Synthesis And Characteristics Of Poly (N-Lauryl Acrylate) For Oil Fractions Spill Removal

Salah F Abdellah Ali, W K Hassan

Abstract: This study is investigating the preparation and characterization of n-lauryl acrylate (LA) to be used in oil spill removing applications. N-Lauryl acrylate was prepared by solution polymerization taking into account the effect of monomer concentration, polymerization time, initiator concentration, cross-linker concentration and polymerization temperature on the yield of lauryl acrylate to optimize the polymerization conditions. Thermal analysis has been done using thermogravimetric analysis (TGA) in the range of 25°C to 600°C and differential scanning calorimetry (DSC) in the range of 35°C to 400°C. The results showed that n-lauryl acrylate is thermally stable to satisfy the requirements of oil spill cleanup applications. The chemical structure of n-lauryl acrylate was confirmed using Fourier Transform Infrared analysis (FTIR). The morphology of n-lauryl acrylate that controls its ability to absorb oil spills was observed using scanning electron microscope (SEM). It was found that n-lauryl acrylate has the ability to absorb gasoline, kerosene, diesel, xylene, octanol and Mobil oil. Sorption capacity of the polymer in dry system, static system and dynamic system in addition to its reusability of sorbent several times were studied.

Key Words: lauryl acrylate, n-lauryl acrylate, oil fractions, oil spill cleanup, oil spill removal, sorption capacity, and reusability of sorbent

1. INTRODUCTION
Oil is very important in industrial applications over worldwide. Oil spills can occur during production, transportation, storage and usage. Oil can reach the marine environment through routine or accidental releases as a result of drilling, manufacturing, transporting, storing and waste. For example, an offshore oil well blowup or pipe line bursts can release huge amounts of oil into the marine environment [1]. However, massive spills are in charge of the most oil spilled annually and they have main environmental and economic outcomes. Spills of oil at the sea are more damaging than those on land; they can spread for hundreds of miles in a thin sleek and cover beaches with a thin layer of oil. This can kill most of sea organisms it coats. Shell fishes and marine birds are the most vulnerable. The spill damaging depends on how the cleanup response takes into effect, climate and sea conditions [2]. Oil spill cleanup is still the main problem because of the restrictions and high cost of current cleanup techniques. Mechanical tools, use of chemical dispersants, burning of oil on water, and synthetic sorbents are the most common ways to remove oil spills [3]. Synthetic sorbents can be used to recover oil via the mechanisms of adsorption, absorption, or both and encourage oil to be trapped into the pores in the absorbent or adsorbant material. To be effective in combating oil spills, sorbents need to be both hydrophobic and oleophilic [4]. The aim of this study is to prepare and characterize new oleophilic hydrophobic acrylate polymer for oil spill cleanup. The study will cover the optimization of synthesis, characterization and valuation of the prepared polymer to be used in oil spill cleanup applications.

2. EXPERIMENTAL

2.1. Materials
Sodium Persulphate (Mwt=238.10) & methylene acrylamide (Mwt=154.17) (Lobachemie Pvt. ltd, Egypt), lauryl acrylate & methanol (SIGMA-AIDRICH company, UK), xylene & 1-octanol & tetrahydrofuran (EL-GOUMHOURIA company for chemicals and medical appliances, Egypt). Mobil special (high performance motor oil), benzene, kerosene and diesel were provided by Exxon Mobil, Egypt.

2.2 Polymerization of lauryl acrylate by solution polymerization
0.05g of initiator sodium persulphate was dissolved in 2 ml water then put 45 ml methanol and 0.5g of methylene acrylamide (cross-linker) then put into a stirred solution for 15 min. at 50°C. 5 ml lauryl acrylate was then added after 3hrs of the reaction in water bath at 60°C. The gel polymer was washed with water and methanol for several times and then dried at 60°C for 72 hrs [7].

2.3 Sorption capacity of different sorption systems
The sorbent was weighted and it was immersed into the oil. After 24 hrs of immersion the sorbent with oil transferred to sintered glass funnel and allow draining and then weighed again. The oil sorption of sorbent on a weight basis was calculated as follow:

\[ \text{Oil sorption\%} = \left(\frac{w_1 - w_2}{w_2}\right) \times 100 \]

Where \( w_1 \) is the weight of sorbent without oil and \( w_2 \) is the weight of sorbent with oil

The percentage of the absorbed oil was investigated for lauryl acrylate polymer for 2.5 ml, 5 ml and 7.5 ml of monomer concentrations at constant polymerization conditions (polymerization time 3 hrs, 0.5g methylene acrylamide, 0.05 g sodium persulphate and polymerization temperature 70°C) for 24hrs in different sorption systems such as dry system (oil was poured into a beaker with no water in it), static system (5 ml oil + 50 ml water) and dynamic system (5 ml oil + 50 ml water) under constant steering (approximately 250 rpm) using an isothermal magnetic stirrer [9].

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2.4 Recovery and reusability of sorbent
After oil sorption test, the sorbent transferred into a beaker contain 20 ml tetra hydrofuran for 3 hrs to remove the oil from the sorbent. The sorbent was dried and weighed then immersed again into the oil and weighed again after 24 hrs [10], [11].

2.5. Methods of characterization
Infrared Spectra (IR, KBr Pellets) were recorded using Perkin-Elmer infrared spectrophotometer (RX IFT-IR system) within the wave-number range of 500 – 4000 cm\(^{-1}\). Differential Thermo-gravimetric analysis (TGA) was observed by SDT Q600 in a temperature range from 35°C to 600°C at a heating rate of 10°C/min. Differential Scanning Calorimetry (DSC) was also carried out according to (DSC, Perkin Elmer). The polymer morphology and its absorption ability were observed by scanning electron microscope (SEM) (JEOL-5300) [12], [13].

All tests were carried out at the Central Laboratory, Faculty of Pharmacy, Alexandria University.

3. RESULTS AND DISCUSSION

3.1 Effect of the polymerization time on the % yield of lauryl acrylate polymer
Effect of polymerization time was investigated by changing the polymerization time from 1hr to 4 hours at constant polymerization conditions, (5 ml of n- lauryl acrylate, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization temperature of 70°C). As shown in Figure 1, % yield of n-lauryl acrylate increased with the increasing of the polymerization time but after 3hrs from the polymerization process, the % yield of lauryl acrylate polymer decreased, so the best polymerization time was 3 hrs.

3.2 Effect of the initiator concentration on the % yield of lauryl acrylate polymer
Effect of the initiator concentration was investigated by changing initiator concentration (0.03 g, 0.05g, 0.07g and 0.1g) at constant polymerization conditions, (5 ml of lauryl acrylate, polymerization temperature 70°C, 0.5g methylene acrylamide, and polymerization time 3 hrs). It was found that the % yield of lauryl acrylate polymer increased as the concentration of the initiator increased as shown in Figure 2.

3.3 Effect of the cross-linker concentration on the % yield of lauryl acrylate polymer
Effect of cross-linker concentration was investigated by changing the cross-linker concentration (0.5g, 0.8g, 1.2g) at constant polymerization conditions, (5 ml of n- lauryl acrylate, polymerization time 3 hrs, 0.05g sodium persulphate, and polymerization temperature 70°C. % yield of n-lauryl acrylate polymer increased as the cross-linker concentration increased as mentioned in Figure 3.

3.4 Effect of the monomer concentration on the % yield of lauryl acrylate polymer
Effect of monomer concentration was investigated by changing the monomer concentration (2.5 ml, 5 ml, 7.5 ml) at constant polymerization conditions, (5 ml of n- lauryl acrylate, polymerization time 3 hrs, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization temperature 70°C. % yield of lauryl acrylate polymer increased as the monomer concentration increased as reported in Figure 4.
3.5 Effect of the polymerization temperature on the % yield of n-lauryl acrylate polymer

Effect of polymerization temperature was investigated by changing the polymerization temperature (from 40°C to 80°C) at constant polymerization conditions, 5 ml of lauryl acrylate, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization time 3 hrs. As shown in Figure 5, the % yield of lauryl acrylate polymer increased as the polymerization temperature increased up to 70°C but it started to decrease at 80°C.

Fig. 5: Effect of the polymerization temperature on the % yield of n-lauryl acrylate polymer

3.6 Fourier transforms infra-red analysis (FTIR)

FTIR showed different peaks for different function groups which confirming the structure of proposed n-lauryl acrylate polymer as reported in Figure 6. Also, Table 1 represents IR peaks of the different function groups of lauryl acrylate polymer [10, 14].

3.7 Effect of the polymerization time on the oil sorption of n-lauryl acrylate polymer

Effect of polymerization time was investigated by changing the polymerization time (from 1 hr to 4 hrs) at constant polymerization conditions, 5 ml of lauryl acrylate, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization temperature 70°C. % oil uptake was investigated for lauryl acrylate polymer after 24 hrs at room temperature for each type of oil. Figure 7 shows a comparison of the effect of the polymerization time for lauryl acrylate polymer on the oil sorption which reached a saturation value at 3 hrs. The polymer network of the lauryl acrylate surface became too dense as the time increased, which resulted in a lower oil sorption and the best polymerization time was 3 hrs.

Fig. 7: Effect of the polymerization time on oil sorption for n-lauryl acrylate polymer

3.8 Effect of the monomer concentration on the oil sorption of n-lauryl acrylate polymer

Effect of monomer concentration was investigated by changing the monomer concentration (2.5 ml, 5 ml, 7.5 ml) at constant polymerization conditions, polymerization time 3 hr, 0.5g methylene acrylamide, 0.05g sodium persulphate and polymerization temperature 70°C. Percentage of oil uptake was investigated for lauryl acrylate polymer after 24 hrs at room temperature for each type of oil. Figure 8 shows a comparison of the monomer concentration on the oil sorption using different types of oils, and indicates that the oil sorption of lauryl acrylate polymer increased as the monomer concentration increased.

3.9 Effect of the cross-linker concentration on oil sorption for n-lauryl acrylate polymer

Effect of cross-linker concentration was investigated by changing the cross-linker concentration (0.5g, 0.8g, 1.2g) at constant polymerization conditions, 5 ml of lauryl acrylate, polymerization time 3 hrs, 0.05g sodium persulphate and polymerization temperature 70°C.

**Table 1: FT-IR peak assignments for 5 ml lauryl acrylate polymer**

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Wave number (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C-H) stretch alkanes</td>
<td>2926</td>
</tr>
<tr>
<td>(C=O) ester</td>
<td>1737</td>
</tr>
<tr>
<td>(C=C) stretch</td>
<td>1652</td>
</tr>
<tr>
<td>(C-H) bend alkane</td>
<td>1461</td>
</tr>
<tr>
<td>(C-O) ester</td>
<td>1120</td>
</tr>
<tr>
<td>(C-H) rock, methyl, seen only in long chain alkanes</td>
<td>722</td>
</tr>
</tbody>
</table>

Fig. 6: FT-IR spectrum of 5 ml n-lauryl acrylate polymer
Fig. 8: Effect of the monomer concentration on oil sorption for
n-lauryl acrylate polymer

Fig. 9: Effect of the cross-linker concentration on oil sorption for
n-lauryl acrylate polymer

% oil uptake was investigated for lauryl acrylate polymer after
24hr at room temperature for each type of oil. Figure 9 shows
a comparison of the cross-linker concentration on the oil
sorption of different types of oils indicates that the oil sorption
decreased when the cross-linker concentration was excessive
and the network surface of lauryl acrylate was too dense to
absorb more oil and reduced the oil sorption.

3.10 Effect of the initiator concentration on oil sorption of
n-lauryl acrylate polymer

Effect of on initiator concentration was investigated by
changing initiator concentration (0.03 g, 0.05g, .07g, 0.1g) at
constant polymerization conditions, 5 ml of n- lauryl acrylate,
0.5g methylene acrylamide, polymerization time 3hrs and
polymerization temperature 70°C. % oil uptake was
investigated for lauryl acrylate polymer after 24hrs at room
temperature for each type of oil. Figure 10 illustrates a
comparison of the initiator concentration on the oil sorption of
different types of oils and indicates that the oil sorption of lauryl
acrylate polymer increased as the concentration of sodium
persulphate increased. Further increase in sodium persulphate
concentration decreased the oil sorption of lauryl acrylate
polymer.

3.11 Sorption capacity of n-lauryl acrylate polymer using
different sorption systems

% oil uptake was investigated for lauryl acrylate polymer at a
different monomer concentration (2.5ml, 5ml, 7.5ml) at
constant polymerization conditions, polymerization time 3hrs,
0.5g methylene acrylamide, 0.05g sodium persulphate, and
polymerization temperature 70°C. After 24hr using different
sorption systems, the sorption capacity increased in each
system (dry system, static system and dynamic) with
increasing the lauryl acrylate concentration as mentioned in
Figure 11.

Fig. 10: Effect of the Initiator concentration on oil sorption n-
lauryl acrylate polymer

Fig. 11: Sorption capacity for n-lauryl acrylate polymer at
different sorption system

3.12 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) analysis in a
temperature range from 35°C to 400°C at a heating rate of 10°C
\ min showed that the melting point of lauryl acrylate is 392.72
°C and the enthalpy value is 53.9 J/g which indicates a high
thermal stability of n-lauryl acrylate polymer as shown in Figure
12.

Fig. 12: DSC curve of 7.5 n-lauryl acrylate polymer
3.13 Thermal Gravimetric Analysis (TGA)
Thermal gravimetric analysis (TGA) in a temperature range from 25°C to 600°C at a heating rate of 10°C/ min shows that the weight loss started at 220.06°C and continued until 588.92°C, residue of lauryl acrylate polymer is 4.427%. The thermal gravimetric curves do not indicate significant weight loss until the temperature reaches 220°C. This implies that lauryl acrylate polymer have high thermal stability and can fully satisfy the demands of various applications as shown in Figure 13.

**Fig. 13: TGA curve of 7.5 ml n-lauryl acrylate polymer**

3.14 Scanning Electron Microscope (SEM) of lauryl acrylate polymer
The morphology of polymer porosity and its ability to absorb oil were observed by scanning electron microscope. SEM micrographs of lauryl acrylate polymer after sorbing in benzene and xylene indicating that the porosity increased as the concentration of monomer increased and the oil sorbed by the polymer causes swelling of the polymer particles as shown in Figures 14-16.

**Fig. 14: SEM image of 7.5 ml LA polymer**

**Fig. 16: SEM of 7.5 ml polymer (xylene sorption)**

3.15 Test for recovery and reusability of sorbent
Tables 2, 3 reported that the polymer has the ability to be recovered and reused several times after transferring the sorbent into a beaker contain 20 ml tetrahydrofuran for 3 hrs to remove the oil from sorbent then dried, and immersed it again into the oil for 24 hrs.

**Table 2: Study of recovery and reusability of LA polymer**

<table>
<thead>
<tr>
<th>No of times of recovery and reusability</th>
<th>Wt of LA polymer after 24 hr in benzene</th>
<th>Wt of recovered and dried LA polymer</th>
<th>Wt of recovered LA polymer after 24 hr in benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.85 g</td>
<td>0.1 g</td>
<td>1.67 g</td>
</tr>
<tr>
<td>2</td>
<td>1.85 g</td>
<td>0.1 g</td>
<td>1.64 g</td>
</tr>
<tr>
<td>3</td>
<td>1.85 g</td>
<td>0.1 g</td>
<td>1.60 g</td>
</tr>
</tbody>
</table>

**Table 3: Study of recovery and reusability of LA polymer**

<table>
<thead>
<tr>
<th>No of times of recovery and reusability</th>
<th>Wt of LA polymer after 24 hr in xylene</th>
<th>Wt of recovered and dried LA polymer</th>
<th>Wt of recovered LA polymer after 24 hr in xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.71 g</td>
<td>0.1 g</td>
<td>1.54 g</td>
</tr>
<tr>
<td>2</td>
<td>1.71 g</td>
<td>0.1 g</td>
<td>1.50 g</td>
</tr>
<tr>
<td>3</td>
<td>1.71 g</td>
<td>0.1 g</td>
<td>1.48 g</td>
</tr>
</tbody>
</table>

4 CONCLUSION
- In this study, we have succeeded in the preparation of oleophilic polymer by polymerization of lauryl acrylate by the solution polymerization to be used in oil spill removing and the optimal polymerization conditions were determined.
- The thermal behavior has been investigated by thermogravimetric analysis and differential scanning calorimeter techniques proving that the lauryl acrylate polymer has good thermal stability to meet the requirements of various applications.
- Lauryl acrylate polymer was found to have a potential to be used for oil sorption in different sorption systems and has the ability to be recovered and reused several times.
5 References:


