Modification and characterization of polyvinyl chloride by graft copolymerization with acrylamide

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Abstract. Polyvinyl chloride (PVC) was dehydrochlorinated in alkali solution (Sodium Hydroxide NaOH) and then grafted with acrylamide (Am) by free-radical polymerization and using benzoyl peroxide (BPO) as an initiator under inert atmosphere. The investigations involved examining the degree of dehydrochlorination on PVC by using different concentration from NaOH in the solution (1, 3 and 5 molarity) and determine the optimum dehydrochlorination and grafting efficiency of acrylamide on pure PVC and different molarity dehydrochlorinated PVC. The dehydrochlorinated polyvinyl chloride (DHPVC) and grafted copolymer (PVC-graft-Acrylamide) was characterized by FTIR, Raman spectrometer, EDX analysis. The results shown that, the highest loss of chlorine by using the 3 M ratio of NaOH and the best grafting was in the use of DHPVC 3M.

1. Introduction
Polyvinyl chloride (PVC) is one of the significant thermoplastic polymers and widely used because of its versatile nature, low price, good performance, wide property range and can be modified within broad limits (from rigid and hard to rubber-elastic and soft). PVC is a polymer that having featured chemicals resistance property, and easily processed in versatile manner with high recyclability [1-3].

PVC degradation occurs at high temperatures, ultraviolet light or high mechanical stresses, all in the presence of oxygen. polymer degradation starts by successive elimination of hydrogen chloride (HCl), which is called dehydrochlorination, giving long-chain polyenes. This consequently causes in an intense discoloration, deterioration of the mechanical properties, and a lowering of the chemical resistance of the polymer [1, 4]. To improve the dehydrochlorination of PVC, some additives were used. One of them was sodium hydroxide (NaOH), the most important additives. The NaOH affected the dehydrochlorination efficiency and could decrease the hydrothermal temperature from 300 °C to 150–250 °C [5, 6]. Many studies have investigated PVC dehydrochlorination by alkaline solution. The maximum rate of the dehydrochlorination for rigid PVC was at 3 M NaOH [7], while for flexible PVC was at 5M NaOH but dropped at 7M NaOH [5]. Also, (1.0 M NaOH/diol solution) effective solvents was investigated previously to improving the dehydrochlorination of PVC, giving in higher yields of dehydrochlorination, lower reaction temperatures (110 –150 °C) and shorter reaction times [8].

For PVC recycling and functionalization purpose, there is different chemical modification methods have been used. These methods include substitution, elimination (dehydrochlorination) and grafting copolymerization. Functionalization of DHPVC can be obtained by its double bonds reaction, which can be activated by a free radical initiator [9, 10]. Conventional free-radical polymerization (FRP) is stay one of the most significant polymeric materials preparation method due to the large extent of monomers can be polymerized and copolymerized, which yields a range of novel materials. The engineering macromolecules of various block and graft structures is excellent approach in obtaining polymers with unique physical and chemical feature [1, 11, 12].
The basic difference between block and graft copolymer synthesis is the sites position and functions at the chain ends or on the chains, respectively. Grafting is a way where in monomers are covalently bonded onto the polymeric backbone. The general methods to investigate grafting copolymers are: (1) grafting-through, in which the macromonomers are copolymerized; (2) grafting-onto, the side chains are prepared, and then attached to the backbone; and finally (3) grafting-from, where the activated sites are randomly created on the long polymeric backbone. These positions are capable of starting the polymerization of a second monomer, leading to grafting copolymers. Grafting-from method advantages are control of the backbone molecular weight with narrow molecular weight distribution and high grafting density, while the difficult control of branch molecular weight, its pronounced drawback [1,11-14].

Initiating radicals in the grafting-from method can be created on a polymer chain upon chemical initiation. In this case, as illustrated in figure 1, a polymeric backbone includes some thermally cleavable bonds such as peroxide bonds. Initiation with peroxides are frequently used in polymer functionalization for free-radical polymerization. If the polymer is heating in the presence of a second monomer, initiation takes place and free radicals produced and transferred to the substrate to react with monomer to form the graft co-polymers. In this systems, homopolymer creation is present due to the conjugate formation of low molar mass radicals [1, 13]. Grafting is an important method to modify the polymeric membranes for separation technology. It is a simple way to achieve tailor-made membranes with special properties. Membrane problems, such as fouling can be solved by grafting appropriate monomers on the polymers [13, 15-17].

![Diagram](image.png)

**Figure 1.** Grafting copolymerization with grafting-from method.

In this work, dehydrochlorination of PVC was investigated at a low to moderate NaOH concentration (1-5) M NaOH at 100 °C temperature in order to partially chlorine removal without damaging the polymer for purpose of grafting copolymerization (grafting-from method via free radical initiator). And investigate the efficiently grafting with acrylamide (hydrophilic monomer), to produce new tailored grafting polymer for membranes separation technology for wastewater treatment.

2. Experimental work

2.1. Materials

Commercial suspension polymerized polyvinylchloride resin (PVC with K-Value: 65-67, bulk density: 570 kg/m³, and partical size: 250 µm) was provided by Sabic Company (Saudi Basic industries corporation, KSA). Acrylamide (AM, 98.0%) and benzoyl peroxide (BPO, 98.0%) were purchased from HiMedia (India). Sodium hydroxide (NaOH, 99.0%) and methanol (99.5%) were supplied by (Scharlau, Spain). Cyclohexanone (99.0%) was purchased from BDH Chemicals Ltd (Poole, England).

2.2. Preparation of Dehydrochlorinated PVC (DHPVC)

PVC was dried in oven at 45 °C for 24h and a weighed quantity of PVC (2 g) and different molar ratios (1, 3, 5 molarity) from NaOH solution (20 ml) were fed into a round-bottom flask fitted with a reflux condenser on magnetic stirrer. Dehydrochlorination process time was (8 hours) at 100 °C temperature. The obtained dehydrochlorination product was filtered and washed with deionised water until all traces
of NaOH was removed followed by drying in a vacuum oven overnight, scheme 1 (a). The product colour is orange and degree orange colour depending on the used solution molarity [10, 18].

2.3. Preparation of graft copolymers

To prepare the grafted PVC, in 250 ml three-neck round-bottom flask fitted with a reflux condenser on magnetic stirrer, dissolving 3 g of polymer (pure PVC, DHPVC 1M, DHPVC 3M and DHPVC 5M) in 25 ml cyclohexanone under inert atmosphere at ambient temperature for 8 hours to achieve a completely dissolving of polymer. An initiator solution is prepared by dissolving 0.45 g of benzoyl peroxide (BPO) in 10 ml cyclohexanone. Also, monomer solution is prepared by dissolving 3 g of acrylamide (Am) in 25 ml cyclohexanone, then it transferred into dropping funnel. The prepared initiator solution is adding directly to dissolve polymer and raising temperature to 70 °C then gradually adding of monomer solution by dropping funnel with continuous stirring. The reaction was then carried out for predetermined time (3 hours) at 70 °C. The mixture was then cooled to the ambient temperature and poured into good-stirred methanol. The produced polymer was precipitated then filtered and washed for several times with methanol, followed by vacuum oven drying overnight. The product was a mixture of homopolymer polyacrylamide (PAM), and grafted copolymer, PVC-g-PAM as in scheme 1(b). Polyacrylamide (PAM) homopolymer was removed by purification the result mixture in deionized water by stirring at 50 °C for 1 hour, then filtered and washing. This purification process was repeated four times to ensure complete PAM removal. The remaining solid (PVC-g-PAM) was dried in a vacuum oven at 60 °C for 30 hours and subsequently characterized.

![Scheme1](image)

Scheme 1. The proposed procedure for (a) dehydrochlorination of PVC and (b) initiation and grafting of PVC with acrylamide.

In this work, from Energy-Dispersive X-ray spectroscopy (EDX) analysis results, we could knowledge the chlorine content before and after dehydrochlorination and find the removed chlorine to calculate the
Dehydrochlorination efficiency (DE%) in a manner similar to other researchers using the removed chlorine content in the liquid of dehydrochlorination treatment [2,5]. Dehydrochlorination efficiency was derived according to the following equation:

\[
(\text{DE} \%) = \frac{\text{removed Cl content}}{\text{Cl content in PVC}} \times 100 \%
\]  

(1)

The grafting parameters could be evaluating by many ways, were the weight of sample before and after grafting used. The efficiency of grafting was found according to the following equation [14,18,19]:

\[
\text{Grafting efficiency (GE \%) = } \frac{\text{Weight of grafted polymer}}{\text{Weight of grafted polymer plus homopolymer}} \times 100 \%
\]  

(2)

2.4. Characterization

Structural changes and chemical characterization of PVC, DHPVC and grafting products were monitored by Fourier transform infrared (FTIR) spectroscopy, Energy-Dispersive X-ray spectroscopy (EDX) and Raman micro spectroscopy.

FTIR spectra of samples were measured with (IR Affinity-1, Shimadzu/ Japan) at a scan number of 10 and a resolution of 4 cm\(^{-1}\) in the range of 3600 cm\(^{-1}\) to 600 cm\(^{-1}\) at room temperature. The samples were prepared by grinding the dry powders with potassium bromide (KBr) and pressed into tablets. EDX is an x-ray technique used to identify the elemental composition of materials. The EDX analysis of samples was performed by using a XFlash-6110/Model (Bruker Co./ Germany) instrument without coating at an acceleration voltage of 10 kV.

Raman spectroscopy is a powerful way to analysis the polymer structure in terms of chemical and phase compositions, and contents of different configurational and conformational states [20]. Raman spectra was measured with Senterra Raman microscope (532nm & 785 nm, Bruker/ Germany) and was recorded at room temperature for four sample: pure PVC, acrylamide monomer, and the samples that showed the efficient dehydrochlorination and grafting as investigated by the FTIR and EDX examination, i.e. DHPVC 3M and graft 3M samples.

3. Results

3.1. Confirmation of Dehydrochlorination and grafting by FTIR

The functional groups of the PVC, DHPVC, AM, and (PVC-g-PAM) were reported by FTIR spectrometer. The spectra of pure PVC and DHPVC (1, 3, 5) molarity are shown in figure 2, it is nearly in agreement with the reported one previously mentioned in the literatures [2,5,21-23]. Table 1 contain stander and experimental bands of pure PVC, acrylamide, also the bands wavenumber variation for DHPVC and grafting samples which given in the range due to the effect of NaOH solution molarity on band shifting and intensity. That was evidenced by the various increasing intensity of band at 1610 cm\(^{-1}\) assigned to \(\nu(\text{C}=\text{C})\) reported that the elimination of HCl during the dehydrochlorination of PVC, and by the various decreasing intensity of bands at 835 cm\(^{-1}\), 758 cm\(^{-1}\), 605.6 cm\(^{-1}\) assigned to \(\nu(\text{C}–\text{Cl})\). Also, the bands at (2970 cm\(^{-1}\)- 2818 cm\(^{-1}\)), 1427 cm\(^{-1}\), 1332 cm\(^{-1}\), 1253 cm\(^{-1}\), and 964 cm\(^{-1}\) were weakened.

In comparison with the FTIR spectrum of the pure PVC, the most significant changes in the FTIR spectrum of all grafted sample (graft pure PVC, graft DHPVC 1M, graft DHPVC 3M, and graft DHPVC 5M) are the appearance of \(\nu(\text{C}=\text{O})\) (amide I) at about (1668-1670) cm\(^{-1}\), \(\delta(\text{NH}_2)\) (amide II) at about (1614.4-1618.2 cm\(^{-1}\)), \(\nu(\text{C}–\text{N})\) (amide III) at 1255.6 cm\(^{-1}\), and \(\nu_3(\text{NH}_2)\) and \(\nu_3(\text{NH}_3)\) at 3375.4cm\(^{-1}\) and 3205.7cm\(^{-1}\), respectively, as shown in figure 3. These bands identical with other researcher [24-28] and verify that the AM monomer was grown onto backbone polymer (PVC) and the graft copolymer was successfully synthesized.

The significant effect of dehydrochlorination and grafting copolymerization in terms of increase or decrease bands intensity showed strongly for DHPVC 5 molarity and moderately for DHPVC 1 molarity. Although, DHPVC 5 molarity showed good grafting results, but it showed adverse dehydrochlorination
results due to NaOH increases which lead to increase transport properties such as density also. Since the solid has become porous, a mass and heat-transfer effect is present due to the solid–liquid contact, as reported that at 7 M NaOH for flexible PVC pellets [5].

Figure 2. FTIR spectrum of pure PVC, DHPVC (1, 3, 5) molarity.

Figure 3. FTIR spectrum of pure PVC with grafted samples.
Table 1. Bands wavenumber variation for PVC, AM, DHPVC and grafting samples.

| Type of bond   | Stander pure PVC peak[5,22,23]/cm⁻¹ | Exp. Pure PVC peak/cm⁻¹ | Stander acrylamide peak[24,36]/cm⁻¹ | Exp. Acrylamide peak/cm⁻¹ | Rang of DHPVC peak/cm⁻¹ | Rang of Grafting peak/cm⁻¹ |
|----------------|-----------------------------------|-------------------------|---------------------------------|---------------------------|-------------------------|---------------------------|
| ν(NH₂)         | ---                               | 3352                    | 3352                            | ---                       | 3755.43                 | 3205.69                   |
| νₐ(NH₂)        | 2969                              | 2970.38                 | ---                             | 2970.4-2972.3             | 2968.4-2970.4           | 2910.6                    |
| ν(CH and CH₂)  | 2915                              | 2908.65                 | ---                             | 2908.7-2910.6             | 2845                    | 2845-2846.9               |
| ν(C=O)         | 2851                              | 2843.07                 | ---                             | 2814                      | 2816.07                 | 2816.07-2818              |
| ν(C=–C)        | 2817                              | 2818                    | ---                             | 1674                      | 1668.43-1670.35         | ---                       |
| ν(C=–C)        | ---                               | 1675                    | 1674                            | ---                       | ---                     | ---                       |
| δ(NH₂)         | 1426                              | 1427                    | 1429                            | 1429                      | 1604.7-1606.7           | ---                       |
| δ(CH₂ and CH)  | 1330                              | 1332.81                 | 1351                            | 1352                      | 1334.7-1336.7           | 1330.88                   |
| ν(C-N)         | 1255                              | 1253.73                 | ---                             | 1253.7-1255.6             | ---                     | ---                       |
| γ(NH₂)         | 1097                              | 1097.50                 | ---                             | 1093.6-1095.6             | 1097.5-1099.4           | ---                       |
| ν(C=O)         | 964                               | 964.41                  | 960                             | 960.55-964.41             | 964.41-966.34           | ---                       |
| ν(C=–C)        | 834                               | 835.18                  | ---                             | 833.25-835.18             | 833.5                   | ---                       |
| ν(C=O)         | 750                               | 758.02                  | ---                             | 758.02                    | ---                     | ---                       |
| ν(C=Cl)        | 607                               | 605.65                  | ---                             | 601.8-609.51              | 613                     | ---                       |

νₛ and νₐ: asymmetric and symmetric stretching, δ: in plane bending, γ: rocking, and w: wagging.

3.2. Energy-Dispersive X-ray spectroscopy (EDX)

The obtained data by EDX analysis include of spectra showing peaks corresponding to the real elements composition of analysed sample. Figure 4 shows EDX of pure PVC, DHPVC and grafting samples, noticed that there is a clear difference in the spectrums of samples in terms of the peaks intensity (increasing or decreasing) of (1) chlorine and carbon between pure PVC and DHPVC samples, and (2) chlorine, carbon, nitrogen and oxygen in grafted samples. The EDX spectrums in conjunction with the elements weight percentage confirm the success of dehydrochlorination and grafting copolymerization in various efficiency due to the molarity of NaOH solution.

Figure 5 and 6 show the effect of NaOH solution molarity on the chlorine contain in produce DHPVC and on the dehydrochlorination efficiency, respectively. From weight percentage of element in table 2 and according to equation (1), dehydrochlorination efficiency (DE%) was about 21.9%, 48.9% and 43.7% for DHPVC 1M, DHPVC 3M and DHPVC 5M, respectively. The weight of produced homopolymer in grafting reaction could be calculated from the weights of grafted samples before and after purification, and according to equation (2), the grafting efficiency (GE%) was about 52.8%, 58.7%, 67.3%, and 51.2% for graft pure PVC, graft 1M, graft 3M and graft 5M, respectively. Figure7 shows the effect of dehydrochlorination at various solution molarity of NaOH on the grafting efficiency.

The EDX and FTIR results with calculations of dehydrochlorination and grafting efficiency given the fact of that 3 molarity of NaOH solution had the significant effect on PVC dehydrochlorination and PVC grafting copolymerization with AM monomer.
Table 2. Weight percentages of element in PVC, AM, DHPVC and grafting samples.

| Sample            | C %  | Cl %  | N %  | O %  |
|-------------------|------|-------|------|------|
| Pure PVC          | 56.89| 43.11 | ---  | ---  |
| DHPVC 1M          | 66.37| 33.63 | ---  | ---  |
| DHPVC 3M          | 78   | 22    | ---  | ---  |
| DHPVC 5M          | 75.75| 24.25 | ---  | ---  |
| Graft pure PVC    | 56.2 | 41.8  | 1.3  | 0.7  |
| Graft 1M          | 66.86| 30.98 | 1.35 | 0.81 |
| Graft 3M          | 77.34| 19.76 | 1.95 | 0.95 |
| Graft 5M          | 75.88| 22.54 | 0.98 | 0.6  |
| Acrylamide        | 61.57| ---   | 34.63| 3.8  |

3.3. Raman spectroscopic

Raman spectroscopy methods for PVC structure were used to analyse and investigate the phase composition, configurational and conformational order, macromolecular orientation, and the degree of chlorine removal [20].

The conjugated double bonds formed during PVC dehydrochlorination can easily be detected due to their resonance enhancement in Raman spectroscopy. The $\nu(C=\mathrm{C})$ and $\nu(C-C)$ vibrations of the conjugated systems are of extremely high intensity in the corresponding spectra, if an appropriate excitation source is used. Detection of conjugated systems is possible down to a level of 0.0001% HCl loss, which is not accessible with any other technique [29].

Raman spectrums of the pure PVC, AM monomer, and the samples that showed typical dehydrochlorination and grafting efficiency, i.e. DHPVC 3M and graft 3M samples, shown in the figure 8, they are nearly in agreement with the reported one previously mentioned in the literatures [29-31]. In comparison with pure PVC, the elimination of HCl during the Dehydrochlorination was evidenced by the strong increasing of $\nu(C=\mathrm{C})$ band intensity at (1508-1513 cm$^{-1}$), and by the decreasing intensity of $\nu(C-\mathrm{Cl})$ bands between (620-715 cm$^{-1}$).

The strong intensity amide group present in the MA monomer at (1628-1648 cm$^{-1}$) is appears in graft 3M at about (1640-1655 cm$^{-1}$). Also, the medium intensity $\nu(\mathrm{NH}_2)$ band present in the MA monomer at about (3332-3342 cm$^{-1}$) is appears as weak intensity in graft 3M at about (3309-3312 cm$^{-1}$). These bands confirmation the successful of Dehydrochlorination and AM grafting onto PVC.
Figure 4. EDX of (a) pure PVC, (b) DHPVC 1M, (c) DHPVC 3M, (d) DHPVC 5M, (e) graft pure PVC, (f) graft 1M, (g) graft 3M and (h) graft 5M.
**Figure 5.** Effect of alkali solution molarity on chlorine content of the produced DHPVC.

**Figure 6.** Effect of NaOH solution molarity on the dehydrochlorination efficiency.

**Figure 7.** Effect of PVC dehydrochlorination at various solution molarity of NaOH on the grafting efficiency.

**Figure 8.** Raman spectra of pure PVC, AM, and the efficient dehydrochlorination and grafting sample.
4. Conclusion

In this work, the goal was to obtain partial dehydrochlorination on PVC without degradation the polymer chain. The increased loss of chlorine in the PVC will lead to formation of a double bond on the polymer chain and increased hydrophobic in PVC. The best results in obtaining the highest loss of chlorine (dehydrochlorination efficiency reached 48.9 %) were when using the 3 M ratio of NaOH. In the preparation of graft PVC from the reaction of acrylamide with pure PVC and DHPVC, the best grafting was in the use of DHPVC 3M (grafting efficiency reached 67.3 %) and as proved by the tests IR spectra, elemental analyses and Raman spectra. Increasing AM will increase hydrophilic in PVC and this will improve its use as a membrane in water treatment.

References

[1] Munnaya K M and Yusuf Y 2009 Handbook of Vinyl Polymers: Radical Polymerization, Process, and Technology 2nd Edition (New York: Taylor & Francis Group) pp 27-440

[2] Tian L, Peitao Z, Meng L and Zhaozhi L 2017 Appl. Sci. 7 256

[3] Poerschmann J, Weiner B, Wośzidło S, Köehler R and Kopinke F D 2014 Chemosphere 119C 682-689

[4] Yu J, Sun L, Ma C, Qiao Y and Yao H 2016 Waste Manag. 48 300–314

[5] Shun M S, Yoshioka T and Okuwaki A 1998 J. Appl. Polym. Sci. 67 2171-2177

[6] Yoshinaga T, Yamaye M, Kito T, Ichiki T, Ogata M, Chen J, Fujino H, Tanimura T and Yamanobe T 2004 Polym. Degrad. Stabil. 86 541–547

[7] Shun M S, Yoshioka T and Okuwaki A 1998 Polymer Degradation and Stability 61 349-353

[8] Tomohito K, Katsuaki I, Guido G, Tadaaki M and Toshiaki 2009 Polymer Degradation and Stability 94 1595–1597

[9] Eun J P, Byoung C P, Young J K, Ali C and Taek S H 2018 Macromolecular Research DOI 10.1007/s13233-018-6123-z

[10] Eun J P, Seung Y L, Ali C and Taek S H 2018 Macromolecular Research DOI 10.1007/s13233-019-7011-x

[11] Hadjichristidis N, Pitsikalis M, Iatrou H, Driva P, Chatzichristidi M, Sakellariou1 G and Lohse D 2010 Encyclopedia of Polymer Science and Technology by John Wiley & Sons, Inc DOI: 10.1002/0471440264.pst150

[12] Temel Ö, Melahat S, Bedrettin S, Mustafa I, Mehmet N A and Baki H 2014 E-Polymers 14 27-34

[13] Bhattacharya A and Misra B N 2004 Prog. Polym. Sci. 29 767–814

[14] Susheel K and Sabaa M W 2013 Springer-Verlag Berlin Heidelberg ISBN 978-3-642-36565-2

[15] Mir M A T, Pawef O and Andrzej K 1996 Elsevier Science Ltd, Polymer 37 18 4149-4154

[16] Tudorachi N and Lipsa R 2006 journal of optoelectronics and advanced materials 8 2 659 – 662

[17] Taghizadeh M T and Ghaffari 2003 Iranian Int. J. Sci. 4 23-36

[18] Wen-Fu L and Cherng-Ching L 1994 Journal of Applied Polymer Science 51 2175-2186

[19] Inge-Willem N, Tori K F and Patrizio R 2018 Processes 6 31

[20] Prokhorov K A, Aleksandrova D A, Sagitova E A, Nikolaeva G Yu, Vlasova T V, Pashinin P P, Jones C A and S J Shilton 2016 Journal of Physics: Conference Series 691 012001

[21] Bakhshali M, Rahim M R and Mehdi J 2016 Polym. Adv. Technol. 27 1056–1063

[22] Jaleel K A, Zuhair J A A and Maha J M A 2015 International Journal of Materials Science and Applications 4 7 21-29

[23] Beltrán M and Marcilla A 1997 European Polymer Journal 33 7 1135-1142

[24] Huseyin A 2014 The Ohio State University Ph.D. theses

[25] Murugan R, Mohan S and Bigotto A 1998 Journal of the Korean Physical Society 32 4 505-512

[26] Neville J 1961 Journal of Molecular Spectroscopy 6 205-214

[27] Faycel A and Faouzi M 2014 Turkish Journal of Chemistry 38 638 – 649
[28] Ameer A A, Mustafa S A, Ahmed A A and Emad A Y 2013 *Journal of Polymer Chemistry* 3 11-15
[29] Andreas G, Peter W and Michael S 2003 *Polymers & Polymer Composites* 11 2
[30] Raghavendra J, Izabela N, Hugh J B, Suzanne M, Robert H and Vincent T 2008 *Applied Optics* 47 2 206-212
[31] Gaurang P, Mundan B S and Purvi P 2015 *Soft* 4 9-24

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