



CrossMark  
click for updates

Cite this: *RSC Adv.*, 2016, 6, 64871

# Highly improved dielectric properties of polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites at elevated temperatures

Kenichi Hayashida

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were incorporated into ten kinds of polymer matrices, and the dielectric properties of the resultant polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites were investigated between 40 °C and 160 °C. We found that the dielectric properties strongly depended not only on the temperatures but also on the kind of polymer matrices. For engineering plastics such as polyetherimide (PEI), the dielectric constant  $\epsilon'_r$  was highly enhanced at around 1 kHz by incorporation of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles owing to Maxwell–Wagner polarization of free electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. This is probably because the  $\pi$  electrons in the aromatic structures of the engineering plastics strongly interact with the electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. Furthermore, the dielectric loss factor  $\epsilon''_r$  for the engineering plastics became small at elevated temperatures because the conductivity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particle was enhanced and therefore the relaxation frequency of Maxwell–Wagner polarization was shifted to higher frequency. PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites exhibited highly improved dielectric properties at around 1 kHz, the high  $\epsilon'_r$  and very low  $\epsilon''_r$  at the elevated temperatures above 120 °C. It was demonstrated that the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite was comparable to the PEI/BaTiO<sub>3</sub> composite in dielectric performance at 160 °C. Because the cost of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is much lower than that of BaTiO<sub>3</sub>, the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite might be promising as a low-cost dielectric material for high-temperature applications.

Received 16th May 2016  
Accepted 3rd July 2016

DOI: 10.1039/c6ra12752e

www.rsc.org/advances

## Introduction

Dielectric materials are mainly used in capacitors to store electrical energy.<sup>1–3</sup> In comparison to ceramic materials, polymer ones have the advantages of low cost, lightweight and high processability. However, the very low dielectric constant  $\epsilon'_r$  of the polymer material strongly prevents improvement of the capacitors. Therefore, polymer/ceramic composite materials have been much studied over the last few decades. Among the ceramics, BaTiO<sub>3</sub> has been most widely used for enhancement in the  $\epsilon'_r$  of polymer materials because of the very high  $\epsilon'_r$  of BaTiO<sub>3</sub>.<sup>4–21</sup> However, the high cost of BaTiO<sub>3</sub> is a serious problem for industrial applications.

On the other hand, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a very low cost ceramic material although  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has not been paid attention as a high  $\epsilon'_r$  filler for polymer materials owing to the low  $\epsilon'_r$  of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; according to the reported literature, the  $\epsilon'_r$  of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is as low as 30.<sup>22–27</sup> Therefore, few studies are available on the dielectric properties of polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites.<sup>28–30</sup> Djoković and coworkers reported dielectric properties of a composites epoxy resin and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods.<sup>28</sup> Also,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods were dispersed in a poly(vinyl alcohol)/poly(ethylene glycol) blend by Sayed *et al.*<sup>29</sup> There are only small improvements of the  $\epsilon'_r$ s of the polymer materials in these studies.

In this paper, we focus on the conductivity  $\sigma$  of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at elevated temperatures. Typically,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is known to have  $\sigma$  of about 10<sup>–5</sup> to 10<sup>–6</sup> S cm<sup>–1</sup> at room temperature.<sup>26</sup> The  $\sigma$  of semiconductors such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is enhanced as temperature is raised because electrons are excited from a valence band to a conductive band.<sup>31</sup> It is expected that the  $\sigma$  of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is especially increased owing to its narrow band gap of 2.1 eV.<sup>32</sup> At elevated temperatures, the enhanced  $\sigma$  of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles would bring a high  $\epsilon'_r$  to a polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite owing to Maxwell–Wagner polarization<sup>33</sup> of the resultant free electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. The polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite might be promising as a low-cost dielectric material for high-temperature applications such as hybrid and electric vehicles.<sup>34,35</sup> In this study,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were incorporated into ten kinds of polymer matrices, and the dielectric properties of the polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites were investigated between 40 °C and 160 °C. We found that the dielectric properties strongly depended not only on the temperatures but also on the kind of polymer matrices. Furthermore, the dielectric performance of one of the polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite was compared with that of a corresponding polymer/BaTiO<sub>3</sub> composite at the elevated temperatures.

## Experimental

### Sample preparation

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were obtained from Kanto Chemical (Japan). The density and specific area of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were

Materials and Processing Dept. II, Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan. E-mail: e1440@mosk.tytlabs.co.jp



determined to be  $4.94 \text{ g cm}^{-3}$  and  $8.71 \text{ m}^2 \text{ g}^{-1}$  using helium pycnometry and a standard BET method, respectively. The average diameter of the  $\alpha\text{-Fe}_2\text{O}_3$  particles was calculated to be 139 nm from the obtained density and specific area data. In the same manner, the density, specific area and average diameter of  $\text{BaTiO}_3$  particles obtained from Wako Pure Chemical Industries (Japan) were determined to be  $5.73 \text{ g cm}^{-3}$ ,  $9.99 \text{ m}^2 \text{ g}^{-1}$  and 105 nm, respectively.

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) were purchased from Wako Pure Chemical Industries (Japan). Poly(2-vinylpyridine) (P2VP) was obtained from Scientific Polymer Products. Styrene/acrylonitrile copolymer (SAN) with 30 wt% of acrylonitrile, polyphenylene ether (PPE), polysulfone (PSF), polyethersulfone (PES) and polyetherimide (PEI) were purchased from Sigma-Aldrich. Styrene/*N*-phenylmaleimide alternating copolymer (St-PMI)<sup>36</sup> and polyarylate (PAR)<sup>37</sup> were synthesized using reported methods, where PAR contained equimolar amounts of isophthaloyl and terephthaloyl moieties.

A series of polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites were prepared by simply blending the  $\alpha\text{-Fe}_2\text{O}_3$  particles with the polymer matrices. First, the  $\alpha\text{-Fe}_2\text{O}_3$  particles and the polymer matrix except PES were homogeneously dispersed in 1,4-dioxane by sonication. The dispersion was quickly frozen by liquid nitrogen, and then freeze-dried under vacuum. For preparation of PES/ $\alpha\text{-Fe}_2\text{O}_3$  composites, dichloromethane was used instead of 1,4-dioxane because PES was insoluble in 1,4-dioxane. Subsequently, all the pre-mixtures thus-obtained were further

kneaded in molten states. Also, PEI/ $\text{BaTiO}_3$  composites were prepared in the same manner. The resultant composites were hot-pressed into disklike specimens with a diameter of 33 mm and a thickness of  $\sim 0.52$  mm. For electrical measurements, two gold electrodes with a diameter of 27 mm were deposited on the top and bottom of the specimens.

## Measurements

Complex permittivity was obtained in the frequency  $f$  range of  $10^2$  to  $10^6$  Hz at 2 V using an LCR meter (E4980A, Agilent) coupled with a rheometer (ARES G2, TA instruments). The temperature of the specimen was controlled in the oven of the rheometer. Direct current (DC) resistance of the specimen was measured at room temperature under a nitrogen atmosphere using a megohmmeter (SM-8220, Hioki), and the value was recorded after 10 minute from application of a voltage of 500 V. The cross-section of the specimen that had been flattened with argon ion beam<sup>38</sup> was observed using an SEM (S-4300, Hitachi) operated at an accelerating voltage of 2 kV.

## Results and discussion

### Dielectric properties of polymer/ $\alpha\text{-Fe}_2\text{O}_3$ composites at 40 °C

We prepared a series of polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with the volume fraction  $\Phi$  of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\Phi = 0.2$ . The chemical structures of the polymer matrices are shown in Fig. 1. All the polymers are

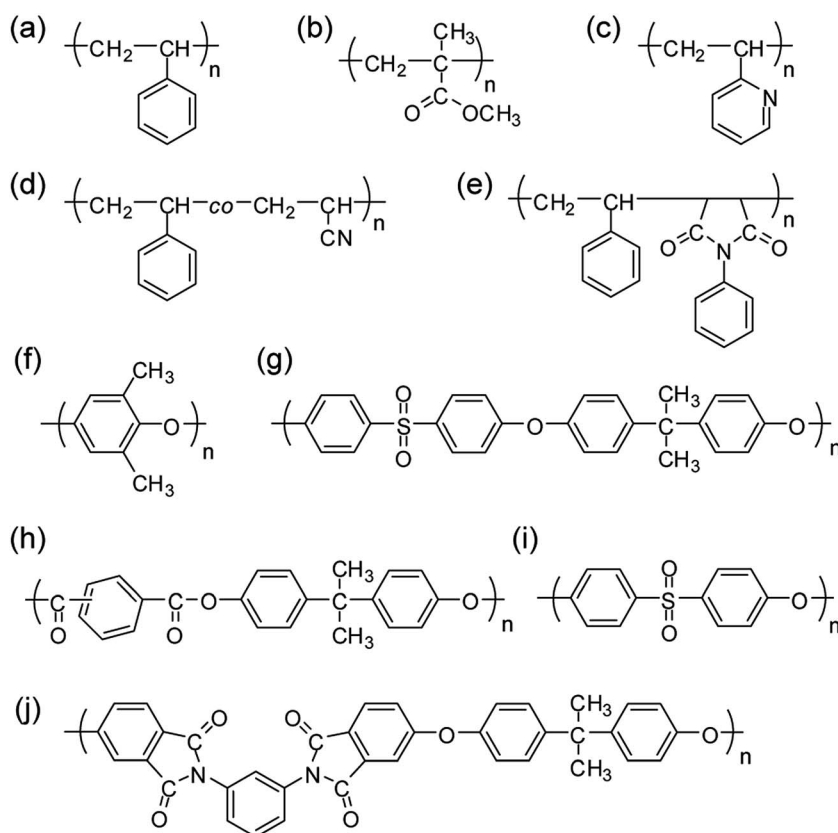


Fig. 1 Chemical structures of polymer matrices used in this study. (a) PS. (b) PMMA. (c) P2VP. (d) SAN. (e) St-PMI. (f) PPE. (g) PSF. (h) PAR. (i) PES. (j) PEI.



**Table 1** Dielectric characteristics (1 kHz) for polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites with  $\Phi = 0.2$  obtained at 40 °C

Polymer	$\epsilon'_r$	$\epsilon''_r$	$\epsilon'_{r \text{ polymer}}^a$	$\epsilon'_{r \text{ Fe}_2\text{O}_3}^b$
PS	4.12	0.123	2.58	27.8
PMMA	5.25	0.453	3.39	31.2
P2VP	6.34	0.447	4.22	33.3
SAN	5.05	0.286	3.03	40.5
PSF	5.71	0.339	3.13	66.2
St-PMI	5.59	0.182	2.88	83.4
PAR	6.52	0.402	3.27	109
PEI	6.23	0.250	3.09	109
PES	7.13	0.475	3.52	116
PPE	5.58	0.162	2.63	120

<sup>a</sup>  $\epsilon'_r$  of the polymer matrix only. <sup>b</sup> Apparent  $\epsilon'_r$  of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> calculated using Lichteneker's logarithmic mixing rule.

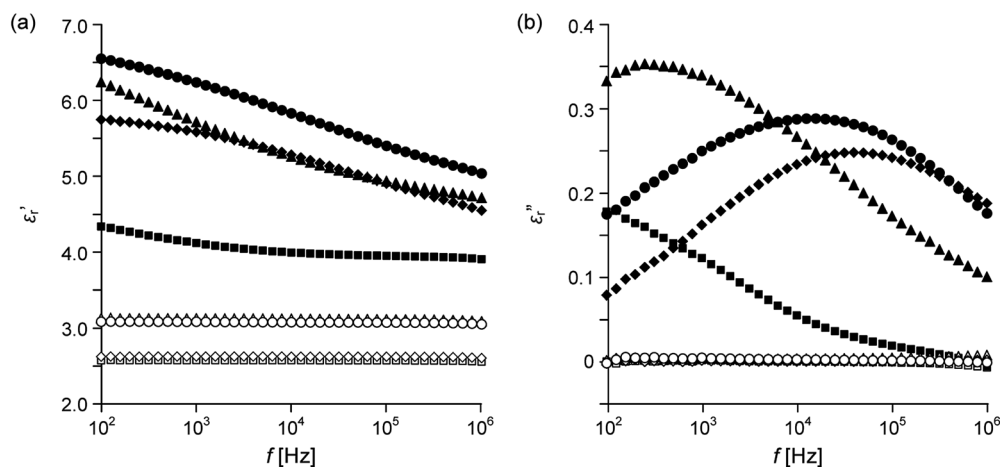
popular, and some of them are engineering plastics that can be used over 150 °C (Fig. 1f–j). The  $\epsilon'_r$  and dielectric loss factor  $\epsilon''_r$  values of the polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites (1 kHz, 40 °C) were listed in Table 1. There is a weak tendency for the  $\epsilon'_r$  of the composites prepared using the engineering plastics to be high. This is an interesting phenomenon that has never been reported. However, it is difficult to correctly evaluate the  $\epsilon'_r$  enhancement effect by direct comparing of the  $\epsilon'_r$  values of the composites because each  $\epsilon'_r$  of the polymer matrix  $\epsilon'_{r \text{ polymer}}$  is different to some extent as shown in Table 1. Therefore, we suggest that apparent  $\epsilon'_r$  of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  is calculated using Lichteneker's logarithmic mixing rule and then compared in order to separate a contribution of the  $\epsilon'_{r \text{ polymer}}$  itself from the  $\epsilon'_r$  of the composite. It is known that the  $\epsilon'_r$  of a polymer/filler composite often obeys Lichteneker's logarithmic mixing rule as follows:<sup>4,7,9,15–17,39</sup>

$$\epsilon'_r = \epsilon'_{r \text{ polymer}}(\epsilon'_{r \text{ filler}}/\epsilon'_{r \text{ polymer}})^\Phi, \quad (1)$$

where  $\epsilon'_{r \text{ filler}}$  and  $\Phi$  are the  $\epsilon'_r$  and volume fraction of the filler. Notice that the  $\epsilon'_{r \text{ filler}}$  is not the  $\epsilon'_r$  of the filler itself but an apparent  $\epsilon'_r$  of the filler particles in the polymer matrix.

Generally, the  $\epsilon'_{r \text{ filler}}$  is much smaller than the  $\epsilon'_r$  of the corresponding bulk compound, mainly because the filler particles do not form a continuous phase in the polymer/filler composite system; the  $\epsilon'_{r \text{ filler}}$  is significantly reduced by the interface between the filler particles. Furthermore, the  $\epsilon'_{r \text{ filler}}$  is affected not only by the size and form of the filler particle but also by the dispersivity of the filler particles in the matrix.<sup>16</sup> For example, the apparent  $\epsilon'_r$  of spherical BaTiO<sub>3</sub> nanoparticles with a diameter of less than 100 nm is reported to be around 100 according to literatures.<sup>8,39</sup>

The calculated  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  is shown in Table 1. There is a strong dependency of the  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  on the polymer matrix; the  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  is about 30 for PS, PMMA and P2VP whereas over 100 for PAR, PEI, PES and PPE. In other word, the  $\epsilon'_r$  for engineering plastics is more enhanced by the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles than that for general-purpose plastics such as PS and PMMA. Fig. 2 shows the frequency  $f$  dependences of the  $\epsilon'_r$  and  $\epsilon''_r$  of four kinds of composites for PEI, PSF, PPE and PS with  $\Phi = 0.2$  obtained at 40 °C. Every  $\epsilon'_r$  is decreased as  $f$  is increased. This is because the dielectric relaxation of a polarization occurs in the  $f$  range, which results in a  $\epsilon''_r$  peak as shown in Fig. 2b. This polarization would be attributed to the interfacial polarization of free electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles, that is Maxwell–Wagner polarization.<sup>33</sup> Because the relaxation frequency becomes high as the  $\sigma$  of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles is high for Maxwell–Wagner polarization, it is suggested that the  $\sigma$  of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles in the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and PPE/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites is higher than that in the PS/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite, resulting in the higher  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  for PEI and PPE over the reported value of  $\sim 30$ .<sup>22–27</sup> This is probably because the  $\pi$  electrons in the aromatic structures of the engineering plastics strongly interact with the electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. Also, it is suggested that the enhanced  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  is caused by the dispersivity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles in the polymer matrix and the interfacial state between the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles and the polymer matrix. However, it is difficult to explain the strong frequency dependence of the dielectric properties as shown in Fig. 2 by these two contributions (the dispersivity and the interfacial state). Therefore, we conclude



**Fig. 2** Frequency  $f$  dependence of (a)  $\epsilon'_r$  and (b)  $\epsilon''_r$  of polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites with  $\Phi = 0$  (open symbols) and  $\Phi = 0.2$  (filled symbols) obtained at 40 °C. The polymer matrices are PEI (circles), PSF (triangles), PPE (diamonds) and PS (squares).



that the enhanced  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  is mainly due to the interaction between the electrons in the  $\alpha\text{-Fe}_2\text{O}_3$  particles and the polymer matrix. From the viewpoint of the molecular structures of the polymer matrix, the  $\alpha\text{-Fe}_2\text{O}_3$  particles might be more effective for fully aromatic polyester and polyimide with long conjugations.

### Dielectric properties of polymer/ $\alpha\text{-Fe}_2\text{O}_3$ composites at 160 °C

The PEI/ $\alpha\text{-Fe}_2\text{O}_3$  and PPE/ $\alpha\text{-Fe}_2\text{O}_3$  composites are not useful at 40 °C owing to the large  $\epsilon''_r$  values over 0.1 (Table 1). Under an electric field  $E$ , the power loss of a dielectric material per unit volume,  $P$  is expressed as,<sup>16</sup>

$$P = E^2 \times 2\pi f \epsilon_0 \epsilon''_r, \quad (2)$$

where  $\epsilon_0$  is the permittivity of vacuum. Because  $P$  is proportional to  $\epsilon''_r$ , the  $\epsilon''_r$  of the material must be low for industrial applications such as capacitors.

The large  $\epsilon''_r$  values of the polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites are drastically reduced at 160 °C. Dielectric characteristics (1 kHz) obtained at 160 °C were listed in Table 2 for six kinds of polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0.2$ . At 1 kHz, all the  $\epsilon''_r$  values are less than 0.05. Furthermore, for PEI, PSF, PAR and PES, the  $\epsilon'_{r \text{ Fe}_2\text{O}_3}$  is more than 150 at 160 °C. For the four kinds of composites, the  $f$  dependences of the  $\epsilon'_r$  and  $\epsilon''_r$  are shown

Table 2 Dielectric characteristics (1 kHz) for polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0.2$  obtained at 160 °C

Polymer	$\epsilon'_r$	$\epsilon''_r$	$\epsilon'_{r \text{ polymer}}^a$	$\epsilon'_{r \text{ Fe}_2\text{O}_3}^b$
St-PMI	5.95	0.0307	2.87	116
PPE	5.71	0.0110	2.61	139
PEI	6.73	0.0321	3.11	157
PSF	6.82	0.0525	3.12	165
PAR	7.29	0.0509	3.31	182
PES	8.32	0.0533	3.53	246

<sup>a</sup>  $\epsilon'_r$  of the polymer matrix only. <sup>b</sup> Apparent  $\epsilon'_r$  of  $\alpha\text{-Fe}_2\text{O}_3$  calculated using Lichteneker's logarithmic mixing rule.

in Fig. 3. Because the dielectric relaxations of Maxwell-Wagner polarization are not started at around 1 kHz as shown in Fig. 3b, the  $\epsilon''_r$  values are small in the lower  $f$  ranges than 1 kHz. This result indicates the  $\sigma$  of the  $\alpha\text{-Fe}_2\text{O}_3$  particle is higher at 160 °C than 40 °C. Fig. 4 shows a variation in the  $f$  dependences of the  $\epsilon'_r$  and  $\epsilon''_r$  of the PEI/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0.2$  between 40 and 160 °C. The  $\epsilon''_r$  peak is shifted to the higher  $f$  until the temperature reaches 120 °C.

For the four polymer matrices, we also prepared polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0.4$ . Fig. 5 shows the  $f$  dependences of the  $\epsilon'_r$  and  $\epsilon''_r$  of polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0.4$  at 160 °C. The  $\epsilon''_r$  of the PEI/ $\alpha\text{-Fe}_2\text{O}_3$  composite remains small whereas for PAR and PES, the  $\epsilon''_r$  becomes very large over all the  $f$  range. In order to elucidate the large  $\epsilon''_r$ , the volume resistivity  $\rho_{\text{DC}}$  of the composites was measured. At  $\Phi = 0.4$ , the  $\rho_{\text{DC}}$  for PAR and PES is much lower than that for PEI and PSF as shown in Fig. 6.  $\epsilon''_r$  is the sum of a loss from  $\sigma$ ,  $\epsilon''_{r(\sigma)}$  and losses from dielectric polarizations  $\epsilon''_{r(\text{DP})}$ :<sup>40</sup>

$$\epsilon''_r = \epsilon''_{r(\sigma)} + \epsilon''_{r(\text{DP})}. \quad (3)$$

Furthermore,  $\epsilon''_{r(\sigma)}$  is described using  $\rho_{\text{DC}}$  as follows:

$$\epsilon''_{r(\sigma)} = 1/(2\pi f \epsilon_0 \rho_{\text{DC}}). \quad (4)$$

It is suggested that because  $\epsilon''_{r(\sigma)}$  is inversely proportion to  $f$  and  $\rho_{\text{DC}}$ , the  $\epsilon''_r$  is highly increased at the low  $f$  range for PAR and PES. The low  $\rho_{\text{DC}}$  for PAR and PES could be attributed to a leak current passing through the conductive networks of the  $\alpha\text{-Fe}_2\text{O}_3$  particles, that is, percolation of the  $\alpha\text{-Fe}_2\text{O}_3$  particles. According to the percolation theory with a random packing of spherical particles, the percolation threshold is calculated to be about 0.30.<sup>41,42</sup> Therefore, it was reasonable that the percolation of the  $\alpha\text{-Fe}_2\text{O}_3$  particles occurred in the polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0.4$ . To the contrary, it was unusual that the PEI/ $\alpha\text{-Fe}_2\text{O}_3$  composite had a high  $\rho_{\text{DC}}$  even at  $\Phi = 0.4$ . We suspected that the dispersivity of the  $\alpha\text{-Fe}_2\text{O}_3$  particles in the polymer matrix was different between

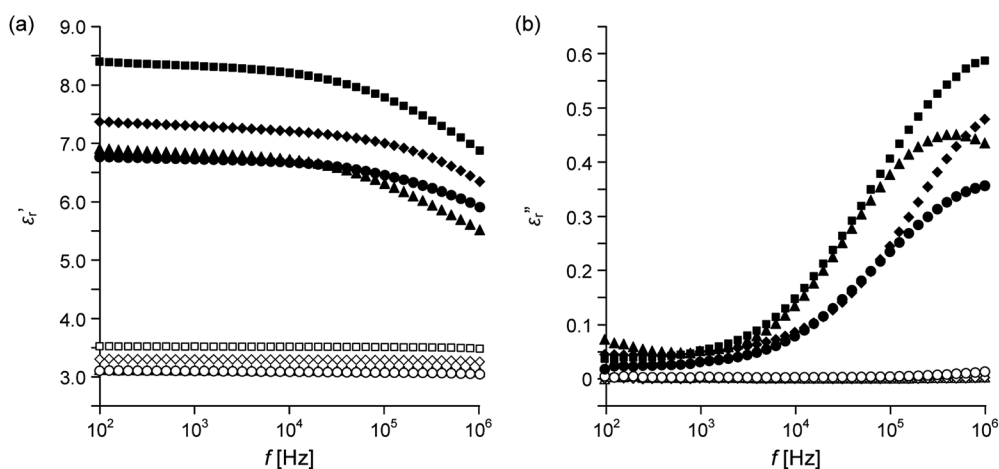


Fig. 3 Frequency  $f$  dependence of (a)  $\epsilon'_r$  and (b)  $\epsilon''_r$  of polymer/ $\alpha\text{-Fe}_2\text{O}_3$  composites with  $\Phi = 0$  (open symbols) and  $\Phi = 0.2$  (filled symbols) obtained at 160 °C. The polymer matrices are PEI (circles), PSF (triangles), PAR (diamonds) and PES (squares).



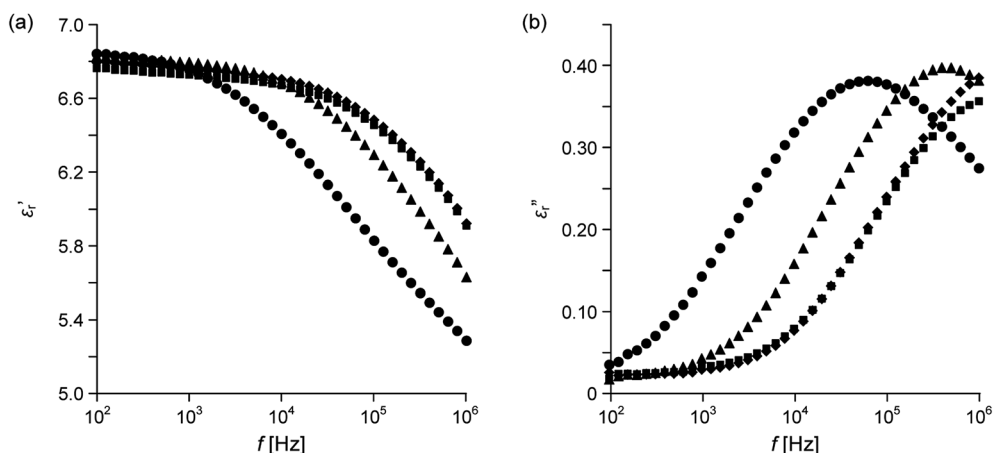


Fig. 4 Frequency  $f$  dependence of (a)  $\epsilon'_r$  and (b)  $\epsilon''_r$  of a PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite with  $\Phi = 0.2$  obtained at 40 °C (circles), 80 °C (triangles), 120 °C (diamonds) and 160 °C (squares).

the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and PAR/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites, and observed it using SEM. Fig. 7 shows SEM images of the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and PAR/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites with  $\Phi = 0.20$  and  $\Phi = 0.4$ . There is no great difference in the dispersivity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles, which means that the significant difference in  $\rho_{DC}$  is not due to the dispersivity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. In the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles would be covered with a PEI layer at a nanometer scale, resulting in the high  $\rho_{DC}$  for PEI owing to inhibition of the tunneling conduction of the free electron<sup>39,43</sup> between the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles.

#### Comparing of dielectric performance for PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and PEI/BaTiO<sub>3</sub> composites

As mentioned above, the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite exhibits the high  $\epsilon'_r$  and very low  $\epsilon''_r$  at the elevated temperature above 120 °C, which might be promising as a low-cost dielectric material for high-temperature applications; PEI has a maximum operating temperature of 200 °C.<sup>35</sup> Therefore, the novel PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite was compared with a conventional PEI/BaTiO<sub>3</sub>

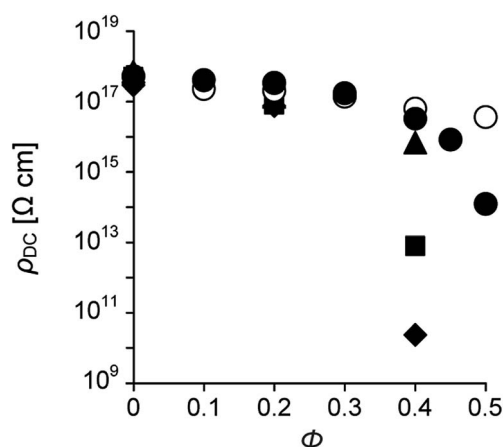


Fig. 6 Volume resistivity  $\rho_{DC}$  of polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (filled symbols) and PEI/BaTiO<sub>3</sub> (open symbols) composites as a function of  $\Phi$ . The polymer matrices are PEI (circles), PSF (triangles), PAR (diamonds) and PES (squares).

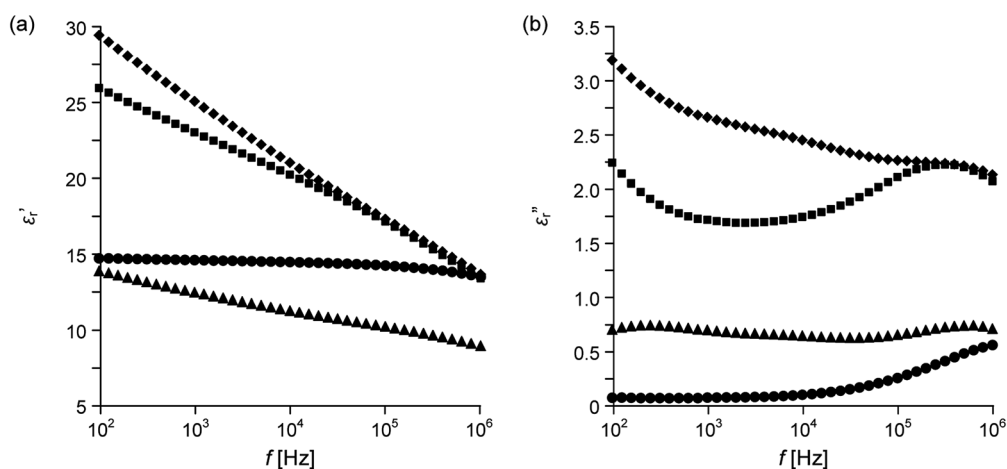


Fig. 5 Frequency  $f$  dependence of (a)  $\epsilon'_r$  and (b)  $\epsilon''_r$  of polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites with  $\Phi = 0.4$  obtained at 160 °C. The polymer matrices are PEI (circles), PSF (triangles), PAR (diamonds) and PES (squares).



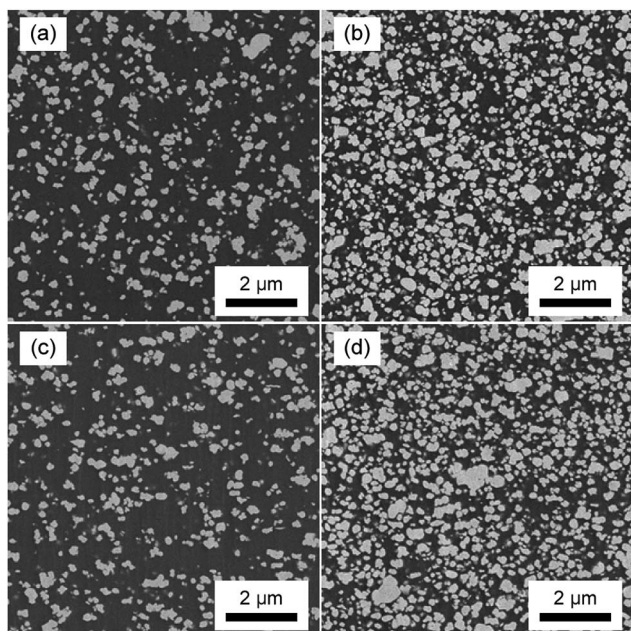


Fig. 7 SEM images of (a and b) PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (c and d) PAR/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites with (a and c)  $\Phi = 0.2$  and (b and d)  $\Phi = 0.4$ .

composite in dielectric performance. As shown in Fig. 6, the  $\rho_{DC}$  values of both the composites are comparable at room temperature when  $\Phi$  is less than 0.4, whereas the  $\rho_{DC}$  of PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is much lower than that of PEI/BaTiO<sub>3</sub> at the higher  $\Phi$ . This is because the interparticle distance becomes small enough for tunneling conduction to occur owing to high loading of particles. Fig. 8 shows the  $f$  dependences of the  $\epsilon'_r$  and  $\epsilon''_r$  of the two types of composites obtained at 40 °C and 160 °C. At 40 °C, although the  $\epsilon'_r$  of PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is higher than that of PEI/BaTiO<sub>3</sub> in the lower  $f$  range, the  $\epsilon''_r$  of PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is much larger than that of PEI/BaTiO<sub>3</sub>. At 160 °C, however,  $\epsilon'_r$  has comparable  $\epsilon''_r$  values to PEI/BaTiO<sub>3</sub> except with  $\Phi = 0.5$ , and higher  $\epsilon'_r$  than PEI/BaTiO<sub>3</sub>. The dielectric characteristics at 1 kHz obtained at 160 °C are plotted as a function of  $\Phi$  in Fig. 9. These results show that the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite was comparable to the PEI/BaTiO<sub>3</sub> composite in dielectric performance at 160 °C. The fitting curves for the  $\epsilon'_r$  of the two types of composites are drawn in Fig. 9a in solid lines using Lichteneker's logarithmic mixing rule. These theoretical curves well fit to the experimental results and give  $\epsilon'_{r, BaTiO_3}$  of 86 and  $\epsilon'_{r, Fe_2O_3}$  of 170, respectively. This value of 86 for BaTiO<sub>3</sub> is

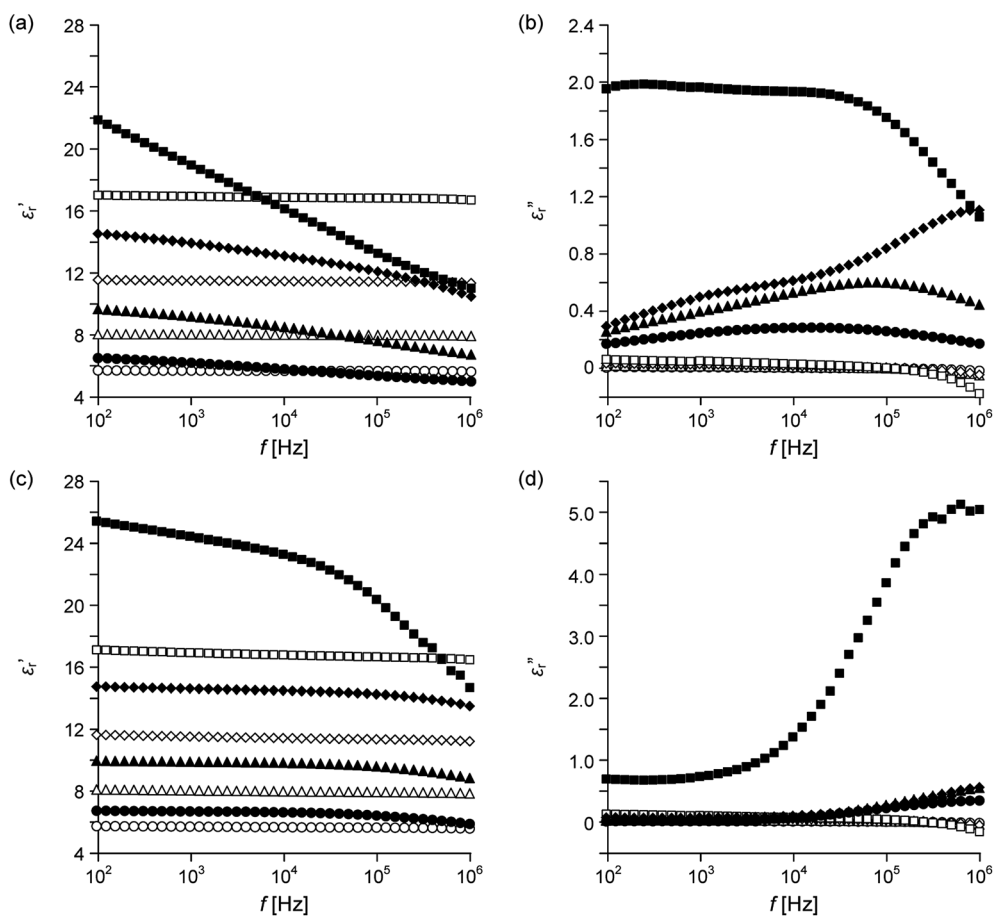


Fig. 8 Frequency  $f$  dependence of (a and c)  $\epsilon'_r$  and (b and d)  $\epsilon''_r$  of two types of composites with  $\Phi = 0.2$  (circles),  $\Phi = 0.3$  (triangles),  $\Phi = 0.4$  (diamonds) and  $\Phi = 0.5$  (squares) obtained at (a and b) 40 °C and (c and d) 160 °C. Open symbols, PEI/BaTiO<sub>3</sub>; filled symbols, PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



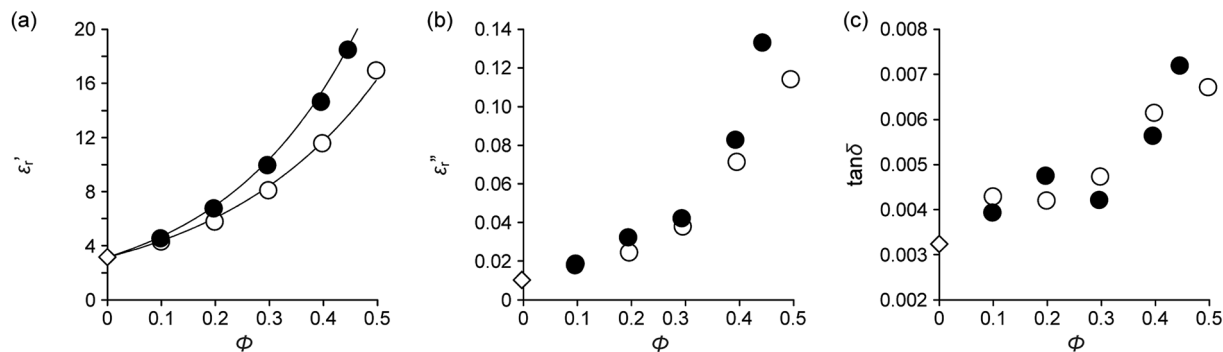


Fig. 9 (a)  $\epsilon'_r$ , (b)  $\epsilon''_r$  and (c) dissipation factor ( $\tan \delta$ ) (1 kHz) of PEI (diamonds) and two types of composites (circles) obtained at 160 °C as a function of  $\phi$ . Open symbols, PEI/BaTiO<sub>3</sub>; filled symbols, PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (a) Solid lines show the fitting curves using Lichtenecker's logarithmic mixing rule.

consistent with some reported results;  $\epsilon'_r$  BaTiO<sub>3</sub> is around 100.<sup>8,39</sup>

## Conclusion

The dielectric properties of polymer/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites strongly depended not only on the temperatures but also on the kind of polymer matrices. For engineering plastics such as PEI, PSF, PAR and PES, the  $\epsilon'_r$  was highly enhanced at around 1 kHz by incorporation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles owing to Maxwell–Wagner polarization of free electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. This is probably because the  $\pi$  electrons in the aromatic structures of the engineering plastics strongly interact with the electrons in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. Furthermore, the  $\epsilon''_r$  for the engineering plastics became small at the elevated temperatures because the  $\sigma$  of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particle was enhanced and therefore the relaxation frequency of Maxwell–Wagner polarization was shifted to higher  $f$ . PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites exhibited highly improved dielectric properties at around 1 kHz, the high  $\epsilon'_r$  and very low  $\epsilon''_r$  at the elevated temperature above 120 °C. It was demonstrated that the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite was comparable to the PEI/BaTiO<sub>3</sub> composite in dielectric performance at 160 °C. Because the cost of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is much lower than that of BaTiO<sub>3</sub>, the PEI/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites might be promising as a low-cost dielectric material for high-temperature applications.

## Acknowledgements

SEM observation was carried out by Mr Yasuhiro Takatani at Toyota Central R&D Labs Inc. The authors appreciate his help.

## References

- W. J. Sarjeant, J. Zirnheld, F. W. MacDougall, J. S. Bowers, N. Clark, I. W. Clelland, R. A. Price, M. Hudis, I. Kohlberg, G. McDuff, I. McNab, S. G. Parler Jr and J. Prymak, in *Handbook of low and high dielectric constant materials and their applications*, ed. H. S. Nalwa, Academic Press, London, 1999, vol. 2, ch. 9, pp. 423–491.
- Q. Wang and L. Zhu, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 1421–1429.
- Z. M. Dang, J. K. Yuan, J. W. Zha, T. Zhou, S. T. Li and G. H. Hu, *Prog. Mater. Sci.*, 2012, **57**, 660–723.
- S. D. Cho, S. Y. Lee, J. G. Hyun and K. W. Paik, *J. Mater. Sci.: Mater. Electron.*, 2005, **16**, 77–84.
- P. Kim, S. C. Jones, P. J. Hotchkiss, J. N. Haddock, B. Kippelen, S. R. Marder and J. W. Perry, *Adv. Mater.*, 2007, **19**, 1001–1005.
- J. Lu and C. P. Wong, *IEEE Trans. Dielectr. Electr. Insul.*, 2008, **15**, 1322–1328.
- K. W. Jang and K. W. Paik, *J. Appl. Polym. Sci.*, 2008, **110**, 798–807.
- P. Kim, N. M. Doss, J. P. Tillotson, P. J. Hotchkiss, M. J. Pan, S. R. Marder, J. Li, J. P. Calame and J. W. Perry, *ACS Nano*, 2009, **3**, 2581–2592.
- Y. Kobayashi, A. Kurosawa, D. Nagao and M. Konno, *Polym. Eng. Sci.*, 2009, **49**, 1069–1075.
- A. Choudhury, *Mater. Chem. Phys.*, 2010, **121**, 280–285.
- L. Xie, X. Huang, C. Wu and P. Jiang, *J. Mater. Chem.*, 2011, **21**, 5897–5906.
- S. Siddabattuni, T. P. Shuman and F. Dogan, *Mater. Sci. Eng., B*, 2011, **176**, 1422–1429.
- M.-F. Lin, V. K. Thakur, E. J. Tan and P. S. Lee, *RSC Adv.*, 2011, **1**, 576–578.
- Y. Song, Y. Shen, H. Liu, Y. Lin, M. Li and C. W. Nan, *J. Mater. Chem.*, 2012, **22**, 16491–16498.
- X. Wu, Z. Chen and Z. Cui, *Compos. Sci. Technol.*, 2013, **81**, 48–53.
- K. Hayashida and Y. Matsuoka, *Carbon*, 2012, **60**, 506–513.
- K. Hayashida, Y. Matsuoka and Y. Takatani, *RSC Adv.*, 2014, **4**, 33530–33536.
- C. Fettkenhauer, J. Glenneberg, W. Münchgesang, H. S. Leipner, G. Wagner, M. Diestelhorst, C. Pienteschke, H. Beige and S. G. Ebbinghaus, *RSC Adv.*, 2014, **4**, 40321–40329.
- W. Lei, R. Wang, D. Yang, G. Hou, X. Zhou, H. Qiao, W. Wang, M. Tian and L. Zhang, *RSC Adv.*, 2015, **5**, 47429–47438.



- 20 W. Yang, S. Yu, S. Luo, R. Sun, W.-H. Liao and C.-P. Wong, *J. Alloys Compd.*, 2015, **620**, 315–323.
- 21 Y. Feng, W. L. Li, Y. F. Hou, Y. Yu, W. P. Cao, T. D. Zhang and W. D. Fei, *J. Mater. Chem. C*, 2015, **3**, 1250–1260.
- 22 R. B. Hilborn Jr, *J. Appl. Phys.*, 1965, **36**, 1553–1557.
- 23 K. Iwachi, S. Yamamoto, Y. Bando and N. Koizumi, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1970, **48**, 159–169.
- 24 D. A. Sverjensky and N. Sahai, *Geochim. Cosmochim. Acta*, 1996, **60**, 3773–3797.
- 25 M. L. Jimenez, F. J. Arroyo, F. Carrique and U. Kaatz, *J. Phys. Chem. B*, 2003, **107**, 12192–12200.
- 26 J. A. Glasscock, P. R. F. Barnes, I. C. Plumb, A. Bendavid and P. J. Martin, *Thin Solid Films*, 2008, **516**, 1716–1724.
- 27 R. A. Lunt, A. J. Jackson and A. Walsh, *Chem. Phys. Lett.*, 2013, **586**, 67–69.
- 28 D. Dudić, M. Marinović-Cincović, J. M. Nedeljković and V. Djoković, *Polymer*, 2008, **49**, 4000–4008.
- 29 A. M. E. Sayed and W. M. Morsi, *J. Mater. Sci.*, 2014, **49**, 5378–5387.
- 30 D. Chen, H. Quan, Z. Huang, S. Luo, X. Luo, F. Deng, H. Jiang and G. Zeng, *Compos. Sci. Technol.*, 2014, **102**, 126–131.
- 31 C. Kittel, in *Introduction to Solid State Physics*, ed. C. Kittel, John Wiley & Sons, New York, 7th edn, 1996, ch. 8, pp. 197–232.
- 32 S. Mohanty and J. Ghose, *J. Phys. Chem. Solids*, 1992, **53**, 81–91.
- 33 A. Schönhals and F. Kremer, in *Broadband Dielectric Spectroscopy*, ed. F. Kremer and A. Schönhals, Springer-Verlag, Berlin, 2003, ch. 3, pp. 59–98.
- 34 D. Tan, L. Zhang, Q. Chen and P. Irwin, *J. Electron. Mater.*, 2014, **43**, 4569–4575.
- 35 Q. Li, L. Chen, M. R. Gadinski, S. Zhang, G. Zhang, H. Li, A. Haque, L. Q. Chen, T. Jackson and Q. Wang, *Nature*, 2015, **523**, 576–580.
- 36 M. N. Teerenstra, P. A. M. Steeman, W. Iwens, A. Vandervelden, D. R. Suwier, B. V. Mele and C. E. Koning, *e-Polym.*, 2003, **3**, 596–607.
- 37 H.-B. Tsai and Y.-D. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 1987, **25**, 1505–1515.
- 38 N. Erdman, R. Campbelle and S. Asahina, *Microsc. Today*, 2006, **14**, 22–25.
- 39 K. Hayashida, *RSC Adv.*, 2013, **3**, 221–227.
- 40 K. Hayashida and Y. Matsuoka, *Carbon*, 2015, **85**, 363–371.
- 41 G. E. Pike and C. H. Seager, *Phys. Rev. B: Solid State*, 1974, **10**, 1421–1434.
- 42 C. D. Lorenz and R. M. Ziff, *J. Chem. Phys.*, 2001, **114**, 3659–3661.
- 43 K. Hayashida and H. Tanaka, *Adv. Funct. Mater.*, 2012, **22**, 2338–2344.

