Reticulated vitreous carbon from polyurethane foam–clay composites

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Abstract

Reticulated vitreous carbon foams were prepared by carbonizing polyurethane precursor foams which were first infused with furfuryl alcohol. The cell size and the fraction of open cells of the precursor foam were controlled by the addition of clay in the polyurethane foam formulation. Addition of clay permitted control of the cell size of carbon foams. The higher open cell content in foams with clay permitted uniform infusion of furfuryl alcohol in the precursor, and thus more uniform carbon foams of higher density. These foams had a lower electrical resistance as compared to foams without clay.
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1. Introduction

Reticulated vitreous carbon (RVC) is a foam composed of glass-like carbon with a high void volume (up to 97%) [1]. High resistance to combustion, resistance to intercalation by materials that disintegrate graphite, good electrical conductivity and chemical inertness to a wide range of acids, bases and organic solvents are some of the special properties of RVC [2]. RVC finds use as porous electrodes [2], as high temperature insulation [2], as filters [3], in storage batteries [4], as scaffolds [5], in semiconductor manufacture [6] and as field emission cathodes [7]. Densified RVCs find use in acoustic control with noise absorption in the range of 250 Hz to 3 kHz.[1]

RVC is synthesized by carbonizing a precursor foam which is impregnated by a thermosetting resin. Open cell polyurethane foams are commonly used as precursors [8]. Open cell foams are those in which the foam lamellae separating neighboring cells are all ruptured, resulting in a structure comprising a network of struts with continuous air passages. The impregnating resins used for polyurethane precursor foams are generally phenolic resins, epoxy resins or furfuryl alcohol. The carbonization rate of furfuryl alcohol impregnated polyurethane foams is found to be higher than that for foams infused with phenolic and epoxy resins [8].

The cell size distribution of the precursor foam is an important factor determining the cell size distribution of the resultant carbon foam [8]. Vinton et al. [9] and Franklin et al. [10] showed that the cell structure of RVC is nearly the same as that of the precursor foam. The production of anisotropic carbon foam having cells of a particular aspect ratio by carbonization of the precursor while it is compressed in one direction has been reported [11]. Thus obtaining RVCs with different cell sizes (usually expressed as pores per linear inch, ppi) from open cell polyurethane foam requires the control of cell size during the foaming of polyurethane.

Addition of a small amount of clay into polymer matrices provides significant improvement in a wide variety of properties [12,13]. The most widely used clay in composite synthesis is montmorillonite (MMT). The clay particles have a layered platelet structure, in which the platelet thickness is about 1 nm and the lateral dimensions are up to 1 μm. Montmorillonite clays have been found to be powerful cell openers for polyurethane foam [14].

In the present study, we synthesized composites of open cell, flexible polyurethane foams with unmodified montmorillonite clay. Addition of a small amount of clay results in more open cells in the foam so that the impregnating reagent can be infused more uniformly into the precursor foam. This foam was then pyrolysed after infusing with furfuryl alcohol to obtain RVC of controlled cell size and enhanced electrical conductivity.

2. Experimental

2.1. Composite formation and its pyrolysis

Commercially available montmorillonite clay (Cloisite Na$^+$, Southern Clay Products, USA) was used to get an intercalated composite foam. The base polyol used was a polyether polyol (Arcol 3553, Bayer). The isocyanate used was an MDI (diphenylmethane 4, 4′-diisocyanate) based one (Suprasec 6456, Huntsman). Other ingredients used were catalysts (Dabco 33LV and Niax A1), silicone surfactant (Tegostab 4113) and cross-linker (diethanolamine). Distilled water was used as blowing agent. Furfuryl alcohol (Riedel-deHaen) was used as the impregnating resin for precursor polyurethane foam and *p*-toluenesulphonic acid (Merck) was used as a catalyst for thermosetting of the resin.

Clay was dried in a vacuum oven at 100 °C for 24 h. The base polyol and various amounts of different clays were mixed in a 1 l, closed stainless steel container for 24 h at 60 °C by gentle stirring. The polyol-clay blend was cooled to room temperature, kept in an environmental chamber along with other ingredients and isocyanate for 1 h, to achieve a temperature of 23 ± 1 °C. The foaming agents were mixed with the polyol-clay blend for 15 s, by stirring at 2500 rpm. This resultant mixture was then added to a specific amount of isocyanate and stirred at a speed of 3000 rpm, for 7 s. The reacting mixture was immediately poured into a stainless steel mould of dimension $40 \times 40 \times 10$ cm^3 and the mould was quickly closed. The mould was opened after 5 min and the foam was removed. The foams were allowed to cure for 2 days at room temperature. The foams thus produced were pyrolysed in an inert atmosphere as follows. One gram of *p*-toluene sulphonic acid was dissolved in 70 ml of acetone. A small piece of the precursor foam was dipped in this solution for about 2 min. The foam was taken out and the excess acetone was removed by compression against a wooden board. After drying in air for 15 min and in oven for 1 h at 100 °C, the foam was taken and dipped into 100 ml furfuryl alcohol for about 2 min. The foam was taken out and the furfuryl alcohol inside the foam was polymerized by heating to 100 °C for 20 h. Pyrolysis of the foam was carried out in a tubular furnace under argon atmosphere at 900 °C for 2 h to obtain the RVC.

2.2. Characterization

The dispersion of clay in PU matrix was investigated using wide angle X-ray diffraction (Cu-K$_\alpha$ rays of wavelength 1.54 Å) using an X-ray diffractometer (X'Pert Pro, PANalytical). The fraction of open cells in the precursor foam was measured from ESEM micrographs and the cell window areas were obtained by analyzing the ESEM images by using an image analysis software (Image Pro Plus). The cell morphology and cell window area of the final carbon foam was also obtained by using ESEM and was analysed by the same image analysis software. The cell windows were designated as open, closed, partially open and with pin holes [15]. Around 100 cell windows per sample were counted. The effective fraction of open cells in precursor foam was measured by the technique proposed by Yasunaga et al. [15] and was calculated as

$$P_{eff} = \frac{N_{open} + 0.5\,N_{partial}}{N_{open} + N_{closed} + N_{pin} + N_{partial}}$$

where, N_{open} is the number of open cells, N_{closed} is the number of closed cells, $N_{partial}$ is the number of partially opened cells and N_{pin} is the number of pin holes. Analysis of the elemental composition of the carbon foam

was done by EDAX (FEI Quanta). The crystalline structure of the carbon foams was investigated by wide angle XRD. The electrical resistivity of the carbon foam was measured by two probe method. In this, all the foams were cut and machined to cubical pieces of dimension $1 \times 1 \times 1$ cm^3. Two opposite flat surfaces of the material were completely coated with silver paste and the two metallic probes were contacted at the centre of the surface. The resistance was measured using a digital multimeter (HP-344014).

3. Results and discussion

Fig. 1(a) shows the wide angle X-ray diffraction patterns of PU foam, clay and the composite. The results indicate an intercalated structure, in which the d-spacing (d 0 0 1 plane) of clay is increased from 12.8 Å in its natural state to 17.1 Å in the clay polyurethane composite with 3 pphp (parts per hundred parts of polyol by weight) clay. The wide angle X-ray diffraction patterns, for carbon foam without clay and the carbon foam with 3 pphp clay in the precursor are shown in Fig. 1(b). The results indicate that the structure of the carbon foam is turbostratic with some graphitic sheet content, which is not altered upon clay addition. The intercalated peaks of clay disappear in these figures owing to the collapse of tactoids at high pyrolysis temperatures (∼900 °C). EDAX analysis (Fig. 2) shows the elemental composition of the carbon foams. The carbon foam without clay in the precursor PU foam
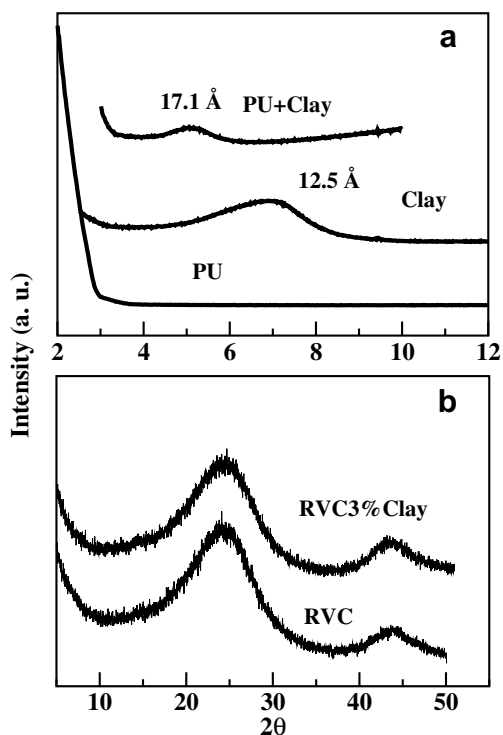

Fig. 1. (a) XRD pattern of polyurethane precursor foam (PU) and the polyurethane clay composite with Cloisite Na$^+$ (PU+Clay). The XRD pattern for Cloisite Na$^+$ (clay) is also shown. (b) XRD patterns of RVC foams obtained from polyurethane foam precursor and its composite with clay.
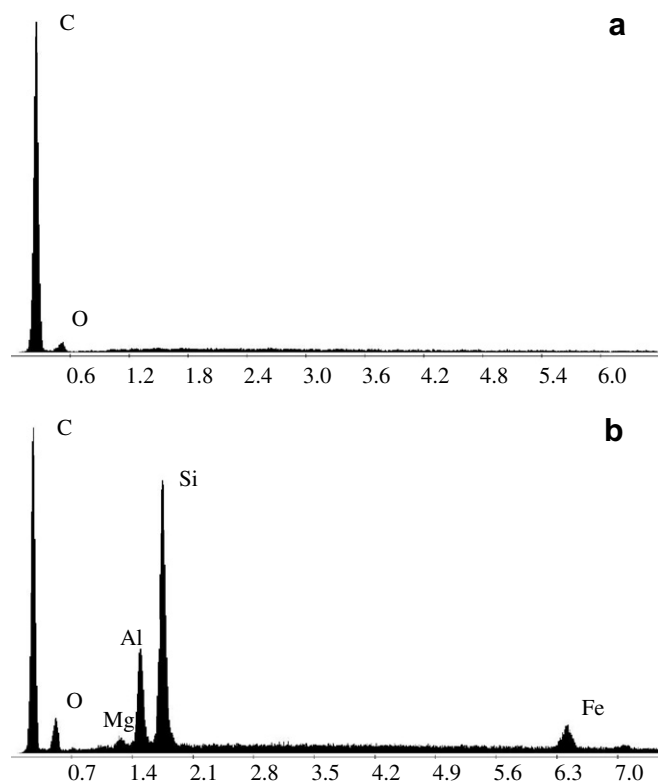
Fig. 2. EDAX scans of RVC. (a) RVC from open cell precursor foam having no clay in it. (b) RVC from open cell precursor foam having 3% clay in it.

shows only carbon whereas the one with clay in the precursor foam shows presence of aluminium, silicon and iron which are the remnants of pyrolysis of clay, which is an aluminosilicate.

The cellular structures of the precursor foams made without clay and with various amounts of clays are shown in Fig. 3. The structure of both foams looks similar. The cellular structures of the carbon foams made from precursor PU foams having no clay and having various amounts of clay are also shown in Fig. 3. It is evident from the figure that the cell size of the carbon foam made from composite foam precursor is smaller than that of carbon foam made from pure PU foam. Also the cells are more uniform in size in the carbon foam made from composite PU precursor foam. Comparing various sub-figures in Fig. 3, it is clear

that the size of the RVC cells is much larger than the precursor PU foam that has no clay. In contrast, the cell size increase on carbonization is comparatively lower for the polyurethane – clay composite precursor foam. This is also evident from the measured cell window areas, an indicator of cell sizes (Table 1) as discussed below.

Table 1 gives the physical characteristics of the precursor foams and the RVCs and the electrical resistivity of the RVCs. The fraction of open cells in the precursor increases with clay content, as reported previously [14]. The mean cell window area decreases with increasing clay content for both precursor foam and RVC (Table 1). The pores per inch (ppi) also increase with clay content for RVC. Further, there is a significant increase in the cell window area when the precursor foam is carbonized to form RVC, at each clay concentration. The increase in cell window area upon carbonization is lower at higher clay content. The above results indicate that the mean cell sizes decrease for both precursor and RVC with increasing clay content and the increase in mean cell size upon carbonization decreases with increasing clay content. The decrease in cell size of the precursor foam with increasing clay content indicates that clay promotes gas bubble nucleation during foaming [16]. This may be also due to the greater number of bubbles dispersed during mixing due to the higher polyol viscosity at higher clay content. More open cells in the precursor foams with higher clay loading result in a smaller increase in cell size upon carbonization. Even though the precursor foam volume shrinks on carbonization, the cell size increases after pyrolysis. This is due to the fact that many of the struts (structural elements separating cells of PU foam) get broken due to the high temperature of pyrolysis, effectively coalescing cells, resulting in coarser cells. If the cells are closed, the struts are not properly coated by the thermosetting resin, which makes the struts vulnerable to breakage at high temperatures. Open cells enable the resin to coat the struts uniformly thus preventing their rupture.

The density of the carbon foam increases with increasing clay content in the precursor foam (Table 1). This is essentially because of a greater infusion of furfuryl alcohol in the foam with a higher fraction of open cells resulting in a lower mass loss. The percentage shrinkage in volume of the foam after carbonization (Table 1) reduces with increasing clay content in the precursor foam. The lower

Table 1
Properties of precursor foam (PU) and RVC

Clay (pphp[a])	Clay in foam (wt.%)	Open cells (%)	Cell window area (mm^2)		Porosity (ppi)	Density (g/cm^3)	Volume shrinkage (%)	Sp. resistivity Ω cm $\pm$ 10%
Polyol	PU	PU	PU	RVC	RVC	RVC	RVC	RVC
0	0	0.56	0.0152 ± 0.005	0.55 ± 0.32	26 ± 6	0.49	58.26	0.48
1	0.6	0.60	0.0123 ± 0.002	0.33 ± 0.18	41 ± 5	0.51	52.98	0.38
2	1.2	0.64	0.0173 ± 0.005	0.11 ± 0.05	54 ± 4	0.60	50.25	0.35
3	1.8	0.72	0.0082 ± 0.004	0.09 ± 0.04	58 ± 2	0.71	49.65	0.27
4	2.4	0.81	0.0059 ± 0.005	0.03 ± 0.01	78 ± 2	0.87	46.66	0.22

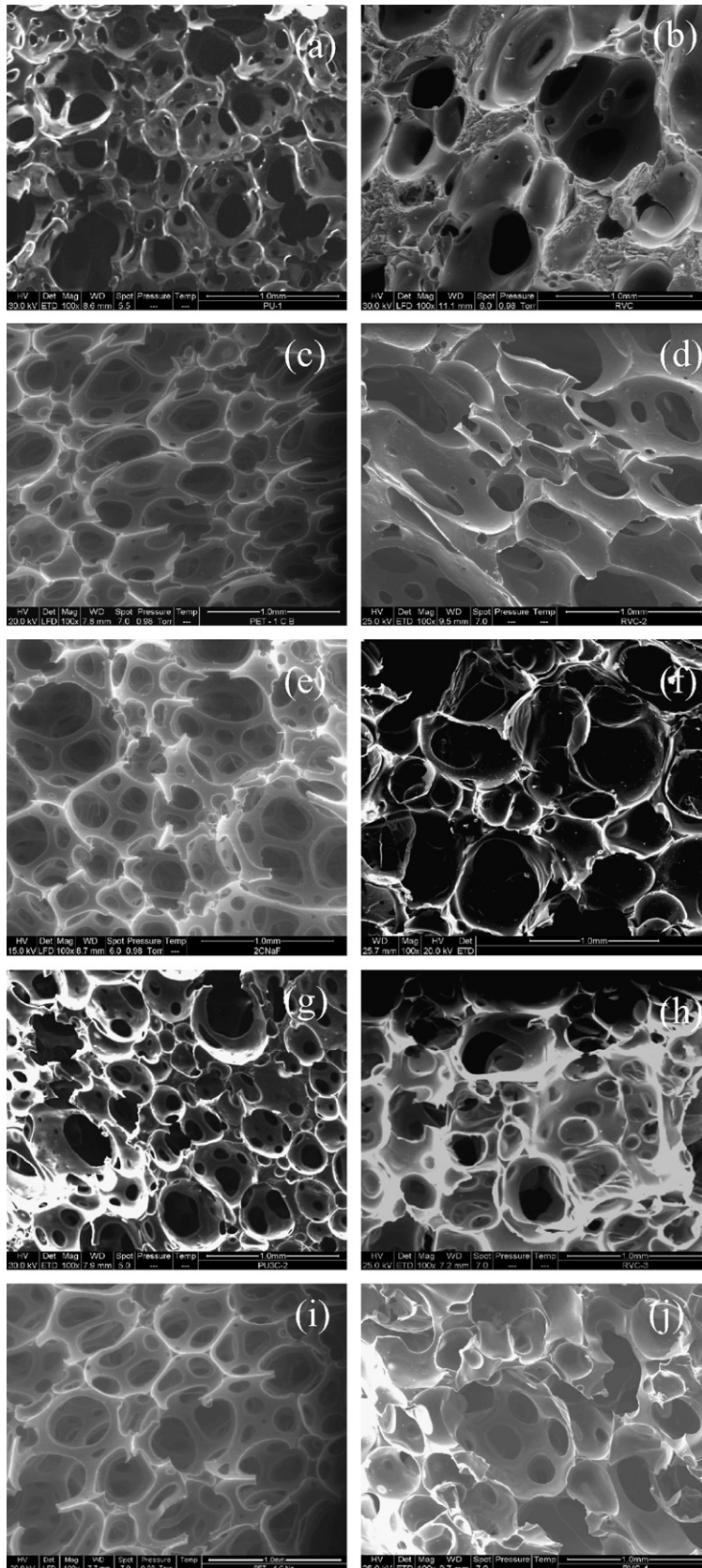[a] pphp = parts per hundred parts of polyol.

Fig. 3. SEM micrographs of precursor polyurethane foams and RVC. (a) PU foam having no clay. (b) RVC from PU foam having no clay (c) PU foam having 1 pphp clay. (d) RVC from PU foam having 1 pphp clay. (e) PU foam having 2 pphp clay. (f) RVC from PU foam having 2 pphp clay. (g) PU foam having 3 pphp clay. (h) RVC from PU foam having 3 pphp clay. (i) PU foam having 4 pphp clay. (j) RVC from PU foam having 4 pphp clay.

volume shrinkage is due to the better infusion of furfuryl alcohol through the greater number of open cells in the precursor foams with higher clay content.

The electrical resistivity of the foam decreases with increasing clay content (Table 1). The primary reason for increase in electrical conductivity of the RVC appears to be due to the increase in RVC density. Zahiri et al. [17] also found that the electrical conductivity increases with foam density.

4. Conclusions

Reticulated vitreous carbon foams have been synthesized by carbonizing clay-composites of open cell polyurethane foams infused with furfuryl alcohol. The combined nucleating and cell opening capacity of the clay in the precursor foam, reduces the cell size providing an effective way to control the cell size of the RVC, thus allowing for various grades. Open cells also result in improved infusion of furfuryl alcohol and thus higher densities of RVC. The resultant RVC foam has been found to have lower a electrical resistivity making the foam more suitable to be used as an electrode material.

Acknowledgements

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