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Effect of amine types and temperature of a natural rubber based composite material on the carbon dioxide capture kinetics

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ABSTRACT

Solid natural rubber (NR) was chosen to prepare a carbon dioxide (CO_2) adsorbent material in order to solve the disadvantage of using NR latex as the adsorbent. Modified silica particles were filled in the NR foam composite material to improve the CO_2 adsorption capacity. The effect of modifier type on the CO_2 adsorption capacity of the NR/silica foam composites was investigated under ambient temperature and pressure. The CO_2 adsorption capacity of the NR/silica foam composite material increased from 1.81 to 6.71 mg/g after filling with silica particles modified by 3-aminopropyltrimethoxysilane. The NR/silica foam composite material filled with silica particles modified with a short chain structure (3-aminopropyltrimethoxysilane) showed a higher CO_2 adsorption capacity than those with a longer modifying chain structure (N-[(3-trimethoxysilyl)propyl]ethylenediamine or N-[(3-trimethoxysilyl)propyl]-diethylenetriamine), due to its low steric hindrance in chemical structure and low heat of reaction. However, increasing the adsorption temperature caused the chains of the long-chain modifier on the silica particle surface to become more flexible, reducing the steric hindrance and resulting in a high selectivity for capturing CO_2 and an increased CO_2 adsorption capacity. The kinetic adsorption of CO_2 on the NR/silica foam composite materials fitted with Avrami's model, suggesting CO_2 adsorption may involve both physisorption and chemisorption. The NR/silica foam composite filled with unmodified or modified silica particles showed a high reusability (more than 10 cycles) compared to NR foam (seven cycles), because the unmodified or modified silica particles improved the thermal properties of the NR foam composite.

Key words: Natural rubber foam; CO_2 adsorption; Physical adsorption; Chemical adsorption

1. Introduction

At present, the carbon dioxide (CO_2) concentration in urban areas tends to be higher than in rural areas, and in particular the CO_2 concentration in indoor air is typically about 650–700 ppm [1, 2]. The American Society of Heating, Refrigerating and Air conditioning Engineers (ASHRAE) reported that a CO_2 concentration lower than ~700 ppm is required for the comfort of occupants inside a building [2, 3], while a CO_2 concentration of 2,000–5,000 ppm adversely affects human health [2, 4, 5]. Accordingly, it is important to solve the problem of high CO_2 levels and develop materials for capturing CO_2 in the atmosphere. The adsorption of gas on a solid media is a well-known process, and the most widely used sorbents are activated carbon [6,7], silica [8,9], graphite/graphene [10,11] and a variety of synthetic zeolite molecular sieves, such as 13X and 5A [12-14]. These kinds of adsorbents can be operated via a physisorption or chemisorption processes that have unique advantages and disadvantages. Physisorbents have a low regeneration energy but their selectivity for CO_2 is too low. Although chemisorbents can adsorb CO_2 very quickly with a high selectivity for CO_2, they consume a high amount of energy for their regeneration [15,16]. Based on these scenarios, it is important to find a suitable material to remove CO_2 from the atmosphere, with the additional challenge that this adsorbent material should be hygienic and regenerative for operation in a real system.

In a previous study, a natural rubber (NR) latex foam composite material was developed as a CO_2 adsorbent [17]. It was observed that NR could adsorb CO_2 under an ambient temperature and pressure and the CO_2 adsorption capacity of the NR latex foam could be increased by the addition of modified silica particles. However, the difficulty of using NR

latex was that it is sensitive to chemical substances [18], resulting in its easy coagulation. Accordingly, solid NR is an alternative choice to solve this problem because it can be easily mixed, stored and transported, making it convenient for the manufacturing of rubber products.

In the present study, solid NR was used to prepare NR foam as a CO_2 adsorbent. To our knowledge, this kind of adsorbent material has not been investigated before. The effect of different amine types (mono-, di- and tri-amine) to modify the silica particles was investigated in terms of the efficiency of CO_2 adsorption by the NR foam and NR/silica foam composite adsorbent materials. Three kinds of modifiers that differed in chain length were used, namely: 3-aminopropyl-trimethoxysilane (NM), N-[(3-trimethoxysilyl)propyl]ethylenediamine (2NM), and N-[(3-trimethoxysilyl)propyl]-diethylenetriamine (3NM), respectively. The modified silica particles were then characterized by solid state ^{13}C- and ^{29}Si-NMR spectroscopy. The morphology of the modified silica particles and NR/silica foam composites was evaluated by scanning electron microscopy (SEM). The relationship between the modified silica particles and the CO_2 adsorption capacity of NR/silica foam composites was investigated under ambient temperature and pressure in a stainless reactor. In addition, the effect of temperature on the CO_2 adsorption capacity and kinetic adsorption of sorbent materials were also estimated and a discussion about the difference between NR latex and solid NR on the CO_2 adsorption is presented. Finally, the reusability of the NR/silica foam composites was studied via the combination of vacuum and temperature swings to reduce the required energy for regeneration.

2. Material and methods

2.1 Materials

The NR (STR 5L) and curing reagents for rubber compounding, such as zinc oxide (ZnO), n-cyclohexyl-2-benzothiazole sulfenamide (CBS), stearic acid and sulfur, were supplied from PI industry, Thailand. *N,N'*-Dinitrosopentamethylenetetramine ($C_5H_{10}N_6O_2$) as a blowing agent was purchased from Shaanxi Pioneer Biotech Co., Ltd., China. Tetraethoxysilane (TEOS), NM, 2NM, and 3NM were rom Sigma-Aldrich (USA). Ammonia solution (28 wt.%) and absolute ethanol (EtOH) were purchased from Qrec Chemical Ltd, (Thailand). All chemicals were used as received without any purification.

2.2 Preparation of modified silica particles

The modified silica particles were prepared via the sol-gel process by mixing 3 mL TEOS, 40 mL EtOH, 1 mL ammonia solution, 7 mL deionized water and the respective modifier (1NM, 2NM or 3NM) at a TEOS: modifier molar ratio of 0.3. The reaction was continuously stirred for 24 h and then the colloidal silica particles were separated by centrifugation at 5000 rpm for 20 min, washed with deionized water and dried at 110 °C in an oven until the weight was constant [19].

2.3 Preparation of the NR/silica foam composites

Table 1 shows the formulation for rubber compounding using a two-roll mill at ambient temperature. The rubber compounding was precured by compressing at 100 °C for 9 min and then the rubber sheet was cured and foamed in an air-circulated oven at 140 °C for 20 min.

Table 1

Formulation of the different rubber compounds.

Ingredient (phr[a])	NR	NR-USi	NR-NSi	NR-2NSi	NR-3NSi
NR	100	100	100	100	100
ZnO	4	4	4	4	4
Stearic acid	2	2	2	2	2
CBS	1	1	1	1	1
$C_5H_{10}N_6O_2$	2	2	2	2	2
Sulfur	3	3	3	3	3
USi[b]	-	10	-	-	-
NSi[c]	-	-	10	-	-
2NSi[d]	-	-	-	10	-
3NSi[e]	-	-	-	-	10

[a]Part by weight per hundred part of rubber, [b]Unmodified silica particles, [c-e]silica particles modified with [c]NM, [d]2NM, and [e]3NM.

2.4 Characterization

The chemical structure of the modified silica particles was investigated by solid state ^{13}C- and ^{29}Si-NMR spectroscopy (Bruker AVANCE III HD, Ascend 400 WB, Germany), operating at Larmor frequencies of 100.62 and 79.51 MHz, respectively.

The morphology of the NR/silica foam composites and modified silica particles inside the rubbery matrix were examined by SEM (JEOL, JSM-6480LV, Japan) operating at 15 kV.

The thermal stability of each NR foam composite was observed by thermogravimetric analysis using a TGA/DTA Perkin-Elmer Pyris Diamond, USA operating at a temperature from 40 up to 800 °C.

The specific surface area of modified silica particles and NR/silica foam composites were calculated using the conventional Brunauer-Emmett-Teller (BET) analysis of nitrogen (N_2) adsorption-desorption, using an Autosorb-1 Quantachrome, Germany.

2.5 CO$_2$ adsorption measurement

The CO_2 adsorption of each NR/silica foam composite was evaluated in a stainless reactor under ambient temperature and pressure. First, the sample was treated at 60 °C under vacuum for 20 min to remove the adsorbed gas in the sample. Then, the sample was cooled down under a N_2 flow to ambient temperature and the mixed gas, 12: 88 (v/v) CO_2: N_2, was flowed in the reactor at 100 mL/min. The sensor detected the CO_2 concentration and the temperature of the gas at the outlet of reactor. The CO_2 adsorption capacity was calculated from the difference in the CO_2 adsorption capacity of the sample and blank based on Eq. (1) [20];

$$q = \frac{1}{M}[\int_0^t Q(co - c)dt]\frac{P}{RT},\qquad(1)$$

where q is the adsorption capacity of CO_2 (mmol/g), M is the mass of adsorbent (g), Q is the gas flow rate (mL/min), c_0 and c are inlet and outlet CO_2 concentration (%vol), respectively, t is the denoted time (min), P is the gas pressure (atm), R is the gas constant (82.0573 $cm^3atmK^{-1}mol^{-1}$) and T is the gas temperature (K).

Raman spectroscopy (DXR Raman microscope, Thermo Scientific, USA) was used to confirm the CO_2 adsorption in the adsorbent. A 780 nm laser was used as the light source

and the spot size was about 3 μm diameter. Raman spectra were recorded from 100–4000 cm^{-1}.

2.6 Regeneration process

The stability of each NR/silica foam composite was studied through the combination of vacuum and temperature swing with N_2 flow process. After absorbing the CO_2, NR/silica foam composite was desorbed of CO_2 by increasing the temperature up to 60 °C followed by decreasing the pressure under a N_2 flow (100 mL/min) for 20 min. After that, the sample was then cooled down and the pressure increased to ambient temperature and pressure. The CO_2 adsorption-desorption was repeated up to 20 cycles.

3. Results and discussion

3.1 Characterization of the modified silica particles

The ^{29}Si-NMR spectra of modified silica particles are shown in Fig. 1(a). The unmodified silica particles (USi) exhibited signals at a chemical shift of -92, -101, and -111 ppm, which were related to the $SiO_2(OH)_2$ (Q^2 sites), $SiO_3(OH)$ (Q^3 sites), and SiO_4 (Q^4 sites), respectively, [21]. The spectra of the modified silica particles (NSi, 2NSi and 3NSi) showed the presence of $C-Si(OSi)_2OH$ (T^3 sites) in the range of -52 to -74 ppm. In addition, the range of the Q^3 and Q^4 sites were both shifted to lower chemical shifts due to the interaction between the silanol groups of the silica particles and the modifier on the silica particle's surface [22].
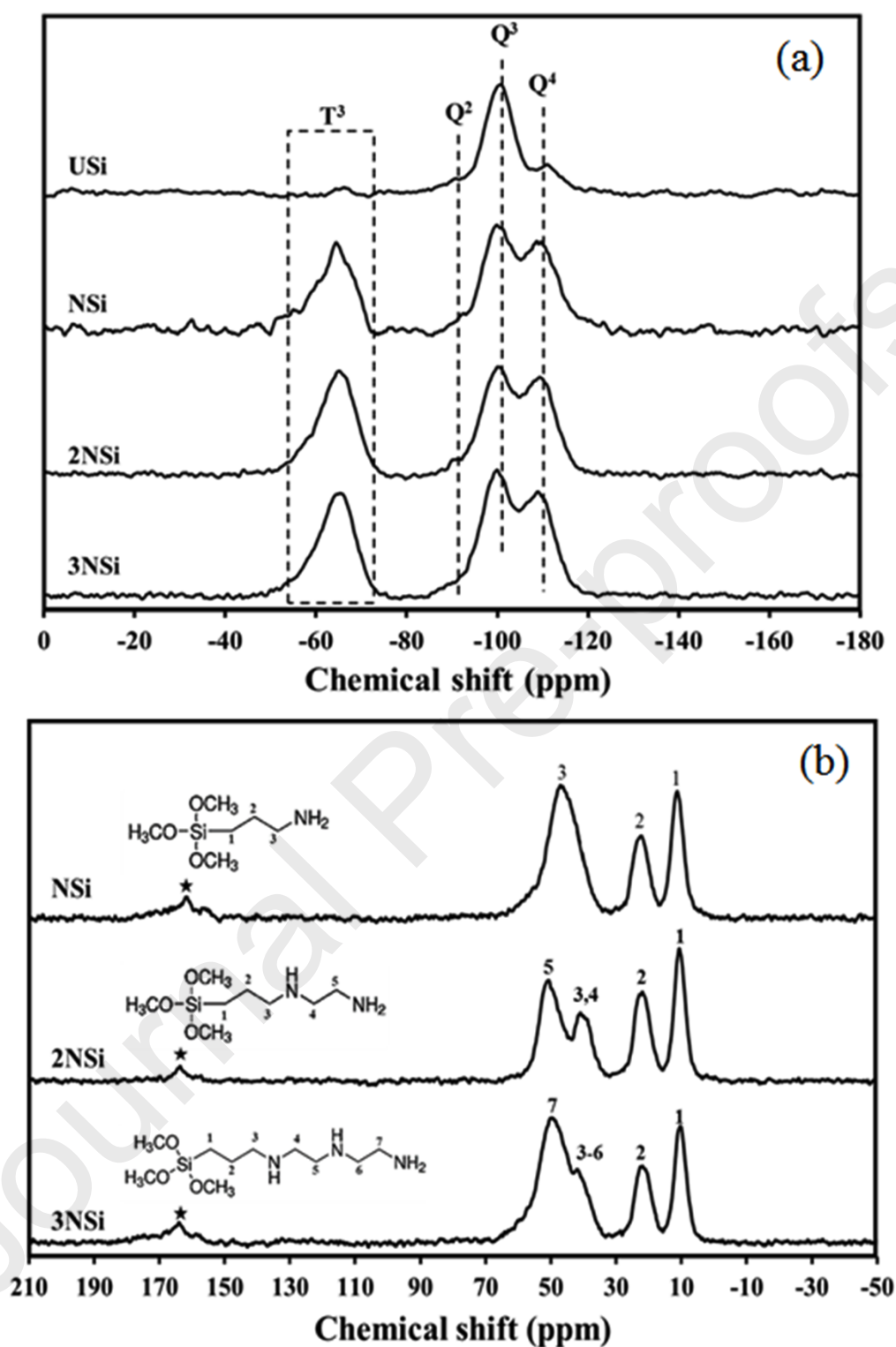
Fig. 1 (a) Representative ^{29}Si-NMR spectra of the unmodified silica (USi) and the different modified silica particles and (b) Representative ^{13}C-NMR spectra of different modified silica particles.

The ^{13}C-NMR spectra of the modified silica particles are shown in Fig. 1(b). The NSi presented signals at a chemical shift of 11 ppm, 24 ppm, and 49 ppm corresponding to the C1, C2, and C3 of the methyl group in the NM chain [23]. The 2NSi showed the signals at a chemical shift of 10 ppm, 22 ppm, 41 ppm, and 51 ppm related to the C1, C2, C3-C4, and C5 of the methyl group in the 2NM chain, while 3NSi showed the signals at a chemical shift of 10 ppm, 22 ppm, 42 ppm, and 50 ppm attributed to the C1, C2, C3-C6, and C7 of the methyl group in the 3NM chain. These results confirmed that aminosilane was covalently bonded with the silanol groups on the silica surface. Moreover, the signal at a chemical shift of 164 ppm was ascribed to carbamate formation, probably due to the reaction between CO_2 in the atmosphere and amine groups on the modified silica surface [24].

3.2 Characterization of the NR/silica foam composites

Fig. 2 shows the morphology of the NR/silica foam composite filled with the USi and different modified silica particles. The NR foam showed a close cell structure and this did not change after filling with USi or the different modified silica particles. However, the cell size of NR/silica foam composites tended to be decreased compared to the NR foam because the modified silica particles might obscure the blowing agent during the foaming process [25]. Additionally, the different morphologies of the modified silica particles in the rubbery matrix was clearly observed, while the USi particles showed aggregates of primary particles in the rubbery matrix, as seen in Fig. 2(b), more aggregates or agglomerates of the modified silica particles were clearly observed, and ranked in the order of 3NSi > 2NSi >

NSi. This was due to the increased basicity of each amine modifier. Accordingly, the

modifier could act as a catalyst to increase the rate of the sol-gel reaction.
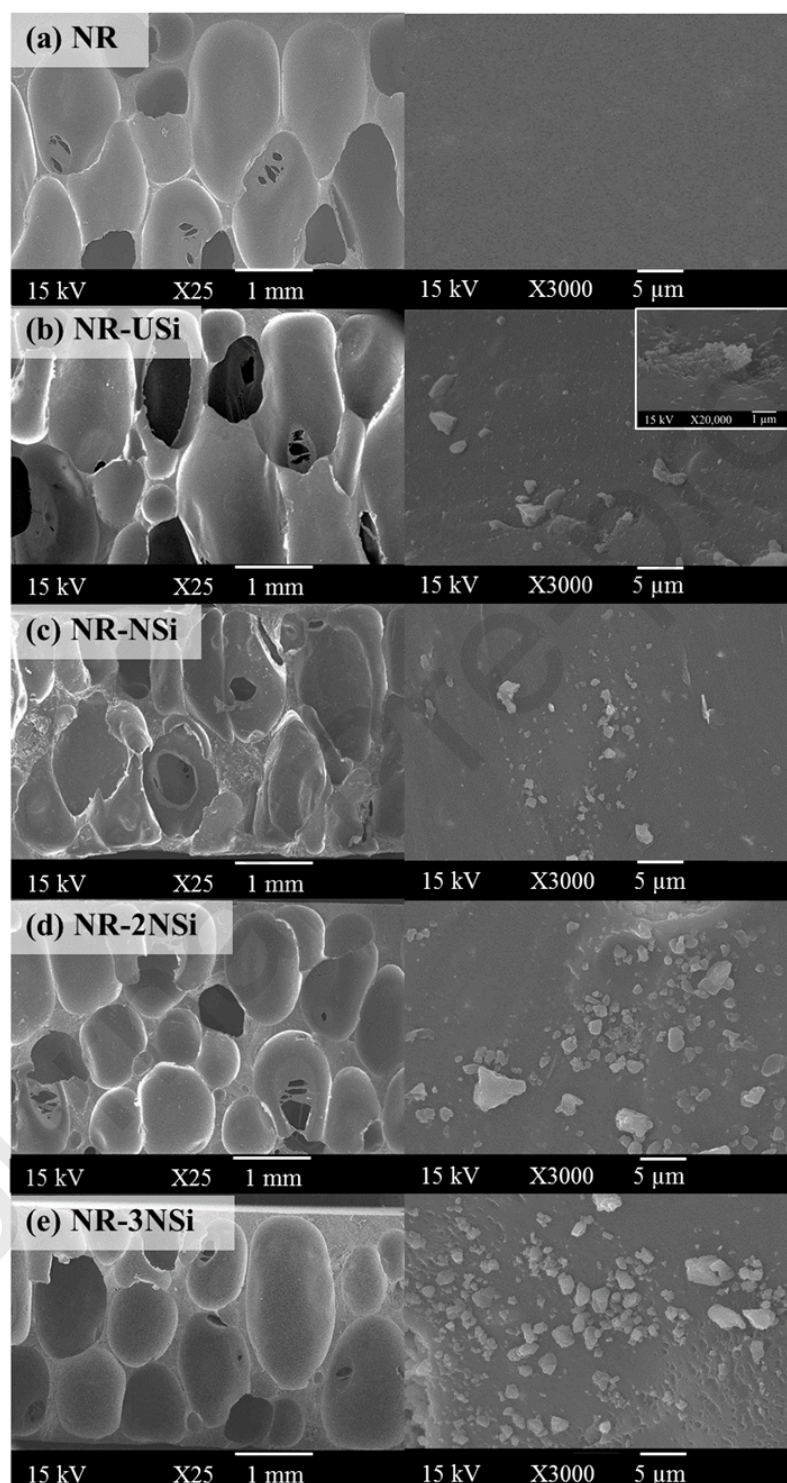
Fig. 2 Representative SEM images (3,000 x magnification) of the NR and different

NR/silica foam composites.

3.3 CO$_2$ capture of the NR and NR/silica foam composites

3.3.1 Effect of the amine content of the modifier on the CO$_2$ adsorption capacity

In this study, mono-, di- and tri-amines (NM, 2NM and 3NM) were used to modify the silica particles in order to increase the functional groups for CO$_2$ capture. Table 2 summarizes the CO$_2$ adsorption capacity of the NR foam and NR/silica foam composites at ambient temperature and pressure. The CO$_2$ adsorption capacity of NR foam in this work prepared from solid NR, was 1.81 mg/g. In a previous study [17], NR latex was prepared as the CO$_2$ sorbent material with a CO$_2$ adsorption capacity of of about 1.42 mg/g, which was 1.27-fold lower than that for the NR foam prepared in this study. This was due to the different curing system for making the rubber foam.

After filling with 10 phr of USi (NR-USi), the CO$_2$ adsorption capacity of NR/silica foam composite material increased 2.68-fold to 4.85 mg/g because the presence of USi increased the adsorbent surface area to capture CO$_2$. For the NR foam filled with the modified silica particles, the CO$_2$ adsorption capacity tended to be increased, due to either the increased physisorption from the porous modified silica particles or from the chemisorption of CO$_2$ on the amine groups on the modified silica particle surface [26, 27]. Although the CO$_2$ adsorption capacity of NR-NSi, NR-2NSi, and NR-3NSi was higher than that of NR-USi, the CO$_2$ adsorption capacity of NR-NSi (modified by mono-amine) showed the highest values compared to NR-2NSi and NR-3NSi (modified by di- and tri-amines). This point should be investigated as to why the di- and tri-amines functionalized on the silica particles result in a lower CO$_2$ adsorption capacity.

Considering the chemical structure of the modifier, the primary amine in NR-NSi reacted with CO_2 faster than the secondary amines in NR-2NSi and NR-3NSi due to the low steric hindrance of the chemical structure and low heat of reaction [28].

Another important factor affecting the CO_2 adsorption is the BET surface area of the modified silica particles. The BET surface area of the NSi particles (168.01 m^2) was higher than that for 2NSi (5.05 m^2) and 3NSi (4.34 m^2). This might be because the modifier with the high amine content, and so a high steric effect, could block the pores of the modified silica particles and so decrease the effective surface area, resulting in a lower CO_2 adsorption. Additionally, the homogeneity of the NR foam porosity should be taken into account for any CO_2 adsorption material, but this is difficult to control.

Table 2

CO_2 adsorption capacity of the NR foam and NR/silica composites under ambient temperature and pressure at a mixed gas flow rate of 100 mL/min.

Sample code	CO_2 adsorption capacity (mg/g)[a]	Degradation temperature (°C)
NR	1.81	310
NR-USi[b]	4.85	330
NR-NSi[c]	6.71	330
NR-2NSi[d]	5.54	325
NR-3NSi[e]	6.16	327

[a]mgCO_2/gNR, [b-e]NR filled with [b]USi particles, [c-e]silica particles with [c]NM, [d]2NM, and [e]3NM.

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It is also important to confirm that CO_2 could be captured in the NR foam or NR/silica foam composite materials. Therefore, in this study raman spectroscopy was used to identify the CO_2 adsorption of the composite material. The raman spectra of the NR/silica foam composites are shown in Fig. 3. The bands at 1665, 1448, and 1374 cm^{-1} were attributed to the stretching of the C=C double bond, CH_2 symmetric bending, and CH_3 twisting of NR [29]. After CO_2 adsorption, the peaks of the NR/silica foam composite at 1370 and 1245 cm^{-1}, corresponding to the O-C-O symmetric stretching of CO_2 molecule [30], and the peak intensity at 1370 and 1245 cm^{-1} tended to be increased, in accord with the high CO_2 adsorption capacity for each sorbent material (Table 2). Accordingly, the NR/silica foam composite material presented in this study can be used as an alternative adsorbent for CO_2 capture.
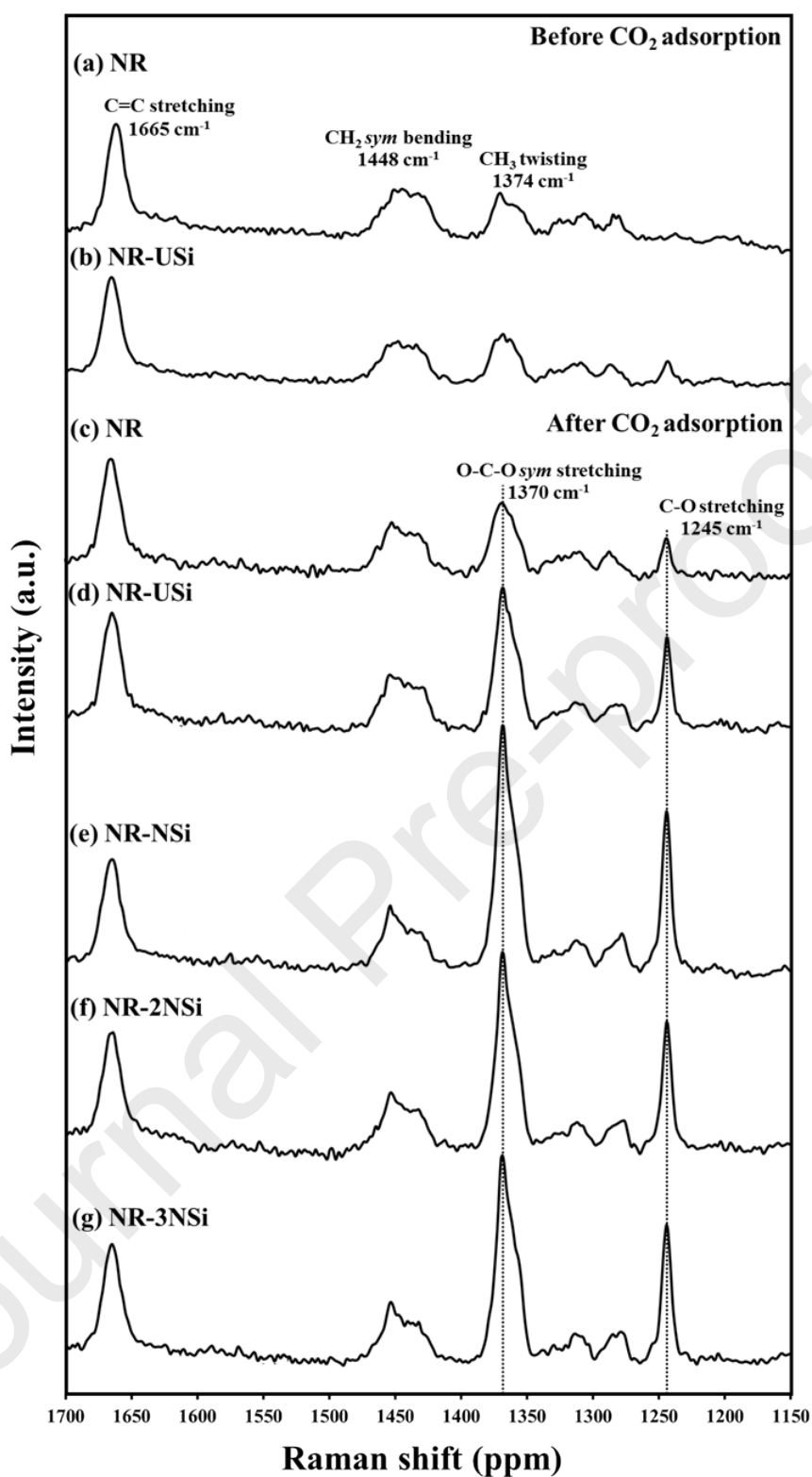
Fig. 3 Representative raman spectra of the NR foam and NR/silica foam composites before

CO_2 adsorption of (a) NR and (b) NR-USi and after CO_2 adsorption of (c) NR, (d) NR-USi,

(e) NR-NSi, (f) NR-2NSi, and (g) NR-3NSi.

3.3.2 Effect of temperature on CO₂ adsorption capacity

Fig. 4(a) shows the adsorption capacity of the NR/silica foam composites at ambient (~ 35 ℃), 45 ℃ and 55 ℃. Negative and positive changes in the slope were observed along the different temperatures. For NR, NR-USi, and NR-NSi, these showed a negative change in the slope due to the exothermic adsorption process. The change in slope of NR-USi was less than that of NR because the USi particles could absorb the heat transfer [31] from NR resulting in improved thermal properties of the NR sorbent material (Table 2), where the degradation temperature of the NR/silica foam composite materials was shifted upwards about 15–20 ℃ compared to NR. However, a marked change in the slope was clearly seen in NR-NSi because after the sample adsorbed the heat, the heat was transferred to the modified silica particles. First, the organic components along the modifier chain might adsorb the heat energy and then transfer this to the NR, which was faster than in the USi particles. For NR-2NSi and NR-3NSi, a different mechanism was clearly observed with a positive change in the slope. When the organic components along the modifier chain received the heat transfer, the long chains covered on the modified silica particle surface become more flexible and resulted in lower chain entanglements, and so chain expansion [32]. Accordingly, the active amine groups along the modifier chain became available to capture CO_2, resulting in the increased CO_2 adsorption capacity. The proposed mechanism of CO_2 adsorption at a high temperature is represented schematically in Fig. 4(b).
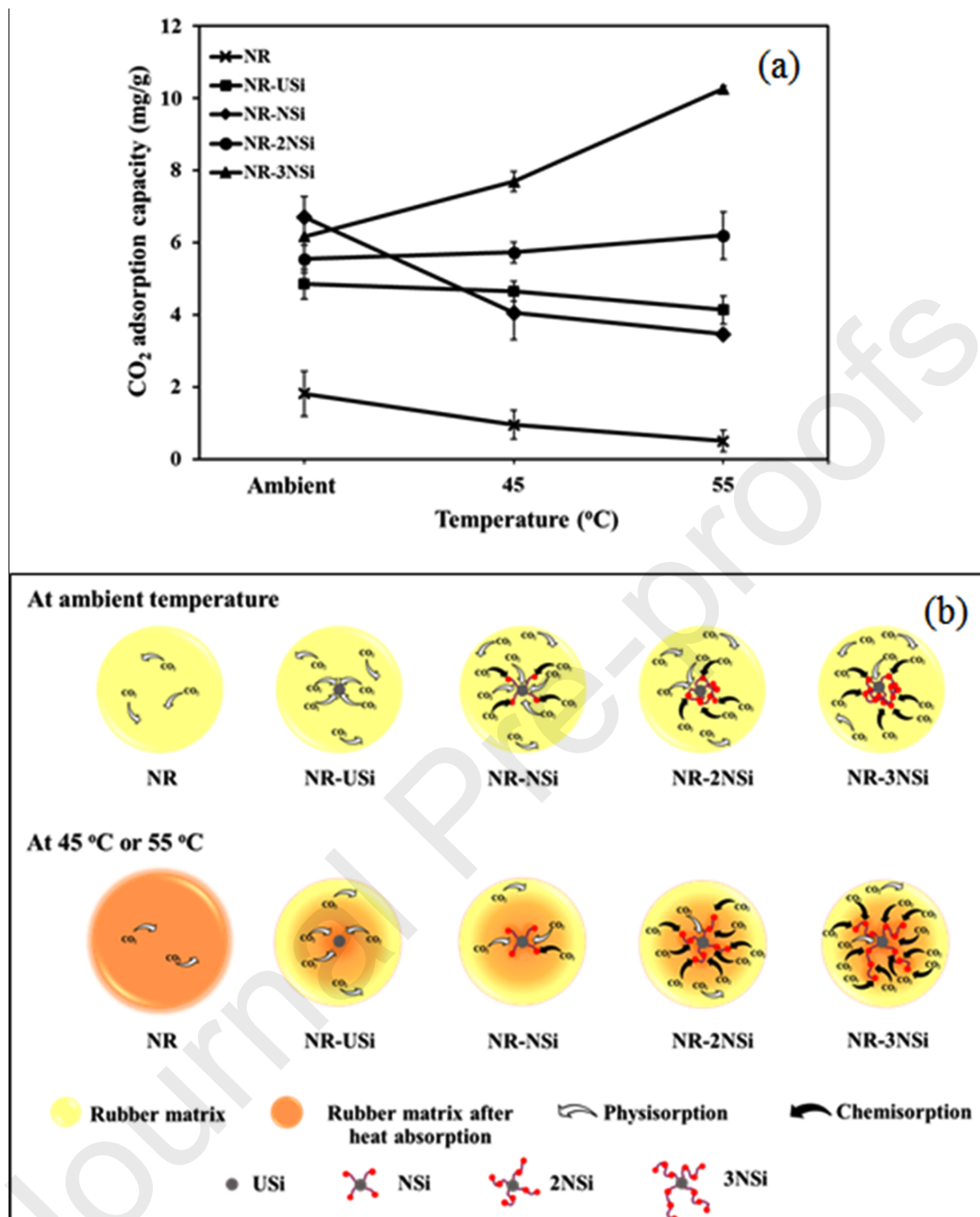
Fig. 4 (a) CO_2 adsorption capacity at various temperatures in a mixed gas flow rate of 100 mL/min and (b) Schematic representation of the CO_2 adsorption mechanism on the NR and NR/silica foam composites at various temperatures and a mixed gas flow rate of 100 mL/min

3.3.3 Kinetic adsorption

Kinetic modeling can explain the possible CO_2 adsorption mechanisms. In this study, the kinetic adsorption behavior of the NR foam composites was studied through pseudo-first order, pseudo-second order and Avrami's models [32,33], as follows:

Pseudo-first order: $\quad q_t = q_e[1 - \exp(-k_1 t))$,

Pseudo-second order: $q_t = \dfrac{k_2 q_e^2}{1 + k_2 q_e t} t$,

Avrami's: $\quad\quad\quad q_t = q_e[1 - \exp(-k_A t)^n]$,

where k_1 (1/min), k_2 (g/mmol min), and k_A (1/min) are the rate constants, q_e (mmol/g) is the adsorption capacity and q_t (mmol/g) is the amount of gas adsorbed in a specific time t (min), and n is the order of the kinetic equation.

Table 3 shows the linear regression parameters of the kinetic data for the CO_2 adsorption on the NR/silica foam composites. A poor linearity for the pseudo-first order and pseudo-second order models was detected (low R^2 value). Generally, the pseudo-first order model is in agreement with only physical adsorption on the surface coverage [33], whilst the pseudo-second order model can be used to assume the chemical adsorption of the adsorbent [34]. However, the interaction between CO_2 and the NR foam composites showed a more complex behavior than the pseudo-first order or pseudo-second order models. Accordingly, Avrami's model was used to explain the kinetic data. The data in Fig. 5 showed a good linearity, in terms of the R^2 value ($R^2 > 0.91$), with a good fitting to the experimental data. This implied that the CO_2 adsorption involved more than one reaction pathway, and may include both physisorption and chemisorption [33]. The n_A of the NR

foam composites ranged between 1.131–2.509, which supported that a complex reaction mechanism occurred in this adsorbent material [35, 36].

Table 3

Linear regression parameters of the kinetic data for CO_2 adsorption.

Sample code	Pseudo-first		Pseudo-second		Avrami		
	R^2	k_1	R^2	k_2	R^2	k_A	n_A
NR	0.6815	0.011	0.4319	1.110	0.9192	0.017	1.304
NR-USi[a]	0.9693	0.014	0.6683	0.635	0.9789	0.011	1.131
NR-NSi[b]	0.9040	0.014	0.2893	0.056	0.9413	0.005	2.509
NR-2NSi[c]	0.8780	0.011	0.7917	0.004	0.9232	0.020	1.502
NR-3NSi[d]	0.8876	0.014	0.5527	0.251	0.9504	0.020	1.412

[a]NR filled with USi particles, or silica particles modified with [b]NM, [c]2NM, or [d]3NM.
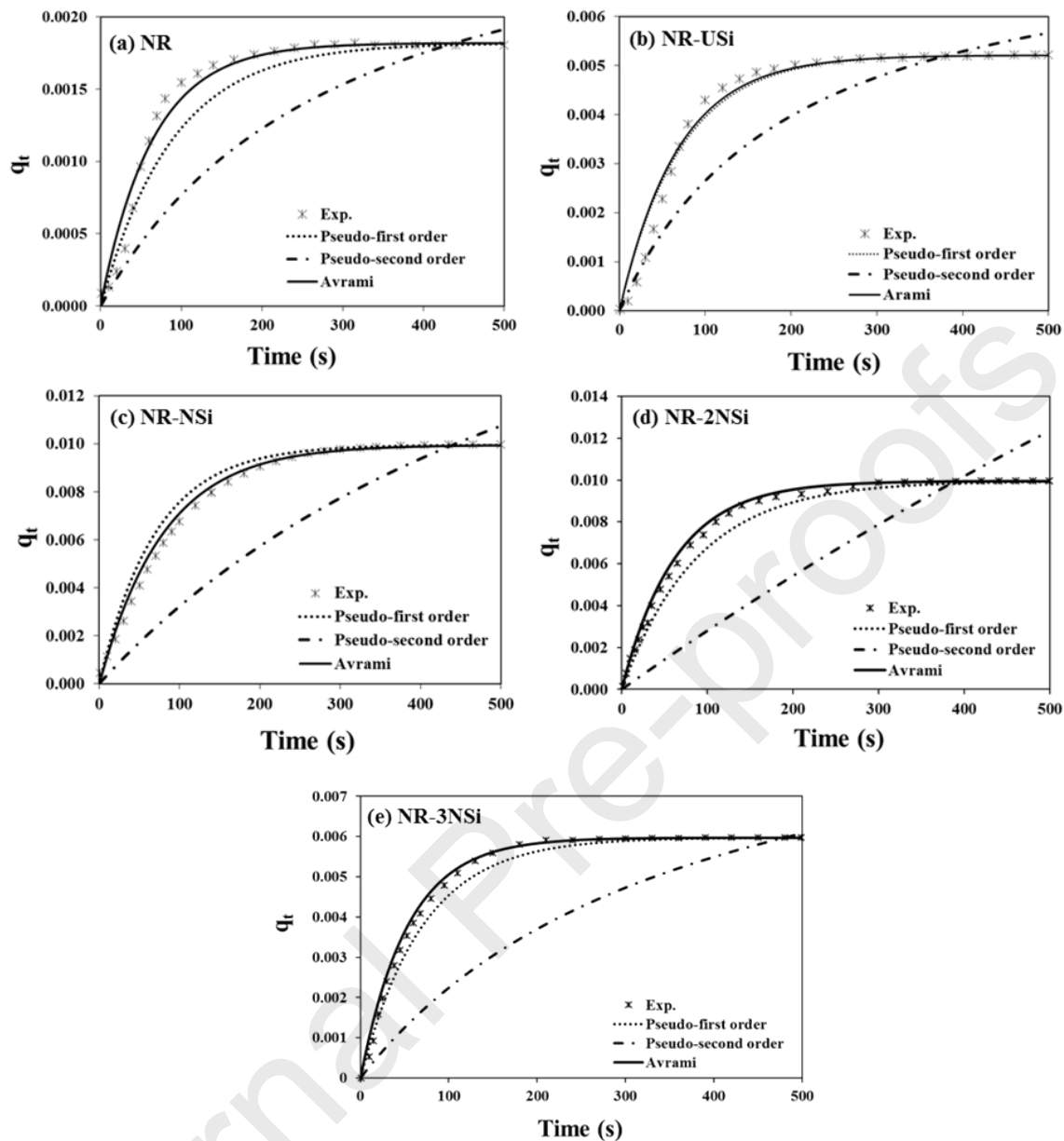
Fig. 5 Experimental CO_2 adsorption capacity on (a) NR, (b) NR-USi, (c) NR-NSi, (d) NR-2NSi, and (e) NR-3NSi, and the corresponding fit to the different kinetic models.

3.3.4 Reusability of the NR/ silica foam composite material

In a real industrial application, not only is a high adsorption capacity of the adsorbent material important but also an excellent reusability in the cyclic adsorption-desorption cycles is required. Accordingly, the stability of the NR/silica foam composite materials was

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studied through the regeneration process. Fig. 6 shows the CO_2 adsorption capacity of the NR/silica foam composites for each adsorption-desorption cycle. The NR foam could be reused for seven cycles, while the NR/silica foam composite filled with unmodified or modified silica particles could be reused for more than 10 cycles. That the NR/silica foam composites showed a higher stability for reusability compared to the NR foam was because the presence of unmodified or modified silica particles could improve either the thermal or the mechanical properties of the NR foam composite [31].
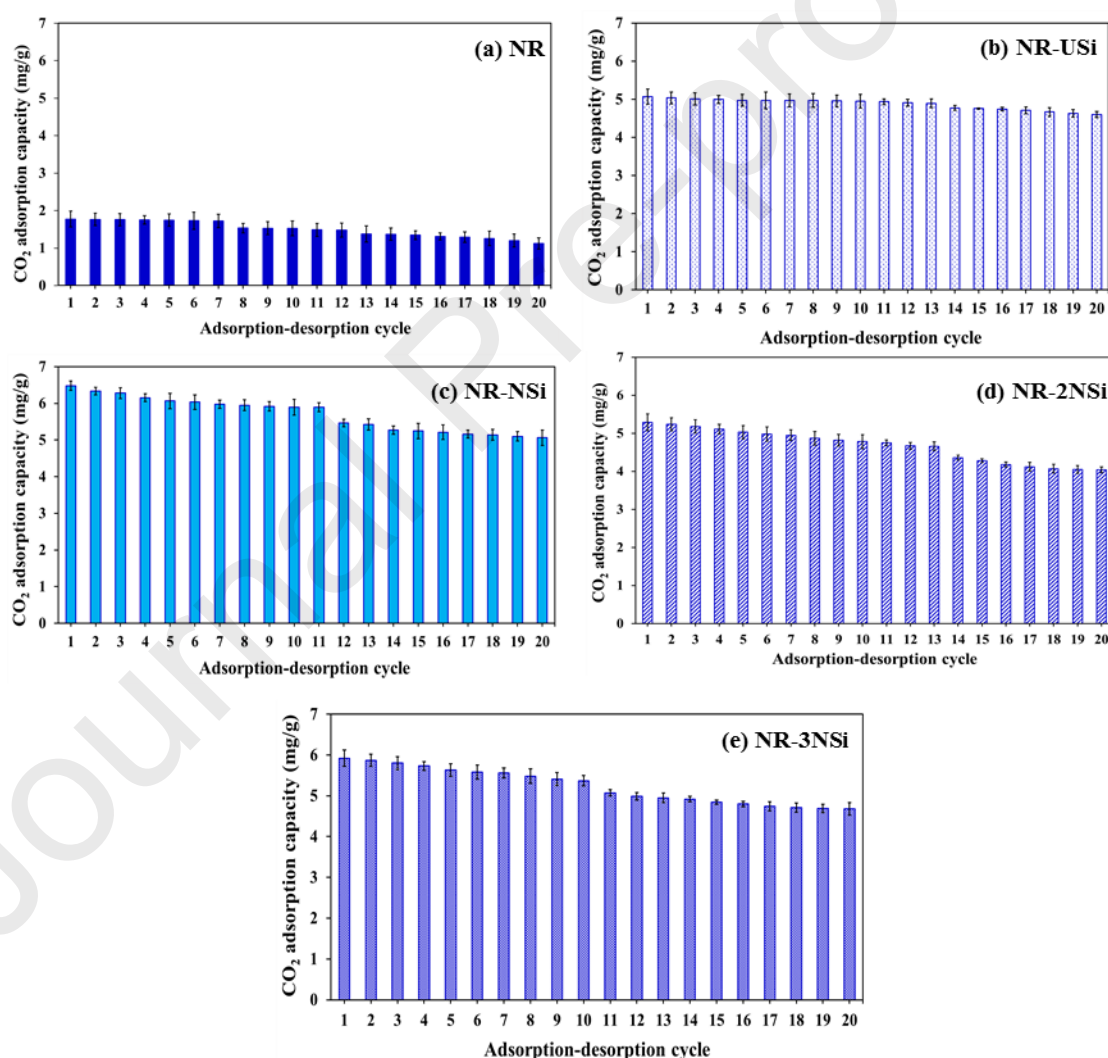
Fig. 6 The cyclic CO_2 adsorption capacity of the NR and NR/silica foam composites over 20 successive adsorption-desorption cycles.

4. Conclusions

In this study, NR foam from solid NR was chosen to prepare as a CO_2 adsorbent. The CO_2 adsorption capacity of the NR foam increased after filling with USi particles or silica particles modified with one of three amine compounds. The NR/silica foam composite filled with the mono-amine NM modified silica particles (NSi) showed an optimum CO_2 adsorbent capacity (6.71 mg/g) under ambient temperature and pressure and a mixed gas flow rate of 100 mL/min. Raman spectra analysis confirmed that the NR/silica foam composite could capture CO_2 in the material. Another factor that affected the CO_2 adsorption capacity was the temperature, which likely influenced the modifier chain structure of the modified silica particles resulting in an increased or decreased CO_2 adsorption capacity of the NR/silica foam composite. The CO_2 adsorption on the NR/silica foam composites was a combination of physisorption and chemisorption, with the experimental data best fitted to Avrami's kinetic model. Finally, the NR/silica foam composites had a high stability for reuse of over 10 cycles. Accordingly, these NR/silica foam composites present alternative CO_2 adsorbents that could potentially be used as a filter for air purification to decrease CO_2 concentration in a building or room with cyclic occupancy (e.g. office).

Conflict of interest

The authors have declared no conflict of interest.

Compliance with ethics requirements

This article does not contain any studies with human or animal subjects.

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Declaration of interests

☒   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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Natural rubber foam composite was prepared from solid natural rubber.

- Amine modified silica particles improved the CO_2 adsorption and thermal properties of natural rubber foam composite.

- Different temperatures showed the significant change of amine modifier structure and CO_2 adsorption in material.

- CO_2 adsorption mechanism of natural rubber foam composite was the combination of physisorption and chemisorption.