JUSAN SCIENCE

Journal of Engineering and Environmental Systems

ISSN (Print): 3135-2510; ISSN (Online): 3135-2529

journal homepage: https://jusanscience.com/journals/jees

Research Article

Engineering Polyvinyl Alcohol-graft-poly(2-hydroxyethyl acrylate-co-ethyl acrylate) [PVA-g-poly(HEA-co-EA)] Films with Tunable Mechanical, Swelling, and Thermal Properties

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https://doi.org/10.66973/jees.26.007

Article info:

Received: 15 May 2026 / Revised: 03 June 2026 / Accepted: 05 June 2026 / Published: 09 June 2026

Rakhmetullayeva R., Nurgaziyeva E., Abutalip M. (2026). Engineering Polyvinyl Alcohol-graft-poly(2-hydroxyethyl acrylate-co-ethyl acrylate) [PVA-g-poly(HEA-co-EA)] Films with Tunable Mechanical, Swelling, and Thermal Properties. *Journal of Engineering and Environmental Systems*, 1, 80–97. https://doi.org/10.66973/jees.26.007

Abstract: In this study, novel polyvinyl alcohol-graft-poly(2-hydroxyethyl acrylate-co-ethyl acrylate) [PVA-g-poly(HEA-co-EA)] films were synthesized through free-radical graft copolymerization of 2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) onto polyvinyl alcohol (PVA) using ammonium persulfate (APS) as an initiator at 75 °C. The effects of thermal treatment and modification conditions on the solubility, swelling behavior, structural characteristics, and physicochemical properties of the resulting films were systematically investigated. The samples were thermally treated at 90 °C for 5–10 h, and their swelling behavior in various solvents was evaluated using the gravimetric method. FTIR spectroscopy confirmed the successful formation of the graft copolymer structure. The synthesized films exhibited pronounced swelling in aqueous media, indicating their potential for biomedical applications, particularly in wound dressing materials. Furthermore, the sorption and release behavior of a model therapeutic agent was studied to assess the drug delivery potential of the films. Kinetic analysis revealed that increasing the EA content enhanced both drug loading and release efficiency. The combination of favorable swelling characteristics, mechanical performance, and controlled drug-release capability demonstrates the potential of HEA-EAPVA graft copolymer films as promising multifunctional materials for biomedical and sustained drug delivery applications.

Keywords: PVA-g-poly(HEA-co-EA); polyvinyl alcohol graft copolymer; free-radical graft copolymerization; polymer films; swelling behavior; mechanical properties; controlled drug release; wound dressing materials.

https://doi.org/10.66973/jees.26.007

1 INTRODUCTION

The development of advanced polymeric biomaterials with tailored physicochemical and biological properties has become an important research direction in modern biomedical and pharmaceutical sciences [1], [2]. Among these materials, wound dressings capable of maintaining a moist healing environment, preventing microbial contamination, absorbing wound exudate, and providing controlled drug release have attracted considerable attention. An ideal wound dressing should combine high water absorption capacity, mechanical flexibility, biocompatibility, gas permeability, structural stability, and the ability to serve as a carrier for therapeutic agents [3], [4], [5]. Polyvinyl alcohol (PVA) is one of the most extensively investigated polymers for biomedical applications owing to its excellent biocompatibility, non-toxicity, hydrophilicity, film-forming ability, and chemical stability [6], [7], [8]. Furthermore, PVA exhibits favorable permeability to oxygen and water vapor, making it suitable for wound-healing and drug-delivery applications. Despite these advantages, conventional PVA films suffer from several limitations, including excessive water solubility, high swelling, limited mechanical durability, and poor dimensional stability under moist conditions [9], [10]. These shortcomings restrict their long-term performance in biomedical environments. To overcome these limitations, various chemical modification strategies have been explored, among which graft copolymerization has emerged as a particularly effective approach. Graft copolymerization enables the incorporation of functional monomer units into the polymer backbone, allowing precise control of mechanical, thermal, swelling, and sorption properties. Acrylic monomers are especially attractive for this purpose because of their versatile functionality and ability to form crosslinked polymer networks [11], [12].

Among acrylic monomers, 2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) offer complementary characteristics. HEA contains hydroxyl groups that enhance hydrophilicity, water uptake, and intermolecular hydrogen bonding, thereby improving biocompatibility and drug-loading capacity. In contrast, EA introduces flexible hydrophobic segments that increase elasticity, toughness, and structural integrity [11,12]. Consequently, the simultaneous incorporation of HEA and EA into a PVA matrix is expected to produce graft copolymer films with a balanced combination of swelling behavior, mechanical performance, and stability.

Previous studies have demonstrated the potential of PVA-based hydrogels and acrylic copolymers for wound dressing, tissue engineering, and controlled drug-release applications [13], [14], 15]. Li et al. reported the grafting of poly(2-hydroxyethyl acrylate) onto PVA, resulting in improved adhesion and film-forming properties due to enhanced intermolecular interactions [16]. Similarly, Kujawski and co-workers demonstrated that crosslinking PVA membranes with sulfosuccinic acid significantly improved water resistance and mechanical stability, although excessive crosslinking led to increased brittleness [17]. Despite these advances, the combined influence of HEA/EA composition and crosslinking treatment on the structure–property relationships of PVA-based graft copolymer films remains insufficiently understood.

Electron-beam irradiation represents an environmentally friendly and efficient crosslinking technique capable of producing three-dimensional polymer networks without the use of additional chemical crosslinkers [18], [19], [20]. Besides enhancing mechanical strength and thermal stability, radiation processing can simultaneously sterilize polymeric materials, making it particularly attractive for biomedical applications [21], [22].

In this study, novel PVA-based graft copolymer films were synthesized through free-radical copolymerization of HEA and EA in the presence of PVA, followed by thermal treatment and electron-beam-induced crosslinking. The effect of the HEA/EA ratio on the structural, morphological, thermal, mechanical, swelling, and drug sorption–desorption properties of the resulting films was systematically investigated. Particular attention was given to establishing composition–structure–property relationships and evaluating the suitability of the developed materials as wound dressing and prolonged drug-release systems. To the best of our knowledge, the combined effect of HEA/EA composition, thermal treatment, and electron-beam radiation crosslinking on PVA graft copolymer films intended for wound dressing and cefazolin release has not been systematically reported.

2 EXPERIMENTAL

2.1 Materials

2-Hydroxyethyl acrylate (HEA) ("Aldrich", USA) with a boiling point of 91°C at under 12 mmHg pressure and a refractive index of $n_D^{20} = 1.4500$ was purified by double vacuum distillation. The purity of the main product was 96%.
Ethyl acrylate (EA) ("Aldrich", USA), with a boiling point of 99°C and a density of 0.9405 g/cm^3, was purified by double vacuum distillation.
Polyvinyl alcohol (PVA) supplied by Fluka Chemie GmbH (Switzerland) with molecular weights of $M_w = 205{,}000$ and 72,000 was used without additional purification.
Ammonium persulfate (APS) obtained from Aldrich (USA), containing 99% active compound, was used without further purification. Distilled water was used for the preparation of all solutions.

2.2. Synthesis of Copolymer Films

Polyvinyl alcohol-graft-poly(2-hydroxyethyl acrylate-co-ethyl acrylate) [PVA-g-poly(HEA-co-EA)] copolymer films were synthesized by free-radical graft copolymerization of 2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) in the presence of polyvinyl alcohol (PVA), using ammonium persulfate (APS) as an initiator. PVA samples with molecular weights of 72,000 and 205,000 g·mol^{-1} and a degree of hydrolysis of 98–99% were used.

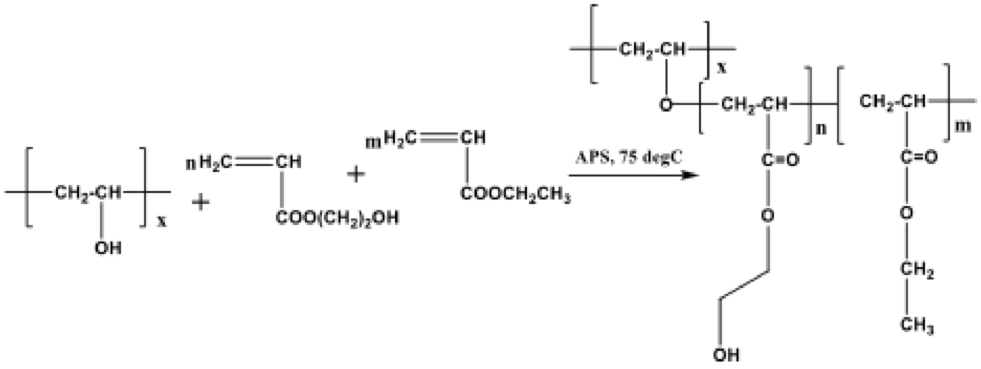
In a typical synthesis, 150 mL of distilled water was placed in a three-necked flask equipped with a reflux condenser, thermometer, and anchor stirrer. Then, 15 g of pre-weighed PVA was gradually added under continuous stirring, and the mixture was heated in a water bath at 70 °C until complete dissolution. After complete dissolution, 0.3 g of APS dissolved in a small amount of distilled water was added to the PVA solution as a radical initiator. Subsequently, the HEA/EA monomer mixture was introduced dropwise through a funnel. In all syntheses, the mass ratio of PVA to the total HEA/EA monomer mixture was kept constant at 1:1, with 15 g of PVA and 15 g of the HEA/EA monomer mixture used in each experiment. The HEA/EA mass ratios were 1.5/13.5 g, 7.5/7.5 g, and 13.5/1.5 g, corresponding to 10:90, 50:50, and 90:10 compositions, respectively. After monomer addition, the reaction mixture was maintained at 75 °C for 3.5 h under continuous stirring.

After completion of the reaction, the mixture was cooled to room temperature. Polymer films were prepared by casting the obtained copolymer solution onto polyethylene plates. The films were first dried in air until mass stabilization and then vacuum-dried at 30 °C until complete removal of residual solvent and constant weight. The thickness of the resulting films was approximately 100–150 μm.

Radiation crosslinking of the films was performed using an ELV-4 industrial electron beam accelerator (Russia). The electron beam current was 5 mA, the dose rate was 1.0 kGy·s^{-1}, and the absorbed dose was 30 kGy. All synthesis experiments were carried out in triplicate, and the reported values represent the average of three independent experiments. The obtained films were repeatedly washed and subsequently dried to remove residual unreacted monomers from the polymer matrix. Following irradiation, the films were immersed in distilled water for 24 h and then dried in air and in a vacuum drying oven at room temperature. The gel fraction % was calculated using the following equation:

$$\text{Gel fraction}(\%) = \frac{W_d}{W_o} \times 100$$

where W_d is the mass of the insoluble film (g), and W_o is the initial mass of the film (g).



Scheme 1. Schematic representation of the free-radical graft copolymerization of 2-hydroxyethyl acrylate and ethyl acrylate onto the polyvinyl alcohol backbone to form polyvinyl alcohol-graft-poly(2-hydroxyethyl acrylate-co-ethyl acrylate) [PVA-g-poly(HEA-co-EA)].

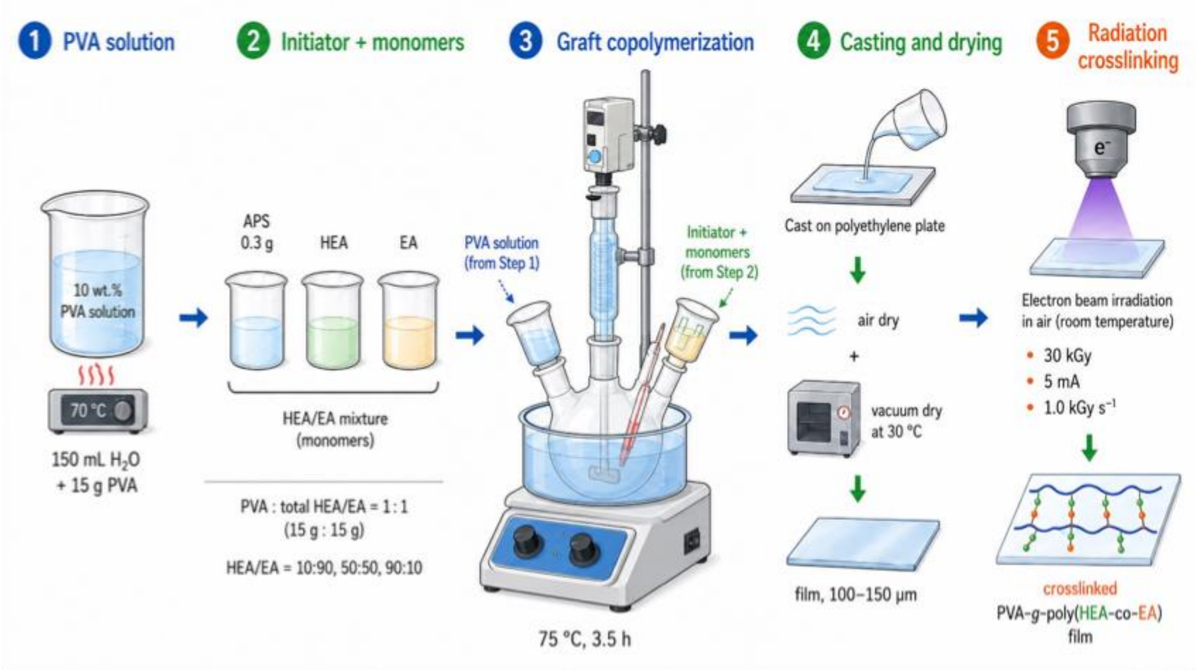


Figure 1. Schematic illustration of the synthesis, film formation, and radiation crosslinking of PVA-g-poly(HEA-co-EA) copolymer films.

Figure 1 shows the schematic workflow for the preparation of polyvinyl alcohol-graft-poly(2-hydroxyethyl acrylate-co-ethyl acrylate) [PVA-g-poly(HEA-co-EA)] copolymer films, including PVA solution preparation, monomer and initiator addition, graft copolymerization, film casting and drying, and electron-beam crosslinking. Scheme 1 illustrates the free-radical graft copolymerization of

2-hydroxyethyl acrylate and ethyl acrylate onto the polyvinyl alcohol backbone to form PVA-g-poly(HEA-co-EA).

2.3 Physicochemical Characterization Methods

To improve the mechanical properties of the synthesized films, thermal treatment was carried out by varying both the treatment temperature and duration over a wide range. The films were thermally treated at temperatures ranging from 90 to 140°C for periods of 1–10 h, and their swelling behavior in various solvents was investigated using the gravimetric method with an ISO 9001-certified analytical balance (Sartorius, Germany). Pre-weighed dry film samples (2 cm × 2 cm) were immersed in distilled water. At predetermined time intervals, the samples were removed, excess surface moisture was carefully blotted with filter paper, and the samples were reweighed.

The swelling degree (α) of the films was calculated using the following equation:

$$\alpha = \frac{W_s - W_d}{W_d} \times 100$$

W_s: Weight of the swollen polymer
W_d:Weight of the dry polymer

Thermal treatment of the films was carried out using a “ShS 80-01 SPU” thermostat (Russia). Initially, the solubility behavior of the untreated films in various solvents was evaluated.

The composition of the PVA-g-poly(HEA-co-EA) copolymers was characterized by ^{1}H-NMR spectroscopy in deuterated dimethyl sulfoxide (DMSO-d_6) using a “Jeol” JNM-ECO spectrometer (Japan).

FTIR spectra of the copolymers were recorded in the range of 4000–800 cm^{-1} using a “Perkin Elmer FTIR Spectrum Two” spectrophotometer (UK).

UV–Vis spectroscopy of the copolymers was performed using a “Specord 200 Plus” spectrophotometer (Analytik Jena, Germany).

Surface morphology and microstructural characteristics of the polymer films were investigated by scanning electron microscopy (SEM) using a MERLIN SEM Carl Zeiss SMT microscope (Germany).

The optical density of the polymer solutions was measured at a wavelength of 400 nm using a “Shimadzu UV/VIS-2401 PC” UV–Vis spectrophotometer (Japan).

Thermal stability of the films was analyzed under a dry nitrogen atmosphere using a “Perkin Elmer 1 TGA” thermogravimetric analyzer (Perkin Elmer Instruments, UK).

Differential scanning calorimetry (DSC) measurements were carried out under a dry nitrogen atmosphere using a “Perkin Elmer Diamond DSC” instrument (Perkin Elmer Instruments, UK).

The mechanical and deformation properties of the films were evaluated using a “Zwick Z010 Model Universal Testing Machine” (Germany) at a crosshead speed of 10 mm/min. Film thickness was measured using a digital Quantum Q-ACC-0010 caliper.

3 RESULTS AND DISCUSSION

The performance of polymeric wound dressing materials is closely related to the balance between hydrophilicity, mechanical integrity, and structural stability. In the developed PVA-g-poly(HEA-co-EA) system, these characteristics are controlled by the relative content of HEA and EA as well as by the extent of thermal and radiation-induced crosslinking. The graft copolymerization process resulted in the formation of a three-dimensional polymer network containing hydrophilic hydroxyl-rich domains originating from PVA and HEA, together with more flexible EA-containing segments. Such structural features are expected to significantly affect the swelling capacity, morphology, thermal stability, elasticity, and drug-release behavior of the films. Therefore, the obtained materials were systematically characterized using spectroscopic, microscopic, thermal, mechanical, and sorption analyses to elucidate the influence of composition on their physicochemical and biomedical properties.

Initially, the solubility of untreated films in various solvents was investigated (Table 1). The study revealed that the films exhibited complete swelling in aqueous media. As the HEA content increased, particularly at 90% HEA composition, the polymer films also swelled in ethanol and n-hexane, whereas films with HEA–EA ratios of 10:90 and 50:50 did not exhibit noticeable swelling in these solvents.

Table 1. Solubility of Polymer Films in Different Solvents

Solvents	HEA-EA mol. %					
	10:90		50:50		90:10	
	12 hours	24 hours	12 hours	24 hours	12 hours	24 hours
Water	swollen	swollen	swollen	swollen	highly swollen	highly swollen
Aceton	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
Tolune	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
Ethylacetate	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
Dimethylformamide	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
Ethanol	slightly swollen	slightly swollen	insoluble	insoluble	insoluble	insoluble
n-Hexane	swollen	swollen	slightly swollen	slightly swollen	insoluble	insoluble

The equilibrium swelling kinetics of films thermally treated at 90°C for 1 with HEA–EA molar ratios of 10:90, 50:50, and 90:10 in the initial monomer mixture were studied in water and ethanol (Figure 2). The results demonstrated that, as the HEA content in the initial monomer mixture decreased, the swelling degree of the films thermally treated for 1 h increased rapidly during the initial stages in water and subsequently reached equilibrium. This behavior indicates a relatively low degree of crosslinking in the obtained films.

For films containing 50% HEA:EA units, the swelling degree of samples thermally treated at 90°C for 1 h was 0.0346 in water and 0.0128 in ethanol. These values indicate lower swelling behavior compared to the previously discussed films.

According to literature data, copolymers containing a higher amount of ethyl acrylate exhibit enhanced elastic properties. Therefore, in this work, films containing 90% EA units in the initial monomer mixture were investigated with respect to their equilibrium swelling kinetics in water and ethanol after thermal crosslinking at 90°C for 1. As shown in the figures, films thermally treated for 1 h exhibited a swelling degree in water of (α= 0.0787) when the ethyl acrylate content in the copolymer reached 90%.

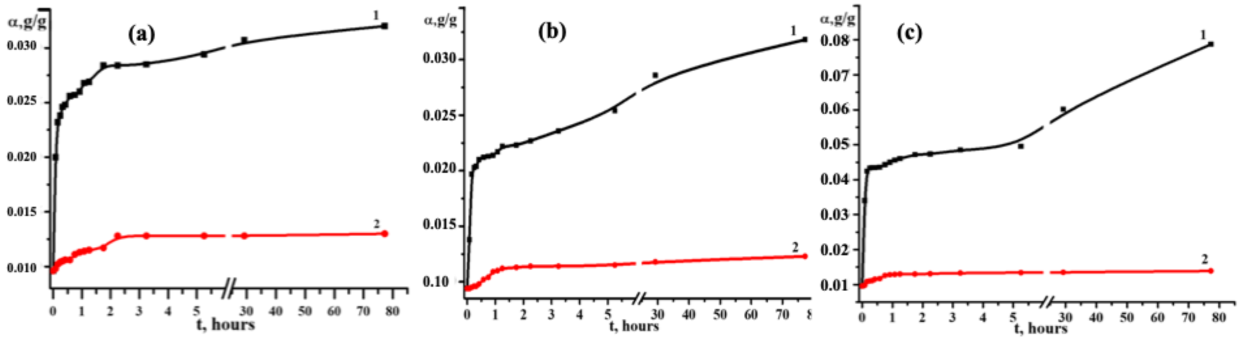


Figure 2. Swelling kinetics of PVA-g-poly(HEA-co-EA) -based films. Conditions: IMM: [HEA–EA] = 90:10 wt.% (a); [HEA–EA] = 50:50 wt.% (b); HEA–EA] = 10:90 wt.% (c); thermal treatment temperature = 90°C; thermal treatment time = 1h. in water (1) and ethanol (2).

The swelling degree of the films in ethanol was relatively low. This behavior can be attributed to the increased concentration of EA units within the copolymer structure, which enhance the elasticity and flexibility of the polymer network due to the plasticizing effect of EA. Similar observations have been reported for acrylic-based copolymer systems, where increased EA content improves segmental mobility and swelling behavior in aqueous media [23], [24].

Among the various polymer crosslinking techniques, radiation-induced crosslinking is considered one of the most efficient and widely utilized methods because it eliminates the need for additional chemical crosslinking agents while ensuring uniform treatment throughout the material. Furthermore, this technique enables precise control over crosslinking density and simultaneously sterilizes the polymeric films during irradiation, making it particularly attractive for biomedical applications.

In the present study, radiation crosslinking of PVA-g-poly(HEA-co-EA) composite films was performed using an ELV-4 industrial electron beam accelerator. Previous studies have demonstrated that irradiation of polymers such as polyvinyl alcohol, polyethylene oxide, poly(N-vinyl pyrrolidone), and polyvinyl ethyl ether induces hydrogen abstraction from CH_2 groups in the polymer backbone, followed by the generation of highly reactive radicals that promote intermolecular crosslinking [25], [26]. Therefore, it is reasonable to assume that crosslinking of the PVA-g-poly(HEA-co-EA) composite films under ionizing radiation proceeds through a similar free-radical mechanism. To evaluate the effectiveness of radiation crosslinking, the dependence of gel fraction yield on the absorbed radiation dose was investigated for copolymers with different monomer compositions (Figure 3). The results clearly demonstrated that increasing the EA content in the graft copolymer enhanced the yield of the crosslinked fraction, indicating improved network formation and structural stability of the polymer matrix.

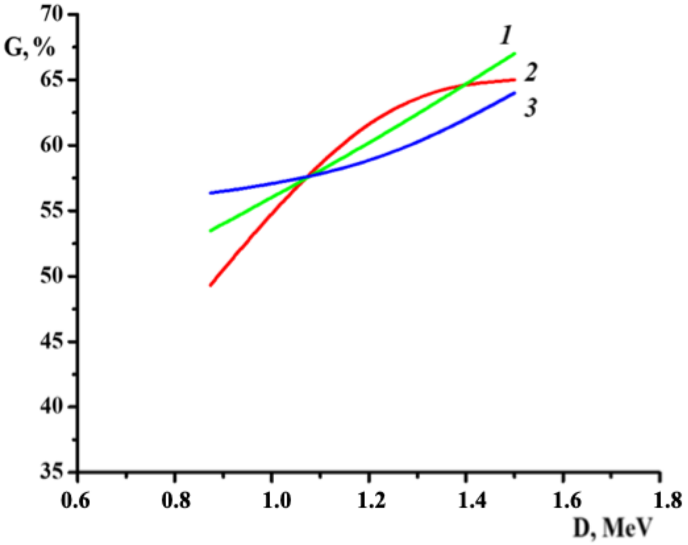


Figure 3. Dependence of the gel-fraction yield of [HEA–EA]/PVA films on the absorbed radiation dose. Conditions: IMM [HEA–EA] = 90:10 (1); 50:50 (2); 10:90 (3) mol.%.

Thus, the obtained results demonstrate that the PVA-g-poly(HEA-co-EA) based films are promising materials for practical applications, particularly as “depot” systems for the controlled release of various therapeutic agents in the treatment of burns and wounds.

3.3 Morphological and Structural Characterization of PVA-g-poly(HEA-co-EA) Composite Films

3.3.1 SEM Analysis of PVA-g-poly(HEA-co-EA) Composite Films

To evaluate the morphology of the polymer films, SEM micrographs were obtained. As shown in Figure 4, the (PVA-g-poly(HEA-co-EA) based films exhibited a porous structure. The high number of pores is associated with the solubility behavior of the films. SEM images also confirmed that the film surfaces were relatively rough and non-uniform, which contributed to the dissolution of the films prior to thermal treatment.

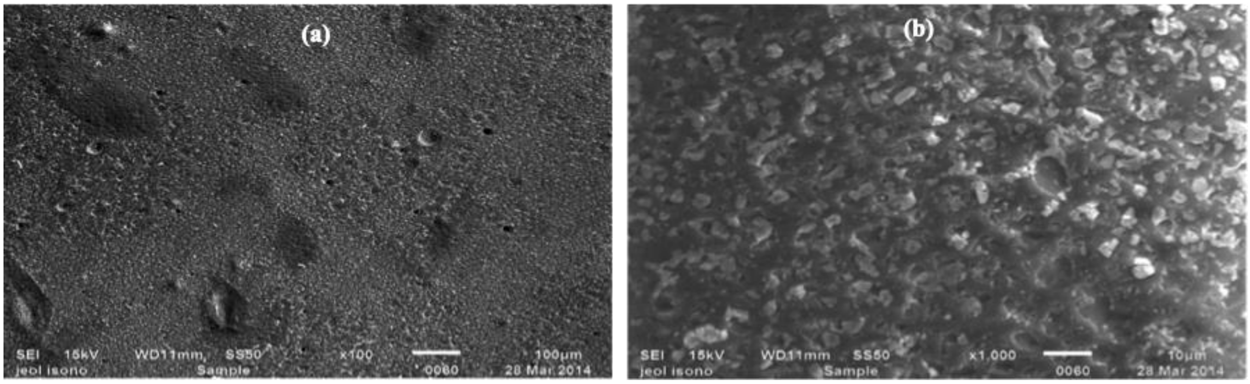


Figure 4. SEM morphology of PVA (a); PVA-g-poly(HEA-co-EA) composite film (b).

3.3.2 NMR Characterization of [HEA–EA]/PVA Composite Films

In this work, the synthesized water-soluble copolymers were characterized by both ^{1}H NMR

(Figure 5) and (^{13}C) NMR (Figure 6) spectroscopy. The spectra of the PVA-g-poly(HEA-co-EA) copolymers were recorded in deuterated dimethyl sulfoxide (DMSO-d6) using a "Jeol" JNM-ECO NMR spectrometer (Japan). The obtained spectra confirmed the successful incorporation of 2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) monomer units into the copolymer structure.

The observed chemical shifts corresponded well to the characteristic functional groups of the PVA-g-poly(HEA-co-EA) copolymers. The signal at 1.1 ppm was assigned to methyl (–CH_3) groups, while the signals at 1.3–1.8 ppm, 1.9–2.1 ppm, 4.1–4.3 ppm, and 6.0–6.2 ppm were attributed to methylene (–CH_2–) groups. Signals observed at 3.7–3.8 ppm and 5.7 ppm corresponded to CH groups, whereas the peak at 3.9 ppm was associated with hydroxyl groups. Overall, the spectral data presented in Figures 5 and 6 confirmed the structural formation of the PVA-g-poly(HEA-co-EA) based films.

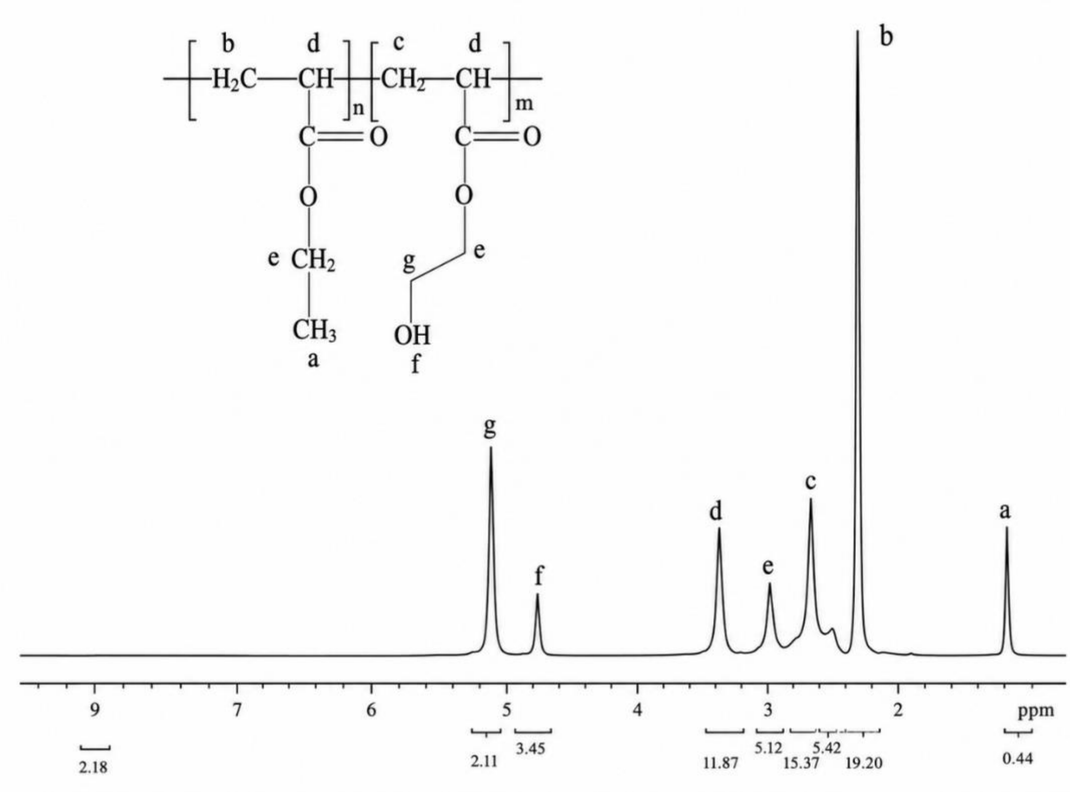


Figure 5. Determination of the structural formula of the HEA–EA copolymer by ^{1}H- NMR spectroscopy. Conditions: IMM [HEA–EA] = 90:10 mol.%; (^{1}H) NMR spectrum.

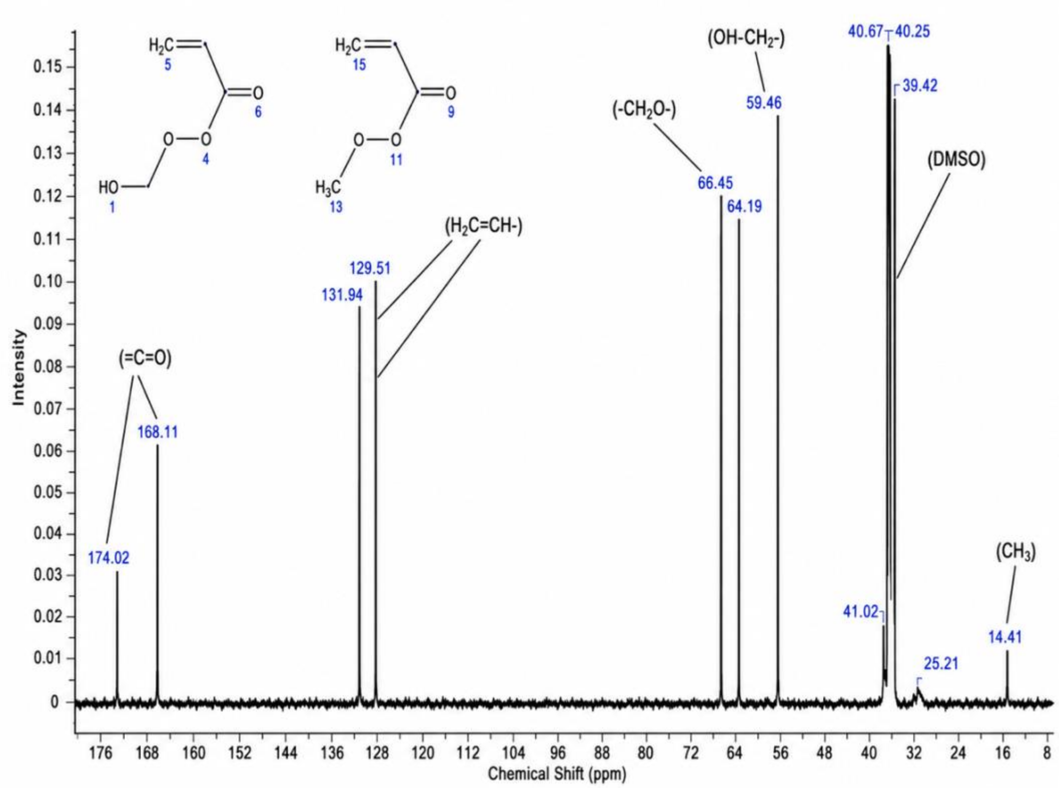


Figure 6. Determination of the structural formula of the HEA–EA copolymer by (^{13}C) NMR spectroscopy. Conditions: IMM [HEA–EA] = 90:10 mol.%; (^{13}C) NMR spectrum.

The ^{1}H NMR and ^{13}C NMR spectra provide important evidence for the formation of the HEA–EA copolymer structure. In the ^{1}H NMR spectrum, the signal at approximately 1.1–1.3 ppm is attributed to the methyl protons of the EA fragments, whereas the signals in the 2.0–2.8 ppm region correspond to the methylene and methine protons of the polymer backbone formed after radical polymerization. The resonances observed at 3.0–4.3 ppm are associated with oxygen-containing methylene groups, including $–OCH_2–$ and $–CH_2OH$ groups from HEA and EA units. The ^{13}C NMR spectrum further confirms the presence of acrylic ester fragments through characteristic carbonyl carbon signals at approximately 168–174 ppm. Signals in the regions of 14–25 ppm, 39–66 ppm, and 64–67 ppm are assigned to methyl, backbone/alkyl, and oxygen-containing methylene carbons, respectively. The combination of these signals confirms the successful incorporation of HEA and EA units into the polymer structure. Together with FTIR analysis, solubility tests, swelling behavior, and the formation of an insoluble network after thermal and radiation treatment, these results support the formation of a grafted PVA-g-poly(HEA-co-EA) polymer system rather than a simple physical blend.

3.3.3 FTIR Analysis of PVA-g-poly(HEA-co-EA) Composite Films

FTIR spectra of the copolymers were recorded in the range of 4000–800 cm using a “Perkin Elmer FTIR Spectrum Two” spectrophotometer (UK).

The obtained spectra demonstrated the appearance of characteristic absorption bands corresponding to alkyl and dialkyl groups in the newly synthesized films. Furthermore, it was observed that the intensity of these bands changed with increasing HEA unit content in the copolymer composition and after thermal treatment (Figure 7).

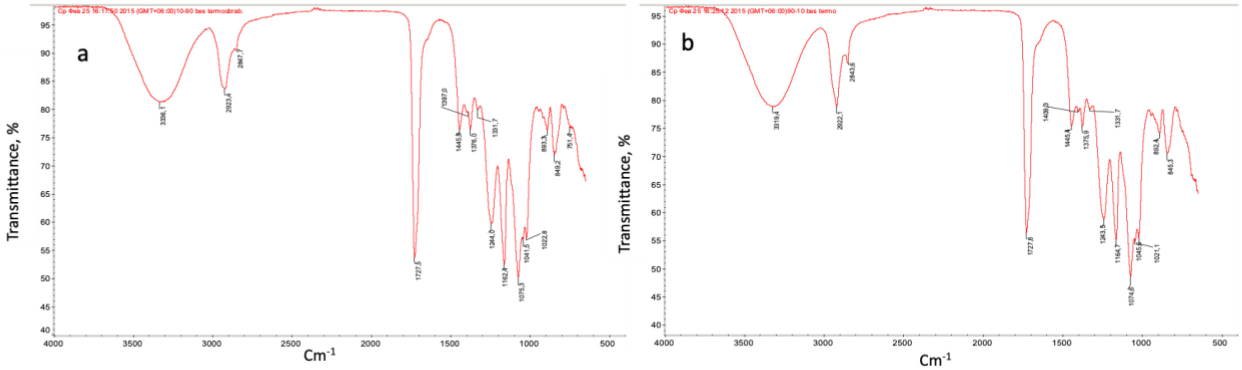


Figure 7. FTIR spectra of with thermally and without thermally treated PVA-g-poly(HEA-co-EA) based films. IMM [HEA–EA] = 10:90 mol.%; (a); [HEA–EA] = 90:10 mol.%; (b)

The broad absorption band observed in the region of 3200–3600 cm⁻¹ is attributed to O–H stretching vibrations originating from hydroxyl groups of PVA and HEA units. Following thermal treatment and radiation crosslinking, a slight broadening and decrease in intensity of this band were observed, suggesting the formation of stronger intermolecular hydrogen-bonding interactions within the polymer network. Similar behavior has been reported for crosslinked PVA-based hydrogels, where hydrogen bonding between hydroxyl and ester groups contributes to increased network stability and reduced chain mobility [27], [28].

The characteristic absorption band at approximately 1720–1730 cm⁻¹ corresponds to the stretching vibration of ester carbonyl (C=O) groups originating from HEA and EA units. The slight shift and broadening of this band after crosslinking indicate changes in the local environment of carbonyl groups due to hydrogen bonding interactions with neighboring hydroxyl groups. Such spectral changes have been widely reported for acrylic ester-containing polymer networks and are commonly associated with enhanced intermolecular interactions and improved compatibility between polymer components [29], [30].

Furthermore, the absorption bands located in the 1000–1300 cm⁻¹ region are assigned to C–O and C–O–C stretching vibrations of alcohol and ester groups. The persistence of these bands after thermal treatment and irradiation confirms the preservation of the graft copolymer structure. The absence of significant new absorption bands suggests that electron-beam treatment mainly promotes crosslink formation through radical recombination rather than introducing new functional groups, which is consistent with previous studies on radiation-crosslinked PVA and acrylic polymer systems.

3.4. Thermal Properties of PVA-g-poly(HEA-co-EA) Composite Films

The thermal behavior of the PVA-g-poly(HEA-co-EA) films was evaluated by simultaneous DSC and TGA analysis, as shown in Figure 8. All samples exhibited a multistage thermal degradation profile, indicating that the films contain several thermally distinguishable structural components. The first mass-loss stage was relatively small, ranging from 2.49 to 2.91%, and occurred at lower temperatures.

This stage can be attributed mainly to the evaporation of physically adsorbed and weakly bound water retained within the hydrophilic PVA/HEA-containing polymer matrix. The second mass-loss stage, ranging from 14.58 to 16.87%, was observed in the intermediate temperature region and is likely associated with the decomposition of thermally labile side groups, dehydration of PVA segments, and partial degradation of the grafted HEA/EA chains. The major degradation stage showed a mass loss of 29.46–34.46%, corresponding to the main decomposition of the polymer network, including cleavage of the grafted chains and degradation of the PVA backbone.

The DSC curves revealed several thermal events in the approximate ranges of 57–70 °C, 148–158 °C, 196–205 °C, 236–237 °C, and 363–372 °C. The low-temperature transitions may be related to moisture removal and relaxation of the polymer chains, whereas the events at higher temperatures are associated with structural rearrangement and progressive thermal degradation of the copolymer network. Comparison of samples (a) and (b), treated for 1 h but prepared with different HEA/EA ratios, shows that increasing the HEA content from 10 to 90 mol.% slightly changes the DSC transition positions and decreases the major mass-loss value from 33.25% to 29.46%. This suggests that the HEA-rich composition may promote stronger intermolecular interactions, most likely through hydrogen bonding between HEA and PVA hydroxyl groups.

For the HEA/EA = 90:10 composition, increasing the thermal treatment time from 1 h to 5 h and 10 h caused only moderate changes in the degradation behavior. The main mass-loss values were 29.46%, 34.46%, and 33.89% for 1, 5, and 10 h treatment, respectively, while the high-temperature DSC event shifted from 362.7 °C to 367.4 °C and 371.6 °C. This gradual shift indicates a moderate improvement in network stability with longer thermal treatment, possibly due to additional structural rearrangement and increased crosslinking density. However, the overall degradation pattern remained similar for all samples, showing that thermal treatment did not fundamentally change the degradation mechanism.

It can be stated that, the DSC and TGA results demonstrate that the synthesized [HEA–EA]/PVA films possess satisfactory thermal stability. The relatively small mass loss below 200 °C indicates that the films are stable under normal biomedical and processing conditions, while the main degradation occurs only at considerably higher temperatures. The results also show that both HEA/EA composition and thermal treatment time can moderately influence the thermal response of the films, mainly by affecting intermolecular interactions and network stability.

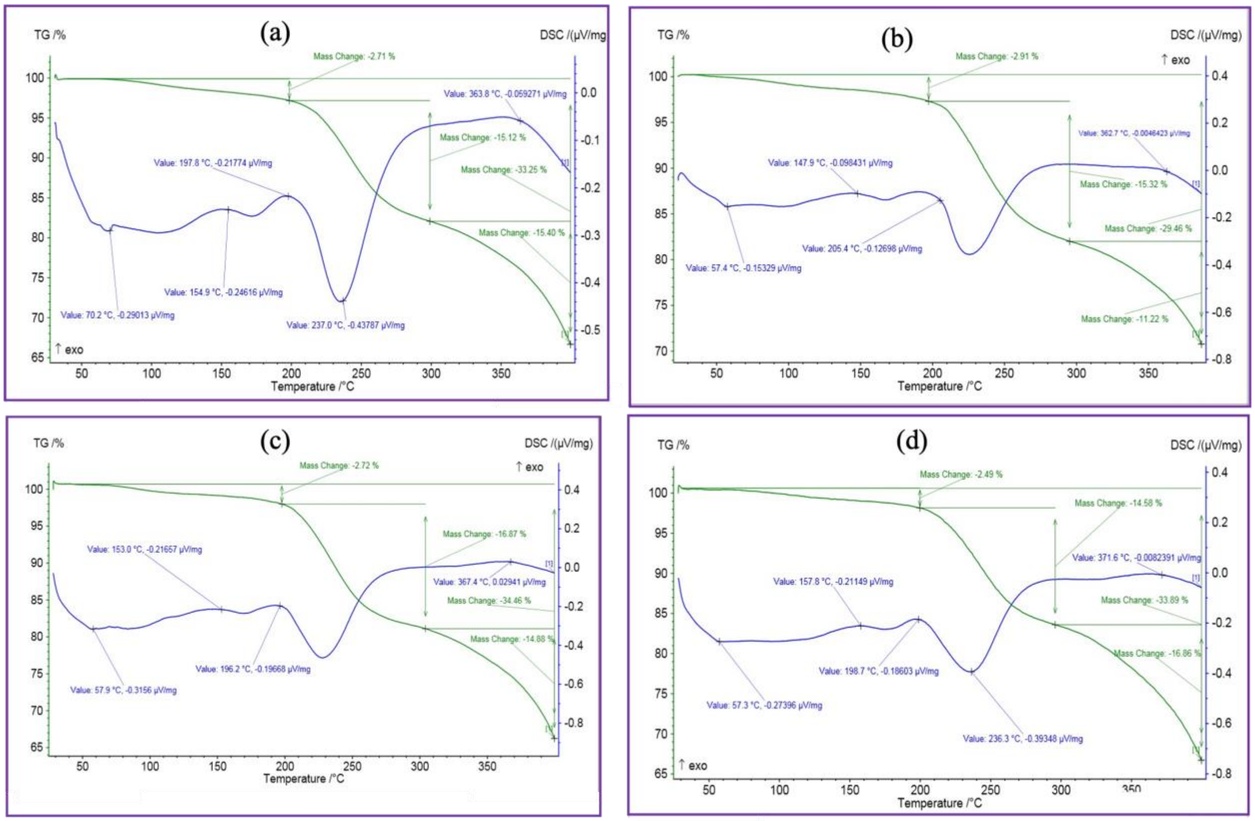


Figure 8. DSC and TGA thermograms of PVA-g-poly(HEA-co-EA) films prepared under different monomer compositions and thermal treatment conditions: (a) HEA/EA = 10:90 mol.% after 1 h thermal treatment; (b) HEA/EA = 90:10 mol.% after 1 h thermal treatment; (c) HEA/EA = 90:10 mol.% after 5 h thermal treatment; and (d) HEA/EA = 90:10 mol.% after 10 h thermal treatment.

3.5 UV–Vis Spectroscopic Analysis and Drug Sorption–Desorption Behavior

The ability of the synthesized films to absorb and release pharmaceutical compounds was evaluated to assess their potential application as wound dressing materials.

The sorption and desorption behavior of the drug-loaded films was investigated by ultraviolet (UV) spectroscopy using a Specord 200 Plus spectrophotometer (Analytik Jena, Germany) (Figure 9). Cefazolin was selected as a model therapeutic agent.

Analysis of the kinetic profiles revealed that films with a higher ethyl acrylate content exhibited improved drug sorption and release performance. These results indicate that the developed modified PVA-based films have strong potential as wound dressing materials and controlled drug-delivery platforms for the treatment of burn wounds.

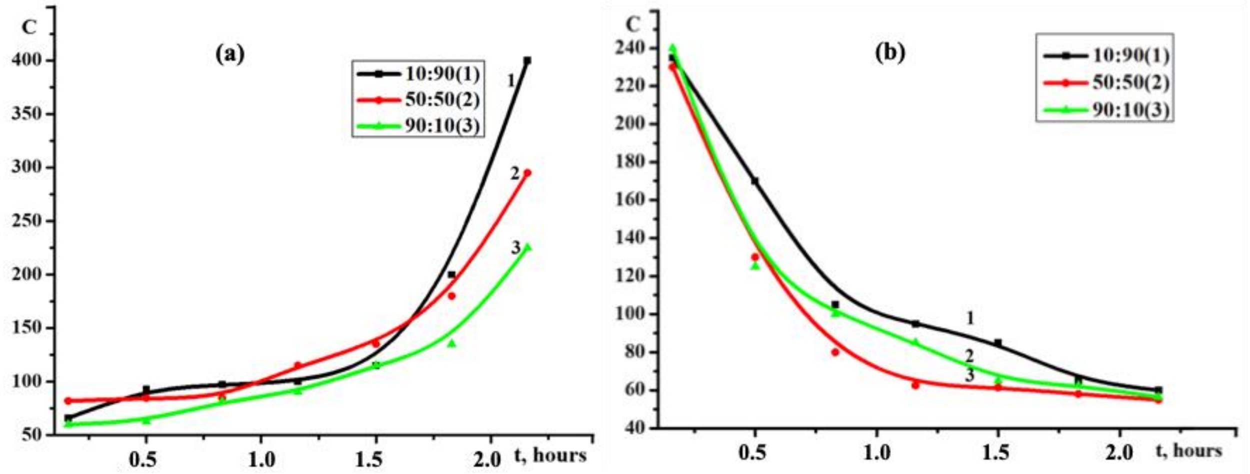


Figure 9. Sorption (a) and desorbtion (b) kinetics of cefazolin in PVA-g-poly(HEA-co-EA) films.

3.6 Mechanical Properties of PVA-g-poly(HEA-co-EA) Composite Films

The mechanical performance of the synthesized films was evaluated using a "Zwick Z010 Model Universal Testing Machine" (Germany) at a crosshead speed of 10 mm/min. Mechanical characterization of polymeric biomaterials is critically important for assessing their suitability in biomedical applications, particularly for wound dressing and flexible film systems, where elasticity, tensile strength, and deformation resistance play key roles in material performance [31].

As illustrated in table 2, the PVA-g-poly(HEA-co-EA) films exhibited excellent mechanical strength combined with high elasticity. Under elevated applied stress, the graft copolymer films demonstrated elongation values reaching approximately 400%, highlighting their remarkable flexibility and deformation resistance. Increasing the EA content in the initial monomer mixture significantly improved the elastic properties of the films, which can be attributed to the plasticizing effect of EA segments within the copolymer matrix. Similar effects have been reported in acrylic-based copolymer systems, where flexible acrylate units enhance chain mobility and reduce intermolecular rigidity [32].

For films with an initial monomer composition of HEA:EA = 10:90, the samples irradiated under Program I (30 kGy) initially exhibited behavior characteristic of semicrystalline polymers, showing minimal deformation up to an applied stress of approximately 1.5 MPa. However, with increasing applied stress, the films displayed highly elastic deformation behavior typical of amorphous polymeric networks. The samples underwent progressive elongation and fractured at approximately 4 MPa with a maximum elongation of nearly 400%.

Films irradiated under Program II (60 kGy) exhibited similar deformation behavior; however, fracture occurred at approximately 2.5 MPa with an elongation of about 250%. In contrast, films irradiated under Program III (90 kGy) withstood significantly higher stress levels due to the formation of a more densely crosslinked polymer network, which restricted chain mobility and reduced elongation. Under these conditions, the maximum elongation of approximately 300% was achieved only at stresses close to 9 MPa. The tensile strength varied from approximately 2.4 to 9.5 MPa depending on the HEA/EA ratio and treatment program. All samples exhibited relatively high elongation at break (230–420%), indicating good flexibility and ductility. The films containing higher amounts of EA generally showed enhanced elasticity due to the plasticizing effect of ethyl acrylate units, whereas increasing the HEA content contributed to higher structural rigidity through hydrogen-bonding interactions. Overall, the combination of moderate tensile strength and high elongation demonstrates that the synthesized HEA–EA/PVA films possess mechanical characteristics favorable for flexible polymer film applications.

Table 2. Tensile strength, elongation at break, and Young's modulus of PVA-g-poly(HEA-co-EA) graft copolymer films.

HEA:EA ratio	**Sample**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Young's modulus (MPa)***
10:90	I	~3.7	~400	~0.005
10:90	II	~2.4	~280	~0.003
10:90	III	~9.5	~280	~0.012
50:50	I	~3.8	~420	~0.003
50:50	II	~5.2	~420	~0.001
50:50	III	~5.5	~270	~0.006
90:10	II	~4.5	~230	~0.002
90:10	III	~3.6	~370	~0.003

CONCLUSION

In this study, PVA-g-poly(HEA-co-EA) graft copolymer films were successfully synthesized through graft copolymerization followed by thermal and radiation-induced crosslinking. FTIR and NMR analyses confirmed the successful incorporation of HEA and EA into the PVA network, while SEM observations revealed porous morphologies favorable for fluid uptake and drug loading.

The physicochemical properties of the films were strongly influenced by the HEA/EA ratio and crosslinking conditions. Increasing EA content enhanced film flexibility and elasticity, with elongation at break reaching approximately 400%, whereas thermal and radiation crosslinking improved structural stability and reduced excessive swelling. Thermal analyses demonstrated good thermal stability and tunable glass transition behavior, with increased monomer content promoting greater polymer chain mobility.

Drug sorption–desorption experiments using cefazolin demonstrated efficient drug loading and sustained release capabilities, particularly for films with higher EA content. The combination of high elasticity, controlled swelling, thermal stability, porous structure, and prolonged drug-release performance highlights the potential of PVA-g-poly(HEA-co-EA) films as multifunctional polymeric materials for controlled drug delivery and related biomedical applications. The combination of high elasticity, favorable swelling behavior, porous morphology, thermal stability, and drug-release capability makes these materials promising candidates for functional polymeric systems and controlled drug delivery applications. However, further biological evaluations, including cytotoxicity, biocompatibility, and antibacterial studies, are required before their suitability for biomedical applications can be confirmed.

Funding

This research received no external funding.

Author Contributions

E.N.: Methodology, Software, Writing; R.K.: Supervision, Writing, Original Draft; M.A.: Supervision, Conceptualization, Writing – Review & Editing.

Ethics Approval and Consent to Participate

This study did not involve human participants or animals. Therefore, ethical approval and informed consent were not required.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

AI Use Disclosure

No AI tools were used to generate scientific results, data, figures, or interpretations. All analyses, conclusions, and scientific content were developed by the authors.

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