

Short communication

High-temperature, polymer–graphite hybrid composites for bipolar plates: Effect of processing conditions on electrical properties

S. Radhakrishnan*, B.T.S. Ramanujam, A. Adhikari, S. Sivaram

Polymer Science and Engineering, National Chemical Laboratory, Pune 411008, India

Received 24 April 2006; accepted 2 August 2006

Available online 13 November 2006

Abstract

High-temperature thermoplastic–graphite composites are prepared using polyphenylene sulfide (PPS) and polyether sulfone (PES) containing natural graphite powder. All samples are prepared by high pressure compaction and heating to high temperatures. The effect of a third additional conducting component on the electrical resistance of these composites is studied. A low resistance of the order of 0.1Ω can be obtained even for a graphite concentration of 50% by addition of the third component. The effect of a mixing/blending technique on the anisotropy of conductivity is investigated. Solution blending of PES with graphite leads to lower anisotropy values than powder mixing and compression moulding. The samples when exposed continuously to a working temperature of 100°C give a small but significant reduction in electrical resistance. X-ray diffraction studies on composites prepared by different techniques indicate that there is restructuring and crystallite re-orientation of the graphite phase in the samples. A large reduction in the crystallite size is observed for samples prepared by solution blending while re-orientation occurs after heat treatment. The changes in electrical properties can be correlated with these structural transformations in the composites.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Conducting polymer; Graphite composites; Bipolar plates; Polyether sulfone; Polyphenylene sulfide; Hybrid materials; Fuel cell

1. Introduction

Bipolar plates are important components of most types of fuel cell whether these are polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cell (DMFCs), or others [1–4]. Conventionally, bipolar plates are made from pure graphite sintered in the form of thick plates that are subsequently machined to form flow channels for hydrogen, methanol, water, etc. In the attempts to reduce the cost as well as the weight of the fuel cell, efforts have been made in recent years to use conducting polymer composites for the fabrication of bipolar plates [5,6]. A few reports mention composites using thermoset resins or bulk moulding compounds [7–9]. For faster and large scale production, however, melt processing such as injection moulding should be more effective.

For better processability by conventional techniques such as injection moulding or compression moulding, a thermoplastic compound with as low a concentration of the conducting graphite additive as possible is preferred. This depends

on the percolation threshold for a particular combination of graphite and the polymer matrix [10]. The polymer matrix is also expected to withstand high temperature and corrosive environments and is therefore chosen from high-temperature thermoplastics such as poly(phenylene sulfide) (PPS), poly(ether ether ketone) (PEEK) and poly(ether sulfone) (PES), or even a liquid crystalline polymer blended with the same [11,12]. In order to achieve optimum electrical properties for these polymer–graphite composites, it is essential to study not only the compositional dependence but also the effect of both processing conditions and continuous exposure to high temperature. This paper reports a study of PPS and PES–graphite composites. These indicate that new methodologies can be adopted to obtain high conductivity and low anisotropy at reasonable loading levels of the conducting additives.

2. Experimental

2.1. Materials

The polymers were commercial grade polyphenylene sulfide (PPS, Ryton V1, Phillips Petroleum, MFI 70) and poly(ether

* Corresponding author. Tel.: +91 20 25893300; fax: +91 20 25893041.
E-mail address: s.radhakrishnan@ncl.res.in (S. Radhakrishnan).

sulfone) (PES, Gafone 3600 P, Gharda Chemicals, India) and were used as such. Graphite was natural grade (better than 200 mesh size powder) obtained from Carbon Enterprises, India, and the carbon black was conducting grade supplied by Degussa, Germany. All the polymer materials were in powder form with particle sizes in the range of 20–25 μm , while the graphite and carbon black were much finer (<2.0 μm).

2.2. Composite blend preparation

Two methods were mainly adopted, namely, powder blending and solution blending, for the preparation of graphite containing PES formulations used in moulding the discs. In the former case, graphite powder in the desired amount was mixed thoroughly with the PES powder (passed through a 120 mesh sieve) in an agate pestle mortar for 1 h. This mix was dried by heating at 50 °C for 2 h prior to compression moulding. In the solution processing, 10 g of PES was completely dissolved in 100 ml of dichloromethane by constant stirring for 12 h in stoppered conical flask. The desired quantity of natural graphite powder was added to the solution and further stirred for 12 h. The mixture was then poured in a trough and the solvent allowed to evaporate so as to form lumps/cake that was washed to remove the solvent. The pieces were crushed, powdered, sieved through 100 mesh, dried at 50 °C for 8 h and finally placed under a vacuum (10^{-3} Torr) for a few hours so as to obtain the graphite–PES mix.

2.3. Compression moulding of discs

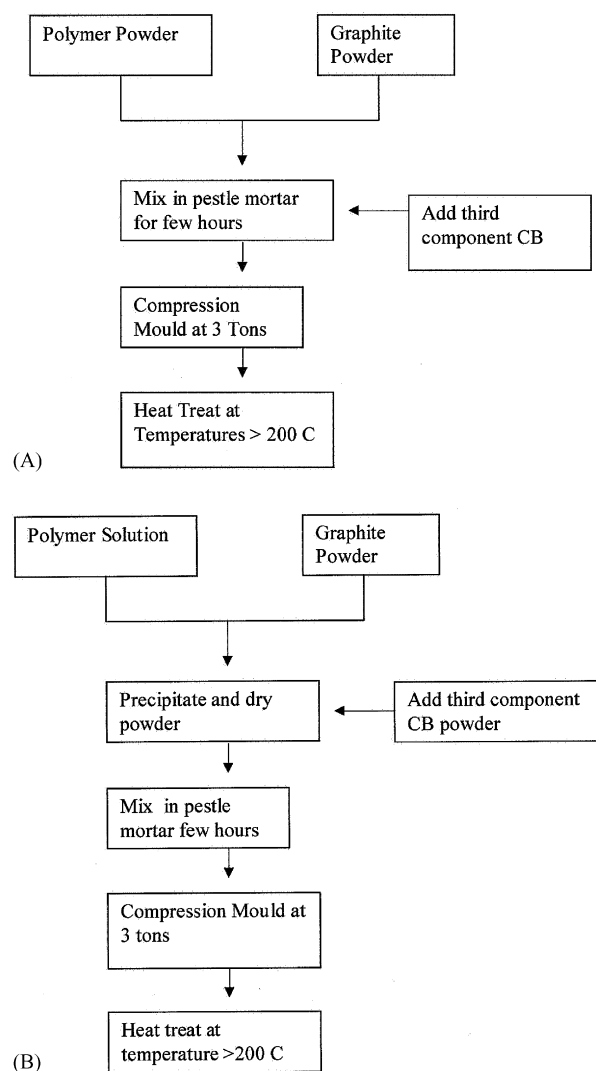
The dried powder (1.0 g) was compression moulded in a single-ended compaction stainless-steel die by applying 3000 kg pressure using a hydraulic press for 3.0 min. The discs (3.0 cm diameter, 1–1.2 mm thickness) were heated to 210 or 240 °C and held at this temperature for different periods that ranged from 1.0–6.0 h [13,14]. The whole process for making these composite discs is depicted in Scheme 1A and B.

2.4. Monitoring electrical and other properties

Samples were tested for electrical conductivity by measuring the resistance by means of a Keithley 6514 electrometer connected to platinum electrodes placed in two directions, viz., across the thickness and along the diameter of the circular disc specimen. The electrical properties were measured in a specially constructed sample holder with carbon cloth and platinum foil (1 cm^2) as contact electrodes and a constant applied pressure of 5 kg cm^{-2} . The structural changes taking place were monitored by recording wide-angle X-ray diffraction with a Philips Diffractometer (PW1780). The details of these measurements are described elsewhere [15–18].

3. Results and discussion

The PES–graphite composite samples obtained after moulding at 210 °C are not hard but easily breakable. By contrast, those obtained at 240 °C exhibit good stiffness, hardness and



Scheme 1.

shiny surfaces with practically no graphite rubbing off the surface. The solution blended PES–graphite (Scheme 1B) has a better surface finish than the powder blended composites.

The electrical conductivity of these discs was monitored with respect to composition, i.e., graphite concentration as well as the third component carbon black additive. Fig. 1 shows the electrical resistance in the perpendicular direction of PES–graphite composites both before and after addition of the third component, while Fig. 2 presents these values for PPS–graphite composites. In both cases, samples prepared by Scheme 1A the resistance decreases rapidly above graphite concentrations of 30 wt.% but a saturation is reached above 60% of graphite. On the other hand, the addition of a third conducting component such as fine carbon black leads to further improvement in electrical conductivity over and above that achieved at high graphite contents. Resistance values of 0.1 Ω are achievable by this method which is desirable for bipolar plates used in fuel cell applications [7,19,20].

The effect of preparation method on the anisotropy of the electrical resistance is indicated in Fig. 3. The anisotropy (defined as the ratio of electrical resistance in the perpendic-

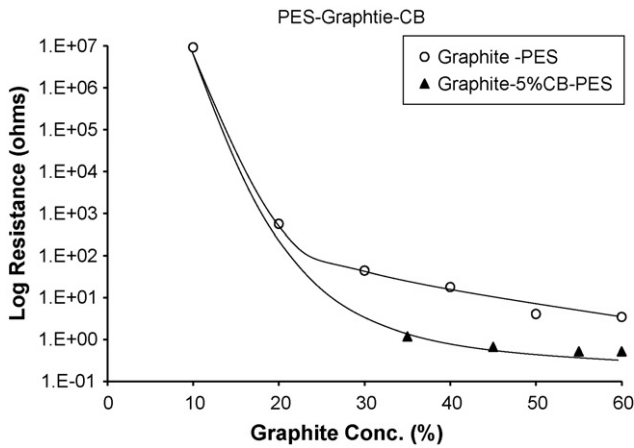


Fig. 1. Compositional dependence of electrical resistance of PES-graphite composite and effect of additional conducting carbon black (5 wt.%).

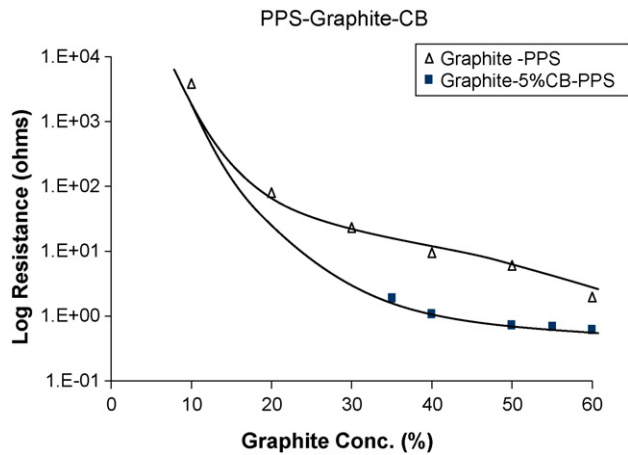


Fig. 2. Electrical resistance of PPS-graphite composites for different graphite concentrations with and without conducting carbon black (5 wt.%).

ular direction to that in the parallel) increases with increase in graphite concentration in the composite. Further, for the samples prepared by Scheme 1A, the anisotropy is higher than that prepared by Scheme 1B. In both cases, however the anisotropy becomes high when the graphite content is above 60%. It may be pointed out that the anisotropy in bonded/sintered graphite plates (>90% graphite) commercially supplied by a few manufacturers is of the order of two to three. In the present case, the

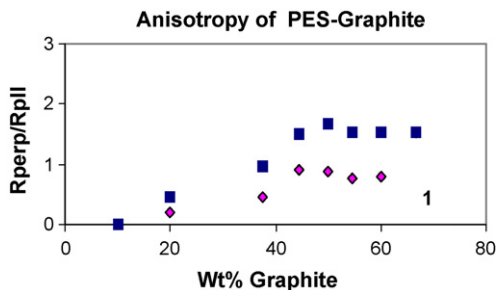


Fig. 3. Anisotropy of conductivity of PES-graphite composites prepared by: (1) solution blending and (2) powder mixing followed by compression moulding.

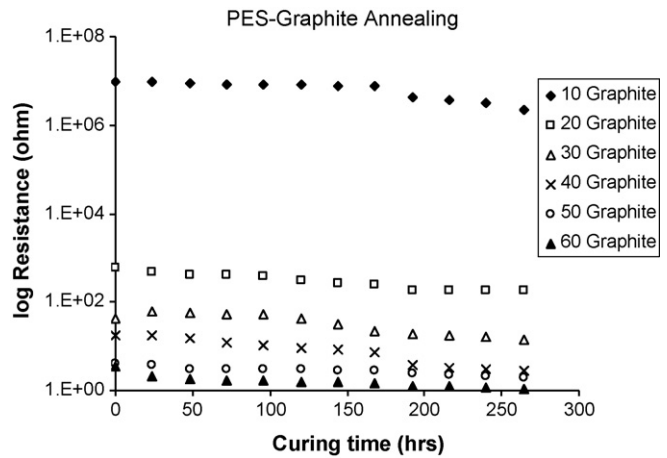


Fig. 4. Effect of continuous exposure to high temperature on electrical resistance of PES-graphite composite disc containing different concentrations of graphite.

anisotropy is much lower. These results are explained later in this paper on the basis of X-ray diffraction data.

The effect of continuous exposure to high temperatures (100 °C) on the electrical resistance of these PES- and PPS-based is shown in Figs. 4 and 5. It is interesting to note that most of these composites exhibit quite stable behaviour and in fact some show a small, but significant decrease in electrical resistance after 200 h. This is somewhat surprising since it is expected that the resistance will increase due to degradation, etc. It should be pointed out, however, that the polymers PES and PPS used in the present case are known to be very stable for up to at least 200 °C, their degradation temperatures are 370 and 400 °C, respectively [21]. Thus, the beneficial changes in electrical resistance in the present case have to be associated with internal morphological/structural changes in the composites.

It is quite well known that polymers can undergo slow deformation under long-term exposure to high temperature (above glass transition temperature) due to re-crystallization, creep, stress relaxation, etc. [22]. This can result in re-orientation of the filler/fibre in the matrix. Since electrical conduction of the composite is dependent on the inter-particulate distance of the

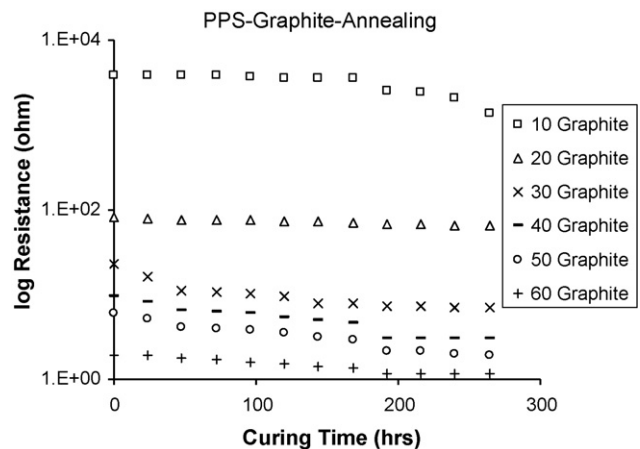


Fig. 5. Effect of high-temperature exposure on electrical resistance of PPS-graphite composite containing different concentrations of graphite.

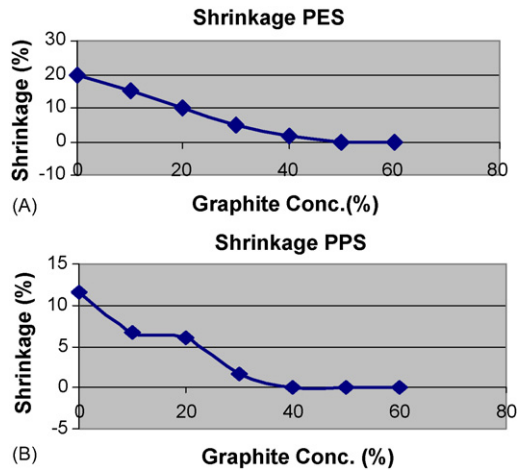


Fig. 6. Shrinkage in PES–graphite (A) and PPS–graphite (B) composite discs after heat treatment.

conducting phase, it is much more sensitive to small changes in this parameter than a mechanical property such as tensile modulus. Hence, significant changes in electrical conductivity are anticipated after prolonged annealing. The fact that the electrical resistivity decreases after this thermal treatment suggests that the filler particles are coming closer to each other rather than going apart. This is in agreement with the observations on shrinkage discussed later.

Fig. 6(A and B) depicts the changes in the physical dimensions of the samples in terms of shrinkage for PES and PPS graphite composites with composition after continuous heat treatment. For low graphite concentrations, there is a large change (>10%) in the degree of shrinkage, while for composites containing >45% of graphite the shrinkage is very low (<0.3%). It is further to be noted that PES–graphite composites have larger dimensional changes than PPS–graphite composites, and that these changes are mainly along the radial direction (parallel to surface) than the thickness. These observations are in keeping with the fact that PPS being semi-crystalline, it is rigid polymer while PES is amorphous and more flexible at higher temperatures above the glass transition temperature [23]. The former would be more dimensionally stable than the latter. At high graphite contents, however, the properties are governed mainly by the high rigidity/low creep due to a reinforcing effect and therefore there will be very little change in the dimensions in both these cases, as is seen in Fig. 6.

In order to investigate the internal structural changes occurring in these composites during and after processing, X-ray diffraction (XRD) studies were conducted. All the XRD scans are not shown here, rather only typical ones are included to bring out the changes that take place. Fig. 7 shows the XRD scan for powder mixed PPS–graphite composite, while Fig. 8(A and B) provides a comparison for PES–graphite composites prepared by powder mixing and solution blending techniques, respectively. The curves 1 and 2 in these figures represent the XRD pattern for samples before heat treatment and after heating to a high temperature. The high, intense sharp peak (002 reflection) of the graphite crystallites occurring at $2\theta = 26.5^\circ$ shifts to a lower 2θ region and becomes a broad peak of lower intensity

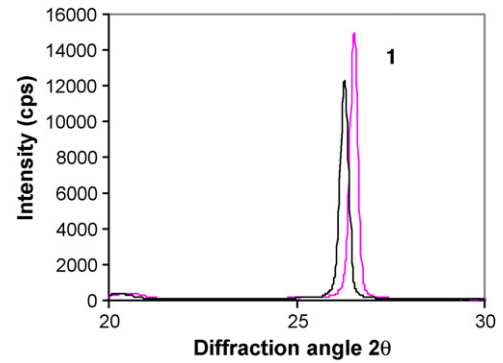


Fig. 7. XRD scans for PPS–graphite composites with 40 wt.% graphite powder mixed and compression moulded: curve (1) before and (2) after heat treatment.

after the heat treatment. The extent of this change in the diffraction peak depends on the processing condition; solution blended PES–graphite samples give the maximum differences. These changes in the XRD patterns indicate that the crystallite size of the graphite particles is reduced (the peak width is increased) [24] by the processing technique adopted. It should be mentioned here that naturally occurring graphite contains stacks of crystallites with a c -axis of 6.79 Å and with an inter-gallery distance of 10–16 Å [25]. On the other hand, the expanded graphite espe-

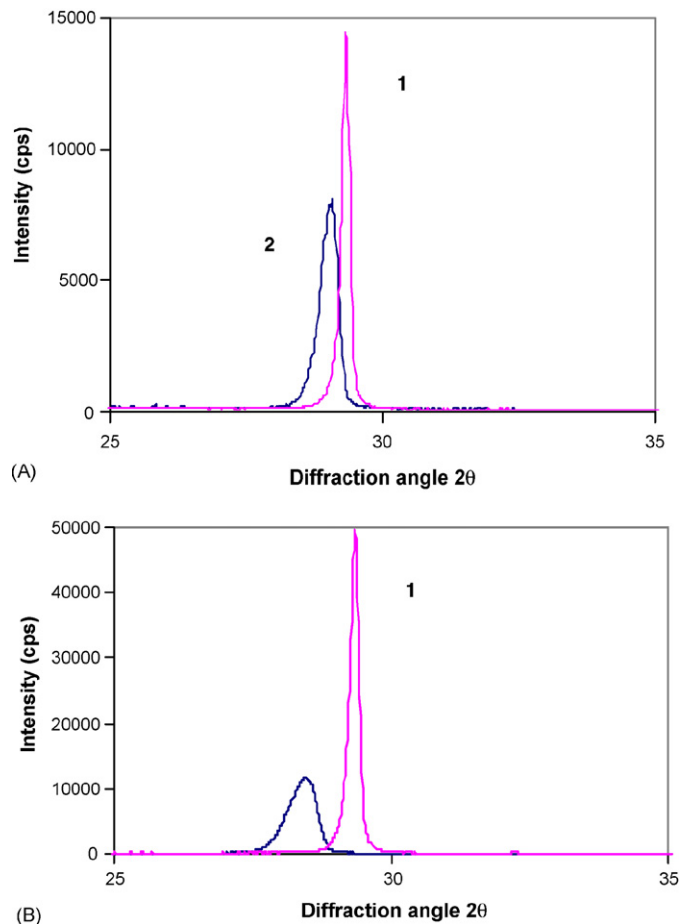


Fig. 8. XRD scans for PES–graphite composites with 44 wt.% graphite powder mixed (top) (A) and solution blended (lower graph) (B) with compression moulding: curve (1) before and (2) after heat treatment.

Table 1
XRD analysis of the PES/graphite solution blended composite before and after heat treatment

Graphite (wt.%)	002 Peak position 2θ ($^{\circ}$)		Intensity (cps)	
	Before heat treatment	After heat treatment	Before heat treatment	After heat treatment
A				
37.50	26.51	26.25	14424	8100
44.44	26.47	25.85	29104	9742
60.00	26.35	25.61	36214	13433
Graphite (wt.%)	Crystallite Size (nm) ^a		Interplanar d -spacing (\AA)	
	Before heat treatment	After heat treatment	Before heat treatment	After heat treatment
B				
37.50	46.20	21.92	3.3560	3.3923
44.44	41.67	17.34	3.3646	3.4438
60.00	20.83	13.86	3.3796	3.4623

^a Crystallite size determined from Scherrer's equation (Ref. [23]).

cially after formation of the composite with polymers, gives rise to a large separation of the crystallites and reduction in their size. In the latter case, the XRD pattern has been found to show a shift in the 002-peak position with broadening [26,27], i.e., very similar to that observed in the present case. The polymer/graphite interaction can thus give rise to a reduction in crystallite size, especially when solution mixing is carried out. Since there is a large reduction in the peak intensity of the 002 reflection, it also suggests that re-orientation of the crystallites after heat treatment is taking place. If a major number of graphite crystallites are stacked with layers parallel to the sample surface or to the c -axis perpendicular with reference to the sample surface, the 002 reflection will be very intense, but for random orientation this will be less intense [28].

Table 1A and B summarizes the XRD data analysis for the above samples. The changes are schematically represented in

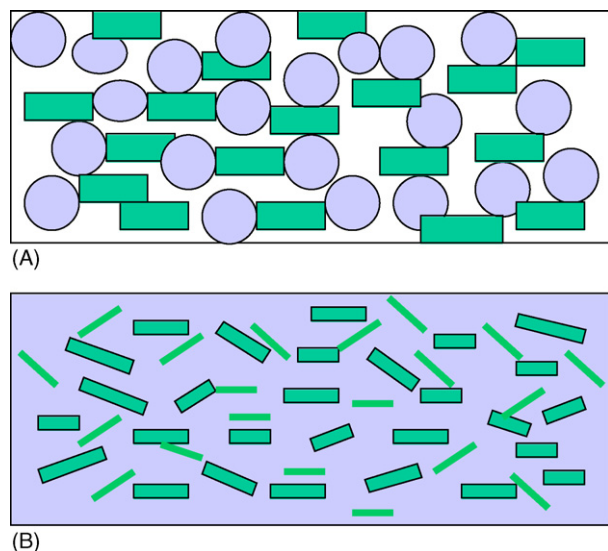


Fig. 9. Schematic representation of graphite-filled polymer composite prepared by: (A) powder mixing and (B) solution blending with compression moulding.

Fig. 9 which depicts the polymer graphite composite prepared by: (A) powder mixing and (B) solution blending. In the former case, the polymer particles have to fuse with each other during compression moulding and heat treatment. In the latter case, the polymer solution delaminates the graphite particles and leads to a reduction in particle size as well as random distribution in the crystallite orientation. This will give rise to lowering of the critical threshold of graphite concentration for conductivity, as well as to low anisotropy in electrical resistivity in the solution blended sample, as has indeed been observed.

4. Conclusions

High-temperature thermoplastic-graphite composites can be prepared by different techniques. A third additional conducting particulate additive gives sufficiently high conductivity at a low graphite loading, which is acceptable for bipolar plates used in fuel cells. The electrical properties for such hybrid composites depend on the processing technique used. Heat treatment at high temperature does not degrade the conductivity. In fact, in few cases, slightly higher conductivity is obtained after such annealing treatment over long time. Although there is some shrinkage after heat treatment, it depends on the graphite concentration and is within acceptable limits at 45% of graphite. The various changes observed in the electrical properties have been explained on the basis of modification of the microstructure in these composites. Solution mixing of graphite with PES followed by moulding of the dried powder leads to a down-sizing of the graphite particles and a more uniform distribution of the conducting phase.

References

- [1] V. Mehta, J.S. Cooper, *J. Power Sources* 114 (2003) 32.
- [2] A. Hermann, T. Chaudhuri, P. Spagnol, *Int. J. Hydrogen Energy* 30 (2005) 1297–1302.
- [3] D. Brett, N. Brandon, *Fuel Cell Rev.* 2 (2005) 15–23.
- [4] M.-S. Lee, L.-J. Chen, Z.-R. He, S.-H. Yang, *J. Fuel Cell Sci. Technol.* 2 (2005) 14–19.
- [5] H.-C. Kuan, C.-C.M. Ma, K.H. Chen, S.-M. Chen, *J. Power Sources* 134 (2004) 7–17.
- [6] F. Mighri, M.A. Huneault, M.F. Champagne, *Polym. Eng. Sci.* 44 (2004) 1755–1765.
- [7] Bulk Molding Compounds Inc., USA, 2004, BMC 940 Data Sheet.
- [8] J. Huang, D.G. Baird, J.E. McGrath, *J. Power Sources* 150 (2005) 110–119.
- [9] R. Leaversuch, *Plast. Technol.* (2002).
- [10] T. Arai, Y. Tominaga, S. Asai, M. Sumita, *J. Polym. Sci., Part B: Polym. Phys.* 43 (2005) 2568–2577.
- [11] H. Wolf, M. Willert-Porada, *J. Power Sources* 151 (2006) 41–46.
- [12] M.K. Bisaria, P. Adrin, M. Abdou, Y. Cai, U.S. Patent 6379795, April 2002 also Editor, *Plastics Technology*, February 2005, p. 68.
- [13] S. Radhakrishnan, V.M. Nadkarni, *Int. J. Polym. Mater.* 11 (1986) 79.
- [14] S. Radhakrishnan, *Angew. Makromol. Chem.* 141 (1986) 49.
- [15] V.M. Nadkarni, S. Radhakrishnan, *Polym. Eng. Sci.* 27 (1987) 547.
- [16] C. Saujanya, S. Radhakrishnan, *Polym. Compos.* 22 (2001) 221.
- [17] S. Radhakrishnan, S.P. Khedkar, *Synth. Met.* 79 (1996) 219.
- [18] S. Radhakrishnan, S. Unde, *J. Appl. Polym. Sci.* 71 (1999) 2059.
- [19] Nedstack Fuel Cell Components BV, *Conduplate LT Data Sheet*, 2003.
- [20] E.A. Cho, U.-S. Jeon, S.-A. Hong, I.-H. Oh, *J. Power Sources* 125 (2004) 178–182.
- [21] J.M. Margolis, *Engineering Thermoplastics: Properties and Applications*, Marcel Dekker, NY, USA, 1985.

- [22] L.H. Sperling, Introduction to Physical Polymer Science, Wiley, NY, USA, 1992.
- [23] J.M.G. Cowie, Polymers: Chemistry and Physics of Modern Materials, Chapman & Hall, London, UK, 1991, p. 350.
- [24] L.E. Alexander, X-ray Diffraction Methods in Polymer Science, J. Wiley, NY, USA, 1969.
- [25] A. Lerf, H.Y. He, M. Forster, J. Klinowshi, J. Phys. Chem., B 102 (1998) 4477.
- [26] G. Zheng, J. Wu, W. Wang, C. Pan, Carbon 42 (2004) 2839.
- [27] T. Sabo, A. Szeri, I. Dekany, Carbon 43 (2005) 87.
- [28] A. Celzard, E. McRae, J.F. Mareche, G. Furdin, M. Dufort, C. Deleuze, J. Phys. Chem. Solids 57 (1996) 715.