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Effect of Polyvinyl Alcohol (PVA) Molecular Weight on the Characteristics of Radiation Synthesized p(AAc/PVA/PEO) Hydrogel Membranes

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ABSTRACT

This study investigates the effect of polyvinyl alcohol (PVA) molecular weight (M.wt) on swelling behavior, X-ray diffraction (XRD) characteristics, thermal stability, and surface morphology of p(AAc/PVA/PEO) hydrogel membranes. The p(AAc/PVA/PEO) hydrogel membranes were prepared using the gamma irradiation crosslinking method. The high-energy gamma rays induced crosslinking reactions within the solution, resulting in the formation of a three-dimensional network structure, or hydrogel, through the formation of chemical bonds between the polymer chains. The swelling behavior of the obtained hydrogel was evaluated at different pH values (3, 5, 7, and 9) and temperatures (20°C and 37.5°C). As the PVA molecular weight increases from 33k to 125k, the swelling degree of the hydrogel membranes also increases. For example, at pH 3 and 10 minutes, the swelling degrees for PVA M.wt 33k, 90k, and 125k are 49 %, 68 %, and 96 %, respectively. Similar trends are observed at pH 5, pH 7 and pH 9. XRD analysis reveals that the degree of crystallinity in the hydrogel membranes increases with increasing PVA molecular weight. Thermal stability analysis demonstrates that higher molecular weight PVA imparts better thermal stability to the hydrogel membranes. These findings contribute to the understanding and design of hydrogel-based materials for various applications in fields such as drug delivery, tissue engineering, and biomaterial development.

Keywords: Gamma irradiation, PVA M.wt , hydrogel membranes and pH.

1. Introduction

Polyvinyl Alcohol (PVA) hydrogels have gained significant attention in various fields, including biomedical engineering, drug delivery, and tissue engineering, due to their excellent biocompatibility, hydrophilicity, and tunable properties (Ghobashy and Mohamed, 2018). One important parameter that influences the properties of PVA hydrogels is the molecular weight of the PVA polymer (Timofejeva *et al.,* 2017). PVA with different molecular weights can exhibit variations in chain length, degree of crystallinity, and mechanical strength, affecting the hydrogel membranes' swelling behavior, thermal stability, and structural characteristics (Zakrzewska *et al.,* 2023). Understanding the relationship between PVA molecular weight and the physiochemical properties of the hydrogel membranes is crucial for tailoring their characteristics to specific applications (Stan *et al.,* 2023). Polyethylene oxide (PEO) and poly (acrylic acid) (pAAc) are two commonly used polymers in the field of hydrogel synthesis and biomaterial development. Each polymer possesses unique properties that make them suitable for different applications.

Polyethylene oxide (PEO) stands out as a water-soluble polymer highly prized in the biomedical realm for its remarkable biocompatibility, low toxicity, and water-attracting characteristics. With an innate resistance to protein adsorption and non-immunogenicity, PEO ensures minimal interference with biological systems. Its unique ability to form hydrogels, owing to a strong affinity for water, makes it an ideal candidate for applications like drug delivery systems, wound healing dressings, and tissue engineering scaffolds. The flexibility of PEO contributes to favorable mechanical properties, while its

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controlled release capabilities in hydrogel form further solidify its role in creating optimal biomedical environments. PEO's versatility positions it as a key player in the development of advanced materials for controlled drug release and regenerative medicine applications (Mustafai *et al.,* 2023) . The key distinction between Polyethylene oxide (PEO) and poly(ethylene glycol) (PEG) lies in their terminal hydroxyl (OH) groups. Poly(ethylene glycol) (PEG) is characterized by having a terminal hydroxyl group at each end of its molecular chain. In contrast, Polyethylene oxide (PEO) exhibits a more diverse range of end groups, which may include hydroxyl, methyl, or other functional groups. This difference in terminal groups contributes to variations in their chemical properties and behavior in different applications. PEG's uniform terminal hydroxyl groups often result in more predictable interactions, making it particularly suitable for certain biomedical and pharmaceutical applications where consistent behavior is essential. On the other hand, PEO's flexibility in end groups allows for tailored modifications, expanding its utility in various industrial and research settings (Dormidontova, 2004) . The influence of the end groups on the phase behavior and properties of PEO in aqueous solutions is minor, similar to infinitely long PEO.

Poly(acrylic acid) (pAAc) is a synthetic polymer derived from acrylic acid monomers. It is known for its pH-responsive behavior, as the carboxylic acid groups present in pAAc can be ionized and form polyelectrolyte complexes (Ghobashy and Mohamed, 2018) . pAAc hydrogels can exhibit swelling and deswelling behavior in response to changes in pH, making them attractive for applications such as drug delivery, biosensors, and smart materials. The pH-responsive properties of pAAc allow for controlled release of drugs or bioactive molecules in response to the acidic or basic environment of targeted tissues or physiological conditions (Ghobashy and Khafaga, 2017) .

Radiation synthesis has emerged as a promising technique for fabricating PVA-based hydrogels. Gamma irradiation crosslinking is widely used to induce crosslinking and stabilize the hydrogel structure. It offers advantages such as rapid and homogeneous crosslinking, scalability, and the ability to control the crosslinking density by adjusting the radiation dose. The radiation technique is a useful method for crosslinked hydrogel (Ghobashy *et al.,* 2021b; Ghobashy *et al.,* 2020b) to be used as a template (Ghobashy *et al.,* 2021a) , semi-permeable membrane (Alshangiti *et al.,* 2019) , and blend polymer (Ghobashy *et al.,* 2017a) hydrogel aims to use as green renewable resources of to protect the environment from negative effects (Madani *et al.,* 2022; Younis *et al.,* 2020; Akram *et al.,* 2016).

This study aims to investigate the effect of PVA molecular weight on the physicochemical properties of p(AAc/PVA/PEO) hydrogel membranes synthesized through gamma irradiation. The swelling behavior of the hydrogels at different pH values and temperatures, providing insights into their responsiveness to environmental conditions, has been evaluated. X-ray diffraction (XRD) analysis is performed to examine the crystallinity of the hydrogel membranes and its correlation with PVA molecular weight. Thermal stability analysis and scanning electron microscopy (SEM) imaging are conducted to assess the stability and surface morphology of the hydrogels, respectively. Furthermore, investigating PVA molecular weight's influence on the physicochemical properties of radiation-synthesized p(AAc/PVA/PEO) hydrogel membranes holds significant importance for several reasons. Firstly, the swelling behavior of hydrogels is a critical parameter that determines their functionality in various applications. Understanding how PVA molecular weight affects the swelling degree at different pH values and temperatures provides valuable insights into the responsiveness and environmental adaptability of the hydrogel membranes. This knowledge enables the developing of hydrogel systems that can efficiently encapsulate and release bioactive molecules, respond to specific physiological conditions, and promote tissue regeneration. The physicochemical properties of PVA hydrogels can be modified by incorporating additional components such as poly(acrylic acid) (pAAc) and poly(ethylene oxide) (PEO), leading to the formation of p(AAc/PVA/PEO) hydrogel membranes. These hydrogels offer versatile platforms for the controlled release of drugs, scaffolds for tissue regeneration, and other biomedical applications. This study aims to contribute to the existing knowledge by investigating the influence of PVA molecular weight on the physicochemical properties of radiation-synthesized p(AAc/PVA/PEO) hydrogel membranes. By examining the swelling behavior, X-ray diffraction (XRD) characteristics, thermal stability, and surface morphology, we can understand how varying PVA molecular weights impact the performance and functionality of the hydrogel membranes.

The outcomes of this study will enhance our understanding of the influence of PVA molecular weight on the properties of radiation-synthesized p(AAc/PVA/PEO) hydrogel membranes. This knowledge can guide the design and optimization of hydrogel-based materials for applications in drug

delivery systems, tissue engineering constructs, and other biomedical fields. Furthermore, the findings contribute to the broader understanding of the relationship between polymer molecular weight and hydrogel performance, facilitating the development of advanced biomaterials with tailored properties and functionalities.

2. Experimental

2.1 Materials

The purchase of Polyvinyl alcohol (PVA) with different molecular weights, Polyethylene oxide (PEO) with a molecular weight of 600,000 g/mol, and acrylic acid monomer from Sigma-Aldrich Chemicals Ltd. Polyvinyl alcohol (PVA) is a synthetic polymer derived from vinyl acetate. It is soluble in water and has excellent film-forming properties. The molecular weight of PVA can vary, and in your case, you have mentioned three different molecular weights: 33,000 g/mol, 90,000 g/mol, and 125,000 g/mol. The molecular weight of PVA affects its properties, such as its solubility, mechanical strength, and viscosity. Polyethylene oxide (PEO), or polyethylene glycol (PEG), is another synthetic polymer with high molecular weight. It is often used as a thickening agent, binder, or lubricant in various industries. PEO with a molecular weight of 600,000 g/mol is a relatively high molecular weight grade, and it possesses different characteristics compared to lower molecular weight variants of PEO. Acrylic acid is a monomer that produces polymers such as polyacrylic acid or poly (methyl acrylate). It is commonly used to manufacture adhesives, coatings, and superabsorbent polymers. The acrylic acid monomer can undergo polymerization to form long-chain polymers with various properties, depending on the specific reaction conditions and other factors. These chemicals were used as received, indicating they were used without further modification or treatment.

2.2. Radiation synthesis of acrylic acid hydrogel-based PVA/PEO Hydrogels

The hydrogel membranes were prepared using a combination of Polyvinyl alcohol (PVA), Polyethylene oxide (PEO), and acrylic acid (AAc) as follows. PVA with different molecular weights (33,000 g/mol, 90,000 g/mol, and 125,000 g/mol) was separately dissolved in distilled water at 80°C for 3 hours. This process allows the PVA to dissolve and form a solution. The concentration of PVA used in the solution was 10% weight. PEO with a molecular weight of 600,000 g/mol was dissolved in distilled water at 40°C for 24 hours. The concentration of PEO used in the solution was 5% weight. The PVA and PEO solutions were combined in a ratio of 70/30 weight percent. This means that 70% of the total weight of the blend solution comes from PVA, while 30% comes from PEO. The mixture was stirred to ensure homogeneity. Acrylic acid (AAc) dissolved in distilled water was added to the PVA/PEO blend solution. The AAc/polymer blend weight ratio was 30% w/w, which means that the weight of AAc was 30% of the total weight of the PVA/PEO blend.

The mixture solution containing PVA, PEO, and AAc was stirred at 80°C for 8 hours. This step ensures thoroughly mixing the components and allows for complete dissolution. After stirring, the solution was irradiated with a single irradiation gamma dose of 30 kGy using a Co^{60} gamma source. Irradiation is a common method to induce crosslinking in polymer materials, enhancing their mechanical properties and stability. The obtained solution after irradiation was poured into glass tubes. Then, a solvent casting technique was employed to obtain polymer membranes. Solvent casting involves evaporating the solvent (water) from the solution to form solid films or membranes. The thickness of the obtained films was measured using a digital micrometer. The films had an approximate thickness of 0.5 mm.

2.2 pH-responsive swelling studies

The swelling kinetics of the investigated hydrogel were studied by immersing dried specimens in buffer solutions with varying pH (3, 5, 7, and 9) at both room temperature (20°C) and human body temperature (37°C). The following steps were followed to determine the swelling ratio. The hydrogel specimens were dried and their initial dry weight (Wd) was measured. The dried specimens were immersed in buffer solutions of different pH values and at the desired temperature. The immersion time varied, ranging from zero to the equilibrium swelling time of 24 hours. After the specified immersion time, the specimens were removed from the buffer solutions, and the weight of the swollen samples (Ws) was determined. This weight represents the weight of the hydrogel after it has absorbed the buffer solution and swelled. The swelling ratio (SR) was calculated using the following equation:

$$SR\% = \frac{W_S - W_d}{W_d} \times 100$$

Where: SR is the swelling ratio, Ws is the weight of the swollen sample, and Wd is the initial dry weight of the specimen. Three measurements were performed for each sample at each pH and temperature condition. The average value of these three measurements was calculated to obtain a representative swelling ratio for each sample.

2.3. Characterization

The characterization techniques provide valuable information about the prepared samples' structural, optical, thermal, and crystallographic properties. They help understand the materials' chemical composition, physical behavior, and potential applications. FTIR spectroscopy was performed using an IRAfinity- Shimadzu instrument. The samples were analyzed in absorbance mode, and the measurements were conducted in the wavelength range from 400 cm-1 to 3500 cm-1. FTIR spectroscopy provides information about the functional groups in the samples and can be used to identify specific chemical bonds or molecular structures. The optical properties of the samples were analyzed using a Shimadzu UV-2600 spectrophotometer. The UV-Vis measurements were conducted in the wavelength range from 200 nm to 900 nm. UV-Vis spectroscopy allows the determination of the absorption characteristics of the samples in the ultraviolet and visible regions of the electromagnetic spectrum. TGA analysis was conducted using a Thermogravimetric Analyzer (TGA-50, Shimadzu). The samples were analyzed under a nitrogen atmosphere from ambient temperature up to 600°C.

The flow rate of nitrogen gas was 50 mL/min, and the heating rate was 20°C/min. TGA analysis measures a sample's weight loss or gains as a function of temperature, providing information about its thermal stability and decomposition behavior. XRD patterns were recorded using a Shimadzu XRD-6000 X-ray diffraction spectrometer. The instrument utilized a copper target (λ = 1.542 Å) operating at 40 kV and 30 mA. The XRD pattern was recorded at a scanning rate of 40/min in the angular range (2θ) of 8 ~ 500. The specific operating conditions included a divergence slit of 10°, scatter slit of 10°, receiving slit of 0.3 mm, and a sample pitch of 0.120. XRD analysis provides information about the samples' crystallographic structure, phase composition, and crystallinity.

3. Results and Discussion

3.1. Fourier transform infrared (FTIR) analysis of p(AAc/PVA/PEO)

Figure 1 provides the Fourier Transform Infrared (FTIR) analysis of p(AAc/PVA/PEO) samples and the interpretation of the corresponding FTIR spectra. Figure 1a shows the characteristic FTIR peak of pure PVA. The FTIR peak located at 2801 cm^{-1} is corresponding to C-H stretching bond. The broad peak at 3255 cm^{-1} corresponds to hydroxyl groups (-OH). The two FTIR peaks at 970 cm-1 and 854 cm-1 correspond to the rocking vibration of -CH_2. The FTIR peak located at 1150 cm^{-1} indicates the presence of polyvinyl acetate (PVAc) instead of PVA. This suggests that the PVA used in the analysis still contains residual vinyl acetate units that have not undergone complete hydrolysis to convert into polyvinyl alcohol (PVA). Polyvinyl alcohol (PVA) is obtained by the hydrolysis of polyvinyl acetate (PVAc), where the acetate groups are converted to hydroxyl groups. The presence of the (C-O) stretching band at 1150 cm-1 and 1099 cm^{-1} attributed to the stretching vibration of the C-O-C in the FTIR spectrum indicates the persistence of some unhydrolyzed PVAc units in the PVA sample. Figure 1b shows the characteristic FTIR peaks of pure PEO at 1078 cm^{-1} and 1193 cm^{-1} attributed to the ether groups. Figure 1c shows the FTIR spectrum of p(AAc/PVA/PEO). It is clear that the -OH peak of PVA at 3255 cm^{-1} was shifted to 3327 cm^{-1}. This shift indicates the formation of intermolecular and intramolecular hydrogen bonds between PVA/PEO and AAc in the obtained hydrogel. The new peak at 1734 cm^{-1} is attributed to the -COOH group of acrylic acid. It suggests the compatibility of AAc with the PVA/PEO molecules and the formation of a network through hydrogen bonding. Based on the observed FTIR spectra, the results indicate specific functional groups and the formation of hydrogen bonds between the polymer components in the p(AAc/PVA/PEO) system. These findings suggest the successful polymerization of AAc onto the PVA/PEO molecules, forming a network structure. The FTIR analysis provides valuable insights into the chemical interactions and structural changes in the polymer blend due to radiation-induced polymerization.

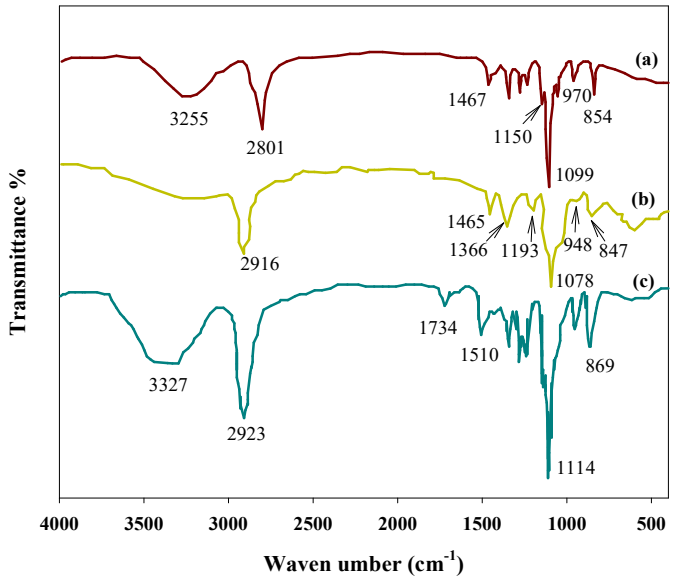


Fig. 1: Show the FTIR of (a) PVA (b) PEO (c) and p(AAc/PVA/PEO)

3.2. The Influence of pH, PVA (M.Wt) and temperature on the Swelling degree (%) of p(AAc/PVA/PEO) Hydrogel Membrane

In Figure 2 (a-d), the effect of pH (3, 5, 7, and 9) and PVA molecular weight (Mw = 33, 90, and 125 k) on the swelling degree of the p(AAc/PVA/PEO) hydrogel membrane is demonstrated. The hydrogel samples, prepared with different PVA molecular weights, were subjected to swelling in buffer solutions at various pH levels and room temperature (37.5 °C). The results indicate that the degree of swelling increases with an increase in PVA molecular weight for all samples tested at different pH values. This suggests that the molecular weight of PVA plays a significant role in determining the swelling behavior of the hydrogel membrane. Figure 2 shows the swelling degree of the p(AAc/PVA/PEO) hydrogel membrane at pH (3, 5, 7, and 9) and PVA molecular weight (Mw = 33, 90, and 125 k). At pH 3, the swelling degree generally increases with increasing PVA molecular weight. For example, at a time of 10 min. the swelling degrees for M.wt 33k, 90k, and 125k are 49.7662, 68.7743, and 96.5068, respectively. At pH 5 and pH 7, the swelling degree shows a similar trend. The hydrogel membrane with higher PVA molecular weight exhibits a higher swelling degree. For instance, at pH 5 and 1.5 hours, the swelling degrees for M.wt 33k, 90k, and 125k are 215%, 539 %, and 552%, respectively. At pH 9, the swelling degree is generally higher than at lower pH values. The hydrogel membrane with the highest PVA molecular weight (M.wt 125k) shows the highest swelling degree. For example, at pH 9 and 2 hours, the swelling degrees for M.wt 33k, 90k, and 125k are 736%, 938 %, and 1030%, respectively. This can be observed by comparing the swelling degrees at different pH values for each PVA molecular weight. For instance, at 1 hour, the swelling degrees at pH 3, 5, 7, and 9 for M.wt 125k are 309%, 484%, 555%, and 680%, respectively. This indicates that the hydrogel membrane exhibits the highest swelling at pH 9 and the lowest swelling at pH 3. The effect of PVA molecular weight: The swelling degree of the hydrogel membrane increases with increasing PVA molecular weight. This can be observed by comparing the swelling degrees at different PVA molecular weights for each pH value. For example, at pH 7 and 0.5 hours, the swelling degrees for M.wt 33k, 90k, and 125k are 201.2288%, 343.4747%, and 401.8122%, respectively. This suggests that the hydrogel membrane containing PVA with a higher molecular weight exhibits a higher swelling degree.

The swelling degree of the hydrogel membrane increases with time for all pH and PVA molecular weight conditions. This is evident by comparing the swelling degrees for each pH and PVA molecular weight at different time points. For example, at pH 5 and M.wt 90k, the swelling degrees increase from 301 % at 20 min. to 1142% at 8 hours and further to 1201 at 10 hours. This indicates that the hydrogel continues to absorb water and swell over time. The swelling degree is influenced by both pH and PVA

molecular weight. At each time, the swelling degree generally increases with higher PVA molecular weight and higher pH. For instance, at 1 hour, the swelling degrees at pH 7 for M.wt 33k, 90k, and 125k are 156.8567%, 276.3915%, and 310.8995%, respectively. This trend suggests that higher molecular weight PVA chains and more alkaline pH conditions promote greater water uptake and swelling of the hydrogel membrane.

From Table 1, we can observe the following comparisons: Effect of PVA Molecular Weight: At pH 3, as the PVA molecular weight increases from 33k to 125k, the swelling degree of the hydrogel membrane also increases (49.8 < 68.8 < 96.5). At pH 5, the difference in PVA molecular weight minimizes swelling (150, 155, 160 %). At pH 7 and 9, the higher the PVA molecular weight, the greater the swelling degree (e.g., 33k < 90k < 125k). Effect of pH: For each PVA molecular weight, the swelling degree generally increases as the pH increases. At PVA M.wt 33k, the swelling degrees at pH 3, 5, 7, and 9 are 49.8, 150, 156.9, and 123.6, respectively. Similarly, at PVA M.wt 90k and 125k, the swelling degrees follow the same trend, indicating that higher pH values lead to increased swelling. These comparisons highlight the combined influence of PVA molecular weight and pH on the swelling behavior of p(AAc/PVA/PEO) hydrogel membranes. The data shows higher PVA molecular weight and alkaline pH conditions generally promote greater swelling.

Table 1: Summarizes the swelling degrees (%) of p(AAc/PVA/PEO) hydrogel membranes at different pH values and PVA molecular weights.

pH / PVA M.wt	33k	90k	125k
pH 3	49.8	68.8	96.5
pH 5	150	155	160
pH 7	156.9	276.4	310.9
pH 9	123.6	207	255.3

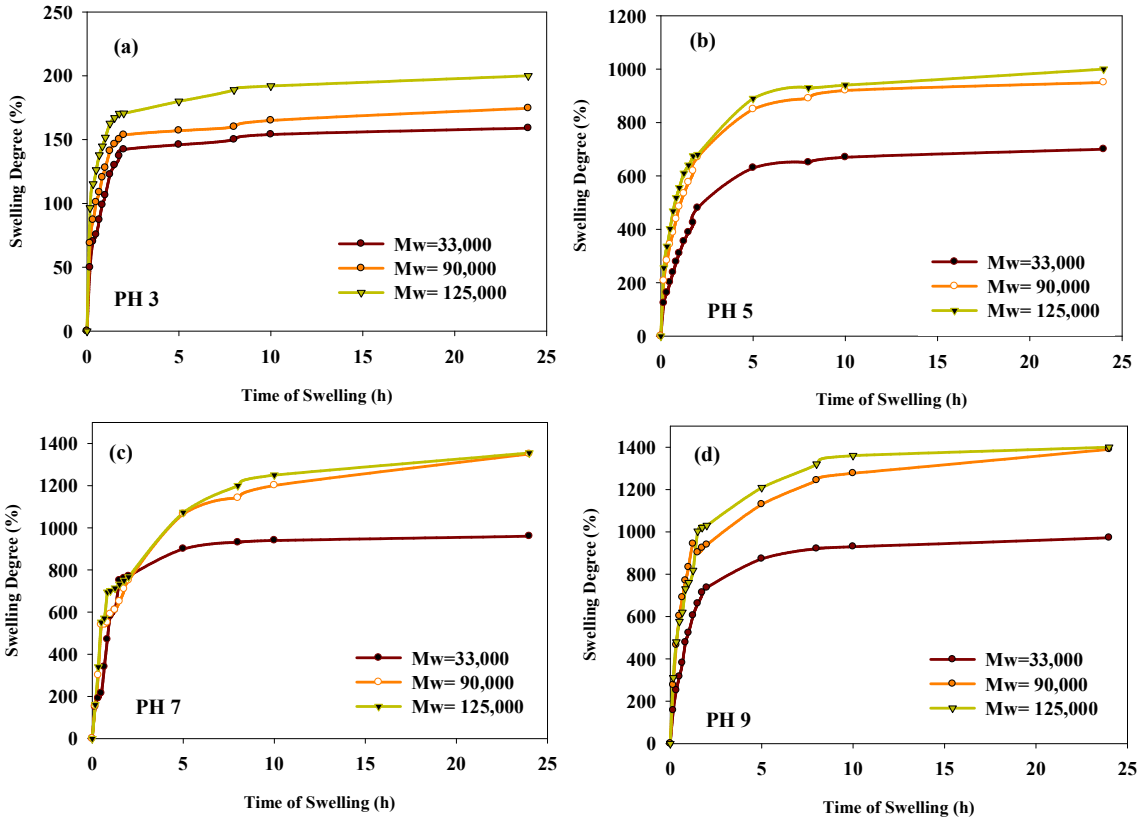
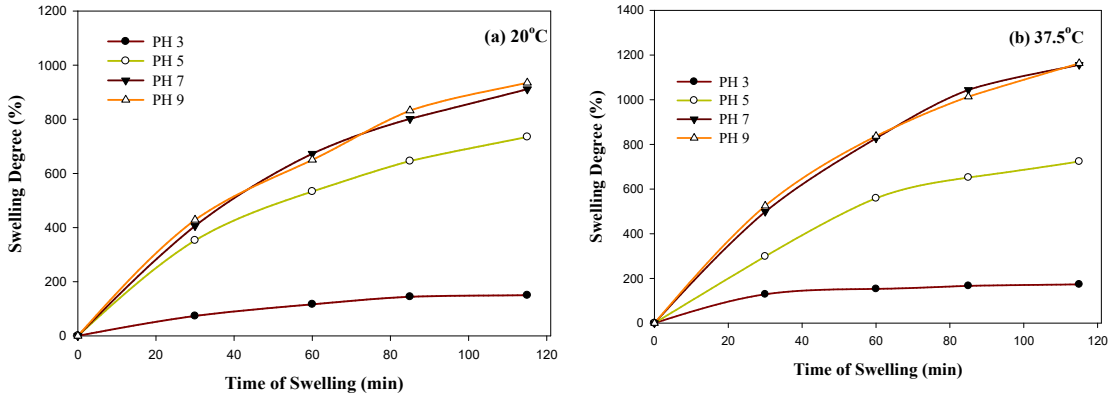


Fig. 2: Show the effect of pH and PVA m.wt in the swelling degree of p(AAc/PVA/PEO) hydrogel membrane.

The formation of a crosslinked network in p(AAc/PVA/PEO) hydrogel membranes is influenced by the adjacent side hydroxyl groups of PVA. As the molecular weight of PVA increases, the chain length between the cross-linking points also increases. This longer chain length provides more opportunities for hydrogen bond formation within the polymer network. The increased chances of hydrogen bond formation lead to an increase in the degree of crystallinity of the hydrogel samples. Crystallinity refers to the arrangement of polymer chains in an ordered and repetitive manner. With higher molecular weight PVA, the polymer chains have a greater tendency to arrange themselves in an ordered fashion, resulting in a higher degree of crystallinity. The higher degree of crystallinity affects the swelling behavior of the hydrogel. Crystalline regions in the hydrogel matrix have limited mobility and are less accessible to water molecules. However, the amorphous regions of the hydrogel, which have more disorderly and flexible polymer chains, have higher water absorption capacity. Therefore, as the degree of crystallinity increases with the increasing molecular weight of PVA, the hydrogel membrane has a higher propensity to absorb larger amounts of water. This is because the amorphous regions can accommodate and retain water molecules more effectively, while the crystalline regions provide structural integrity to the hydrogel network. It's important to note that the relationship between molecular weight, crystallinity, and water absorption can be complex and depend on various factors, such as the specific composition of the hydrogel, processing conditions, and environmental parameters. The above observations provide a general understanding of how molecular weight and crystallinity influence the water absorption behavior of p(AAc/PVA/PEO) hydrogel membranes.

In Figure 3a, which represents the time-dependent swelling behavior of the p(AAc/PVA/PEO) hydrogel at 20°C, it is observed that the maximum degree of swelling occurs at pH 7 and 9 compared to pH 3 and 5. This suggests the hydrogel exhibits enhanced water absorption and swelling capacity under neutral to slightly basic conditions. At low pH values (pH 3 and 5), the carboxylic acid groups (COOH) of pAAc tend to be more ionized, resulting in an increased concentration of negatively charged carboxylate ions (COO-) in the hydrogel. These carboxylate ions can form hydrogen bonds with the adjacent hydroxyl groups (OH) of PVA/PEO. The formation of hydrogen bonds between the carboxylate ions and hydroxyl groups promotes the interaction between the polymer chains, leading to a more compact and restricted network structure. This restricts the hydrogel's swelling ability and limits water uptake.

On the other hand, at pH 7 and 9, the environment becomes more alkaline, and the ionization of the carboxylic acid groups decreases. As a result, there are fewer carboxylate ions available for hydrogen bonding. This allows the hydrogel to have a more open and flexible network structure, facilitating the absorption and retention of a larger amount of water. The hydroxyl groups (OH) of PVA/PEO can also interact with the carbonyl groups (C=O) of pAAc through hydrogen bonding. These intermolecular interactions contribute to the swelling behavior of the hydrogel. Overall, the pH-dependent swelling behavior observed in Figure 3a suggests that the ionization of carboxylic acid groups and the formation of hydrogen bonds between different functional groups play a significant role in controlling the water absorption capacity of the p(AAc/PVA/PEO) hydrogel. Figure 3b, which represents the swelling behavior of the samples at 37.5°C, may provide additional insights into the effect of temperature on the swelling properties of the hydrogel. Figure 3b does not show any significant change in the swelling degree between 20°C and 37.5°C, it suggests that the temperature within this range does not have a pronounced effect on the swelling behavior of the p(AAc/PVA/PEO) hydrogel. The swelling properties of the hydrogel may remain relatively stable within this temperature range.



(a) **(b)**

Fig. 3: The swelling time dependent of p(AAc/PVA/PEO) hydrogel membrane at tow temperature (a) 20 °C and (b) 37.5 °C.

3.3. SEM analysis of p(AAc/PVA/PEO)

The SEM image depicted in Figure 4 reveals a smooth surface of the p(AAc/PVA/PEO) hydrogel membrane without any visible spots or pores. This observation suggests good miscibility and compatibility between polyacrylic acid (pAAc), polyvinyl alcohol (PVA), and polyethylene oxide (PEO) within the hydrogel matrix. The absence of distinct boundaries or phase separation indicates a homogeneous distribution of the polymer components, supporting the formation of a well-blended system. The smooth surface morphology also suggests that the hydrogel membrane possesses a uniform structure, which can be advantageous for various applications.

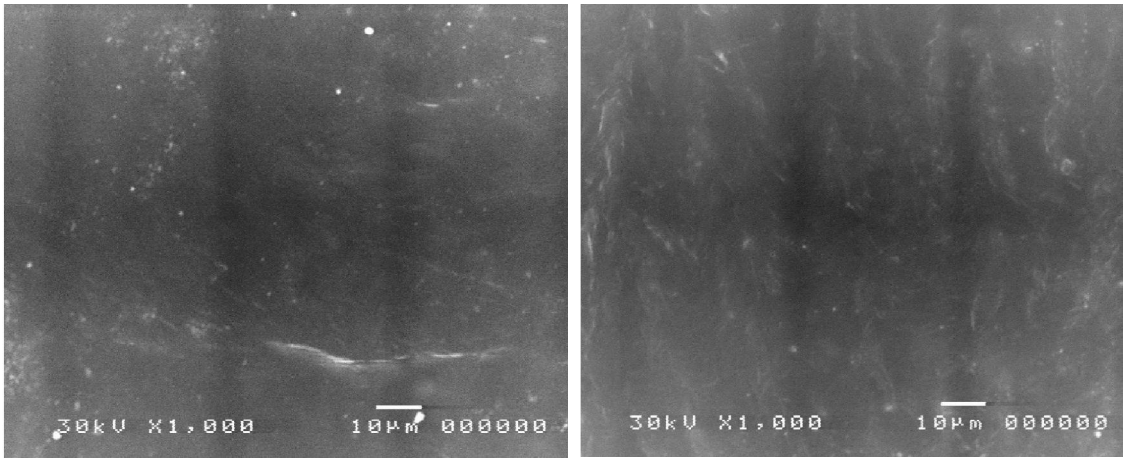


Fig. 4: The SEM image of p(AAc/PVA/PEO) hydrogel membrane

3.4. Thermogravimetric Analysis (TGA) of p(AAc/PVP/PEO)

Thermogravimetric analysis (TGA) is a valuable technique for studying thermal stability and decomposition behavior of polymeric materials. TGA involves subjecting the material to a controlled temperature ramp in an inert atmosphere, typically nitrogen, while continuously monitoring its weight change as a function of temperature. The weight loss observed during TGA can provide insights into various processes occurring within the material, such as the initial scission of crosslinked polymeric chains, degradation of chemical bonds, phase transitions, and the loss of volatile components like water. The TGA data can be obtained by analyzing important information about the material's thermal stability, decomposition temperature, and degradation kinetics. This can help understand the material's behavior under different temperature conditions, determine its thermal stability limits, and evaluate its suitability for specific applications. TGA is widely used in polymer science, materials characterization, and quality

control to assess polymeric materials' thermal properties and stability (Ghani *et al.,* 2022; Ghobashy, 2017b) .

Figure 5a presents the TGA curves of radiation crosslinked p(AAc/PVA/PEO) hydrogels with different molecular weights of PVA (33, 90, and 125 k). The TGA thermograms exhibit two distinct stages of thermal degradation. The first stage, occurring between 50 and 400 °C, is attributed to the degradation of the main polymer chains. During this stage, the polymeric chains decompose, breaking into smaller molecules. This process typically involves releasing volatile components, such as water and other small organic molecules. The weight loss observed in this stage reflects the extent of degradation and polymer mass loss. The second stage, between 400 and 600 °C, is primarily associated with decarboxylation. Here, the carboxyl groups in the acrylic acid moieties undergo thermal decomposition, releasing carbon dioxide (CO2) and water (H2O). This stage represents the further degradation of the polymer structure and the elimination of residual carboxyl groups.

By analyzing the TGA thermograms of the radiation crosslinked p(AAc/PVA/PEO) hydrogels with different molecular weights of PVA (33, 90, and 125 k), valuable information can be obtained regarding the thermal stability and decomposition behavior of the hydrogels. The presence of two distinct stages of degradation indicates that significant chemical changes occur within specific temperature ranges. These changes include main chain scission and decarboxylation processes. Understanding the thermal properties and stability of the hydrogel system based on the molecular weights of PVA is essential for optimizing its performance in various applications. The TGA analysis provides insights into the temperature ranges at which these chemical changes occur, allowing for the design and development of hydrogels with improved thermal stability and controlled decomposition behavior.

In the given Table 2, it can be observed that the hydrogel containing PVA with a lower molecular weight of 33,000 (M.wt =33,000) exhibits lower characteristic temperatures Ti and Tf compared to the hydrogels with higher molecular weights of PVA (Mw=90,000 and M.wt =125,000). This indicates that the hydrogel with lower M.wt PVA has lower thermal stability, as it starts to decompose at a lower temperature and completes decomposition at a lower temperature. On the other hand, the hydrogel with higher M.wt PVA shows higher T_i and T_f values, suggesting increased thermal stability. Therefore, the molecular weight of PVA significantly influences the thermal stability of the p(AAc/PVA/PEO) hydrogel, with higher molecular weights generally associated with higher thermal stability. The higher values of Ti (the characteristic temperature at the beginning of decomposition) generally indicate higher thermal stability for the material. The table shows that as the molecular weight of PVA increases from 33,000 to 125,000, the T_i values also increase from 232°C to 290°C. This indicates that the hydrogel with higher molecular weight PVA (Mw=125,000) exhibits higher thermal stability than the hydrogel with lower molecular weight PVA (Mw=33,000). Therefore, the trend in T_i values supports the statement that higher Ti values correspond to a higher thermally stable material. The weight loss (Δw %) between T_i and T_f was calculated and the average specific rate of decomposition (%/°C) was determined from the relation

$$v = \frac{\Delta w}{T_f - T_i}$$ and the results are summarized in Table (1).

The T10 values listed in Table 2 indicate the temperature at which 10% weight loss occurs for each sample. The table shows that as the molecular weight of PVA increases from 33,000 to 125,000, the T10 values also increase from 245°C to 309°C. This suggests that the hydrogel containing higher molecular weight PVA exhibits higher thermal stability than those with lower molecular weight PVA. The longer PVA chains in the higher molecular weight PVA contribute to enhanced thermal stability, providing more thermal degradation resistance. Therefore, the trend in T10 values supports the statement that higher molecular weight PVA leads to higher thermal stability in the hydrogel system.

The Horowitz-Metzger method is commonly used to determine the activation energy of thermal degradation by analyzing the thermogravimetric (TG) data. By applying this method to the TG curves obtained for all the samples, the activation energy (Ea) can be calculated. The activation energy provides valuable information about the energy barrier required for the degradation process. It is an important parameter for understanding the materials' thermal stability and degradation kinetics. By comparing the calculated activation energies for the different samples, insights can be gained into the effect of PVA molecular weight on the degradation behavior and stability of the hydrogel system.

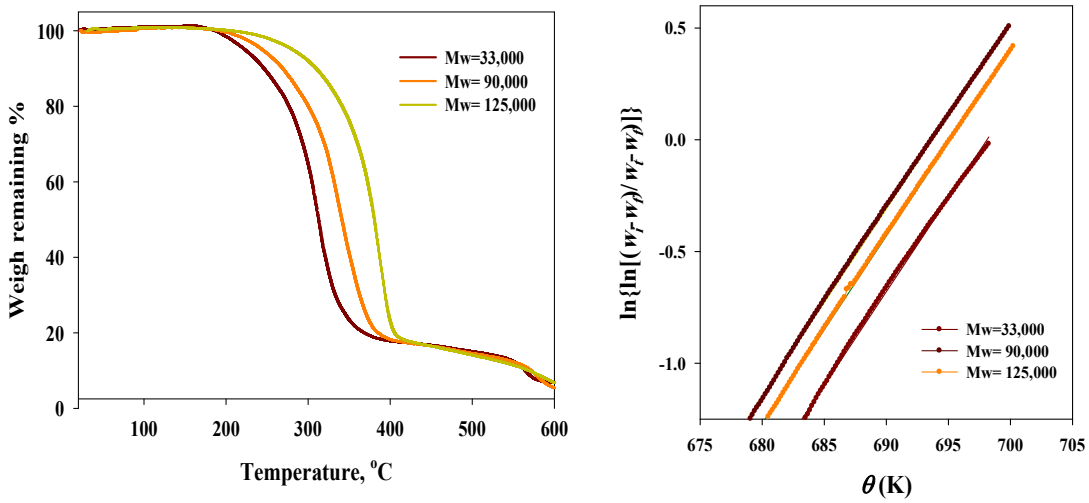
The Horowitz–Metzger (HM) relation used to evaluate the degradation kinetics is:

$$\ln[\ln(w_o - w_e)/(w_t - w_e)] = E_a \theta / RT_{\max}^2 \qquad (1)$$

where w_o is the initial weight of the sample, w_e is the final weight of the sample, w_t is the remaining weight of the sample at given temperature, T, E_a is the activation energy, $\theta = T - T_{max}$ and R is the gas constant (R= 8.314 $JK^{-1}mol^{-1}$). The plot of $\ln[\ln(w_o - w_e)/(w_t - w_e)]$ versus θ for all samples is presented in Figure 5b, which gives a straight line whose slope is equal to $E_a / RT_{\max}^2$.

E_a were calculated for all samples and presented in Table 2.

The obtained activation energy (Ea) values of 137.5 kJ/mol, 125.4 kJ/mol, and 121.6 kJ/mol for the samples with PVA molecular weights of 33,000, 90,000, and 125,000, respectively, indicate that the activation energy increases with increasing PVA molecular weight. This suggests that the hydrogel containing higher molecular weight PVA requires more energy to initiate the thermal degradation. The higher activation energy values indicate a stronger chemical bond structure and increased thermal stability in the hydrogel system. The trend of increasing activation energy with higher PVA molecular weight further confirms the correlation between PVA molecular weight and the thermal stability of the hydrogel.



(a) (b)

Fig. 5: The TGA thermogram and activation angry plot of p(AAc/PVA/PEO) hydrogel membrane.

Table 2: Temperature, weight loss characteristics and the energy of activation (E_a) of P(AAc/PVA/PEO) at different Mw of PVA.

	Temperature [°C]			Δw [%]	v [%/°C]	E_a [kJ mol^{-1}]
	T_i	T_f	T_{10}			
Mw=33.000	232	352	245	71.52	0.596	138.2
Mw=90.000	260	387	286	72.24	0.569	127.6
Mw=125.000	290	408	309	74.48	0.631	123.4

3.5. XRD analysis of p(AAc/PVA/PEO)

The XRD analysis of the p (AAc/PVA/PEO) blend in Figure 6 revealed distinct diffraction peaks corresponding to pure PVA, PEO, and polyacrylic acid (pAAc). The peaks characteristic of PVA appeared at 2θ = 14.09°, 15.63°, 19.50°, and 40.10° (Hong *et al.,* 2011; Todica *et al.,* 2014) (Ghobashy and Mohamed, 2018) , while PEO as known, exhibited peaks at 2θ = 18.9° and 23.79° (Gupta *et al.,*

2013) . However, in Figure 6, only the peak at 23.79° is visible, indicating that the other peak at 2θ = 18.9° may not be as prominent or have merged with other peaks in the blend. The visibility of specific peaks can vary depending on factors such as the concentration and arrangement of the components in the blend and the sensitivity and resolution of the XRD measurement. Also, the characteristic peak of polyacrylic acid is located at 2 θ ~ 22 ° , 17 ° and 35 ° (Swain and Prusty, 2018), (Ghobashy, 2017a ; Ghobashy and Khafaga, 2017) . In Figure 6, the XRD peak corresponding to polyacrylic acid (pAAc) is appears at 36.55°, which is slightly shifted from the typical position of 35°. This shift in peak position suggests that some changes or interactions may occur in the pAAc structure within the p(AAc/PVA/PEO) blend. Factors such as the presence of other components, molecular interactions, and the preparation process can influence the peak position in XRD analysis. The shift in peak position indicates a modification or deviation from the expected crystallographic arrangement of pAAc in the blend. In the XRD analysis of the p(AAc/PVA/PEO) blend, the distinct peaks corresponding to pure PEO at 2θ = 18.9° and pAAc at 17° and 22° appear to merge with the peaks of PVA and PEO. As a result, only a single diffraction peak is observed at around 2θ = 19.5° for PVA and 2θ = 23.79° for PEO in Figure 6. This merging of peaks suggests that there are interactions and structural modifications occurring between the components in the blend, leading to the formation of new crystallographic arrangements and the loss of individual peak characteristics for PEO and pAAc. Furthermore, the XRD analysis of the p(AAc/PVA/PEO) blend indicates the presence of new peaks at 2θ = 26.73° and 28.24°. These peaks suggest the formation of new crystal planes in the hydrogel membrane, resulting from the crosslinked interactions between PVA, PEO, and pAAc. The cross-linking process, likely induced by the gamma irradiation (Ghobashy *et al.,* 2020a) , leads to forming a network structure within the blend, resulting in these additional XRD peaks. These findings further support the strong intermolecular interactions and the formation of a crosslinked network in the p(AAc/PVA/PEO) hydrogel membrane. Based on the XRD analysis results presented in Figure 6, it can be concluded that polyacrylic acid (pAAc) exhibits strong interactions with both polyvinyl alcohol (PVA) and polyethylene oxide (PEO) in the p(AAc/PVA/PEO) blend. The merging of XRD peaks and the formation of new crystallographic arrangements indicate that pAAc interacts with PVA and PEO, potentially through hydrogen bonding or other intermolecular interactions. These interactions between the polymers contribute to the blend's overall structural properties and behavior, suggesting a strong crosslinked interaction between pAAc, PVA, and PEO in the hydrogel system. As well as the intensity of two crystalline peaks at 2θ = 19.5° and 2θ = 23.79° are increased with the molecular weight of PVA increased from (33, 90 and 125 k), this indicates that the increased of crosslinked density induced by gamma radiation.

Furthermore, it can be observed that the intensity of the two crystalline peaks at 2θ = 19.5° and 2θ = 23.79° increases with an increase in the molecular weight of PVA (33, 90, and 125 k). This indicates that the crosslinked density within the p(AAc/PVA/PEO) blend is enhanced with higher molecular weight PVA when subjected to gamma radiation. The increased crosslinked density is likely due to the higher number of crosslinking sites available in the higher molecular weight PVA, leading to a more densely interconnected network structure. The elevated crosslinked density can have implications for the mechanical and structural properties of the hydrogel membrane, potentially influencing its performance in various applications.

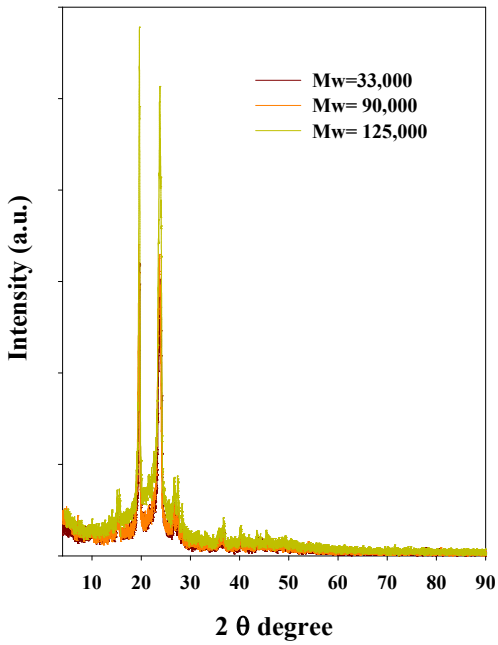


Fig. 6: The XRD pattern of p(AAc/PVA/PEO) hydrogel membrane.

4. Conclusion

The study investigated the swelling behavior of p(AAc/PVA/PEO) hydrogel membranes under different pH conditions and with varying PVA molecular weights. The results revealed several important findings:

1. Effect of pH: The hydrogel exhibited the highest swelling degree at pH 7 and 9 compared to pH 3 and 5. This suggests the hydrogel has enhanced water absorption and swelling capacity under neutral to slightly basic conditions. Carboxylic acid groups (COOH) ionization at low pH values increased, leading to more carboxylate ions (COO-) in the hydrogel. The formation of hydrogen bonds between these ions and adjacent hydroxyl groups (OH) of PVA/PEO restricted the swelling ability of the hydrogel. In contrast, at higher pH values, the reduced ionization allowed for a more open and flexible network structure, facilitating increased water uptake and retention.
2. Time-Dependent Swelling: The swelling degree of the hydrogel increased over time for all pH and PVA molecular weight conditions. This indicates that the hydrogel continued to absorb water and swell as time progressed.
3. Temperature Effects: The swelling behavior of the hydrogel did not show significant changes between 20°C and 37.5°C. This suggests that within this temperature range, the swelling properties of the hydrogel remained relatively stable.
4. Effect of PVA Molecular Weight:

4.1. Swelling Behavior: The results indicate that the swelling degree of the hydrogel increases with increasing PVA molecular weight. As the molecular weight of PVA increases, the chain length between cross-linking points also increases. This leads to more crystallinity and enhanced hydrogen bonding within the hydrogel network. The increased crystallinity and hydrogen bonding allow for greater hydrogel water absorption and swelling capacity. Consequently, hydrogel membranes containing higher molecular weight PVA exhibit higher swelling degrees.

4.2. Thermal Stability: The thermal stability of the hydrogel is influenced by the molecular weight of PVA. Higher molecular weight PVA chains form a more compact and well-organized network structure. This enhanced network structure provides better thermal stability to the hydrogel. As a result, hydrogel membranes with higher molecular weight PVA show improved thermal stability and a higher thermal degradation resistance.

4.3. XRD Characteristics: The XRD analysis provides insights into the crystalline structure of the hydrogel. The results indicate that the degree of crystallinity increases with increasing PVA

molecular weight. As the molecular weight of PVA increases, the chain length between cross-linking points increases, leading to a higher degree of crystallinity. This is attributed to the increased chances of hydrogen bond formation between PVA chains. The higher degree of crystallinity observed in hydrogels with higher molecular weight PVA suggests a more ordered and compact arrangement of polymer chains within the network structure.

Finally, the study demonstrates that PVA molecular weight plays a significant role in determining the swelling behavior, thermal stability, and XRD characteristics of the p(AAc/PVA/PEO) hydrogel. Higher molecular weight PVA leads to increased swelling, improved thermal stability, and enhanced crystallinity. These findings provide valuable insights for designing and optimizing hydrogel systems for various applications such as drug delivery, tissue engineering, and biomaterial development.

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