

Modified Silica- Starch hybrids for oil absorption

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Abstract- Mesoporous silica particles were modified using cross linked starch. The hydrophobic character was introduced by further coating with Polydimethylsiloxane (PDMS). Pore structure of prepared hybrid structure is strongly influenced by concentration of added starch and the type of cross linking reagent. A clear correlation is observed between amount of absorbed oil and porosity. The molecular structure of the PDMS-silica –starch hybrid was characterized by FTIR and XRD. The effect of variation in crosslinking agent on textural properties of the hybrid was studied using BET.

Key words - Hydrophobic coating, cross linked starch, silica –starch hybrid, oil absorption.

I. INTRODUCTION

Petroleum refining and petrochemical plants are the major industrial source of oil waste [1]. Oil spills found in water can be detrimental for the marine and aquatic ecosystems. In order to avoid such disasters an immediate measure is essential. Numerous studies have been carried out with novel materials like sawdust [2], aquatic plants [3], carbon [4], PVC [5] etc. for “water oil separation”. Recently developed oleophilic foam systems and CNT [6,7] though shows high absorption efficiency but require expensive materials for their fabrication and involve lengthy preparation procedure. Hydrophobic silica aerogels which are known to be highly porous and have the lowest density and highest surface area have been studied for the sorption of oil spills [8, 9], dispersed oil droplets in water [10]. Reynolds et al. [11] used a hydrophobic aerogel to remove crude oil from a 3% salt water and Prudhoe Bay crude oil mixture. Rao et al. [12] used a super hydrophobic aerogel to absorb oils resulting in a very high uptake capacity of about 20.64 g/g.

Recently, adsorbents containing natural polymers have been studied as an alternative to expensive hydrophobic materials with super oleophilicity. For example, polydimethylsiloxane (PDMS) was cured with sugar particles which were later removed resulting in the formation of highly porous PDMS particles with high absorption capacity for oils [13]. Compared to conventional sorbents like activated carbon; ion exchange resins etc. the sorption using polysaccharide-based materials for removing pollutants from solution, offers several advantages. The polysaccharide-based sorbents are low-cost materials which are obtained from natural resources whereas the ion-exchange resins are derived from petroleum-based raw materials. Sorbents containing polysaccharides possess a high rate of absorption. Since they have repetitive functional groups, their absorption

capacity can be improved by substitution onto the polymer backbone. A crosslinking agent is known to create a network between the polymer chains which induces a steric effect. Modification of starch by cross-linking improves many properties of starch that results in high oil absorption. These natural polymers after cross linking have been used as sorbents for the economic treatment of effluent containing dyes [14]. Polycarboxylic acids such as tartaric acid (TA) could function as nontoxic alternative being of low cost. The aim of this study is to investigate the effect of addition of cross linked starch to mesoporous silica which was later hydrophobically modified using PDMS to study oil absorption properties.

II. EXPERIMENTAL

A. Reagents

Epichlorohydrin was obtained from Sigma Aldrich. 25% ammonia solution (purity 99.5%), Sodium silicate, POCl_3 and tartaric acid were provided by Merck, starch was obtained from Himedia. Vegetable oil was purchased from local market. All chemicals, reagents used were of analytical grade.

B. Synthesis of crosslinked starch

For the synthesis of cross-linked starch, a modified procedure as given by Simkovic et al. [15,16] was followed where $\text{Ca}(\text{OH})_2$ was chosen as a base instead of NH_4OH and sonication step was introduced before and after addition of epichlorohydrin. About 20 ml of $\text{Ca}(\text{OH})_2$ (50% w/w) was heated to 50°C and later 5 g of starch was added under vigorous stirring in order to avoid lump formation. This mixture was subjected to sonication at 40°C for 3 hours. To the same solution, a desired amount of epichlorohydrin and $\text{Ca}(\text{OH})_2$ were added drop wise under stirring. This mixture was once again subjected to sonication at 40°C for 30 min. After sonication, the viscosity of the mixture increased slowly leading to a solid

polymer. Three different crosslinking agents have been used for the synthesis of cross linked starch.

C. Synthesis of mesoporous silica

For the preparation of mesoporous silica, required amount of sodium silicate was mixed with 70 ml of ethyl alcohol and 2 ml of 0.01N hydrochloric acid solution was added to the reaction mixture (A). The resulting solution was agitated for 30 min. The required amount of cross linked starch (0.25g-1g) was slowly dropped into solution A and then homogenized for 5 min. The solution thus obtained was heated for 1 h at 80°C in a round bottom flask. After attaining a highly viscous solution the heating was continued for another hour to get fine particles on cooling. In order to study the correlation between volume of absorbed oil and silica concentration, silica-starch hybrids with different concentrations of silica (0.5- 2.0 mol/l) were prepared.

For generating hydrophobicity in the synthesized mesoporous silica particles, a further coating with a hydrophobic layer is required. PDMS solution (10 wt. %) was prepared by mixing PDMS with toluene (90 ml) under stirring to get a homogenous clear solution (solution B). The starch-silica particles were dispersed in 5 ml toluene (solution C). The final solution of PDMS-silica was obtained after mixing B into C. The coated silica particles were dried at room temperature and heated at 100°C for 24 hrs. The same procedure was adopted to prepare silica-starch hybrids with different silica concentrations (0.5- 2.0 mol/l) so as to study correlation between volume of absorbed oil and silica concentration.

D. Oil absorption capacity (OAC) and Water absorption capacity (WAC)

The oil-absorption capacity of the samples is given by a simple ratio ($OAC = m_{max}/m_s$), where the numerator m_{max} is the maximum absorbed oil and m_s stands for mass of cross-linked starch. In order to find OAC, vegetable oil drops were slowly added to cross linked starch placed in a watch glass until the excess oil droplets drips down without getting absorbed.

Water absorption capacity of porous starch was measured by the centrifugation method as described by Abbey and Ibeh [17]. About ten ml of water was added to 1 g of the starch sample in a pre-weighed centrifuge tube. The mixture was allowed to stand for about 30 min and later centrifuged. The supernatant was discarded. The tube along with the residue was weighed and the gain in weight was taken as the water absorption capacity. The starch slurry with starch from different origin was hydrolyzed with and without ultrasound and a quantitative data on water and oil absorption was calculated. To increase the hydrophobic character the porous starch granules, the synthesized cross linked starch was mixed with silica.

E. Material Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K α radiation of 0.15406 nm wavelength. The nitrogen sorption experiments were performed at -196°C on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were out-gassed at 120°C for 6 h. Scanning electron microscopy (SEM) was performed using Jeol, JSM 5600 microscope operated at 15 kV. Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer.

III. RESULT AND DISCUSSION

A. FTIR

Fig 1a shows IR spectrum of silica without cross linked starch. The peak observed at 466 cm^{-1} is due to symmetric oxygen stretching vibrations of surface silanol sites, and a sharp peak at 802 cm^{-1} is due to symmetric Si-O-Si stretching vibrations. The peak at 1093 cm^{-1} can be assigned to asymmetric stretching modes, while an Si-O bending vibration is seen at 478 cm^{-1} [18]. Si-O-H stretching can be seen at 3417 cm^{-1} . Fig 1b shows the spectra of PDMS-silica-starch hybrid that shows additional peaks at 1109 and 1174 cm^{-1} suggesting that additional C=O and C-C bonds were introduced after adding cross linked starch. A significant reduction in the intensity of symmetric Si-O-Si is also seen after crosslinking. The characteristic absorption bands of -CH₃ for PDMS at 2982 and 780 cm^{-1} were observed in the FTIR spectra of the PDMS-silica particles. After the PDMS coating, two additional peaks at 3000 and 2900 cm^{-1} appeared which could be attributed to the C-H stretching vibrations of PDMS. The Si-C stretching and CH₃ rocking bands appeared at 750-900 cm^{-1} . The results show that in PDMS-silica-starch hybrid, the molecular framework of PDMS was preserved even after heating.

B. XRD

The XRD data in Fig 2 illustrates the amorphous nature of synthesized silica particles and a similar pattern was found for all samples. The peak at $2\theta = 24^\circ$ indicates mesoporous structure. The XRD patterns of silica with and without cross linked starch are almost similar indicating surface immobilization with unchanged internal molecular arrangement. The amorphous silica particles consist of aggregates having an approximate size of 10 μm as confirmed from SEM.

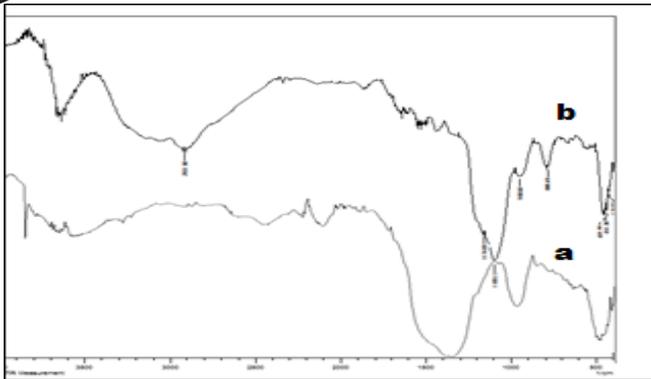


FIG 1 IR SPECTRUM OF (A) SILICA WITHOUT CROSS LINKED STARCH, (B) PDMS- SILICA-STARCH HYBRID

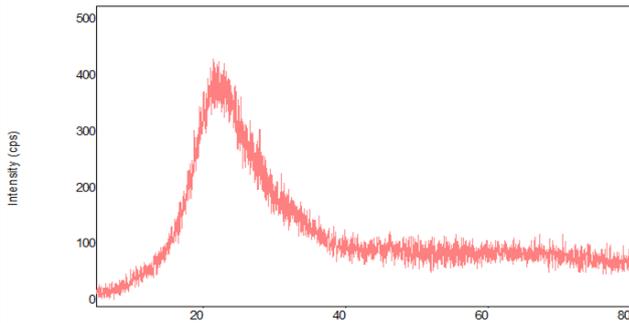


FIGURE 2. XRD OF AS-SYNTHESIZED SILICA POWDER

C. SEM

SEM micrograph in Fig 3(a) shows an aggregate structure of silica prepared as such without adding starch. The addition of cross linked starch and PDMS treatment results into porous silica structure as evident from Fig 3b. It can be concluded that starch incorporation did not affect the texture of the hybrid much except its porous matrix as it shows more porosity and inter granular voids. Small pores within the particles appearing as dark regions can be clearly distinguished in SEM micrographs (Fig. 3b).

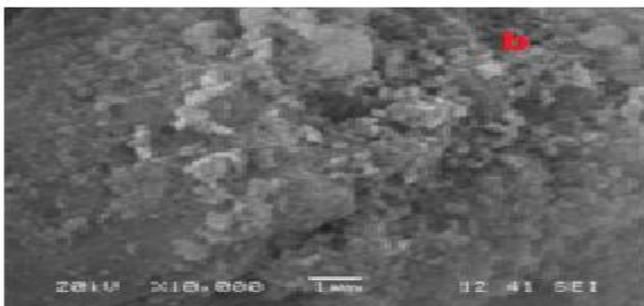
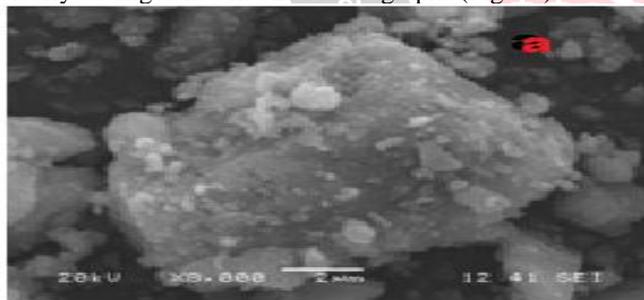


FIG 3 SEM OF SILICA (A) BEFORE ADDING STARCH (B) AFTER ADDING STARCH AND PDMS

D. Surface Area

The porosity of the synthesized silica hybrid before and after modification was investigated by nitrogen sorption analysis. The N₂ sorption isotherms and pore size distribution shows type IV isotherm pattern, characteristic of mesoporous silica. Addition of starch and PDMS caused a remarkable increase in surface area and pore volume. The BET specific surface area as seen from Table 1 shows a consistent increase from 120.3 to 337 m²g⁻¹ while pore volume increased from 0.126 to 0.558 cm³g⁻¹ after adding starch. The increased surface area can be attributed to an increased density of pores leading to higher pore volume in the silica matrix. The same trend was seen for all type of starch samples, particularly for rice starch.

TABLE I
 TEXTURAL CHARACTERISTICS OF PDMS-SILICA-STARCH HYBRID

Starch source	Silica before adding starch			Silica after adding starch and PDMS		
	Pore diameter (nm)	BET Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	BET Surface area (m ² /g)	Pore volume (cm ³ /g)
potato	5.85	122.8	0.115	4.98	213.6	0.264
corn	7.42	119.1	0.134	4.37	228.1	0.321
rice	5.14	120.3	0.126	2.32	337	0.558

E. Oil absorption Capacity(OAC)

Table 2-4 summarizes the data for oil absorption capacity of cross linked starch with and without sonication.

TABLE 2. FUNCTIONAL CHARACTERISTICS OF STARCH WITH AND WITHOUT CROSSLINKING USING EPICHLOROHYDRIN

Starch source	Water absorption capacity (ml/100g)		oil absorption capacity (ml/100g)	
	Without crosslinking	After crosslinking	Without crosslinking	After crosslinking
potato	71.46±2.34	82.39±3.11	76.41±3.04	87.39±3.24
corn	76.25±3.31	84.54±3.32	78.53±3.23	86.60±2.39
rice	78.13±3.04	87.16±2.73	73.81±2.11	87.48±2.20

TABLE 3. FUNCTIONAL CHARACTERISTICS OF STARCH WITH AND WITHOUT CROSSLINKING USING POCL₃

Starch source	Water absorption capacity (ml/100g)		oil absorption capacity (ml/100g)	
	Without crosslinking	After crosslinking	Without crosslinking	After crosslinking
potato	72.23±2.04	83.16±3.23	77.87±3.62	89.16±3.12
corn	77.39±3.42	85.16±3.17	78.89±3.13	87.05±2.27
rice	78.87±3.13	88.30±2.29	74.14±2.09	87.92±2.69

TABLE 4. FUNCTIONAL CHARACTERISTICS OF STARCH WITH AND WITHOUT CROSSLINKING USING TARTARIC ACID

Starch source	Water absorption capacity (ml/100g)		oil absorption capacity (ml/100g)	
	Without crosslinking	After crosslinking	Without crosslinking	After crosslinking
potato	73.24±2.82	84.11±3.36	78.32±3.81	90.16±3.17
corn	77.88±3.17	86.09±3.14	79.01±3.13	87.86±2.44
rice	79.43±3.54	88.85±2.21	74.87±2.35	88.07±2.25

The oil absorption capacity was found to be maximum in samples that were subjected to sonication. It was observed that the viscosity of starch under sonication showed a significant improvement probably due to generation of partial cross linking during starch degradation [19]. Since, the absorbing capacity is affected by the degree of hydrolysis, more the hydrolysis, more C-C bonds of starch granules will be destroyed leading to more specific surface area and finally better absorption. Hence sonication is an important factor in increasing absorbing capacity. The OAC of samples after sonication ranged between 86.60±2.39 and 90.16±3.17ml/100g for all type of starch samples with different cross linking agents. The effect of change in concentration of starch on oil absorption capacity of PDMS-silica-starch hybrid was studied by varying the starch content from (0.25-1.0 g).

Fig 4-6 summarizes the data for oil absorption capacity of PDMS-silica-starch hybrid for different types of starch samples. The maximum oil absorption capacity was found to be 96.2± 1.2 in samples containing 1g rice starch. The increased surface area found in rice starch is evidently playing a role here. The increased density of pores which results in higher pore volume in the silica matrix provides highest oleophilicity when rice starch was used. During the sorption process, the oil fills the inter-particle voids occupied by air initially and then penetrates further into the pores of hybrid structure. A similar trend was seen on varying silica content from 0.5- 2.0 mol/l as seen in Fig 7. A continuous rise in OAC of rice starch confirms the

presence of a highly porous structure. However, the potato starch showed a reversal effect at higher silica content.

F. Water Absorption Capacity (WAC)

Table 2-4 summarizes the data for water absorption capacity of cross linked starch with and without sonication. The WAC was maximum in rice starch samples cross linked using tartaric acid after sonication. The WAC of samples after sonication ranged between 82.39±3.11 and 88.85±2.21ml/100g for all type of starch samples with different crosslinking agents. All data are Mean ±SD of three replicas.

Fig 4-6 shows a drastic decrease in WAC from 79.43 to 2.1 ml/100g of PDMS-silica-starch hybrid. A uniform PDMS coating is responsible for this remarkable reduction in water absorption capacity. The highest reduction in WAC was seen in hybrids containing 1g rice starch. During the absorption process, not only the pores, but also the inter-particle air spaces get filled with oil and therefore repel water. Hence PDMS-silica-starch hybrid may serve as an excellent oil absorber and can be used for oil spill clean-up.

IV. CONCLUSION

Starch from different sources differed significantly in oil absorbing property. Rice starch showed a maximum OAC of 90.16±3.17 ml/100g. Cross linked polysaccharides like starch can act as an effective oil absorber when mixed with mesoporous silica matrix followed by PDMS coating. Thus by incorporating a natural polymer in an inorganic material, hybrid structures of increased oil absorption capacity could be achieved. The oleophilic nature was found to increase significantly in rice starch cross linked by tartaric acid because of its highest surface area and pore volume. These cross linked structures can be used as sorbents in hybrid form for the economic treatment of effluent containing oil. This work can be further extended to study absorption and treatment of other pollutants in aqueous medium.

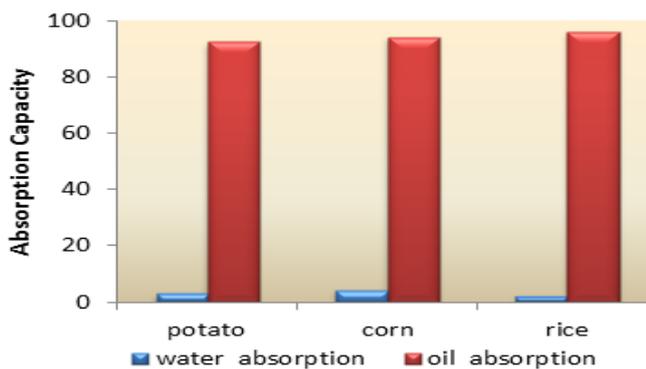


FIG 4 OAC/WAC OF PDMS-SILICA-STARCH WITH

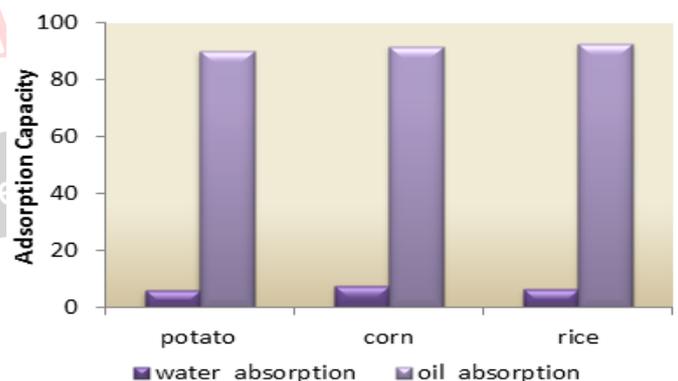


FIG 5 OAC/WAC OF PDMS-SILICA-STARCH WITH POCL3 TARTARIC ACID

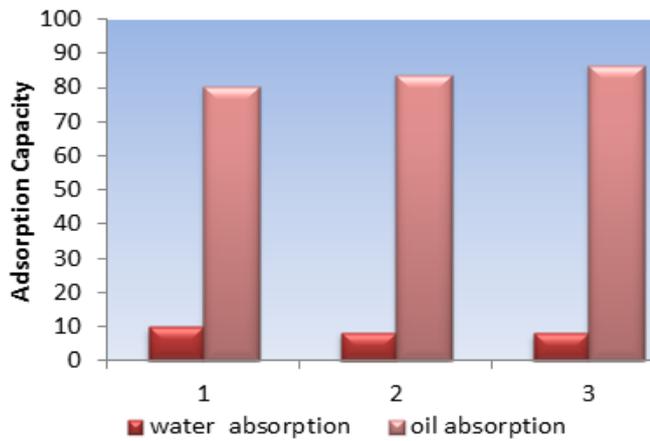


FIG 6 OAC/WAC OF PDMS-SILICA-STARCH WITH EPICHLOROHYDRIN

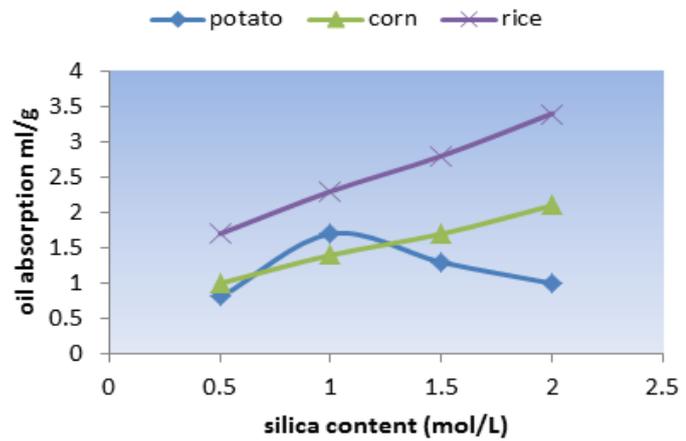


FIG 7 VARIATION IN OAC OF PDMS-SILICA-STARCH WITH SILICA CONTENT

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