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Novel Method of Oil/Water Separation Using Composite of Polymethylacrylamide Hydrogel-Coated Metal Mesh

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Abstract

Different compositions of hydrogels composed of mathacrylamide homopolymer (60 and 90% of PMAM) were prepared using the free radical polymerization technique, with and without methylene bisacrylamide as crosslinker (0 and 3%). Several parameters and properties were studied to evaluate their performance as oil/water separators. Many parameters are used, such as residual oil in water, water recovery, separation time, hydrogels coated percentages, swelling parameters, mechanical properties, microscopic and photographic images, and scanning electron microscopy. The results showed that water recovery (87-97), Separation efficiency (96.2-99.6 %), separation time (6-9.5 min.), hydrogels coated percentages (18-23 %), water content (70-97 %), and tensile test (63-90 MPa). The effect of polymer crosslinking density, mesh pore size, and polymer composition on the parameters and properties mentioned above were also studied. The results showed that the separation efficiency of 1000 micron mesh composite is better than 500-micron mesh composites.

Keywords: Hydrogel, composite, oil/water separation, separation efficiency.

1. Introduction

Separating oil and water mixtures is a important task, the key for the clean-up of the environment after oil spillages [1]. The separation of oil/water mixture is a serious issue that many industries must consider. Many new methods to separate oil from water are designed as the production of oil/water mixtures increases in the worldwide [2]. These methods include API gravity separator, centrifuge, hydro-cyclone, induced gas floatation, and membrane filter [3-7]. Membrane filter is usually made of hydrogel material, the term "hydrogel" refers to the hydrophilic polymeric networks that are insoluble in water and can absorb it from 25% to many times their dry weight because of the presence of a three-dimensional network. Existing hydrogel materials, which are claimed to be helpful in some critical applications, such as the separation of oils from water, are derived almost exclusively from hydrophilic monomers such as acrylamide derivatives, acrylic acid, ethylene glycol, vinyl alcohol, ethylenimine, vinyl pyrrolidone, and hydroxyl ethyl methacrylate [8, 9]. The swelling parameters in water, mechanical and thermal properties, and many other properties are also affected by the degree of crosslinking in the polymer network [10, 11]. Many works in this field have been used hydrogels and other materials as membrane filters for oil/water separation. Kalaleh *et.al.* have prepared a novel and superabsorbent hydrogel composed of a copolymer of acrylamide with sodium acrylate. The composite of these hydrogels with steel meshes shows outstanding performance as an oil/water separator; the separation efficiency reached 97 % [12].

On the other hand, Crick *et.al.*have mentioned the application of hydrophobic polymeric material for separating hydrophobic solvents such as hexane, petroleum ether, and toluene from water. In this study, the coated mesh was designed to prevent water from passing through it, whereas hydrophobic solvents are allowed to pass through the hydrophobic layer (polysilicon) [13]. This work aims to synthesize crosslinked methyl acrylamide hydrogels, to prepared composites composed of the prepared crosslinked polymers hydrogels and meshes with different pore sizes, and study the properties and performance of the prepared coated meshes for separation of oil from water.

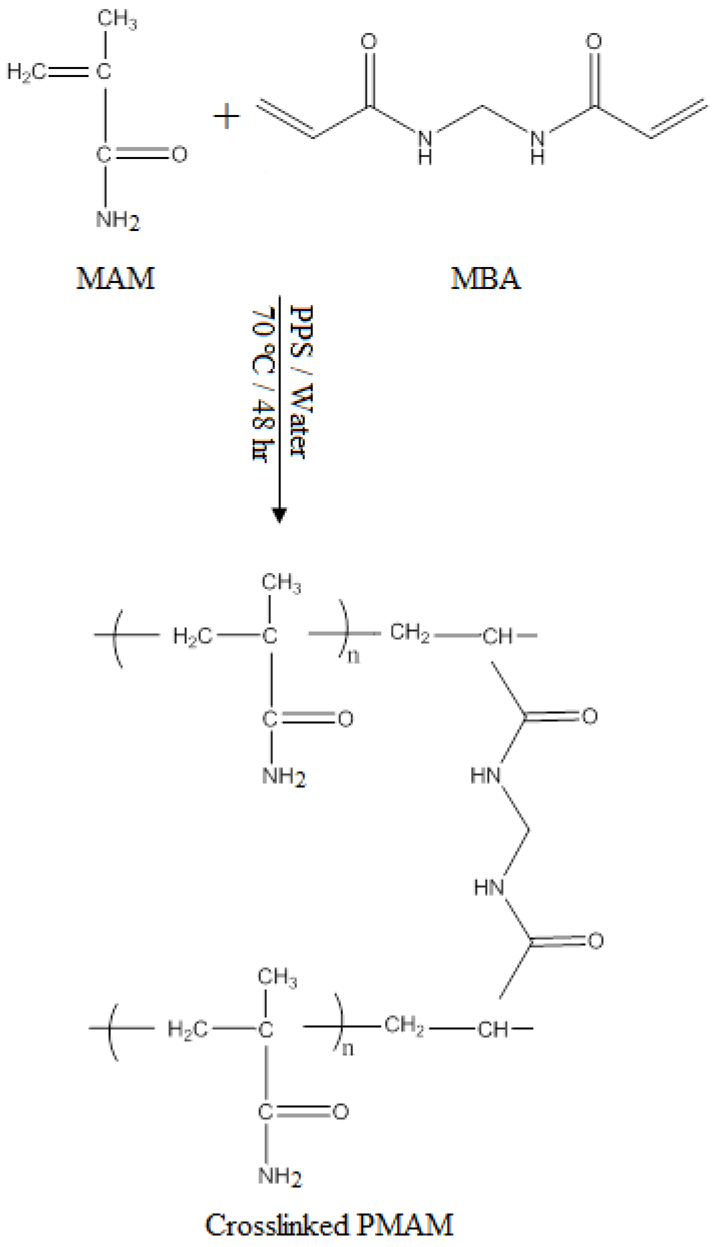
2. Experimental Section

Materials

The monomer methacrylamide (MAM) and the crosslinker methylene bisacrylamide (MBA) were obtained from Aldrich-oma chemical Co and purified by recrystallization from chloroform. Potassium persulfate (PPS) was supplied by Aldrich-oma chemical Co and recrystallized twice from methanol before use. Corn oil was collected from the local market. All solvents were used as received.

Preparation of Hydrogels

Based on the monomers and crosslinking agent concentrations, two compositions of hydrogels have been prepared. The mixture was produced according to the desired composition (Table 1) in a small stopper flask. The mixture was stirred for 15 minutes before being transferred to glass ampoules. All oxygen was removed from the tubes by purging them with nitrogen for 15 minutes. To ensure complete conversion of the monomers and produce to polymer forms, free radical initiated reactions were preferred at conventional temperatures ranging from about room temperature to about 100 °C. To minimize the formation of bubbles in the polymers, polymerization was usually started at a temperature of 30-80 °C. The glass ampoules were placed in the water bath at 70°C for two days for polymerization. The temperature was then raised, and the tubes were placed in a 90°C oven for another day [14]. The reaction is shown in (**Scheme 1**).



Scheme 1. Reaction of crosslinked poly (MAM)

Table 1. Feed compositions of poly (MAM) hydrogels

Exp.	methacrylamide % MAM wt./mixture wt.	potassium persulfate % PPS wt./mixture wt.	methylene bisacrylamide % MBA wt./mixture wt.	Solvent (water) vol ml
1	60	0.40	0.0	15
2	90	0.40	0.0	15
3	60	0.40	3.0	15
4	90	0.40	3.0	15

Preparation of Mesh-Hydrogels Composites

The prepared hydrogels were then fabricated with metal meshes having different pore sizes (500 and 1000 microns). The prepared coated meshes were tested for separating oil from water. The polymer solution is put into a square dish to make covering the mesh pieces easier. The clean mesh was carefully submerged in the solution of prepared hydrogel for about 30 seconds before being slowly and horizontally removed with the solution adhered to its surface, as shown in **Figure 1.** The mesh was dipped and baked for one day at 80°C to thoroughly polymerize the solution. This enabled the coated solution to be thermally initiated and converted into a polymerized hydrogel. The coated mesh was washed with distilled water after polymerization to remove the impurities such as unreacted initiator, monomers, and any other byproducts left over from the preparation procedure.

Figure 1. Preparation of mesh-hydrogels composites

Separation of Oil from Water Using Mesh-Hydrogels Composites

In a beaker, 50 mL of 10% oil /90% water mixture was prepared by mixing the amounts of the two components and stirring at 500 rpm for 25 minutes to form the emulsion, as shown in Figure 2. The mixture was then poured onto the upper glass tube on the hydrogel-coated mesh, sandwiched between two loose plastic pieces (30 mm in diameter. The oil remained in the upper coated mesh, whereas the water passed through the hydrogels.

Figure 2. Separation process of oil/water mixture

Characterization

Parken Elmer-1650 spectrophotometer was used to determine the functional groups in the copolymers using a KBr disk method at a wavenumber range of 400 to 4000 cm-1. Shimadzu-3600 UV spectrophotometer was used to estimate the concentration of the oil after filtration according to a standard procedure.

Water Recovery and Reclaimed Oil

After separation, the amount of water recovered and the amount of reclaimed oil was evaluated. The water recovery is measured using equation 1, whereas reclaimed oil % was estimated using equation 2

$$Water\ Recovery = \frac{(Vwater)filtrate}{(Vwater)initial} \times 100 \qquad (1)$$

Where (Vwater) initial is the volume of water in the initial feed mixture, and (Vwater) filtrate is the volume of water in the filtrate solution.

$$Reclaimed\ Oil = 1 - \frac{(Voil)filtrate}{(Voil)initial} \times 100 \qquad (2)$$

Where (Voil) filtrate is the volume of oil in the filtrate solution and (Voil) initial is the volume of the oil in the initial feed mixture.

Duration Time of Separation Process

Separation time was measured directly during the experiments; therefore, no additional calculations were required. The separation time was calculated by counting the seconds from the time the combination was placed on top of the coated mesh until no fluid droplets could be seen dripping from the mesh's bottom for at least three seconds.

Calculation of Coating Percentage with Hydrogel

The coating percentage with hydrogel was calculated using equation 3 [15].

Wb is the mass of the uncoated mesh before immersion in the hydrogel, and Wa is the mass of the coated mesh after polymerization. The percentage of hydrogel-coated mesh was calculated based on varied mesh pore diameters (500 and 1000 microns).

Estimation of the Residue Oil-in-Water

The residue oil-in-water after must be analyzed after separation. The oil was first extracted from water by using a suitable organic solvent (hexane). The organic layer was separated from the aqueous layer using a separator funnel. After separation, the oil content was calculated using the oil calibration curves in the hexane. The concentration of the oil after filtering was determined using a UV-VIS spectrophotometer in the separation system, according to a standard method.

Swelling

The gels were dried at room temperature for several days before being put in a vacuum oven at 50°C until they reached constant weight. The dried discs were weighted and put in (50 ml) sample vials. The swelling time was counted from when the deionized water was added to the vial. The weight increment of the discs as a function of time was used to record the swelling gravimetrically. The swollen piece of hydrogel was regularly removed from the water, gently placed between two pieces of filter paper to remove excess water from the surface, and then weighed before being returned. The equilibrium water content (EWC) of a hydrogel was calculated using the weight of discs after (30 days of being completely hydrated) and the weight of the same discs after being dried in an oven at 50 °C for (48 hr). EWC was calculated as follows for the same sample [16]:

Where Ws and Wd are the weights of the swollen sample after 30 days of complete hydration and after 48 hours of drying in a 50°C oven, the following relation was used to calculate the weight reduction of the xerogels:

Where W0 and Wd are the weights of the xerogel sample and the dried sample after 48 hours in a 40°C oven.

Scanning Electron Microscopy (SEM) and Light Microscopy

The surface topography of the sample was investigated using SEM. An acceleration voltage of 5 to 10 kV captured the images. Carbon tape was used to secure the coated mesh (0.5 cm) test specimens on aluminum stubs. Before the measurements, the samples were sputter coated with 10 nm gold using a high-resolution sputter coater. To assess the droplet size, 5 mL of oil was placed under light microscopy (EVOS fl digital inverted microscope), and 5 images were taken randomly from different places using a camera microscope.

Tensile Testing

The tensile test was used to determine the mechanical properties of the coated mesh. These tests were carried out on an Instron 3366 machine in accordance with ASTM 3039. The load was run at a constant speed of 2 mm/min until the sample was broken. The coated meshes were cut with dimensions of (100 mm in length and 9-10 mm in width).

3. Results and Discussion

The structures of the poly MAM are shown in **Figure 3**. The absorption bands are as follows: MAM's carbonyl absorption of 1665 (amide C=O). The N-H asymmetrical stretching vibration of the amide group in MAM was detected as a broad band at 3320 cm-1. MAM's C-N and N-H stretching vibrations were found in a band at 1320-1390 cm-1. The C-N stretch vibration of MAM is responsible for the sharp band at 1425 cm-1. Furthermore, the absence of an olefinic double bond peak in the copolymers, which appeared in the FTIR of the monomer at about 1555 cm–1, confirms the polymer formation.

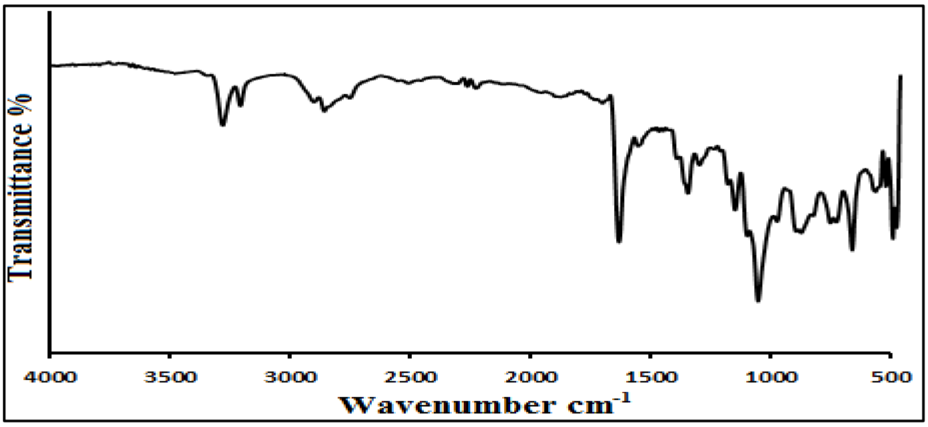


Figure 3. FTIR spectrum of poly MAM

Evaluation of Separation Process

Water Recovery

Figure 4 shows the water recovery percentage based on two MAM concentrations (60 and 90 percent) in the PMAM hydrogel-coated mesh for different mesh sizes (500 and 1000 m) (with and without crosslinker). When the MAM concentration in PMAM is increased from 60% to 90%, the water recovery improves as the hydrogel thickens. As the polymer concentration increases, the viscosity of the solutions grows as well. On the other hand, the polymer with a crosslinker is less water recovery than without a crosslinker. A larger MBA concentration generally resulted in a stronger gel with less water. The increase in crosslinker density reduces the migration of water molecules into the gel network, which was expected. Therefore, the hydrogel, which contains a crosslinker (MBA), absorbs a small amount of water in the swollen equilibrium state. This finding has been frequently reported in many other investigations [17, 18].

On the other hand, water recovery varied and fluctuated depending on mesh sizes and monomer concentrations, as seen in **Figure 4**. Water recovery for the two mesh sizes was between 87 and97 percent. Water recovery cannot exceed 97 percent since the hydrogel holds some water.

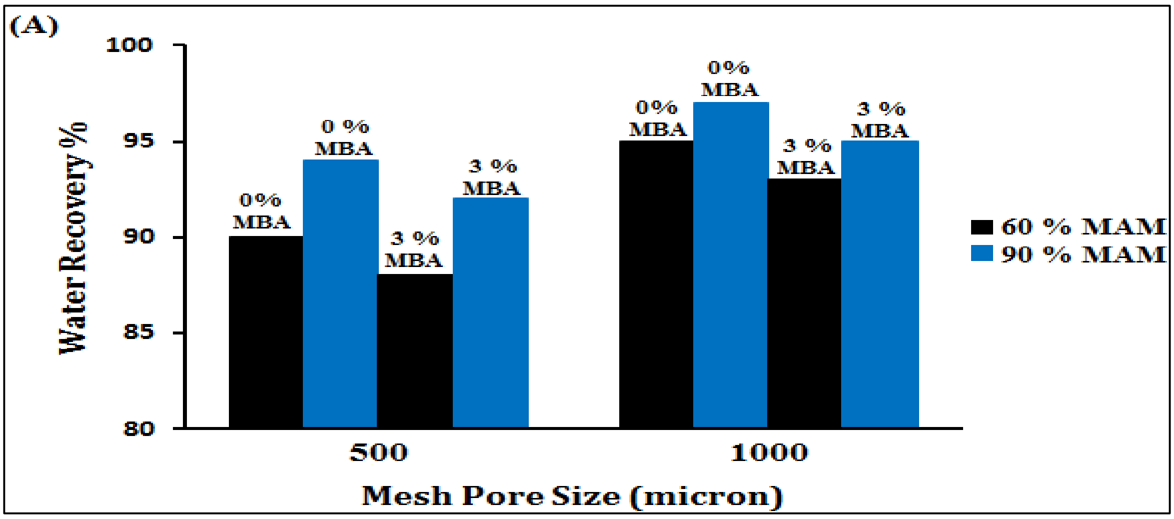


Figure 4. Water recovery of PMAM with different composition

Residual Oil in Water

The probable presence of residual oil in the filtrated water was tested using UV-visible spectroscopy to confirm the excellent separation efficiency. **Figure 5** shows the separation efficiency of poly MAM. The highest separation efficiency was for 90%MAM with 3%MBA in based on 1000 micron mesh was calculated as 99.4. These values did not change when hydrogel was prepared with using crosslinker (MBA).

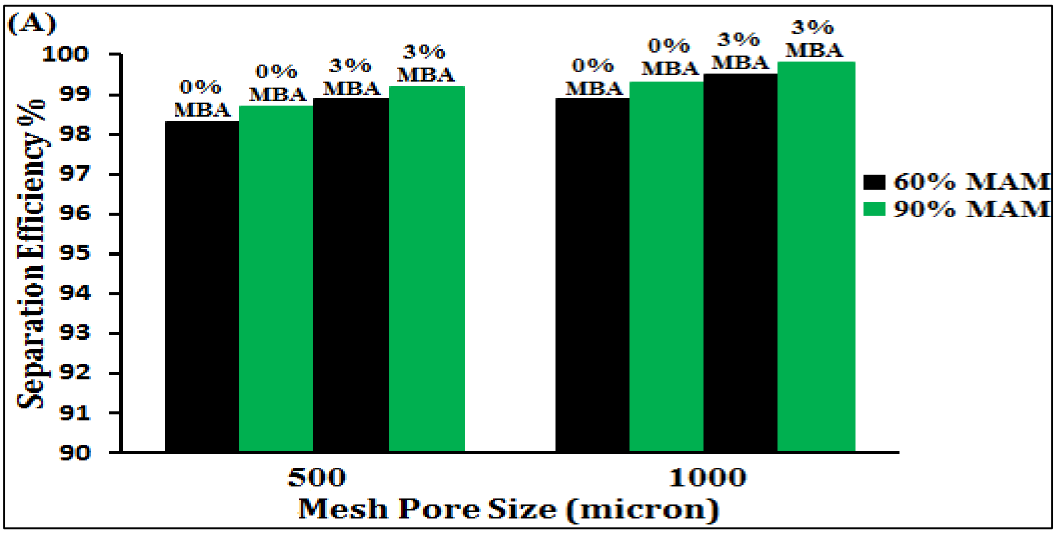


Figure 5. Separation efficiency of MAM/EMA copolymer with different composition

As demonstrated by light microscopy images, there is also a considerable difference in phase composition between the feed and the filtrate, as illustrated in **Figure 6**, where the collected filter (right) is transparent compared to the original mixture (left).

Figure 6. Microscopic and photographic images before (left) and after separation (right) based on the 1000 micron mesh

Duration Time of Separation Process

The separation time has decreased as the increasing mesh pores for 500 and 1000 microns **Figure 7**. The PMAM with 60 % MAM monomer was separated the fastest. This happens because the hydrogel layer becomes thin using low monomer concentration, resulting in faster separation. However, as the hydrogel became thicker, the separation time increased as the monomer content in the hydrogel increased. Thus, 90PMAM is more separation time than 60PMAM. In addition, it was observed that increasing the crosslinker (MBA) amount in the copolymer increases the separation time. This result was expected since the crosslinker decreased the swelling ability of hydrogels.

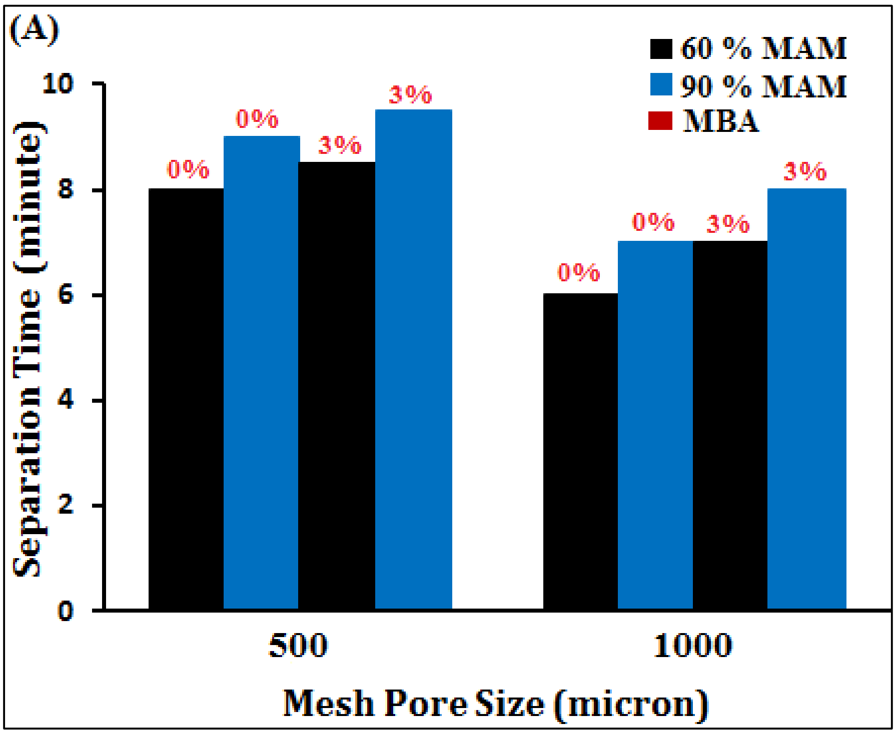


Figure 7. Separation time of MAM homopolymers

Coating Percentage with Hydrogel

The lowest mesh pore size was covered with gel more than the coarse mesh pore size, as seen in **Figure 8**, which increased the hydrogel's absorption ability and improved oil/water separation. Furthermore, raising the hydrogel concentration increases the fraction of hydrogel-coated mesh. The hydrogel was thinner with low monomer content than with a greater monomer concentration. Thus, hydrogels composed of 90% MAM were thicker than hydrogels consisting of 60% MAM. Moreover, it can be observed that the crosslinker concentration increased from 0 to 3%, and the coating percentage increase. These results may be explained by increasing the crosslinking density of the hydrogels so that the hydrogel layer will be thicker. Hydrogel coating percentage measurements verified the effect of monomer and crosslinker concentrations on the hydrogel thickness.

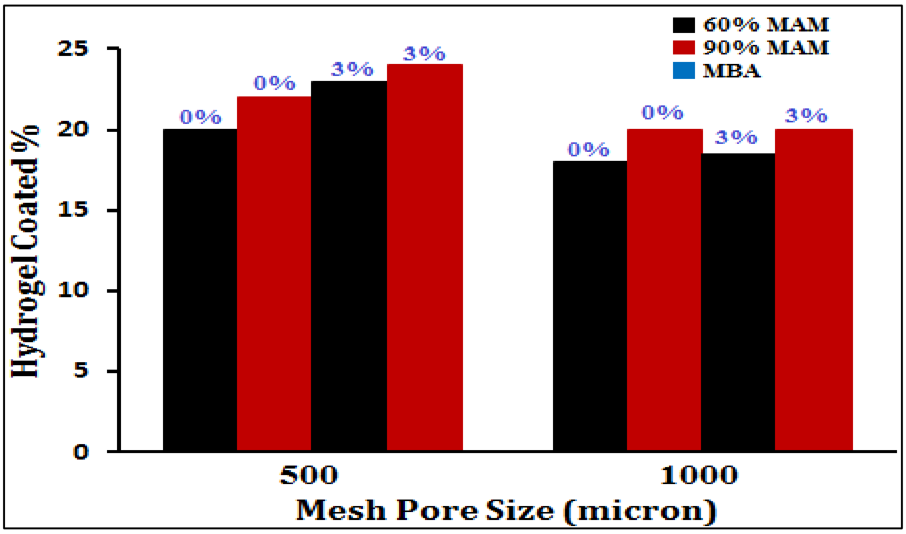


Figure 8. Hydrogel Coated % of 90MAM and 60MAM as a function of mesh sizes

Swelling Parameters

The EWC values of the hydrogels are shown in **Table 2**. They are in the range of (97.01 – 70.22%). 60% of PMAM with 3%MBA had the lowest swelling capacity, while 90% of PMAM without MBA had the highest EWC. The crosslinker (MBA) absence in the hydrogel structure allows water molecules to diffuse easily outside the gel phase. As expected, weight loss during swelling in the prepared hydrogels decreases with increasing MBA contents.

Table 3. Water content, EWC at different times for PMAM90 and PMAM60 gels with and without MBA

Time	**EWC %**			
	Poly methacryamide 90 0% methylene bisacrylamide	**Poly methacryamide 90 3% methylene bisacrylamide**	**Poly methacryamide 60 0% methylene bisacrylamide**	**Poly methacryamide 60 3% methylene bisacrylamide**
1 (hr)	90.11	86.33	71.21	66.43
2 (hr)	91.01	86.88	71.79	66.99
3 (hr)	91.97	87.55	72.61	67.22
4 (hr)	92.55	87.77	72.91	67.88
5 (hr)	92.95	88.22	73.22	68.55
6 (hr)	93.43	88.91	73.71	69.22
8 (hr)	93.79	89.21	74.01	69.90
11 (hr)	94.55	89.88	74.32	70.33
13 (hr)	95.88	90.11	74.92	70.94
20 (hr)	96.41	90.76	75.41	71.59
24 (hr)	97.31	90.99	75.88	71.79
2 (day)	98.12	91.52	76.19	72.67
3 (day)	99.07	91.90	76.77	72.96
6 (day)	98.53	91.33	76.11	71.55
9 (day)	98.12	91.01	75.41	71.08
13 (day)	97.98	90.88	75.01	70.60
15 (day)	97.54	90.51	74.88	70.09
19 (day)	97.23	90.08	74.55	70.02
24 (day)	97.08	90.00	74.07	70.05
27 (day)	97.06	90.10	74.05	70.10
30 (day)	97.01	90.06	74.17	70.22

Mechanical Tests (Tensile Testing)

The results of tensile tests reveal that as MAM concentration increases, stress modulus increases. So, the stress of 500 microns mesh coated with 90% PMAM (**Figure 10)** is more than 60% PMAM (**Figure 9**). This behavior could be attributed to an increase in the monomer (MAM) concentration, which led to increased interaction with the mesh. On the other hand, when the crosslinker amount was 3% for 90% PMAM (**Figure 11**), the stress was more than 90% PMAM without the crosslinker (**Figure 10**). The obtained results could be explained in terms of increasing the crosslinker amount will restrict the mobility of the polymer chain. Thus the polymer will be stronger [19, 20]. **Figures (11 and 12)** show the effect of the mesh pore size on the mechanical properties of 90% PMAM+3% MBA. The mechanical properties enhance as the pore size of the mesh decrease from 1000 to 500 microns. These results could be attributed to the interaction between 500-micron mesh and polymer is more than 1000 micron mesh.

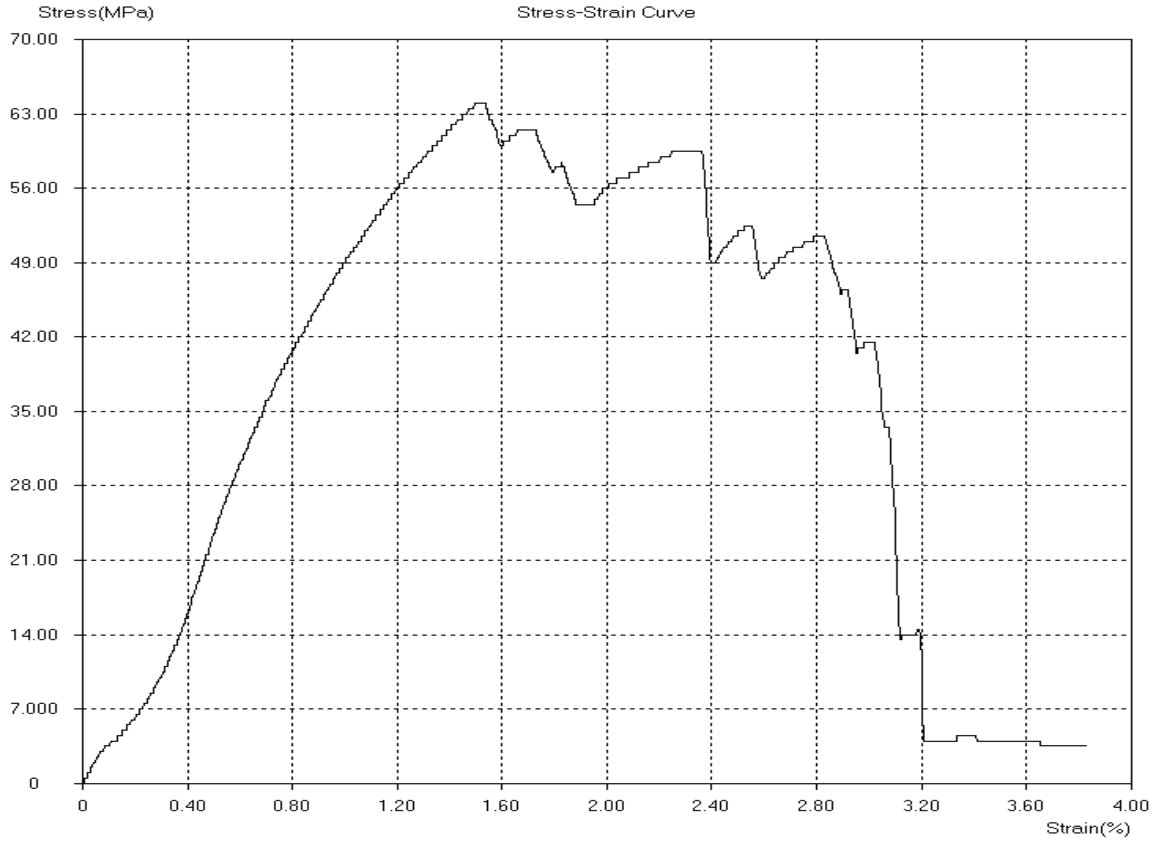


Figure 9. Tensile test of 500 micron pore size mesh coated with 60%PMAM

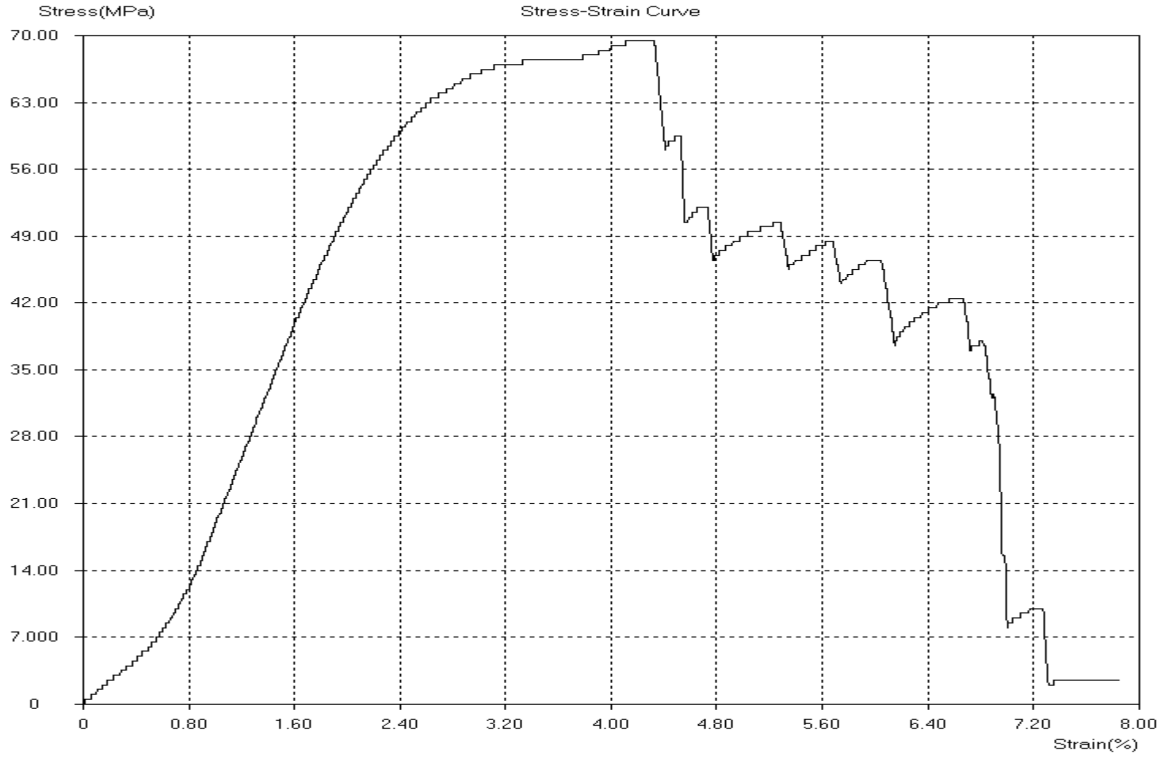


Figure 10. Tensile test of 500 micron pore size mesh coated with 90%PMAM

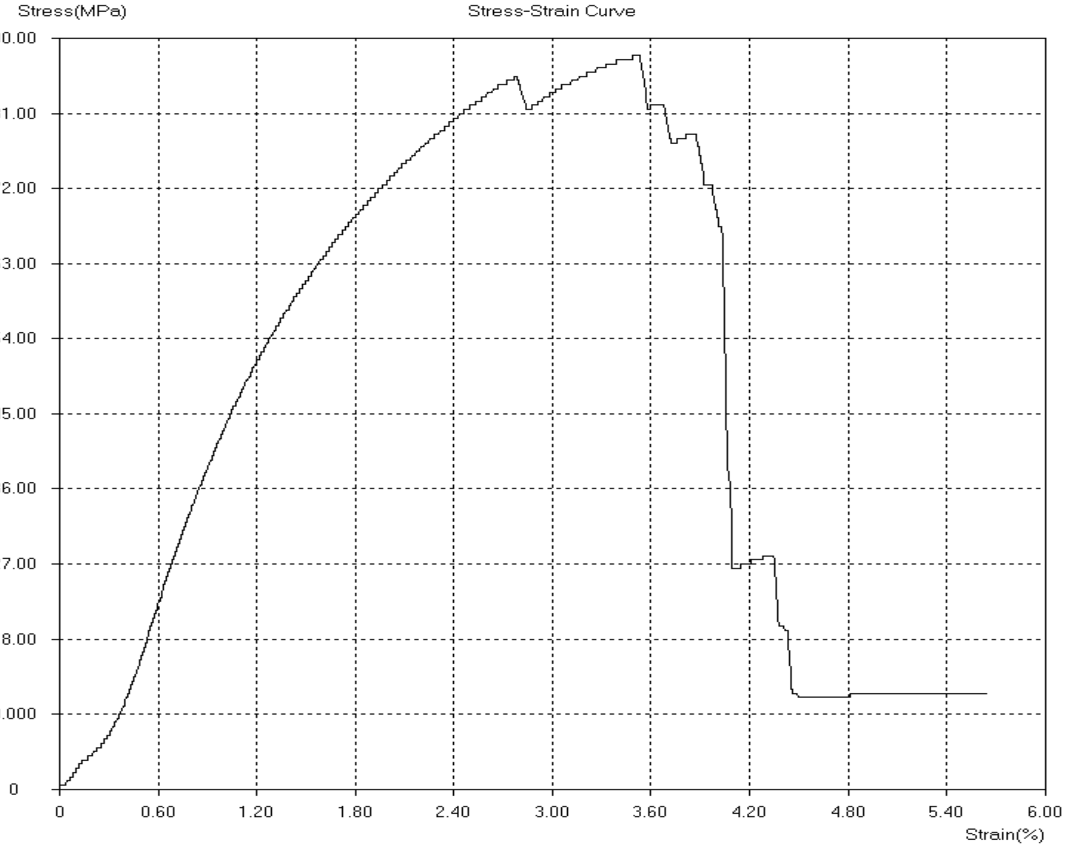


Figure 11. Tensile test of 1000 micron pore size mesh coated with 90%PMAM + 3% MBA

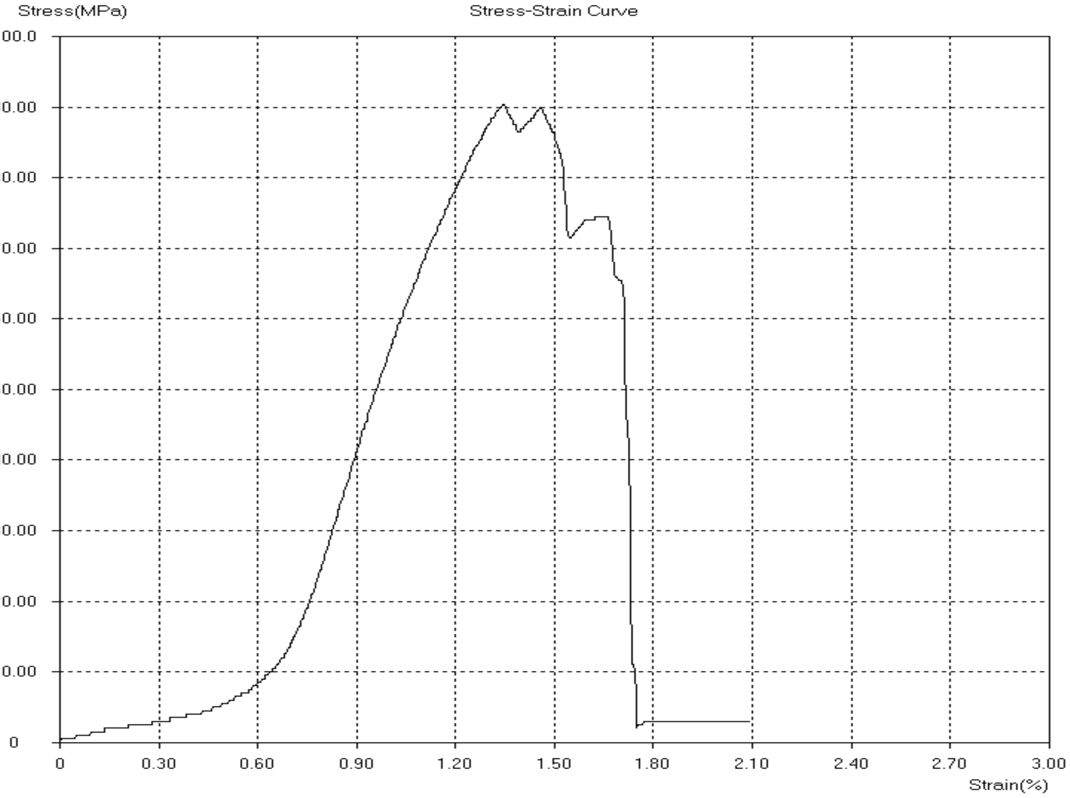


Figure 12. Tensile test of 500 micron pore size mesh coated with 90%PMAM + 3% MBA

Scanning Electron Microscopy (SEM)

Figure (A) shows typical photos of uncoated mesh substrates with 1000 micron pores, indicating that the original meshes had smooth and clean surfaces. **Figure 13** (B and C) shows the SEM images of PMAM polymer (60% MAM and 90% MAM) with a 3% crosslinker coating mesh with a pore diameter of about 1000 microns. The surface of the 60 %t MAM +3 %t MBA hydrogel was less rough and smother than the mesh with 60 % MAM +3 % MBA, as shown in SEM photos in **Figure 3.36**.

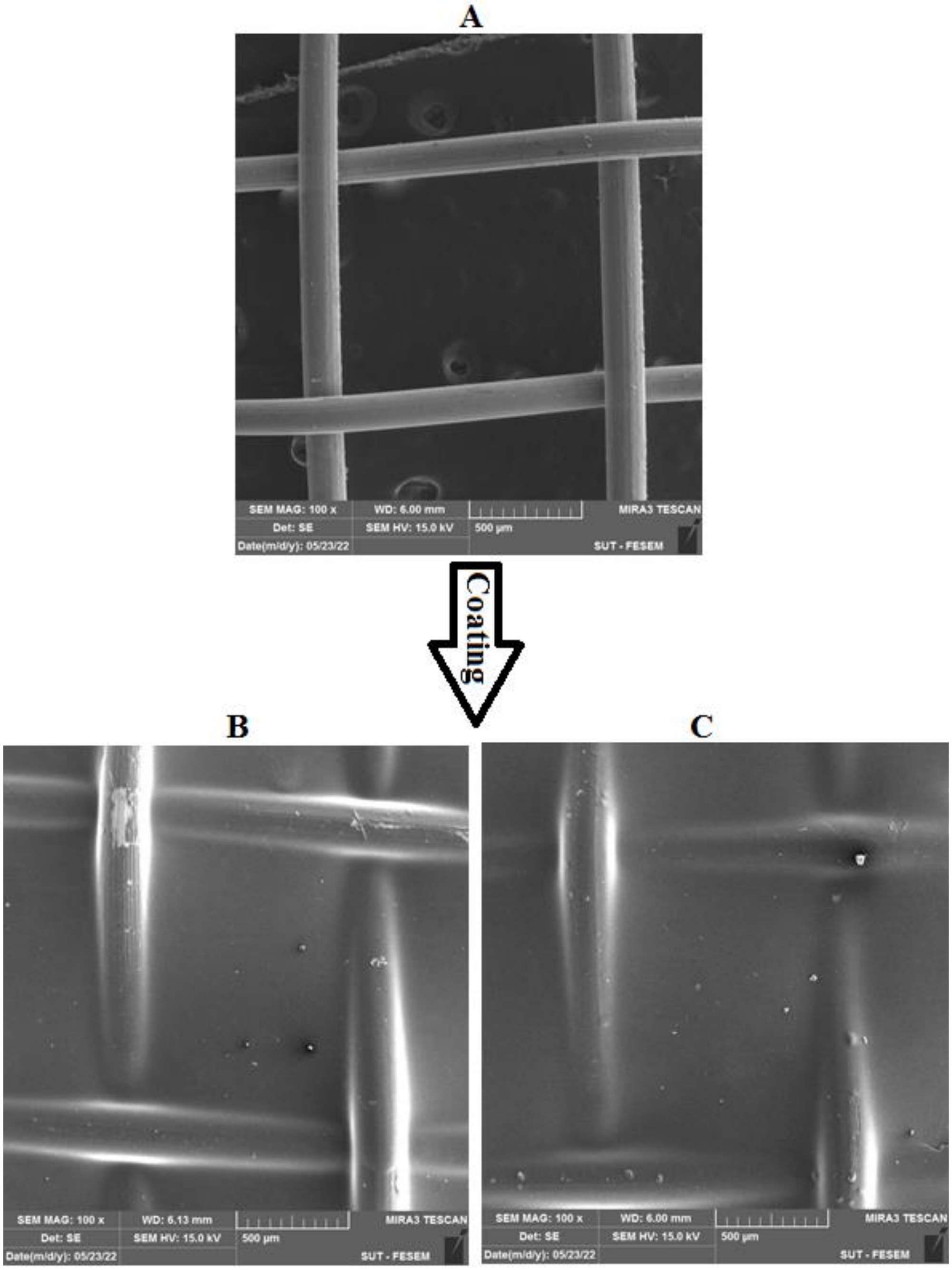


Figure 13. SEM images of A- uncoated mesh (1000) microns, B- mesh coated with 60% MAM /3%MBA, C- mesh coated with 90%MAM/3% MBA

4. Conclusion

Hydrogels of poly methyl acrylamide were successfully prepared. The preparation process was achieved with and without MBA as a crosslinker. The prepared hydrogels were successfully fabricated with meshes having different pores sizes. The fabricated meshes were then used to separate the oil/water mixture. Several properties and parameters were studied to evaluate the coated meshes' performance for the separation process. The composition 90%MAM with 3%MBA shows good performance when coated with meshes having 1000 micron pore size. Finally, the mechanical properties of the prepared coated meshes could be improved by using the crosslinker in the preparation of the hydrogels.

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