Development of Polymeric Aerogel using Plastic Wastes for Oil Cleanup from Wastewater

Junaid Saleem, Usman Bin Shahid, and Gordon McKay

Abstract—**The overall aim of this project is to develop a recyclable polymer aerogel for an effective utilization of plastic waste and to use it for oil clean up from wastewater. The waste utilization from one source (plastic waste) to reduce waste from another source (oil clean up from wastewater) will take the world one step closer to the sustainability.**
A huge proportion of municipal solid waste accumulated all over the globe is composed of plastic wastes and a large volume of it is either incinerated, disposed of into landfill or leaked into the ocean. The plastic leakage into the seawater has created further problems as around 13m tonnes of plastic is ingested by seabirds and fish. In addition, it is estimated that 20,000 plastic bottles are produced per second and less than 10% of them are recycled. With this rate, it is projected that if proper recycling measures are not taken then by 2050 ocean will contain more plastic by weight than fish. In this work, we have provided a sustainable solution to this problem by utilizing the plastic waste to produce a polymeric aerogel which is then used for an efficient oil clean-up from wastewater. To achieve this goal, different grades of plastic wastes have undergone solvent blending using shear mixing and solvent extraction using lyophilization to form polymer aerogel. Unlike traditional methods in which either virgin polymer is used to synthesize aerogels or high carbon number and high boiling point solvent is used to synthesize polymer films, our research has used plastic wastes as a precursor to produce polymeric aerogels in combination with a low carbon number, lower boiling point, and low freezing point solvent. It is anticipated that it will lead to open up a new direction of using plastic waste as a highly efficient oil-sorbent aerogel. As this is an ongoing project, we expect to provide more results before the start of July 2018.

Index Terms— **Plastic wastes, lyophilization, aerogel, and oil sorbent**

I. INTRODUCTION

The main objective in this study is to prepare polymeric aerogel using plastic waste for oil cleanup from waste water. This research leads to the production of polymeric aerogel for oil cleanup from wastewater. The main precursor of this product is the plastic waste of various types including PET, HDPE, PP, and LDPE. This work addresses two sources of environmental pollution. The first one is related to the pollution generated by plastic waste while the second one is about contaminated wastewater containing oil. The overall aim of this research is to develop a recyclable polymer aerogel for an effective utilization of plastic waste and to use it for oil clean up from wastewater.

Plastic waste constitutes around 15% of total municipal solid waste produced all over the globe [1] and a large volume of it is leaked into the ocean. This leakage has created further problems as around 13m tonnes of plastic is ingested by seabirds and fish [2–4]. In addition, it is estimated that 20,000 plastic bottles are produced per second and less than 10% of them are recycled. With this rate, it is projected that by 2050 ocean will contain more plastic by weight than fish, if proper recycling measures are not taken [5]. Another key issue related to plastic wastes is the screening of their different grades. They require greater processing for recycling than metal or glass. In order to be mixed efficiently, they need to be of identical or nearly identical composition. This information discloses that while plastic products are convenient to use, their accompanying environmental issues must be dealt appropriately. Henceforth plastic waste needs to be effectively utilized [6].

Incineration and landfill have so far been the most employed procedure to treat plastic wastes [7,8]. However, landfilling will ultimately be diminished due to the inadequacy of land [9]. Similarly, incineration produces toxic fumes which necessitate further treatment [10]. Pyrolysis of plastic wastes has also been considered and explored [11,12]. However, high energy requirements have limited the extensive utilization of pyrolysis in waste plastics industry [6].

Plastic wastes as Oil Sorbents

Another potential utilization of plastic wastes is to make oil sorbents. Aboul-Gheit et al. [13] used polyethylene (PE) and polypropylene (PP) powders and subjected them with gamma irradiation to prepare oil sorbent. As their key objective was to present oil and water separation efficiency, the oil uptake and retention capacities were not measured. Also, Polyurethane (PU) foams were prepared by means of chemical conversion route using plastic waste but retention values after dripping were not reported [14]. Grafting of polystyrene (PS) on waste polyurethane (PU) foams was also performed with oil uptake values of 20-50 g/g were achieved [15].

In another work, an oil absorbent was produced using grafting technique on polypropylene fibers [16]. The oil uptake capacity of 20g/g was obtained. Further, fibers were produced from polystyrene waste utilizing peeled citrus

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ISBN: 978-988-14049-0-9
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

extract. The resultant fibers possessed high oleophilicity and hydrophobicity [17]. Recently, our research team has produced thin polymer films from HDPE plastic bottles with extremely high oil retention values (90g/g) [1,18].

Virgin polymers for oil sorbent aerogels (including foams and sponges)
One of the most effective strategies to improve oil sorption capacity of polymers is to produce aerogels, foams or sponges as these materials enjoy high surface area, high pore volume, and extremely high porosity. Polymer foam was synthesized [19] for oil remediation with 30g/g oil uptake capacity. Also, polypropylene sponge was synthesized [20] with 700 -2000 % weight gain after oil sorption. Likewise, several sponges and foams were produced for oil spill clean-up including PDMS (poly-dimethyl siloxane) sponge [21], polyurethane [22–25], melamine sponges [22] and polystyrene foams [26].

Our approach and novelty

As presented above, all previous studies either produce aerogels (including foams and sponges to cover broader area) using virgin polymers or produce oil sorbents using plastic wastes. While the utilization of plastic wastes as aerogels for oil sorption has been mainly unexplored, its limitation as oil sorbents is already discussed in section 2.2.1 except the key differences in the previous studies of our team members and the proposed study.

The previously published work by our team members was related to the production of thin films using plastic waste. The procedure adopted in these papers was lengthy, involving many steps including pre-mixing, extrusion, hot-press, initial solvent extraction, sequential bi-axial stretching, and final solvent extraction. It is more time and energy consuming than the proposed methodology. Moreover, the porosity of the films was in the range of 65-70% while the proposed polymer aerogel will be more than 99% porous. Lastly, recyclability of these thin films was also not reported while our proposed methodology will focus on regeneration and recyclability of polymer aerogels. We are targeting to produce more than 99% porous polymer aerogel using simple and repeatable methodology with multiple recyclability. Uptake kinetics is expected to be super-fast, as proven in the previous works of our team members, with oil saturation will be reached within few seconds.

Hence, having presented the above information, we can safely say that as far as authors are aware, utilization of plastic wastes as an efficient and effective oil sorbent aerogels has by and large been relatively unexplored. The major focus has been on their low cost elimination instead of their sustainable recyclability by means of value added products. The proposed project will explore the feasibility of converting plastic wastes into an efficient oil sorbent aerogel.

Some of the key benefits of this product for end user and manufacturer are as follows:

- Low cost sorbent
- High porosity, light weight, and easily portable
- Simple and easily repeatable methodology with minimum chemicals
- Multiple recyclability with near 100% efficiency
- Effective utilization of plastic waste
- Effective oil clean up from wastewater
- High retention capacity after prolonged dripping
- Super-fast uptake kinetics
- Complete Dripping profile

2. PRELIMINARY STUDIES

Based on the existing literature, polymer type and its proportion in plastic waste was identified. Table 1 depicts the classification of plastic wastes [6,9,27]

Table1: Classification of plastic wastes

Polymer	% Plastic Wastes
LDPE/LLDPE	20.6
PP	20
HDPE	17.4
PET	11.7
PS	10.9
PVC	10.9
PU	2.7
Others	9.8

We have shortlisted the following plastics (Table 2) based on a preliminary literature review and initial experimentation:

1) HDPE (High Density Polyethylene)
2) PET (Polyethylene terephthalate)
3) LDPE (Low Density Polyethylene)
4) PP (Polypropylene)

Table 2: Type of Plastic waste selected

S.N	Plastic Waste	Recycling Image
1	PET	
2	HDPE	
3	LDPE	
4	PP	

This list is generated based on an ongoing parallel project for the production of thin polymer films using plastic wastes [1,6,18]. The source of plastic waste was from thermoplastic class of polymers with 'linear chains' as these polymers would undergo swelling when mixed with solvent. Examples of other thermoplastics are polyamide/nylon, polystyrene, poly methyl methacrylate. There is another class of plastics which are called Thermosets. They get permanently deformed on heating and hence are generally considered as non-recyclable. Examples of thermosets are

ISBN: 978-988-14049-0-9
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

urea formaldehyde, polyurethane (it can be thermoplastic as well), melamine formaldehyde, polyester resin ,epoxy resin, phenol-formaldehyde/Bakelite [6].
Secondly, solvent was selected in consideration of lyophilization process and from the literature [28] it was found that Xylene is the ideal choice for this project because of the following attributes:

- It comprises of low carbon chain
- has low freezing point and
- It fully dissolves the plastic waste especially linear chain hydrocarbon

In order to make an effective oil sorbent from plastic waste, some of the essential attributes that need to be considered before the start of the production are presented in Figure 1.

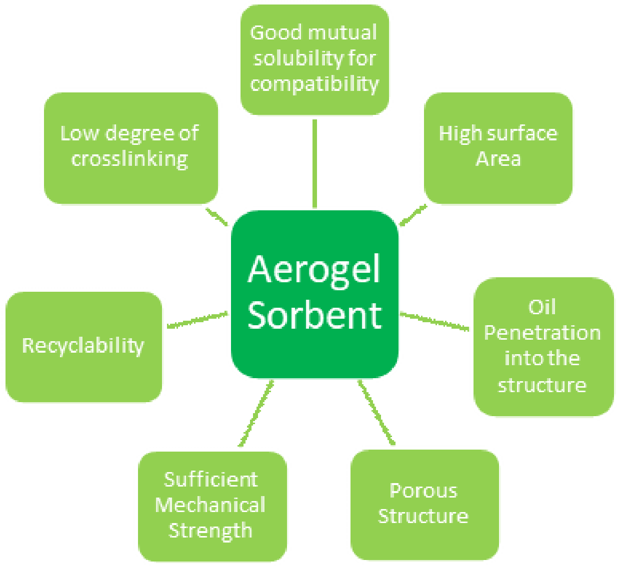

Fig. 1. Essential attributes of polymeric aerogel for oil sorption

In order to determine the melting temperature (Tm), heat of fusion (ΔH) and % crystallinity of different plastic wastes, Differential Scanning Calorimetery (DSC) was performed. Herein, a preliminary study using HDPE plastic bottle is presented as shown in Table 3. In order to fully dissolve the plastic waste into the solvent, the solution should be mixed near or above the melting temperature of polymer.
Our previous study [1,18] on HDPE, which has become the basis of this project, has revealed that plastic wastes can become super oil sorbent by achieving high surface area and by the formation of pores and void spaces. Figure 2 [1] gives the sorption capacity of polymer sorbent film using different oils.

Table 3: DSC results of HDPE waste bottle

Sample	Tm (°C)	ΔH (J/g)	% Crystallinity
HDPE	131	171	59

Oil uptake mechanism can follow a combination of absorption, adsorption, cohesion, and adhesion [1,6]. This combination results in an extremely high values of oil uptake.

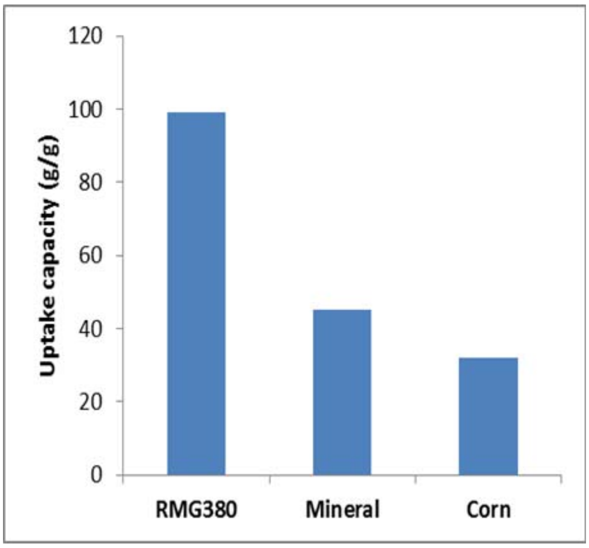

Fig. 2. Oil uptake capacity of polymer film made from HDPE plastic bottles

Methodology:

The following production route has been utilized and will be further exploited to complete the project.
Plastic waste is mixed with Xylene in the presence of antioxidant in a round bottom flask under constant magnetic/mechanical stirring at 130 °C. Isopropyl alcohol is then used for precipitation and the resultant mixture is freeze-dried to obtain aerogel. The amount of plastic waste and solvent are optimized. The trace amount of additive in the form of ultra-high molecular weight polyethylene (UHMWPE) is then added to compare strengths of aerogels with and without additive.

Optimization of Process Variables:
Amount of plastic waste, amount of solvent, mixing conditions, mixing temperature, and freeze drying operating conditions are optimized

Recyclability:
For oil sorption studies, the polymer aerogel is regenerated by placing it into hexane bath followed by washing with acetone and drying in oven. For organic solvent studies, the polymer aerogel is heated above the boiling point of solvent to regenerate polymer aerogel. It is anticipated that the above mentioned recycling techniques will lead to multiple recyclability with almost 100% efficiency [29].

Oil sorption studies are performed by using in-house setup as shown in Figure 3.

As this is an ongoing project, we expect to provide more results before the start of July 2018.

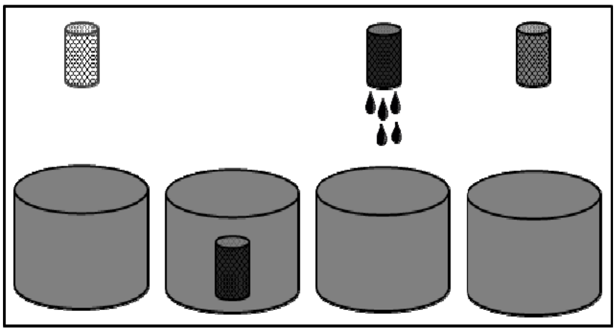

Fig. 3. Process of sorbate uptake using polymer aerogel: (i) Pre-weighed aerogel about to be placed in container, (ii) Aerogel immersed in sorbate, (iii) Loosely attached sorbate molecules are allowed to drain off, and (iv) Equilibrium is reached

ACKNOWLEDGMENT

Authors acknowledge the financial support from Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar.

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