JTE
HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNICAL EDUCATION SCIENCE
Ho Chi Minh City University of Technology and Education
Website: https://jte.edu.vn
Email: jte@hcmute.edu.vn

Effect of Linear Polyacrylamide on the Properties of semi–IPN Hydrogels Based on N, N'–Dimethylacrylamide, and Maleic Acid

Thi Cam Phan Bui[1], **Nguyen Anh Tuan Huynh**[2*]
[1]*University of Science, Vietnam National University Ho Chi Minh City, Vietnam*
[2]*Ho Chi Minh City University of Technology and Education, Vietnam*

[*]Corresponding author. *Email: tuanhna@hcmute.edu.vn*

ARTICLE INFO

Received:	19/08/2023
Revised:	02/09/2023
Accepted:	07/09/2023
Published:	28/12/2023

KEYWORDS

Semi–IPN hydrogel;
Swelling behavior;
N, N'–Dimethylacrylamide;
Maleic acid;
Polyacrylamide.

ABSTRACT

In this work, the semi–interpenetrating polymer network hydrogels based on Polyacrylamide; N, N'–Dimethylacrylamide, and Maleic acid were synthesized and investigated by changing the content of linear polyacrylamide in the obtained materials. The chemical properties, morphology, swelling behaviors in distilled water, and mechanical properties of the hydrogels were investigated. Fourier transform infrared spectra confirmed the polymerization ability of monomers, scanning electronic microscopy images showed that the pore size could be controlled by the added volume of linear polyacrylamide was in the range of 252.8 ± 5.0 ~ 888.5 ± 3.5 µm. The swelling ratio and the mechanical properties of the hydrogels increased with increasing linear polyacrylamide content. All of the results in this work showed that semi–interpenetrating polymer network hydrogels based on Polyacrylamide; N, N'–Dimethylacrylamide, and Maleic acid had a high swelling ratio, good water retention, thermal properties, and mechanical properties. Potential applications of the obtained hydrogels are in progress.

Doi: https://doi.org/10.54644/jte.80.2023.1454

1. Introduction

Hydrogels are three-dimensional polymeric networks that can absorb and maintain a high content of water. The presence of networks enables hydrogels to swell in aqueous media without dissolving [1]. Hydrogels can be classified based on the type of networks (i.e., single, semi-interpenetrating, interpenetrating, double network, or mechanically interlocked) [2]. An interpenetrating polymer network (IPN) is a polymer comprising two or more networks that are at least partially interlaced on a molecular scale but not covalently bonded to each other, and cannot be separated unless chemical bonds are broken [3]. The semi–interpenetrating polymer network (semi–IPN) is a polymer comprising one or more networks and one or more linear or branched polymer(s) characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules [3]. Semi–IPN hydrogels are versatile materials with tunable properties, making them suitable for various applications. Their combined properties of hydrophilic, swelling capability, and mechanical strength make them potentially useful in areas such as biomedical engineering [4], drug delivery systems [5], tissue engineering [6], agriculture [7], and other fields where water-responsive materials with tailored mechanical properties are desired. In general, there are many factors affecting the properties of a semi-IPN hydrogel such as the nature of the monomers, the ratio of different monomers inside the copolymers, the cross-linker and the linear polymer content introduced in the network structure.

In general, hydrogels of N-substituted polyacrylamides refer to hydrogel materials that are composed of polyacrylamide polymers with N-substituted functional groups. Polyacrylamide is a polymer derived from acrylamide monomers, and the N-substituted polyacrylamides have additional substituents attached to the nitrogen atom in the acrylamide units. The N-substituted functional groups in polyacrylamides can vary and include a wide range of chemical moieties, such as methyl, ethyl, propyl, butyl, or other alkyl groups [8]. Hydrogels made from N-substituted polyacrylamides are typically formed through the process of polymerization, where the acrylamide monomers are cross-linked to form a three-dimensional network structure [9]. This crosslinking can be achieved through various methods, such as chemical crosslinking agents [10], [11] or physical crosslinking techniques like temperature or pH-induced gelation [12]. The presence of N-substituted groups in the polyacrylamide backbone can introduce specific properties to the hydrogel such as hydrogels of N-isopropyl-acrylamide exhibit a lower critical solution temperature (LCST) behavior, where they undergo a phase transition from a swollen state to a collapsed state above a certain temperature called the LCST [13]. Overall, hydrogels of N-substituted polyacrylamides offer a versatile platform for developing smart materials with tailored properties, making them valuable in various fields of research, and applications [14]–[17].

N, N'–Dimethylacrylamide (DMA) is a non-ionizing monomer, easy to polymerize, highly reactive, and the reaction initiation temperature is low, which is favorable for the copolymerization process [18]. DMA can also be used as a monomer in the synthesis of semi–IPN hydrogels. Semi–IPN hydrogel-based DMA combines the properties of both hydrogel networks and linear polymers, resulting in materials with unique properties. They can exhibit enhanced mechanical properties compared to traditional hydrogels, such as increased tensile strength, toughness, and elasticity, which makes them suitable for applications where mechanical properties are required highly [19].

Maleic acid (MA) is a multifunctional organic compound that has the unique properties of enhancing the hydrophilicity of the polymer network, improving compatibility, and forming hydrogen bonds to complement the network structure [20]. In addition, MA is cheap, saving input costs. Semi–IPN synthesis-based MA, MA is often mixed with a monomer or pre-polymer containing functional groups that are capable of reacting with –COOH. This mixture is then polymerized to form a polymer network. Then, a linear polymer was added to form a semi–IPN structure. Maleic acid can form covalent bonds with functional groups of monomers or pre-polymers, resulting in cross-linking networks that can increase tensile strength, toughness, and elasticity for semi–IPN materials [21].

Polyacrylamide (PAM) is a polyolefin, which can be viewed as polyethylene with amide substituents on alternating carbons [22]. Due to the presence of amide groups ($–CONH_2$), the carbon atoms interspersed in the framework are stereospecific, so PAM can exist in atactic, syndiotactic, and isotactic. Linear PAM is a water-soluble polymer [23]. Polyacrylamide can be copolymerized with other monomers, such as N, N'–Dimethylacrylamide, and Maleic acid to form hydrogels. The hydrogel composition can affect the overall properties of the material, such as water absorption, and mechanical strength. Hydrogel-based PAM possesses several attractive features. Firstly, they exhibit a high water absorption capacity, allowing them to swell, and retain large amounts of water without dissolving [24]. Secondly, the mechanical properties can be adjusted, from flexible to stiff, and elastic, depending on the degree of crosslinking, and molecular weight [25], [26].

As mentioned, semi–IPN hydrogel is a type of hydrogel that exhibits unique properties due to the presence of two distinct polymer networks in the same structure. The properties of semi–IPN hydrogels, such as mechanical properties, thermal properties, and swelling properties, can be influenced by various factors. One of the factors that can be mentioned is the linear polymer content introduced into the structure. In our previous publications, the effects of monomer nature and the ratio of different monomers have been studied [27]–[29]. However, in our understanding there has been no research on the impact of linear polymer PAM on the properties of semi–IPN hydrogel.

In this work, the impact of linear PAM on the properties of semi–IPN hydrogel based on DMA, MA and Methylenebisacrylamide (MBA) will be studied. The chemical structures, morphology, mechanical properties, and glass transition temperature (T_g) were investigated. Finally, the swelling behaviors of hydrogels were investigated in pure water by weighing method. The change in properties of semi–IPN hydrogel is explained based on the effect of linear PAM. These results will contribute useful information about the main factors affecting the properties of the obtained semi–IPN hydrogel.

2. Materials and Methods

2.1. Materials

N, N'–Dimethylacrylamide (DMA, C_5H_9NO, 99%) was supplied by Aldrich Chemical Corp (USA); Maleic acid was received by Shanghai Zhanyun Chemical Co (MA, $C_4H_4O_4$, 99%); Polyacrylamide (PAM; $C_{3x}H_{5x}N_xO_x$; 99%) was supplied by Shanghai Macklin Biochemical Technology Co., Ltd; Ammonium persulfate (APS, $(NH_4)_2S_2O_8$) as a catalyst was purchased from Aencore Chemical Pty. Ltd.

(Australia); N, N, N', N'–Tetramethylethylenediamine (TEMED, $C_6H_{16}N_2$) as a promoter, and N, N'–Methylenebisacrylamide (MBA, $C_7H_{10}N_2O_2$) as a crosslinker were purchased from Alfa Aesar Co (USA). All reactants were used as received without any further purification.

2.2. Method

The preparation of semi–IPN hydrogels with different PAM ratios, called PAMx, is illustrated in *Figure 1*. It was prepared by free radical polymerization in the aqueous solution of PAM, DMA, and MA, employing APS/TEMED as a catalyst promoter, respectively. The feed ratios are given in *Table 1*.

Firstly, semi–IPN hydrogels were prepared by mixing the solution 1% w/w of linear polymer PAM, and DMA with various volume-designated ratios, 0.12 mg MBA, 1.392 g MA, 7.2 mL solution of APS and a specified volume of water in a vial under iced-water bath condition. After that, the obtained mixtures were vacuumed for 30 minutes until the solution became homogeneous. In the next step, 7.2 mL solution of TEMED was added as a redox initiator pair to initiate the final reaction mixture. The solution was mixed thoroughly, and then quickly poured into a cylindrical plastic mold with the dimension of 12×5 mm, sealed immediately, and kept at 3 – 5 °C for 24 hours. The obtained hydrogels were carefully removed from the mold and were washed with distilled water continuously for 7 days at room temperature to remove unreacted substances. The purified samples were dried at 45 °C until constant mass to obtain final hydrogels.

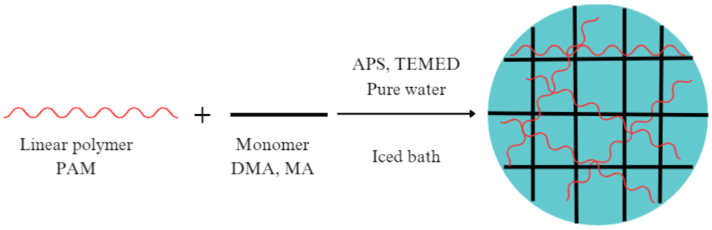


Figure 1. *Preparation scheme of semi–IPN hydrogels*

Table 1. *Composition of raw materials used for the preparation of semi–IPN hydrogels*

Sample	PAM[a] (mL)	DMA (mL)	MA (g)	MBA (mg)	APS[b] Solution (mL)	TEMED[c] Solution (mL)	Pure water (mL)	Total volume (mL)
PAM 6	5.4	9.0	1.392	0.12	7.2	7.2	12.6	41.4
PAM 8	7.2	9.0	1.392	0.12	7.2	7.2	10.8	41.4
PAM 10	9.0	9.0	1.392	0.12	7.2	7.2	9.0	41.4
PAM 12	10.8	9.0	1.392	0.12	7.2	7.2	7.2	41.4
PAM 14	12.6	9.0	1.392	0.12	7.2	7.2	5.4	41.4

[a] *solution of 2.5 g PAM/247.5 g H_2O;* [b] *Solution of 0.4792 g APS/25 mL H_2O;* [c] *Solution of 4 mL TEMED/25 mL H_2O*

2.3. Characterization

Fourier transform infrared (FTIR) spectra was measured by a Jasco FT/IR – 4700 FTIR instrument (Japan) within 4000 – 400 cm^{-1} having a scan resolution of 4.00 cm^{-1}. The ATR technique was applied directly to the monomers, linear polymers, and dried hydrogels. Background measurements were performed, and subtracted for all the samples.

Scanning electronic microscopy (SEM) images of freeze-dried hydrogels were taken by a Hitachi Table Microscope, TM4000Plus (Hitachi, Tokyo, Japan) to investigate the interior morphology. The hydrogels were immersed in distilled water to an equilibrium swelling state and freeze-dried at -45 °C to observe the morphology by SEM. All samples were sputter-coated with platinum to enhance the conductivity, and SEM images were acquired at an accelerating voltage of 10.0 kV. The pore sizes and porosity were analyzed by ImageJ. The porosity (%) of hydrogels was estimated through ImageJ/Adjust/Threshold/Analyze Particles function with a fixed area of 1280 pixel × 960 pixel.

The rheological properties of the hydrogel with dimensions 12×5 mm were performed on the HAAKE RheoStress 1 (Thermo Fisher Scientific, USA). The value of storage modulus (G'), loss modulus (G"), and viscosity (η*) are measured from 50 – 180 sec at 25 °C. The test parameters are set including a frequency of 1.00 Hz and a gap between the two discs of 3.2 mm. The mechanical properties measurement on the CT3 Texture Analyzer (Brookfield, USA) at 25 °C. The compressive stress test was performed by a 7 mm diameter flat probe on 12×5 mm cylindrical hydrogels at a measurement rate of 0.05 mm/sec. The stress is determined at the point where the hydrogel begins to break.

The T_g of the hydrogels was determined using a DSC 214 Polyma (NETZSCH, Germany). Approximately 12 – 15 mg of dried hydrogel was tested at a rate of 5 °C/min in the temperature range of 50 – 220 °C. Nitrogen gas was used for analysis.

The swelling kinetics of the hydrogels were studied using the weighing method. Dried hydrogels were immersed in pure water at room temperature. At predetermined time points, swelling hydrogels were eliminated from the excess water by filter paper and weighing. The swelling ratio (SR, %) was calculated according to the following equation [30]:

$$\mathrm{SR} = \frac{\mathrm{W_s} - \mathrm{W_d}}{\mathrm{W_d}} \tag{1}$$

where W_s is the weight of the swelling hydrogel, and W_d is the weight of the freeze-dried hydrogel.

Furthermore, swelling kinetic curves created as a result of dynamic swelling tests were assumed to have a second degree, the following equation was applied [30]:

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \mathrm{k_S}.(\mathrm{S_{max}} - \mathrm{S})^2 \tag{2}$$

where dS/dt is the swelling speed of hydrogels; S_{max} (%) is the swelling value of hydrogel at equilibrium; S is the swelling value at time t, and k_s ($g_{hydrogel}/g_{H2O}$.min) represents swelling speed constant.

Recently, the mechanisms of water diffusion in swelling polymeric systems have received considerable attention, because of their important applications in drug delivery, the environment, and the agriculture field. To determine the nature of water diffusion was conducted based on Fickian diffusion law for the onset stage of swelling [30]:

$$\mathrm{F} = \frac{\mathrm{M_t}}{\mathrm{M_\infty}} = \mathrm{kt^n} \tag{3}$$

where M_t is the total amount of water intake at time t, M_∞ is the total amount of water intake at an equilibrium state which is determined by a weighing method, k is a swelling coefficient which is a parameter correlated with the polymeric network structures, and n is an exponent characteristic of the swelling which represents solvent diffusion modes inside hydrogels. Based on "n" values, the release mechanism involved in it can be arbitrated as ($n \leq 0.45$: Fickian diffusion) where the rate of diffusion is less than the rate of relaxation, ($0.45 < n < 0.89$: non-Fickian diffusion) where diffusion and relaxation rates are comparable ($n > 0.89$: Case II diffusion) where rate of diffusion is faster than the relaxation rate of the polymer, and ($n = 1$) the release mechanism follows the first order kinetics [31]. Moreover, the diffusion coefficient value (D, cm^2/min) calculated for the cylindrical hydrogels was determined with the following equation [30]:

$$\mathrm{D} = \pi.\mathrm{r}^2.\left(\frac{\mathrm{k}}{4}\right)^{1/\mathrm{n}} \tag{4}$$

where r represents the radius of the hydrogel (cm).

3. Results and Discussion

3.1. FTIR Measurements

FTIR spectroscopy results of monomer DMA, monomer MA, linear PAM, hydrogel PAM 6, PAM 8, PAM 10, PAM 12, and PAM 14 were shown in *Figure 2*. Firstly, in the DMA spectrum, oscillations appear including C–H at 2935 cm^{-1}, C=O of the carbonyl group at 1644 cm^{-1}, 973 cm^{-1} representing the $CH=CH_2$, and 1050 – 1147 cm^{-1} representing the C–N [32]. Next, in the MA spectrum, the characteristic oscillations were observed including C=O of the carboxyl group at 1706 cm^{-1}, C=C at 1628 cm^{-1}, –OH at 2381 – 3328 cm^{-1} (due to link overlap =C–H sp^2 at 3053 cm^{-1}) [33]. In the PAM spectrum, the deformation N–H oscillation was shown at 1601 cm^{-1}; 1661 cm^{-1} represents the C=O oscillation of the carbonyl group, and prolonged N–H oscillation occurred at 3182 cm^{-1} [34]. For PAM 6, PAM 8, PAM 10, PAM 12, and PAM 14, the $CH=CH_2$ binding characteristic at 973 cm^{-1} was disappeared. The characteristic peak of the C=O (carbonyl) at 1608 – 1616 cm^{-1} were observed in both PAMs and hydrogels. However, the peak area of the hydrogels was clearly larger than that of PAM. This result shows that the incorporation of PAM into the hydrogels network has been successful. All hydrogels appeared C=O (carboxyl) at 1712 – 1725 cm^{-1}, indicating that the copolymerization between DMA and MA has been performed.

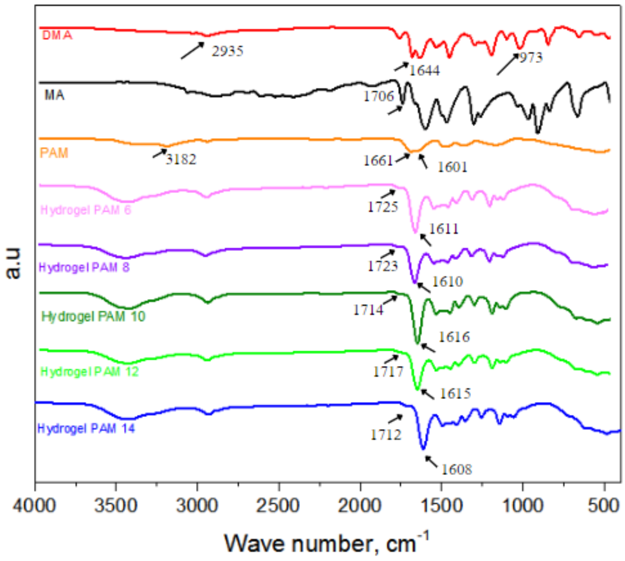
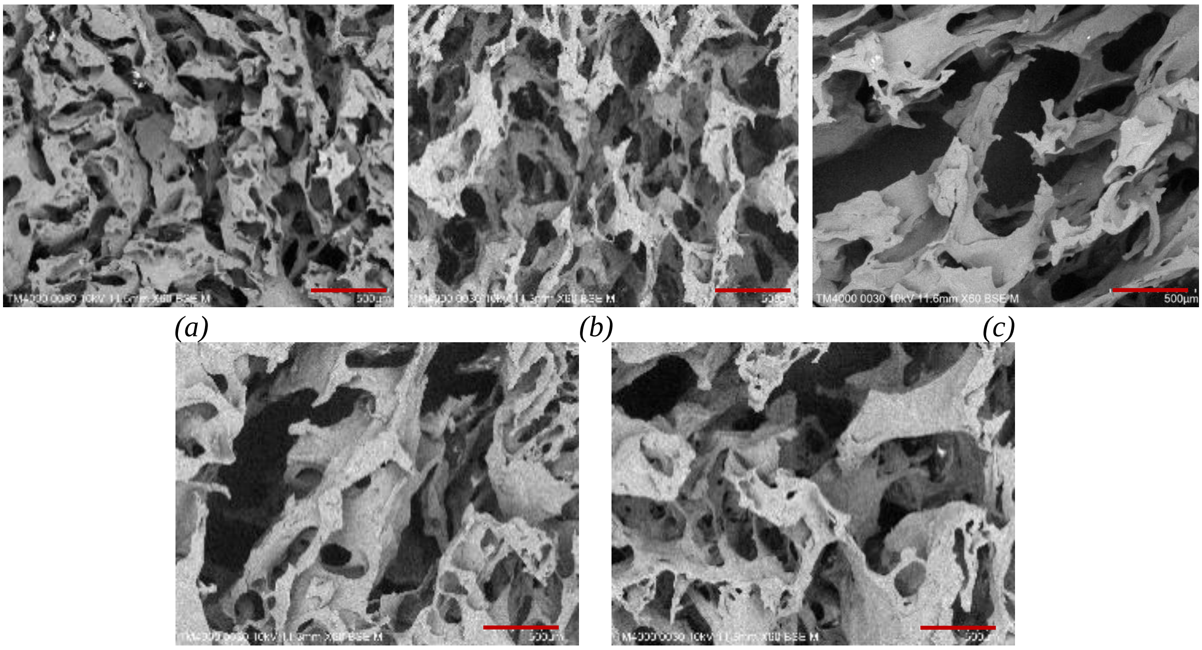


Figure 2. *FTIR spectra of monomers, linear polymer, and hydrogels*

3.2. Interior morphology



(a) *(b)* *(c)*

(d) *(e)*

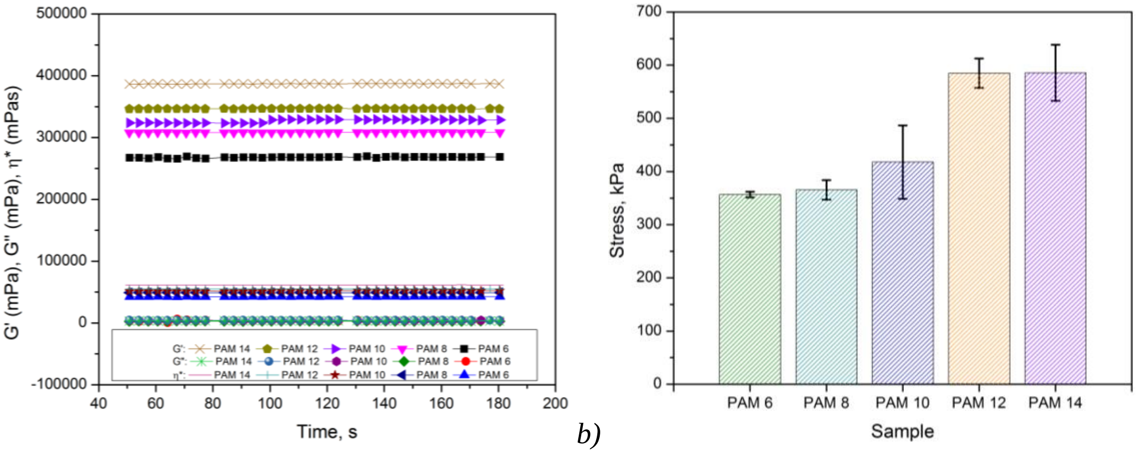
Figure 3. *SEM images of (a) PAM 6, (b) PAM 8, (c) PAM 10, (d) PAM 12, and (e) PAM 14*

The morphology of hydrogels were shown in *Figure 3*. SEM observation results show that the hydrogel samples have a fairly uniform pore structure with the average pore size and porosity listed in Table 2. The results show that PAM 14 has a much larger porosity than PAM 6, which is evidenced by the porosity of PAM 14 being 49.95%, and PAM 6 being 42.92%. The presence of linear PAM in the semi–IPN structure can facilitate the formation of interconnected channels or pathways for water diffusion. These pathways allow faster, and more efficient water transport in the hydrogel, which increases swelling porosity. Besides, the same report by Wei et al has concluded that the size of porosity increases with increasing linear Salecan [35].

Table 2. *Pore size, and porosity of semi–IPN hydrogels*

Sample	Pore size, µm	Porosity, %
PAM 6	252.8 ± 4.0	42.92
PAM 8	333.3 ± 12.1	42.94
PAM 10	664.5 ± 9.0	48.24
PAM 12	679.9 ± 2.2	48.26
PAM 14	888.5 ± 4.8	49.95

3.3. Mechanical properties



a) *b)*

Figure 4. *(a) Rheology, and (b) Mechanical properties of hydrogel*

The rheological properties of hydrogels were shown in Figure 4a. The G, G”, and η* values of the hydrogels were listed in Table 3. From 50 to 180 s at 25 °C, the G’ value does not change significantly, and it is always greater than the G” value, which indicates that the hydrogel is a viscoelastic material [36]. As the PAM content increased, the hydrogel network became denser due to the increasing presence of polymer chains, and entanglement. The network is denser so more efficient energy storage, and transmission during deformation leads to an increase in G’. In addition, higher PAM content, increased polymer density, and entanglement impede the movement of polymer chains. This leads to greater internal friction, and energy dissipation during deformation, causing an increase in G”. A higher G” value indicates that a larger percentage of the input energy is dissipated as heat within the material, which is typical for more viscoelastic behavior. Finally, the increased PAM content results in restriction of the movement of solvent molecules, and polymer chains in the hydrogel, increasing the viscosity.

Table 3. *Mechanical properties of PAM 6, PAM 8, PAM 10, PAM 12, and PAM 14*

Sample	G’, mPa	G’’, mPa	η*, mPas	Stress, kPa
PAM 6	339682.0 ± 9239.7	2445.9 ± 170.0	54091.4 ± 1485.7	356.6 ± 5.4
PAM 8	346768 ± 19579.7	3370.8 ± 48.8	55944.4 ± 3116.1	365.5 ± 18.4
PAM 10	406165.0 ± 4416.2	5991.5 ± 132.9	64648.1 ± 705.0	414.7 ± 68.9
PAM 12	410327.0 ± 15676.2	6022.54 ± 66.0	65542.7 ± 2494.1	584.84 ± 27.5
PAM 14	410581.0 ± 10921.4	6124.4 ± 658.3	66353.1 ± 1736.8	585.8 ± 52.8

The stress value of hydrogels were shown in Figure 4b, and Table 3. The results show that the stress of PAM 6 is significantly different from that of PAM 14. It can be seen that when PAM is present in the hydrogel structure, it will establish water channels, helping the amount of water absorbed in the network to move easily transferred from high-stress areas to non-stressed areas, increasing the capacity of the hydrogel to withstand compressive stress [37]. Besides, PAM also contributes to efficient energy dissipation due to the high viscosity of polymer chains, thereby contributing to increased stability, and limiting structural collapse [37]. In addition, the PAM chains interact with the existing polymer network to form additional physical or chemical crosslinking. This enhanced bonding contributes to a stiffer, and stronger hydrogel structure, resulting in increased stress. Finally, the combination of PAM, and the existing polymer network in the semi–IPN structure produces a synergistic effect. The PAM chain can complement the properties of an existing hydrogel matrix, which improves mechanical performance. The synergistic effects arise from the unique combination of the two polymers, leading to enhanced stress [38], [39].

3.4. Thermal properties of hydrogels

The DSC curves of hydrogels were shown in *Figure 5*. The T_g of PAM 6, PAM 8, PAM 10, PAM 12, and PAM 14 were 109.2, 119.9, 122.8, 123.3, and 123.7 °C, respectively. Thereby, it was found that the T_g between hydrogels tended to increase when increasing linear PAM content. When PAM is added to the hydrogel network, PAM can have a reinforcing effect on the network structure, leading to an increase in T_g. Linear PAM can form additional crosslinking points in the hydrogel network. The increased crosslinking density can restrict the movement of the polymer chains, enhance the structural integrity of the hydrogel, and increase T_g. On the other hand, the PAM chain can interact with the polymer chain in the hydrogel, enhancing intermolecular interactions such as hydrogen bonding. These additional interactions enhance physical or chemical entanglement in the network, leading to increased T_g. Furthermore, the presence of PAM can improve the arrangement, and spatial organization of the hydrogel network. PAM incorporation can promote a more ordered structure, which requires higher energy for chain rearrangement, resulting in elevated T_g [38], [40]. This result is completely consistent with the mechanical properties presented above.

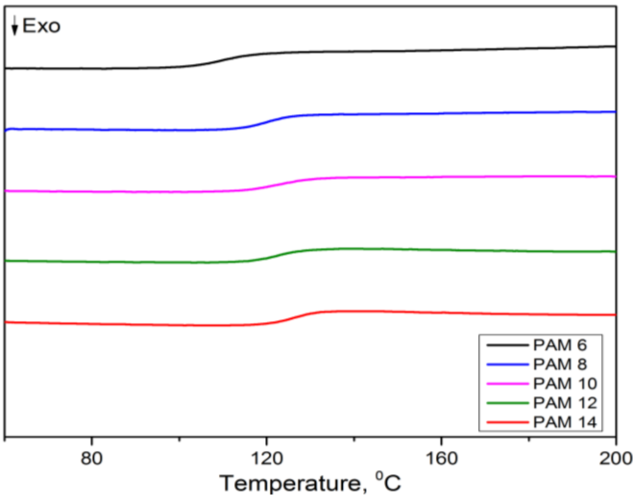


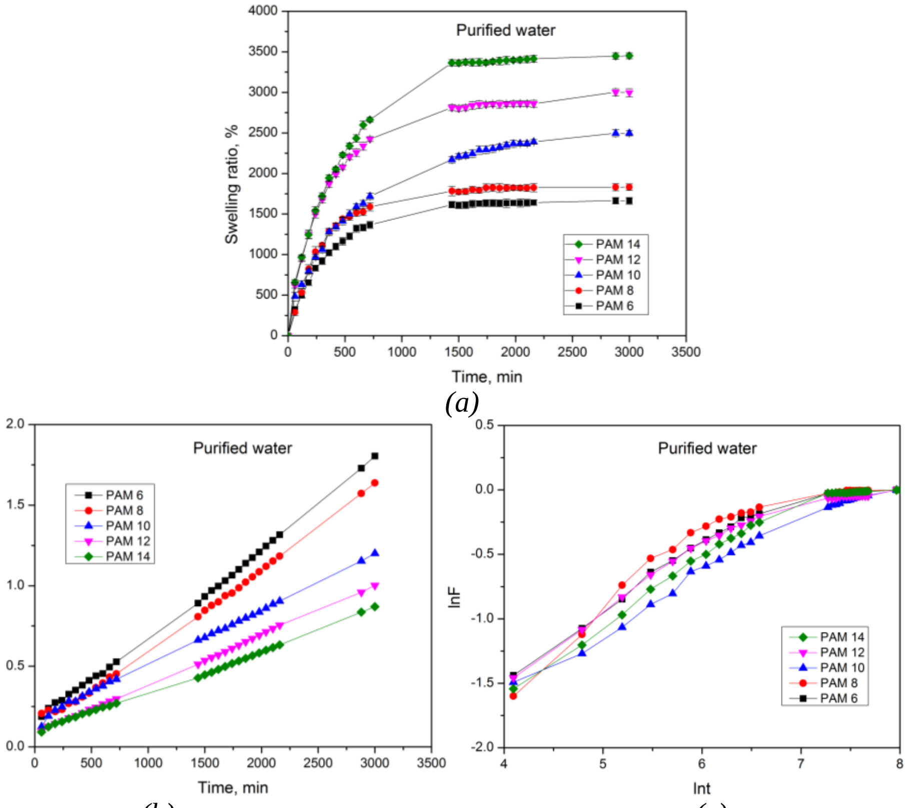
Figure 5. *DSC curves of the hydrogels*

3.5. Swelling behavior

The swelling kinetic curves of hydrogels were shown in *Figure 6a*. The maximum swelling ratio (SR_{max}) of hydrogels were listed in *Table 4*. Specifically, PAM 6 has SR_{max} = 1665.14%, PAM 8 has SR_{max} = 1831.90%, PAM 10 has SR_{max} = 2994.56%, PAM 12 has SR_{max} = 3001.62%, and PAM 14 has SR_{max} = 3450.22%. This difference can be explained based on the effect that linear PAM incorporated into the hydrogel. Firstly, linear PAM is hydrophilic and has a high affinity for water, when PAM is integrated into hydrogel will enhance the hydrophilic properties of the overall structure. The increased hydrophilic promotes water absorption of the hydrogel, resulting in enhanced swelling properties. Moreover, linear PAM is a flexible polymer with a relatively loose structure, when PAM is incorporated into the semi–IPN structure, flexible polymer chains are added to the hydrogel, these chains allow for a more mobile, and extended hydrogel structure, facilitating increased swelling behavior. Moreover, the addition of linear PAM can increase the porosity of hydrogel. PAM chains can create space in the semi –IPN structure, which provides more space for water absorption. The increased porosity allows for greater water infiltration, and retention, resulting in enhanced swelling properties. These observations were similar to those reported in X. Hu's study when the linear salecan was incorporated into the poly(DMAA-co-HEMA) structure, the linear making the hydrogel structure more hydrophilic, and hydrophilic more consumption leads to increased swelling rate [37].

The plot of t/S vs. t of hydrogels in pure water were shown in *Figure 6b.* The calculation results of the swelling at equilibrium (S_{max}), and the swelling speed constant (k_s) were listed in *Table 4*. The S_{max} of PAM 6, PAM 8, PAM 10, PAM 12, and PAM 14 is 1862.2, 2024.29; 2840.91; 3355.70, and 3984.06%, respectively. This is compatible with the experimental data obtained.

Besides, the plot of lnF vs. lnt of hydrogels were shown in *Figure 6c*. The diffusion exponent (n), the swelling coefficient (k), and the diffusion coefficient (D) were calculated in *Table 4,* it is found that the value of n ranges from 0.33 to 0.40 ($n \leq 0.45$), so it can be determined that water diffuses into the hydrogel according to the Fickian mechanism, the hydrogel swelling is shown by the diffusion mechanism, and the polymer network loosens [30], [41].



(a)

(b) *(c)*

Figure 6. *(a) Swelling kinetic curves, (b) The plot of t/S vs. t, and (c) The plot of lnF vs. lnt of hydrogels in pure water at 25 °C*

Table 4. *The swelling kinetics parameter of hydrogels in pure water at 25℃*

Sample	$SR_{max,}$	$S_{max,}$	k_s	n	k	D
PAM 6	1665.14	1862.20	1.93×10^{-4}	0.34	0.078	2.65×10^{-5}
PAM 8	1831.90	2024.29	2.12×10^{-4}	0.34	0.082	2.80×10^{-5}
PAM 10	2994.56	3355.70	7.60×10^{-5}	0.35	0.067	2.64×10^{-5}
PAM 12	3001.62	3267.97	1.14×10^{-4}	0.33	0.079	2.95×10^{-5}
PAM 14	3450.22	3984.06	7.11×10^{-5}	0.39	0.054	5.96×10^{-5}

4. Conclusions

In this work, semi–IPN hydrogels based on PAM, DMA, and MA were synthesized and investigated. The chemical structure was confirmed by FTIR. A uniform porous structure of the semi–IPN hydrogels was confirmed by SEM. The equilibrium swelling ratio was influenced by the content of PAM introduced into hydrogel: increasing the PAM content led to an increased swelling ratio. Moreover, this work also confirmed that the mechanical properties, T_g of PAMx also increase with increasing PAM content. Further application of semi–IPN hydrogels based on PAM, DAM, and MA are in progress.

Acknowledgments

We are grateful to Polymer Chemistry Lab., Faculty of Chemical and Food Technology, Ho Chi Minh City University of Technology and Education, Vietnam for facilities support of this work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

REFERENCES

[1] R. Foudazi, R. Zowada, I. M. Zloczower, and D. L. Feke, "Porous Hydrogels: Present Challenges and Future Opportunities," *Langmuir*, vol. 39, no. 6, pp. 2092-2111, 2023.

[2] L. F. Hart, J. E. Hertzog, P. M. Rauscher, B. W. Rawe, M. M. Tranquilli, and S. J. Rowan, "Material properties and applications of mechanically interlocked polymers," *Nature Reviews Materials*, vol. 6, no. 6, pp. 508-530, 2021.

[3] N. Zoratto and P. Matricardi, "Semi-IPNs and IPN-based hydrogels," in *Woodhead Publishing Series in Biomaterials, Polymeric Gels*, Kunal Pal, Indranil Banerjee, U.K.: Woodhead Publishing, 2018, pp. 91-124.

[4] Y. Li *et al.*, "Novel fast thermal-responsive poly (N-isopropylacrylamide) hydrogels with functional cyclodextrin interpenetrating polymer networks for controlled drug release," *Journal of Polymer Research*, vol. 22, pp. 1-14, 2015.

[5] Z. S. Huang, J. W. Shiu, T. F. Way, and S. P. Rwei, "A thermo-responsive random copolymer of poly (NIPAm-co-FMA) for smart textile applications," *Polymer*, vol. 184, p. 121917, 2019.

[6] O. Erol, A. Pantula, W. Liu, and D. H. Gracias, "Transformer hydrogels: A review," *Advanced Materials Technologies*, vol. 4, no. 4, p. 1900043, 2019.

[7] S. Mantha *et al.*, "Smart hydrogels in tissue engineering and regenerative medicine," *Materials*, vol. 12, no. 20, pp. 3323, 2019.

[8] S. Wu and R. A. Shanks, "Synthesis and characterisation of hydrophobic modified polyacrylamide," *Polymer International*, vol. 53, no. 11, pp. 1821-1830, 2004.

[9] N. Jain, "A Review On Acrylamide Based Hydrogel-Structural Feature, Chemistry, Synthesis and Its Application.", *International Journal of Engineering Science Invention*, vol. 6, no. 11, pp. 67-74, 2017.

[10] J. Maitra and V. K. Shukla, "Cross-linking in hydrogels-a review," *Am. J. Polym. Sci.*, vol. 4, no. 2, pp. 25-31, 2014.

[11] P. Sapuła, K. B. Was, and K. Malarz, "Are Natural Compounds a Promising Alternative to Synthetic Cross-Linking Agents in the Preparation of Hydrogels?," *Pharmaceutics*, vol. 15, no. 1, p. 253, 2023.

[12] Z. He, C. Liu, J. Zhao, F. Guo, and Y. Wang, "Enhanced gelling properties and hydration capacity of ginkgo seed proteins by genipin cross-linking," *Food Chemistry*, vol. 399, p. 133924, 2023.

[13] M. J. Ansari *et al.*, "Poly (N-isopropylacrylamide)-based hydrogels for biomedical applications: A review of the state-of-the-art," Gels, vol. 8, no. 7, p. 454, 2022.

[14] A. Chan, R. P. Orme, R. A. Fricker, and P. Roach, "Remote and local control of stimuli responsive materials for therapeutic applications," *Advanced drug delivery reviews*, vol. 65, no. 4, pp. 497-514, 2013.

[15] S. Chaterji, I. K. Kwon, and K. Park, "Smart polymeric gels: Redefining the limits of biomedical devices," *Progress in polymer science*, vol. 32, no. 8-9, pp. 1083-1122, 2007.

[16] H. F. Darge, A. T. Andrgie, H. C. Tsai, and J. Y. Lai, "Polysaccharide and polypeptide based injectable thermo-sensitive hydrogels for local biomedical applications," *International journal of biological macromolecules*, vol. 133, pp. 545-563, 2019.

[17] S. L. Loo, L. Vásquez, A. Athanassiou, and D. Fragouli, "Polymeric Hydrogels - A promising platform in enhancing water security for a sustainable future," *Advanced Materials Interfaces*, vol. 8, no. 24, p. 2100580, 2021.

[18] D. Alpaslan, T. E. Dudu, S. Kubilay, and N. Aktas, "Synthesis and characterization of biocompatible poly (maleic acid-co-citric acid) microparticles as a smart carrier for thiamine," *Polymer Bulletin*, vol. 78, no. 11, pp. 6305-6320, 2021.

[19] A. Akhmetzhan *et al.*, "A short review on the N, N-Dimethylacrylamide-based hydrogels," *Gels*, vol. 7, no. 4, p. 234, 2021.

[20] F. Jamali, N. E. Esfahani, and A. Rahmati, "Maleic acid as an important monomer in synthesis of stimuli-responsive poly (acrylic acid-co-acrylamide-co-maleic acid) superabsorbent polymer," *Scientific Reports*, vol. 13, no. 1, p. 3511, 2023.

[21] W. Huang *et al.*, "A semi-interpenetrating network polyampholyte hydrogel simultaneously demonstrating remarkable toughness and antibacterial properties," New Journal of Chemistry, vol. 40, no. 12, pp. 10520-10525, 2016.

[22] S. D. Ittel, L. K. Johnson, and M. Brookhart, "Late-metal catalysts for ethylene homo-and copolymerization," *Chemical Reviews*, vol. 100, no. 4, pp. 1169-1204, 2000.

[23] M. W. Scoggins and J. W. Miller, "Determination of water-soluble polymers containing primary amide groups using the starch-triiodide method," *Society of Petroleum Engineers Journal*, vol. 19, no. 3, pp. 151-154, 1979.

[24] A. Tangri, "Polyacrylamide based hydrogels: synthesis, characterization and applications," *International Journal of Pharmaceutical, Chemical & Biological Sciences*, vol. 4, no. 4, 2014.

[25] Z. Bao, C. Xian, Q. Yuan, G. Liu, and J. Wu, "Natural polymer-based hydrogels with enhanced mechanical performances: preparation, structure, and property," *Advanced Healthcare Materials*, vol. 8, no. 17, p. 1900670, 2019.

[26] B. Yi, Q. Xu, and W. Liu, "An overview of substrate stiffness guided cellular response and its applications in tissue regeneration," *Bioactive materials*, vol. 15, pp. 82-102, 2022.

[27] N. A. T. Huynh, "Swelling behavior of hydrogels based on N, N'-Diethylacrylamide," *Journal of Technical Education Science*, no. 59, pp. 39-48, 2020.

[28] H. N. A. Tuan and V. T. T. Nhu, "Synthesis and properties of pH-thermo dual responsive semi-iPN hydrogels based on N, N'-diethylacrylamide and itaconamic acid," *Polymers*, vol. 12, no. 5, p. 1139, 2020.

[29] H. N. A. Tuan and H. Phuong, "Characterization and swelling behavior of hydrogels from N-isopropylacrylamide, N, N′-diethylacrylamide, acrylic acid, and its use for drug release," *Canadian Journal of Chemistry*, vol. 101, no. 1, pp. 799-812, 2023.

[30] T. E. Dudu, D. Alpaslan, and N. Aktas, "Superabsorbent hydrogels based on N, N-dimethylacrylamide and maleic acid for applications in agriculture as water purifier and nitrogen carrier," *Polymer Bulletin*, vol. 79, no. 10, pp. 8551-8573, 2022.

[31] N. Thombare, S. Mishra, R. Shinde, M. Z. Siddiqui, and U. Jha, "Guar gum based hydrogel as controlled micronutrient delivery system: Mechanism and kinetics of boron release for agricultural applications," *Biopolymers*, vol. 112, no. 3, p. e23418, 2021.

[32] M. Rezaei, H. A. Panahi, S. Nasrollahi, E. Moniri, and N. T. Fard, "Synthesis and Characterization of Zinc Oxide Nanoparticles Grafted Poly [(N, N-Dimethylacrylamide)-co-(Allyl Acetoacetate)] for Removal of Pb (II) in Environmental and Biological Samples," *Separation Science and Technology*, vol. 58, no. 8, pp. 1516-1526, 2023.

[33] B. Akkaya, R. Akkaya, S. I. Celikkaya, N. Sarıaydin, and K. Y. Raheem, "Doxorubicin loaded pH-responsive chitosan-poly (acrylamide-maleic acid) composite hydrogel for anticancer targeting," *Journal of Molecular Structure*, vol. 1274, p. 134536, 2023.

[34] Z. Jing *et al.*, "Tough, stretchable and compressive alginate-based hydrogels achieved by non-covalent interactions," *RSC advances*, vol. 10, no. 40, pp. 23592-23606, 2020.

[35] W. Wei *et al.*, "Smart macroporous salecan/poly (N, N-diethylacrylamide) semi-IPN hydrogel for anti-inflammatory drug delivery," *ACS Biomaterials Science & Engineering*, vol. 2, no. 8, pp. 1386-1394, 2016.

[36] S. P. Rwei, H. N. A. Tuan, W. Y. Chiang, and T. F. Way, "Synthesis and characterization of pH and thermo dual-responsive hydrogels with a semi-IPN structure based on N-isopropylacrylamide and itaconamic acid," *Materials*, vol. 11, no. 5, p. 696, 2018.

[37] X. Hu *et al.*, "Synthesis and characterization of a novel hydrogel: salecan/polyacrylamide semi-IPN hydrogel with a desirable pore structure," *Journal of Materials Chemistry B*, vol. 2, no. 23, pp. 3646-3658, 2014.

[38] X. J. Liu *et al.*, "Highly stretchable and tough pH-sensitive hydrogels with reversible swelling and recoverable deformation," *Rsc Advances*, vol. 6, no. 6, pp. 4850-4857, 2016.

[39] D. L. Merlin and B. Sivasankar, "Synthesis and characterization of semi-interpenetrating polymer networks using biocompatible polyurethane and acrylamide monomer," *European Polymer Journal*, vol. 45, no. 1, pp. 165-170, 2009.

[40] Y. R. Kwon *et al.*, "Semi-IPN superabsorbent polymer based on itaconic acid and polyvinyl alcohol with improved gel strength and salt resistance," *Polymer Engineering & Science*, vol. 63, no. 7, pp. 1943-1952, 2023.

[41] S. Dash, P. N. Murthy, L. Nath, and P. Chowdhury, "Kinetic modeling on drug release from controlled drug delivery systems," *Acta Pol. Pharm.*, vol. 67, no. 3, pp. 217-23, 2010.

Dr. Huynh Nguyen Anh Tuan received B.E. degree in Chemical engineering from the University of Technology of Ho Chi Minh City, Vietnam, in 2003 and M.E. degree in Polymeric and Composite Material from the same University in 2006. In 2018, he received a PhD. degree from the National Taipei University of Technology (Taipei Tech), Taipei, Taiwan with a major in Polymeric and Organic Materials. He worked as a researcher and lecturer at the University of Technology and Ton Duc Thang University in Ho Chi Minh City, Vietnam. Since 2011, he has been working as a lecturer in the Department of Chemical Engineering, Faculty of Chemical and Food Technology at the University of Technology and Education, Vietnam. His research interest includes the synthesis of dual-responsive hydrogel and its applications. Moreover, he also focus to fabricate polymer-based composite materials which were reinforced by agricultural waste. Email: tuanhna@hcmute.edu.vn. ORCID: https://orcid.org/0000-0003-4861-7678.

Master student Bui Thi Cam Phan received a B.E. degree in Chemical engineering from the University of Technology and Education, Ho Chi Minh City, Vietnam, in 2020. She is a master student in Materials Science at the University of Science, Viet Nam National University Ho Chi Minh City. Email: buithicamphan98@gmail.com, ORCID: https://orcid.org/0009-0000-3981-873X.