

# Polyaniline Encapsulated Microporous Polymer Beads and their Vapor and Gas Adsorption Behavior

Pramil C. Deb,\* Lalit D. Rajput, Pravin K. Singh

Advance Materials Department, Naval Materials Research Laboratory, MIDC Area, Ambernath (E), Maharashtra 421506, India

Received 17 June 2006; accepted 28 September 2006

DOI 10.1002/app.25597

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Styrene-maleic acid copolymer beads and styrene-divinylbenzene beads were encapsulated with polyaniline by *insitu* oxidative polymerization of aniline. These beads both in unmodified and encapsulated forms were studied for their organic vapor and hydrogen adsorption behavior at 30°C and reduced pressure. Enhanced

adsorption of hydrogen to the extent of 4.9 mass % was observed for encapsulated styrene-maleic acid copolymer beads. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 297–303, 2007

**Key words:** copolymerization; encapsulation; adsorption

## INTRODUCTION

Science and technology of storage and release of hydrogen as energy provider is an area of global interest and a challenge to material science. Among various methods of storage of hydrogen,<sup>1</sup> those involving physisorption by zeolite type materials,<sup>2,3</sup> molecularly porous metal organic frameworks, MOF<sup>4–6</sup> and carbon nanotubes<sup>7</sup> are making steady progress. However, targets of achieving 4–10% hydrogen adsorption by mass of adsorbing material under not too stringent conditions appear elusive. Recent claim<sup>8,9</sup> of about 3% uptake at 78 K at low pressure and 1% uptake at 298 K and 20 bar have aroused immense interest in these materials. It has been anticipated<sup>8</sup> that introduction of large organic linkers in isoreticular metal organic frameworks (IRMOF) may further increase the extent of hydrogen adsorption and reach the targeted level. In contrast to variety of binding sites in zeolites,<sup>2,3</sup> these materials are characterized by having well-defined binding sites<sup>8</sup> at the metal and the linkers. It is anticipated that the electrochemical component responsible for adsorption of hydrogen in carbon nanotubes<sup>10,11</sup> can possibly be utilized in conducting polymer such as polyaniline and polypyrrole.

We have recently<sup>12</sup> shown that transition metal based crosslinked styrene-maleic acid complexes show considerable promise for adsorption of vapor and gas under ambient conditions. These materials appear to contain finely dispersed metal in complex form in the

polymer matrix, particularly in titanium complex and possess easy release behavior. While these materials are being fully evaluated, we have recently encapsulated polyaniline in polymer beads. In the present communication we report our preliminary results on the preparation and vapor and gas adsorption behavior of polyaniline encapsulated polymer beads.

## EXPERIMENTAL

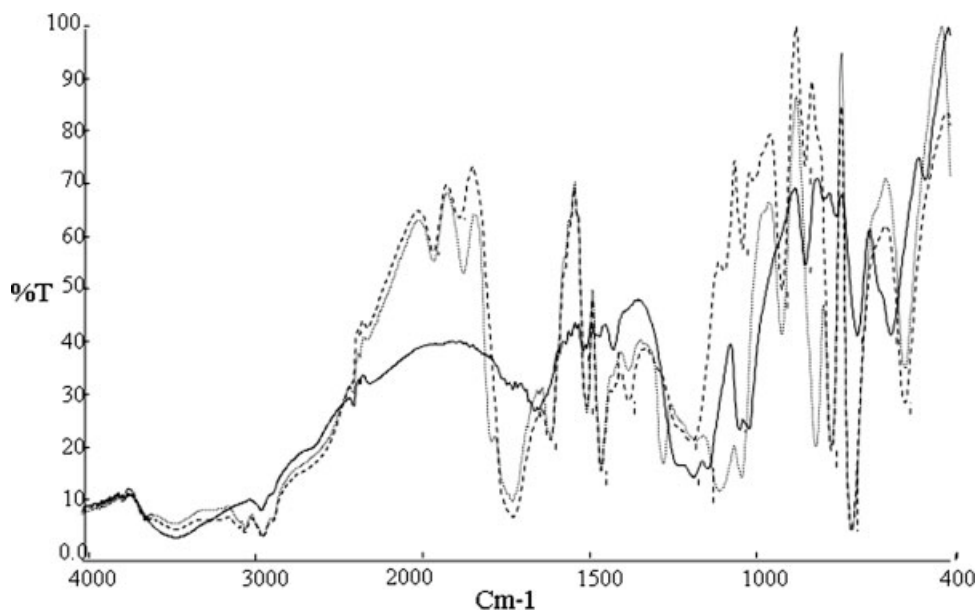
### Polyaniline encapsulation

Synthesis and characterization of styrene-maleic acid copolymer beads and metal-polymer complexes in nonaqueous medium have already been described.<sup>12,13</sup> Polyaniline encapsulated styrene maleic acid copolymer beads were prepared by modification of the method of Palaniappan et al.<sup>14</sup> as follows: Styrene-maleic acid copolymer beads were suspended in acetone solution of recrystallized benzoyl peroxide (0.8M) and evacuated to expel the entrapped air in the beads and facilitating entry of acetone solution. Supernatant acetone solution was decanted out and the beads were washed twice with acetone to remove surface adhered benzoyl peroxide. Freshly distilled aniline in aqueous acetone was added slowly to the beads at room temperature and the mixture was stirred. Color of the beads changed from yellowish white to brownish black and then to purple black in about 4 h. The mixture was left for 24 h and thereafter the liquid containing very little fine black particles was decanted off. The beads were washed repeatedly with acetone and finally Soxhletted with acetone and dried at 50°C under reduced pressure for 24 h.

Sulfonated styrene-divinyl benzene polymer beads were similarly treated to get uniformly brownish to

\*Present address: Defence Institute of Advanced Technology, Girinagar, Pune-411025, India.

Correspondence to: P. C. Deb (pramil\_cd@yahoo.co.in).



**Figure 1** FTIR spectra of SMA copolymer (---) PANI-encapsulated SMA copolymer (...) and PANI-encapsulated SDVBSA polymer (—).

greenish black beads indicating incorporation of polyaniline in the beads. They were purified by soxhletting with acetone and dried under reduced pressure.

### Characterization

IR spectra of the crushed beads were taken in KBr using a FTIR instrument (Perkin-Elmer, 1650). Scanning electron micrographs of crushed beads were taken in LEO 1455.

Nitrogen contents in the beads were estimated using a CHNS analyzer (Perkin-Elmer 2400).

### Vapor/gas adsorption

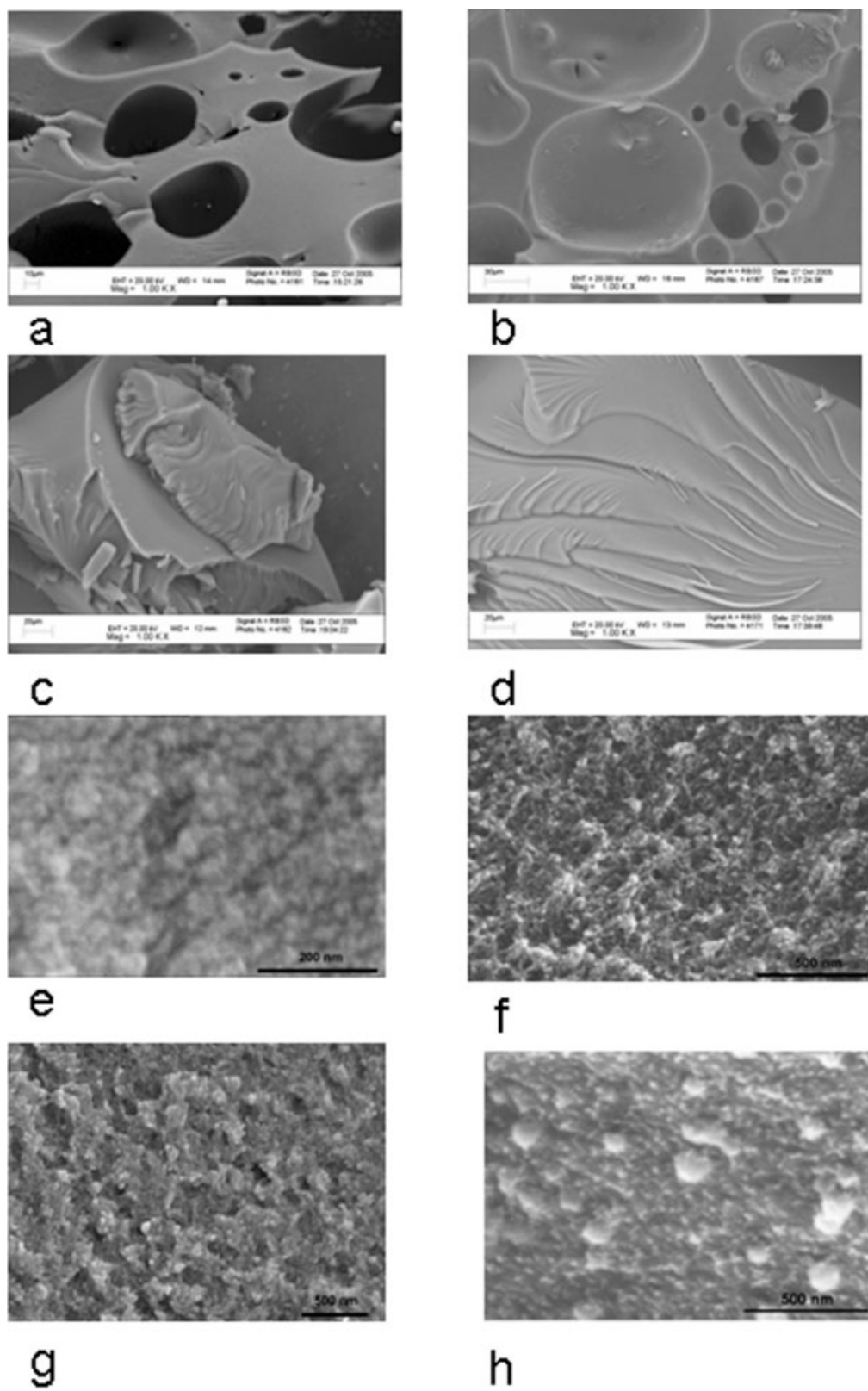
Appropriate amounts of beads were exposed to saturated vapor of methyl ethyl ketone, toluene and ethanol in separate desiccators and kept at 25°C for 24 h to equilibrate. The beads were wiped dry quickly to ensure removal of condensed vapor on outer surface and were weighed at regular intervals to measure extent of adsorption and desorption. This was continued for about 90 min after which negligible loss/gain was observed.

Hydrogen gas adsorption studies were carried out in a SORPTOMATIC 1990 instrument of THERMO FINNIGAN, ITALIA that records the fall in pressure of gases over adsorbing surface as a function of pressure and automatically converts the same into amount of gas adsorbed. Details of measurement have been already reported.<sup>12</sup> The instrument was standardized with hydrogen, nitrogen as well as helium to determine the dead volume.

## RESULTS AND DISCUSSION

Styrene-maleic acid copolymer beads (SMA) had a carboxyl equivalent of about 350 showing presence of more styrene units in the copolymer chain than a truly alternating copolymer and extensive crosslinking. Polyaniline encapsulated SMA copolymers contained 0.4–0.5% nitrogen indicating 2.5–3% polyaniline in the beads. In contrast styrene-divinyl benzene sulfonic acid (SDVBSA) beads contained as high as 1.4% nitrogen indicating about 9% polyaniline encapsulation. It has been shown earlier that polyaniline exists in doped form in presence of maleic and other organic acids<sup>15–18</sup> and the same is expected in the copolymer beads where the acid exists in the form of substituted succinic acid. Both nitrogen content and color showed fast polyaniline formation by benzoyl peroxide oxidation and is in tune with the findings of Palaniappan.<sup>14</sup> We also carried out a few experiments using aqueous potassium persulfate for oxidative polymerization of aniline in the beads.<sup>15</sup> Even though there was indication of encapsulation, the rate and extent of encapsulation were relatively low and inconsistent.

FTIR spectrum of polyaniline encapsulated copolymer bead is shown in Figure 1 along with the spectrum of unmodified bead. They are essentially same having a broad peak at 3440  $\text{cm}^{-1}$  and a moderate peak at 1703  $\text{cm}^{-1}$  for the carboxylic group. The striking difference is in the appearance of a peak at 1250  $\text{cm}^{-1}$  for the C—N stretching in the spectrum of PANI-encapsulated material.<sup>16</sup> This peak confirms the presence of polyaniline in the copolymer beads. IR spectrum of polyaniline encapsulated styrene-divinyl benzene



**Figure 2** SEM photographs: (a) SMA copolymer, (b) PANI-encapsulated SMA, (c) SDVBSA polymer and (d) PANI-encapsulated SDVBSA polymer, FESEM photographs: (e) PANI-encapsulated SDVBSA, (f) SMA copolymer, (g) PANI-encapsulated SMA and (h) Ti-complexed SMA.

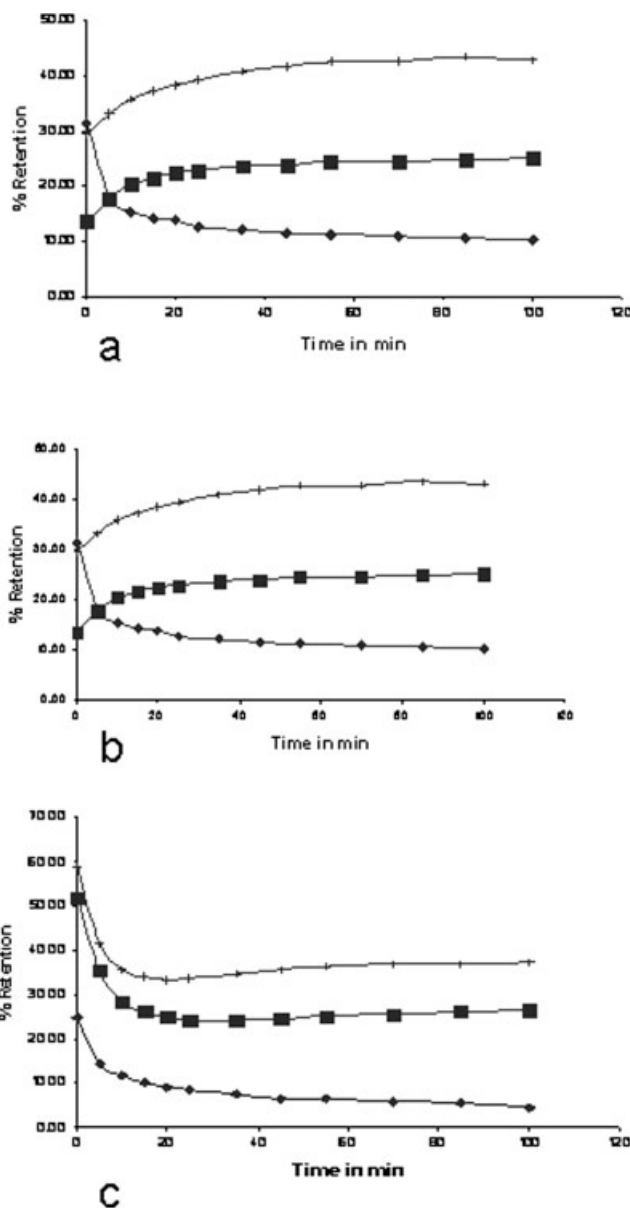
sulfonate is shown in the same figure for comparison. The spectrum is characterized by the presence of a small peak at about  $2360\text{ cm}^{-1}$  because of  $\text{NH}_2^+$  stretching indicating the presence of doped polyaniline in the polymer beads. However, the C—N stretching peak at  $1250\text{ cm}^{-1}$  could not be detected.

Figure 2(a–d) shows scanning electron micrographs of broken surface of raw and encapsulated beads of both the copolymers. As is evident, while the SDVBSA bead and its PANI-encapsulated form offer fairly uniform surface with little porosity in micron range, SMA beads both in unmodified and encapsulated form are quite porous. FESEM pictures shown in Figure 2(e–h) clearly indicate highly porous nature of the raw and encapsulated beads of SMA having interconnected pores of varying sizes of  $<5\text{ nm}$  to about  $100\text{ nm}$ . The SDVBSA encapsulated bead on the other hand does not show this feature which is expected to lead to differences in vapor and gas uptake behavior. For reference FESEM picture is also shown for Ti-complexed SMA bead that also indicates porous structure but substantially occupied by Ti in bound form as the same could not be removed through conventional processes.<sup>12</sup> Distribution of pore sizes in the nanometer ranges should prove to be important in these materials for gas adsorption. Attempts are being made to quantify the possible distribution with beads of various sizes and various pore size distributions by varying synthesis conditions.

### Vapor uptake and release

Figure 3(a–c) shows methyl isobutylketone, toluene and ethanol vapor adsorption/desorption behavior of encapsulated beads at room temperature and atmospheric pressure. For comparison, adsorption-desorption characteristics of unmodified SDVBSA beads are also shown. SDVBSA beads and their polyaniline encapsulated form show distinctly different behavior compared to those of SMA beads.<sup>12</sup> While adsorption of vapor was carried out in sealed desiccators, desorption studies were made in open atmosphere having a relative humidity of about 85%. In absence of any other component being progressively adsorbed, it is evident that the continuous increase in weight is due to moisture picked-up by SDVBSA beads from atmosphere, which in case of nonencapsulated beads is at least 12% (neglecting toluene release due to its being a very good solvent for polystyrene). In case of PANI-encapsulated forms, the same trend is observed though the adsorption of toluene is considerably reduced presumably due to resistance to entry of toluene into the interior now being substantially blocked by polyaniline molecules.

PANI-encapsulated SMA beads in contrast show expected behavior as observed earlier for unencapsulated and metal encapsulated beads<sup>12</sup> with an initial



**Figure 3** Vapor adsorption behavior of polymer beads: (a) PANI-SMA/MIBK ( $\blacklozenge$ ), SDVBSA/MIBK ( $+$ ), PANI-SDVBSA/MIBK ( $\blacksquare$ ). (b) PANI-SMA/toluene ( $\blacklozenge$ ), SDVBSA/toluene ( $+$ ), PANI-SDVBSA/toluene ( $\blacksquare$ ). (c) PANI-SMA/ethanol ( $\blacklozenge$ ), SDVBSA/ethanol ( $+$ ), PANI-SDVBSA/ethanol ( $\blacksquare$ ).

fast release followed by slow release after about 10 min. Adsorption-desorption curves follow the same behavior as mentioned above also for MIBK, a liquid having a higher dipole moment indicating not so significant role of polarity in desorption behavior of the beads although the extent of adsorption is slightly higher for the more polar liquid.

Adsorption-desorption behavior of the SDVBSA beads for ethanol shows a totally different trend. An initial fast release with substantial retention of ethanol is followed by a minute uptake of moisture after about 10 min. Ethanol being a nonsolvent for polystyrene is released rapidly except for the hydrogen

**TABLE I**  
**Data Acquisition Parameters (DAP) for Adsorption of Hydrogen by Various Porous Copolymer Beads at 30°C and 900 Torr Saturation Pressure**

DAP code	$P/P_0$ region	Equilibrium time (min)	Equilibrium deviation (Torr)
A	0–0.3	2	0.5
	0.3–0.6	10	0.3
	0.6–0.9	10	0.3
B	0–0.3	1	0.5
	0.3–0.6	1.5	0.2
	0.6–0.9	1.5	0.5
C	0–0.3	1.5	0.08
	0.3–0.6	1.5	0.08
	0.6–0.9	1.5	0.08

bonded part and after initial desorption, moisture uptake competes with the release of ethanol resulting in attainment of steady state quite early. Desorption of ethanol from PANI-encapsulated SMA beads was as observed for untreated beads.<sup>12</sup>

### Hydrogen adsorption

Hydrogen adsorption behavior of polymer beads was followed by allowing the beads to be in contact with the gas for different times (through variation of equilibrium pressure deviations) in discreet pressure ranges within 0–900 Torr. Schedule of three adsorption programs is shown in Table I. Accordingly, the total time for attaining the preset saturation pressure of 900 Torr could be varied. However, in none of cases saturation could be achieved even after prolonged exposure for as many as 15 days when small deviation of equilibrium pressure was allowed at each experimental point. Table II shows the extent of adsorption and time taken for the original and encapsulated polymer beads under different experimental conditions. While the extent of adsorption of hydrogen by the present materials can be compared with values reported for various materials, comparison of rates of adsorption cannot be made in view of nonavailability of such data

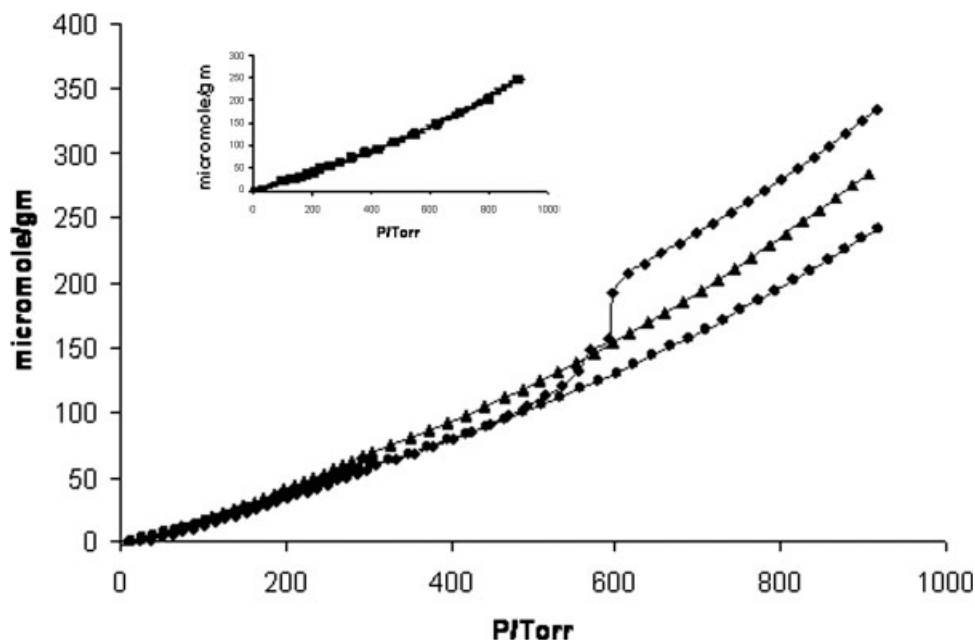
in literature. As is evident from Table II, saturation could not be achieved in hours and sometimes in days irrespective of the acquisition parameters used for adsorption studies. It is also apparent that adsorption and its rates (approximate) for SMA and PANI-encapsulated SMA copolymers are higher than for SDVBSA polymers indicating the role of polymer type. Porosity and pore size distribution are also expected to play important role. This is being studied in some detail and will for part of future communication.

As pointed out earlier for metal complexed copolymer beads,<sup>12</sup> in the case of PANI-encapsulated SMA beads, appearance of appreciable positive adsorption starts in the range of 350–500 Torr for different polymers. Thereafter, it appears as though the polymers follow a path of fast adsorption preceded by a state of negligible adsorption with a very slow change in equilibrium pressure. The state of negligible adsorption has been found to continue for as much as 8–12 h in good number of cases, particularly when very small equilibrium deviation is allowed during adsorption somewhat similar to relaxation processes in polymers. It appears as if a slow process of chain segment rearrangement is induced under these conditions to open up small pores to accommodate hydrogen gas. This process seems to be sensitive to incremental pressure change.

Figure 4 shows adsorption isotherm of few instances where limiting pressure was reached without saturation in 2–5 h. These are similar to typical type-III adsorption indicating multiplayer adsorption and condensation in pores and capillaries. Inset shows reversibility for one such case (desorption is shown by large solid squares). Figure 5 shows a typical case of enhanced adsorption by PANI-encapsulated SMA beads under specific acquisition parameter (B). Continued adsorption was allowed for almost 15 days (refer Table II, SMA-PANI: B) but no saturation was achieved. Adsorption achieved was 2.45 mol % i.e., 4.9 mass % of hydrogen (mols and/or mass of hydrogen gas adsorbed by 100 gms of polymer beads as the

**TABLE II**  
**Rates of Hydrogen Adsorption of Unmodified and PANI-Encapsulated Copolymer Beads**

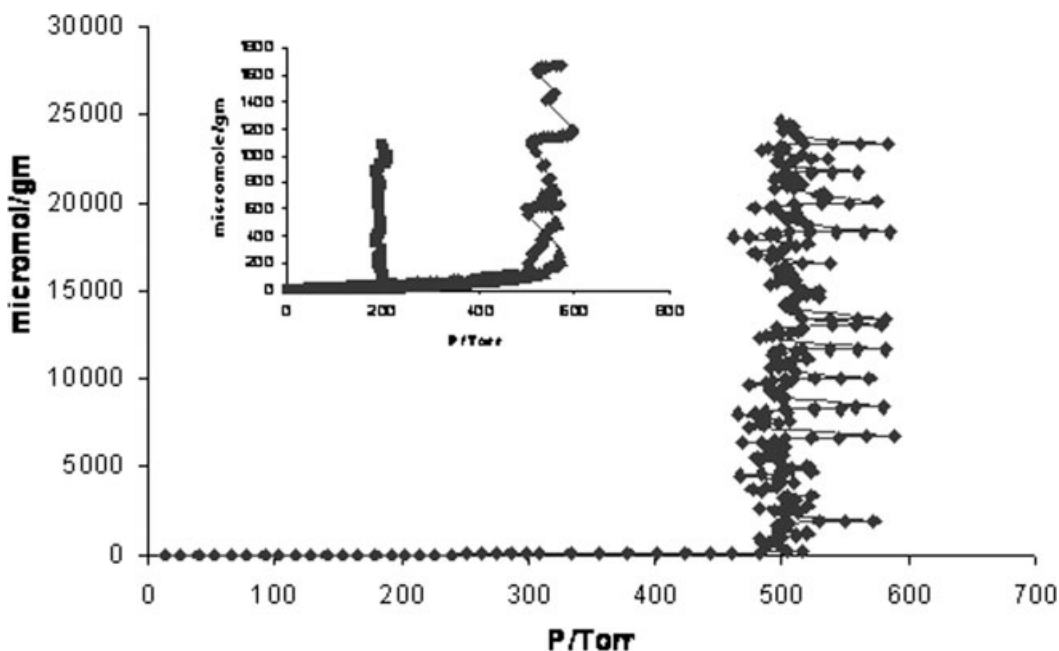
Polymer	Acquisition parameter code	Total time of adsorption (h)	Rate of adsorption (mass %/h 10 <sup>3</sup> )	Saturated/unsaturated
SMA	A	47.00	2.70	Unsat.
	B	1.65	3.00	Unsat.
	C	77.00	4.50	Unsat.
SMA-PANI	A	6.25	5.23	Unsat.
	B	355.7	13.80	Unsat.
	C	8.3	5.44	Unsat.
SDVBSA	A	47.11	2.70	Unsat.
	B	1.78	3.20	Unsat.
SDVBSA-PANI	A	83.15	2.17	Unsat.
	B	4.27	1.56	Unsat.



**Figure 4** Hydrogen adsorption behavior of polymer beads: 100–200  $\mu\text{m}$  Raw-SMA (●), SDVBSA (▲), PANI-SDVBSA (◆).

dead volume has been automatically subtracted) at an equilibrium pressure of about 450–600 Torr. To the best of our knowledge, this is the highest recorded physisorption of hydrogen by any material at room temperature. To confirm, these experiments were repeated number of times with freshly prepared unmodified as well as encapsulated SMA beads. Inset shows a few traces of such results. One such case shows enhanced adsorption starting at as low as 200 Torr for PANI-encapsulated SMA beads of different bead and

pore size. They all substantiate the typical pattern shown in Figure 5 although the experiments were continued to a period of about 50–100 h in some cases and saturation was not achieved. We have also carried out adsorption studies with other acquisition parameters and it is observed that in certain cases SDVBSA also behaves similarly though the extent of adsorption and rates are lower. It will be too unsound to conclude about the type of adsorption in these cases. These experiments however, indicate that adsorption is con-



**Figure 5** Hydrogen adsorption behavior of polymer beads showing enhanced adsorption for PANI-SMA beads.

trolled by the porosity and dimension of pores in the prepared beads in addition to encapsulation. These aspects will be studied in detail for a definite conclusion regarding influence of various factors responsible for enhanced adsorption of hydrogen in encapsulated SMA copolymer beads.

Presently, metal organic framework compounds,<sup>8</sup> carbon nanotubes<sup>9,19</sup> and polymer-dispersed metal hydrides (PDMH)<sup>20,21</sup> are being extensively studied as promising materials for hydrogen storage. Adsorption to the extent of about 2 and 3.2 mass % of hydrogen at high pressures and ambient temperature is recently reported for inter-reticular metal organic framework (IRMOF) and carbon nanotubes<sup>8,19</sup> respectively. It is indicated that there is possibility of higher adsorption with larger organic linkers in IRMOFs. For the PDMHs, the role of polymer in modifying the hydrogen storage capacity of a metal hydride is not yet known. A combination of various chemical bonding including van der Waals interaction and participation of free radicals in hydrogen movement in the materials is generally postulated. It has also been demonstrated that for physisorption, large adsorption capacity is obtained only with adsorbents containing large volume of micro pores with suitable diameter so that overall pore volume can be in the range of 1 mL/g and above.<sup>21</sup> Our preliminary studies using field emission scanning electron microscopy (FESEM) for SMA as shown in Figure 2(e–h) confirm that they are highly porous with varying pore diameter ranging from <5 to 100 nm and above. There is ample scope to vary the pore sizes and their distribution depending on the conditions of suspension polymerization and can be controlled.

### CONCLUSIONS

Crosslinked Styrene-maleic acid copolymer and styrene divinylbenzene sulfonic acid beads were encapsulated with polyaniline through oxidative polymerization. Organic vapor adsorption characteristics of the two types of beads show different behavior because of difference in functional groups. Hydrogen adsorption of the two types of beads shows different behavior mostly because of difference in their porosity and data acquisition parameters used. PANI encapsulated styrene-maleic acid copolymer beads show enhanced ad-

sorption to the extent of 4.9% without attaining saturation at 450–600 Torr. It appears a pressure sensitive no-adsorption stage extending to hours follows the period of adsorption. This behavior has been found to be characteristic of polymer beads. Extent and rate of adsorption are dependent on porosity and condition of adsorption study. Adsorption isotherms indicate multilayer adsorption with condensation in pores.

Authors thank Dr. J. Narayanas, Director NMRL for his keen interest and permission to publish this paper. Thanks are also due to Mr. A. Kumar for experimental assistance and Parijat Deb of Materials Engineering Department of Purdue University, USA, for FESEM.

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