2

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Investigation and Evaluation of Poly (N- butyl acrylate) for Oil Fractions Spill Removal Applications

Salah F. Abdellah Ali*[1, 2] and W. K. Hassan[2]

[1]*Chemistry Department, College of Science and Arts, Jouf University, Al-Qurrayat, Saudi Arabia.*
[2]*Materials Science Department, Institute of Graduate Studies & Research, Alexandria University, Egypt.*

THIS WORK is aiming at investigating the preparation and characterization of n-butyl acrylate (BA) to be used in oil spill removing applications. N-Butyl 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 n- butyl 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- butyl acrylate is thermally stable to satisfy the requirements of oil spill cleanup applications. The chemical structure of n- butyl acrylate was confirmed using Fourier Transform Infrared analysis (FTIR). The morphology of n- butyl acrylate that controls its ability to absorb oil spills was observed using scanning electron microscope (SEM). It was found that n-butyl 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.

Keywords: Oil spill removal, N-butyl acrylate, Oleophilic gel polymers, Sorption system, Butyl acrylate and oil spill cleanup.

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 (3, 4) are the most common ways to remove oil spills. 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 absorbant or adsorbant material. To be effective in combating oil spills, sorbents need to be both hydrophobic and oleophilic (5, 6). 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.

Experimental

Materials

Sodium Persulphate (Mwt = 238.10) & Methylene Acrylamide (Mwt = 154.17) (Lobachemie Pvt. ltd, Egypt), Butyl 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.

Polymerization of butyl acrylate by solution polymerization

0.05g of initiator sodium persulphate was dissolved in 2 ml water. 45 ml methanol and 0.5g of methylene acrylamide (cross-linker) were added into a stirred solution for 15 min. at 50°c. After 3hrs of the reaction in water bath at 60°c, 5 ml butyl acrylate was added. The gel polymer was washed with water and methanol for several times and then dried at 60°c for 72 hrs [9, 10].

Sorption capacity of different sorption systems

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

$$\text{Oil sorption\%} = (w_t - w_o) / w_o * 100 \quad [11]$$

(Where w_o is the weight of sorbent without oil and w_t is the weight of sorbent with oil)

The percentage of the absorbed oil was investigated 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 stirring (approximately 250 rpm) using an isothermal magnetic stirrer (11).

Recovery and reusability of sorbent

After oil sorption test, the sorbent was transferred into a beaker containing 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 (12,13).

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) [7, 8]. All tests were carried out at the Central Laboratory, Faculty of Science, Alexandria University.

Results and Discussion

Effect of the polymerization time on the % yield of n-butyl acrylate polymer

Effect of polymerization time was investigated by changing the polymerization time from 1hr to 4 hrs at constant polymerization conditions, (5 ml of n- butyl acrylate, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization temperature of 70°C). As shown in Figure 1, it was found that the % yield of n-butyl acrylate increased with the increasing of the polymerization time. After 3hrs from the polymerization process, the % yield of butyl acrylate polymer started to decrease showing the best polymerization time at 3 hrs.

Effect of the initiator concentration on the % yield of n-butyl acrylate polymer

Effect of the initiator concentration was investigated by changing initiator concentration (0.03 g, 0.05g, .07g and 0.1g) at constant polymerization conditions, (5 ml of butyl acrylate, polymerization temperature 70°c, 0.5g methylene acrylamide, and polymerization time 3 hrs.

The % yield of n-butyl acrylate polymer increased as the concentration of the initiator increased as shown in Figure 2.
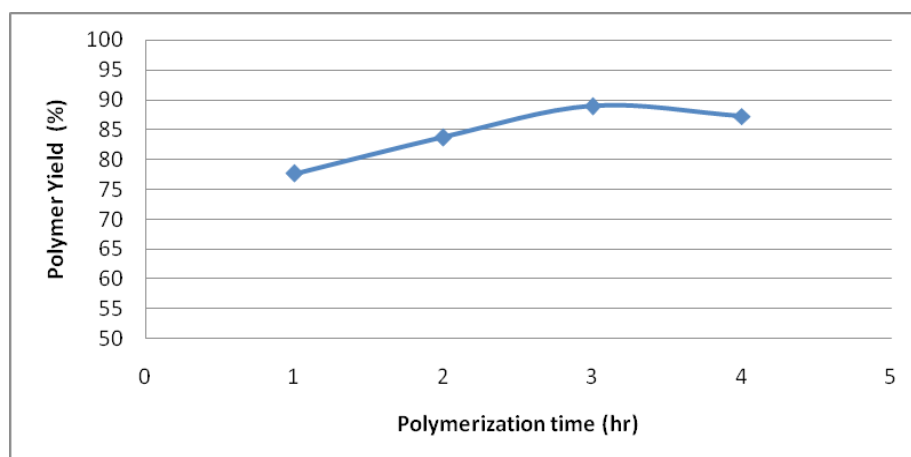
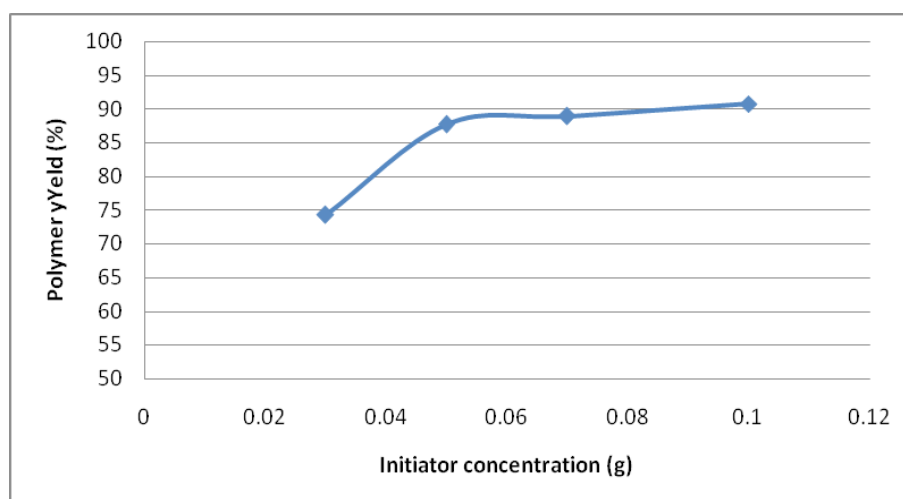**Fig. 1. Effect of the polymerization time on the % yield of n-butyl acrylate polymer.**

Fig. 2. Effect of the initiator concentration on the % yield of n-butyl acrylate polymer.

Effect of the cross-linker concentration on the % yield of n-butyl 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- butyl acrylate, polymerization time 3 hrs, 0.05g sodium persulphate, and polymerization temperature 70°C.

The % yield of n-butyl acrylate polymer increased as the cross-linker concentration increased as mentioned in Figure 3.

Effect of the monomer concentration on the % yield of n-butyl 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 hrs, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization temperature 70°C.

The % yield of butyl acrylate polymer increased as the monomer concentration increased as illustrated in Figure 4.

Effect of the polymerization temperature on the % yield of n-butyl 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 butyl acrylate, 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization time 3 hrs. As shown in Figure 5, the % yield of butyl acrylate polymer increased as the polymerization temperature increased up to 70°C but it started to decrease at polymerization temperature of 80°C.
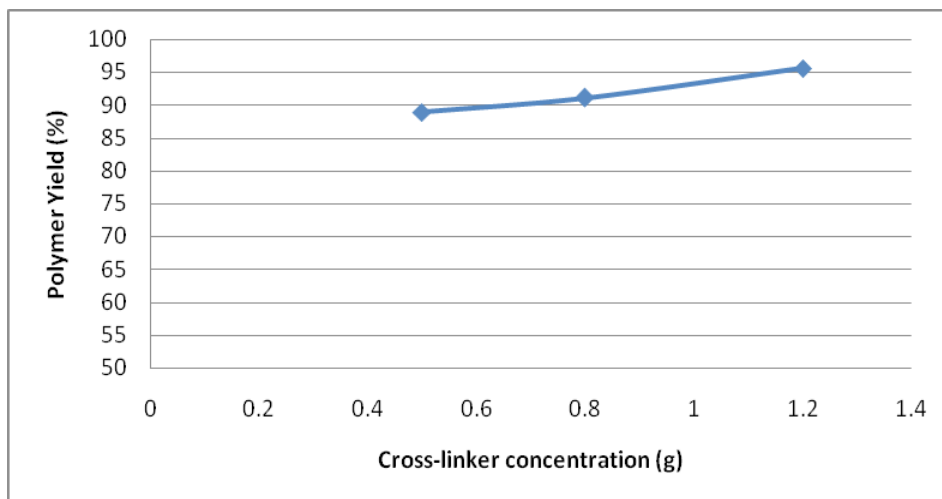
SALAH F. ABDELLAH ALI AND W. K. HASSAN

Fig. 3. Effect of the cross-linker concentration on the % yield of n-butyl acrylate polymer.
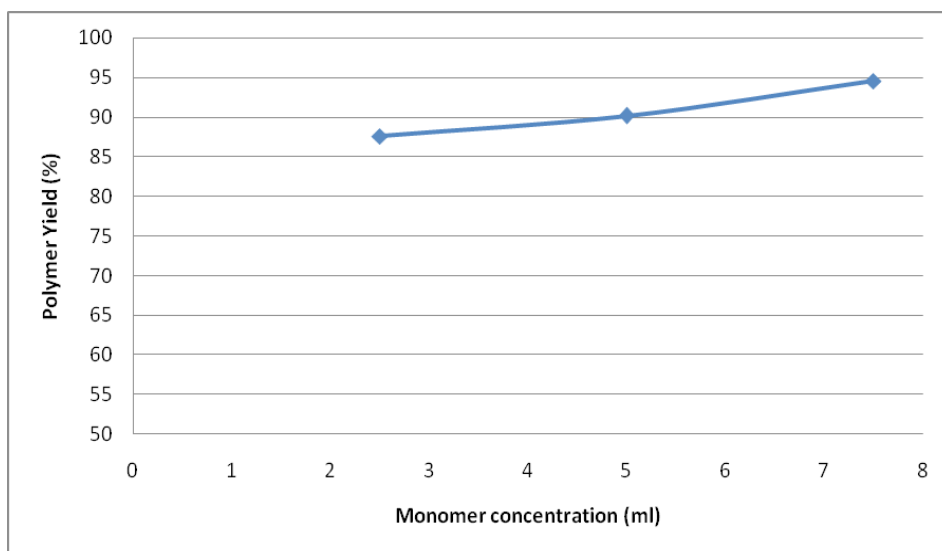

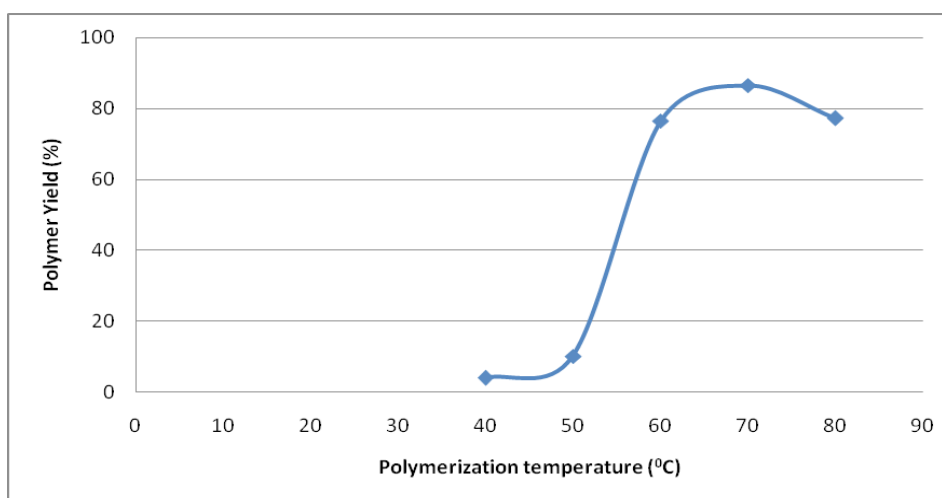**Fig. 4. Effect of the monomer concentration on the % yield of n-butyl acrylate polymer.**

Fig. 5. Effect of the polymerization temperature on the % yield of n-butyl acrylate polymer.
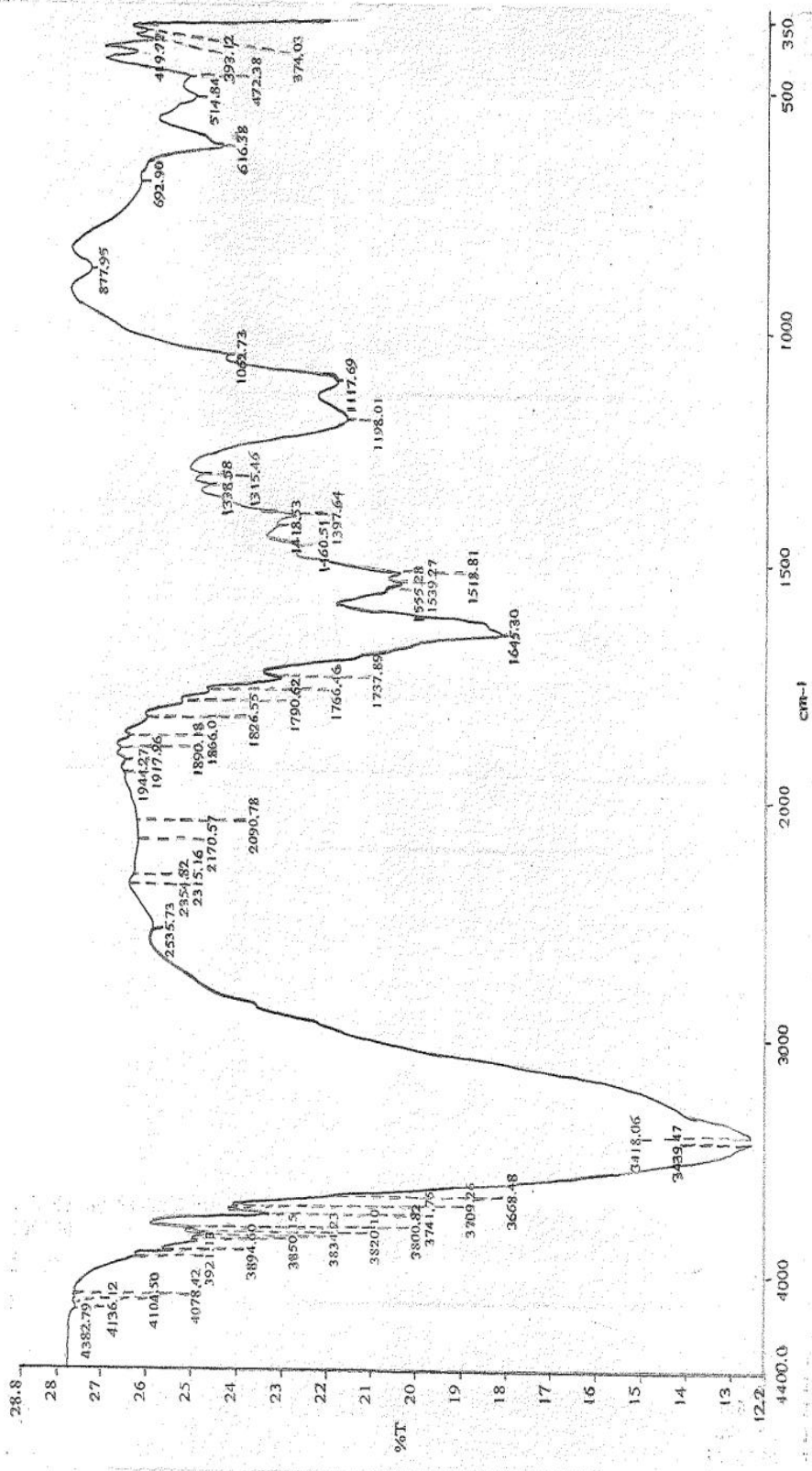
Fig. 6. FT-IR spectrum of n-butyl acrylate polymer.

Fourier transforms infra-red analysis (FTIR)

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

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

Effect of polymerization time was investigated by changing the polymerization time (from 1hr to 4 hrs) at constant polymerization conditions, 5 ml of butyl acrylate , 0.5g methylene acrylamide, 0.05g sodium persulphate, and polymerization temperature 70°C. % oil uptake was investigated for butyl acrylate polymer after 24hrs at room temperature for each type of oil. Table 2 shows a comparison of the effect of the polymerization time of n-butyl acrylate polymer on the oil sorption which reached saturation value after 3hrs. The polymer network of the n-butyl acrylate surface became too dense as the time increased resulting in a lower oil sorption and the best polymerization time was 3 hrs.

Effect of the monomer concentration on the oil sorption of n- butyl 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 butyl acrylate polymer after 24 hrs at room temperature for each type of oil. Table 3 shows a comparison of the monomer concentration on the oil sorption using different types of oils and indicates that the oil sorption of n-butyl acrylate polymer increased as the monomer concentration increased.

Effect of the cross-linker concentration on oil sorption for n-butyl 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 butyl acrylate, polymerization time 3 hrs, 0.05g sodium persulphate and polymerization temperature 70°C. % oil uptake was investigated for n-butyl acrylate polymer after 24hr at room temperature for each type of oil.

\TABLE 1. FT-IR peak assignments for 5 ml n-butyl acrylate polymer.

Assignments	Wave number (cm-1)
(C=O) ester	1737
(C=C) stretch	1645
(C-H) bend	1460
(C-O) ester	1198

TABLE 2. Effect of the polymerization time on oil sorption of n-butyl acrylate polymer.

Polymerization time (hrs)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
1	510	460	270	140	90	48
2	850	630	320	190	130	70
3	1210	770	360	230	175	78
4	780	540	290	160	110	65

TABLE 3. Effect of the monomer concentration on oil sorption of n-butyl acrylate polymer.

Monomer concentration (ml)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
2.5	810	620	250	190	90	64
5	1209	770	360	230	175	78
7.5	1320	1100	400	260	196	88

Table 4 reports a comparison of the cross-linker concentration on the oil sorption of different types of oils and indicates that the oil sorption decreased with excessive cross-linker concentration as the network surface of n-butyl acrylate was too dense to absorb more oil and reduced the oil sorption.

Effect of the initiator concentration on oil sorption of n-butyl 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- butyl acrylate, 0.5g methylene acrylamide, polymerization time 3hrs and polymerization temperature 70°C.

% oil uptake was investigated for butyl acrylate polymer after 24hrs at room temperature for each type of oil. Table 5 illustrates a comparison of the initiator concentration on the oil sorption of different types of oils and indicates that the oil sorption of butyl acrylate polymer increased as the concentration of sodium persulphate increased. Further increase in sodium persulphate concentration showed a decrease of the oil sorption of n-butyl acrylate polymer.

Sorption capacity of n-butyl acrylate polymer using different sorption systems

% oil uptake was investigated for butyl 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 (dry system, static system and dynamic system) with increasing the butyl acrylate concentration as mentioned in Table 6.

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 butyl acrylate is 392.72°C and the enthalpy value is 53.9 J/g indicating a high thermal stability of n-butyl acrylate polymer as shown in Figure 7.

TABLE 4. Effect of the cross-linker concentration on oil sorption of n-butyl acrylate polymer.
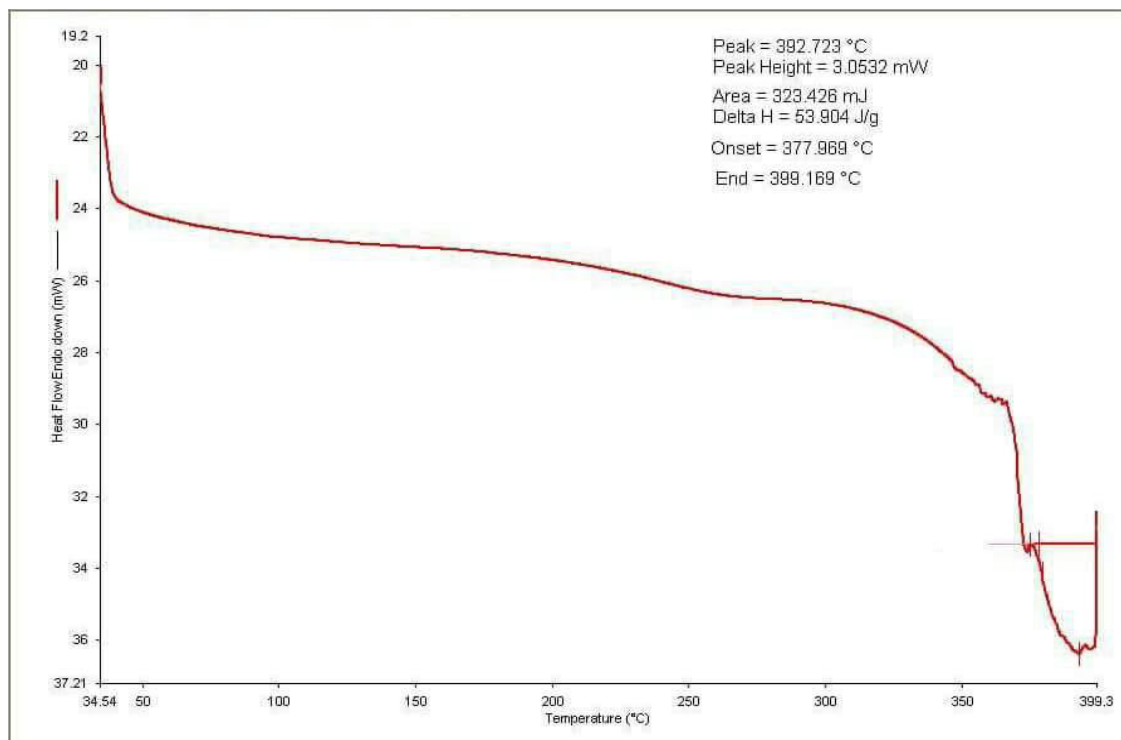
Cross-linker concentration (g)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
0.5	1211	769	360	230	175	78
0.8	830	560	230	160	123	57
1.2	620	410	170	120	82	45

TABLE 5. Effect of the initiator concentration on oil sorption of n-butyl acrylate polymer.

Initiator concentration (g)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
0.03	400	310	260	95	85	65
0.05	810	450	300	150	154	70
0.07	1210	770	360	230	176	79
0.1	920	580	310	180	165	72

TABLE 6. Sorption capacity of n-butyl acrylate polymer in different sorption systems.

Monomer concentration (ml)	Percentage of Gasoline uptakein dry system	Percentage of Gasoline Uptake in static system	Percentage of Gasoline Uptake in dynamic system
2.5	200	220	170
5	290	320	260
7.5	340	370	300

Fig. 7. DSC curve of n-butyl acrylate polymer.

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 n-butyl acrylate polymer is 4.427%. The thermal gravimetric curves do not indicate significant weight loss until the temperature reaches 220°C. This implies that n-butyl acrylate polymer have high thermal stability and can fully satisfy the demands of various applications as shown in Figure 8.

Scanning Electron Microscope (SEM) of n-butyl acrylate polymer

The morphology of polymer porosity and its ability to absorb oil were observed by scanning electron microscope. SEM micrographs of n-butyl acrylate polymer after sorbing in benzene and xylene showing that the porosity was increased as the concentration of monomer increased and the oil sorbed by the polymer causes swelling of the polymer particles as appeared in Figures 9-11.

Test for recovery and reusability of sorbent

Tables 7, 8 showed that n-butyl acrylate polymer has the ability to be recovered and reused several times after transferring the sorbent into a beaker contain 20 ml tetra hydrofuran for 3 hrs to remove the oil from sorbent then dried, and immersed it again into the oil for 24 hrs.

Conclusion

In this study, we have succeeded in the preparation of oleophilic polymer by polymerization of butyl 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 thermo-gravimetric analysis and differential scanning calorimeter techniques proving that the n-butyl acrylate polymer has good thermal stability to meet the requirements of various applications. N-Butyl 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.
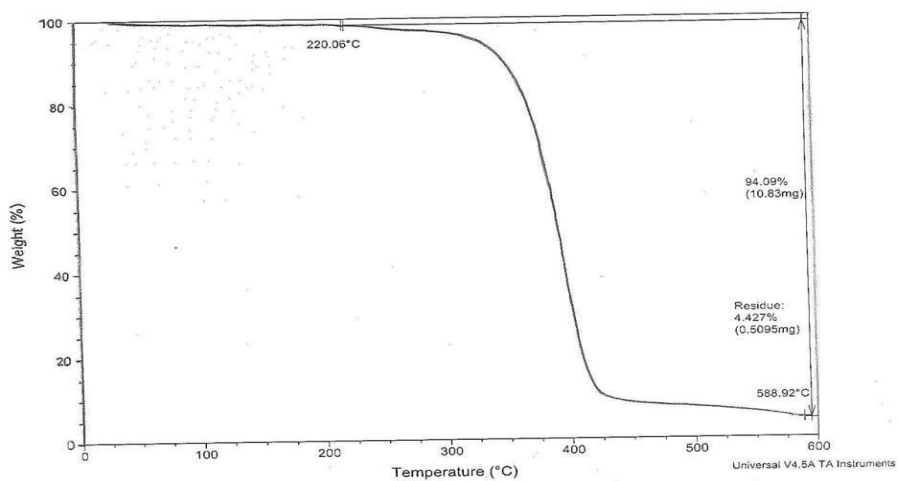
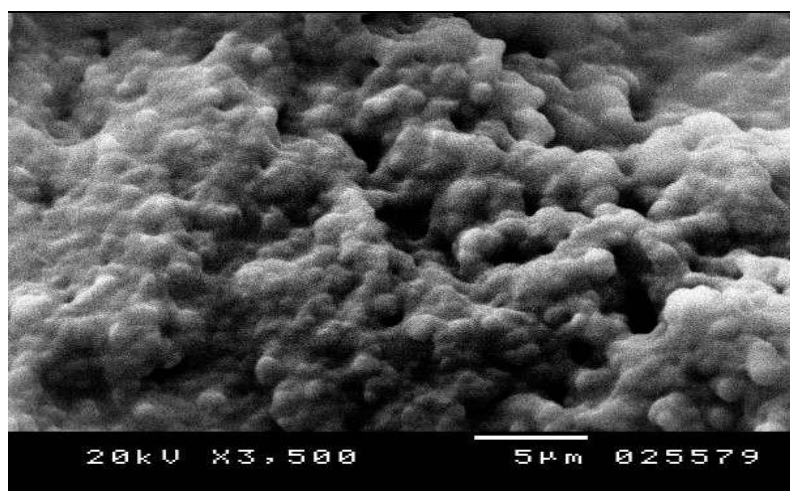**Fig. 8. TGA curve of 7.5 ml n-butyl acrylate polymer.**

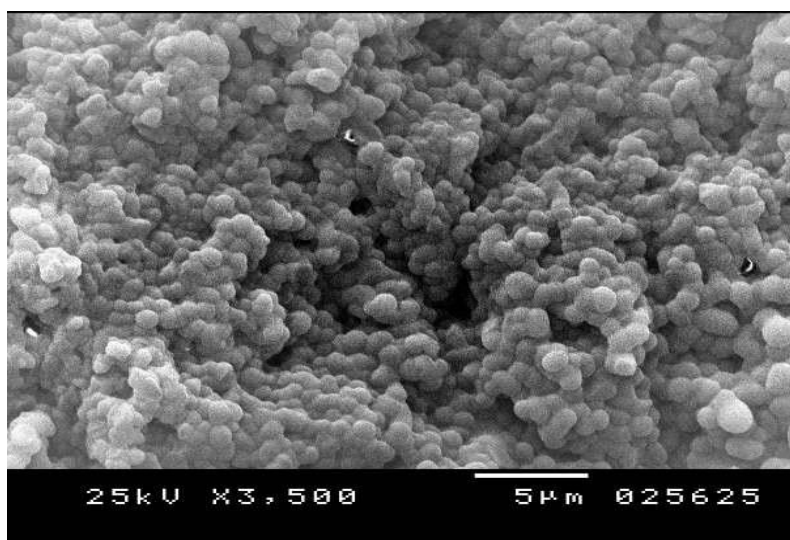**Fig. 9. SEM image of 7.5 ml n-butyl acrylate polymer.**

Fig. 10. SEM image of 7.5 ml n-butyl acrylate polymer (benzene sorption).
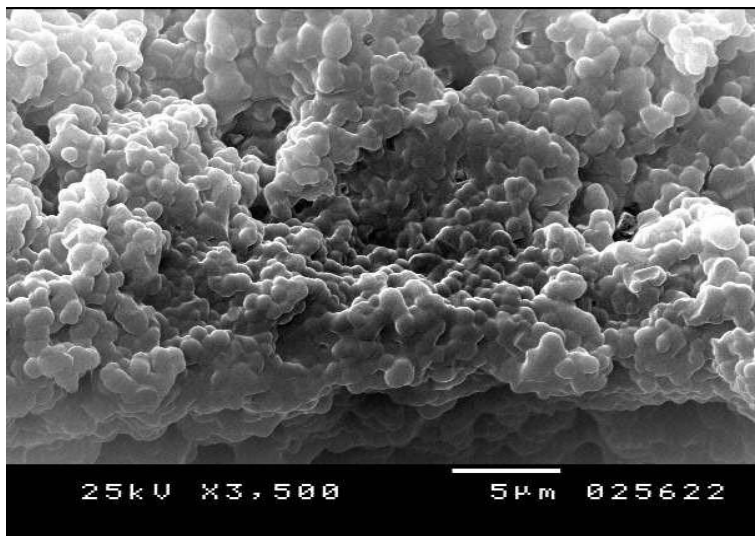
Fig. 11. SEM image of 7.5 ml n-butyl acrylate polymer (xylene sorption).

TABLE 7. Study of recovery and reusability of n-butyl acrylate polymer in gasoline.

Number of times of recovery and reusability	weight of BA polymer after 24 hrs	weight of recovered and dried BA polymer	weight of recovered BA polymer after 24 hrs
1	0.50 g	0.1 g	0.42 g
2	0.50 g	0.1 g	0.40 g
3	0.50 g	0.1 g	0.38 g

TABLE 8. Study of recovery and reusability of n-butyl acrylate polymer in xylene.

Number of times of recovery and reusability	weight of BA polymer after 24 hrs	weight of recovered and dried BA polymer	weight of recovered BA polymer after 24 hrs
1	1.42 g	0.1 g	1.33 g
2	1.42 g	0.1 g	1.29 g
3	1.42 g	0.1 g	1.25 g

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