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Modified polymethyl methacrylate as a sustainable medium for capturing carbon dioxide

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ABSTRACT

This study evaluates the potential of modified polymethyl methacrylate (PMMA) materials, which incorporate organotin moieties pendant on the polymeric chains, as media for carbon dioxide storage. The PMMA containing a triphenyltin moiety has the largest specific surface area ($S_{\text{BET}}=11.618 \text{ m}^2/\text{g}$) in comparison to the polymers containing tributyl (5.287 m^2/g) and trimethyl (4.881 m^2/g) residues. The PMMA with the triphenyltin moiety proved to be the most efficient material in capturing carbon dioxide (34.8 cm^3/cm^3 , 6.8 wt%), which is attributed to its relatively high surface area and pore volume and diameter compared to the others.

1. Introduction

Carbon dioxide (CO_2) is a major threat to the environment. It traps heat in the atmosphere, causing global warming. Global temperatures have been continuously rising since the mid-20th century [1]. Rising temperatures can have severe consequences, such as melting polar ice caps, causing floods and droughts. Fossil fuels have contributed significantly to human development but have also caused a rise in CO_2 emissions, leading to atmospheric warming and increased ocean acidity with the potential for ecological damage [2].

Reducing CO_2 levels in the atmosphere is a primary challenge. One effective way is to use renewable energy sources like nuclear, biomass, wind, and solar power. However, the scale of these sources needed to meet global demand is extensive, and cost-wise, they need to compete with fossil fuels [3,4]. A new method to reduce CO_2 levels involves storing it in specially designed materials [5]. Solid gas storage is gaining attention due to its potential in various applications, including handling gas supply fluctuations. It provides a reliable solution by injecting gas into a storage material during low demand and releasing it when demand increases [6].

High concentrations of CO_2 can be mitigated through capture and storage techniques [7]. Compared to alternative methods, this approach can cost-effectively and efficiently reduce CO_2 emissions, ultimately helping combat climate change. Therefore, building on our research on

the use of different materials as storage media for gases [8–10], we were interested in the application of PMMA for gas storage. The current study introduced a chemically modified polymethyl methacrylate containing a triphenyltin moiety as an efficient material for capturing CO_2 . Indeed, modified PMMA can efficiently capture CO_2 under mild conditions [11].

2. Experimental methods

The Brunauer-Emmett-Teller (BET) method has been utilized to determine the specific surface area (S_{BET}) of the solids. The nitrogen (N_2) adsorption and desorption isotherms were determined using a Quantachrome analyzer. The samples were dried under dry N_2 at 200°C for 5 h before the measurements [10]. The pore size distribution has been established using the Barrett-Joyner-Halland (BJH) theory. The pore volumes were calculated at a relative pressure (P/P°) of 0.98. The CO_2 uptake was carried out on an H-sorb 2600 high-pressure volumetric adsorption analyzer (40 bars, 323 K). Nitrogen gas adsorption and desorption of PMMA 1–3 were carried out on a surface area measurement device at 77 K and 40 bar. A Tescan Mira3 LMU system at an accelerating voltage of 25 kV was used to capture the scanning electron microscopy (SEM) images. A Veeco instrument was used to record the atomic force microscopy (AFM) images.

The modified PMMA materials 1–3 (Fig. 1a) were synthesized as previously reported [12]. They were dried under nitrogen flow in a

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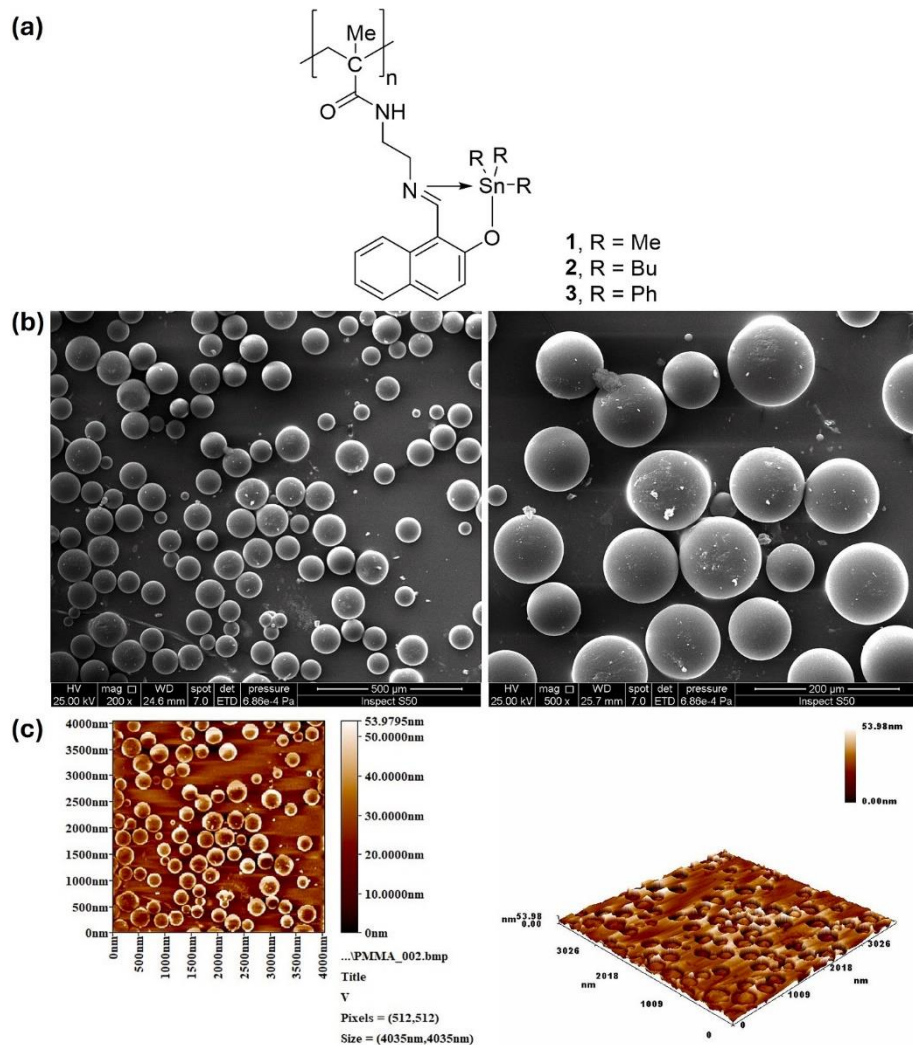


Fig. 1. (a) Structures of modified PMMA 1–3, (b) SEM images of 3, and (c) AFM images of 3.

vacuum oven (70 °C, 6 h).

3. Result and discussion

The FTIR spectra of modified PMMA 1–3 confirmed the presence of NH moiety that appeared at the region of 3327–3334 cm^{-1} as broad bands. The C=O and the CH=N groups appeared as strong absorption bands at 1728–1729 cm^{-1} and 1611–1617 cm^{-1} regions, respectively. In addition, the Sn–N and Sn–O moieties appeared at 503–505 cm^{-1} and 439–446 cm^{-1} region, respectively [12].

The SEM images proved that the surfaces of the modified PMMA 1–3 were uneven and had pores that varied in shape and size. Fig. 1b shows the SEM images of 3. AFM is a highly advanced tool used to provide accurate details of porosity and roughness within the surfaces of materials. It allows for a complete understanding of the lattice structure and evaluates the three-dimensional geometric characteristics of individual particles. Rough surfaces are ideal for gas adsorption compared to smooth ones. The AFM images of PMMA 1–3 showed uneven surfaces in both 2-D and 3-D. Fig. 1c shows the AFM images of 3, which had a macro pore size. The roughness factors for PMMA 1, 2, and 3 were 125, 164, and 242 nm, respectively. Due to its highest rough surface, PMMA 3 was expected to be more efficient in capturing CO_2 than the other two PMMAs.

The pore size distribution of PMMA 1–3 was determined using the BJH method, and the S_{BET} was calculated using the BET method. The

Table 1

Surface area (S_{BET}) and pores volume and diameter of PMMA 1–3.

PMMA material	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (nm)
1	4.881	0.042	31.651
2	5.287	0.067	33.153
3	11.618	0.096	54.971

properties of PMMA 1–3 are shown in Table 1. The average pore diameter for PMMA 1 and 2 lies between 2 and 50 nm, which corresponds to mesopore size in general [13]. On the other hand, PMMA 3 has an average pore diameter (55 nm) corresponding to macropore size, indicating that its surface is rougher compared to the other two. It is believed that the aromatic moiety within 3 plays a role in increasing the surface area of PMMA compared with the aliphatic substituents in 1 and 2. In general, higher S_{BET} would be associated with smaller pore size, but it can be influenced by different factors such as pore shape.

The efficiency of modified PMMA 1–3 toward CO_2 storage capacities was assessed on the high-pressure volumetric device at 323 K and 40 bar. The existence of volatiles and solvents in a sample occludes most of the voids in the porous structure. Therefore, the volatiles were removed before the CO_2 storage capacity of PMMA was determined. The results showed that PMMA material 3 (34.8 cm^3/g) had a better storage capacity than 2 (25.9 cm^3/g) and 1 (22.8 cm^3/g) under the same

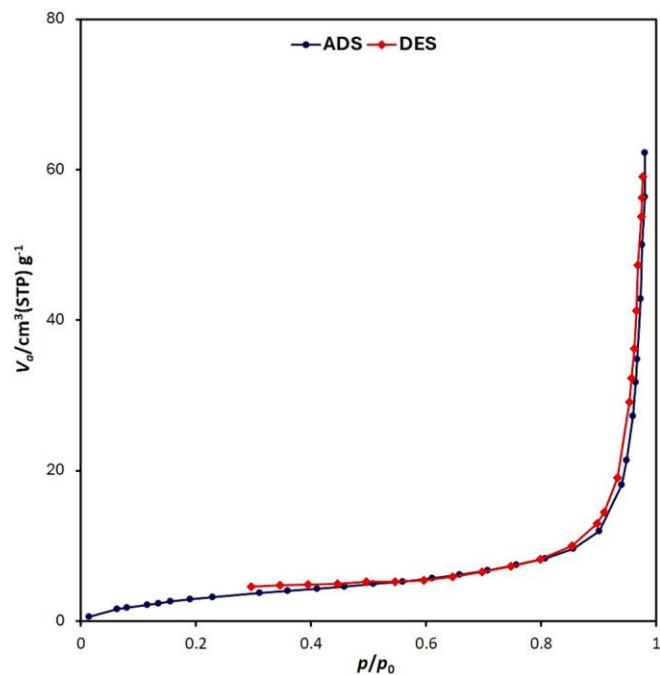


Fig. 2. The N₂ adsorption (ADS) and desorption (DES) isotherms for 3.

Table 2				
Modified PMMA 1-3	CO ₂ uptake capacity over various adsorbents. (wt%)	T (K), P (bar)	Ref	
Modified PMMA 1-3	6.8	323, 40	Current	
Carvedilol-metal complexes	2.1-3.5	323, 40	8	
Fusidate-metal complexes	6.3-7.2	323, 50	9	
Valsartan-metal complexes	4.8-6.8	323, 40	10	

conditions. The observation is consistent with PMMA 3 having a larger BET surface area. It also has a larger pore volume and diameter compared with 1 and 2. The three PMMA showed a CO₂ storage capacity of 6.8 wt%. Fig. 2 shows the N₂ adsorption and desorption isotherms for 3.

PMMA 3 showed the highest capacity for storing CO₂, possibly because of its large pore sizes as well as its rough surface, resulting in the highest S_{BET}. The amount of gas adsorbed is dependent on the porosity properties of PMMA. Additionally, the charges of the tin and the heteroatoms of the organic moieties play a role in the capture of CO₂. For example, the attractive interactions (e.g., van der Waals or electrostatic forces) and electrostatic forces (e.g., surface field-molecular dipole interactions and polarization force) between the organotin moiety and CO₂ could contribute to the higher gas uptake [9]. Clearly, the three modified PMMA showed a CO₂ capture efficiency that is comparable to those reported for organometallic complexes under similar conditions (Table 2) [8-10].

4. Conclusions

Polymethyl methacrylate materials containing trisubstituted tin moieties on the polymeric chains act as improved storage media for carbon dioxide. The polymeric material comprising a highly aromatic triphenyltin moiety has the largest specific area, pore volume, and diameter. The material is more effective in capturing carbon dioxide (34.8 cm³/cm³; 6.8 wt%) than those containing tributyl and trimethyl

residues.

CRedit authorship contribution statement

Hanan A. Ibraheem: Writing – original draft, Investigation, Data curation. **Gamal A. El-Hiti:** Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis, Data curation. **Emad Yousif:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Dina S. Ahmed:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Benson M. Kariuki:** Writing – review & editing, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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