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FULL LENGTH ARTICLE

Synthesis and characterization of oil sorbent based on Hydroxypropyl Cellulose Acrylate

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Abstract The present work deals with the preparation of some oil sorbers based on cellulose derivatives to control petroleum oil spills. In this respect, hydroxypropyl cellulose HPC was used to synthesize hydroxypropyl cellulose acrylate HPCA macromonomer by esterification of HPC with acryloyl chloride. Then the produced HPCA monomer was copolymerized with octadecyl acrylate (ODA) in the presence of two types of crosslinkers to produce oil gel. The chemical structures of both HPC and HPCA were confirmed by using FTIR and ^{1}HNMR spectroscopic analysis. Whereas the thermal properties of the crosslinked oil absorbents were investigated using TGA. Furthermore, morphological properties of prepared crosslinked copolymers were studied using SEM. Several parameters were considered to evaluate the oil sorbers, such as: monomers feed ratio, type and concentration of the applied crosslinkers. Finally, the swelling efficiency of oil gel was thoroughly investigated in light and heavy oil. It observed that as the octadecyl acrylate content increased the oil absorbency also increased and reached a maximum value at monomer feed ratio 10/90 HPCA/ODA. It is found that the maximum oil absorbency measured with MBA at a monomer feed ratio 10/90 HPCA/ODA are 29.7 and 18.6 g/g for toluene and crude oil, respectively.

1. Introduction

Petroleum crude oil is one of the most important energy and raw material sources for the synthesis of synthetic polymers and chemicals worldwide [1]. The processes of oil exploration, production and transportation may result in oil spillage. In recent years, tremendous increases of accidental and intentional oil spillage have occurred during different oil processes [2]. Oil pollution, particularly of sea and navigable waters, has stimulated more public concern than other waste or spilt materials. Oil pollution of the sea has been raised with the increase in oil consumption. The total annual influx of petroleum hydrocarbons is about 10 million metric tons. The bulk of this influx is due to the transportation-related activities. Oil spill occurs from tanker loading and uploading operations, pipeline rupture, which may be because of industrial waste as leakage from engines, incorrect operation of valves, and discharge of

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oily wastes. Oil pollution of the shore, in addition to the reduction of amenity, also affects marine, shore life, and vegetation [3]. Crude oil spilt in the marine environment undergoes a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photochemical oxidation, microbial degradation, and adsorption onto suspended materials, agglomeration, etc. The methods commonly used to remove oil involve oil booms, dispersants, skimmers, sorbents etc. [4].

One of the most economical and efficient methods for combating oil spills is oil sorption by sorbents. Oil sorbents are able to concentrate and transform liquid oil to the semisolid or solid phase, which can then be removed from the water and handled in a convenient manner without significant oil draining out. The preferable sorbent materials are those which, besides being inexpensive and readily available, demonstrate fast oil sorption rate, high oil sorption capacity (oleophilicity or lipophilicity), low water pickup, and high oil retention capacity during transfer, high recovery of the absorbed oil with simple methods, good reusability, high buoyancy, and excellent physical and chemical resistances against deformation, photodegradation, and chemical attacks [5]. There are three major classes of oil sorbents, namely, inorganic mineral products, organic synthetic products and organic natural products [6].

There are many natural products used for the preparation of oil sorbers by different chemical modifications such as chitosan, rosin and cellulose. Cellulose is a nontoxic, renewable resource and one of the most abundant polymers on earth [7]. By chemical modification of this polymer, new characteristics can be introduced, e.g., improved solubility in various solvents. This opens up a broad range of applications in which modified cellulose can be used, e.g., in paint, food, and pharmaceutical industry [8,9]. To achieve the desired properties, the hydroxyl groups along the polymer chain are substituted with different groups, e.g., carboxymethyl or methyl, or with a mixture of different groups, e.g., hydroxypropyl and methyl groups. The properties of the modified cellulose will thus not only depend on the chain length but also on the nature of the substituent, the degree of substitution (DS) and for some types of substituents, the length of the side chains. In addition, the distribution of the substituents along the backbone will influence the polymer properties [10,11].

Among the cellulose derivatives, HPC is an alkyl-substituted hydrophilic cellulose derivative with advantages such as excellent film forming properties, degradability, biocompatibility etc. [12,13]. It also has a particular phase transition behavior in aqueous solution and some solvents [14–17]. Because of these unusual and desirable properties, and its prospects in industrial applications, HPC has been a focus of many researches [18–20].

In this study, we attempt to prepare natural modified biodegradable oil sorbents containing segments that act as targeted sites for biodegradation. This is accomplished by the use of HPC (cellulose derivatives) to prepare a crosslinked copolymer of hyddroxypropyl cellulose acrylate/octadecyl acrylate HPCA/ODA as the oil sorbent. The prepared oil sorbents were characterized and evaluated in the presence of light and heavy oil. Furthermore, the chemical structure of the prepared sorbents was thoroughly investigated and correlated to their efficiency.

2. Experimental

2.1. Materials

Hydroxypropyl cellulose (HPC) was obtained from Aqualon Co. as industrial grade reagent with M_w 370,000. Other chemicals used in this study were purchased from Aldrich chemical Co. as analytical grade reagents and used as received. They include Acryloyl chloride, 2,2′azobisisobutyronitrile (AIBN), Octadecyl acrylate (ODA), Divinyl benzene (DVB), Triethyl amine (TEA), Methylene bisacrylamide (MBA) Dimethylformamide (DMF) and Tetrahydrofuran (THF), Toluene. The crude oil was obtained from PETRODARA OIL Co.

Company: Dara Petroleum, well name: Arta-60 and its specifications are listed in Table 1.

2.2. Synthesis of hydroxypropyl cellulose acrylate (HPCA)

Hydroxypropyl cellulose acrylate (HPCA) was synthesized by the reaction of hydroxypropyl cellulose with acryloyl chloride in the presence of DMF. Hydroxypropyl cellulose (5.99 mmol based on hydroxypropylated anhydroglucose unit (HPAGU)) was added to 100 ml of DMF with vigorous stirring at room temperature. After complete dissolution of hydroxypropyl cellulose, the solution was transferred into a 500 ml four-necked flask fitted with a mechanical stirrer, thermometer, and Nitrogen inlet and dropping funnel. Then 36 mmol of TEA was added as an acid acceptor, the solution was cooled to zero temperature. After that 36 mmol acryloyl chloride was added dropwise in a period of about 60 min. The solution was stirred at 40 °C for 6 h. A yellowish precipitate of TEA hydrochloride was formed during the reaction. The reaction mixture was poured into a beaker containing 400 ml of THF. White hydroxypropyl cellulose acrylate coagulated. The product was filtered, washed with THF, and dried at 40 °C under vacuum.

Table 1 Specifications of petrodara crude oil.

Experiment	Method	Result
Density, @ 15.56C	ASTMD-1298	0.9492
Specific gravity		0.9502
API gravity @ 60 F		17.42
Kinematic viscosity, cSt, @149 F	ASTM D-445	61.58
Hydrogen sulfide, ppm	ASTM D-3327	Nil
Mercapten, ppm	ASTM D-3327	Nil
Residual sulfur, ppm	ASTM D-3327	3793.72
Total sulfur, wt.%	ASTM D-4294	3.09
Asphalten content, wt.%	IP-143	10.6
Wax content, wt.%	UOP-64	2.87
Bs& W, vol.%	ASTM D-96	2
Salt content, ptb	ASTM D-3230	490.8
Water content, vol.%	ASTM D-95	1.55
Pour point, C	ASTM D-97	6
Carbon residue, wt.%	ASTM D-189	12.83
Flash point	ASTM D-93	42
Copper corrosion	IP 154	1a
Ash content, wt.%	ASTM D-482	0.096