View Online

Expanding the potential for waste polyvinyl-alcohol†

Andrew J. Hunt, Vitaly L. Budarin, Simon W. Breeden, Avtar S. Matharu and James H. Clark*

Received 3rd April 2009, Accepted 26th May 2009
First published as an Advance Article on the web 12th June 2009
DOI: 10.1039/b906607a

Downloaded by City College of New York on 22 November 2010
Published on 12 June 2009 on http://pubs.rsc.org | doi:10.1039/B906607A

Expanded polyvinyl-alcohol (PVA) was successfully prepared using a similar process to that of starch expansion. The addition of an iodine solution was necessary to facilitate expansion and led to surface areas of up to 143.1 m^2 g^{-1}. The use of recycled material from LCD screens required no additional iodine and produced an expanded material with high surface areas (95.0 m^2 g^{-1}) and total pore volumes (0.56 cm^3 g^{-1}). The PVA–iodine complexes were found to better mimic the interactions between amylose and amylopectin in starch expansion.

Introduction

Polyvinyl-alcohol (PVA) is a versatile, environmentally-benign and readily available commercial polymer.[1] Global consumption of PVA exceeded one million metric tons in 2006.[1] PVA is used in a multitude of applications ranging from adhesives to state-of-the-art large area liquid crystal display (LCD) televisions.[1] As many consumer goods reach their end of life, PVA is becoming more evident in the polymer waste stream, but applications of this waste material are limited.

LCDs are fast becoming a rich source of PVA consumption. PVA is extensively used in polarizing films that are applied to the front and rear glass surfaces of an LCD panel. The PVA is doped with iodine and usually trapped between two sheets of triacetyl cellulose protective polymer. LCD sales revenues topped $100 billion in 2008 and are forecast to reach a staggering $150 billion by 2012.[2] The phenomenal success of LCDs during the last decade has also led to a noticeable amount of LCDs entering in the waste electrical and electronic equipment (WEEE) waste stream. It is estimated that 2.5 billion LCDs are approaching their end of life and LCD WEEE is the fastest growing waste stream in the European Union.[2] LCD recycling is a global concern as many contain mercury backlights.[2] In 2002, the European Parliament and the Council on waste electrical and electronic equipment passed the WEEE directive 2002/96/EC, which essentially requires LCDs with an area greater than 100 cm^2, and those containing mercury backlights, to be disassembled prior to incineration or land-filling.[3] Currently, the LCD panel comprising glass, liquid crystal and PVA-impregnated polarising films is sent for incineration or land-fill.[2]

Interestingly, due to the inherent biocompatibility of PVA, it may be ideally suited as support material for enzyme immobilisation, tissue scaffolds and as drug delivery systems.[4] Such applications require high substrate surface area, which may be achieved through a process of expansion that is already used for naturally-derived starch to achieve surface areas of 180 m^2 g^{-1}.[5] The expansion of starch involves three stages: gelatinisation, retrogradation and dehydration *via* solvent exchange, during which the amylose and amylopectin polymer chains re-organise in to a largely, mesoporous structure.[6] To the best of our knowledge, this expansion process has not been applied to a synthetically-derived polymer, such as PVA.

Herein, we investigate the expansion of synthetically-derived PVA mimicking the procedures used for the expansion of starch as a potential high surface area substrate. We demonstrate that the expansion process can be applied to both virgin PVA and PVA isolated from polarising films of waste LCD panels. We also show that addition of iodine to virgin PVA is essential in changing the micro-structure of PVA and, thereby, allowing expansion to take place.

Experimental

Starting material

The PVA from LCD screens was prepared by soaking the polarising film in warm water (50–60 °C) for 30 minutes, after which the triacetyl cellulose outer layers were separated to reveal the inner PVA layer. The resulting PVA film was dried in a vacuum oven at 40 °C for 12 hours. Other reagents including iodine, potassium iodide and virgin PVA (average *Mw* 18 000–23 000) were purchased from Sigma-Aldrich. Ethanol (96%) was obtained from Fischer Scientific.

Preparation of expanded PVA from virgin material

PVA (average *Mw* 18 000–23 000; 200 mg) and distilled water (4 ml) were added to a 7.5 mL laboratory microwave reaction vessel (CEM Discovery model), sealed and irradiated at 180 °C for 10 minutes. On completion, an aqueous solution of I_2/KI (1 ml, 0.1 mol dm^{-3}/0.3 mol dm^{-3}) was added to the warm PVA solution. The PVA/iodine solution was allowed to retrograde at 4 °C for 12 hours, added to ethanol (100 ml) and stirred for 3 hours. The resulting PVA/iodine precipitate was isolated, solvent exchanged with ethanol and dried in a vacuum oven at 40 °C for 12 hours, as previously reported for starch.[6]

Department of Chemistry, The University of York, Heslington, York, UK. E-mail: jhc1@york.ac.uk; Fax: +44 (0)1904 432705; Tel: +44 (0)1904 432559

† The authors would like to acknowledge the partners of project REFLATE for providing defunct LCD screens for this project and Berr for their financial support.

This journal is © The Royal Society of Chemistry 2009

View Online

Published on 12 June 2009 on http://pubs.rsc.org | doi:10.1039/B906607A
Downloaded by City College of New York on 22 November 2010

Preparation of expanded PVA from waste PVA

LCD PVA film (200 mg) and distilled water (4 ml) were added to a 7.5 mL CEM microwave reaction vessel, sealed and irradiated at 180 °C for 10 minutes. The sample was then irradiated at 180 °C for 10 minutes. The PVA/iodine solution was allowed to retrograde at 4 °C for 12 hours, added to ethanol (100 ml) and stirred for 3 hours. The resulting PVA/iodine precipitate was isolated, solvent exchanged with ethanol and dried in a vacuum oven at 40 °C for 12 hours, as previously reported for starch.[6]

Material characterisation

Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2010 instrument at 77 K. Samples were outgassed at 50 °C for 6 h under vacuum ($p < 10^{-2}$ Pa) and subsequently analysed. The linear part of the BET equation (relative pressure between 0.05 and 0.22) was used for the determination of the specific surface area. The pore size distribution was calculated from the adsorption branch of the N_2 physisorption isotherms and the Barret–Joyner–Halenda (BJH) formula.[7] The characteristic energy of adsorption (E_{DA}) was calculated from the Dubinin–Astakhov adsorption isotherm equation.[8]

Samples were viewed using a scanning electron microscope Hitachi S-2400. Samples were Au coated on a high resolution sputter SC7640 at a sputtering rate of 1500 V min^{-1}, up to a 7 nm thickness.

Results and discussion

The use of iodine in the expansion of virgin PVA

Fig. 1 and Table 1 summarise the influence of experimental conditions on textural properties of expanded virgin PVA. Gelatinisation of PVA at 180 °C without retrogradation gave low surface areas (15.2 m^2 g^{-1}, Table 1 PVA 1, Fig. 1). When the process was repeated with a 6 hour retrogradation period, the surface area of the material increased (24.1 m^2 g^{-1}, Table 1 PVA 2, Fig. 1); however, this is still significantly less than expanded starches.[6] Retrogradation results in increasing the sample's crystallinity and thereby aids in forming mesoporous structures.[6]

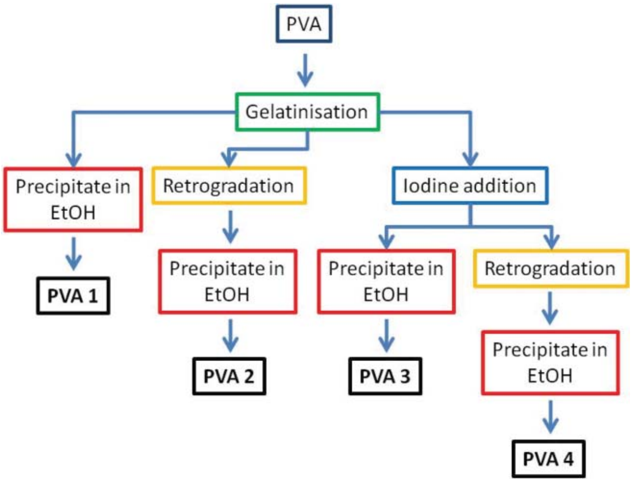

Fig. 1 Expansion conditions.

Table 1 Porosimetry data for expanded PVA both with and without iodine

	PVA 1	PVA 2	PVA 3^b	PVA 4^c
S_{BET}/m^2 g^{-1}	15.2	24.1	12.4	87.2
Microporous volume/cm^3 g^{-1a}	0.008	0.013	0.007	0.05
Adsorption average pore diameter/nm	8.7	6.8	9.5	7.3
Total pore volume/cm^3 g^{-1}	0.07	0.08	0.06	0.33
Micro/mesoporous ratio	0.11	0.16	0.12	0.15
E_{DA}/kJ mol^{-1a}	7.8	7.6	8.0	7.6

[a] Calculated through the Dubinin–Astakhov model. [b] Addition of a 1 ml (0.1 mol^{-1} dm^{-3} I_2/0.3 mol^{-1} dm^{-3} KI) solution, followed by precipitation in ethanol. [c] Addition of a 1 ml (0.1 mol^{-1} dm^{-3} I_2/0.3 mol^{-1} dm^{-3} KI) solution, followed by 6 hours retrogradation and precipitation in ethanol.

One possibility to increase the structural organisation of the virgin PVA solution is by the addition of iodine.

It is well known that iodine forms a blue coloured complex with polymers, including starch and PVA.[9] Two structural models have been proposed, the helical and aggregation models.[10,11] Although there is still some discussion over the actual nature of this complex, there is little dispute that linear polyiodine ions such as I_3^- and I_5^- are formed due to interactions of iodine with free hydroxyl groups of PVA unused in the formation of intermolecular hydrogen bonds.[12] One possibility is that two networks are formed, a PVA polymer chain network and a fibril network.[13] It has been suggested that microfibrils consist of crystalline lamellar and amorphous regions alternatively stacked between these microfibrils. It is believed that amorphous layers in the lamellar structure contain tie chains that interconnect the crystallite and, as such, PVA–iodine complexes act as junction points between PVA microfibrils in the network.[13] The resulting effect of forming PVA–iodine complexes is that they contribute to the structuring of the microfibrillar network. As such, the formation of PVA–iodine complexes is believed to better mimic the restructuring that occurs during retrogradation in the starch expansion process.

Therefore, iodine was added to two virgin PVA solutions immediately after microwave heating, in an attempt to improve the surface area and better mimic the structural changes that occur in starch expansion. The first PVA–iodine solution was immediately precipitated in ethanol forming a yellow material with low surface area (12.4 m^{2}g^{-1}, Table 1 PVA 3, Fig. 1). The second PVA–iodine solution was retrograded for 6 hours, thereby forming a dark blue gel indicative of a PVA–iodine complex.[9] The resulting gel was precipitated in ethanol yielding a blue material possessing enhanced surface areas (87.2 m^2 g^{-1}, Table 1), total pore volumes (0.33 cm^3 g^{-1}, Table 1), greater microporosity and improved mesoporosity (PVA 4, Fig. 1).

Influence of preparation time and temperature

It was found that as the temperature of gelatinisation increased so did too the surface area of the material (Fig. 2A). The greatest BET surface areas were observed for samples heated at 180 °C with a 12 hour retrogradation (116 m^2 g^{-1}, Fig. 2A). Samples

Downloaded by City College of New York on 22 November 2010
Published on 12 June 2009 on http://pubs.rsc.org | doi:10.1039/B906607A

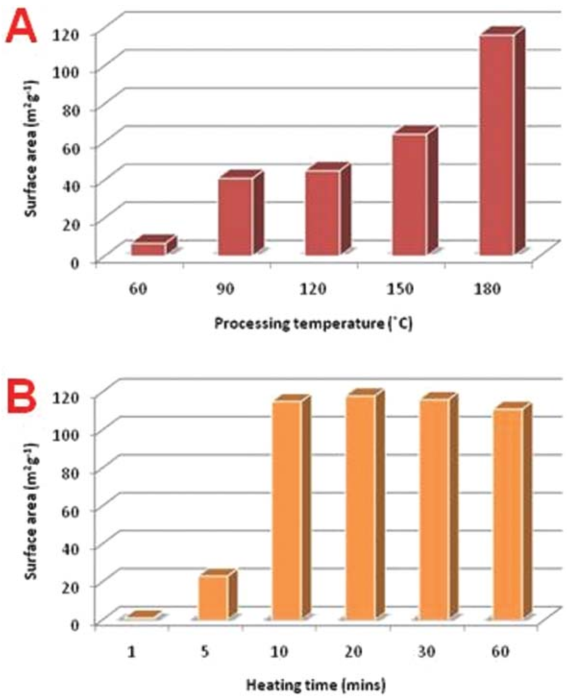

Fig. 2 (A) Effect of gelatinisation temperature on expansion. (B) Effect of gelatinisation time on expansion (180 °C).

heated at only 60 °C did not completely dissolve, this was also observed for samples that were heated in the microwave at 180 °C for less than 5 minutes. Microwaving for 10 minutes was sufficient and minimised energy consumption (Fig. 2B).

Retrogradation

The retrogradation process was found to be enhanced at lower temperatures (Fig. 3A), optimal retrogradation temperature was found to be similar to that of starch (4 °C). Samples were held at the retrogradation temperatures for 1 hour. The colour of the material on addition of ethanol (ranging from dark blue at 4 °C to yellow at 50 °C) was a qualitative indicator of the surface area, with darker blue samples having greater surface areas (Fig. 3B).

Interestingly, the time needed for the PVA retrogradation was shorter than that of high amylose corn starch. Amylose can retrograde in hours although the more complex chains of amylopectin require longer retrogradation times. Typically, the retrogradation time for this starch is 48 hours; however, in PVA, this process is completed within 12 hours (Fig. 3C).

Solvent exchange

Solvent exchange is needed to dehydrate the material, whilst avoiding collapse of the material on drying. Increasing the number of ethanol washes up to three had a positive effect on the surface area (Fig. 4A). However, further solvent exchanges had a negative effect on the surface area.

It is known that propanol can bond to hydroxyl groups in PVA, thereby disrupting the intermolecular hydrogen bonds and inhibiting gel formation.[12] As PVA–iodine complex formation is dependent on formation of aggregates, it is possible that addition of an excess of ethanol in solvent exchanging would disrupt the micro-structure in PVA and therefore hinder expansion. Initially, longer polyiodine chains such as I_5^- are formed in the PVA–iodine complex. On exposure to an aqueous alcoholic solution, these I_5^- chains are broken down to form shorter I_3^- chains, in good agreement with the colour changes of the material (from blue to purple to pink) during solvent exchanging (Fig. 4B). The use of a polar aprotic solvent, such as acetone, as an exchange solvent led to a substantial loss in surface area.

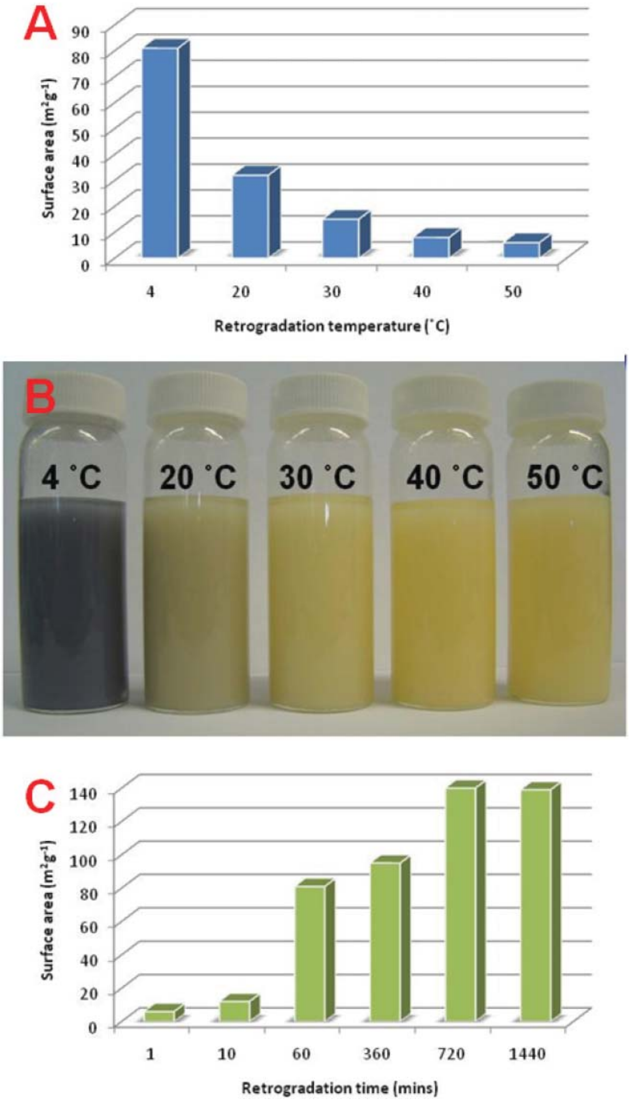

Fig. 3 (A) Effect of retrogradation temperature on PVA expansion. (B) A photograph of resulting materials post retrogradation. (C) Effect of retrogradation time on PVA expansion.

Optimised expansion and recycled PVA

By combining the knowledge of the three expansion stages, it was possible to optimise the material manufactured to give an expanded virgin PVA sample of 143.1 m^2 g^{-1} (Table 2).

These optimised conditions are: heating by microwave irradiation at 180 °C for ten minutes, addition of iodine solution and retrogradation at 4 °C for 12 hours followed by precipitation in ethanol and three ethanol solvent exchanges. This led to the formation of a synthetic polymer with similar porous structure to that of expanded starch.

This journal is © The Royal Society of Chemistry 2009

View Online

Downloaded by City College of New York on 22 November 2010
Published on 12 June 2009 on http://pubs.rsc.org | doi:10.1039/B906607A

Table 2 Porosimetry data for the expansion of LCD PVA and optimised expansion of virgin PVA

	Expanded PVA	LCD PVA
S_{BET}/m^2 g^{-1}	143.1	95.0
Microporous volume/cm^3 g^{-1a}	0.09	0.05
Average pore diameter adsorption/nm	6.9	11.7
Total pore volume/cm^3 g^{-1}	0.47	0.56
Micro/mesoporous ratio	0.19	0.09
E_{DA}/kJ mol^{-1a}	6.2	7.5

[a] Calculated through the Dubinin–Astakhov model.

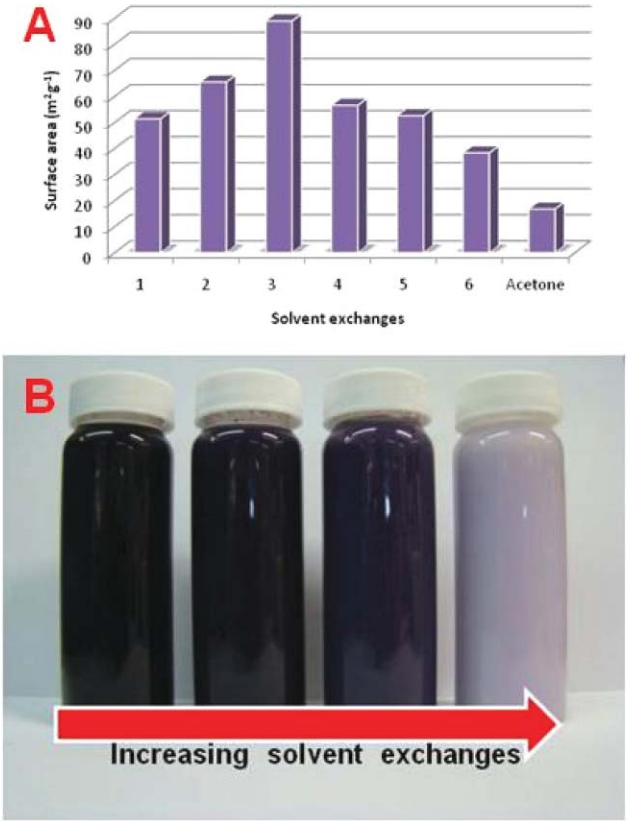

Fig. 4 (A) Effect of solvent exchanging on the expansion of PVA. (B) Photograph of resulting materials during solvent exchanging.

The use of waste LCD polarisers may provide a cheap and abundant source of PVA, which already contains the iodine essential for expansion. On applying the optimised expansion conditions to LCD PVA, it was possible to obtain an expanded form of the material with no need for additional iodine solution. Porosity measurements of the LCD expanded material (Table 2) gave a surface area of 95.0 m^2 g^{-1}. The adsorption isotherms for both the virgin and recycled materials are of type V in the IUPAC classification (Fig. 5A).[14]

The isotherm for the recycled material shows a greater total pore volume, but a larger average pore diameter compared to that of the expanded virgin PVA. The porous distributions of the two materials are similar, although there are differences in the mesoporous region (Fig. 5B).

The LCD expanded PVA appears to be lamellar like with several thin sheets or layers of film on top of each other (Fig. 6B). These sheet/film features are not seen in the material prepared from virgin PVA, which predominantly comprises large agglomerates formed from smaller particles (Fig. 5A). However, the expanded recycled PVA retains some properties of the original film and both materials show a porous surface texture (Fig. 6).

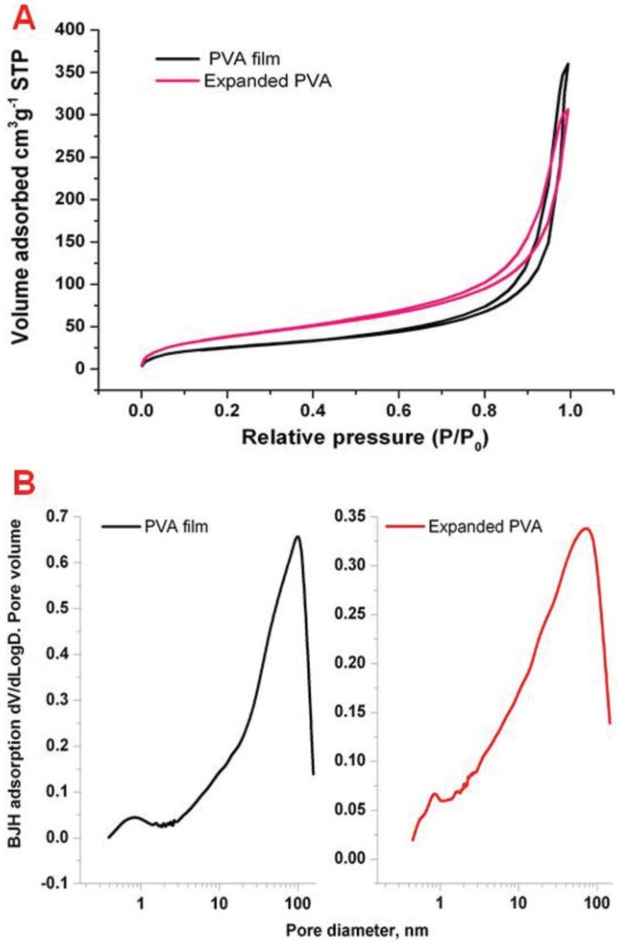

Fig. 5 (A) Adsorption isotherms and (B) porous distributions for expanded virgin PVA and LCD PVA.

Conclusions

The waste electrical and electronic equipment (WEEE) directive places a responsibility on the manufacturer to take back their goods and to disassemble prior to disposal. Liquid crystal displays represent a significant and rapidly increasing proportion of this waste and, as such, utilisation of any of this waste stream is of both environmental and commercial interest. We have developed a process that modifies the low value PVA contained in this waste to produce a structured mesoporous material with high surface areas. We have shown that it is possible to expand virgin PVA using a similar process to that of starch expansion. The addition of an iodine solution was necessary to facilitate micro-structuring of the PVA, resulting in materials of increased surface areas (up to 143.1 m^2 g^{-1}). The use of recycled material from LCD screens requires no additional iodine and produces an expanded material with high surface areas (95.0 m^2 g^{-1}) and total pore volumes (0.56 cm^3 g^{-1}). These materials may find use in

View Online

Downloaded by City College of New York on 22 November 2010
Published on 12 June 2009 on http://pubs.rsc.org | doi:10.1039/B906607A

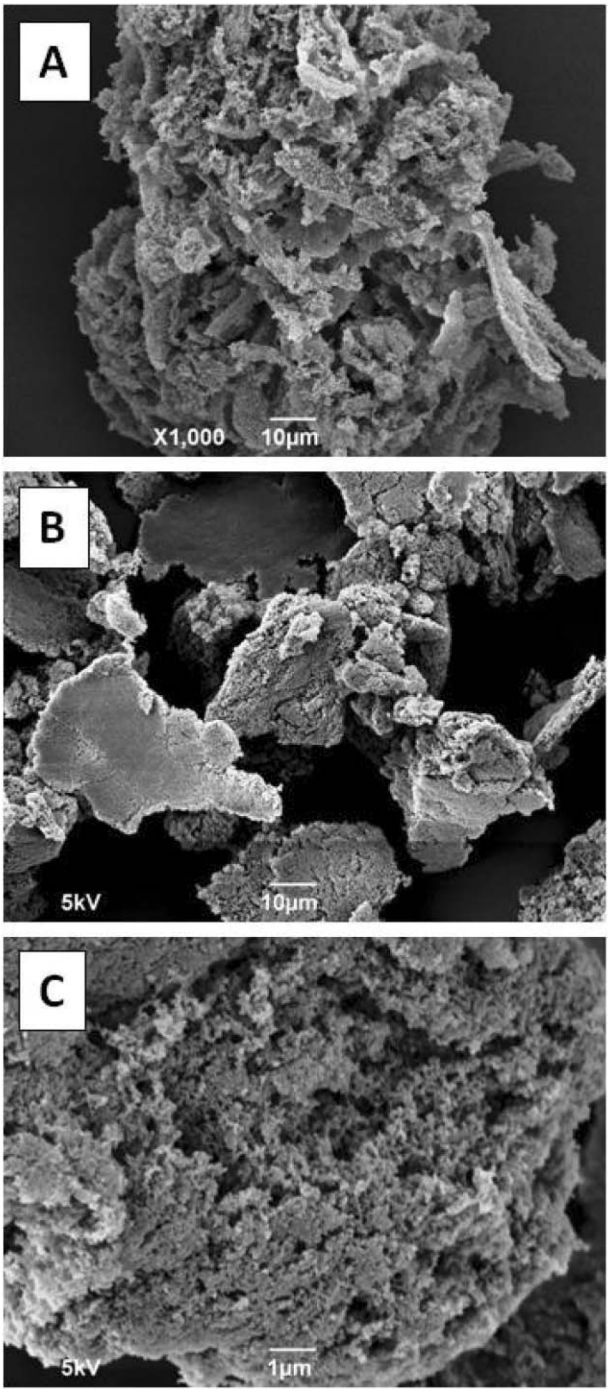

Fig. 6 SEM images of (A) virgin expanded PVA (10 μm). (B) Expanded PVA from waste LCD (10 μm) and (C) expanded PVA from waste LCD (1 μm).

a wide range of applications, in particular as tissue scaffolds, due to the high surface area and compatibility of both PVA/iodine (required for the expansion process) with the human body. The effect of additives and small molecules present in recycled material is the subject of continued investigation with regard to their use in biomedical applications.

Notes and references

1 (*a*) I. Sakurada, in *Polyvinyl alcohol fibers*, Marcel Dekker, New York, 1985; (*b*) H. Chinn, Y. Inoguchi and U. Loechner, *SRI Consulting CEH Report Polyvinyl Alcohol*, 2007, Menlo Park, California; (*c*) E. Chiellini, A. Corti, S. D'Antone and R. Solaro, *Prog. Polym. Sci.*, 2003, **28**, 963.

2 (*a*) A. S. Matharu, Y. Wu, in *Electronic Waste Management, Issues in Environmental Science and Technology*, ed. R. E. Hester and R. M. Harrison, RSC Publishing, Cambridge UK, 2008, 26; (*b*) R. Martin, B. Simon-Hettich, W. Becker, *Safe recovery of liquid crystal displays (LCDs) in compliance with WEEE*, Electronics goes green 2004+, Berlin, 2004.

3 Union, T.E.P.a.t.C.o.t.E., *WEEE – Directive 2002/96/EC of the European Parliament and of the Council*, 2007.

4 (*a*) L. Wu, X. Yuan and J. Sheng, *J. Membr.Sci.*, 2005, **250**, 167–173; (*b*) C. R. Nutterman, S. M. Henry and K. S. Anseth, *Biomaterials*, 2002, **23**, 3617–3626; (*c*) J. Drobnik, *Adv. Drug Del. Rev.*, 1989, **3**, 229–245.

5 (*a*) M. Glen, D. J. Stern, *US Pat.* 5,958,589, 1999; (*b*) S. Doi, J. H. Clark, D. J. Macquarrie and K. Milkowski, *Chem. Commun.*, 2002, **22**, 2632; (*c*) V. Budarin, J. H. Clark, F. E. I. Deswarte, J. J. E. Hardy, A. J. Hunt and F. M Kerton, *Chem. Commun.*, 2005, 2903; (*d*) J. H. Clark, F. E. I. Deswarte, J. J. E. Hardy, A. J. Hunt, F. M. Kerton, K. Milkowski, *PCT Patent Application*, PCT/GB2004/003276; (*e*) R. J. White, V. L. Budarin and J. H. Clark, *ChemSusChem*, 2008, **1**, 408–411.

6 P. Calvert, *Nature*, 1997, **389**, 338; D. R. Daniels and A. M. Donald, *Biopolymers*, 2003, **69**, 165; D. R. Daniels and A. M. Donald, *Macromolecules*, 2004, **37**, 1312–1318.

7 E. P. Barret, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.

8 S. G. Chen and R. T. Yang, *Langmuir*, 1994, **10**, 4244–4249.

9 (*a*) W. O. Herrmann and W. Haehnel, *Ber. Deutsch. Chem. Ges.*, 1927, **60**, 1658; (*b*) H. Staudinger, K. Frey and W. Starck, *Ber. Deutsch. Chem. Ges.*, 1927, **60**, 1782.

10 L. G. Teblev, G. F. Kikul'skii Ye, P. Korchagina and S. A. Glikman, *Vysokomol. Soedin, Ser. A.*, 1965, **7**, 1231.

11 M. M. Zwick, *J. Appl. Polym. Sci.*, 1965, **9**, 2393.

12 (*a*) H. Noguchi, H. Jodai and S. Matsuzawa, *J. Poly. Sci B*, 1997, **35**, 1701–1709; (*b*) H. Yang and F. Horii, *Polymer*, 2008, **49**, 785–791.

13 (*a*) K. Miyasaka, *Adv. Polym. Sci.*, 1993, **108**, 91; (*b*) T. Miyazaki, S. Katayama, E. Funai, Y. Tsuji and S. Sakurai, *Polymer*, 2005, **46**, 7436–7442; (*c*) H. Takamiya, Y. Tanahashi, T. Matsuyama, T. Tanigami, K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, 1993, **50**, 1807; (*d*) Y. Kojima, K. Furuhata and K. Miyasaka, *J. Appl. Polym. Sci.*, 1985, **30**, 1617; (*e*) T. Miyazaki, A. Hoshiko, M. Akasaka, M. Sakai, Y. Takeda and S. Sakurai, *Macromolecules*, 2007, **40**, 8277–8284; (*f*) T. Miyazaki, A. Hoshiko, M. Akasaka, T. Shintani and S. Sakurai, *Macromolecules*, 2006, **39**, 2921–2929.

14 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. Mc Eneaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633–2656.

This journal is © The Royal Society of Chemistry 2009