Molecular design, synthesis and analysis of new hydrophobic seafoams with augmented uptake capacity

Rasha A. Azzam* and Tarek M. Madkour

Abstract - The development of new urethane seafoams to be used in the clean-up of oil spills is the subject of this study. PU prepolymer blends that are hydrophobic in nature are excellent candidates for this technology. The hydrophobicity of the prepolymer ensured maximum encapsulation of the oil droplets within the foam cells during the foaming of the polyurethane materials, which will allow the sea area to be restored to its original state without harming its surrounding habitat or inhabitants. The advantage of the liquid state of the prepolymer blends is to only solidify and foam upon getting in contact with water, which will facilitate its application using fire hoses mounted on fireboats. In order to test the best materials for this type of application, hundreds of organic substrate candidates were tested using molecular modeling techniques in order to evaluate their miscibility with hydrocarbon oil. Elected organic structures based on their higher miscibility with oil will be synthesized in the laboratory and used as the building blocks for the polyurethane prepolymers. The more hydrophobic the prepolymer, the more encapsulation of the oil droplets within the foam cells during the foaming process is expected to be. The organic substrate candidates of various R groups, various diols of different types and lengths, and various hard block sequence length distribution have been modeled in order to evaluate their miscibility with hydrocarbon oil. Prepolymer structures of optimum miscibility with oil and immiscibility with water identified as possible chemical designs and prototypes for this type of application were synthesized in the lab and analyzed. The prepolymers were all analyzed using FTIR and NMR spectroscopic techniques in order to validate the results of the modeling investigation.

Keywords - Computer simulation, miscibility, molecular dynamics, oil spill, urethane prepolymer

I. INTRODUCTION

Oil Pollution is a serious environmental problem associated with the increasing levels of oil production all over the world. Under certain conditions, it may have severe adverse impacts on the environment including marine life, air quality, soil properties and surface, and subsurface water. The Gulf of Guinea region is a great inlet of the Atlantic Ocean on the western African coast and encompasses a dozen African nations all exploring for oil. It represents a stressed ecosystem since it is situated within the richest oil reservoir in this part of the world. Oil-related activities that range from exploration to exportation result in a wide range of adverse effects that cause significant damage to the components of the ecosystem such as coral reefs, algal mats, mangrove and others.

While it is one of the necessities of modern industrial life, oil production and transportation have their negative side. Under control, it is efficient, versatile, and productive. However, when oil becomes out of control, it can be one of the most devastating substances in the environment. Max [1] has indicated that the reality of oil technology (its extraction, its transport, its refinery and use) has outpaced laws to control the technology and prevent oil from polluting the environment. When spilled on sea water, oil spreads for kilometers around causing major economic and environmental problems.

Oil spills not only impact marine habitats and inhabitants but also impact air quality and industrial facilities, which depend on the intake of clean seawater such as desalination plants.

There have been many oil spills resulting from mechanical failure of equipments, human errors and misjudgments. Examples of major oil spills as reported by Maclean [2] and Balawi [3] include (i) Amoco Cadiz spill in 1978, which spilled 275 thousand m^3 of light Arabian crude oil in the English Channel and (ii) Exxon Valdez spill in Alaska in 1989, which was the worst oil spill in the history of United States, spilling approximately 45 thousand m^3 of Alaskan heavy crude oil into the sea.

The Kuwait oil spill in 1991, the largest spill ever recorded had about 1.7 million m^3 oil spilled from oil terminals and tankers off the Kuwaiti and Saudi Arabian coast during the 1991 Gulf war. Long-term environmental harm of oil spills are tremendous and include destruction of land and marine wildlife, damage to property and beaches, air pollution, contamination of water supplies as well as several other losses. Therefore, public concern throughout the world toward oil spills has increased, leading to serious international endeavors to come up with efficient ways to combat oil spills and their environmental impact.

Commonly used methods for the clean-up of oil spills are: skimmers, [4-6] dispersants, [7-11] absorbents, [12-14] standard booms and industrial vacuum equipment. Other methods, such as burning, [15-17] sinking and biodegradation [18,19] are less widely used due to their major limitations or due to their environmental impact. The performance of any of these methods, as reported

[20] in the study done by the National Research Council, Washington, D.C., can be severely limited by oceanic conditions and weather, including currents, waves, and wind, and by the nature of the oil slick. While absorbent technology is promising, recovery of oil from absorbents such as straw, sawdust, clay, kenaf, feather, pads and peat are not easily accomplished [13]. The use of polymeric porous materials such as polyurethane offers a better alternative to this problem since polyurethane foams, in general, are easily squeezable. However, the direct use of ready-made PU foams on the surface of the oil spill may prove cumbersome as illustrated by the Canadian Petroleum Association evaluation report on Foam-X sorbent [21]. Tests on Foam-X sorbents with potential to absorb retain spilled oil and to reduce the hydrocarbon's flammability were described. The sorbent is placed on the surface of an oil slick where the spilled oil is recovered by either adsorption or absorption. Foam sorbents have a distinct cellular structure which does not depend on the nature of various oils to provide coherence of the oil/sorbent mixture. Open cell polyurethane foams supply a large surface area of porous material with open ended interconnected pores. Potential problems with Foam-X sorbents included but not limited to: (i) its low density corresponding to large foam volume and thus requiring huge transportation, and (ii) the difficulty of the oil droplets to penetrate through the pores of the PU foams thus affecting the absorption efficiency of the foam.

Recently, foaming polyurethanes (PU) on the top of an oil spill has been described [22] as an alternative method for oil spill clean-up. The foaming process usually starts with high volume–low pressure treatment of the liquid PU prepolymer on the top of the oil spill through a simple spray gun currently used by various applicators such as Seafoam, Inc., Houston, Texas. The foaming process on the top of the oil spill forces the oil droplet to enter through the pores of the foaming sorbent. The sorbent is then removed using existing spill recovery methods and can either be destroyed in controlled settings or squeezed for partial recovery of the oil as outlined by Brown [23]. The hope for this technology is to allow for the sea area to be restored to its original state without harming its environment. The easily transportable liquid polyurethane prepolymers contain the main ingredient for making the polyurethane foams.

The second reaction in Fig. 1 describes the reaction of the sprayed polyurethane prepolymers with sea water for the production of carbon dioxide gas. The steady reaction will cause the gas bubbles to enlarge within the forming polymer matrix and cause the polymeric material to foam with the oil droplets encapsulated within the foam cells under the influence of the favorable miscibility interactions of the prepolymer with the oil droplets. Tests conducted so far on these foams include: Canadian standards absorbency test, water column visual analysis, surface oil retention visual analysis, and gas chromatograph vapor analysis [21]. These tests were done on the foams, peat moss and vermiculite sorbents and the results were compared. It was concluded that the foam sorbent is capable of absorbing/adsorbing significant amounts of oil per unit weight of sorbent with relatively short contact times. Oil was fairly recovered from the foams. However, due to the hydrophilic nature of the polyurethane used to make the foams, more water than oil was absorbed alongside the oil droplets. This is natural and should be excepted since most of the major ingredients used to prepare the PU prepolymer are either polyether or polyester-based. Furthermore, the reaction of PU prepolymer with water produces the highly polar urea groups, which engages with the sea water in a complex hydrogen bonding network causing the water molecules to remain attached to the PU foam surface. In order to improve the efficiency of the polyurethane sorbents to absorb and retain oil droplets on the expense of the sea water molecules, the foam must be made hydrophobic. This way, the produced foam will repel the water molecules and attract the hydrocarbon ones.

The basic chemical reactions for producing polyurethane foams are shown:
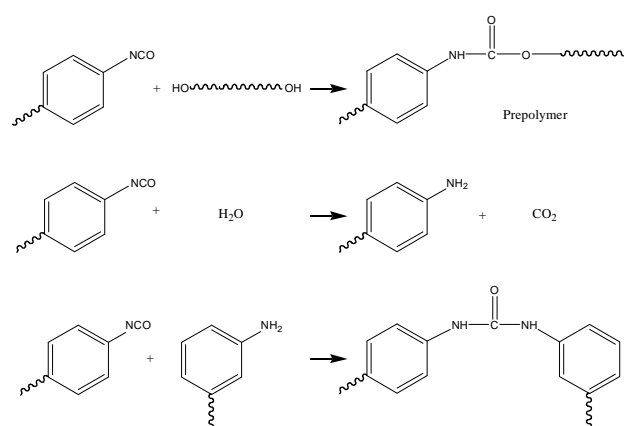

Fig. 1 Basic chemical reactions for producing urethane foams.

This study aims at the development of new PU foam for the clean-up of oil spills. Polyurethane prepolymer blends that are hydrophobic in nature are excellent candidates for this technology. The hydrophobicity of the prepolymer will ensure maximum encapsulation of the oil droplets within the foam cells during the foaming of the polyurethane materials. The blends, being in the liquid forms, will only solidify and foam upon getting in contact with water, which will facilitate its application using fire hoses mounted on fireboats. In order to elect the best candidates for this type of applications, several combinations of organic substrate candidates, various diols of different types and lengths, and various hard block sequence length distribution have been tested using molecular modeling techniques in order to evaluate their miscibility with hydrocarbon oil.

II. METHODOLOGY

Various binary systems have been simulated using Materials Studio software package, Molecular Simulation, inc. The COMPASS forcefield was used with all hydrogen atoms explicitly considered. A single

polymer chain of 500 repeat units was used in order to minimize the effect of chain ends on the results of the simulation. Initial configurations with periodic boundary conditions were generated in the simulation box as to enable the simulations to be carried out in such a way that the atoms experience forces as if they were in the bulk phase.
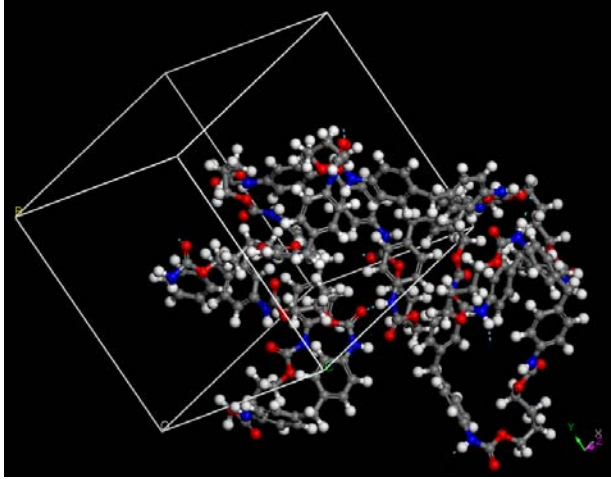

Fig. 2 3D modeling trajectory of a PU chain.

Reliable representations of the trajectories can thus be simulated and analyzed, Fig 2, according to the following the simulation model of Depner and Schürmann [24]. The polymer segments are subject to the bond-stretching potential, E_b:

$$E_b = K_b(1 - l_o)^2/2 \qquad (2)$$

where l_o is the equilibrium bond length and K_b is the bond stretching constant. The deformation of the bond angle θ between successive pairs of bonds from its equilibrium value θ_o is governed by the potential E_θ:

$$E_\theta = K_\theta (\cos\theta - \cos\theta_o)^2/2 \qquad (3)$$

with K_θ is the bond-bending constant. The torsional potential, E_ϕ, is modeled as

$$E_\phi = K_\phi (1 + \cos(n\phi - \tau)] \qquad (4)$$

where K_ϕ is the torsional constant, height of the energy barrier, n is the periodicity and τ the phase angle. Out-of-plane deformations modeled as a special case of the torsion equation with $\tau = 0$ and $n = 2$ and is given by, E_x [24]:

$$E_x = K_x[1 + \cos(2\phi)] \qquad (5)$$

The out-of-plane potential acts to keep the connected atom in the plane defined by the other three atoms. K_x is the out-of-plane deformation constant. Non-bonded Lennard-Jones interactions between atoms separated by four bonds or more are given by E_{nb}:

$$E_{nb} = 4\varepsilon^* \left[\left(\frac{r^*}{r_{ij}} \right)^{12} - \left(\frac{r^*}{r_{ij}} \right)^6 \right] + C \qquad \text{for } r_{ij} = 1.5\ r^* \qquad \text{and}$$

$$E_{nb} = 0 \qquad \text{for } r_{ij} > 1.5\ r^* \qquad (6)$$

The Lennard-Jones parameters between different atoms A and B are assumed to satisfy the Lorentz–Berthelot mixing rules defined by:

$$r_{AB}^* = (r_A^* + r_B^*)^{1/2} \text{ and } \varepsilon_{AB}^* = (\varepsilon_A^* \varepsilon_B^*)^{1/2} \qquad (7)$$

where r^* and ε^* are the Lennard-Jones radius and potential. The electrostatic interactions between atoms carrying partial charges are given by E_{ij}:

$$E_{ij} = \frac{q_i q_j}{4\pi\varepsilon\ r_{ij}} \qquad (8)$$

where q_i and q_j are the partial atomic charges on atoms i and j, respectively, r_{ij} is the distance between them and ε is the dielectric constant. The partial charges calculated [25] using the semiemperical molecular orbital method, MNDO, are used. The COMPASS forcefield was used with all hydrogen atoms explicitly considered. A single polymer chain of 500 repeat units was used in order to minimize the effect of chain ends on the results of the simulation. Initial configurations with periodic boundary conditions were generated in the simulation box as to enable the simulations to be carried out on relatively small molecular systems in such a way that the atoms experience forces as if they were in the bulk phase. In order to enhance the sampling efficiency in calculating the diffusion coefficients, ten gaseous molecules of each type were inserted into the cells. This was done to ensure a reliable representation of the trajectories. The equilibrium molecular dynamics simulations were usually performed using microcanonical ensembles. For every structure, the simulations were run several times; usually four runs, for better averaging. The self-diffusion coefficients of the gas molecules were calculated from the Einstein relation [25]:

$$D_o = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \left\langle \left[r_i(t) - r_i(0) \right]^2 \right\rangle \qquad (9)$$

where r_i is the position vector of atom i and N is the number of all gas molecules. The angular brackets denote averaging over all choices of time origin and over all particles. The diffusion coefficients of the penetrant molecules were only considered in evaluating the permeability through the different structures.

The evaluation of the enthalpic contributions to the free energy of mixing are based on the cohesive energy density approach [26] since the Flory-Huggins interaction parameter is unknown for most of these systems. These enthalpic contributions were evaluated from the solubility

parameters of the various components in the pure states according to:

$$\Delta H_{mix}/V = ((\Delta E_1 /V_1)^{1/2} - (\Delta E_2 /V_2)^{1/2})^2 \, \phi_1 \phi_2 \qquad (1)$$

or,

$$\Delta H_{mix}/V = (\delta_1 - \delta_2)^2 \, \phi_1 \phi_2 \qquad (2)$$

where ΔE_1 and ΔE_2 are the energies of vaporization of component 1 and 2 of the binary blend, respectively, V_1 and V_2 are the molar volume of the two species. The cohesive energy density, CED, is the ratio of the energy of vaporization calculated from the molecular dynamics runs to the molar volume of the species. The solubility parameter, δ, has been defined as the square root of the cohesive energy density and describes the attractive strength between molecules of the material. Evaluation of the cohesive energy densities of the various prepolymers could be used in conjunction with the above equation to investigate the influence of the molecular characteristics on the miscibility of the prepolymers with both oil and water. This investigation is being considered with respect to:

1. Various urethane scaffolds based on aliphatic, aromatic or heterocyclic groups.
2. Various diols of different types and lengths.
3. Various hard block sequence length.

III. SYNTHESIS AND SPECTRAL ANALYSIS

4,4'-diphenylmethane diisocyanate (MDI), 4,4'-methylenebisbenzeneamine (MDA), monoethylene glycol (MEG), low molecular weight poly(ethylene glycoladipate), butanediol, hexamethyleneglycol were all purchased from Aldrich Chemical Co. The poly(propylene glycol) oligomer and the heterocyclic diamines 2,6-diamino-pyridine, 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole, 2,2'-bis(p-aminophenylene-6,6'-dibenzothiazolyl)-methane were provided through ICI-Polyurethanes, Belgium. Triethylene diamine (Dabco EG), the urethane catalyst, was supplied from Air Products and Chemicals, PA, USA. Prior to use, MDI was melted at 80 ^{o}C for 24 hr and kept thereafter at 50 ^{o}C under a nitrogen blanket. The diols were all heated to 70 ^{o}C under vacuum for 18 hr to ensure the removal of all air bubbles and water vapor that may otherwise interfere with the isocyanate reactions. The three heterocyclic diamines were purified through crystallization and recrystallization. Polyurethanes are normally produced by reacting three basic monomers, diisocyanate, long chain diols known as polyols, and chain extenders, which are either diols such as ethylene glycol or diamines. The structure, therefore, of polyurethane is dependant on the choice of these components and their reactivity. With regards to the diisocyanate compounds, the organic isocyanate functional group is capable of a surprisingly diverse range of chemical reactions. Organic isocyanates include aliphatic, cycloaliphatic, aromatic and heterocyclic polyisocyanate. The most important aromatic diisocyanates are toluene diisocynate (TDI) and methylene diphenyl diisocyanate (MDI). Important aliphatic isocyanates include 1,6-hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI). While aliphatic isocyanates are widely used in the coatings industry due to their high resistance to outdoor weathering conditions such the ultraviolet light, aromatic diisocyanates are normally used in making PU foams for the extra stability and toughness they provide the foams with.

The reactions of isocyanates belong to two main categories: (i) active hydrogen donors and (ii) non-active hydrogen reactions. Several authors[20,23] described the first category as it requires at least one co-reagent containing one ore more hydrogen atoms that are potentially exchangeable (or labile) under the conditions of the reactions. A typical example for this category is the reaction of isocyanates with hydroxyl groups of either the diols or polyols such as the isocyanate reaction with alcohols and phenols to form urethanes as shown below:

$$R-N=C=O \; + \; HO-R' \; \rightleftharpoons \; R-NH-\overset{\overset{\textstyle O}{\|}}{C}-OR'$$
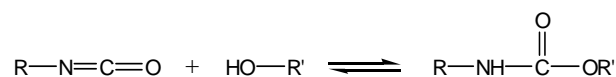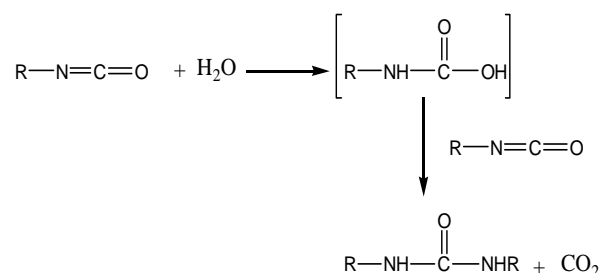
Reaction with phenols is significantly slower than that with aliphatic alcohols and yields a less stable urethane.

Non-active hydrogen reactions constitute the second broad category and involve breaking the susceptible carbon-nitrogen bond. Primary and secondary amines react vigorously with isocyanates to yield urea as illustrated herewith:

$$R-N=C=O \; + \; H_2N-R' \; \rightleftharpoons \; R-NH-\overset{\overset{\textstyle O}{\|}}{C}-NHR'$$
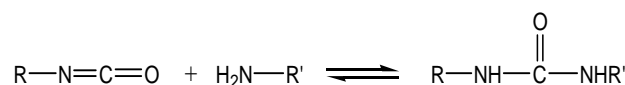
The reaction between isocyanate and water is a special case of an alcohol/isocyanate reaction. The primary product is the carbamic acid, which is quite unstable and decomposes to the corresponding amine and carbon dioxide. The amine formed will then react immediately with another isocyanate group to form a urea linkage. The evolved CO_2 causes the material to foam resulting in a much lower density porous material:

$$R-N=C=O \; + \; H_2O \longrightarrow \left[R-NH-\overset{\overset{\textstyle O}{\|}}{C}-OH \right]$$
$$\downarrow R-N=C=O$$
$$R-NH-\overset{\overset{\textstyle O}{\|}}{C}-NHR \; + \; CO_2$$

Long chain macroglycols with a molar mass from 400 to 5000 g mol-1 compose the soft segments of any polyurethane material. They include polyethers, polyesters, polydienes or polyolefins, and polydimethylsiloxanes. Polyurethane elastomers have traditionally been made from polyether or polyester soft segments as was explained in the 'Handbook of Polyurethane'.[19] While, it is well-known that polyester-

based urethanes have relatively good material properties, they are rather susceptible to humidity and hydrolysis which could be an obstacle when used in vigorous oceanic conditions. When the application requires good environmental stability, a polydiene based soft segment is a good candidate. Polydienes, which are hydrophobic in nature, should also increase the hydrophobicity of the PU prepolymers and thus their absorbing efficiency of the spilled hydrocarbon material. The processing of these materials, however, is known to be quite difficult.

The third component of making polyurethanes is the diol and diamine chain extenders. Diamine chain extenders are much more reactive than diol chain extenders and produce polyurethanes with superior properties. This is since PU hard segments of urea nature has a higher density of hydrogen bonding, which results in a higher glass-transition temperature as well as higher thermal stability. Generally, polyurethanes chain extended with an aliphatic diol or diamine produce softer PU material than polyurethanes chain extended with an aromatic diol or diamine. Common chain extenders for polyurethane synthesis are 1,4-butandiol, 1,6-hexandiol, ethyleneglycol, ethylenediamine and 4,4'-methylenebis(2-chloroaniline). The FTIR spectra were recorded at room temperature using a Nicolet 550 FTIR system coupled to a computer. The spectra were collected over the range 4000-400 cm^{-1} by averaging 128 scans at a maximum resolution of 2 cm^{-1}. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC-250 spectrometer at 250 and 62.5 MHz, respectively, in DMSO-d_6 using tetramethylsilane as an internal reference. The chemical shift (δ) and coupling constant (J) data are quoted in ppm and Hertz, respectively. The following abbreviations were used to describe the peak patterns where appropriate: s = singlet, d = doublet, q = quartet and m = multiplet.

IV. RESULTS AND DISCUSSION

According to the above equation, which describes the relationship between the solubility parameters of two components and the enthalpic contributions to the free energy of mixing, and hence, their influence on the miscibility of a mixture of both, it is apparent that maximum miscibility would occur when δ_2 is as close as possible in value to δ_1, i.e. the difference of ($\delta_1 - \delta_2$) is as small as possible. Close inspection of the simulated solubility parameter values of the various recommended polyurethanes prepolymers in comparison to those of oil and water would identify the most hydrophobic urethanes suitable enough for the current investigation.

Oil is known to be a mixture of various hydrocarbons such as n-Pentane, n-Hexane, n-Heptane and n-Dodecane. Table I lists the solubility parameter values of various oil components as well as that of water [27]. As mentioned earlier, various polyurethane prepolymers of various urethane scaffolds based on aliphatic, aromatic or heterocyclic groups, various diols of different types and lengths, and various hard block sequence length were simulated and studied. Polyurethanes are normally

prepared from a polyether or polyester macrodiol (with molecular mass ranging from a few hundred to a few thousand) coupled with an excess of a conventional diisocyanate, usually of the aromatic series, to give a diisocyanate polymeric precursor, which is chain-extended by a conventional diol or diamine to produce the final polymer.

Table I. Solubility parameters of various solvents

Solvent	(MPa)$^{1/2}$
n-Pentane	14.4
n-Hexane	14.9
n-Heptane	15.3
n-Dodecane	16.0
Water	48.0

Table II lists various polyurethane prepolymers of various urethane scaffolds based on aliphatic and aromatic groups.

Table II. Polyurethane prepolymers containing aliphatic and aromatic moieties

PU	Diiso-cyanate	Diol	Aliphatic aromatic extender	Simulated solubility parameter
1	MDI	s-PEGA	PPG	22
2	MDI	EG	PPG	24
3	MDI	BD	PPG	24
4	MDI	HD	PPG	20
5	MDI	BD	-	27
6	MDI	HD	MDA	21
7	MDI	HD	-	25
8	MDI	EG	-	23
9	MDI	BD	MDA	23

s-PEGA = low molecular weight poly(ethylene glycoladipate)

EG = ethyleneglycol
BD = Butanediol
HD = hexamethyleneglycol
MDI = 4,4'-diphenylmethane diisocyanate
PPG = poly(propylene glycol) oligomer
MDA = 4,4'-diphenylmethane diamine

The observed changes in the solubility parameters are obviously modest because on the one hand they correspond to a relatively minor change in the overall polymeric structure (the polyether portion coming from the macrodiol remains an important fraction), and on the other hand the heterocyclic moieties are accompanied by lateral methylene groups, which introduces a considerable degree of rotational freedom. As the heterocyclic material is less well introduced into the backbone, the consequences of this modification on the properties are mostly reflected by an increase in the columbic interactions. For PU structures with the heterocyclic ring moved completely outside the backbone as a side group, the resulting materials are homogeneous and amorphous since the chains do not normally pack correctly because

of the bulkiness of the ring and its asymmetric position and therefore becomes very soft, stretchable and mixable.

Table III lists various polyurethane prepolymers of various urethane scaffolds based on heterocyclic groups.

Table III. Polyurethane prepolymers containing heterocyclic moieties

PU	Diiso-cyanate	Diol	Hetero-cyclic diamine	Simulated solubility parameters
1	MDI	s-PEGA	DAP	21
2	MDI	s-PEGA	DAI	28
3	MDI	s-PEGA	APO	24
4	MDI	s-PEGA	m-ASM	29
5	MDI	s-PEGA	p-ASM	24
6	MDI	EG	APO	30
7	MDI	HD	APO	31
8	MDI	HD	p-ASM	30

DAP = 2,6-diamino-pyridine
DAI = N,N'-bis(p-aminohexyl-pyromellitimide)
APO = 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole
p,m-ASM = 2,2'-bis(p-and m-aminophenylene-6,6'-dibenzothiazolyl)-methane
s-PEGA = low molecular weight poly(ethylene glycoladipate)
EG = ethyleneglycol
HD = hexamethyleneglycol
MDI = 4,4'-diphenylmethane diisocyanate

Since it is the objective of this study to find polyurethane structures with the solubility parameters as close as possible to oil and as far away as possible from water, it is apparent from Table 2 and 3, that the following three polyurethanes, with the lowest value for the Hansen solubility parameters are the most hydrophobic PU prepolymer. These are:
i.)   PU-1: MDI/HD/PPG
ii.)   PU-2: MDI/HD/MDA
iii.)   PU-3: MDI/s-PEGA/DAP

In addition to these prepolymers, other ones were also synthesized in order to provide a variety of materials for a subsequent study of the miscibility of these systems with both oil and water as a means of validating the results of the molecular modeling investigation. Eight polyurethane prepolymers were synthesized according to standard procedures [28]. After synthesis of the urethane prepolymer is complete, the residual isocyanate monomer was removed by the wiped film distillation technique [28] to less than 0.1%. The free isocyanate content of the prepolymer was determined by reacting a pre-weighed sample with excess di-n-butylamine in toluene, digested for 10 min and titrated against HCl in accordance with the procedures outlined in ASTM D2572-97. The synthesized polyurethane prepolymers are all listed in Table IV. The synthesis of these urethane prepolymers, which are hydrophobic in nature are to be utilized in the clean-up of oil spills. The hydrophobicity of the prepolymer will ensure maximum encapsulation of the oil droplets within

the foam cells during the foaming of the polyurethane materials. Other prepolymers were also synthesized in order to be tested in a subsequent study for their miscibility with oil and water as a means of validating the results of the modeling investigation performed earlier

Table IV. Polyurethane prepolymers containing different types of diols and chain extenders

PU	Diiso-cyanate	Diol	Aliphatic/aromatic chain extender
1	MDI	HD	PPG
2	MDI	HD	MDA
3	MDI	BD	MDA
4	MDI	s-PEGA	DAP
5	MDI	s-PEGA	APO
6	MDI	s-PEGA	p-ASM
7	MDI	EG	APO
8	MDI	HD	p-ASM

PEGA = low molecular weight poly(ethylene glycoladipate)
EG = ethyleneglycol
BD = Butanediol
HD = hexamethyleneglycol
MDI = 4,4'-diphenylmethane diisocyanate
PPG = poly(propylene glycol) oligomer
MDA = 4,4'-diphenylmethane diamine
DAP = 2,6-diamino-pyridine
APO = 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole
p-ASM = 2,2'-bis(p-aminophenylene-6,6'-dibenzothiazolyl)-methane

The NMR analytical data obtained for the various prepolymers are as follows:

Prepolymer 1: (MDI-PPG-MDI-HD-MDI-PEGA-MDI-HD-MDI-PPG-MDI)
^{1}H NMR (300 MHz, DMSO-d_6): 7.30-7.21 (m, 18H); 7.05 (broad, 4H); 6.80-6.74 (m, 8H); 4.20-4.11 (m, 8H); 3.84 (s, 6H); 1.71-1.42 (m, 8H).
^{13}C NMR (75 MHz, DMSO-d_6): 152.6, 152.1, 119.5 (CO); 138.9, 138.0, 135.6, 133.2, 131.8 (ArC); 131.3, 129.8, 124.5, 116.7 (ArCH); 73.08 (CH); 69.6, 68.9, 67.5, 65.3, 40.5, 39.9, 27.7, 25.1 (CH$_2$).

Prepolymer 2: (MDI-MDA-MDI-HD-MDI-PEGA-MDI-HD-MDI-MDA-MDI)
^{1}H NMR (300 MHz, DMSO-d_6): 7.85 (broad, 6H); 7.50-7.00 (m, 20H); 6.83-6.70 (m, 12H); 4.20 (t, $J_3 = 8.1$ Hz, 4H); 3.83 (s, 8H); 1.71-1.63 (m, 4H); 1.46-1.40 (m, 4H).
^{13}C NMR (75 MHz, DMSO-d_6): 152.6, 152.3, 119.5 (CO); 138.9, 138.4, 138.2, 135.6, 135.2, 133.2 (ArC); 131.3, 131.2, 129.8, 124.4, 121.0, 116.7 (ArCH); 65.4, 40.5, 27.7, 25.1 (CH$_2$).

Prepolymer 3: (MDI-MDA-MDI-BD-MDI-PEGA-MDI-BD-MDI-MDA-MDI)
^{1}H NMR (300 MHz, DMSO-d_6): 7.95 (broad, 6H); 7.48-7.10 (m, 20H); 6.83-6.73 (m, 14H); 4.10 (t, $J_3 = 8.1$ Hz, 4H); 3.85 (s, 8H); 2.05-1.95 (m, 4H).

^{13}C NMR (75 MHz, DMSO- d_6): 152.6, 152.3,119.5 (CO); 138.8, 138.2, 135.5, 135.1, 133.3 (ArC); 131.2, 131.1, 129.9, 124.5, 121.1, 116.8 (ArCH); 65.0, 40.4, 25.7 (CH_2).

Prepolymer 4: (MDI-DAP-MDI-PEGA-MDI-PEGA-MDI-PEGA-MDI-DAP-MDI)

^{1}H NMR (300 MHz, DMSO- d_6): 9.03 (broad, 4H); 7.77 (d, J_3 = 8.0 Hz, 2H); 7.59-7.17 (m, 18H); 6.80-6.74 (m, 8H); 4.40-4.26 (m, 8H); 3.90 (s, 6H).

^{13}C NMR (75 MHz, DMSO- d_6): 165.5, 154.3, 153.4, 120.0 (CO); 153.2, 138.3, 138.0, 135.6, 135.2, 133.2, 131.8 (ArC); 138.4, 131.3, 131.2, 129.8, 124.5, 121.0, 116.9, 104.8, 103.5 (ArCH); 66.2, 62.3, 62.2, 40.5, 34.4, 23.5 (CH_2).

Prepolymer 5: (MDI-APO-MDI-PEGA-MDI-PEGA-MDI-PEGA-MDI-APO-MDI)

^{1}H NMR (300 MHz, DMSO- d_6): 7.55 (d, J_3 = 8.5 Hz, 2H); 7.25 (d, J_3 = 8.5 Hz, 2H); 7.50 (broad, 6H); 7.45-7.17 (m, 18H); 6.81-6.71 (m, 9H); 4.39-4.27 (m, 8H); 3.85 (s, 6H).

^{13}C NMR (75 MHz, DMSO- d_6): 165.2, 153.4, 152.6, 119.9 (CO); 165.6, 142.5, 138.8, 138.4, 138.0, 135.6, 135.2, 133.2, 121.6 (ArC); 131.3, 131.2, 129.8, 129.4, 124.5, 121.74, 121.0, 117.2 (ArCH); 65.9, 61.9, 40.3, 34.3, 23.8 (CH_2).

Prepolymer 6: (MDI-ASM-MDI-PEGA-MDI-PEGA-MDI-PEGA-MDI-ASM-MDI)

^{1}H NMR (300 MHz, DMSO- d_6): 8.10 (s, 2H); 8.08 (d, J_3 = 8.3 Hz, 2H); 7.56-7.15 (m, 32H); 6.95-6.75 (m, 8H); 4.11 (s, 4H); 3.82 (s, 6H).

^{13}C NMR (75 MHz, DMSO- d_6): 165.2, 153.3, 152.3, 151.9, 120.0 (CO); 166.2, 151.9, 139.8, 138.8, 138.2, 137.9, 135.6, 135.2, 133.8, 131.8, 131.5, 127.8 (ArC); 131.2, 131.1, 129.5, 124.5, 122.2, 121.0, 119.9, 119.8, 119.4, 117.1 (ArCH); 66.2, 62.2, 62.1, 40.5, 39.4, 34.2, 24.0 (CH_2).

Prepolymer 7: (MDI-APO-MDI-EG-MDI-PEGA-MDI-EG-MDI-APO-MDI)

^{1}H NMR (300 MHz, DMSO- d_6): 7.54 (d, J_3 = 9.0 Hz, 4H); 7.15 (d, J_3 = 9.0 Hz, 4H); 7.52 (broad, 6H); 7.45-7.15 (m, 16H); 6.81-6.74 (m, 8H); 4.31 (s, 4H); 3.80 (s, 6H).

^{13}C NMR (75 MHz, DMSO- d_6): 153.3, 152.7, 120.0 (CO); 165.1, 142.3, 138.8, 138.1, 137.8, 135.3, 133.0, 131.7, 121.5 (ArC); 131.3, 131.2, 129.7, 129.1, 124.2, 121.7, 120.8, 117.2,(ArCH); 66.0, 40.3, (CH_2).

Prepolymer 8: (MDI-ASM-MDI-HD-MDI-PEGA-MDI-HD-MDI-ASM-MDI)

^{1}H NMR (300 MHz, DMSO- d_6): 8.06 (s, 2H); 8.04 (d, J_3 = 8.3 Hz, 2H); 7.48-7.15 (m, 34H); 6.83-6.76 (m, 8H); 4.17 (t, J_3 = 7.5 Hz, 4H); 4.10 (s, 6H); 1.69-1.66 (m, 4H); 1.45-1.41 (m, 4H).

^{13}C NMR (75 MHz, DMSO- d_6): 153.2, 152.5, 119.9 (CO); 166.0, 151.9, 139.4, 138.5, 138.3, 138.2, 135.5, 133.2, 131.8, 127.7 (ArC); 131.3, 131.1, 129.8, 129.7, 124.5, 122.1, 121.0, 119.7, 119.6, 119.1, 116.7 (ArCH); 65.5, 40.6, 39.3, 27.8, 25.1 (CH_2).

According the above outlined synthesis procedures; all synthesized prepolymers must be end-capped with isocyanate functional groups to allow the prepolymers to complete their polymerization reactions upon contact with sea water, hence the use of the term prepolymer. Upon contact with sea water, the isocyanate groups will undergo chemical reactions with the water molecules as described above to produce an amine group and a CO_2 molecule. The amine-terminated compounds would continue to react with other isocyanate group present in the medium. The molecules will continue to react while linking themselves to each other as to produce the final polyurethane polymer. The carbon dioxide gas will cause the polymer to foam and expands while creating open cells throughout the porous structure. As the prepolymer polymerize, it is expected that the resulting polymer molecules will mix with the hydrocarbon molecules driven by the favorable thermodynamic forces due to the hydrophobicity of both PU and oil. The final oil-encapsulated PU foam could thus be collected and treated as described earlier.

The IR spectra showed sharp peaks at 1730 cm^{-1} corresponding to the free urethane and/or ester carbonyl groups and at the 1710 cm^{-1} corresponding to the bound urethane groups and/or ester carbonyl groups. For prepolymers containing diamine chain extenders, sharp peaks at 1694 cm^{-1} corresponding to the free urea, strong sharp peaks at 1640 cm^{-1} corresponding to the bifurcated urea carbonyl groups and broad bands at the range of 1690-1660 cm^{-1} were observed indicating the loosely ordered hydrogen bonds.

The presence of NH and methylene (CH_2) groups were verified by ^{1}H NMR analysis for all the investigated compounds. In the ^{1}H NMR spectrum, the proton of NH in both urea and urethane groups appear as a broad signal in the region between δ 7 to δ9 ppm. While the two protons of three methylene groups in three MDI molecules appears as a singlet signal in region from δ4.10 to δ3.85 ppm. For the carbonyl C-atom, CO, of both of urea and urethane groups in all investigated compounds, two signals were observed in ^{13}C NMR spectrum in region between δ165.2 to δ151.9 ppm. On the other hand, two C-atoms of NCO groups in two MDI molecules were normally observed in ^{13}C NMR spectrum in region δ120.0 to δ119.5 ppm as one signal. Furthermore ^{13}C NMR showed the presence of carbon atoms of three methylene groups in three MDI molecules as one signal in a region from δ40.6 to δ40.3 ppm.

The 1H NMR spectrum of compound **2** proved the existence of four protons of two CH_2 groups attached to urethane group which appears as a one triplet signal (t, J_3 = 8.1 Hz, 4H) at δ4.20 ppm due to their coupling with two protons of adjacent methylene groups in hexamethyleneglycol molecule. The same coupling was observed in compound **3** at δ4.10 ppm as triplet signal (t, J_3 = 8.1 Hz, 4H) for two methylene groups attached to urethane group in butanediol molecule. The doublet signal (d, J_3 = 8.0 Hz, 2H) at δ7.77 ppm in ^{1}H NMR spectrum of compound **4** which related to two protons in pyridine ring proved the presence of pyridine ring in that compound. Moreover, two doublet signals (d, J_3 = 8.5 Hz, 2H) and (d, J_3 = 8.5 Hz, 2H) at δ7.55 and δ7.25 ppm,

respectively, in ^{1}H NMR spectrum of compound **5** showed the existence of two benzene rings of 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole molecule in that compound. The ^{1}H NMR spectrum of compound **6** indicated the presence of two protons at δ8.10 ppm as a singlet signal and two protons at δ8.08 ppm as a doublet signal (d, J_3 = 8.3 Hz, 2H) which proved the existence of two benzothiazol rings. The four protons of two benzene rings in 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole molecule have been recognized in ^{1}H NMR spectrum of compound **7** as two doublet signals (d, J_3 = 9.0 Hz, 4H) and (d, J_3 = 9.0 Hz, 4H) at δ7.54 and δ7.15, respectively. Furthermore, ^{1}H NMR spectrum of compound **7** showed the presence of four protons of two CH2 groups of ethyleneglycol molecule as a singlet signal at δ4.31 ppm. The ^{1}H NMR spectrum of compound **8** showed the presence of two protons at δ8.06 ppm as a singlet signal and two protons at δ8.04 ppm as a doublet signal (d, J_3 = 8.3 Hz, 2H) which proved the existence of two benzothiazol rings. Moreover, the ^{1}H NMR spectrum of compound **8** proved the existence of four protons of two CH_2 groups attached to urethane group which appears as a one triplet signal (t, J_3 = 7.5 Hz, 4H) at δ4.17 ppm due to their coupling with two protons of adjacent methylene groups in hexamethyleneglycol molecule.

In ^{13}C NMR spectrum of **2**, **3**, **7** and **8**, the carbon atom of two methylene groups attached to urethane group appeared in the region between δ66.0 to δ65.0 ppm as one signal thus confirming the chemical structures of the synthesized prepolymers.

V. FUTURE ELABORATION

Future elaboration and continuation of this work must include the following:

A. Environmental studies on the impact of prepolymers on marine habitat and inhabitants

To assess the effect of prepolymers on fish histopathology, toxicity, oxidative stress and DNA fragmentation index, the response of fish populations to the contaminants will be monitored at a selected exposure levels. At this stage, fish will be exposed to prepolymers at varying time periods and several biological parameters will be considered:

1. Fish mortality, weight, and behavior will be monitored.
2. Histopathological changes in the gills, liver and kidneys as assessed by histological and ultrastructural changes
3. Oxidative stress as indicated by the loss of antioxidant enzymes such as superoxide dismutase, catalyses, glutathione peroxidase, glutathione-s-transferase, and glutathione reductase will be monitored.

Also several markers for the oxidative damage will be observed such as lipid peroxidation and protein carbonyl formation as well as DNA fragmentation and oxidation.

4. Hepatotoxicity as evaluated by high levels of cytochrome P450, CB5 and NAPH-reductase and low activities of EROD.

At the end of this step, possible environmental impact of the prepolymers on fish habitat and inhabitants will be identified and reported.

B. DryAdd simulation of the PU foaming process

To simulate the foaming reaction of the prepolymer, a well-know computational package, DryAdd, will be employed to determine the optimum isocyanate value (NCO) of the prepolymer that produces the required hard block content and the best urethane/urea ratio. Isocyanate groups' reaction with water will be simulated to form carbon dioxide. If the evolution of this gas is controlled correctly as the system gels, it can be used to produce water-blown environmentally-friendly foam. A polyol with average OH functionality of 2.5 (represented as two materials, with functionality 2 and 3) and molecular weight of 1000 will be mixed with polymeric MDI with average functionality of 2.3. Allowed reactions will include that of the water and isocyanate to form amine and CO_2, followed by the rapid reaction of the amine with isocyanate to give a urea linkage. Isocyanate plus polyol will give urethane links. Other side reactions to give allophanates and biurets will also be included unless considered, in special cases, insignificant. If the water molecules are set up with two phantom groups - amine and CO_2 - then the evolution of CO_2 can be monitored, and compared with the molecular weight buildup. Here, the amount of each is calculated alongside the rise in secondary cycles, a sure indicator of the onset of gelation. By adjusting reaction rates using catalysts the evolution of CO_2 can be controlled with respect to gelation and the hard block content as well as the urethane/urea ratio will be evaluated.

At the end of this step, compositions that produce the desired hard block sequence length distribution, which matches the prepolymer prototypes (elected in the previous phase), will be identified.

C. Development of PU foaming technology

The polyurethane foams will contain the following components and be mixed in the following proportions:

- A polyether or polyester polyol.
- An aliphatic chain extender to enhance the hydrophobicity of the resultant foams.
- A quasi-prepolymer with an NCO content as low as possible to produce the desired hardness and physical properties.
- An index 100 for the polyurethane system formulation.
- An amine catalyst to catalyze the system to between 20 and 40 seconds.
- Match the viscosity of the isocyanate to the polyol blend to improve mixability.

Due to the functionality of the reactants, a high degree of crosslinking occurs and a foam results. Bubbles of gas

cause the polymer matrix to foam resulting into a cellular flexible foam. In order for the foam to form well, the gas evolution process and the polymer formation must occur at a matched rate. This is why a catalyst is used. The block copolymer acts as a foam stabilizer during the early stages of foam formation when the polymer is still weak. The walls of the foam cells are particularly weak and break under the pressure during the gas evolution causing the foam to have an open-cell morphology and shaping the way for the oil droplets encapsulation.

At the end of this step, a PU foaming technology would have been developed and finalized, and used to produce final foams using these prepolymers in order to test the ultimate properties of these materials.

D. Thermal and mechanical characterization of the resultant foams

Synthesized polyurethane foams will be evaluated based on their thermal and mechanical characteristics. Properties such as thermal conductivity, thermal expansion, strength in tension and in compression, and shear strength of the synthesized foams will be evaluated. Cell morphology which is important for oil encapsulation will be characterized using scanning electron microscopy.

It is desired to synthesize foams with maximum efficiency in absorbing oil while allowing minimum encapsulation of water. Therefore the density and the efficiency of the synthesized foams in encapsulating oil and water will be determined. Rate of encapsulation of oil into the foams will be determined. Seawater and crude oil from a local petroleum company will be used. Effects of different types of crude oil (light or heavy) will be investigated.

At the end of this step, thermal and mechanical properties of the synthesized foams will be determined. Optimum foam will be determined based on evaluated characteristics.

E. Environmental studies on the impact of oil-encapsulated foams on marine habitat and inhabitants

Introduction of a large quantity of chemicals onto the sea water and the environment require a safety precautions and biomonitoring programs. Assessment of the response of fish populations to contaminants usually involves monitoring of selected exposure at several levels of biological organization from biomolecular level to the community levels. At this stage, fish will be exposed to oil-encapsulated foams at varying time periods and similar biological parameters to the previous study will be evaluated.

At the end of this step, possible environmental impact of the oil-encapsulated polyurethane foams on fish habitat and inhabitants, in particular possible toxic effects of the oil-encapsulated foams on fish histopathology, toxicity, oxidative stress and DNA fragmentation index will be identified and reported.

F. Large scale production of PU prepolymers

To examine on a large scale, the production of the prepolymer blend. This is will be done using existing polyurethane technologies normally used to produce MDI-based prepolymers commonly known as polymeric MDI. The prepolymer blend will contain large amount of the monomeric methylene diisocyante (MDI) as to control both the NCO value of the blend and hence its reactivity with water as well as the blend's viscosity.

At the end of this step, large quantities of PU prepolymer blends of various hydrophobicity would have been prepared and ready to be used on a pilot scale experiment.

G. Evaluation of a pilot scale for the clean up of crude oil from water surface using the foaming technology

In order to evaluate this technology, a pilot scale representing the foaming technology will be designed, constructed and tested with the synthesized polyurethane foams of optimum quality. Performance of any recovery method can be severely limited by oceanic conditions and weather, including currents, waves, and wind, and by the nature of the oil slick. Therefore, the pilot scale will include a container with simulated wave generation capability to represent as close as possible the actual sea conditions. It will also include delivery system to deliver the liquid prepolymer to the water surface. The pilot scale will also include containment, recovery and compressibility capabilities for the separation/recovery of oil from the foams.

At the end of this step, a pilot scale prototype of the foaming technology will be designed, constructed, and tested. Effectiveness of the foaming technology to clean up oil spills from seawater will be evaluated.

H. Solutions for containment, clean up and recovery of a large scale oil spill using PU foaming technology

Although spilled oil may originate from a small localized source, it can rapidly spread to cover large area of water. How thick the resulting slick would be depends on the amount of time the oil spends on the surface, the type of oil spilled, and its viscosity at ambient temperature. A principal factor in removing oil expeditiously and effectively is the thickness of the oil spill. The rate of oil recovery by any method decreases with decreasing oil thickness. Thus rapid response with coordinated use of oil-containment booms, transfer pumps, and temporary storage is required for the recovery to be successful. Large scale design of the foaming technology will be considered in details taking into consideration the containment, clean up, recovery, storage and potential use of oil and foams. Detailed economic analysis of the large scale process will be performed.

At the end of this step, the large scale design of the foaming technology will be accomplished. Economic study of the large scale foaming technology will be conducted.

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