Iraqi Journal of Market Research and Consumer Protection
(2022) 14(2): 26-33
DOI: http://dx.doi.org/10.28936/jmracpc14.2.2022.(4)
Turki et al.,

المجلة العراقية لبحوث السوق وحماية المستهلك

# SYNTHESIS AND CHARACTERIZATION OF NEW DEMULSIFIER FROM NATURAL AND SYNTHETIC POLYMER

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**Received 19/ 6/ 2022, Accepted 28/ 7/ 2022, Published 31/ 12/ 2022**

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## ABSTRACT

**This research included the preparation and characterization of new demulsifies from natural and synthetic polymers of chitosan and polyvinyl alcohol that are environmentally friendly and at the same time have high efficacy comparable to emulsifiers. imported foreign. The prepared compounds were examined using infrared spectroscopy and nuclear magnetic resonance spectroscopy, and all the spectral signals of the polymers were in good agreement with the chemical composition of the polymers. And the melting and decomposition that occur on polymers at high temperatures. The effect of the length and type of side chain in the compositions of polymers on the process of water separation of oil emulsions was studied, and they had an important impact on the levels of water separation. The solubility behavior of polymers was also known, so that there was a solubility difference in Different organic solvents according to the type of the side chain of a hydrocarbon nature, and the best solubility of the prepared polymers was a solvent (dimethyl sulfoxide). The best polymerization time was found (12) h, as well as the best temperature at which polymerization takes place is (70 °C) and the prepared emulsion was compared with The commercial emulsifier was evaluated for its efficiency in separating water from crude oil (crude oil Basra) and compared to the commercial emulsifier, it was more efficient than the commercial one in separating water from oil.**

**Keywords:** Demulsifier, chitosan, polyviny alcohol ،crude oil Basra.

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# تحضير وتشخيص كاسرات أستحلاب جديدة من بوليمرات طبيعية وصناعية

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## الخلاصة

**تضمن هذا البحث تحضير وتشخيص كواسر استحلاب جديدة من بوليمرات طبيعية وصناعية من الكيتوسان والبولي فينيل الكحول صديقة للبيئة وفي نفس الوقت ذات فعالية عالية تضاهي كواسر الاستحلاب الأجنبية المستوردة. تم فحص المركبات المحضرة باستخدام التحليل الطيفي بالأشعة تحت الحمراء والمطياف بالرنين المغناطيسي النووي وكانت جميع الاشارات الطيفية للبوليمرات تتوافق بشكل جيد مع التركيب الكيميائي للبوليمرات وكذلك تم دراسة الاستقرار الحراري للبوليمرات المشتركة المستحلبة باستعمال التحليل الوزني الحراري لمعرفة التحولات الحرارية ودرجة الانتقال الزجاجي وفقدان الوزن من خلال أطوار التبلور والانصهار والتحلل الذي يطرأ على البوليمرات عند درجات حرارة عالية، كما تمت دراسة تأثير طول ونوع السلسلة الجانبية في تراكيب البوليمرات على عملية فصل الماء للمستحلب النفطي فكان لهما تأثير مهم في مستويات فصل الماء .كما تم معرفة سلوك الذوبانية للبوليمرات بحيث كان هناك تفاوت بالذوبان في المذيبات العضوية المختلفة تبعا لنوع السلسلة الجانبية ذات الطبيعة الهيروكاربونية وكانت أفضل إذابة للبوليمرات المحضرة هو مذيب (ثنائي مثيل سلفوكسايد)، لقد وجد أفضل زمن للبلمرة (١٢) ساعة وكذلك أفضل درجة حرارة عندها تتم البلمرة هي70م، كما تمت مقارنة المستحلب المحضر مع المستحلب التجاري وقيمت كفاءتها في فصل الماء عن النفط الخام (نفط الخام البصرة) ومقارنتها مع كاسر الاستحلاب التجاري فكانت أكثر كفاءة من التجاري في فصل الماء عن النفط**

**الكلمات المفتاحية:** مزيل استحلاب ، كيتوسان ، بولي فنيل الكحول ، نفط خام البصرة.

## INTRODUCTION

Pollution in the environment is increasing as new technologies are developed. The amount of oil consumed increases as industrial development occurs. These problems are significant in the oil industry, including refining, storage, and transportation. These issues are severe in the oil industry, refining, storage, and transportation. As a consequence, treating oil-water is required**(Abdulredha *et al.*, 2018)**, There are several methods for removing water from oil. Oil-water pollution has the largest effect on drinking water , groundwater atmospheric pollution and crop production. Since China has a major portion of oily wastewater, there is an urgent need for oil waste water treatment **(Adewunmi & Kamal, 2019)** , Oil-in-water or water-in-oil emulsion is another name for oily wastewater. When water and oil are combined in the presence of a stabilizing ingredient, these emulsions form. These emulsions are also used in several industries, such as the pharmaceutical and cosmetic industries. Water is combined with oil in petrochemical industries to minimize viscosity so that oil may be transported easily **(Atehortúa *et al.*2019)**. There are primarily two forms of oil-water emulsions: water-in-oil (W/O) emulsions and oil-in-water (O/W) emulsions **(Behroozi *et al.*, 2019; Contreras Ortiz *et al.*, 2018)**. The stability mechanisms of both emulsions differ. For example, oil-in-water emulsions can be stabilized by both steric and electrostatic repulsion, but water-in-oil emulsions are stabilized by steric forces due to their poor conductivity. Emulsions are thermodynamically metastable systems. When a surfactant is applied as a stabilizer, oil and water can be categorized based on the diameter (d) of the dispersed phase as free oil and water when d>150μm, dispersion when d is between 20μm and 150μm, and emulsion when d is less than 20μm **(Feitosa *et al.*, 2019; Delgado *et al.*, 2016; Fang *et al.*, 2016)**. The separation rate is the rate at which the emulsion separates into oil and water phases. The emulsion has several advantages for a specific production facility, including increasing the rate of water droplet flocculation, increasing the solubility of emulsifying agents and thus destabilizing the emulsion, and decreasing emulsion viscosity, which increases the probability of coalescence according to Stoke's law. The most common approach for handling crude oil emulsion is demulsification with chemical demulsifiers. The addition of reagents (demulsifiers) destroys the protective effect of hydrophobic emulsifying agents, allowing water droplets to coalesce **(Fang *et al.*, 2016; Fridjonsson *et al.*, 2014).**

Chemical demulsification is a process that uses demulsifiers to increase the rate of film thinning while decreasing emulsion stability. Chemical demulsifiers are categorized into three groups based on their chemical structures and applications: polymeric surfactants, ionic liquids, and nanoparticles **(Adewunmi & Kamal, 2019; Atehortúa *et al.*, 2019; Behroozi *et al.*, 2019; Hazrati *et al.*, 2018)** that dendrimers have been widely explored since they are effective in diverse emulsions **(Goodarzi *et al.*, 2019)**. Nanoparticles modified polymeric surfactants are widely recognized to be more effective than equivalent polymeric surfactants **(Hazrati *et al.*, 2018).**

Demulsifier concentration, temperature, and other parameters can all affect demulsification efficiency. A demulsifier's hydrophilicity or lipophilicity is the crucial feature in establishing the optimal dose for breaking an emulsion **(Li *et al.*, 2017).**

## MATERLALS AND METHODS

### Chemicals

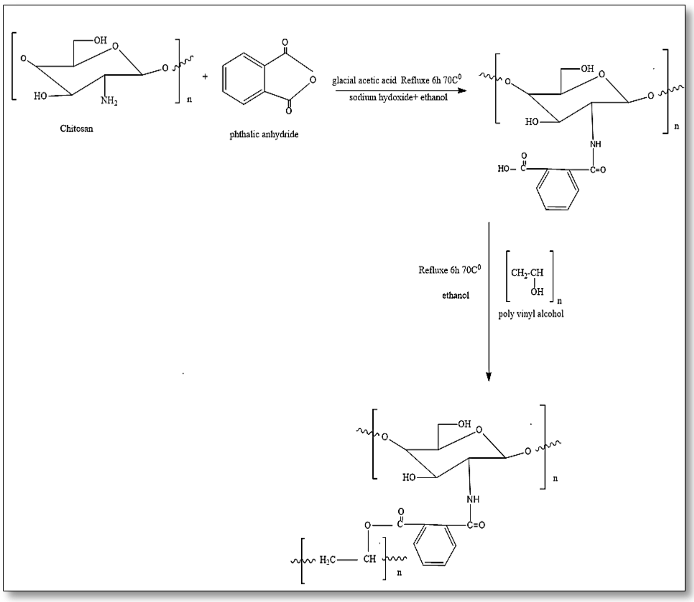
Chitosan (96%), phthalic anhydride (98%), sodium hydroxide (99%), Glacial acetic acid (99%), poly vinyl alcohol (98%), Diethyl Ether (98%), Dimethyl Sulfoxide (DMSO) (99%), Absolute Ethanol (99%).

### Preparation of (*Chit-CO- Pth*) From (chitosan and phthalic anhydride )

Add 1 g of chitosan in 50 mL of glacial acetic acid (1%) and stirred at 30°C for 2 h then 0.016 mol (2 g) of phthalic anhydride mixed with chitosan, the mixture was stirred and heated in a water bath at 70°C for 6 h. 5% of sodium hydroxide drops are added until precipitation of the desired compound. The transparent white precipitate was collected and washed with 10 mL diethyl ether to remove any remaining materials. The product was filtered and dried in a vacuum oven at 60°C overnight as a solid, brown-colored was obtained with a yield of 80% and the melting point was measured as 90-94°C **(Mhatre *et al.*, 2018)**.

### Synthesis of -CO- (Chit-Pth-PVA)

Mixture of 3.64 g of (chph) and 2g of poly vinyl alcohol dissolved in (EtOH+$H_2O$) were reflux for 6 h. The crystalline solid was filtered and recrystallized from EtOH. The product washed with 10 mL diethyl ether to remove any remaining materials, filtered and dried at 70°C, a transparent white precipitate was obtained, collect the formed residue, with a yield of 60% and the melting point was measured as 70-73°C as (Scheme 1) **(Mhatre *et al.*, 2018)**.



**Scheme (1):** Synthesis of -CO- (Chit-Pth-PVA) **(Mhatre *et al.*, 2018)**.

### Preparation of W\O Emulsion

In a 500 mL beaker W/O emulsion is prepared by adding 30-vol% water contains 1 g from NaCl to form water similar to In the properties of oil wells water to the 70-vol% Basra crude oil and then the two phases are mixed at room temperature. After that W/O emulsion is completely stirred at high speed for 2h. At last, the emulsion was left for 30 min under homogenization to ensure the formation of one phase emulsion. the Prepared emulsion showed high stability at 25°C **(Mhatre *et al.*, 2018)**.

### Demulsification performance Test

The demulsification performance test is evaluated according to EC2134A (Commercial demulsifier). the polymer is dissolved in an organic solvent (Dimethyl Sulfoxide) and prepared into a demulsifier solution with concentration of 0.1 g/100 mL **(Nikkhah *et al.*, 2015)** from this concentration, the following concentration were prepared (10, 20, 30, 40, 50, 60, 70 and 80 ppm). Firstly, an amount of demulsifier is added into 70/30 wt% of W\O emulsion, then the cylinder is shaken vigorously 200 times by hand within 2 min. and kept it stable for 30 min. Afterward, the cylinder is immediately returned into the as-settled hot water bath. The demulsifying efficiency is measured by calculating the amount of water remove from the emulsion sample **(Zolfaghari *et al.*, 2016)**, as shown in (Table, 1)

**Table (1):** Amount of water separated from the demulsifier

| **Demulsifier(chphpv)** | Temp. | 10 ppm | 20 ppm | 30 ppm | 40 ppm | 50 ppm | 60 ppm | 70 ppm | 80 ppm |
|---|---|---|---|---|---|---|---|---|---|
| **room Temperature** | 20°C | 25 mL | 26 mL | 27 mL | 28 mL | 29 mL | 30 mL | 31 mL | 32 mL |
| **Hot water bath** | 80°C | 35 mL | 37 mL | 40 mL | 42 mL | 43 mL | 45 mL | 47 mL | 49 mL |
| **Commercial demulsifier** | 80°C | 21 mL | 23 mL | 24 mL | 25 mL | 26 mL | 28 mL | 29 mL | 30 mL |

## RESULT AND DISCUSSION

Synthesized (chphpv) Showed higher demulsification rate and efficiency for the crude oil/water emulsion (70/30 vol %) than that for the commercial demulsifier. Increasing the Demulsifier dose from (10 to 80 ppm) leads to elegant rise in the demulsification efficiency. This can be assigned to the raise in the demulsifier adsorption on the W/O interface. which gradually replace asphaltene (native emulsifiers) and diminish the mechanical stability of the interfacial coating, resulting in displacement and then collapsing of water droplets.After that droplets are formed and then fuse, they are stable droplets.

### Separation Efficiency

The effect of EC2134A and -CO-(Chit-Pth-PVA) on water separation efficiency over time is shown in (Table 2) show an increase in water separation for Re-SOLV ®EC2134A until it reaches 70 min, after that the separation levels off and the separation rate is low. The best separation recorded for was 80% EC2134A after 120 min and increase in water separation for compound 2 over time. The separation rate of water was high only for the first 30 min, where after it decreased significantly. The best separation recorded for -CO-(Chit-Pth-PVA) was 85% after 100 min. The minimal additional increase in separation after 70 min that was observed for (Chi pth PVA) because the active chemical groups (OH, COOH, C=O,) on the polymer chains are fully engaged are not available to improve separation.

The infrared spectra of the compound-1-(Chit-CO-Pth) (Figure 1) show a strong intensity bands at the range of 3398 cm$^{-1}$ which refer to the stretching vibrations of hydroxyl groups, a weak intensity band at 3008 and 2920 cm$^{-1}$ due to the (=CH) Ar, respectively, and (C-H) Alph, showed peaks at 1705 cm$^{-1}$ assigned to (C=O) stretching of carboxylic groups and at 1647 cm$^{-1}$ assigned to characteristic absorption of (C=O) amid, 1545 cm$^{-1}$ peak of (C=C) of aromatic ring. while at 1257 cm$^{-1}$ band refer to (C-N) and show strong band at 1010 cm-$^{1}$ due to the (C-O). The infrared spectra of the compound-2-CO-(Chit-Pth-PVA) (Figure 2) the low intensity at the range of 3271.27 cm$^{-1}$ which refer to the stretching vibrations of hydroxyl groups, show bands at 2912-2805 cm$^{-1}$ due to the stretching vibrations of (CH,CH2) Alph, band at 1712.79 cm$^{-1}$ medium the stretching vibrations of (C=O ester), while at 1631 cm$^{-1}$ which refer to (C=O amid), 1597.06 cm$^{-1}$ which refer to the (C=C) of aromatic ring. for these compound as stretching vibrations appeared at 1242 cm$^{-1}$ of (C-N) and 1018 cm$^{-1}$ were due to the bending vibrations of (C-O).

**Table (2):** FTIR spectra for the compounds(1,2).

| Comp. | OH | CH,CH2 | C=O ester | C=O carboxylic | C=O amide | C=C | C-N | C-O |
|---|---|---|---|---|---|---|---|---|
| **1** | 3398 | 2800-2900 | --- | 1705 | 1647 | 1545 | 1257 | 1010 |
| **2** | 3271 | 2927-2850 | 1712 | ---- | 1631 | 1597 | 1242 | 1018 |

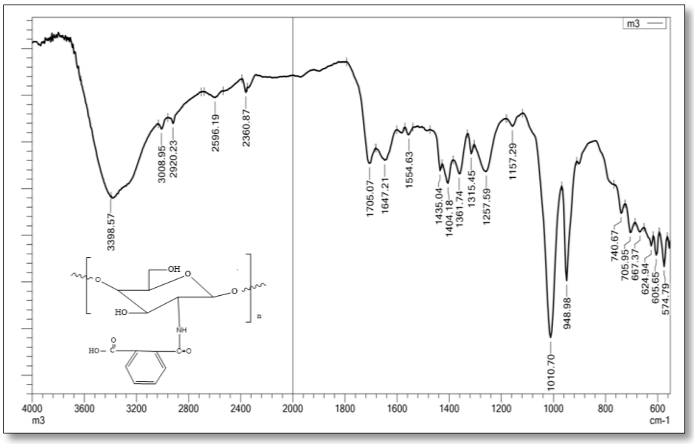


**Figure (1):** FTIR of (Chit-CO- Pth) compound-1-.

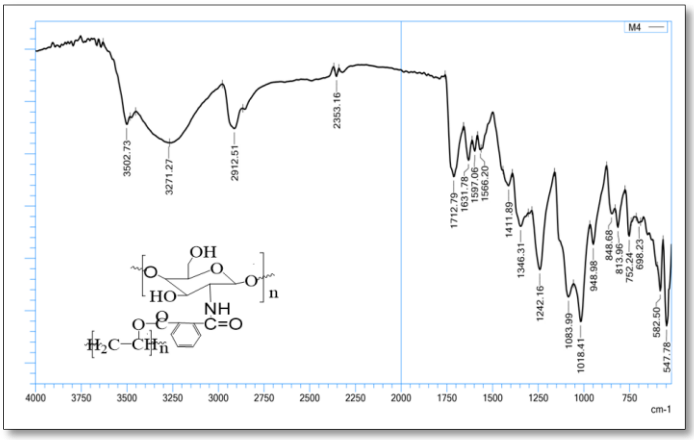


**Figure (2):** FTIR of -CO-(Chit-Pth-PVA) compound-2-.

### $^1$H-NMR of -CO-(Chit-Pth-PVA)

$^1$H-NMR spectra of the prepared polymers of compound-2-CO- (Chit-Pth-PVA) is shown in (Figure 3) which gives the following proton signals:

1-δ (1.5-2.52) ppm (m, 9H, $CH_2$,CH)

2-δ (3.3-3.5) ppm (s, 2H, $CH_2$ OH)

3-δ (3.8 -4.3) ppm (t, 2H, $CH_2O-C=O$ ester)

4- δ (7.47) ppm (m, 4H, for different environment aromatic protons)

5- δ (8.14) ppm (s, 1H, HN-C=O amide)

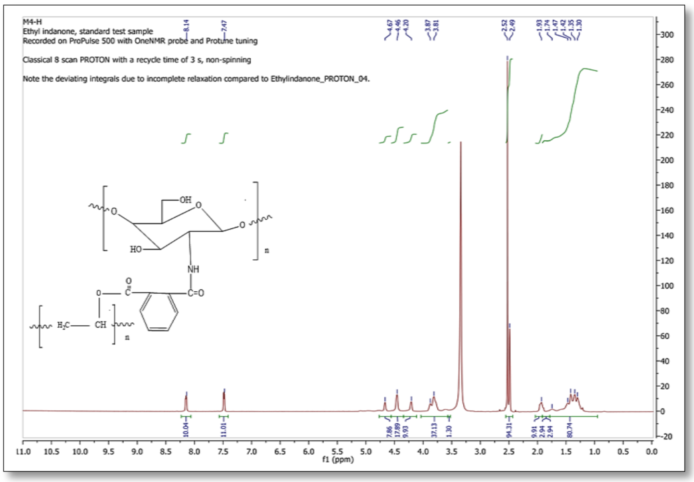
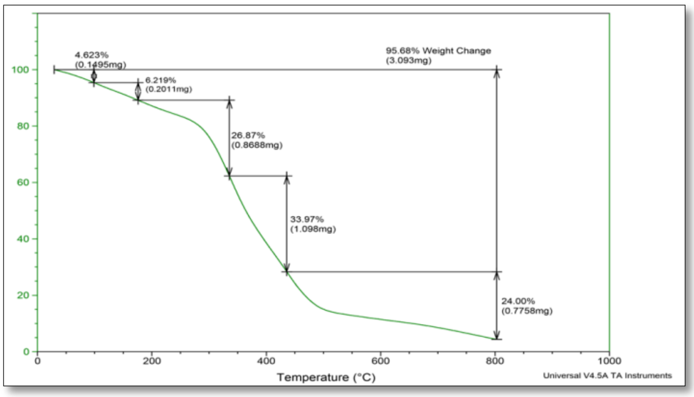


**Figure (3):** $^1$H-NMR of -CO-(Chit- Pth-PVA) compound-2-.

**Thermal analysis of -CO-(Chit-Pth-PVA)**

Thermal gravimetric analysis of this compound (Figure 4) showed four stages of weight loss, which were as follows:

1. The first stage, which was at 120.23°C, which is attributed to the evaporation of water present in the form of moisture or crystallized in the compound, with a weight loss 5%.
2. The second stage, which was at 220.98°C, which is attributed to the decomposition of chitosan bonds with phthalic anhydride and decomposition of (co-polymer), with a weight loss 7%.
3. The third stage included a loss of 26.87% at 380.10°C, which is attributed to the decomposition of the bonds forming chitosan
4. The fourth stage, which is the last stage, which included the largest weight loss 24% at 808.38°C, which indicates the continued degradation of chitosan and the emission of carbon dioxide.



**Figure(4):** Thermal analysis -CO-(Chit-Pth-PVA) compound-2-.

## CONCLUTIONS

Practically, this study could prepared other new design natural and synthetic polymers due to their outstanding merits, have received more attention in the field of emulsification, modification of natural and synthetic polymers gave them new or improved property. Modified polymers is of great importance and develop various dimulsifers systems, according to the current study which represent an applicable and empirical study, there are several conclusions that can be drawn; firstly, increasing the separation time of the tested c leads to increase the separation of water; secondly, the concentration of demulsifer can play an important role in limiting the separation of water. lastly, increasing the dosage of dimulsifers will increase the efficiency of separation of water accordingly, a coalescence process of water droplets is taken place when the polymer is add into the W\O emulsion.

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