

In situ Catalytic Bulk Copolymerization of Maleate Surfmer-Methyl Methacrylate Using TiO₂ and V₂O₅ at Different Conditions

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Abstract

Non-ionic Maleate surfmer (M1) prepared via ring opening reaction of maleic anhydride followed by esterification with polyethylene glycol. Surfmer was homopolymerized and copolymerized with methyl methacrylate (M2) at different conditions using TiO₂ and V₂O₅ as catalysts in presence of O₂ or N₂. The chemical structure of the prepared surfmer was confirmed by FTIR, ¹³C and ¹H NMR. The produced copolymers were also confirmed and characterized by Gel Permeation Chromatography (GPC) after cleaning polymers. Also, thermal gravimetric analysis (TGA) indicated higher thermal stability for M1M2TN and M1M2VO composites relative to pure PMMA. Scanning and transmission electron microscope (SEM and TEM) for PMMA and M1M2TN may confirm homogeneous and controlled enchainment of M1-M2 copolymer using TiO₂ at the optimum conditions. The polymer conversion% was calculated and discussed. The optimum conditions resulted in 64.2% and 63.8% conversion using 20% TiO₂ in N₂ and 10% V₂O₅ in O₂ respectively at 80°C after 4h with M1/M2 molar ratio of 1:1. The interfacial tension properties for the prepared surfmer and its copolymer were evaluated.

Keywords: Catalytic copolymerization; Maleate surfmer; Methyl methacrylate; Interfacial Tension; HNMR

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Introduction

A significant number of studies have been undertaken on the polymerization of surfmers. Surfmer molecules present the advantage of combining the physical behavior of surfactants with the reactivity of monomers [1-3]. A wide variety of surfmer structures that differ with respect to polar functional groups (that is, hydrophilic and lipophilic balance) and the location of the polymerizable moiety have been reported. Examples include anionic, cationic, zwitterionic and nonionic surfactants [4-7]. The conventional polymerizable compounds that have been used include styrene, acrylic, methacrylic, and acrylamides [8-10]. The polymerizable surfactants are interesting in various fields. Several investigations have been carried out on maleic anhydride copolymers to be used as polymeric surfactants [11-13]. It was asserted for many years that 1,2-disubstituted ethylene does not polymerize, while maleic anhydride shows only a small tendency for radical polymerization [14]. Braun et al. [15] used various radical initiators to polymerize maleic anhydride; they observed

partial decarboxylation and obtained a polymer which consists mainly of cyclopentanone derivatives. Heseding and Schneider [16] prepared maleic anhydride homopolymer by γ -irradiation. The polymer obtained by initiation via irradiation showed the anhydride structure without decarboxylation and discoloration. These results were in good accord with the findings from the work of Lang et al. [17]. Synthesized catalysts for industrial purposes consume a billion-dollar and account for the manufacture of 60% of chemicals that are utilized for most chemical transformations. Catalytic processes enable the production of many substances such as polymers, plastics, pharmaceuticals, detergents and many others [18-23]. For example, fabricated electrospun TiO₂ has been designed, synthesized and used as green catalyst for save chemical process by Shrikant et al. [24].

Polymer-inorganic nanocomposites have a great attention recently due to their importance in different fields. It is known that TiO₂ and V₂O₅ have good thermal and photo-catalytic activities in different chemical processes such as polymerization

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and environmental treatment reactions [25,26]. Also nano-TiO₂ has bioactivity behaviors and thus polymer-TiO₂ nanocomposites can be used in industrial and medical areas [27-29]. The functionality of PMMA/CaSO₄ nanocomposites has been studied to be used as support for gentamicin antibiotic in bone substitute material and antibiotic vehicle [30]. Maleic anhydride (MA)-copolymers have been used as polymer-drug conjugates [31,32]. These copolymers are usually prepared in organic solvents which have cytotoxicity effect. The simple maleate surfmer (i.e. the neutralized hemi ester of a fatty alcohol) was used to prepare seeds of polystyrene latex which were grown with a shell of film-forming polymers [33].

This investigation describes a novel method for catalytic copolymerization of nonionic maleate surfmer with methyl methacrylate using *in situ* bulk polymerization technique to keep away from terrible effects of organic solvent. Copolymerization process was carried out using TiO₂ and V₂O₅ in presence of O₂ or N₂ atmosphere at different reaction temperature, reaction time and molar ratios of monomers. Also, the mechanism of this reaction with and without catalyst was estimated.

Experimental Section

Materials

All chemicals were purchased from Aldrich Co. First of all, linear hexanol was dried using magnesium sulphate (MgSO₄) then distilled under atmospheric pressure. Also, maleic anhydride (MA) was refluxed with chloroform and filtered to remove any traces of maleic acid. Finally, the product was then crystallized three times from chloroform to yield white needles with a melting point of 53°C. Polyethylene glycol 200 (PEG₂₀₀) and p-toluene sulphonic acid were used as received from Merck-Schuchardt. Methyl Methacrylate (MMA) was purified to remove the hydroquinone inhibitor by following the previous method [33,34]. TiO₂ and V₂O₅ are purchased from Sigma Comp.

Synthesis of the non-ionic maleate surfmer (M1)

The maleate surfmer as shown in **Scheme 1** was prepared in two steps. Firstly is the preparation of the hemiester of maleic anhydride via ring opening reaction. Maleic anhydride (0.1 mole) was placed in one necked flask and 0.12 mole of hexanol was added and then the reaction mixtures stirred at 80°C for one hour. Heptane was added to the reaction mixtures and stirred to dissolve the unreacted maleic anhydrides. This process was repeated three times. The unreacted hexanol was removed by dissolving reaction mixture in appropriate amount of ethyl acetate and wash three times with super saturated NaCl solution. Ethyl acetate was evaporated and the prepared hemiesters were collected.

The second step is the preparation of maleate surfmer (maleate diester) by esterification of 0.1 mole of hemiester with 0.1 mole of PEG₂₀₀. The reaction was performed in presence of 1% p-toluene sulphonic acid as a catalyst and xylene as a solvent. When the reaction completed, the solvent was distilled off under reduced pressure and the pure surfmer was obtained. Unreacted

polyethylene glycol was removed by mixing the product with isopropanol and then extraction with a solution of 5% sodium carbonate. Isopropanol was then removed by distillation under reduced pressure in a rotary evaporator. The produced diester surfmer (MANS₂₀₀) was left to dry overnight on anhydrous sodium sulphate and will be denoted as M1 in discussion.

Catalytic bulk polymerization of M1 and copolymerization of M1 and M2

Surfmer monomer (M1) 3.6 g and previously purified MMA (M2) 1.0 g with molar ratio of 1:1 was mixed in test tube of 20 ml capacity, then the catalyst samples TiO₂ or V₂O₅ were added with different weight% (2, 10 and 20%) with respect to the total monomers weight. Dry nitrogen or oxygen were passed through the reaction mixture then the reaction test tube was tightly closed and put in adjusted water bath at the required temperatures (60, 80 and 100°C) for different times (2, 4, 8 and 12 h) and different molar ratios (1:2 and 2:1). When the reaction completed, the product container cooled to 25°C, opened and the produced copolymer was dissolved in acetone to separate copolymer solution from the catalyst by filtration. This copolymer precipitated by running in methanol then filtered and dried under vacuum at 40°C till stable weight. Maleate surfmer monomer (M1) also polymerized using the two catalysts in N₂ and O₂ atmosphere for comparison. The conversion% of product was calculated by the following equation:

$$\text{Conversion\%} = (\text{weight of copolymer} / \text{total weight of monomers}) * 100$$

Characterization of non-ionic maleate surfmer M1, its polymer (PM1) and its copolymer (M1M2)

The prepared copolymers were characterized by using Gel Permeation Chromatography (GPC) to determine the number-average molecular weights (Mn), weight-average molecular weights (Mw), and polydispersity index (Mw/Mn) for different produced copolymer samples and as described previously [25]. Nuclear magnetic resonance ¹H, ¹³C NMR spectra of the prepared non-ionic maleate surfmer, its homopolymer and co-polymers were recorded in chloroform using a Varian NMR-400-Mercury 400 MHz spectrometer with TMS as an internal standard. Fourier transform infrared (FTIR) spectra were measured using polymer/KBr disks with a Perkin Elmer 1500 Fourier transform spectrometer.

Interfacial tension measurements

The interfacial tension measurements were carried out using tensiometer K10ST, from KRUSS, at temperature of 298 K, by using the Du Nouy method. Different molar concentrations of the prepared non-ionic maleate surfmer and co-polymers were dissolved in toluene. The aqueous phase was a solution of distilled water. The interfacial tensions were quantified for 15 min after putting the oil and water phases in contact. The CMCs of the prepared surfactants were determined by the method adopted [35].

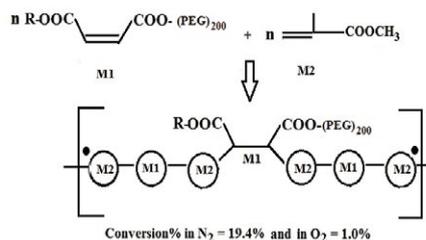
Results and Discussion

Polymerization of maleate surfmer and its copolymerization with MMA

Maleate surfmer homo-polymerized and copolymerized with methyl methacrylate through bulk technique with and without catalysts (TiO_2 or V_2O_5) at different molar ratios, catalyst weight, reaction time, reaction temperature under O_2 or N_2 atmosphere.

Noncatalytic M1 polymerization and M1-M2 copolymerization:

Table 1 represents the conversion% of bulk homo-polymerization of surfmer (PM1) and its copolymerization with M2 (M1M2 with molar ratio 1:1) in O_2 and N_2 atmosphere with/without TiO_2 or V_2O_5 at 80°C for 4 h. The results indicate that the non-ionic maleate surfmer M1 gave nil polymer in both O_2 and N_2 atmospheres without catalyst [36]. While mixing of MMA monomer (M2) with maleate surfmer M1 increased the conv.% from nil to 1.0 and 19.4% in O_2 and N_2 atmospheres respectively producing copolymers M1M2O and M1M2N. Previous publications indicated that MMA can be polymerized in both O_2 and N_2 with higher conversion% in oxygen by oxidative polymerization mechanism [25,37]. These observations indicate that M1 and M2 are mostly activated thermally at the reaction temperature and produce free radicals according to Sudha et al. [38]. **Scheme 2** suggests the free radical mechanism for bulk copolymerization of M1-M2 by producing M2 free radical (MMA*) which initiate

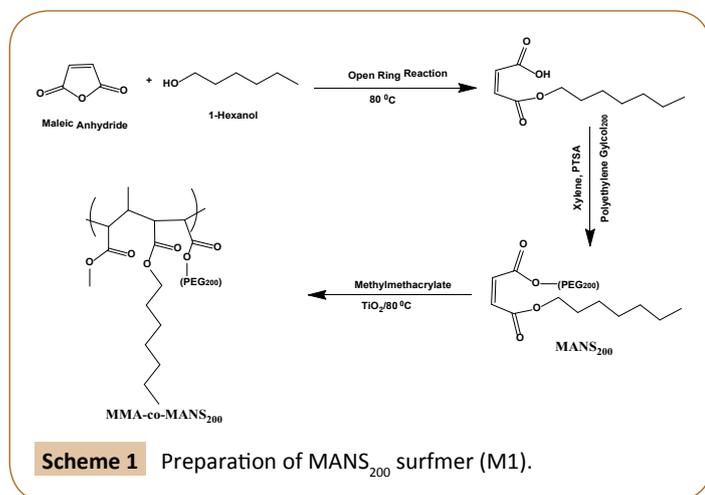


Scheme 2 M1-M2 copolymerization in N_2 atmosphere.

M1 molecules and produce the first free radical unit (*M2-M1*) which capable of starting initiation and propagation steps in N_2 atmosphere [39]. On the other hand, M1 homopolymerization and its copolymerization in O_2 gave nil and 1% respectively mostly due to formation of epoxides on double bond (C=C) of M1. This epoxide is stable due to its conjugation with the two carbonyl (C=O) of two ester arms which can act as electron withdrawing groups. These stable epoxides cannot break to free radicals and thus block the created MMA free radicals and inhibit maleate surfmer homo-polymerization and its copolymerization with MMA. It can be concluded that MMA activated the double bond of maleate monomer in N_2 while O_2 form stable epoxides and block created free radicals. Also M1 and M2 have different activity with oxygen, the first inhibited while the second is activated in their polymerization process.

Catalytic M1 polymerization and M1-M2 copolymerization:

Homo-polymerization of M1 using TiO_2 and V_2O_5 in O_2 or N_2 atmospheres and its copolymerization with M2 at the same abovementioned conditions exhibited acceptable conversion% of polymers (**Table 1**). So, this work was to be intent on catalytic *in situ* bulk copolymerization of M1-M2 at different conditions and its comparison with M1 homo-polymerization results at the optimum conditions. The results on handing in **Table 1** inform that, catalytic copolymerization of M1-M2 using TiO_2 in N_2 and O_2 produce M1M2TN and M1M2TO copolymers with conv.% values 64.2 and 31.6% respectively at the abovementioned conditions. The conv.% increased due to TiO_2 activity in N_2 and O_2 with values of ~ 44 and 30% relative to copolymers without catalyst (M1M2N and M1M2O respectively). It is clear that TiO_2 have better concert in N_2 relative to O_2 environments in M1-M2 copolymerization process. Previous publication for bulk polymerization of MMA using CuO/TiO_2 at 80°C for 5 h indicated that the conv.% of PMMA were 20 and 24% using TiO_2 in N_2 and O_2 environment respectively [25]. These previous results indicated the probability of an oxidative polymerization mechanism for MMA in such conditions [25]. Comparison between these previous results and present work confirm that TiO_2 which is a semiconductor, can be activated thermally and creates its e_{CB}^- that capable of opening the olefin double bond of M1 and M2 to start the initiation step through free radical mechanism in N_2 atmosphere. The concept that M1 also initiated by TiO_2 is confirmed from its homo-polymerization results in N_2 and O_2 with conv.% values of 21.5 and 18.4% respectively and nil without TiO_2 from **Table 1**. These observations confirm that O_2 may be forms stable epoxides with the olefin double bond of maleate monomer specially and the



Scheme 1 Preparation of MANS_{200} surfmer (M1).

Table 1: Effect of metal oxide and reaction atmosphere (O_2 and N_2) on the conversion% of M1 homo-polymerization and M1M2 copolymerization at 80°C for 4 h.

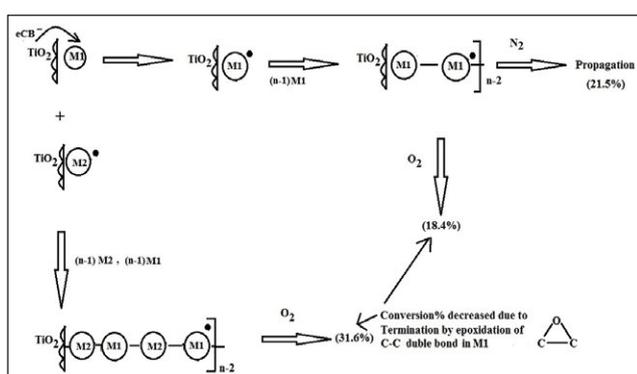
Nanocomposite Code	Catalyst Type and weight%	Atmosphere	Conv.%
M1	No	O_2 and N_2	0.0
M1M2N	No	N_2	19.4
M1M2O	No	O_2	1.00
M1TN (20%)	20% TiO_2	N_2	21.5
M1TO (20%)	20% TiO_2	O_2	18.4
M1M2TN (20%)	20% TiO_2	N_2	64.2
M1M2TO (20%)	20% TiO_2	O_2	31.6
M1M2VN (20%)	20% V_2O_5	N_2	43.3
M1M2VO (20%)	20% V_2O_5	O_2	63.8

rate of initiation step by TiO_2 is higher than the rate of epoxidation of $\text{C}=\text{C}$. So, propagation step retarded slightly and gave conv% value of 18.5% in oxygen environment.

On the other hand, results in **Table 1** inform that V_2O_5 promotes copolymerization reaction in O_2 better than in N_2 atmospheres and the corresponding conv.% are 63.8 and 43.3, so the actual conv.% due to V_2O_5 activity are 24 and 62.8% relative to M1M2N and M1M2O respectively. It is concluded that TiO_2 and V_2O_5 have different routes in this reaction. The electronic distribution of V_2O_5 surface mostly modified due to adsorption of oxygen and creates more active sites which accelerate initiation and propagation rates, so conv.% increased from 1% in O_2 to 63.8% due to the catalytic effect of oxygen and V_2O_5 . It is concluded that TiO_2 is more dependable than V_2O_5 in this reaction because TiO_2 without oxygen give the same conv% (~64%) using V_2O_5 in oxygen. Also, maleate homo-polymerization have different route and give lower conv% in O_2 atmosphere versus MMA using catalysts. So, the effect of catalyst weight will be studied in N_2 environment. **Scheme 3** gives a suggestion for initiation and propagation mechanism of M1 and M1-M2 polymerization in N_2 using TiO_2 as a catalyst. Mostly, M1-M2 copolymer have an alternating units (-M1-M2-M1-M2-) in these conditions.

Effect of catalyst weight%: **Table 2** represents the conv.% of M1-M2 copolymerization using different weight% of TiO_2 and V_2O_5 in N_2 atmosphere. The conv.% increased from 19.4% without catalyst to 41.8, 56.3 and 64.2% using 2, 10 and 20 wt% of TiO_2 and to 34.5, 47.2 and 43.3% using the same wt% of V_2O_5 respectively. The optimum weight% of TiO_2 and V_2O_5 is 20 and 10% respectively.

Molecular weight distribution of produced polymers indicates that as TiO_2 wt% increased; α_w and α_n are increased but the polydispersity index ($\Delta w/\Delta n$) is nearly the same. These results indicate that number of active sites, number of polymer chains (Δn) and thus initiation and propagation rate are increased. Also, Δw and Δn increased by increasing V_2O_5 wt% but 10% give the maximum conv.% and better polydispersity index ($\Delta w/\Delta n=1.99$). These observations indicate better controlling using V_2O_5 mostly due to catalytic chain transfer [38]. So, conv% decreased by increasing wt% of V_2O_5 .



Scheme 3 Catalytic homo-polymerization of maleate surfmer (M1) and its copolymerization with MMA (M2) using TiO_2 in N_2 and O_2 atmospheres.

Effect of M1/M2 molar ratio, reaction temperature and reaction time: **Table 3** show the effect of M1/M2 molar ratios (1/2, 1/1 and 2/1), effect of reaction temperature (60, 80 and 100°C) and effect of reaction time (2, 4, 8 and 12 h) on conv.% of M1-M2 copolymerization in N_2 atmosphere using TiO_2 as catalyst. The optimum molar ratio of M1/M2 is 1:1. Also, conv.% due to molar ratio of 1:2 is better than 2:1 (45.8 and 30.5% respectively) as shown in **Table 3**. These observations confirm that M2 (MMA) initiate M1 and they may be repeated alternately (-M2-M1-M2-M1-) as suggested in **Scheme 3**.

Table 3 shows the conv.% at reaction temperatures 60, 80 and 100°C are 27.2, 64.2 and 30.5%. Also, conv.% after reaction time 2, 4, 8, 12 h are 37.4, 64.2, 62.2 and 32.5% respectively. The optimum reaction temperature and time are 80°C and 4 h. The conv.% decreases with longer reaction time and higher reaction temperature may be due to higher rate of chain transfer reaction [37] and/or epoxidation rate. Two ester groups of maleate surfmer unit can act as π -acceptor for the neighboring π -bond ($\text{C}=\text{C}$) electrons, which mostly resulted in stabilization of epoxides and thus inhibition of propagation step.

Characterization

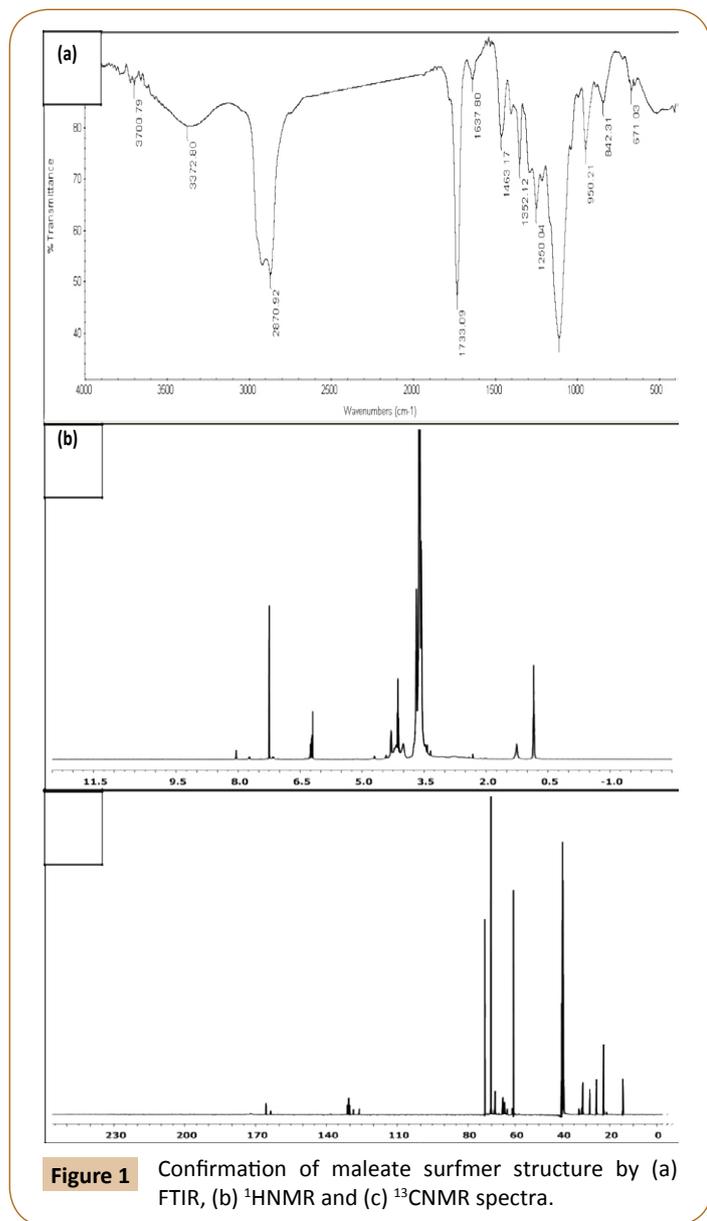
Verification the chemical structure of the prepared non-ionic maleate surfmer (M1): The chemical structure of the prepared non-ionic surfmer (M1) was defined by FTIR, ^1H and ^{13}C NMR as shown in **Figure 1a-1c** respectively. Figure 1a shows the FTIR of M1 surfmer which indicates the presence of a band at 1733

Table 2: Effect of weight% of TiO_2 and V_2O_5 catalysts in N_2 atmosphere at 80°C for 4 h on conversion% of M1M2 copolymers.

Nano-composite Code	Wt.% of Catalyst	Conv.% of Copolymers	Molecular weight distribution		
			α_w	α_n	α_w/α_n
M1M2TN(2)	2% TiO_2	41.8	251280	116618	2.16
M1M2TN(10)	10% TiO_2	56.3	267303	129649	2.06
M1M2TN(20)	20% TiO_2	64.2	307294	143293	2.1
M1M2TO(20)	20% TiO_2	31.6	323218	148064	2.18
M1M2VN(2)	2% V_2O_5	34.5	167133	76294	2.2
M1M2VN(10)	10% V_2O_5	47.2	173377	87149	1.99
M1M2VN(20)	20% V_2O_5	43.3	196320	95542	2.06
M1M2VO(20)	20% V_2O_5	63.8	168458	88888	1.89

Table 3: Effects of M1/M2 molar ratio, reaction temperature and reaction time on conversion% of M1M2 copolymer using optimum wt% TiO_2 in N_2 atmosphere.

Nanocomposite Code	M1/M2 Molar Ratio	Temperature (°C)	Conv.%
M1/M2TN(20)	1/2	80	45.8
M1M2TN(20)	1/1	80	64.2
M1M2TN(20)	2/1	80	30.5
M1M2TN(20)	1	60	27.2
M1M2TN(20)	1	80	64.2
M1M2TN(20)	1	100	30.5
M1M2TN(20)	1	80	37.4
M1M2TN(20)	1	80	64.2
M1M2TN(20)	1	80	62.2
M1M2TN(20)	1	80	32.5



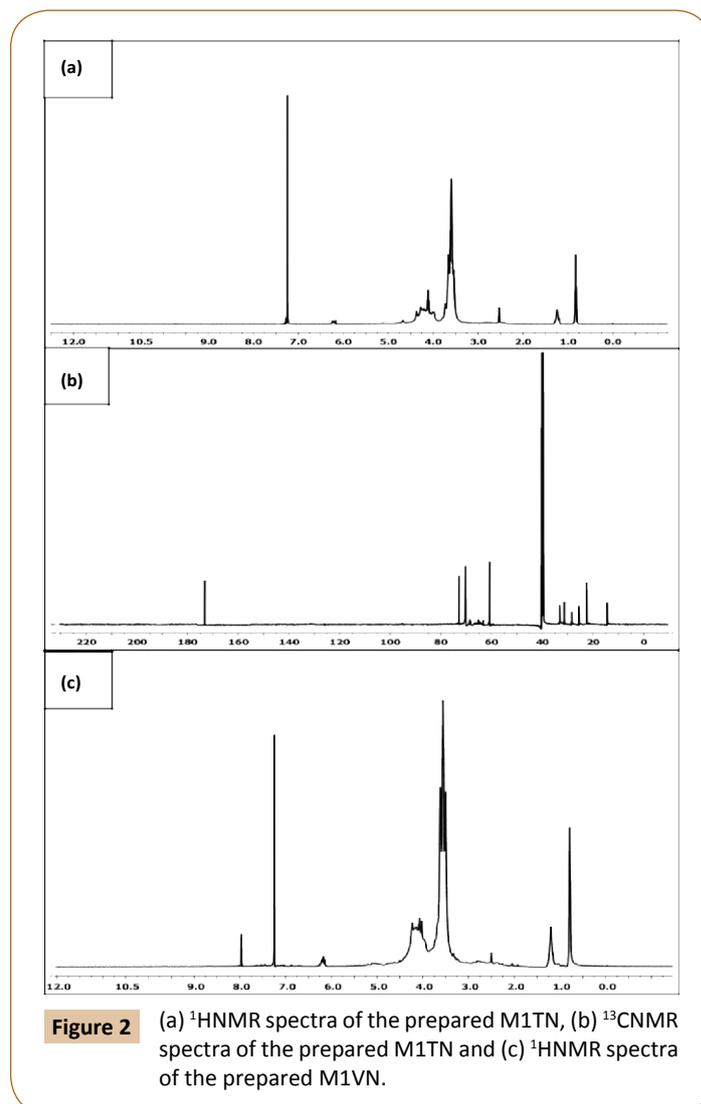
cm⁻¹ due to carbonyl group of the prepared diesters and two bands at 2870 and 2999 cm⁻¹ due to symmetric and asymmetric methylene group. Disappearance of two characteristic bands at 1810 and 1780 cm⁻¹ of the two arms of anhydride group of maleic anhydride confirms the formation of diester. Whilst the presence of OH stretching at 3372 cm⁻¹ indicates that PEG is one of the constituents of the prepared monomer in addition to the band at 1100 cm⁻¹ due to the ethereal bond C-O-C [31]. Also, the olefinic bond=CH₂ still present and appeared at 1637 cm⁻¹.

¹H NMR of M1 in **Figure 1b** confirms M1 structure as follow: a chemical shift appears at δ=0.851 and 1.261 ppm due to the terminal (CH₃-) and (-CH₂)_n of 1-hexanol respectively, the chemical shift resulted from the double bond of two protons of maleate appeared at 6.233 ppm. Three characteristic chemical shifts at 3.621, 4.13, and 4.701 ppm due to PEG moiety are appeared.

The chemical structure of the prepared surfmer is also justified through ¹³C NMR spectra as shown in **Figure 1c**. The figure shows chemical shifts at 13.8, 22.0, 30.9, 25.0, and 27.9 ppm due to

the alkyl chain of hexanol (CH₃CH₂CH₂CH₂CH₂-) respectively, a chemical shifts due to double bond of maleate surfmer at 130.0 ppm, a chemical shift of carbonyl group due to ester formation at 165 ppm, and finally chemical shifts of PEG at 64, 72, and 60 ppm. It can be concluded that all confirmation methods for the prepared M1 monomer structure are coincided together.

Confirmation of M1 homopolymer and M1-M2 copolymers using ¹³C and ¹H NMR spectra: Maleate surfmer was homo-polymerized using 20% w/w TiO₂ and V₂O₅ as catalysts in nitrogen atmosphere at 80°C for 4 h and produce M1TN and M1VN respectively. The ¹H NMR spectra of M1TN and M1VN samples and ¹³C NMR of M1TN sample are shown in **Figure 2a-2c** respectively. It can be seen from ¹H NMR that the spectrum of M1TN and M1VN differs from that of the monomer M1 (**Figure 1b**) in terms of the appearance of a triplet band at 2.5 ppm which represents the (-CH-CH-) protons in the polymer backbone and disappearance for the band of double bond maleate surfmer (-CH=CH-) which confirm homopolymerization of M1. The ¹³C NMR in **Figure 2b** for M1TN sample shows a chemical shift at δ=30.896 ppm due to polymerized (-CH-CH-) of maleate surfmer and confirm ¹H NMR results.



The maleat surfmer (M1) also copolymerized with methyl methacrylate (M2) with molar ratio of 1:1 in presences of TiO_2 and V_2O_5 under oxygen or nitrogen atmosphere at 80°C for 4 hrs. ^1H NMR spectra of copolymers (M1M2TN and M1M2VN) and ^{13}C NMR of M1M2TN are presented in **Figure 3a-3c** respectively. From the comparison of M1M2TN copolymer with M1TN homo-polymer, it is of interest to mention that $-\text{CH}-$ band due to backbone of surfmer shifted from 2.5 ppm in M1TN to 2.719 ppm in M1M2TN and be stronger and broader band. In addition, disappearance of the two olefinic protons ($\text{C}=\text{C}$) at $\delta=6.2$ ppm confirm copolymerization of surfmer with MMA. The chemical shift of the ($-\text{OCH}_3$) of acrylate appeared at $\delta=3.3$ ppm and also, the characteristic bands of PMMA which appeared between 0.0 and 2.0 ppm confirm copolymerization of MMA. The abovementioned results confirmed by ^{13}C NMR of copolymer (M1M2TN) in **Figure 3c**. From this figure it can be observed a new chemical shifts at $\delta=33$ ppm due to copolymerization, chemical shift at $\delta=19.0$ and 52.3 ppm due to the methyl group (CCH_3) of hexyl chain and methoxy (OCH_3) of methyl methacrylate respectively.

It is concluded that ^1H NMR of M1 contain $-\text{CH}=\text{CH}-$ characteristic band at chemical shift of 6.233 ppm. This band disappears in ^1H NMR spectra of M1 homo-polymer and M1M2 copolymers. ^1H NMR of M1 contain ($-\text{CH}_2-$)_n and terminal $-\text{CH}_3$ characteristic bands due to hexyl chain at 1.261 and 0.851 ppm respectively.

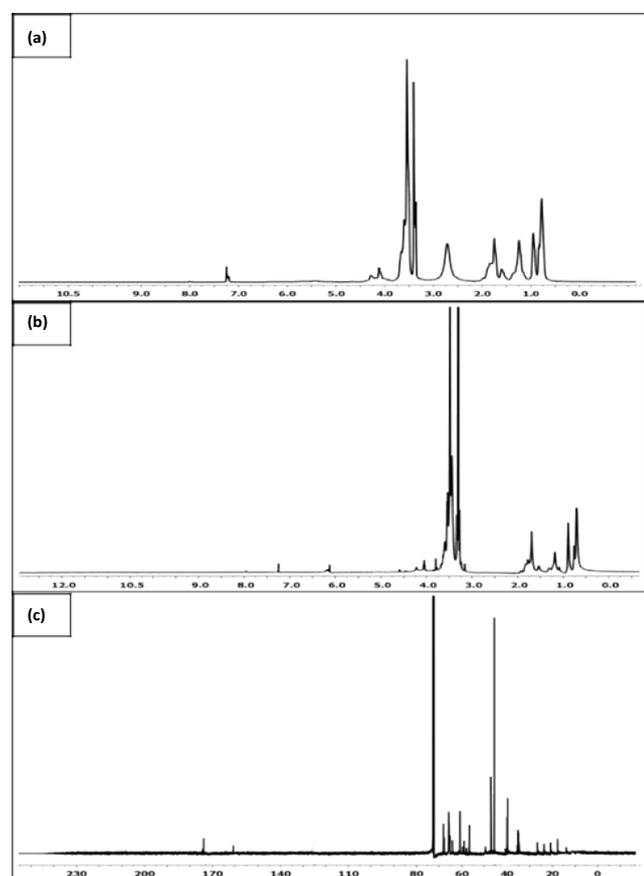


Figure 3 ^1H NMR spectra of (a) M1M2TN, (b) M1M2VN and ^{13}C NMR of M1M2TN (c).

These bands still present in all spectra of M1 homo-polymer and M1M2 copolymers. These observations confirm homopolymerization of M1 and its copolymerization with MMA. PMMA have singlet bands at 0.85, 1.03, 1.22 ppm due to (rr), (mr) and (mm) respectively. Multiple bands appeared between 1.8 -2.3 ppm due to (rrr), (mrr), (mrr) and (mrm) respectively. These bands appear in samples M1M2VN and M1M2TN and disappear in samples M1M2VO and M1M2TO spectra. The band of $-\text{OCH}_3$ due to PMMA appear at 7.278 ppm in spectra of M1M2VO and M1M2TO but sharply decreased in M1M2VN and M1M2TN. These observations may indicate that O_2 and N_2 environments have different effect on M1-M2 repeating. The two monomers M1 and M2 may be repeated as M1M2M2M2M1 in N_2 which resulted in appearing of the multiple bands. On the other hand, these multiple bands disappear in spectra of M1M2TO and M1M2VO. Also $-\text{OCH}_3$ band appeared in spectra of these samples. These observations may indicate that M1 and M2 are repeated in their copolymer as M1M2M1M2. It is concluded that O_2 environment affect as co-initiator which give more controlled enchainment process.

Thermogravimetric analysis (TGA): **Figure 4** shows the thermogravimetric analysis of pure PMMA, M1-M2 copolymer at optimum conditions using 20% titanium oxide in nitrogen atmosphere (M1M2TN) and using 10% vanadium pentoxide in oxygen atmosphere (M1M2VO). The figure shows the higher thermal stability of the two copolymer composite samples relative to PMMA.

Scanning and transmission electron microscope: **Figure 5a-5d** show TEM of pure PMMA and SEM of M1M2TN sample with different magnification factors (X50, X200 and X2000) respectively. TEM of PMMA show pure film of PMMA matrix. SEM of M1M2TN in **Figure 5b** show interacted TiO_2 particles with M1-M2 copolymer matrix. This interaction be clear by higher magnification in **Figure 5c and 5d**. This figure is clearly show homogeneous copolymer matrix centered around points which are mostly the catalyst particles.

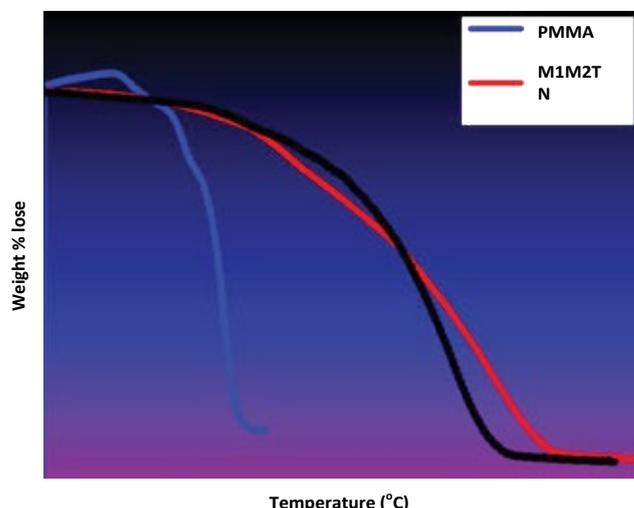


Figure 4 Thermogravimetric analysis of pure PMMA, M1M2TN and M1M2VO.

Interfacial properties for prepared surfmer and its corresponding copolymer:

The effect of the surfmer and its copolymer concentrations ($\ln C$) on the reduction of the interfacial tension (γ) of the toluene-water interface at 298 K is showed in **Figure 6**. Two curves presented similar expected behavior for surfactants. First, a linear decreasing in the interfacial tension is observed with increasing the surfactants concentration, which means that the adsorption of the prepared surfactants molecule at the toluene-water interface is in accordance with the Gibbs adsorption isotherm. The interfacial activity was available by the rate of the interfacial tension decreasing to the increasing in the natural \ln of the surfactants concentration, and it was got from the angular coefficient of the linear curves in $\gamma-\ln C$ plot.

$$a = -d\gamma / d \ln C$$

where: a is the interfacial activity, N/m; γ is the interfacial tension, N/m; and C is the concentrations of prepared surfactants mol/kg. From a certain concentration, the interfacial tension value became constant. It was assumed that the saturation of the prepared surfactants molecule at the interface was reached and micellization took place, by the self-aggregation of surfactants molecules. The CMC value was got by the intersection of two segments prolongation in $\gamma-\ln C$ plot. According to data obtained from interfacial tension curves and listed in **Table 4**, it can be observed that, for the prepared copolymer, the interfacial tension for them less than the corresponding prepared surfmer, this may be due to increasing the hydrophobic portion which

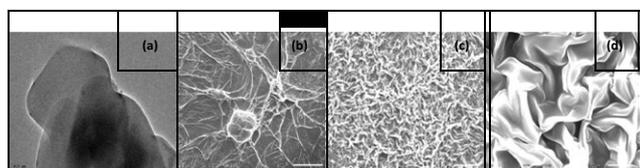


Figure 5 (a) TEM of pure PMMA and SEM of M1M2TN composite with different magnification (b) X50, (c) X200 and (d) X2000.

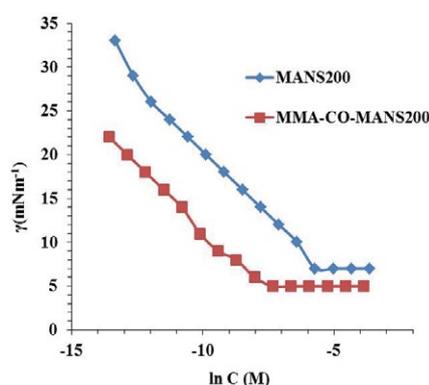


Figure 6 Variation of the interfacial tension with \ln concentrations of synthesized nonionic surfmer (M1) and its copolymer with methylmethacrylate between water and toluene at 25°C.

leads to easily oriented to the interface and adsorbed on it which leads to a continuous shift of the CMC to lower values [40].

The maximum surface excess (Γ_{\max}) was calculated from the relationship:

$$\Gamma_{\max} = \frac{1}{RT} \left(\frac{-\delta\gamma}{\delta \ln C} \right) T,$$

Where $(-\delta\gamma/\delta \ln C)T$ is the slope of γ versus $\ln C$ plots at a constant absolute temperature T and $R=8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The data of Γ_{\max} are shown in **Table 5**. For the surfmer the Γ_{\max} values are higher than the corresponding values for the copolymers derived from them. This may be attributed to a higher degree of packing for the molecules of the surfmer than that of the molecules of the corresponding polymeric surfactant.

The Γ_{\max} values were used for calculating the minimum area A_{\min} in nm^2 per molecule at the interface using the following equation:

$$A_{\min} = \frac{10^{16}}{N\Gamma}$$

Where, N is Avogadro's number, the values of the A_{\min} for the prepared surfactants calculated and listed in **Table 4**. A_{\min} for prepared copolymeric surfactant is higher than the corresponding surfmers; this may be due to increasing its molar mass which leads to increase in the radius of gyration of the molecule [41,42].

The standard free energy of micellization (ΔG_{mic}) determination has played an important role in developing a clear understanding of the process of micellization, which is important for discerning clarification, the impacts of effects of structural and environmental factors on the value of the CMC and for predicting the effects on it of new structural and environmental variations [43]. It can be determined by the following equation:

$$\Delta G_{\text{mic}} = RT \ln CMC$$

By analyzing the values of standard free energy of micellization (ΔG_{mic}) in **Table 5**, it may conclude that, the values of standard free energy of have negative charge this mean that the micellization process is spontaneous ($-\Delta G_{\text{mic}}$). The values of ΔG_{mic} for MMA-co-MANS₂₀₀ more negative than the corresponding surfmer and this may be due to increasing the hydrophobic moiety, the increase in hydrophobic chain length increases its distortion motion in the solution, so the free energy increases. The increase of the free energy expressed by $-\Delta G_{\text{mic}}$ evidence this concept.

Table 4: Interfacial properties for the synthesized surfmer and its copolymer from interfacial tension measurements at 25°C.

Surfactants	CMC $\times 10^4$ (mol L ⁻¹)	γ_{CMC} (mNm ⁻¹)	Π_{CMC} (mNm ⁻¹)	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	A_{\min} (Å ²)
M1	32.70	7	29.1	-1.22	135.25
M1M2TN(20)	6.48	5	31.1	-1.19	139.14

Table 5: The free energy of micellization, the free energy of adsorption and the hydrophobic-lipophilic balance (HLB) for the synthesized surfactants.

Surfactants	ΔG_{mic} (kJ mol ⁻¹)	ΔG_{Ads} (kJ mol ⁻¹)	$\Delta G_{\text{mic}}-\Delta G_{\text{Ads}}$	HLB
M1	-14.16	-16.53	2.37	10.47
M1M2TN(20)	-18.16	-20.77	2.61	8.29

The Standard free energy of adsorption (ΔG_{ads}) was calculated by the use of ΔG_{mic} values from the relationship [44]:

$$\Pi_{CMC} A_{CMC} \Pi_{CMC} A_{min} = \Delta G_{mic} - \Delta G_{ad}$$

i.e. the $\pi_{CMC} A_{min}$ product expresses the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle. The ΔG_{ad} values are all negative as listed in **Table 5** and are more negative than ΔG_{mic} , indicating that adsorption at the interface is associated with a decrease in the free energy of the system.

The differences between ΔG_{mic} and ΔG_{ad} from previous equation can be written as

$$0.6023 A_{min} \pi_{CMC} = \Delta G_{mic} - \Delta G_{ad}$$

where the product $A_{min} \pi_{CMC}$ expresses the work involved in transferring a surfactant molecule from a monolayer zero surface pressure to a micelle; ΔG_{mic} and ΔG_{ad} values are listed in **Table 5**. It is apparent that the work of transfer, which measures the ease of adsorption to form a monolayer at zero surface pressure relative to ease of micellization, shows observed change with increasing the hydrophobic moiety for copolymer than the corresponding surfmer. The positive values of $\Delta G_{mic} - \Delta G_{ad}$ reflect that, the prepared surfactants are more readily adsorbed at interface. This in turn could account for investigating these surfactants in petroleum application.

The HLB values were calculated using the general formula for non-ionic surfactants,

$$HLB = [M_H / (M_H + M_L)] * 20$$

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where M_H is the formula weight of the hydrophilic portion of the surfactant molecule and M_L is the formula weight of the hydrophobic portion. The calculated HLB listed in **Table 5**. When the hydrophobic moiety increases by copolymerization, the HLB decrease and this give conception on good solubility of copolymers in oil.

Conclusion

Nonionic maleate surfmer was synthesized in two steps and used as a monomer (M1). The first is the ring opening by hexyl alcohol and the second is the esterfaction reaction with PEG₂₀₀. The chemical structure of the prepared surfmer M1 was confirmed by FTIR, ¹H and ¹³CNMR spectroscopy. M1 homo-polymerization give nil conv.% but copolymerized with MMA with conv.% of 19.4 and 1% in N₂ and O₂ atmosphere respectively without catalyst. Also, M1 homo-polymerized in presence of TiO₂ as catalyst in N₂ and O₂ with conv.% of 21.5 and 18.4% respectively. It is also copolymerized with methyl methacrylate in presences of TiO₂ and V₂O₅ as catalyst in N₂ and O₂ at 80°C for 4 hours. The chemical structure of the prepared clean polymers was confirmed by FTIR, carbon and hydrogen nuclear magnetic resonance (¹³C and ¹H NMR) and characterized by gel permeation chromatography (GPC). The thermal stability of pure PMMA and the composites M1M2TN and M1M2VO show higher thermal stability of composites relative to PMMA. Also, TEM of PMMA and SEM of M1M2TN confirm a homogeneous enchainment of M1-M2 copolymer centered around TiO₂ catalyst particles. The optimum conditions resulted in 64.2% and 63.8% conversion using 20% TiO₂ in N₂ and 10% V₂O₅ in O₂ respectively at 80°C after 4h with M1/M2 molar ratio of 1:1.

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