes increasingly granular, with more pronounced clustering of BaSO₄ particles. At higher concentrations (30%BaSO₄ to 40%BaSO₄), the particles are densely packed, resulting in rougher surfaces with agglomerated particles. The polymer matrix struggles to encapsulate and uniformly disperse the high volume of BaSO₄, causing the particles to cluster together due to attractive forces, such as van der Waals interactions [14]. These aggregated clusters cannot be fully integrated into the polymer chains, leading to a granular and rough morphology. The agglomerates act as micro-sized protrusions, giving the surface its rough, grainy appearance.

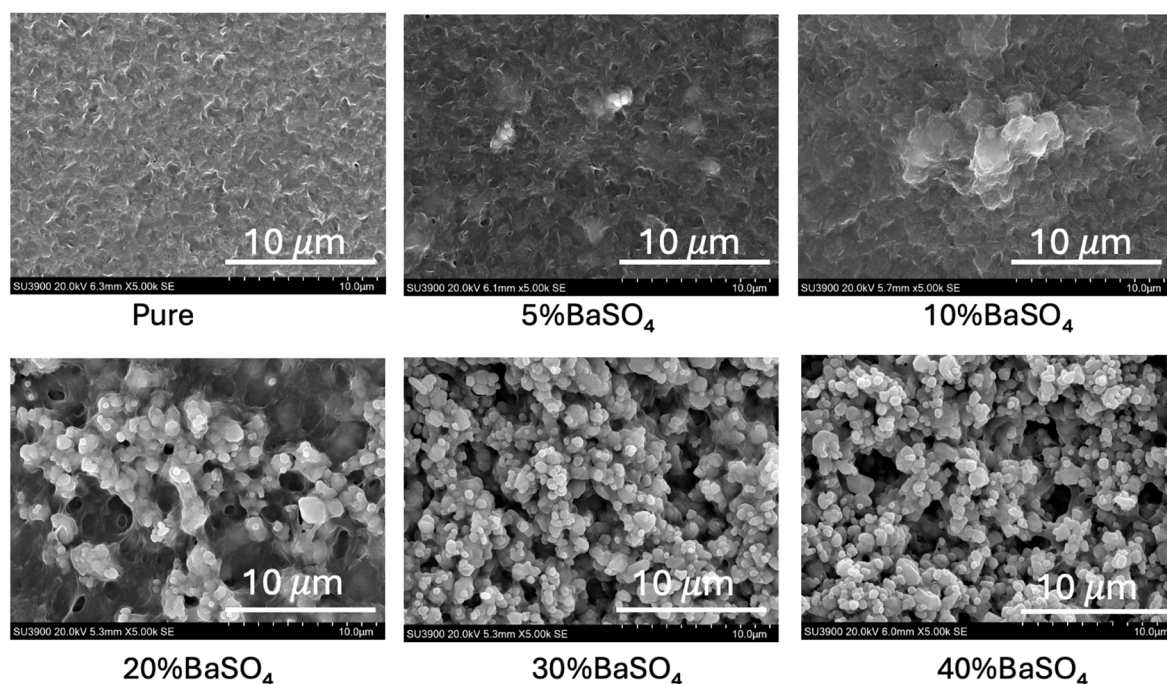


Figure 2. SEM micrographs of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films.

AFM analysis

AFM analysis was conducted to further support the surface morphology observations. The AFM images reveal that the BaSO₄/P(VDF-HFP) composite films exhibit significant surface roughness on a large scale. Figure 3 presents the AFM images of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films, with the corresponding surface roughness values (*R_q*) listed in Table 1. The AFM image of pure P(VDF-HFP) shows a relatively smooth surface with minimal height variation. The surface roughness is quite low (*R_q*: 66.57 nm), which is consistent with the SEM micrographs and the previously reported morphology of pure P(VDF-HFP) films. This smoothness suggests that in the absence of BaSO₄ fillers, the polymer chains form a dense and uniform film during the solution casting process. It also indicates that the polymer matrix can crystallize uniformly when there is no filler particles present to disrupt the structure. For BaSO₄/P(VDF-HFP) composites, surface roughness increases with BaSO₄ content. The results clearly show a progressive increase in surface roughness as the BaSO₄ content rises from 5% to 40%. This is due to the growing number of BaSO₄ particles in the polymer matrix, which raises the likelihood of particle aggregation, leading to an uneven topography.

At lower concentrations of BaSO₄, such as 5% to 10%, the AFM images reveal a slight increase in surface roughness compared to the pure polymer. Small bumps or granular formations appear, indicating the presence of dispersed BaSO₄ particles. However, the surface remains relatively smooth, suggesting that the BaSO₄ particles are well-dispersed and have not significantly disrupted the uniformity of the polymer matrix. At 20%BaSO₄, the *R_q* value (180.66 nm) increases significantly compared to the 10% BaSO₄/P(VDF-HFP) sample, indicating that larger clusters have formed, introducing greater height variations and resulting in a rougher surface, as also shown in the SEM results. At higher concentrations (30% to 40%), surface roughness is dominated by BaSO₄ particle

agglomerates, as the polymer matrix can no longer maintain an even dispersion of the filler. This results in a highly irregular and rough surface texture. The polymer’s capacity to encapsulate and uniformly disperse BaSO₄ is exceeded at these concentrations, leading to large-scale agglomeration and the formation of surface protrusions. This change in morphology can affect the microstructural and mechanical properties of the composite films, which is important to consider for x-ray absorption applications.

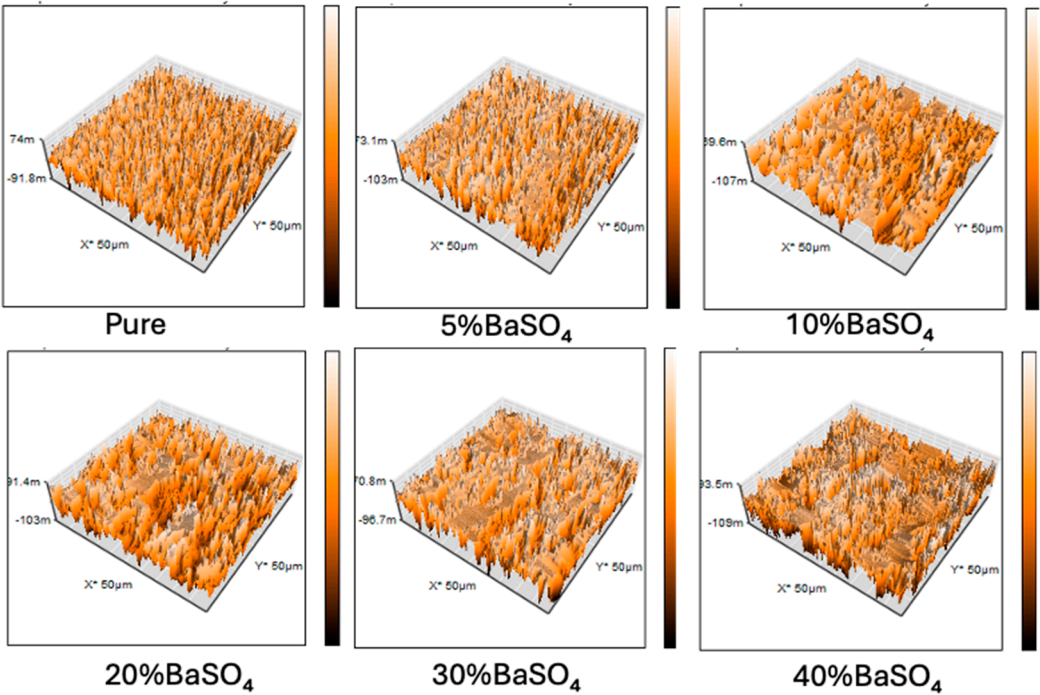


Figure 3. AFM images of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films.

Table 1. Porosity, root mean square roughness, crystallinity values of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films.

Sample	Porosity (%)	Root means square roughness (R_q) (nm)	Crystallinity (X_c) (%)
Pure	0.30	66.57	60.10
5% BaSO ₄	1.60	138.93	71.24
10% BaSO ₄	4.67	139.96	73.81
20% BaSO ₄	15.05	180.66	79.00
30% BaSO ₄	20.40	237.45	80.44
40% BaSO ₄	25.21	590.32	83.53

3.2. Hydrophobicity

For X-ray shielding materials, surface wettability can impact performance, particularly in environments where moisture exposure is a concern (e.g., medical devices, protective clothing). Hydrophobic surfaces may resist moisture better, protecting the integrity of the shielding material over time. The water contact angle (WCA) measures how water interacts with a surface. A WCA below 90° indicates hydrophilicity, between 90° and 150° indicates hydrophobicity, and above 150° indicates superhydrophobicity, reflecting how well a surface repels or attracts water [28]. WCA is inversely related to surface energy (SE), which influences a material’s behavior, including adhesion, durability, and interaction with other materials [29].

Figure 4 presents the WCA and SE results for pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films. For pure P(VDF-HFP), the WCA is 93.28° ± 1.42°, and the SE is 24.18 ± 0.39 mJ/m²,

indicating a slightly hydrophobic surface. The relatively high SE contributes to moderate wettability. This confirms the hydrophobic nature of P(VDF-HFP), attributed to the presence of CF_3 and fluorine atoms, which make fluorine-containing polymers naturally hydrophobic. Additionally, SEM in the previous section showed a smooth polymer surface with minimal roughness, as expected in a uniform polymer matrix. AFM would likely confirm minimal nanoscale roughness, consistent with the relatively low WCA. As BaSO_4 was incorporated (from 5% to 20%), the WCA gradually increased from $94.26^\circ \pm 1.42^\circ$ to $99.27^\circ \pm 1.37^\circ$, suggesting a slow shift toward greater hydrophobicity. Simultaneously, the SE decreased steadily from 23.36 ± 0.44 to $21.48 \pm 0.19 \text{ mJ/m}^2$, implying that BaSO_4 nanoparticles were lowering the surface tension. SEM revealed dispersed BaSO_4 particles within the polymer matrix, likely contributing to slight surface roughness. AFM also indicated a subtle increase in nanoscale roughness, correlating with the gradual rise in WCA. For the composite with the highest BaSO_4 content (40%), the WCA reached $120.85^\circ \pm 0.47^\circ$ and SE dropped to $12.25 \pm 0.06 \text{ mJ/m}^2$, indicating significant hydrophobicity approaching superhydrophobic behavior. Although BaSO_4 itself is hydrophilic [30], which would normally decrease WCA and increase SE, the observed behavior can be attributed to substantial aggregation of BaSO_4 particles, as revealed by SEM and AFM images. These particles likely formed rough micro- and nanoscale structures, increasing surface roughness, which ultimately enhanced WCA and reduced SE. This outcome can be explained by Young's and Wenzel's equations, both of which relate surface roughness to wettability [31]. Young's equation describes the equilibrium contact angle (θ) for a liquid droplet on an ideal, smooth surface, taking into account interfacial free energies (surface tensions) between solid, liquid, and gas phases. However, this model assumes a homogeneous (for pure P(VDF-HFP)), flat surface, making it less applicable to rough surfaces like those observed in BaSO_4 /P(VDF-HFP) composites. The Wenzel equation, an extension of Young's model, considers surface roughness by introducing a roughness factor, which amplifies the natural wetting behavior of a surface. According to the Wenzel model, for hydrophobic surfaces, increased roughness leads to higher contact angles as the liquid follows the contours of the rough surface [32]. Thus, the high BaSO_4 content created an uneven, rough surface that amplified the material's hydrophobicity, as predicted by the Wenzel model, even though BaSO_4 itself is hydrophilic. This suggests that surface morphology, rather than the inherent chemical nature of BaSO_4 , dominated the wettability properties of the composite, driving it towards greater hydrophobicity.

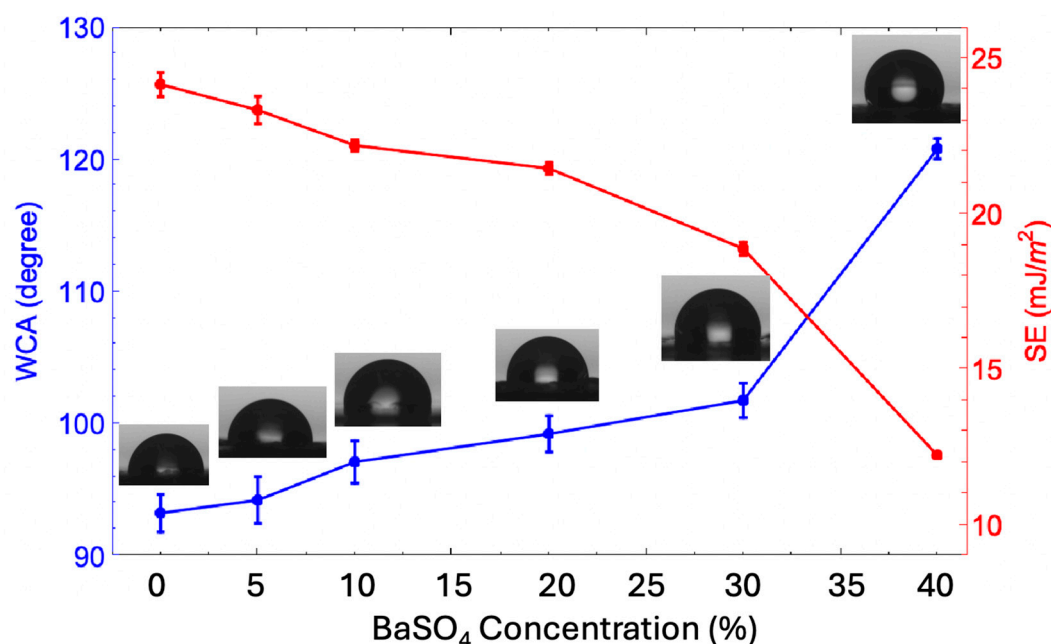


Figure 4. Water contact angle (WCA) and surface energy (SE) of pure P(VDF-HFP) and BaSO_4 /P(VDF-HFP) composite films.

3.3. Crystal Structure

FTIR analysis

FTIR spectroscopy is a crucial tool for analyzing the crystal structure of polymers, enabling optimization of mechanical and thermal properties in X-ray shielding materials. By assessing phase composition and crystallinity, FTIR analysis supports the development of durable, efficient materials that meet strict safety and performance standards for radiation protection. Figure 5 shows FTIR peaks associated with the crystal structures of both P(VDF-HFP) and BaSO₄ in the composites. For pure P(VDF-HFP), vibrational peaks are observed at 431 cm⁻², 481 cm⁻², and 531 cm⁻² (CF₂ bending); 614 cm⁻² (CF₂ bending and skeletal bending); 762 cm⁻² (in-plane bending/rocking); 834 cm⁻² (CH₂ rocking and CF₂ asymmetric stretching); 873 cm⁻² (CH₂ rocking); 975 cm⁻² (CH out-of-plane deformation); 1,069 cm⁻² (CF₃ out-of-plane deformation); 1,171 cm⁻² (CF₂ antisymmetric stretching); 1,231 cm⁻² (CF out-of-plane deformation); and 1,402 cm⁻² (CH₂ scissoring). These peaks confirm the semi-crystalline nature of P(VDF-HFP), with both amorphous and crystalline regions contributing to its structure [33–35]. In BaSO₄ powder, the sulfate group exhibits four fundamental vibrational modes: one nondegenerate mode (ν_1), one doubly degenerate mode (ν_2), and two triply degenerate modes (ν_3 and ν_4). The FTIR spectrum of BaSO₄ typically displays several significant bands, with intense bands associated with asymmetric stretching and bending (ν_3 and ν_4) and weaker bands representing symmetric stretching and bending (ν_1 and ν_2). In the FTIR spectrum, bands in the range of 1,078–1,193 cm⁻² and a shoulder at 983 cm⁻² correspond to the symmetric stretching of the SO₄²⁻ group. The SO₄²⁻ group's stretching vibration is identified at 1,543 cm⁻² (ν_3), while peaks at 610 and 639 cm⁻² correspond to out-of-plane bending. The absorption peak at 3,401 cm⁻², attributed to the H₂O stretching vibrations at vacant Ba sites, is evident in pure BaSO₄ but absent in the composites, suggesting the elimination of hydration-related vibrations during composite formation. Peaks around 2,064 cm⁻² represent overtones and combinations of stretching and bending of sulfur-oxygen bonds powder [36,37].

In the FTIR spectra of BaSO₄/P(VDF-HFP) composites with varying BaSO₄ concentrations, characteristic peaks from both the P(VDF-HFP) polymer matrix and BaSO₄ are retained, indicating successful integration of BaSO₄ within the polymer structure. Key BaSO₄ peaks, including SO₄²⁻ bending vibrations at 610 and 639 cm⁻² and symmetric stretching vibrations within the range of 1078–1193 cm⁻², remain stable across all concentrations, underscoring the sulfate group's structural integrity in the composite. As BaSO₄ concentration increases, these specific peaks grow in intensity, reflecting the increasing BaSO₄ content. Meanwhile, prominent P(VDF-HFP) polymer peaks, such as CF₂ bending at 531 and 614 cm⁻², CF₂ in-plane bending or rocking at 762 cm⁻², and CH₂ rocking at 834 cm⁻², are preserved across all composite spectra. This suggests that BaSO₄ does not significantly disrupt the semi-crystalline structure of P(VDF-HFP), allowing the composite to retain the structural and mechanical properties of the polymer [21]. Additionally, peak shifts observed in the FTIR spectra of the composites may indicate changes in the chemical environment around specific functional groups due to interactions between BaSO₄ and the P(VDF-HFP) matrix. When BaSO₄ is incorporated into P(VDF-HFP), the particles interact with the polymer chains, potentially altering local electronic distributions and bond strengths within the polymer. Such interactions could cause slight shifts in the CF₂ bending or CH₂ rocking peaks of P(VDF-HFP), reflecting molecular-level interactions that affect the polymer's structural arrangement. These shifts provide valuable insight into the compatibility and interaction between the phases within the composite material [20]. The absence of the 3401 cm⁻² peak, associated with H₂O stretching vibrations in pure BaSO₄ powder, suggests that hydration in BaSO₄ is eliminated during composite formation, likely due to thermal processing or polymer-particle interactions that reduce the presence of free water molecules. This elimination of water content is advantageous as it enhances the composite's durability and thermal stability, making it suitable for applications in environments where moisture could affect material performance. Overall, the composite retains the structural integrity of P(VDF-HFP) alongside the stability of BaSO₄, highlighting its balanced integration, mechanical flexibility, and suitability for radiation-shielding applications.

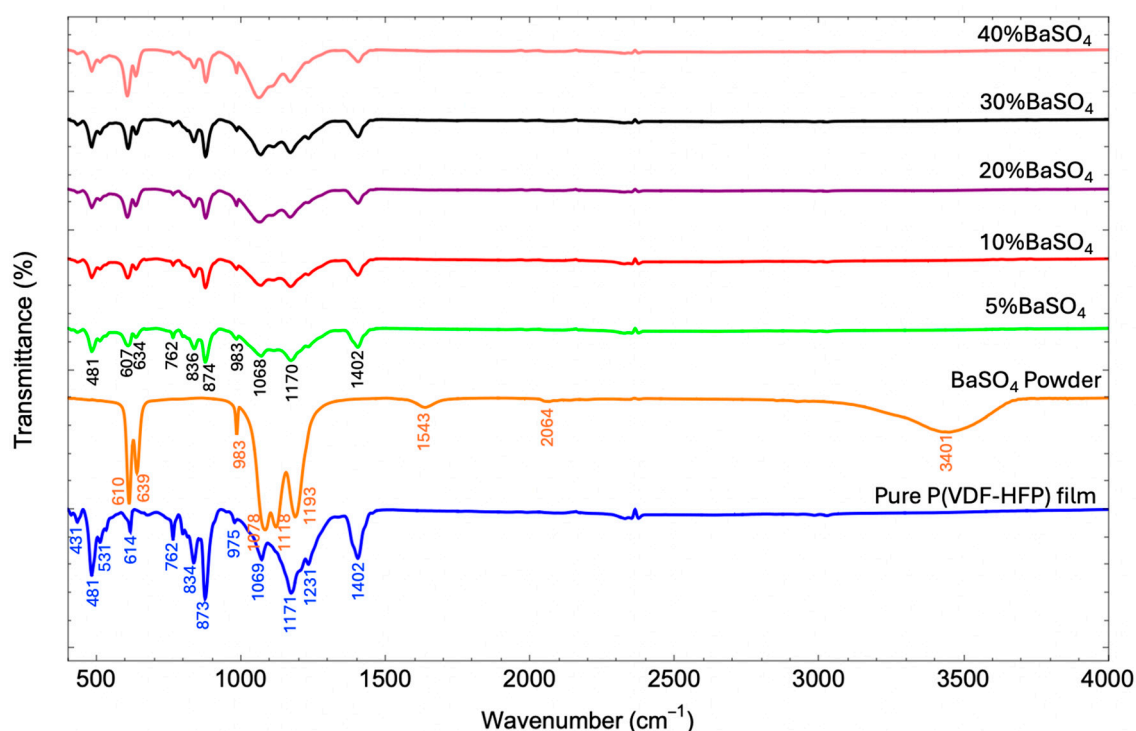


Figure 5. FTIR patterns of pure P(VDF-HFP) and BaSO₄P(VDF-HFP) composite films.

XRD analysis

The crystalline data for pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composites provides key insights into how BaSO₄ loading affects the overall crystalline structure of the composite material. Figure 6 shows the XRD intensity data at various 2θ angles for pure P(VDF-HFP), BaSO₄ powder and BaSO₄-P(VDF-HFP) composite films with different BaSO₄ concentrations. Table 1 lists the crystallinity levels evaluated from XRD results using Equation 2. The P(VDF-HFP) consists of alternating segments of vinylidene fluoride (VDF) and hexafluoropropylene (HFP), with a structural formula represented as: $[-CH_2-CF_2-]_n - [-CF_2-CF(CF_3)-]_m$, where n and m represent the relative ratios of the VDF and HFP units in the copolymer. The P(VDF-HFP) structure combines crystalline (from VDF) and amorphous (from HFP) regions, resulting in a semi-crystalline copolymer that can exhibit multiple crystalline phases, primarily the α, β, and γ phases, depending on the polymer chain configuration [38]. The XRD pattern of the pure P(VDF-HFP) film reveals broad, low-intensity peaks, indicating its semi-crystalline structure. These peaks, associated with the crystalline α-phase of P(VDF-HFP), are relatively weak and broad, reflecting a moderate crystallinity level of 60.1% [39]. This semi-crystalline structure combines rigid crystalline domains and flexible amorphous regions. However, with light elements like carbon, hydrogen, and fluorine, pure P(VDF-HFP) has limited X-ray shielding capability due to its low atomic number composition. To investigate the BaSO₄ powder, its XRD pattern reveals sharp, high-intensity peaks at specific 2θ values, reflecting its crystalline structure. According to Sifontes's research [36], BaSO₄ powder typically exhibits prominent, sharp peaks in its diffraction pattern, characteristic of a crystalline material. This pattern confirms BaSO₄'s orthorhombic crystal structure and highlights its high degree of crystallinity. The recorded XRD data display peaks at defined 2θ positions, particularly between 10° and 80°, which correspond to characteristic diffraction angles of BaSO₄. The peak intensity underscores the material's purity and structural integrity, distinguishing it from less crystalline or amorphous forms. Additionally, the sharpness and intensity of these peaks indicate the stable sulfate ion arrangement within the lattice, which is essential for applications requiring materials with high thermal stability and low reactivity.

The XRD patterns of BaSO₄/P(VDF-HFP) composites reveal that increasing BaSO₄ content impacts the crystalline structure of the P(VDF-HFP) matrix. When BaSO₄ is incorporated, changes in both XRD patterns and crystallinity demonstrate its influence on the composite's structure.

Additional peaks, characteristic of BaSO₄'s crystalline structure, appear in the XRD patterns, confirming its successful integration and dispersion within the matrix. The broad α -phase peak of P(VDF-HFP) around $2\theta \approx 20^\circ$ is absent, indicating that slight changes in intensity suggest structural modifications within the polymer matrix. As BaSO₄ concentration rises, the XRD peaks sharpen and intensify, particularly around BaSO₄'s characteristic angles, indicating an increase in overall crystallinity. This effect is likely due to BaSO₄ acting as a nucleating agent, promoting the formation of crystalline domains within the P(VDF-HFP) matrix. This nucleation enhances polymer chain organization, leading to a more crystalline structure. The resulting higher crystallinity improves material rigidity and stability, which is beneficial for applications requiring a more robust composite material. Furthermore, the inclusion of BaSO₄, with its high atomic number, increases the composite's density and enhances its potential for X-ray attenuation. Higher BaSO₄ concentrations improve X-ray shielding, as evidenced by the persistent BaSO₄ peaks in the XRD patterns, which confirm its presence and distribution within the matrix. The broadening and reduction of P(VDF-HFP) peaks contribute to effective X-ray absorption and shielding. This increased density and enhanced X-ray shielding make these composites suitable for lightweight radiation protection applications.

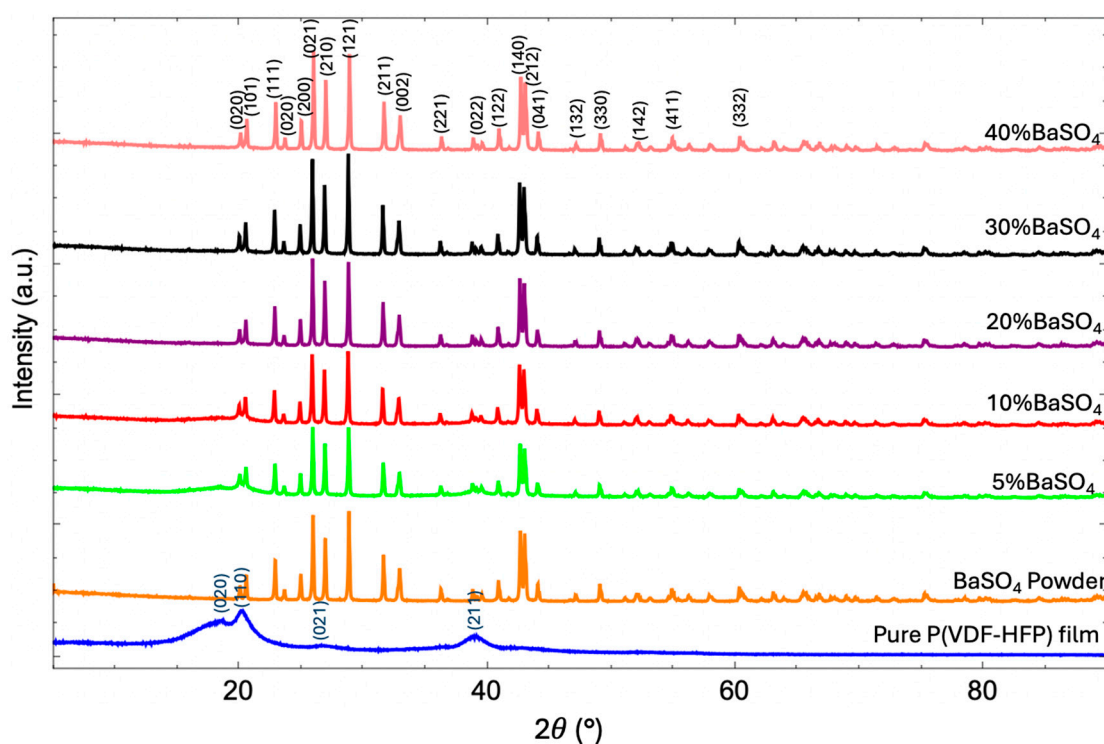


Figure 6. XRD patterns of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films.

3.4. Mechanical Property

The mechanical properties of polymer composite films are crucial for practical applications, especially in contexts such as X-ray shielding, where both strength and flexibility are required. Adding BaSO₄ filler to P(VDF-HFP) significantly affects these properties. To achieve optimal mechanical performance, it's essential to control BaSO₄ content and ensure uniform particle dispersion within the composite. Standard tensile tests reveal the impact of BaSO₄ on tensile properties, including Young's modulus, tensile strength, and elongation at break, as illustrated in Figure 7. For pure P(VDF-HFP), the stress-strain curve displays an initial elastic phase, followed by a peak stress that transitions into plastic deformation, with minimal resistance to further stretching. This behavior is characteristic of a ductile polymer. The tensile properties show a Young's modulus of 6.3 MPa, indicating low stiffness and high flexibility. With a tensile strength of 11.59 MPa and an elongation at break of 22.61%, pure P(VDF-HFP) is highly flexible but lacks mechanical strength due

to the absence of reinforcement. Upon introducing BaSO₄, the stress-strain curves of the 5%-20% BaSO₄/P(VDF-HFP) composites retain a similar shape to that of pure P(VDF-HFP), but with enhanced stiffness and tensile strength. As BaSO₄ content increases, both Young's modulus and tensile strength rise, reaching 12.6 MPa and 19.45 MPa, respectively, at 20% BaSO₄. The elongation at break, however, decreases from 20.07% to 12.45%, indicating reduced ductility as the material stiffens. These composites offer a balance of strength and flexibility, suitable for X-ray shielding applications where moderate stiffness and improved tensile strength are advantageous. For the 30%-40% BaSO₄/P(VDF-HFP) composites, the stress-strain curves indicate substantial increases in tensile strength and rigidity, showcasing the strong reinforcing effect of BaSO₄. With Young's modulus values of 13.4 MPa and 16.4 MPa, and tensile strengths reaching 43.33 MPa and 48.59 MPa for 30% and 40% BaSO₄, respectively, these composites demonstrate high load-bearing capacity. However, the elongation at break falls to 9.41% and 8.73%, signifying increased brittleness and decreased flexibility. These properties make the 30%-40% BaSO₄ composites ideal for applications requiring robust strength and rigidity, although they may be less suitable for environments needing flexibility. As noted by Xiaolei Chen et al. [18] in studies on BaSO₄-filled polymer composites, the Young's modulus and tensile strength of these materials increase progressively, while elongation decreases with higher BaSO₄ content. When inorganic particles are embedded within a polymer matrix, stress can transfer from the matrix to the particles, thereby enhancing yield stress. The tensile yield stress in particle-filled polymers is primarily influenced by filler content and interfacial interactions, which depend on factors such as interfacial adhesion, particle size, and dispersion within the matrix. BaSO₄ nanoparticles, in particular, benefit from their hydrophobic surface, which allows better dispersion in the polymer matrix. Consequently, as BaSO₄ content rises, the interface transfers more stress from the matrix to the inorganic particles, leading to increased tensile yield stress in the composite.

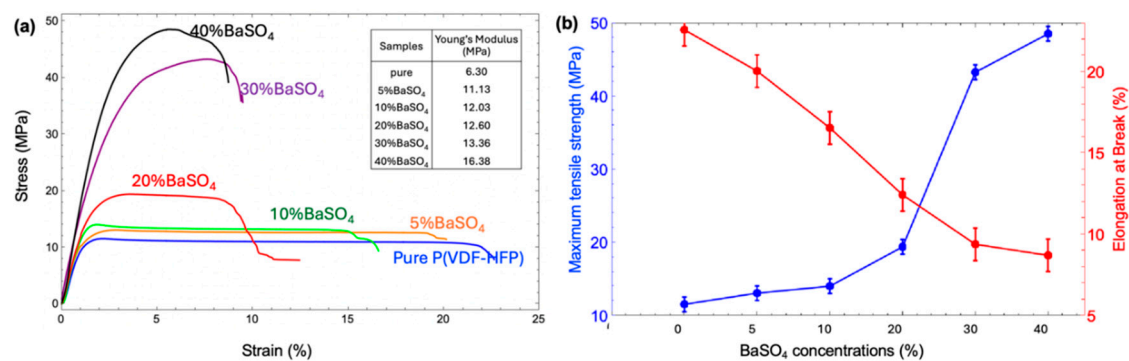


Figure 7. (a) Stress-strain curves and Young's modulus (inserted table) and (b) Values of tensile properties (Tensile strength and elongation at break) of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films.

3.5. Thermal Stability

The thermal stability evaluation of P(VDF-HFP) and BaSO₄/P(VDF-HFP) composites for X-ray shielding involves key measurements such as decomposition temperature, weight loss rate, and residual mass. A high decomposition temperature and low weight loss rate indicate heat resistance, while stable residual mass reflects BaSO₄'s durability as a filler. This analysis helps optimize BaSO₄ content to enhance thermal resilience and ensure reliable shielding performance. The thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves for pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films, shown in Figure 8 and summarized in Table 2, reveal differences in decomposition temperature, weight loss rate, and residual mass between the pure polymer and the composites. From Figure 8(a), pure P(VDF-HFP) begins significant weight loss around 469°C, indicating relatively low thermal stability. In contrast, BaSO₄/P(VDF-HFP) composites display higher decomposition temperatures, starting at approximately 479°C for the 5% BaSO₄ composite and reaching around 498°C for the 40% BaSO₄ composite. Additionally, the weight loss

rate decreases with increased BaSO_4 content, indicating slower degradation in composites. For instance, the 30% BaSO_4 composite shows a more gradual weight loss, demonstrating BaSO_4 's heat-resistant effect, which stabilizes the polymer matrix and delays degradation. Furthermore, the residual mass after thermal decomposition is minimal for pure P(VDF-HFP), as it fully degrades, leaving little residue. However, BaSO_4 /P(VDF-HFP) composites retain progressively higher residual mass with increased BaSO_4 content, with the 40% BaSO_4 composite showing the highest residual mass. This residual mass is mainly due to the thermally stable BaSO_4 , which remains intact and provides a durable framework even after the polymer matrix has decomposed, enhancing the composite's suitability for high-temperature applications.

In Figure 8(b), the DTG data provide additional information on the thermal decomposition behavior of pure P(VDF-HFP) and BaSO_4 /P(VDF-HFP) composites, specifically peak decomposition temperature, maximum weight loss rate, and final residual mass for each sample. The peak decomposition temperature, where each sample experiences the maximum weight loss rate, is around 499°C for pure P(VDF-HFP), indicating lower thermal stability compared to the composites. With increasing BaSO_4 content, the peak decomposition temperature gradually rises, reaching 504°C for the 5% BaSO_4 composite, 507°C for the 20% BaSO_4 composite, and 513°C for the 30% BaSO_4 composite. This increase in peak temperature with higher BaSO_4 content suggests that BaSO_4 stabilizes the polymer matrix, delaying thermal decomposition. The maximum weight loss rate, representing the steepest part of the decomposition curve, is highest for pure P(VDF-HFP) at 27.55 %/min, suggesting rapid degradation under thermal stress. As BaSO_4 content increases, the weight loss rate decreases significantly, with the 5% BaSO_4 composite at 21.36 %/min and the 40% BaSO_4 composite at 7.73 %/min, indicating improved resistance to sudden thermal breakdown. The residual mass represents the material left after heating to the final temperature, indicating the stability of the inorganic BaSO_4 component. Pure P(VDF-HFP) has negligible residual mass, as it fully degrades without leaving a stable residue. In contrast, BaSO_4 /P(VDF-HFP) composites retain progressively higher residual mass with increased BaSO_4 content. For instance, the 5% BaSO_4 composite has a small residual mass, while the 30% BaSO_4 composite retains a much larger amount. This residual mass is primarily composed of thermally stable BaSO_4 , which does not decompose and remains intact, providing structural stability even after polymer degradation. These results indicate that increasing BaSO_4 content in P(VDF-HFP) composites raises the peak decomposition temperature, reduces the maximum weight loss rate, and increases the final residual mass, demonstrating BaSO_4 's role in enhancing the thermal stability and durability of the composite for high-temperature X-ray shielding applications requiring prolonged structural integrity.

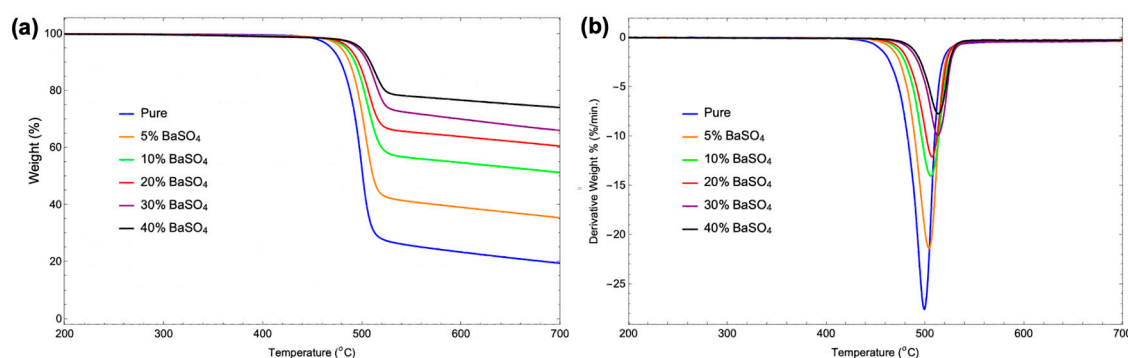


Figure 8. (a) TGA and (b) DTG thermograms of pure P(VDF-HFP) and BaSO_4 /P(VDF-HFP) composite films.

Table 2. Decomposition temperature, weight loss rate, and residual mass evaluated from TGA and DTG thermograms of pure P(VDF-HFP) and BaSO₄/P(VDF-HFP) composite films.

Sample	TGA Analysis Results			DTG Analysis Results		
	Decomposition Temperature	Weight Loss Rate	Residual Mass	Peak Decomposition Temperature	Maximum Weight Loss Rate	Residual Mass
	(°C)	(%/°C)	(%)	(°C)	(%/min)	(%)
pure	468.87	0.55	19.58	499.09	27.55	-0.06
5% BaSO ₄	478.78	0.46	35.50	503.72	21.36	-0.07
10% BaSO ₄	483.38	0.34	51.34	505.7	14.03	-0.28
20% BaSO ₄	486.69	0.27	60.60	506.86	12.10	-0.16
30% BaSO ₄	495.29	0.24	66.15	512.65	9.93	-0.19
40% BaSO ₄	498.26	0.18	74.11	513.15	7.73	-0.23

3.5. Absorption Performance

The linear attenuation coefficient is a parameter that is used to describe the fraction of attenuated incident X-ray photons per unit thickness of material. In general, the primary interactions within shielding materials encompass the photoelectric effect, Compton scattering, and pair production [40]. However, pair production occurs when the energy of the incident photon exceeds 1.022 MeV. Since this study employed low-energy photons (60 – 100 keV), the potential interaction mechanisms should be photoelectric and Compton scattering. In the case of the photoelectric effect, all the energy of the incident photon is absorbed by an atomic electron, unlike Compton scattering, where the energy transferred to an electron depends on the scattering angle [41]. The linear attenuation coefficient (μ), a crucial factor in evaluating the absorption capacity of shielding materials, is influenced by several key variables. These include the atomic number of the shielding material, its physical density, and the energy of the incident X-ray photon. BaSO₄ is comprised of a high atomic number of Ba. So, the increase in BaSO₄ concentration was found to increase the linear attenuation coefficient, as shown in Figure 9. Each value of μ was calculated from the slope of the linear equation $\ln \frac{I_0}{I}$ and the thickness of the shielding (x). The results show that the increase of BaSO₄ causes a linear attenuation coefficient increase. This phenomenon occurs because there is an increased likelihood that X-ray photons will collide with electrons within the atoms of barium, which has a high atomic number, resulting in the photoelectric effect.

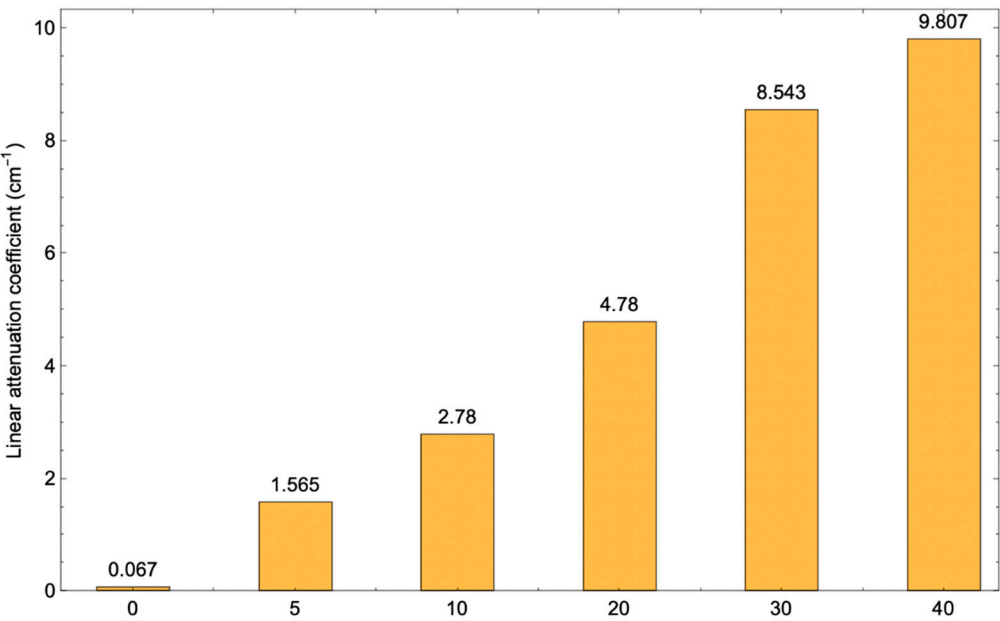


Figure 9. Relation between BaSO₄ concentration in PVDF-HFP composite film and linear attenuation coefficient (μ).

Considering the radiation absorption capability of this shielding material, it was found that as the linear attenuation coefficient increases, the radiation passing through the shielding decreases, as shown in Table 3. The percentage attenuation was calculated as the percentage of the difference between the intensity of the incident and the transmittance of X-ray photons. The results show that the performance of X-ray shielding material made of BaSO₄/P(VDF-HFP) depends on the concentration of BaSO₄ in the shielding sheet. Furthermore, the increase in shielding thickness can increase the efficiency of X-ray protection as well. The results found from this research show that the highest percentage of attenuation from X-ray source of 60 keV and 0.1 mA was 71/52 % at the BaSO₄ concentration of 40% and the thickness of 0.12 cm.

Table 3. Attenuation of X-ray photons due to the component of BaSO₄ in BaSO₄/P(VDF-HFP) composites.

Thickness (cm)	Attenuation (%)				
	5%BaSO ₄	10%BaSO ₄	20%BaSO ₄	30%BaSO ₄	40%BaSO ₄
0.02	1.48	4.95	10.99	19.48	22.71
0.04	4.92	8.96	19.05	36.65	39.81
0.06	7.65	14.65	26.11	47.27	49.77
0.08	10.47	19.26	31.68	54.54	58.49
0.1	13.87	24.02	39.32	61.39	65.64
0.12	15.50	27.41	44.95	66.25	71.52

The investigation of the percentage attenuation of the shielding at different concentrations of BaSO₄ in BaSO₄/P(VDF-HFP) shielding sheets by the high energy of X-ray photons is shown in Table 4. These results show that the ability of the shielding decreases while radiating with high energy. It is possible that the main part of X-ray photons was scattered and moved through the shielding. This phenomenon leads to a decrease in the linear attenuation coefficients of the shielding.

Table 4. Attenuation of X-ray photons due to the component of BaSO₄ in BaSO₄/P(VDF-HFP) composites at different X-ray energy photon.

X-ray energy (keV)	Attenuation (%) of the 0.2 mm thickness				
	5%BaSO ₄	10%BaSO ₄	20%BaSO ₄	30%BaSO ₄	40%BaSO ₄
60	1.48	4.95	10.99	19.48	22.71
80	2.28	2.12	7.33	10.96	13.95
100	0.04	1.20	3.74	6.29	7.89

4. Conclusions

Polymer composite shielding offers an alternative approach to mitigate the risk of X-ray radiation exposure. In this method, a selected polymer acts as a matrix, while a high atomic number particle serves as a filler to absorb the X-ray photons. BaSO₄/P(VDF-HFP) composite shielding sheets were produced with varying concentrations of BaSO₄. Post irradiation with X-ray photons, these sheets were analyzed to assess their photon absorption capacity, surface characteristics, and bulk properties. The results indicated that increasing the concentration of BaSO₄ in BaSO₄/P(VDF-HFP) enhances the linear attenuation coefficient of the shielding sheet when exposed to 60 keV and 0.1 mA X-ray generator. However, the linear attenuation coefficient decreases with higher X-ray generator power at 80 and 100 keV. Additionally, higher BaSO₄ concentrations led to rougher and more hydrophobic surfaces on the shielding sheets. Furthermore, tensile and thermal tests showed improvement in the shielding sheet's properties.

Data Availability Statement: The processed data required to reproduce these findings is available from the authors upon reasonable request.

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