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REGULAR ARTICLE

Temperature and Ph-sensıtıve Super absorbent Polymers based on Modıfıed Maleıc Anhydrıde

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Abstract. Maleic anhydride was modified with 1-decanol at two different ratios to obtain derivatives named MD-75 (75% modified) and MD-100 (100% modified). By using these derivatives and acrylamide (AAm), many hydrogels with different AAm/MD ratios were synthesized. Ammonium persulphate (APS), N,N,N′,N′-tetramethyl ethylenediamine (TMEDA) and N,N′-methylene bisacrylamide (MBAAm) were used as initiator, catalyts and crosslinker agent respectively in the synthesis reaction. The modification reactions were clarified by FTIR and ^{1}H-NMR methods. Swelling behaviours, swelling capacities and effect of temperature, pH of the swelling medium and hydrogel composition on these parameters were studied. The swelling capacity of the hydrogels increased up to 82700% with decreasing the AAm/MD ratio. Temperature and pH of the swelling medium and the composition of the hydrogels were found to have a strong effect on the swelling behaviour and the swelling capacity of the hydrogels. The gels showed low swelling capacity with single-step swelling behaviour at low temperatures (T≤50 °C) and high swelling capacity with two-step swelling behaviour at higher temperatures. The swelling and diffusion kinetics of the hydrogels were also determined. All of the synthesized hydrogels showed uniform diffusion type at low temperatures while two types of diffusion observed at high temperatures.

Keywords. Maleic anhydride; hydrogel; pH; temperature; super absorbent polymer.

1. Introduction

Hydrogels are cross-linked polymers capable of swelling in water and can hold much more water in their structure than their own weight. The basis of swelling in hydrogels is based on H-bonds and Van der Waals forces between hydrogels and water. These polymers can absorb water through hydrophilic groups such as –OH, -COOH, -NH_2 and -SO_3H in their structure.[1] Hydrogels capable of holding at least as much water as their own weight (with swelling capacity ≥100%) are called super absorbent polymers (SAPs).[2] The high water content of the superabsorbent polymers makes them biocompatible.[3] The swelling capacity of such polymers is influenced by many factors such as composition and crosslink density of the polymer and pH, ionic strength and temperature of the swelling medium. These materials were also called smart hydrogels or stimuli-responsive hydrogels.[4] These intelligent hydrogels have gained more attention in the last decade because of their applications in chemical separation,[5,6] hygiene products,[7,8] wastewater treatment,[9–12] drug delivery system,[13–15] medical fields,[16–21] etc.

Hydrogels contain both hydrophilic and hydrophobic groups in their own network are being affected by temperature. Hydrogels affected by temperature changes are called temperature-sensitive hydrogels.[22] Hydrogels, whose swelling capacity increases as the temperature increases, are called positive temperature-sensitive hydrogels. Temperature-sensitive hydrogels have been studied extensively for use in controlled drug release.[23–26] Because the release agents used in drug release are affected by temperature.

Hydrogels synthesized using monomers with ionizable acidic or basic groups are pH-sensitive hydrogels. Such hydrogels can adjust their structure and natural properties depending on the pH of the medium and their swelling capacities are affected by variation in environmental pH. The pH-sensitive hydrogels containing acidic groups are referred to as 'polyanions'.[27] Because they lose their protons at high pH (basic medium) values and form a negatively charged polymer backbone. The pH-sensitive hydrogels have many applications in drug delivery and medical field due to their biocompatibility.[28]

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Acrylamide (AAm) is the best choice for the synthesis of SAPs as acrylamide is a hydrophilic monomer and its hydrogels exhibit a high swelling capacity. Due to its basic properties, its hydrogels being both temperature-sensitive and resistant to salts.[29,30] Homopolymer hydrogels of acrylamide have a high swelling capacity. But this property lowers their hydrolytic stability and tensile strength. As a result, their technological applications remain limited. Modification of the amide groups by hydrophobic groups or copolymerization of acrylamide with hydrophobic monomers improves the mechanical stability of the acrylamide based hydrogels.[31,32]

Maleic anhydride (MA) has two reactive groups: double bond an anhydride group. Maleic anhydride is both an electron donor and electron acceptor monomer capable of forming alternating copolymers with α-olefins due to double bond in its structure.[33,34] Copolymers of maleic anhydride have a wide range of applications such as enzyme immobilization,[35,36] biosensors[37,38] and controlled drug release systems.[39,40] The maleic anhydride can also be easily modified by both primary amines and alcohols and complexed with metal ions due to its reactive anhydride groups.[41–44] There are many applications of modified maleic anhydride based copolymer hydrogels in literature such as tissue engineering,[45] drug release[46,47] and full wound healing.[48]

In this study, synthesis and characterization of pH and thermoresponsive AAm/Modified MA (MD) based hydrogels were performed. MA was modified with decanol by esterification technique to enhance its hydrophobicity and then copolymerized with AAm by using ammonium persulphate (APS) as an initiator in the presence of N,N'-methylene bisacrylamide (MBAAm) as a crosslinking agent. Maleic anhydride was modified with decanol in two different ratios. The modification reaction was monitored by thin-layer chromatography (TLC). Then hydrogel synthesis with different AAm / MD ratios was performed. Structures of the hydrogels were characterized by FT-IR spectroscopic method. Dynamic swelling behaviour, the effect of pH, temperature and hydrogel composition on swelling behaviour, swelling and diffusion kinetics of the hydrogels were also investigated.

2. Materıal and method

2.1 *Material*

Maleic anhydride and MBAAm were purchased from Sigma-Aldrich. Maleic anhydride was purified by recrystallization in chloroform before using in experiments. MBAAm was used without further purification. Decanol (modification agent), 1,4-dioxane (solvent in modification reaction), AAm, sodium dodecylsulfate (homogenizer in hydrogel synthesis rection), sodium chloride (homogenizer in hydrogel synthesis rection), APS (initiator) and N,N,N′,N′-tetramethylethylene diamine (TMEDA)(catalyst in hydrogel synthesis rection) were purchased from Merck and used as received. All of the acids (HCl; 37%, CH_3COOH; 99%; H_2CO_3; 99.7%, and H_3PO_4; 85%) and bases (NaOH; 98% and NH_3; 28%) used for buffer solution preparation were supplied from Merck and used without further purification.

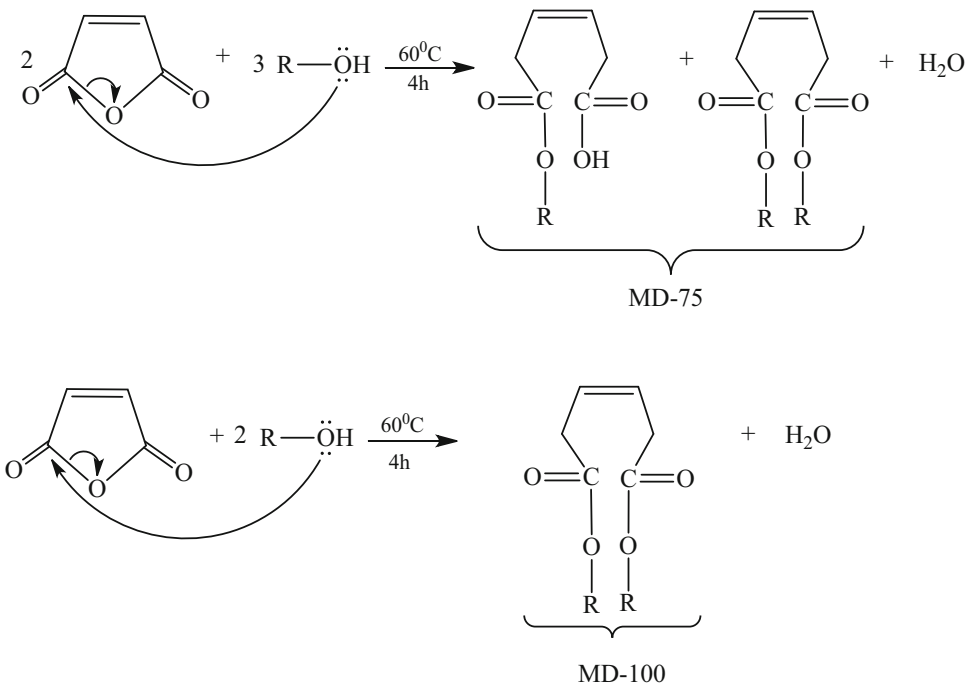
2.2 *Method*

2.2a *Modification of maleic anhydride*: 0.75 g of maleic anhydride was dissolved in 10 mL of 1,4-dioxane. 2.25 mL (MA/Decanol mol ratio: 2/3) or 3.00 mL (MA/Decanol mol ratio: 1/2) of 1-decanol dissolved in 2.5 mL of 1,4-dioxane was added to this homogeneous mixture. A magnetic stirrer was thrown into the mixture prepared in the synthesis tube and its mouth was closed with a stopper. The reaction was carried out at 60 °C constant temperature oil bath and monitored by thin-layer chromatography. The reaction was completed after 4 h. The solvent 1,4-dioxane and unreacted 1-decanol were removed from the reaction medium by rotary evaporator after completion of the modification reaction. The modified MA was used for hydrogel synthesis. The modification reaction mechanism is shown in Scheme 1.

The product in which the maleic anhydride was completely modified was named as MD-100 (100%) and the product in which 3 of the 4 groups were modified was called MD-75 (75%).

2.2b *Hydrogel synthesis*: The hydrogels were synthesized by free radical solution polymerization technique. The solutions MBAAm (1% by mass), TMEDA (1% by mass) and APS (8% by mass) were prepared in water. In hydrogel synthesis, the amounts of AAm and MD were changed by keeping the total mole number and concentration of the monomers constant ($6x10^{-3}$ mol; 1.0 M) in order to keep the crosslink density constant. Chemicals used in hydrogel synthesis are given in Table 1.

0.15 g NaCl was dissolved in 5 mL of water in a 100 mL beaker at room temperature. 0.35 g of SDS was added to the NaCl solution and mixed with a magnetic stirrer until a homogeneous solution was



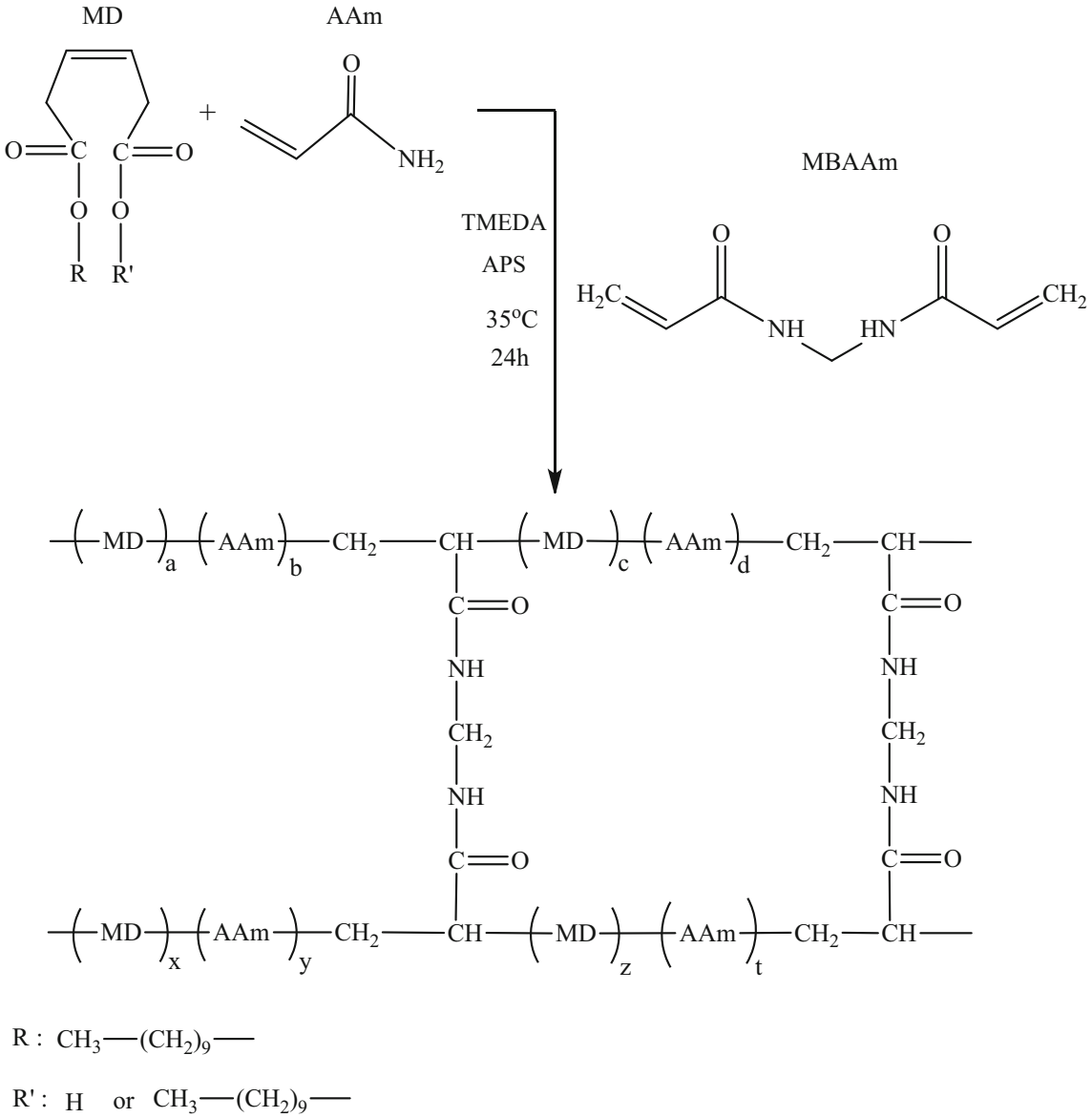
Scheme 1. Reaction mechanism for modification of MA with decanol at different ratios.

Table 1. Chemicals used in hydrogel synthesis and codes of the synthesized hydrogels.

Gel code	Monomer mole ratio (AAm/MD)	MD-75 (μL)	MD-100 (μL)	AAm (g)	MD (M)	AAm (M)
A/MD-75: 10/1	10/1	312	–	0.390	0.091	0.909
A/MD-75: 20/1	20/1	164	–	0.408	0.048	0.952
A/MD-75: 30/1	30/1	111	–	0.415	0.032	0.968
A/MD-75: 50/1	50/1	67	–	0.420	0.020	0.980
A/MD-75: 80/1	80/1	45	–	0.423	0.012	0.988
A/MD-100: 10/1	10/1	–	400	0.400	0.091	0.909
A/MD-100: 20/1	20/1	–	220	0.418	0.048	0.952
A/MD-100: 30/1	30/1	–	142	0.426	0.032	0.968
A/MD-100: 50/1	50/1	–	87	0.431	0.020	0.980
A/MD-100: 80/1	80/1	–	55	0.435	0.012	0.988

formed at 35 °C in an oil bath. Then required modified maleic anhydride (MD-75 or MD-100) was added and stirred for 2 h. AAm was then added and stirred for 30 minutes. Finally, 250 μL 1%$TMEDA_{(aq)}$, 50 μL 8% $APS_{(aq)}$ and 100 μL 1% $MBAAm_{(aq)}$ solutions were added respectively and mixed. The molar concentrations of $TMEDA_{(aq)}$, $APS_{(aq)}$ and $MBAAm_{(aq)}$ in all solutions are 3.6 mM, 2.92 mM and 1.1 mM respectively. The resulting mixture was transferred to 2 mL of polyethylene pipettes with one end closed. The pipettes were sealed with parafilm and kept at 35 °C oil bath for 24 h. After 24 h, the hydrogels formed were removed from the pipettes and cut into small cylindrical pieces, washed and allowed to dry for characterization. The washing process was carried out in two steps. In the first step, it was washed 3 times with 1-4 dioxane to remove the excess MD component. In the second step, the gels were washed 5 times with water to remove the water-soluble components (AAm, APS, TMEDA, NaCl, SDS and MBAAm) and the uncrosslinked polymer. Hydrogels were dried at 40 °C in a vacuum oven until constant weight. The conversion in hydrogel synthesis was calculated for all of the hydrogels and found as higher than 99%. Hydrogel synthesis reaction is shown in Scheme 2.

2.2c *FT-IR analysis*: The modification reaction was confirmed by FT-IR spectroscopy with Perkin-Elmer Spectrum One ATR model FT-IR spectrometer. The FT-IR spectra of MA, decanol, MD-75 and MD-100



Scheme 2. Synthesis mechanism of poly(AAm-*co*-MD) hydrogels.

were recorded in the wavenumber range of 450-4000 cm^{-1}.

2.2d *^{1}H-NMR analysis*: The modification reaction was also confirmed by ^{1}H-NMR spectroscopy with JEOL 6X-400 (400 MHz) spectrometer. ^{1}H-NMR spectra of both MD-100 and MD-75 were recorded.

2.2e *Swelling studies*: A dried piece of gel was weighed and immersed into a beaker filled with pure water or buffer solution (pH:2, 4, 6, 7, 8, 10 or 12; in case of studying pH dependency) at 25 °C or different temperatures (40, 50, 60, 70 or 80 °C; in case of studying temperature dependency). At regular periods the gel removed from the beaker, dried with filter paper to remove the surface water, weighed and immersed again into the water or buffer solution. This process was continued until the swollen gel came to constant weight. A picture of the dry and swollen state of a gel sample is given in Figure 1.

The buffer solutions were prepared by using suitable acid-base pairs. Every swelling study was carried out three times and the average value was used in calculations. The swelling ratio (S) of the hydrogels was calculated by using the following equation.

$$S = (W_t - W_0)/W_0 \quad (1)$$

Where $\mathbf{W_t}$ and $\mathbf{W_0}$ are the weights of the swollen gel at time **t** and dry gel respectively.

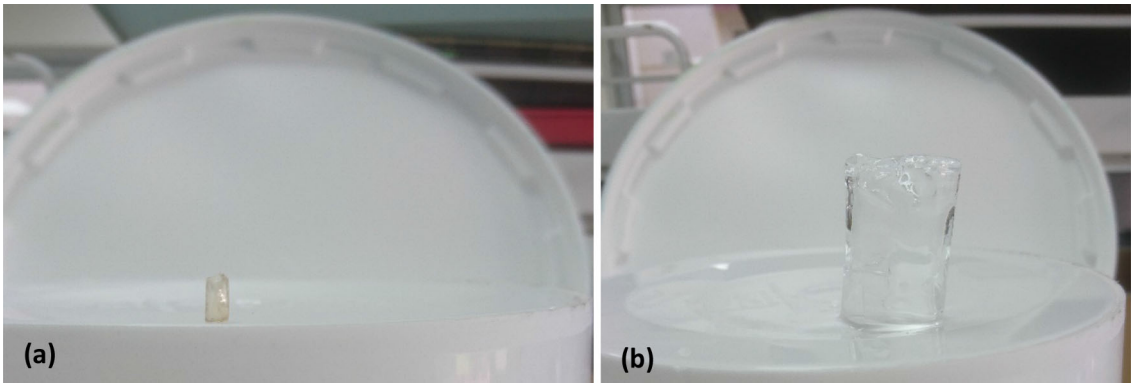


Figure 1. A picture of the dry (a) and swollen (b) state of a gel sample.

3. Results and Discussion

3.1 *FT-IR analysis*

FT-IR spectroscopy alone is not sufficient to determine the structure of the compounds. However, it is very useful in determining whether there is a reaction or not and in clarifying of the reaction mechanism. In this study, FT-IR was used to elucidate the mechanism of the modification reaction. FT-IR spectra of maleic anhydride, decanol and the modified product were recorded and represented in Figure 2 for comparison.

It can be seen from Figure 2 that weak C-H stretching at 3070 cm^{-1}, strong and broad symmetric C=O stretching at 1780 cm^{-1} and weak but sharp asymmetric C=O stretching bands at 1850 cm^{-1} are evident in MA.[40] The most prominent bands in decanol are OH stretching band between 3150 and 3450 cm^{-1} and C-H stretching bands at 2850 and 2920 cm^{-1}. The observation of the OH stretching band in the MD-75 spectrum and being wider than decanol indicates the presence of the COOH group. The band at 1750 cm^{-1} shows the presence of the C=O group, while the absence of the band of maleic anhydride in 1850 cm^{-1} indicates that it is not maleic anhydride. The loss of the OH stretching band in MD-100 and the increase in absorbance of the C=O stretching band at 1750 cm^{-1} indicate that the carboxyl group is absent and the structure is completely esterified.

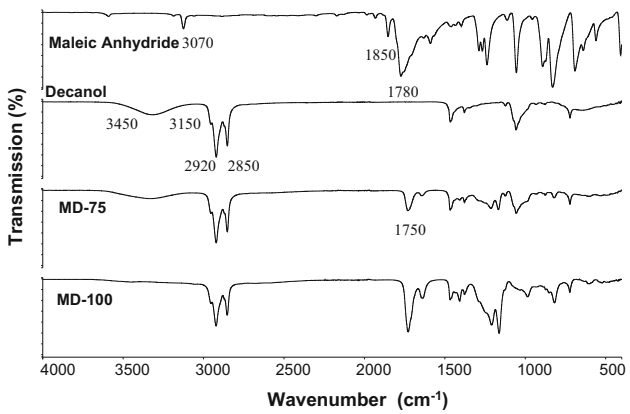


Figure 2. Comparison of FT-IR spectra of maleic anhydride, decanol and the modified products MD-75 and MD-100.

3.2 *^{1}H-NMR analysis*

The ^{1}H-NMR spectra of MD-75 and MD-100 were taken in $CDCl_3$ and are given in Figure 3 comparatively.

In Figure 3, the peak between 0.6 - 1.0 ppm corresponds to CH_3 protons, and the peaks between 1.0-1.9 ppm correspond to CH_2 protons of decyl groups. The doublet peak between 6.0-7.0 ppm belongs to CH protons between two carbonyl groups. The peak around 10.5 ppm belongs to the OH proton of the carboxylic acid group. The disappearance of the peak at 10.5 ppm and the increase in the areas of the peaks of the -CH_2 and -CH_3 protons in the MD-100 spectrum are evidence of the absence of the -OH group in the structure and the increase in the number of decyl groups.

3.3 *Swelling studies*

One of the most important properties of hydrogels is the swelling capacity. Swelling capacity is known as the swelling ratio of the hydrogel at equilibrium. Swelling behavior of hydrogels synthesized with different AAm/MD mole ratios (range between 10/1 and 80/1) in water at 25 °C are shown in Figure 4.

Figure 4 shows that swelling capacity of the hydrogel is decreased by increasing of AAm/MD mole ratio (which means increased AAm content)

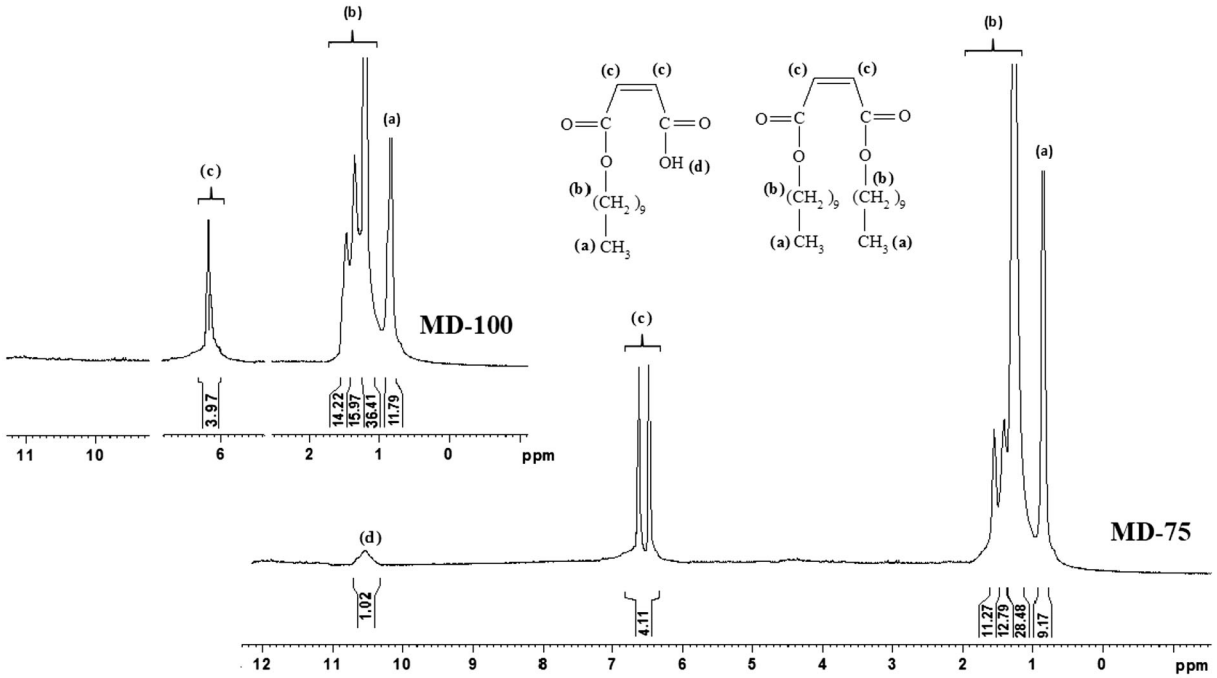


Figure 3. ^{1}H-NMR spectra of MD-75 and MD-100 taken in $CDCl_3$.

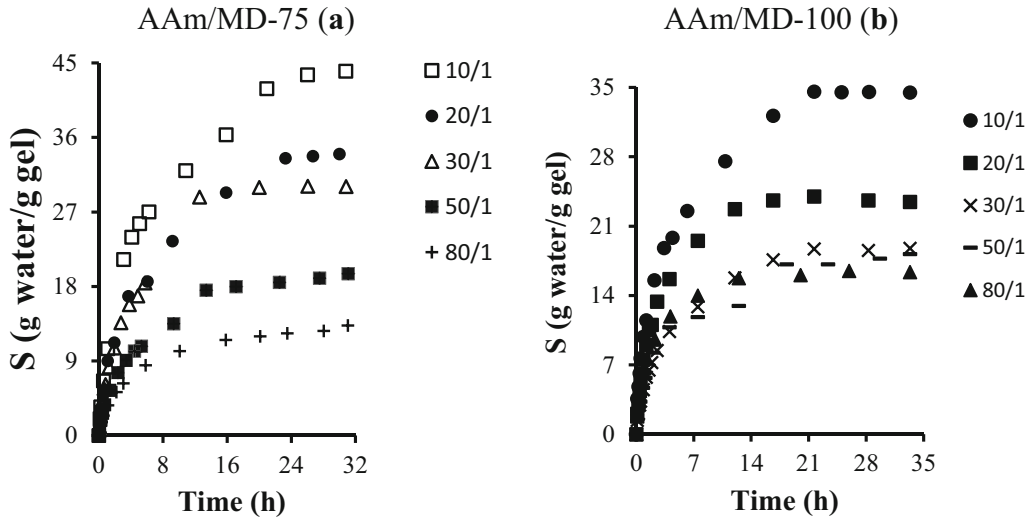


Figure 4. Swelling behaviour of (a) AAm/MD-75 (b) AAm/MD-100 hydrogels with different AAm/MD mole ratios ranging between 10/1 and 80/1 in water at 25 °C.

from 10/1 to 80/1. When the acrylamide content of the hydrogel is high, the H-bonds between the acrylamide molecules are being strong. H-bonding interactions occur among the -NH_2 and C=O groups within the hydrogel provides a compact H-bonded structure to the hydrogel. Because of these properties, acrylamide creates an effect like a hydrophobic effect. This effect limits the movement of the polymer chains and prevents the entrance of the solvent into the hydrogel.[49,50]

3.4 *Effect of temperature*

One of the parameters that can affect the swelling capacity of the hydrogels is temperature. Copolymer hydrogels synthesized in this study have both hydrophilic (NH_2 and COOH groups) and hydrophobic (decyl groups) in their own network. Swelling studies of the synthesized hydrogels were carried out at different temperatures and similar results were obtained for all hydrogels. Therefore, the result of only

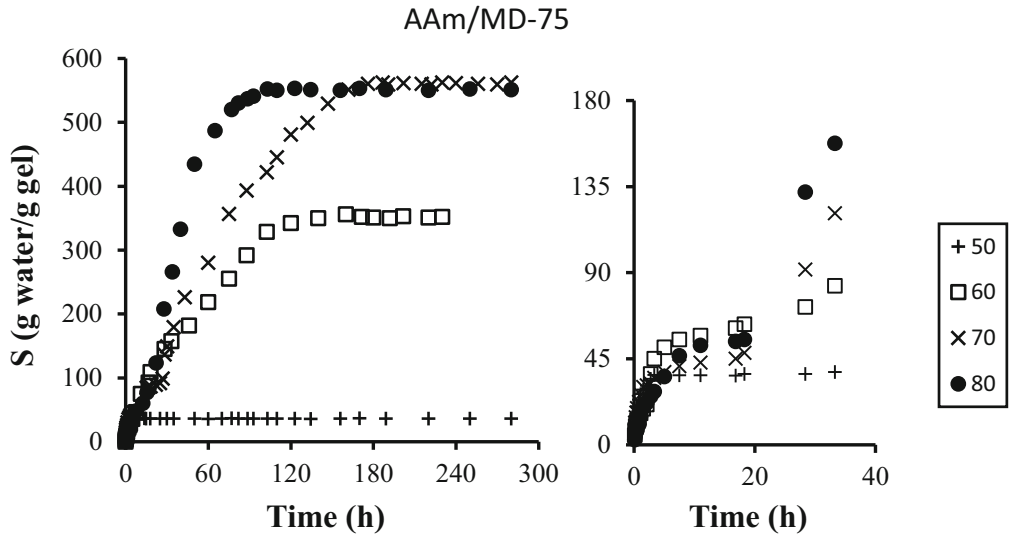


Figure 5. Variation of swelling ratio with time at different temperatures (50, 60, 70 and 80 °C) for AAm/MD-75: 30/1 hydrogels in water.

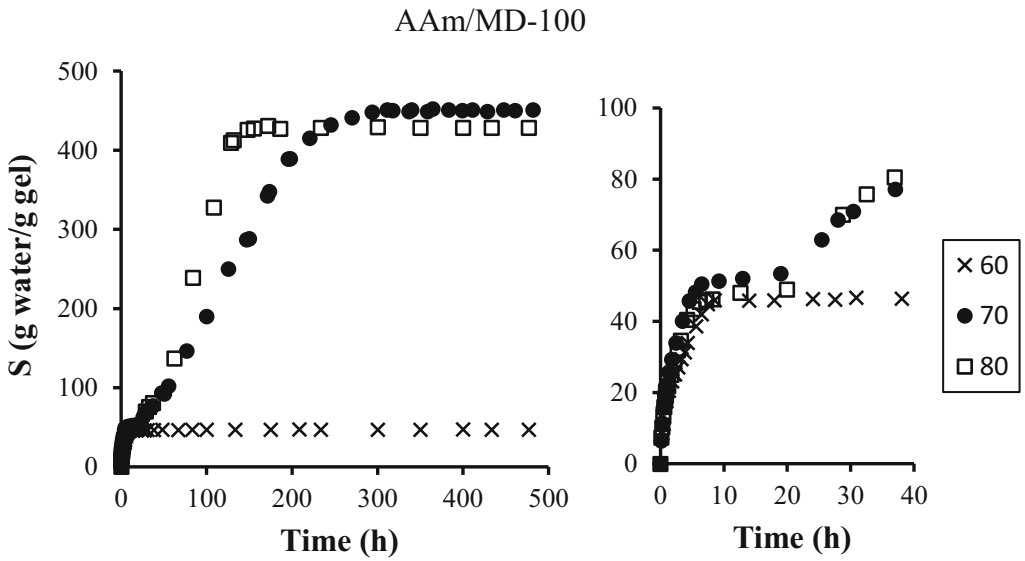


Figure 6. Variation of swelling ratio with time at different temperatures (60, 70 and 80 °C) for AAm/MD-100: 30/1 hydrogels in water.

AAm/MD: 30/1 hydrogels are represented in Figure 5 and Figure 6.

Figure 5 and Figure 6 show the swelling behaviour of the AAm/MD-75: 30/1 hydrogels at 50, 60, 70 and 80 °C and AAm/MD-100: 30/1 at 60, 70 and 80 °C, respectively. Swelling studies were carried out at 25, 37, 50, 60, 70 and 80 °C for each hydrogel. Since the behaviours obtained at 50 °C and lower temperatures same, only the results of one of the same results and temperatures having different behaviours are given in the figures. A single step behaviours with low swelling capacity were obtained at 50 °C for AAm/MD-75 and 60 °C for AAm/MD-100 and below temperatures, while two-step behaviors with high swelling capacity were obtained at temperatures higher than these temperatures. The swelling capacity of the hydrogels at a critical temperature where the swelling behaviour changes, and lower temperatures are being low due to the strong H-bonding between the acrylamide units. At temperatures above critical temperatures, these H-bonds are weakened because of the temperature, entrance of the water and the repulsion forces of the hydrophobic decyl groups. Thus, water can easily enter into the hydrogel and its swelling capacity is

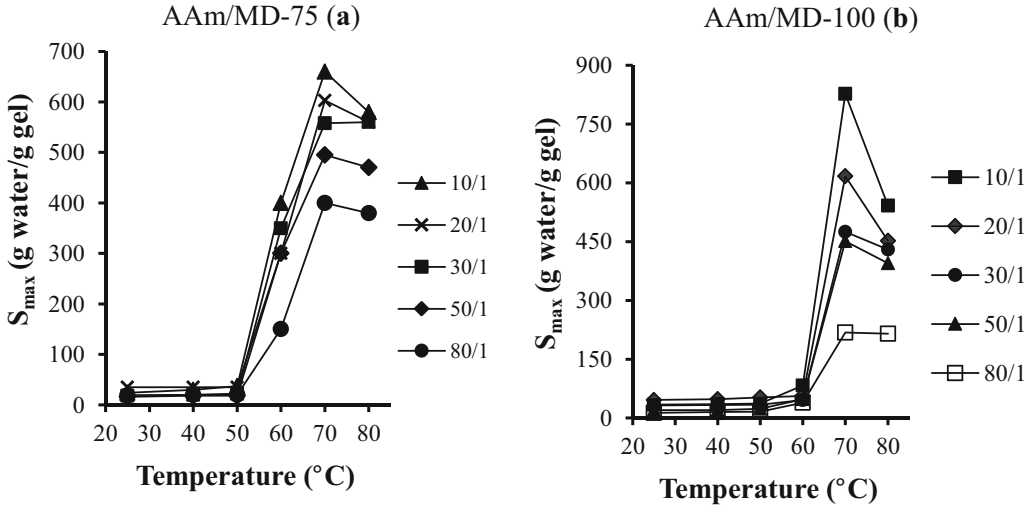


Figure 7. Variation of swelling capacity with temperature for (a) AAm/MD-75 and (b) AAm/MD-100 hydrogels in water.

increased. It takes about 20 h at these temperatures for the H-bonds between the acrylamide units to be completely weakened. During this period the gel appears to be reached equilibrium. At the end of the said period, the H-bonds between the acrylamide units are weakened, so the acrylamide units begin to form H-bonds with water molecules more easily and the activity, which is called the second step, begins. When AAm/MD-75 and AAm/MD-100 are compared with each other, the swelling behaviour is similar but the critical temperature of AAm/MD-75 is 10 °C lower than AAm/MD-100. This result can be explained by the fact that AAm/MD-75 contains the -COOH groups and these groups tend to make H-bonds with AAm units. Thus, the H-bonds between AAm units can be weakened more easily. Swelling capacities of the hydrogels were calculated using the experimental results of swelling studies and illustrated in Figure 7.

It is understood from Figure 7 that swelling capacity increases with increasing temperature up to 70 °C and decreases again at 80 °C. Swelling capacity was reached its maximum value of this study (660 g water/g gel for AAm/MD-75: 10/1 and 827 g water/g gel for AAm/MD-100: 10/1) at 70 °C. The decreasing of the swelling capacity at 80 °C can be explained by the reduction of the interactions between the water and hydrogel molecules at this temperature.

3.5 *Effect of pH*

Swelling studies of the synthesized hydrogels at different pH (between 2 and 12) media were carried to explore the variation of the swelling capacities of the hydrogels with pH of the environment. Since ionic strength is one of the parameters affecting the swelling capacity while preparing buffer solutions, the ionic strength was kept constant at μ = 0.03 mol-ion/L and the amounts of the components were adjusted. The obtained results are given in Figure 8.

It can be seen that from Figure 8(a) the swelling capacities of the AAm/MD-75 hydrogels at low pH values (acidic media) are being low. This is because the carboxyl groups of the hydrogel can not ionize as well in acidic media. Due to low ionization, carboxyl groups show hydrophobic character at low pH values.[49] In basic media (high pH values), carboxyl groups ionized well and the hydrogel negatively charged. Repulsive interactions among the ionized carboxyl groups result in the expansion of the gel and the swelling capacity is increased.[51] In Figure 8(b), the swelling capacities of the AAm/MD-100 hydrogels are not affected by the pH of the swelling media. This means that the AAm/MD-100 hydrogels are not pH-responsive hydrogels. Because there are no acidic or basic groups that can ionize in the structure of AAm/MD-100 hydrogels. Viscoelastic properties of polymers are not affected by the pH of the environment. Because the parameters that affect the viscoelastic properties in hydrogels are the crosslink density and accordingly the amount of water contained in the hydrogel.

3.6 *Swelling and diffusion kinetics*

Swelling kinetics of the synthesized hydrogels have been studied using the following equation proposed by Wu *et al.*[52]

$$t/S = A + Bt \quad (2)$$

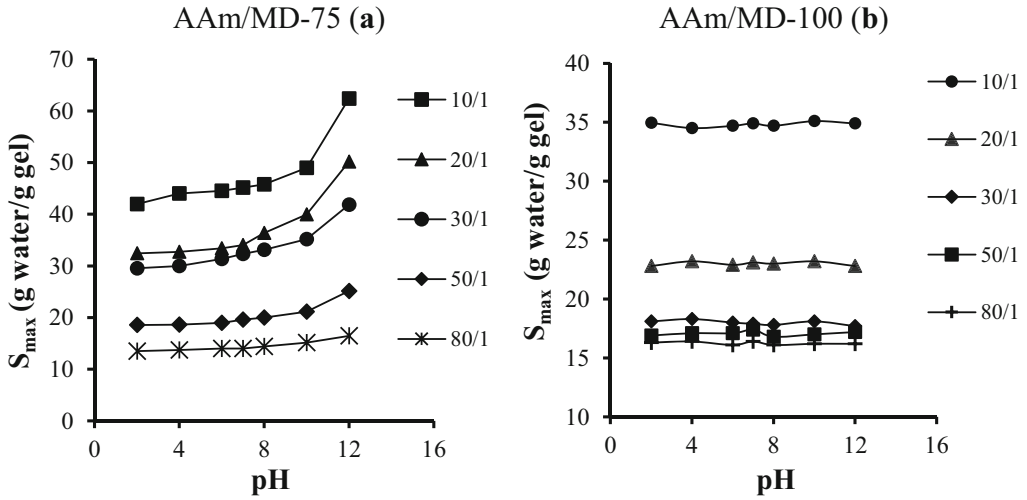


Figure 8. variation of swelling capacity with pH of the medium for (a) AAm/MD-75 and (b) AAm/MD-100 hydrogels at 25 °C.

Where S is the water uptake at time t, $B = 1/S_{eq}$ is the inverse of maximum or equilibrium swelling and $A = 1/(k_s.S_{eq}^2)$ is the reciprocal of the initial swelling rate $[(dS/dt)_0]$ of the hydrogel, and k_s swelling rate constant. Swelling kinetics studies were performed for all synthesized hydrogels. The kinetic behavior of the gels showing single-step swelling behavior appeared similar. Gels that have two-step swelling behavior also showed consistent behavior. Figure 9 shows kinetic curves obtained using Equation 2 for all AAm/MD-75 hydrogels at 25 °C, and for AAm/MD-75: 30/1 hydrogels at 70 and 80 °C.

In Figure 9b, two straight lines were obtained, one before the 20th hour and the other after the 60th hour, while a single line was obtained in Figure 9a. These results support the swelling behaviour results.

Diffusion of the water into the hydrogels was studied using the well known Fickian diffusion law[53,54] given in Equation 3 to determine the type and nature of the diffusion process.

$$F = M_t/M_\infty = K.t^n \quad (3)$$

In Equation 3, M_t and M_∞ are the amount of water absorbed by the gel at time t and at equilibrium respectively. K is the diffusion rate constant, t is the elapsed time after swelling has started and n is the diffusion exponent giving information about the diffusion type. Diffusion kinetics curves of the AAm/MD-75 hydrogels at 25 and 70 °C are given in Figure 10 as an example and the results of all of the hydrogels are given in Table 2 and Table 3.

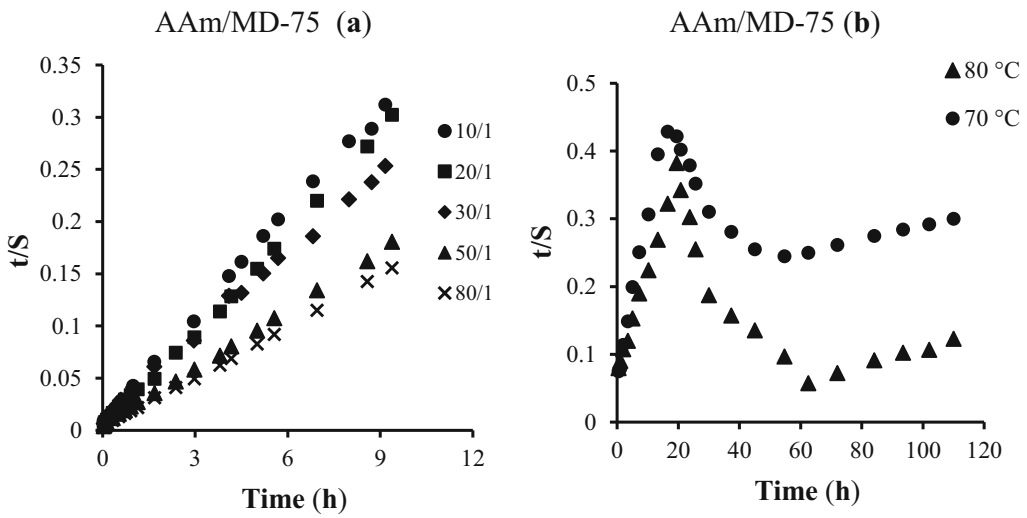


Figure 9. Swelling kinetics curves for (a) AAm/MD-75 hydrogels at 25 °C and (b) AAm/MD-75: 30/1 hydrogels at 70 and 80 °C in water.

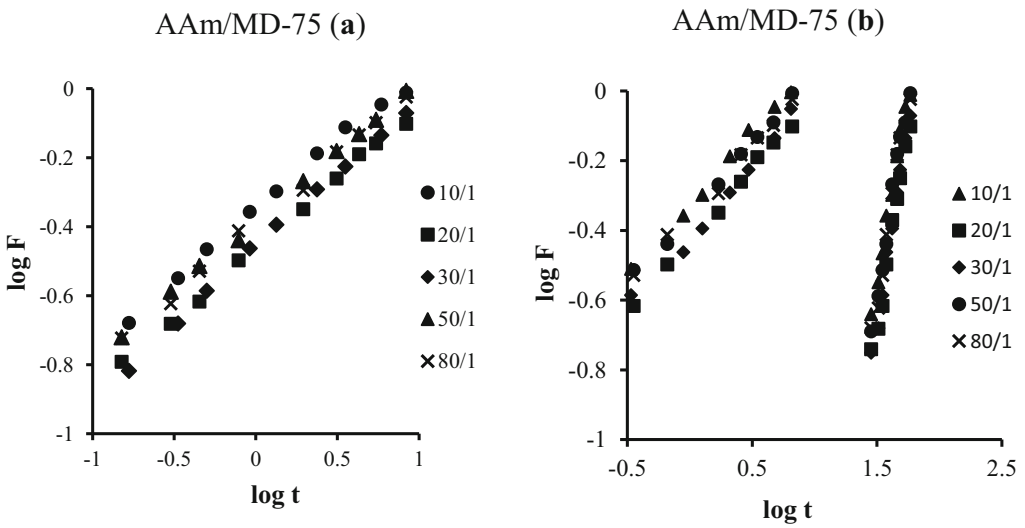


Figure 10. Diffusion kinetics curves for AAm/MD-75 hydrogels (a) at 25 °C and (b) at 70 °C.

Table 2. Diffusion kinetics parameters of AAm/MD-100 hydrogels.

AAm/MD-100	Temperature (°C)	n_1	n_2	$K_1 \times 10^2$	$K_2 \times 10^6$	S_{eq} (Theoretical)	S_{eq} (Exp.)
10/1	25	0.48	–	3.9	–	38	35
20/1		0.49	–	4.3	–	27	24
30/1		0.45	–	2.7	–	20	19
50/1		0.46	–	4.4	–	17	17
80/1		0.42	–	8.3	–	17	16
10/1	40	0.47	–	4.2	–	41	39
20/1		0.48	–	5.8	–	33	31
30/1		0.47	–	4.6	–	27	25
50/1		0.46	–	4.9	–	24	23
80/1		0.48	–	9.1	–	21	21
10/1	50	0.38	–	4.8	–	51	48
20/1		0.41	–	7.1	–	46	44
30/1		0.38	–	8.4	–	35	33
50/1		0.43	–	5.4	–	28	29
80/1		0.44	–	10.9	–	26	26
10/1	60	0.47	–	5.2	–	87	83
20/1		0.45	–	7.4	–	66	61
30/1		0.48	–	9.1	–	54	47
50/1		0.45	–	6.7	–	43	42
80/1		0.47	–	11.5	–	37	35
10/1	70	0.43	1.27	0.48	47.3	836	827
20/1		0.45	1.29	0.46	27.1	621	617
30/1		0.46	1.31	0.39	17.8	460	450
50/1		0.41	1.48	0.26	18.4	448	445
80/1		0.39	1.47	0.33	23.2	222	218
10/1	80	0.38	1.12	0.61	56.1	545	542
20/1		0.47	1.09	0.28	138	461	452
30/1		0.45	1.07	0.37	313	432	428
50/1		0.46	1.08	0.16	54.3	401	395
80/1		0.48	1.02	0.22	120	220	215

Table 3. Diffusion kinetics parameters of AAm/MD-75 hydrogels.

AAm/MD-75	Temperature (°C)	n_1	n_2	K_1 x 10^2	K_2 x 10^6	S_{eq} (Theoretical)	S_{eq} (Exp.)
10/1	25	0.5	–	1.2	–	44	44
20/1		0.59	–	2.1	–	35	34
30/1		0.65	–	1.5	–	32	30
50/1		0.58	–	2.2	–	20	20
80/1		0.58	–	2.4	–	12	13
10/1	40	0.57	–	1.8	–	51	49
20/1		0.60	–	2.3	–	38	37
30/1		0.65	–	2.1	–	34	32
50/1		0.57	–	2.4	–	26	25
80/1		0.55	–	2.3	–	21	20
10/1	50	0.58	–	2.4	–	57	57
20/1		0.60	–	2.0	–	43	41
30/1		0.64	–	2.1	–	35	36
50/1		0.52	–	2.7	–	36	33
80/1		0.54	–	2.3	–	32	28
10/1	60	0.52	1.09	3.7	24.2	412	400
20/1		0.51	1.04	3.1	16.5	371	365
30/1		0.56	1.05	4.3	63.4	363	353
50/1		0.63	1.05	1.3	18.6	303	300
80/1		0.51	1.08	3.4	23.7	158	150
10/1	70	0.59	1.13	0.42	13.5	672	660
20/1		0.58	1.24	0.38	9.05	610	603
30/1		0.56	1.73	0.23	9.36	560	561
50/1		0.52	1.17	0.35	6.96	505	495
80/1		0.60	1.28	0.61	13.0	408	400
10/1	80	0.61	2.78	0.11	3.2	582	571
20/1		0.58	2.83	0.07	2.1	569	560
30/1		0.61	1.38	0.05	2.3	563	551
50/1		0.64	2.15	0.06	2.7	481	470
80/1		0.65	2.25	0.08	2.4	392	380

It is clear from Figure 10 that gels exhibiting two-step swelling behavior (Figure 10b) have different kinetics at each step. However, gels that swell in one step (Figure 10a) have uniform kinetics.

According to Fick's Law, diffusion type of the water into the hydrogel depends on the diffusion rate ($R_{diff.}$) of the water and relaxation rate (R_{rlx}) of the hydrogel.[55] In case of $R_{rlx} >> R_{diff.}$ then the diffusion is Fickian type and $n < 0.5$. If $R_{diff.} >> R_{rlx}$ the diffusion is relaxation controlled that non-Fickian type and $0.5 \leq n < 1.0$. If the diffusion rate and the relaxation rate are very close to each other ($R_{diff.} \approx R_{rlx}$) then the diffusion is super case diffusion and $n \geq 1.0$. all of the kinetic parameters obtained for the hydrogels are given in Table 2 and Table 3.

When the results in Table 2 are evaluated, one *n* value was found for AAm/MD-100 hydrogels at temperatures ($T \leq 60$ °C) with a single-step swelling behavior. Since this *n* value is less than 0.5 for all of the AAm/MD-100 hydrogels, the type of diffusion was determined as the Fickian type diffusion. On the other hand, two *n* values were found, one less than 0.5 and the other greater than 1.0 for AAm/MD-100 hydrogels at temperatures (70 and 80 °C) where two-step swelling behavior was observed. In this case, the diffusion type was found as Fickian type for the first step and super case for the second step. Diffusion kinetic parameters of AAm/MD-75 gels are given in Table 3. The results are similar to those of AAm/MD-100 gels. Differently, the diffusion type at temperatures ($T \leq 50$ °C) in which single-step swelling behaviour was observed and the first steps of the temperatures ($T \geq 60$ °C) where two-step swelling behavior was observed were determined as non-Fickian type diffusion. Theoretical and experimental swelling capacities of hydrogels seem to be compatible with each other.

4. Conclusions

Several hydrogels of modified maleic anhydride and acrylamide were synthesized. All of the synthesized hydrogels exhibited different swelling behaviours and kinetics at low and high temperatures. All hydrogels

exhibited two-step swelling behavior at 60 °C and higher temperatures, while they showed single-step swelling behavior at temperatures below this temperature. Hydrogels using the derivative in which maleic anhydride is modified by 75% (AAm/MD-75) are highly affected by the pH of the medium since they have -COOH groups. Hydrogels with high AAm/MD ratio showed low swelling capacity due to H-bonds between acrylamide molecules. At temperatures above 50 °C, these H-bonds were weakened and swelling capacity increased very quickly. Diffusion of water into hydrogels at low temperatures and at the first step of high temperatures were determined as Fickian type diffusion for AAm/MD-100 hydrogels and non-Fickian type diffusion for AAm/MD-75 hydrogels. It was found as a super case diffusion type for all hydrogels in the second step at high temperatures where two-step swelling behavior was observed.

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