Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 1510−1516

polymer

www.elsevier.com/locate/polymer

High dielectric constant polyaniline/epoxy composites via in situ polymerization for embedded capacitor applications

Jiongxin Lu [a], Kyoung-Sik Moon [a], Byung-Kook Kim [b], C.P. Wong [a,*]

[a] School of Materials Science and Engineering, Packaging Research Center, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332-0245, USA
[b] Materials Science and Technology Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

Received 13 August 2006; received in revised form 13 January 2007; accepted 19 January 2007
Available online 31 January 2007

Abstract

Polyaniline (PANI)/epoxy composites with different polyaniline (PANI) contents were successfully developed by in situ polymerization of aniline salt protonated with camphorsulfonic acid within epoxy matrices and fully characterized. The influence of PANI loading levels on various properties was also explored. Dielectric and electrical properties of PANI/epoxy composites were studied for samples in parallel plate configuration. A PANI/epoxy composite prepared in this fashion reached a high dielectric constant close to 3000, a dielectric loss tangent less than 0.5 at room temperature and 10 kHz. The hardener type was also found as a critical parameter for the dielectric properties of PANI/epoxy composites. The distribution of the conductive element clusters within the polymer matrix was studied by SEM and correlated to the dielectric behavior of the composite films.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: High dielectric constant; Conductive polymer; In situ polymerization

1. Introduction

The growing demand for the miniaturization and performance in electronic devices has been driving research and development activities for embedded passives (such as resistors, capacitors and inductors). By eliminating surface mount components and embedding into the substrate boards, embedded passive components offer various advantages over traditional discrete ones, including higher component density, increased functionality, improved electrical performance, increased design flexibility, improved reliability and reduced unit cost [1,2]. For embedded capacitor applications, study on ferroelectric ceramic/polymer composites with high dielectric constant (k) has been actively explored, since polymers meet the requirements for the low cost organic substrate process such as low temperature processibility and mechanical flexibility [3,4]. However, some challenging issues in these polymer composites for high k applications have been addressed, such as limited dielectric constants, low adhesion strength and poor processibility. Dramatic increase of dielectric constant close to the percolation threshold observed in the conductor−insulator percolative system arouses interest of developing conductive metal/polymer composites as candidate materials for embedded capacitor applications. Various metal fillers, such as silver, aluminum, nickel, have been used to prepare the metal/polymer composite or three-phase percolative composite system [5−11]. This material option represents advantageous characteristics over the conventional ceramic/polymer composites, specifically, ultra-high k with balanced mechanical properties including the adhesion strength.

Polyaniline (PANI) and its derivatives are regarded as one of the most promising conducting polymers because of its high polymerization yield, controllable electrical conductivity, good environmental stability and relatively low cost [12−16]. PANI/polymer composites have attracted considerable attention because low concentration of PANI can make the material

---

* Corresponding author. Tel.: +1 404 894 8391; fax: +1 404 894 9140.
E-mail address: cp.wong@mse.gatech.edu (C.P. Wong).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.01.057

achieve conductive or semiconductive capabilities which enable the development of thin, light, flexible and inexpensive organic electronics applied in display, sensor, and solar technologies [17–23]. For instance, PANI/polyurethane composite containing 8.4 wt% of PANI was reported with a conductivity of 2.17×10^{-10} S cm^{-1} [17]. The electrical conductivity of PANI/PU-epoxy composites with 1–5 wt% of PANI was in the range of 10^{-9}–10^{-3} S cm^{-1} [18]. PANI nanorod/liquid crystal epoxy composites showed electrical conductivity varied from 10^{-5} to 10^{-3} S cm^{-1} [19]. The conductivities for PANI/epoxy-amine system were in the range of 10^{-12}–10^{-6} S cm^{-1}, which was lower due to the deprotonation effect of amine [20]. Oligomeric PANI/epoxy resin composites cured with amine could be doped with protonic acids to achieve the electrical conductivity in the range of 10^{-5}–10^{-3} S cm^{-1} [21]. Besides the electrical behaviors, dielectric properties of PANI and its composites have been of interest as well. PANI was reported to possess a *k* value larger than 104 in a partially crystalline system for which an inhomogeneous disorder model was proposed [22]. High *k* values ranging from 200 to 1000 were reported for a PANI/polyvinyl alcohol composite, where the dispersed PANI particles of submicron size were suspended in the insulating polyvinyl alcohol matrix [14]. A PANI/polyurethane composite with a *k* value around 1120 at 1 kHz and 433 at 10 kHz was also reported [15]. But no data about dielectric loss of this system were found. For electroactive applications, 23 vol% of insulating polymer coated PANI particulates in a poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer matrix can reach a *k* value more than 2000 and a dielectric loss tangent around 1.75 at 100 Hz [23]. These results suggest the possibility of using conducting polymer as conductive elements instead of the metal fillers to achieve ultra-high dielectric constant and the worthwhileness of further study.

Epoxies have been of particular interests for embedded capacitor applications because of its compatibility with printed circuit board (PCB) manufacturing process. However, there is limited information concerning PANI composites prepared within thermoset polymer matrix. Therefore, it is worthwhile to explore the feasibility of incorporate high-loading level PANI into the epoxy matrix and the properties of PANI/epoxy composites. In this study, camphorsulfonic acid (CSA) was chosen as a protonating agent because the PANI protonated with CSA has relatively high crystallinity, high electrical conductivity and high miscibility with another polymer matrix [24,25]. In situ polymerization of protonated aniline in the epoxy matrix was employed to prepare PANI/epoxy composites. Compared with traditional simple solution blending method by mixing the doped PANI and epoxy resin [20,25–27], the in situ polymerization method rendered the possibility of better miscibility between PANI and epoxy resins and the higher PANI loading.

The influence of PANI loading levels and the hardener type on dielectric properties of PANI/epoxy composites was discussed. Frequency dependency of dielectric properties for PANI/epoxy composites was also presented in the range of 10 kHz–10 MHz. Scanning electron microscopy (SEM) was used to characterize the morphology of PANI/epoxy composites. The correlation of the microstructure with the corresponding dielectric properties was discussed.

2. Experimental

2.1. Materials

EPON 828 (Shell Chemicals Co.) was used as a matrix resin. Hexahydro-4-methylphthalic anhydride (HMPA, Lindau Chemical Co.), Ancamine 2167 (Air Product) and Anchor 1040 (Air Product) were selected as anhydride, amine and amine complex type hardeners, respectively. 1-Methylimidazole (Aldrich Chemical Co.) was employed as a catalyst. Aniline, camphorsulfonic acid (CSA) and ammonium persulfate (APS) were purchased from Aldrich Chemical Co.

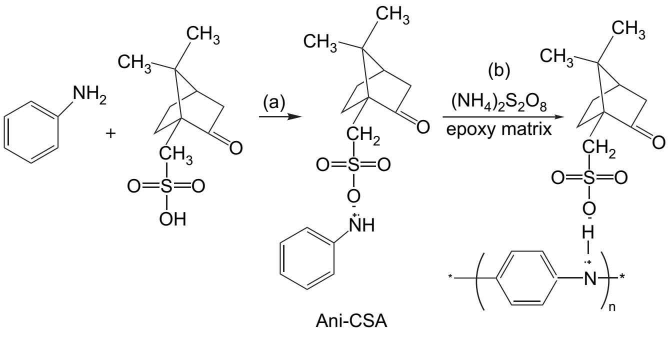
2.2. Preparation of aniline salt monomer

Aniline (0.05 mol, 4.6565 g) and CSA (0.05 mol, 11.515 g) were dissolved in a mixture of methanol and water by stirring. The aniline salt monomer Ani-CSA was obtained as a tan-white solid by recrystallization.

2.3. In situ polymerization of aniline salt within epoxy matrices

Ani-CSA (1.537 g) in 10 ml of chloroform was mixed with 3.5 g of epoxy in 5 ml of chloroform. An aqueous solution of 1.426 g of APS was added into the mixture dropwise with stirring over 1.5 h. The resulting mixture was stirred for another 5 h in an ice bath, and then washed with distilled water until the neutralization of the system to remove the excess amount of CSA and APS. A dark green viscous 20 wt% PANI/epoxy composite was obtained after storing in a vacuum oven overnight. The 8 wt%, 15 wt% and 25 wt% PANI/epoxy composites were prepared in the same manner.

After the addition of a hardener (if not other specified, HMPA by default), the composites were cured at 100 °C for 0.5 h and at 125 °C for 1 h (Scheme 1).



Scheme 1. Syntheses of aniline salt monomer Ani-CSA and PANI/epoxy composites via in situ polymerization of Ani-CSA in the epoxy matrix.

2.4. Instrumental analysis

Fourier transform infrared (FT-IR) and ultraviolet–visible (UV–vis) spectra were recorded on a Nicolet Magna-IR 560 spectrometer and a Beckman DU 520 General purpose UV–vis spectrophotometer, respectively. The ^{1}H NMR spectrum of aniline salt Ani-CSA monomer was obtained on a 300 MHz Varian Mercury Vx 300 NMR spectrometer. The glass transition temperatures (T_gs) of materials were determined by a modulated differential scanning calorimeter (DSC, TA Instruments 2920) at a heating rate of 5 °C/min under a nitrogen atmosphere. Thermogravimetric analysis was conducted on a TGA (TA Instruments 2050) at a heating rate of 5 °C/min under a nitrogen atmosphere. Scanning electron microscopy (SEM) measurements were carried out on a JEOL 1530 equipped with a thermally assisted field emission gun operated at 10 keV. Parallel plate capacitors of the formulated high k composite materials were fabricated on a copper clad FR-4 board and copper top electrodes were coated by DC sputtering. The capacitance and dissipation factor of the capacitor were then measured with a HP 4263A LCR meter. The thickness of the dielectric films was in the range of 55–88 μm measured with a profilometer (Alpha-Step Co.) and used to calculate the dielectric constant of the sample. Electrical measurements were conducted at room temperature by the four-probe technique using a Keithley 2000 Multimeter.

3. Results and discussion

3.1. Characterization of aniline salt monomer

Fig. 1(a) shows FT-IR spectrum of the Ani-CSA monomer. Aromatic C=C ring stretching observed at 1600 cm^{-1} and C–N stretching of benzenoid amine at 1509 cm^{-1} are consistent with the presence of the aniline ring. A peak at 1745 cm^{-1} is assigned to the C=O stretch of the carbonyl group in the camphor moiety. Peaks at 2640 cm^{-1} (N–H stretch), 1302 cm^{-1} and 1180 cm^{-1} (S=O symmetric stretch) are also consistent with the presence of the secondary sulfonamide in the Ani-CSA monomer. These results confirm that CSA has been successfully attached to aniline.

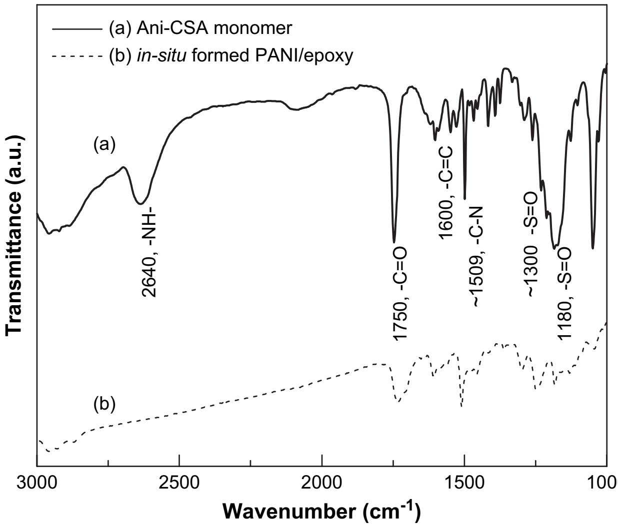


Fig. 1. FT-IR spectra of (a) Ani-CSA monomer and (b) in situ formed PANI/epoxy composite.

Fig. 2 presents the ^{1}H NMR spectrum of the Ani–CSA in $CDCl_3$ which is found to be fully consistent with the proposed structure. The aryl proton is observed at 7.6–7.2 ppm, as expected for the presence of the aniline moiety. The integration of other hydrogen is also consistent with the structure as listed in Table 1. It is another strong evidence for the successful preparation of the Ani-CSA monomer.

3.2. Characterization of in situ formed PANI/epoxy composites

The FT-IR result of the in situ formed PANI/epoxy composite is displayed in Fig. 1(b). The peak at 2640 cm^{-1} due to N–H stretching is not visible in the spectra, giving the evidence of the in situ polymerization of PANI within the epoxy matrix. Peaks at 1750 cm^{-1} assigned to the C=O stretching of the carbonyl group in the camphor moiety and at 1180/1300 cm^{-1} due to S=O symmetric stretching can be observed, indicating that CSA is still attached to PANI within the epoxy matrix.

The UV–vis spectrum of the green solution of in situ formed PANI/epoxy composite in dimethylsulfoxide (DMSO)

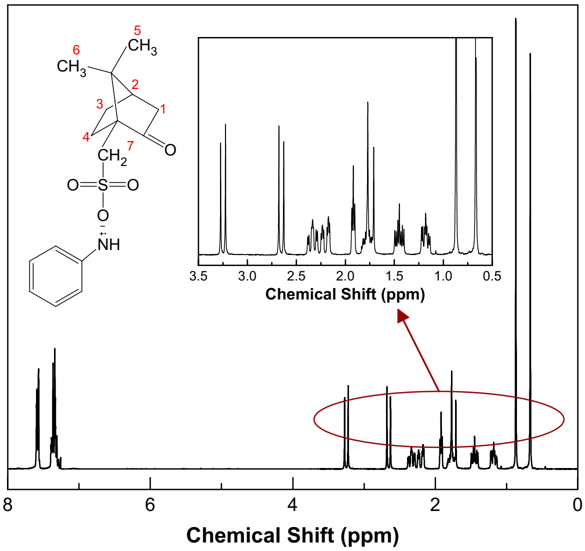


Fig. 2. ^{1}H NMR spectrum of Ani-CSA monomer in $CDCl_3$.

Table 1
^{1}H NMR data for Ani-CSA monomer in $CDCl_3$

Hydrogen	Chemical shift (ppm)	Peak multiplicity	Integration
Aryl	7.6–7.2	m	5H
H^{10}	3.2, 2.65	dd	2H
H^5, H^6	2.35, 1.5	Overlapping m	4H
H^4	1.9	m	1H
H^3	1.8	dd	2H
Geminal CH_3	0.87, 0.68	s	6H

s = Singlet, dd = doublet of doublets, and m = multiplet.

is shown in Fig. 3. An intense peak at ca. 330 nm is attributed to the transition from π band to π* band, while the shoulder at ca. 435 nm is the typical transition between polaron band and π* band which is generally observed for emeraldine salts. The broad absorption band at ca. 900 nm is assigned to the combination of transition from π band to polaron band and "free-carrier tail" which stems from the formation of delocalized polarons. The results indicate that PANI remains in its doped state and adopts a mixture of compact and expanded coil-like conformations in the composites [28].

The DSC thermograms of cured neat epoxy and in situ formed PANI/epoxy composites with different PANI contents are shown in Fig. 4. The T_g of the neat PANI is difficult to be detected by DSC. As compared to the neat epoxy, a slight decrease of T_g is observed for various in situ PANI/epoxy composites with increasing PANI content, indicating that no obvious phase separation occurred in the composites.

The thermal stability behavior of neat PANI and in situ formed PANI/epoxy with different PANI contents is shown in Fig. 5. The TGA diagram of the neat PANI shows a certain weight loss below 200 °C, which is attributed to the loss of water and oligomers. The weight loss between 220 °C and 320 °C may correspond to the loss of the bound CSA. This can explain the weight loss in the same temperature range for all the in situ formed PANI/epoxy composites.

3.3. Morphological study of in situ formed PANI/epoxy composites

Morphologies of the composites were observed by SEM. Fig. 6 displays SEM micrographs of in situ formed PANI/epoxy composites with different PANI contents. In contrast to the composites prepared by simple mixing in which the agglomeration of PANI occurred, no obvious phase separation is observed in the in situ formed PANI/epoxy composites and this observation is consistent with the DSC results. The fracture surface of the PANI/epoxy composite with 8 wt% PANI resembles that of a typical neat epoxy fracture surface with a few different structures as conductive salt-rich regions [13]. The existence of the conductive salt clusters is more obvious in composites with higher concentrations of PANI. The morphological study suggested that the in situ polymerization method to prepare the PANI/epoxy composites is useful to achieve good dispersion and high miscibility of PANI with the epoxy matrix.

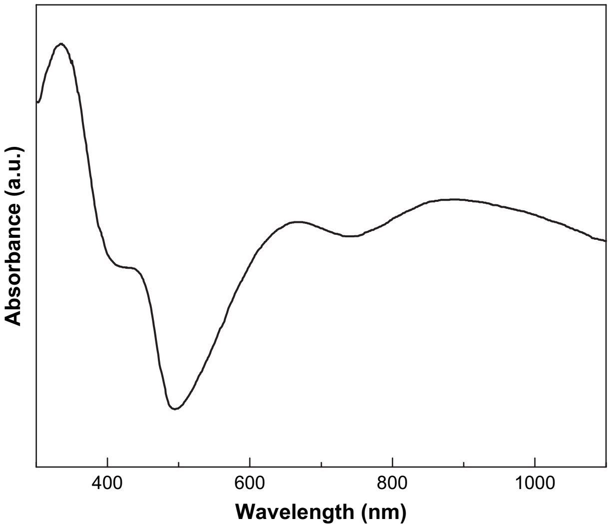


Fig. 3. UV–vis spectrum of an in situ formed PANI/epoxy in DMSO.

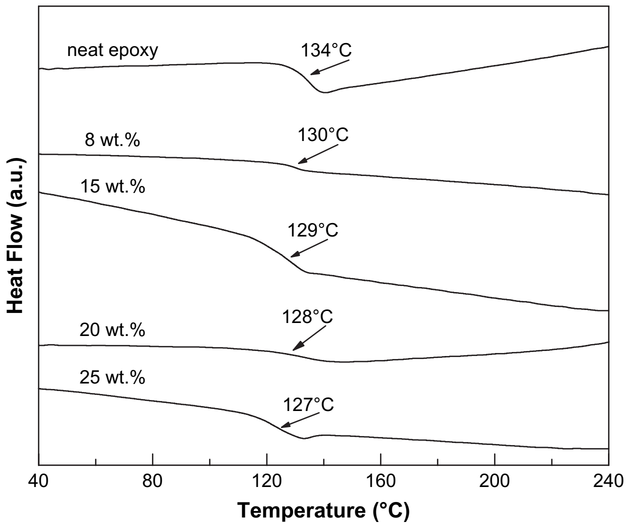


Fig. 4. DSC curves of neat epoxy and in situ formed PANI/epoxy composites with different PANI contents.

3.4. Dielectric and electrical property study of in situ formed PANI/epoxy composites

Dielectric and electrical properties of in situ formed PANI/epoxy composites with different PANI contents were studied on samples with parallel plate capacitor configuration. The electrical conductivity of the composite containing 25 wt% PANI was 5×10^{-6} S cm^{-1}. While the resistance of the other composites with lower contents of PANI was beyond the range

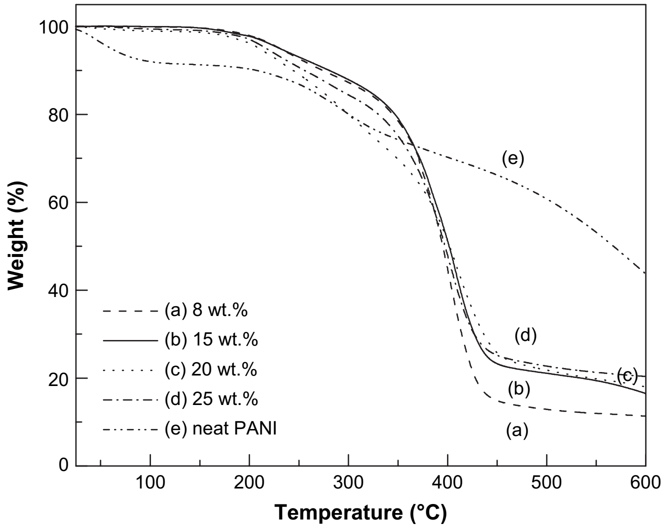


Fig. 5. TGA diagrams of in situ formed PANI/epoxy composites with different PANI contents and neat PANI.

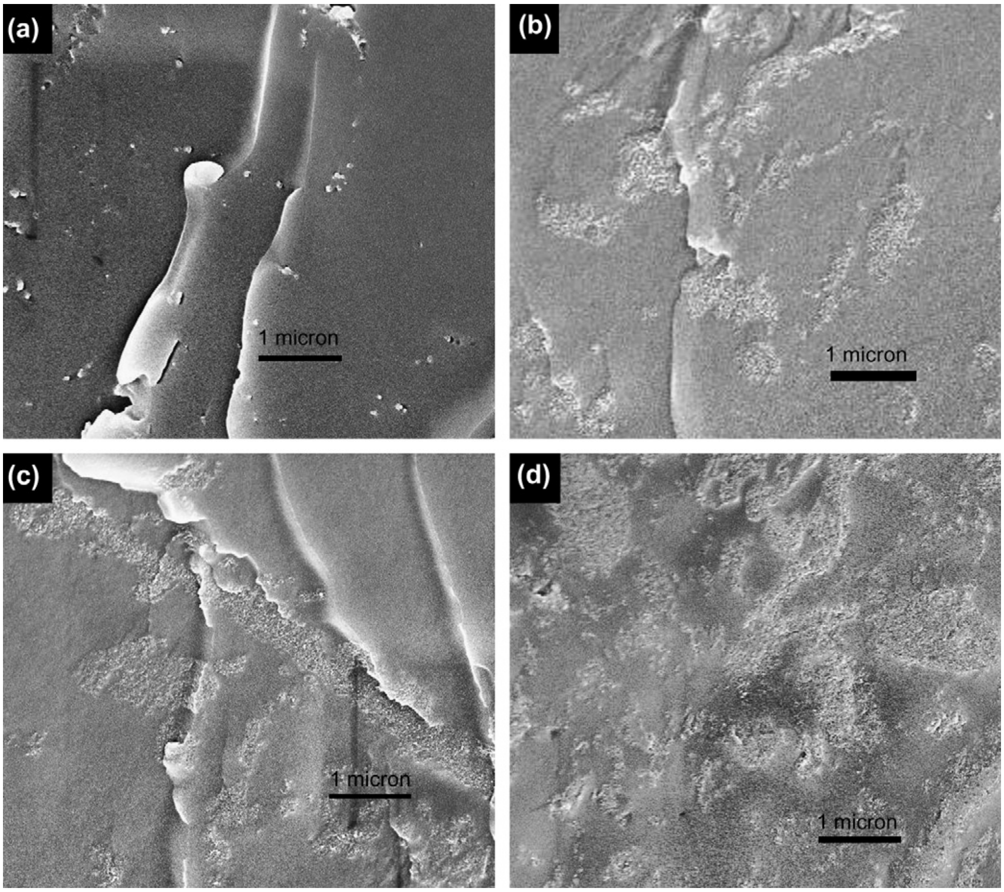


Fig. 6. SEM micrographs of in situ PANI/epoxy composites with (a) 8 wt%, (b) 15 wt%, (c) 20 wt%, and (d) 25 wt% PANI.

of the equipment (over $10^7\ \Omega$), demonstrating conductivity values below $10^{-7}\ \mathrm{S\,cm^{-1}}$. Compared to the values ranging from 10^{-10} to $10^{-3}\ \mathrm{S\,cm^{-1}}$ reported for other PANI/polymer composites, the conductivity values of these in situ formed PANI/epoxy composites are reasonable as the conductive properties of these composites vary considerably resulting from the differences in PANI loading, doping state and level, molecular organization of the conductive clusters with respect to the polymer matrix and so on.

The values of *k* and dielectric loss tangent (dissipation factor, Df) at 10 kHz are listed in Table 2. The *k* values increase significantly with the increase of PANI contents in the composites. As revealed from the data, the *k* value increases about 300-fold from ∼10 with 8 wt% PANI to ∼2980 with 25 wt% PANI. The elimination of PANI agglomerates and the formation of a fine PANI network surrounded by epoxy matrix lead to enhanced dielectric properties of the composites. The relatively high dielectric loss tangent is due to the motion of free charge carriers and interfacial polarization relaxation attributed to the conductive salt clusters within the composites.

Fig. 7 depicts the effect of the AC frequency on the values of *k* and Df of in situ formed PANI/epoxy composites with different PANI contents. It shows that the *k* values decrease with the AC frequency for all the composites, which is an expected phenomenon as reported in other PANI/polymer composites [14,15,17]. The results indicate that more PANI dipoles and charge carriers within the composites fail to keep up with the electric field of the increasing frequency. Another effect might contribute to this relaxation process is that the AC-conductivity exhibited at higher frequency will increase with frequency and thus decrease charge storing capability [18]. The composite containing the largest amount of PANI showed the strongest frequency dependency of dielectric properties, which might be due to its highest conductivity. In Fig. 7(b) which shows the frequency dependence of dielectric loss tangent in the experimental frequency range, the peaks are possibly related to interfacial polarization relaxation effects, which correspond to the relaxation of *k* value shown in Fig. 7(a) as well.

The hardener type was also found as a critical parameter for the dielectric properties of PANI/epoxy composites. Table 3 lists the dielectric properties of in situ formed PANI/epoxy composites with 15 wt% PANI cured with different types of hardeners. The composites cured with alkaline type hardener (amine) showed a low dielectric constant, and this may be due to the dedoping effect of PANI salt by amine, which can react

Table 2
Dielectric properties of in situ formed PANI/epoxy composites with different PANI contents at 10 kHz

PANI content	8 wt%	15 wt%	20 wt%	25 wt%
k	10	192	916	2980
Df	0.08	0.48	0.55	0.48

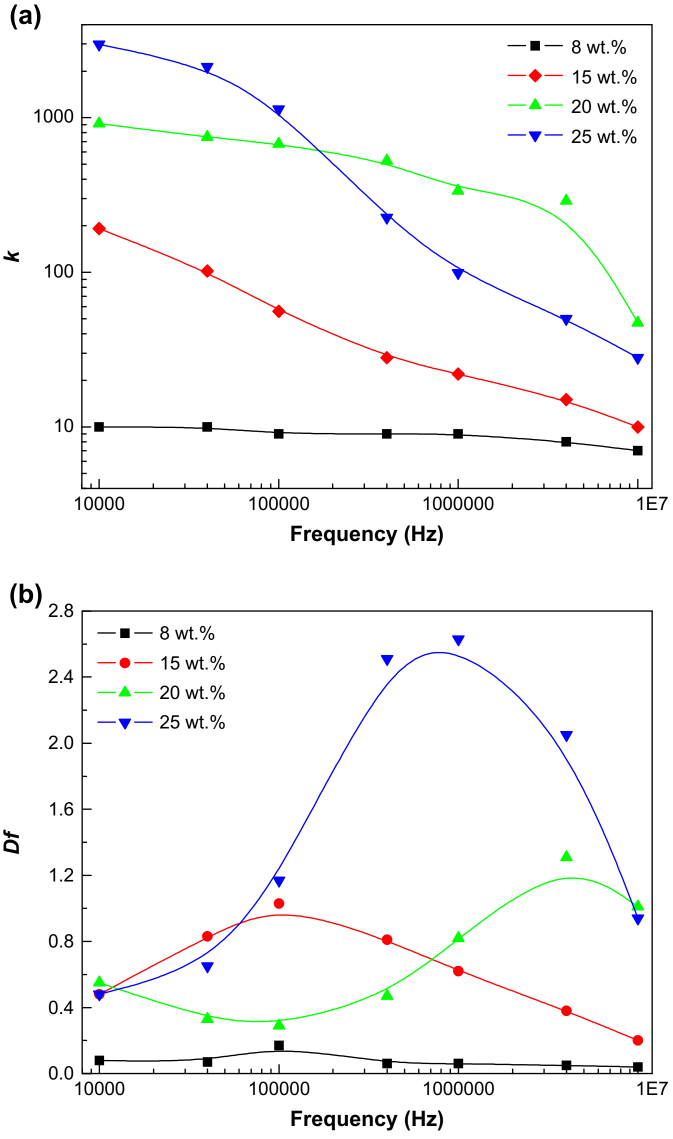


Fig. 7. Frequency dependence of (a) *k* and (b) Df of in situ formed PANI/epoxy composites with different PANI contents.

with the dopant of PANI and thus lead to the deprotonation of the conductive salt. The color change from green to blue by the addition of alkaline hardener was observed for the composites throughout the mixing procedure, suggesting that a conversion from a conductive PANI–CSA emeraldine salt to a nonconductive PANI emeraldine base occurred due to the basic character of the alkaline hardener. While using acidic type hardeners such as anhydride and amine complex, which retain the doping state of the PANI salt, led to a much higher dielectric constant. The results are consistent with the finding that the acidic curing agents support the conductive character of PANI, while alkaline hardeners conflict this property [29].

4. Conclusions

The in situ polymerization of an aniline salt within epoxy matrices was successful to prepare PANI/epoxy composites with various PANI contents. A PANI/epoxy composite prepared in this fashion exhibited a high dielectric constant close to 3000, a dielectric loss tangent less than 0.5 at 10 kHz and at room temperature. The morphological study by SEM suggested that the in situ polymerization method to prepare the PANI/epoxy composites was useful to achieve good dispersion and high compatibility of PANI with the epoxy matrix. The elimination of agglomerates surrounded by insulating matrix and the formation of a fine network led to enhanced dielectric properties of the composites. The hardener type was also found as a critical parameter for the dielectric properties of PANI/epoxy composites. Accordingly, the dielectric properties of the composites could be tailored by the doping level and the appropriate hardener selection.

Table 3
Dielectric properties of 15 wt% in situ formed PANI/epoxy composites cured with various hardeners at 10 kHz

Hardener	Anhydride	Amine	Amine complex
k	192	8.1	200
Df	0.48	0.03	0.39

Acknowledgements

The authors would like to express grateful acknowledgement to the National Science Foundation and Korean Institute of Science and Technology for their financial support.

References

[1] Ulrich RK, Schaper LW. Integrated passive component technology. New Jersey: IEEE Press, Wiley-Interscience; 2003.
[2] Prymark J, Bhattacharya S, Paik K, Tummala RR. Fundamentals of microsystems packaging. New York: McGraw-Hill; 2001.
[3] Gregorio R, Cestari JM, Bernardino FE. J Mater Sci 1996;31:2925–30.
[4] Bai Y, Cheng ZY, Bharti V, Xu HS, Zhang QM. Appl Phys Lett 2000;76:3804–6.
[5] Rao Y, Wong CP. IEEE Proceedings of the 52nd electronic components and technology conference, San Diego, CA, USA; 2002. p. 920–3.
[6] Xu J, Wong CP. IEEE Proceedings of the 53rd electronic components and technology, New Orleans, LA, USA; 2003. p. 173–81.
[7] Lu JX, Moon KS, Xu JW, Wong CP. J Mater Chem 2006;16:1543–8.
[8] Qi L, Lee BI, Chen S, Samuels WD, Exarhos GJ. Adv Mater 2005;17:1777–81.
[9] Dang ZM, Lin YH, Nan CW. Adv Mater 2003;15:1625–9.
[10] Dang ZM, Shen Y, Nan CW. Appl Phys Lett 2002;81:4814–6.
[11] Choi HW, Heo YW, Lee JH, Kim JJ, Lee HY, Park ET, et al. Appl Phys Lett 2006;89:132910.
[12] Tsotra P, Friedrich K. Synth Met 2004;143:237–42.
[13] Tsotra P, Gryshchuk O, Friedrich K. Macromol Chem Phys 2005;206:787–93.
[14] Dutta P, Biswas S, De SK. Mater Res Bull 2002;37:193–200.
[15] Chwang C, Liu C, Huang S, Chao D, Lee S. Synth Met 2004;142:275–81.
[16] Chiou WC, Yang DY, Han JL, Lee SN. Polym Int 2006;55:1222–9.
[17] Tabellout M, Fatyeyeva K, Baillif PY, Bardeau JF, Pud AA. J Non-Cryst Solids 2005;351:2835–41.
[18] Suelho K, Dinant NF, Magana S, Clisson G, Francois J, Dagron-Lartigau C, et al. Polym Int 2006;55:1184–90.
[19] Deligoz H, Tieke B. Macromol Mater Eng 2006;291:793–801.
[20] Moreira VX, Garcia FG, Soares BG. J Appl Polym Sci 2006;100:4059–65.
[21] Yang X, Zhao T, Yu Y, Wei Y. Synth Met 2004;142:57–61.

[22] Joo J, Long SM, Pouget JP, Oh EJ, MacDiarmid AG, Epstein A. J Phys Rev B 1998;57:9567–79.
[23] Huang C, Zhang QM, Su J. Appl Phys Lett 2003;82:3502–4.
[24] Łuzny W, Banka E. Macromolecules 2000;33:425–9.
[25] Han MG, Im SS. Polymer 2001;42:7449–54.
[26] Jang J, Bae J, Lee K. Polymer 2005;46:3677–84.
[27] Yang QH, Wei SG, Cheng GX. Polym Compos 2006;27:201–4.
[28] Xia Y, MacDiarmid AG. Macromolecules 1994;27:7212–4.
[29] Tsotra P, Gatos KG, Gryshchuk O, Friedrich K. J Mater Sci 1995; 40:569–74.