

Photoinduced Grafting of Methyl Methacrylate onto Dehydrochlorinated poly (Vinyl Chloride) Using A Combination Of Dimethylaniline And Benzoyl Peroxide As Initiator System

El-Sayed A. Abdel-Razik¹, Ahmed E. Shehata¹, Ibrahim M. El-Sherbiny^{1,2,*}

¹Polymer Laboratory, Chemistry Department, Faculty of Science, ET-35516, Mansoura University, Egypt;

²Center for Materials Science, University of Science and Technology, Zewail City of Science and Technology, 6th October City, 12588 Giza, Egypt

ABSTRACT: Polyvinyl chloride (PVC) has been dehydrochlorinated in alkaline medium followed by photo-induced graft copolymerization of methyl methacrylate. The grafting has been achieved using a combination of dimethyl amine and benzoyl peroxide, as radical initiator system. The effects of various parameters such as concentrations of monomer, initiator, substrate, and solvent as well as time of light irradiation on the grafting yield, expressed as grafting percentage and grafting efficiency, have been investigated, and the optimum grafting conditions were determined. The dehydrochlorinated PVC and graft products were characterized using FTIR, TGA, DTA, XRD and SEM and the mechanism of grafting was proposed.

Keywords: Benzoyl peroxide, Dehydrochlorinated polyvinyl chloride, Dimethyl amine, Methyl methacrylate, Photo-induced grafting, Polyvinyl chloride

I. INTRODUCTION

Polyvinyl chloride (PVC) is one of the world's largely produced plastic polymers due to its use in a wide range of applications. For instance, PVC is beneficial in many construction purposes because of its efficiency as compared to traditional materials such as copper, iron or wood. PVC can be made flexible and softer via addition of plasticizers. The flexible PVC has been utilized to replace rubber in applications such as insulation of electrical cables, clothing and upholstery, and in inflatable products [1].

Grafting of certain acrylate monomers onto PVC backbone would increase its impact strength and also assists in its processing without the addition of plasticizers. Grafting onto PVC has been achieved through various approaches. These include; (a) radical chain transfer reaction, such as grafting of PVC with methyl methacrylate [2], butyl acrylate [3] and glycidyl methacrylate [4], (b) ionic polymerization from labile chlorine in PVC, such as grafting of PVC with isobutylene [5], (c) by mechanochemical reaction, such as grafting of PVC with vinyl alcohol [6], (d) with the aid of a polyperoxy radicals [7], and (e) by using a polymer radicals produced by γ -irradiation, such as the grafting of PVC with acrylic acid [8], acrylamide [9], styrene [10], and methyl methacrylate [11].

Attempts for increasing the number of radical sites onto PVC backbone via dehydrochlorination, and consequently increasing the extent of grafting have been reported. For instance, Mukherjee et al [12] have dehydrochlorinated PVC in pyridine before its grafting with styrene using benzoyl peroxide (BPO). Sharma and Varma [13] also reported the use of dehydrochlorinated PVC in nitrobenzene for grafting of styrene in presence of a cationic initiator.

In the present study, the number of radical sites onto PVC has been increased through its dehydrochlorination in alkaline medium in order to increase the extent of its photo-induced grafting with methyl methacrylate (MMA) monomer in the presence of a combination of dimethyl amine (DMA) and benzoyl peroxide (BPO), as a radical initiator system, in cyclohexanone and in the presence of air and visible light. Such a modified PVC resulting from the current study can be blended with virgin PVC to a level where the grafted poly(methyl methacrylate) (PMMA) side chains can behave as impact modifier as well as a processing aid. In this study, attempts have also been made to determine the optimum conditions for achieving maximum grafting of MMA onto PVC.

II. MATERIALS AND METHODS

2.1. Materials

PVC resins of average molecular weight of 100,000 Da were supplied by BHD (Malaysia). The monomer, MMA was provided by Merck (Darmstadt, Germany) and was ready for grafting process after removal of its polymerization inhibitor via its washing with 5% aqueous NaOH solution followed by distilled water, and then drying over calcium chloride. DMA and BPO were purchased from Sigma-Aldrich (Saint Louis, USA). Benzene, NaOH, cyclohexanone and methanol were of good grade and used as received.

2.2. Methods

2.2.1. Preparation of dehydrochlorinated PVC (DHPVC)

Pre-weighted amounts of PVC resin (1g) and 10 ml of NaOH solution (25%) were fed into a round-bottom flask fitted with a reflux condenser. Then, the dehydrochlorination process was carried out for 6.5 h at 100°C. The resulting dehydrochlorinated powder (DHPVC) was washed extensively with distilled water to remove any traces of alkali, dried under vacuum at 40°C for 12 h, and then stored until further investigation.

2.2.2. Grafting of MMA onto DHPVC

The predetermined amounts of DHPVC, MMA, DMA and BPO were added portion wise with stirring to cyclohexanone and then the entire reaction mixture was transferred to Pyrex cell. The graft copolymerization was then initiated by irradiation with pair of incandescent broad-spectrum lamps (Philips, 40 W), positioned 20 cm away from the cells containing the reaction mixture. Irradiation was continued for variable predetermined periods (0.5–3 h). The grafting and polymerization processes were terminated by adding hydroquinone aqueous solution (3%). The crude product was precipitated by methanol, filtered, dried and weighed. The formed homopolymer (PMMA) was extensively extracted by refluxing with benzene for 24 h. The residual PMMA-g-DHPVC copolymer was washed with benzene, and dried at 40°C until constant weight. Experiments with the same procedures were also carried out in the dark at room temperature. The grafting parameters such as grafting percentage (GP%) and grafting efficiency (GE%) of the resulting copolymer, as well as the Homo% were calculated according to the following relationships:

$$\text{Grafting percentage(GP\%)} = \frac{A - B}{B} \times 100$$

$$\text{Grafting efficiency(GE\%)} = \frac{A - B}{C} \times 100$$

$$\text{HOMO\%} = \frac{D}{C} \times 100$$

Where A, B, C, and D are the weights of graft copolymer, DHPVC, MMA, and the homopolymer (PMMA), respectively.

2.2.3. Viscosity measurements

Viscometric measurements were carried out for the solutions of PVC, DHPVC, PMMA, and the resulting PMMA-g-DHPVC copolymers using cyclohexanone as a solvent with the aid of an Ostwald viscometer at 27±0.1°C. The following equation was used to obtain the values of intrinsic viscosity [14].

$$[\eta] = \frac{\sqrt{2}}{c} \sqrt{\eta_{sp} - \ln \eta_{rel}}$$

2.2.4. Instrumental analysis

The UV spectra of the used initiator system were obtained using UV-visible spectrophotometer (Perkin Elmer Lambda 3B) and the λ_{max} values in the visible region were determined. The chemical structure of the grafted copolymers was examined by FTIR spectrometer (Perkin Elmer 1430). The dried samples were pressed with KBr and their FTIR spectra were recorded at 25°C in the range of 400–4000 cm⁻¹. The thermal characteristics of the developed PMMA-g-DHPVC copolymers were investigated using thermal analyzers (Shimadzu DTA-50 and Shimadzu TGA-50H) under nitrogen atmosphere. The X-ray diffraction patterns of the prepared copolymer specimens were performed using a beam monochromator and Cu K α radiation at $\lambda = 1.542 \text{ \AA}$. The applied voltage was 40 kV and the current intensity was 40 mAs. The 2 θ angle was measured in the range of 0–50° and the X-ray runs were carried out at scanning speed of 2°/min. Surface morphology of the obtained copolymer samples was examined using a scanning electron microscope (JEOLJSM-5500LV SEM, JEOL Ltd, Japan) and the measurements were carried out using high vacuum mode. Copolymer samples were placed on aluminum mount, sputtered with gold using Bal-tec. scd. 050 sputter coater and then scanned at an accelerating voltage of 20 kV.

2.2.5. Statistical analysis

The collected grafting data was analyzed and expressed as average values of triplicates. The effect of various reaction conditions on the grafting parameters was statistically analyzed by one-way ANOVA using Excel (Microsoft Office 2007). Differences were considered significant at the level of $p < 0.05$.

III. RESULTS AND DISCUSSION

3.1. Preparation and characterization of DHPVC and PMMA-g-DHPVC copolymer

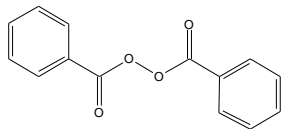
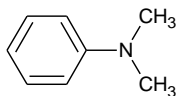
In the present study, the number of radical sites on the PVC molecules has been increased via dehydrochlorination process in an alkaline medium in order to increase the grafting extent of MMA monomer onto DHPVC using a combination of DMA and BPO, as radical initiator, in cyclohexanone and in the presence of air and visible light irradiation.

Preliminary experiments were carried out in the dark and in the presence of visible light as well as in the presence of either the initiator mixture or only one of the initiator constituents. The results presented in Table 1 showed that the presence of visible light has improved the GP% from 15% to 25% after irradiation for 3 h instead of 24 h in the dark. The results shown in Table 1 also demonstrate that the combination of BPO and DMA is essential for occurrence of grafting and use any of them alone would not be enough for the grafting process. Therefore, it became necessary to examine the UV-vis spectra of both DMA and BPO and the results are shown in Table 2. From the table, the results revealed that BPO has two absorption peaks; a broad one at 300 nm and a small one at 380 nm, whereas, the DMA has showed three absorption bands at 246 nm, 300 nm and 383 nm.

Table 1. Graft copolymerization of MMA onto DHPVC in the presence of BPO/DMA as initiator system in cyclohexanone as a solvent: DHPVC 20 g/l, MMA 1.86 mol/l, and the initiator system (BPO 0.02 mol/l and DMA 0.02 mol/l)

Initiator system	Conc.(mol/l)	Condition	GP %	GE%
BPO + DMA	0.02+0.02	Dark (24h)	15%	1.59%
BPO	0.02	Dark (24h)	0%	0%
DMA	0.02	Dark (24h)	0%	0%
BPO + DMA	0.02+0.02	Visible (3 h)	25%	2.67%
BPO	0.02	Visible (3 h)	0%	0%
DMA	0.02	Visible (3 h)	0%	0%

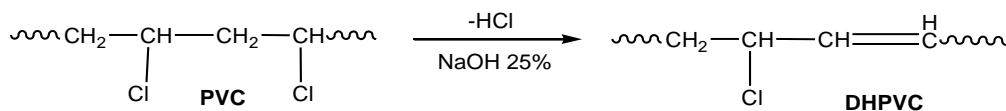
Table 2. Results of the UV-visible spectra of the initiator mixture (BPO and DMA) in cyclohexanone at room temperature

Name	Structure	λ_{\max}	Absorbance
BPO		300 nm	1.08
		380 nm	0.22
DMA		246 nm	2.75
		300 nm	2.46
		383 nm	0.15

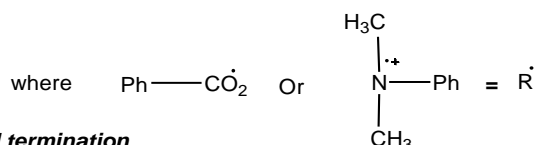
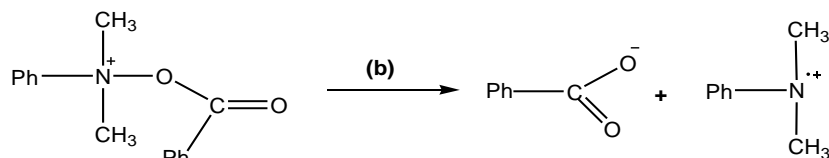
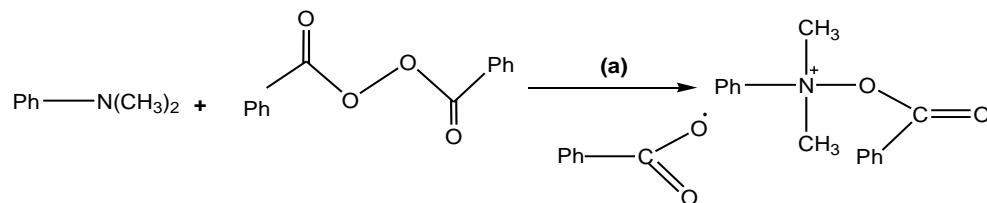
The dehydrochlorination and grafting processes are illustrated in Scheme 1. From the scheme, the free radicals produced from the combination of DMA and BPO have reasonable efficiency in initiating the grafting of MMA onto DHPVC in cyclohexanone and under visible light irradiation.

(a) Grafting of MMA onto DHPVC

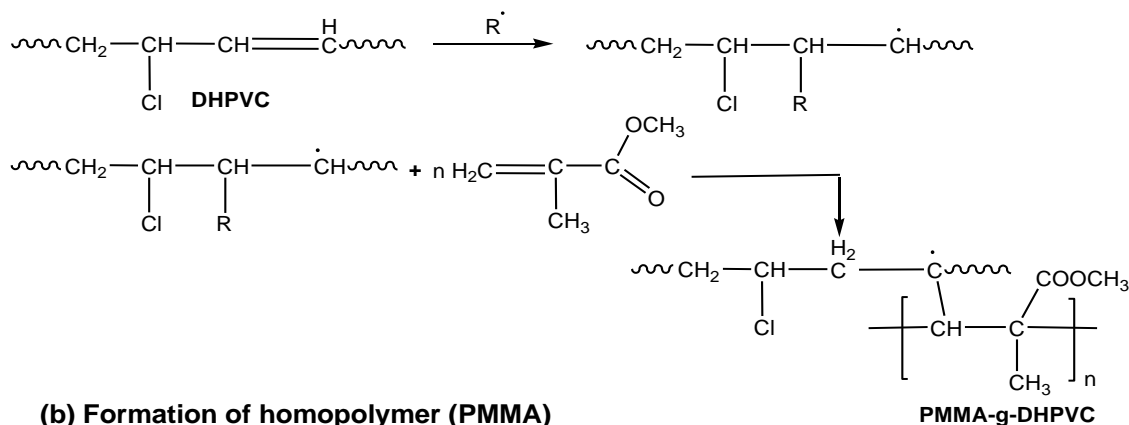
i- Dehydrochlorination of PVC



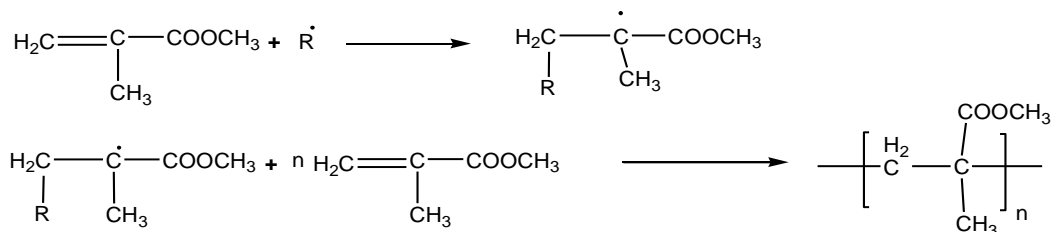
ii- Initiation



iii- Propagation and termination



(b) Formation of homopolymer (PMMA)



Scheme 1. A schematic illustration of the dehydrochlorination, the grafting of MMA onto DHPVC, and the formation of the homopolymer (PMMA) in the presence of BPO/DMA as initiator system and in cyclohexanone as a solvent

3.2. Proof of grafting

There are some experimental evidences that confirm the occurrence of the grafting process of MMA onto DHPVC. The higher weights of the graft products as compared with that of the starting DHPVC after the extensive removal of the homopolymer (PMMA) can be taken as evidence of grafting. Occurrence of grafting can be also deduced from the reduction noted in the viscosity of the resulting graft copolymers as compared

with that of the starting DHPVC as shown in Table 3. As apparent from the table, the reduction in the viscosity increased with increasing the GP (%).

Table 3. Intrinsic viscosity of different samples (0.5 g dissolved in 100 ml of cyclohexanone)

Samples	GP(%)	Intrinsic viscosity [η] (dL/g)
PVC	-	1.367
DHPVC	-	1.2492
PMMA-g-DHPVC	5	0.757
PMMA-g-DHPVC	20	0.744
PMMA-g-DHPVC	45	0.617
PMMA-g-DHPVC	65	0.544
PMMA	-	0.033

3.3. FTIR spectroscopy

The FTIR spectra of PVC before and after dehydrochlorination process in addition to that of the resulting PMMA-g-DHPVC copolymer are illustrated in Fig 1. As apparent from the figure, both PVC and DHPVC showed similar spectra with the band at about 1670 cm^{-1} became stronger in the IR spectrum of DHPVC which indicates the formation of long polyene sequences in the PVC chains [15].

The IR spectrum of the resulting PMMA-g-DHPVC copolymer shows a new strong carbonyl band at about 1730 cm^{-1} (Fig 1c), indicating the presence of PMMA grafted side chains. Moreover, the absorption band of polyene sequences in the DHPVC at 1670 cm^{-1} became much weaker which also confirms the occurrence of grafting process.

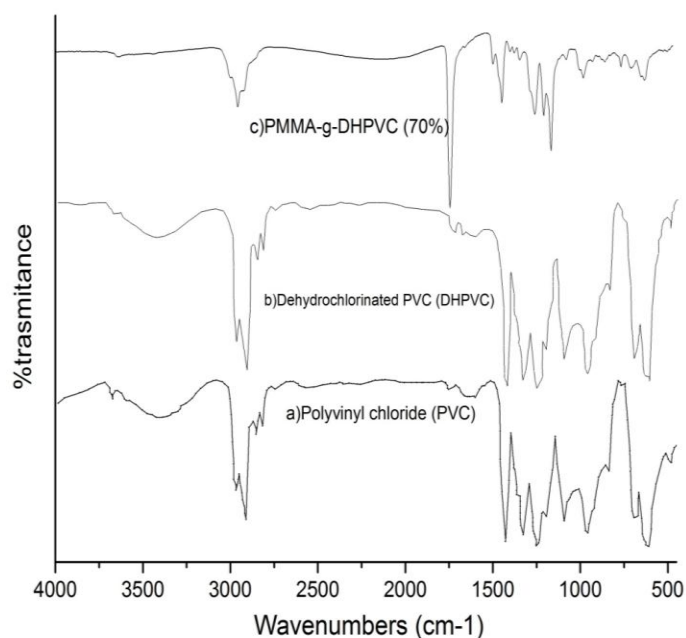


Fig 1. FTIR spectra of a) polyvinyl chloride (PVC), b) dehydrochlorinated polyvinyl chloride (DHPVC), and c) PMMA-g-DHPVC (70%)

3.4. Thermal analysis

The thermal characteristics, as determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DTA), of the prepared PMMA-g-DHPVC (GP%; 20% and 70%) as compared to DHPVC are shown in Table 4 and Fig 2. As apparent from Table 4, the initial decomposition temperature (IDT) and the final decomposition temperature (FDT) of the DHPVC are 174.11°C and 559.14°C , respectively. This IDT value has increased to 195.86°C and 204.33°C in the PMMA-g-DHPVC copolymers of GP 20% and 70%, respectively. Whereas, the FDT value of the DHPVC has decreased to 547.86°C and 479.14°C in the PMMA-g-DHPVC copolymers of GP 20% and 70%, respectively. This increase in IDT and decrease in the FDT values tend to show that the thermal stability of DHPVC is more or less influenced by the grafting process. From Fig 2, the TGA thermogram of DHPVC showed three stages of decomposition. In the first stage, a high weight loss (about 60.37%) was recorded between the temperature range of 174.11°C and 389.83°C . Further degradation of DHPVC was noted above 390°C with a second weight loss of about 20.99% followed by a third stage of weight

loss of about 15.83% that started at about 559.14°C. In the case of PMMA-g-DHPVC copolymers, the TGA thermogram showed four stages of decomposition; three of them are common with that of DHPVC but with higher IDTs and relatively lower FDTs (Fig 2). The first stage was found between 80.3°C and 203.47°C with a weight loss of about 8%. In the second stage, a large weight loss (~50%) has occurred between 204.3°C and 356.5°C due to the complete dehydrochlorination of DHPVC [16], whereas the third weight loss (22.34%) was noted between 356.5°C and 478.16°C. Further degradation was recorded between 479.14°C and 672.21°C with a weight loss of 15%. This difference in the thermal behavior of PMMA-g-DHPVC as compared to DHPVC and other polymers such as PMMA and PVC, and even their physical mixtures (PMMA + DHPVC), as shown in Table 4, tends to confirm the occurrence of grafting.

The DTA thermogram of DHPVC showed two moderate exothermic peaks at temperature 459.69°C (15.25µV) and 533.10°C (15.14µV), respectively as shown in Fig 2, and Table 4. The DTA thermogram of PMMA-g-DHPVC copolymer (GP 70%) also showed two exothermic peaks but at different temperatures of 444.81°C (12.4 µV) and 621.63°C (12.8µV), respectively. This obvious difference in the µV values and the peak positions between DHPVC and PMMA-g-DHPVC (Table 4) tends to suggest occurrence of a change in the micro-structure of DHPVC due to grafting.

Table 4. TGA and DTA data of the prepared PMMA-g-DHPVC copolymers as compared to that of the starting materials

Sample	GP%	TGA		DTA Exothermic peaks at temperature (µV)
		IDT*	FDT**	
PVC	-	203.67°C	559.35°C	361.57°C (24.75 µV) 541.58°C (19.85 µV)
DHPVC	-	174.11°C	559.14°C	459.69°C (15.25 µV) 533.10°C (15.14 µV)
PMMA	-	-	-	208.82°C (4.2 µV)
PMMA-g-DHPVC	20%	195.86°C	547.86°C	453.66°C (11 µV) 468.90°C (11.8 µV) 568.92°C (15 µV)
PMMA-g-DHPVC	70%	204.33°C	479.14°C	444.81°C (12.4 µV) 621.63°C (12.8 µV)
PMMA + DHPVC [#]	-	195.26°C	490.45°C	389.20°C (17.65 µV) 506.01°C (7.95 µV)

*IDT: Initial decomposition temperature; ** FDT: Final decomposition temperature; [#](1:1w/w physical mixture)

3.5. Scanning electron microscopy

The surface morphology of the synthesized PMMA-g-DHPVC copolymer (GP 70%) as compared to DHPVC is illustrated in Fig 3. As apparent from Fig 3a, DHPVC has irregular plate-like structure with relatively smooth surface. Grafting of MMA onto the DHPVC (Fig 3b) results in relatively irregular clusters with dense surface rigidity. This change insurface morphology may also confirm occurrence of the grafting.

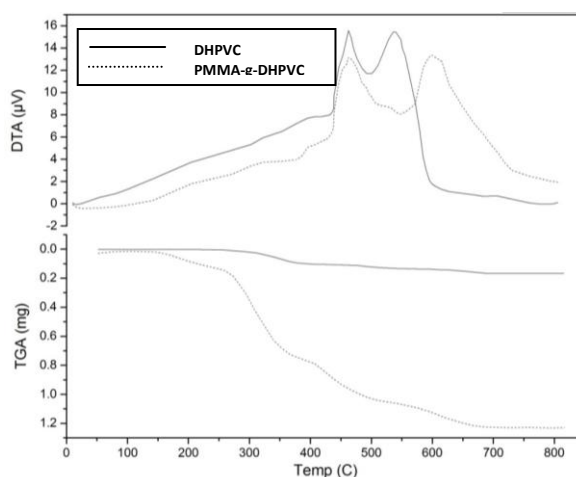


Fig 2. Thermal analysis (TGA and DTA) of the prepared PMMA-g-DHPVC copolymer (GP 70%) as compared to that of DHPVC

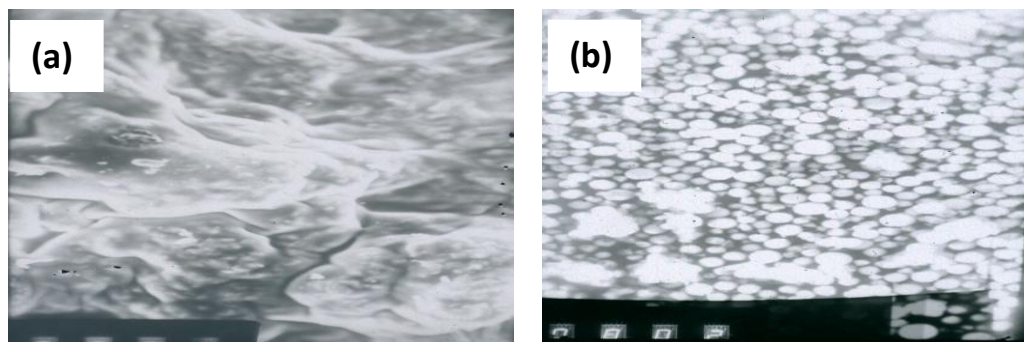


Fig 3. SEM micrographs of (a) DHPVC and (b) PMMA-g-DHPVC (70%) at X100

3.6. X-ray Diffraction

The X-ray diffraction (XRD) patterns of PVC and its prepared derivatives, DHPVC and PMMA-g-DHPVC were investigated as shown in Fig 4. As apparent from the figure, the diffractograms of both PVC and DHPVC showed two different broad bands in the 2θ ranges between $14-18^\circ$ and between $22-26^\circ$, respectively, indicating two distinct short range ordering of chains as usually found in the commercial PVC [17,18]. In the diffractogram of the PMMA-g-DHPVC (GP 20%), these two broad bands disappeared indicating a highly amorphous nature of the resulting copolymer. The amorphous character of the PMMA-g-DHPVC may be attributed to incidence of the grafting process in a random way along the DHPVC backbone leading to destroying the partial regularity of the packing of the original PVC chains. Additionally, it is known that PMMA has an amorphous nature [19]. This finding leads to the conclusion that grafting of PMMA causes the disruption of the less amount of ordering found in the DHPVC. The obtained difference in the diffraction patterns between DHPVC and the PMMA-g-DHPVC can be also taken as additional evidence on the occurrence of grafting.

3.7. Grafting Study

3.7.1. Effect of reaction time

The effect of reaction time in the range 0.5-3 h on the grafting of MMA onto DHPVC is shown in Fig 5. As can be noted from the figure, the grafting parameters (GP% and GE%) increased with increasing the reaction time. For instance, the GP% and GE% have increased after 3 h of irradiation time to reach 25% and 2.7%, respectively. The HOMO%, however, was found to be almost constant until 1 h of reaction then increased with time to attain 9.6% after 3 h. The reaction time generally affects the extent of chain transfer process. It seems from Fig 5 that, at the beginning of the reaction and until 1 h, the chain transfer occurs mainly to DHPVC chains and consequently the grafting process of MMA onto DHPVC chains was the predominating and almost no homopolymerization occurred. Beyond 1 h of reaction, the formed larger molecules of PMMA-g-DHPVC which increases the solution viscosity may encourage other chain transfer reactions towards more homopolymerization.

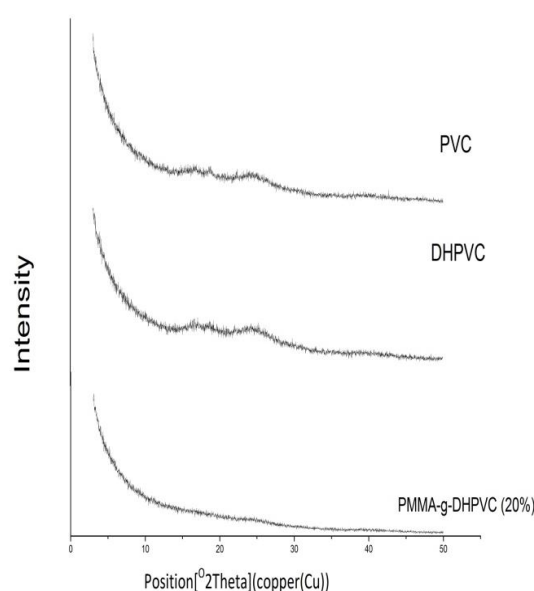


Fig 4. X-ray diffraction patterns of PVC, DHPVC, and the resulting PMMA-g-DHPVC (20%)

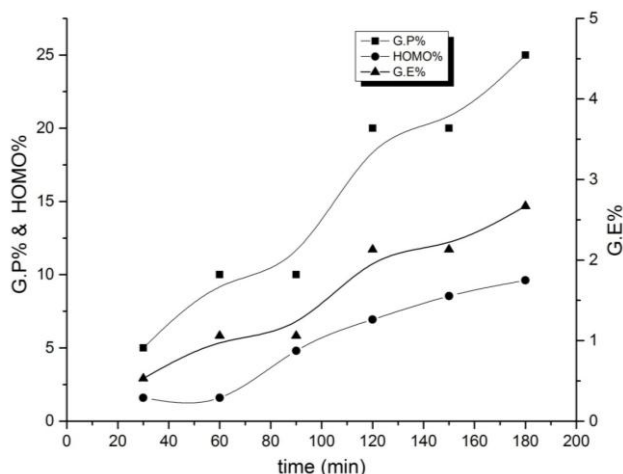


Fig 5. Effect of reaction time on the photoinduced grafting of MMA onto DHPVC using BPO/DMA in cyclohexanone, as initiator system: DHPVC (20 g/l), MMA (1.86 mol/l), initiator system (BPO 0.02 mol/l and DMA 0.02 mol/l).

3.7.2. Effect of monomer concentration

The graft copolymerization of MMA onto DHPVC was conducted at various concentrations of MMA in the range between 0.465 and 2.79 mol/l as shown in Fig 6. As apparent from the figure, there is an increase in both GP% and GE% upon increasing the MMA concentration up to a certain value (about 2.5 mol/l under the experimental conditions) and then they either leveled off (as GP%) or decreased (as the case of GE%) with the monomer further increasing. These obtained results may be attributed to the relatively limited number of active sites available for grafting on the DHPVC chains, then upon increasing the monomer amount, more competition takes place between MMA molecules for the same active sites on DHPVC leading to increasing the grafting extent (increased GP% and GE%) until saturation of the DHPVC backbones. At higher MMA concentrations, however, the excessive MMA molecules could induce drastically more chain transfer and termination reactions leading to more homopolymerization instead of graft copolymerization [20-22]. This assumption was confirmed by the observed increase in HOMO% up to 20.29% which showed an adverse effect on GE% values where its highest value did not exceed more than 5.5%. Moreover, once the PMMA-g-DHPVC copolymer is formed, the excess MMA may shield the graft copolymer, which may reduce the grafting rate [20].

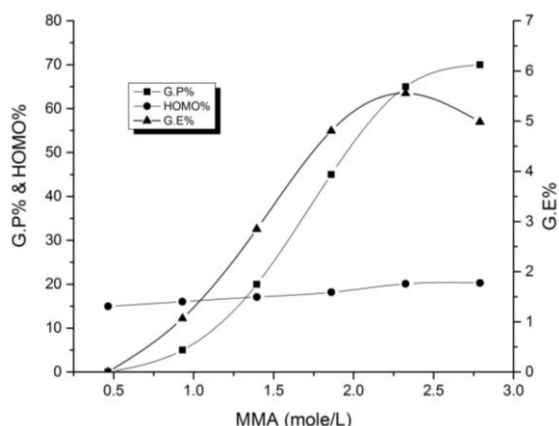


Fig 6. Effect of monomer(MMA) content on the photoinduced grafting of MMA onto DHPVC using BPO/DMA in cyclohexanone, as initiator system: DHPVC (20 g/l), initiator system (BPO 0.033 mol/l and DMA 0.047 mol/l), and irradiation time (3 h).

3.7.3. Effect of initiator system

3.7.3.1. Effect of BPO concentration

The effect of the initiator (BPO) content on the photoinduced grafting of MMA onto DHPVC in the presence of DMA is shown in Fig 7. The grafting results showed that, with keeping all the other parameters constant including the DMA concentration, increasing the BPO content was accompanied by increasing in both GP% and GE% until maximum values at BPO content of 0.033 mol/l followed by a decrease in the GP% and

GE% with further increase in the BPO content. This behavior can be attributed to occurrence of chain transfer reactions to the monomer upon increasing the BPO content which encourage homopolymerization instead of graft copolymerization. This can be confirmed from the increase in the HOMO% with increasing the BPO content.

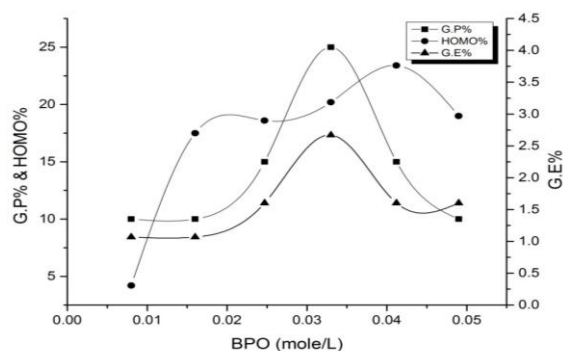


Fig 7. Effect of benzoyl peroxide (BPO) content on the photoinduced grafting of MMA onto DHPVC using BPO/DMA in cyclohexanone as initiator system: DHPVC (20 g/l), initiator system (DMA 0.02 mol/l), MMA (1.83 mol/l), and time 3 h.

3.7.3.2. Effect of DMA concentration

The effect of DMA content on the grafting reaction of MMA onto DHPVC in presence of constant amount of BPO and in the presence of visible light was studied and the results are shown in Fig 8. From the figure, it is apparent that increasing the DMA concentration (mol/l) was accompanied by an increase in the GP% and GE% until reaching the optimum condition at DMA concentration of 0.047 mol/l then the grafting yield (GP% and GE%) decreased with the further increase in the DMA content. This finding may be due to the chain transfer to monomer which was accompanied by increasing the homopolymer formation as appeared from the relative increase in the values of HOMO%.

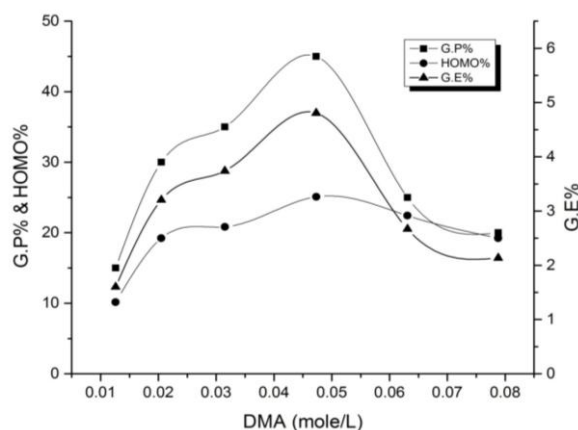


Fig 8. Effect of dimethylaniline (DMA) content on the photoinduced grafting of MMA onto DHPVC using BPO/DMA in cyclohexanone as initiator system: DHPVC (20 g/l), initiator system (BPO 0.033 mol/l), MMA (1.83 mol/l) and time 3 h.

3.7.4. Effect of DHPVC concentration

The dependence of grafting on the content of DHPVC was studied in the range of 10-60 (g/l) at constant contents of initiator and monomer as illustrated in Fig 9. From the figure, it can be noted that with increasing the DHPVC concentration the GP% and GE% steadily decreased. This noted reduction in the grafting yield was accompanied by a slight increase in the HOMO% values (increased from 19.2 to 22.1%). These results can be attributed to the increase in the viscosity of the medium upon increasing the DHPVC content, which consequently reduces the mobility of the macro free radicals, that resulting in a reduction in grafting and encouraging the homopolymer formation.

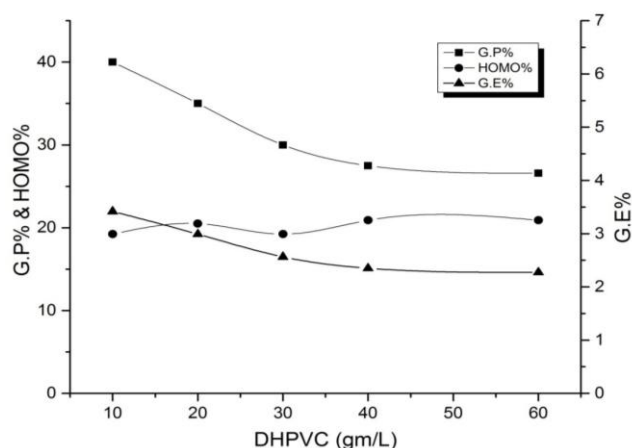


Fig 9. Effect of DHPVC content on the photoinduced grafting of MMA onto DHPVC using BPO/DMA in cyclohexanone as initiator system: MMA (1.83 mol/l), initiator system (BPO 0.033 mol/l, DMA 0.047 mol/l), and time 3 h.

3.7.5. Effect of solvent, cyclohexanone

The effect of solvent, cyclohexanone, on the grafting of MMA onto DHPVC was investigated using BPO and DMA as combined photoinitiator in the presence of visible light. The increase of cyclohexanone in the range between 0.19 and 1.15 mol/g was accompanied by a significant decrease in the values of GP%, GE% and HOMO% as shown in Fig 10.

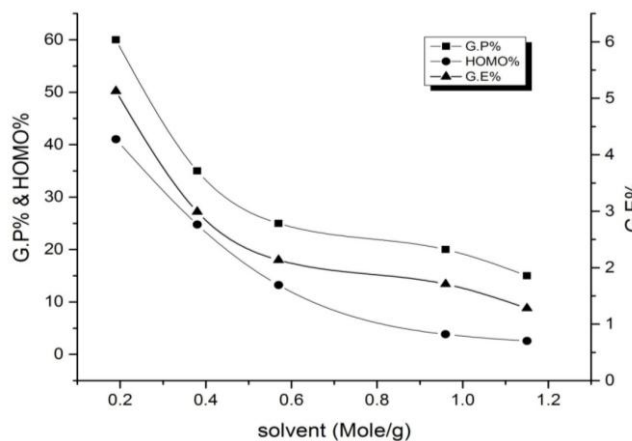


Fig 10. Effect of solvent (cyclohexanone) on the photoinduced grafting of MMA onto DHPVC using BPO/DMA in cyclohexanone as initiator system: MMA (0.011 mol/l), initiator system (BPO 0.00016 mol/l, DMA 0.00023mol/l), and time 3 h.

IV. CONCLUSIONS

In the current study, photo-induced grafting of MMA onto the prepared DHPVC was achieved at different experimental conditions in the presence of a combination of DMA and BPO, as a radical initiator system, in cyclohexanone. The effect of the various experimental conditions on the grafting yield has been extensively investigated and the optimum grafting conditions were investigated.

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