Synthesis and characterization of polyaniline nanorods as curing agent and nanofiller for epoxy matrix composite

Jyongsik Jang*, Joonwon Bae, Kyungtae Lee

Hyperstructured Organic Materials Research Center, School of Chemical Engineering, College of Engineering, Seoul National University, Shinlimdong 56-1, Seoul 151-742, South Korea

Abstract

Novel PANI nanorods with average diameter of 21–53 nm and length of 0.5–1 μm were synthesized by dispersion polymerization method. The morphology of obtained PANI nanorods was significantly dependent on the type of salt, stirring, and polymerization temperature. Dispersion polymerization with $FeCl_3$ produced longer nanorods than ammonium persulfate (APS) and magnetic stirring decreased the length of nanorods. While the average diameter of PANI nanorods decreased with increasing reaction temperature, the electrical conductivity dropped considerable at high polymerization temperature due to the increment of insulating emeraldine base. Dynamic differential scanning calorimetry (DSC) study showed that the heat of cure was independent of heating rate. On the contrary, the heat of cure was proportional to the content of PANI nanorods as a role of curing agent. Isothermal DSC study revealed that the cure behavior of LCE/PANI nanorod system was an auto-catalyzed reaction. Thermogravimetric analysis (TGA) indicated that the thermal stability of cured LCE/PANI nanocomposite was significantly dependent on the PANI nanorod composition. In addition, the electrical conductivity of LCE/PANI nanocomposite materials was higher than that of conventional epoxy composites. Therefore, PANI nanorods played a role of curing agent owing to the existent amine group and acted as reinforcing filler for cured LCE nanocomposites.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Curing agent; Nanofiller; Composite

1. Introduction

Recently, various nanoscale applications have motivated the synthesis of one-dimensional (1-D) conducting nanomaterials such as nanofibers, nanotubes, and nanorods [1,2]. Especially, polyaniline (PANI) nanomaterials have attracted great attention because of their enhanced conductivity, environmental stability, and color change corresponding to diverse redox states. They have been fabricated using template method, self-assembly method, electrochemical polymerization and electrospinning method [3–5]. However, these methods have offered a limited scale synthesis of PANI nanomaterials. On the other hand, dispersion polymerization is known to provide the mass production of micro-size spherical polymers. Nevertheless, 1-D

nanostructured polymeric materials could not been obtained from the dispersion technique without purification of byproducts [6].

One of the most promising applications of PANI is conducting nanofiller for nanocomposites, especially thermoset matrix composites [7–12]. However, there has been limited information concerning conducting polymer nanocomposites, prepared with thermoset polymer as matrix. Recently, we have examined the cure behavior and properties of various LCE/carbon nanotube and LCE/carbon black systems [13,14]. When the advantageous properties of LCE resin [15–24] such as mechanical durability, chemical inertness, and hardness are combined with those of PANI nanomaterials, the resulting nanocomposites can be applied to diverse electronic devices, electromagnetic shielding materials, and conducting adhesives. Even though the LCE is a representative electrically insulating material, the incorporation of electrically conducting fillers into the LCE matrix could produce conducting polymer nanocomposite [25]. Therefore, it is worthwhile to understand the

cure kinetics and properties of LCE/PANI nanorods nanocomposite system.

Herein, we report the first example for large-scale production of PANI nanorods using dispersion polymerization in high yield without undesired by-products. The effect of synthetic conditions on the morphology of resulting PANI nanorods was extensively studied. We also investigated the cure behavior of the LCE/PANI nanorod system and the thermal and electrical properties of the prepared LCE/PANI conducting nanocomposites. It was expected that PANI nanorods could play roles of curing agent and reinforcement filler without restricting cure reaction owing to the nanoscale architect.

2. Experimental

2.1. Materials

A liquid crystalline epoxy (LCE) resin, diglycidyl ether of 4,4′-dihydroxy-α-methyl stilbene (DGE-DHAMS) was employed as matrix resin. The synthesis, physical and chemical properties, and potential applications of the DGE-DHAMS based epoxy resin have been addressed in literature [26–29]. The chemical structures of LCE and aniline were shown in Fig. 1. The epoxy equivalent weight (EEW) of the LCE resin is about 175 g/mol. The electrically conducting filler, PANI nanorods were synthesized by dispersion polymerization at ambient condition [30].

2.2. Synthesis of PANI nanorods

The PANI nanorod was synthesized by dispersion polymerization using hydrochloric acid (HCl) as a dopant and ammonium persulfate (APS) as an oxidant. In a typical procedure, 20 ml of 35 wt% HCl and 2.0 g of aniline were dispersed in 200 ml of distilled water. The [HCl]/[aniline]

(a) Liquid Crystalline Epoxy (DGE-DHAMS)

(b) Aniline

Fig. 1. Chemical structures of epoxy resin and aniline: (a) diglycidyl ether of 4,4′-dihydroxy-α-methyl stilbene; (b) aniline.

ratio was fixed at 6. The HCl is one of the strongest dopant for the polymerization of aniline monomer, thus it is suitable to increase the electrical conductivity of PANI nanorods. Then, 4.8 g of ammonium persulfate (APS) was added into the solution. Subsequently, 3.75 g of ferric chloride was also used for the formation of PANI nanorod. The polymerization of PANI proceeded with stirring for 3 h at 30 °C. Ethanol was added into the resulting product to remove the residual HCl and APS. The upper solution was discarded and the remaining product solution was dried in vacuum oven overnight at 45 °C. The yield was higher than 90%. The effect of experimental parameters such as oxidant, stirring, and temperature was thoroughly examined.

### 2.3. Preparation of sample mixtures for cure

The weight ratios of the PANI nanorod to LCE in the samples were made to be 1, 5, 10, 15, 20, and 25 wt%. The sample mixtures were prepared by dispersing the LCE and PANI nanorod in acetone, and sonicating the mixtures for 1 h. Then, the solvent was evaporated in a vacuum oven. The sample mixtures were cured at 150 °C for 4 h and post-cured at 200 °C for 1 h for complete cure.

2.4. Instrumental analysis

The dynamic differential scanning calorimetry experiments were conducted with a thermal analyzer DSC2920 at heating rates of 2.5, 5, 10, and 20 °C/min. The heat of cure was determined from the area under the cure thermogram. The isothermal DSC experiments were carried out in the temperature range of 160–200 °C. Below the range, the curing rate is too low to monitor the cure reaction, whereas a small amount of thermal degradation occurs over the range. Infrared spectra were recorded on a Bomem MB100 Fourier Transform Infrared (FT-IR) spectrometer. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA7 at a heating rate of 10 °C/min under nitrogen atmosphere. The electrical conductivity of cured samples were measured by the standard four-probe method under ambient conditions. TEM analysis was performed with a JEOL JEM-200CX transmission electron microscope. SEM images were obtained with a JEOL 6700 scanning electron microscope. The EDX analysis was performed using JEOL JSM 5410 LV.

3. Results and discussion

The scanning electron microscope (SEM) image of PANI nanorods obtained at [HCl]/[aniline]=6 at 30 °C was exhibited in Fig. 2(a). The average diameter of PANI nanorods was 34 nm and showed little size distribution. Under acidic condition, the acid–base reaction occurs with basic aniline molecules and the resultant products, amphiphillic monomer ions such as anilinium ions, form anilinium
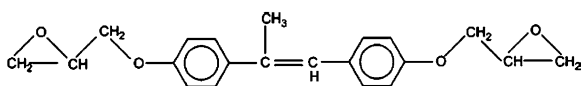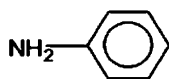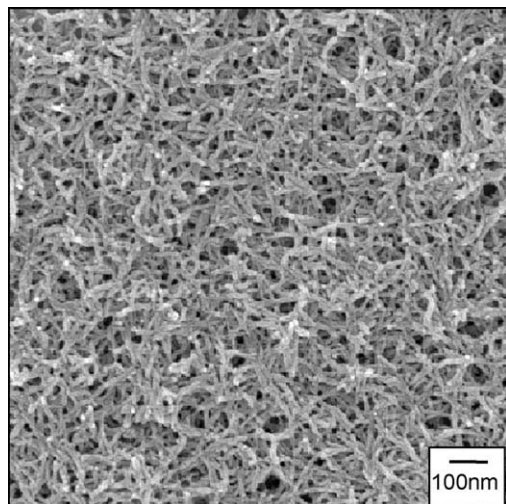
Fig. 2. Scanning electron microscope (SEM) image of polyaniline nanorods synthesized by dispersion polymerization at [HCl]/[aniline]=6 at room temperature.

Fig. 3. FT-IR spectrum of polyaniline nanorods.

micelles in aqueous solution [31,32]. When the molar ratio of [HCl]/[aniline] is higher than 1, free aniline molecules disappear in aniline/HCl aqueous solution and most of aniline monomers are transformed into amphiphillic anilinium ions. The formation mechanism of PANI nanorods is related to effect of salts on the micelle structure. Micelles grow in the presence of salts from spherical, rodlike to cylindrical aggregates or wormlike micelles [33]. The amphiphillic anilinium ion micelles were polymerized with the morphological transition from spherical to cylindrical morphology owing to existent salt ions such as Fe^{3+}, $S_2O_8^{2-}$, NH_4^+, Cl^-, and H^+ in reaction medium. This sphere-to-cylinder micellar conversion has also been reported by our group [34]. In addition, the electrostatic interaction between the chlorine anion of HCl and the quinoid imine as well as the H-bonding interaction between the benzenoid amine and H_2O coexist in the PANI doped with HCl [35]. The anilinium micellar transformation by salt ions and two kinds of interaction in the polymer chain backbone drive the PANI to grow into nanorod morphology. Under these experimental conditions, the yield of PANI nanorods (approximately 5–10 g) was higher than 90%. The high yield formation of PANI nanorods using anilinium micelles and dopant interactions is a characteristic of our synthetic method, which makes it different from other approaches. To the best of our knowledge, this is the first experimental evidence for the large-scale fabrication of PANI nanorods using surfactant-free polymerization.

Fig. 3 exhibits the FT-IR spectrum of PANI nanorods, which shows the vibrational bands 1483 and 1567 cm^{-1} associated with quinoid and benzenoid structures of PANI. The peaks at 1246 and 1300 cm^{-1} were attributed to C–H stretching from aromatic conjugation. Elemental analysis (EA) exhibited the presence of carbon (57.8%) and nitrogen (11.6%). Since an aniline has one nitrogen (N) and six
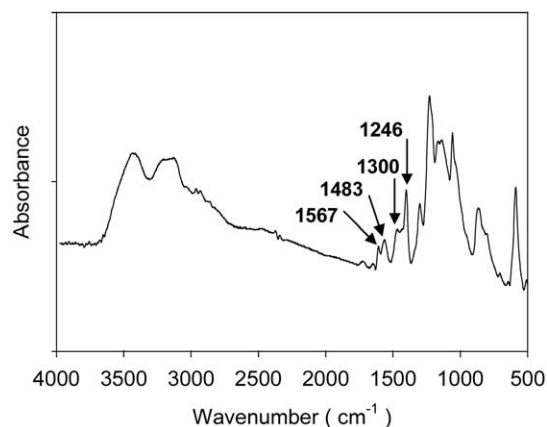
carbons (C), N/C atomic ratio is approximately 0.17. EA data was consistent with the N/C ratio of bulk PANI. Considering these facts, it is obvious that PANI was successfully synthesized using dispersion polymerization.

Fig. 4(a) and (b) displays transmission electron microscopy (TEM) images that confirm the effect of oxidant type concerning the length control of PANI nanorods. The average length (500 nm) of PANI nanorods polymerized with FeCl$_3$ was larger than that (200 nm) polymerized with ammonium persulfate (APS). Compared with different oxidant types, Fe^{3+} oxidizes one electron from a monomer and $S_2O_8^{2-}$ oxidizes two electrons from a monomer. In other words, the molar ratio of [oxidant]/[monomer] in the FeCl$_3$ oxidation polymerization system required twice as much as that of the APS system. In addition, Fe^{3+} has larger charge number than $S_2O_8^{2-}$. Therefore, the more anions under the FeCl$_3$ system emerge as compared with APS system and the ionic strength of Fe^{3+} is larger than $S_2O_8^{2-}$. This is because FeCl$_3$ induces the PANI nanorods that have longer length. It has good agreement with the previous result that micelles reach a larger growth at higher charge number and concentration of ions [36]. When FeCl$_3$ was used as oxidant, the average length of nanorods was 500 nm under magnetic stirring condition of 300 rpm (Fig. 4(b)), whereas the average length of nanorods was 1 μm without magnetic stirring (Fig. 4(c)). This means that the length of PANI nanorods could be tuned through appropriate selection of oxidant species and stirring condition.

Table 1
Average diameter, conductivity and yield of PANI nanorods as a function of polymerization temperature

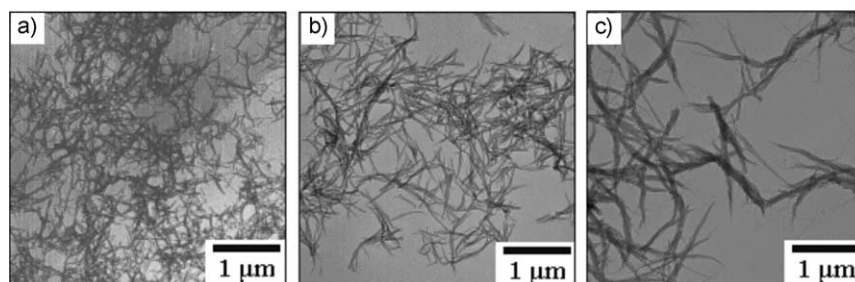| Temperature (°C)	Average diameter (nm)	Conductivity (S/cm)	Yield (%)
−20	53.0	89.7	>50
3	47.6	24.5	>60
30	34.5	10.9	>90
50	23.1	8.1	>95
70	21.1	1.5	>95

Fig. 4. Effect of oxidant and stirring condition on the average length of PANI nanorods polymerized with: (a) 0.005 mol of APS at 300 rpm magnetic stirring (average length: 300 nm), (b) 0.01 mol of FeCl₃ at 300 rpm magnetic stirring (average length: 500 nm), (c) 0.01 mol of FeCl₃ without magnetic stirring (average length: 1 μm).

The polymerization temperature also affected conductivity, the average diameter, and yield of nanorods (Table 1). The average diameter of PANI nanorods decreased from approximately 53 to 21 nm with increasing polymerization temperature up to 70 °C. The conductivity of synthesized PANI nanorods was in inverse proportion to polymerization temperature [37]. Fig. 5 represents the TEM images of PANI nanorods prepared at 3 and 50 °C. At −20 °C, the conductivity of PANI nanorods was approximately 90 S/cm. There are no reports describing the preparation of PANI nanomaterials with conductivity of 10^1–10^2 S/cm without the polymer agglomerations. The polymerization rate was faster at higher temperatures and this was indirectly observed through rapid color change of reaction medium from transparent into blue color. Because the fast polymerization shortened the growth time of PANI, the thickness of PANI nanorods became thin and the yield was high (> 95%) without undesired shapes.

The temperature dependence of PANI conductivity was also explained by X-ray diffraction (XRD) patterns in Fig. 6. XRD pattern of PANI nanorods at 70 °C confirms the peaks applicable to both emeraldine base (0.5, 0.46, and 0.39 nm) and emeraldine salt (0.44, 0.42, and 0.29 nm). Contrarily, as the polymerization temperature decreases at low temperature (−20 °C), the PANI nanorods reveal only two peaks at 0.42 and 0. 35 nm, which were attributed to emeraldine salt as a conducting material [38]. These data indicated the presence of emeraldine base as an insulating material at high temperature.

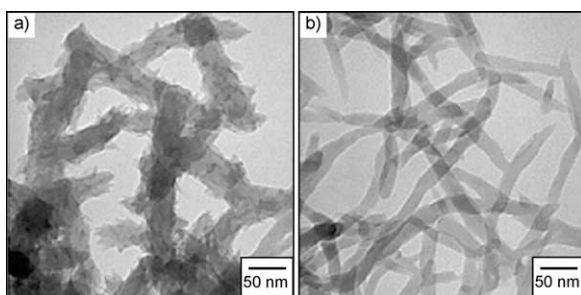To study the cure behavior and properties of LCE/PANI

nanorods system, PANI nanorods with average diameter of 34.5 nm and conductivity of 10.9 S/cm were employed. The weight ratio of PANI nanorod to LCE was fixed at 25 wt%. The dynamic DSC thermograms of the LCE/PANI nanorod as a function of heating rate are presented in Fig. 7. The peak temperature and the initial cure temperature increased with increasing heating rate in LCE/PANI nanorod system. Table 2 represents the maximum peak temperature (T_p), heat of cure, and activation energy of LCE/PANI nanorod system. It was clear that the heat of cure was nearly independent of the heating rate. While it was reported that the heat for cure of LCE/curing agent system was ca. 140 kJ/mol epoxide [13], heat of cure for LCE/PANI nanorod system was evaluated to be approximately 125 kJ/mol epoxide. Since the heat of cure is proportional to the extent of cure reaction at constant curing agent concentration, PANI nanorods retarded cure reaction slightly. The steric hindrance from the presence of PANI nanorods resulted in the slight retardation effect on cure reaction. However, the PANI nanorods did not act as a heat sink.

The activation energy of the LCE/PANI nanorod system can be evaluated using Ozawa equation [39,40]:

$$\log \varphi = C - 0.4567 E_a / R T_p$$

where φ is the heating rate, E_a the activation energy, and T_p

Fig. 5. TEM images of polyaniline nanorods obtained from [HCl]/[aniline]=6 at different polymerization temperatures: (a) 3 °C, (b) 50 °C.
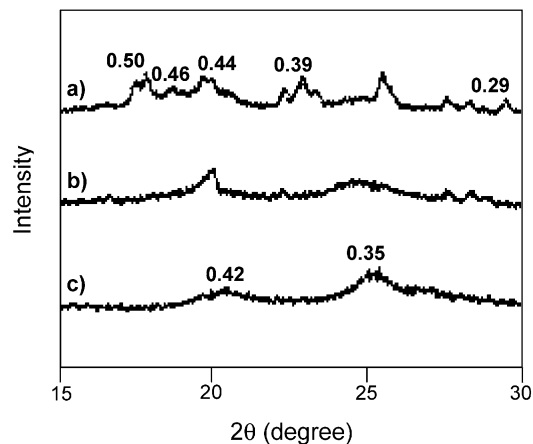

Fig. 6. X-ray diffraction patterns of PANI nanorods as a function of polymerization temperature: (a) 70 °C; (b) 30 °C; (c) −20 °C.
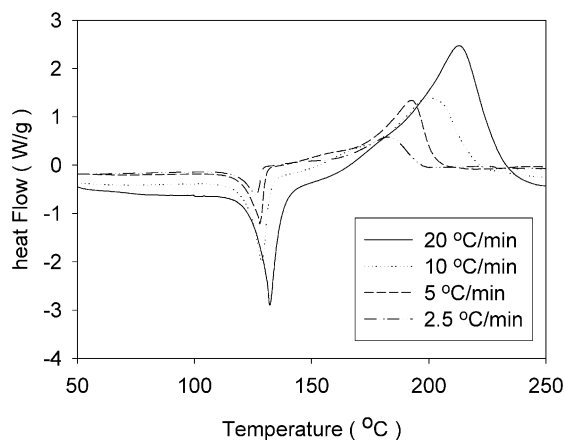
Fig. 7. Dynamic DSC thermograms of LCE/PANI nanorod system as a function of heating rate.

Fig. 8. Dynamic DSC thermograms of LCE/PANI nanorod system as a function of PANI composition.

the peak temperature. Activation energy can be calculated from the slope of log φ vs. $1/T_p$. The activation energy of LCE/PANI nanorod was 116.60 kJ/mol epoxide, which was about 10% higher than that of LCE/curing agent system (105 kJ/mol) [13]. The activation energy increment means that the curing reaction of LCE/PANI nanorod system occurrs at a higher temperature range. This phenomenon was clearly reflected in the shift of peak temperatures in Table 2. That is, the cure kinetics of LCE/PANI nanorod system was not significantly affected by the introduction of PANI nanorods. Dynamic DSC results revealed that the PANI nanorods could be successfully employed as curing agent.

Fig. 8 shows the dynamic DSC curves for LCE/PANI nanorod system as a function of the composition of PANI nanorod at a constant heating rate of 10 °C/min. Peak temperatures decreased with increasing the amount of PANI nanorod at the same heating rate. It showed that the curing reaction occurred readily at high PANI nanorod composition. Heat of cure and peak temperatures was summarized in Table 3. The heat of cure increased slightly with increasing the amount of PANI nanorod. Therefore, the extent of cure increased with increasing the composition of PANI nanorod. This phenomenon arose from the increased composition of amine group taking part in cure reaction. The curing agent reacts with the epoxide through nucleophilic addition reaction. Partially positive carbon atom in epoxide group is a electrophile while amine group is a nuclephile. Owing to the large number of existent amine groups, it is facile for the amine groups in PANI to form
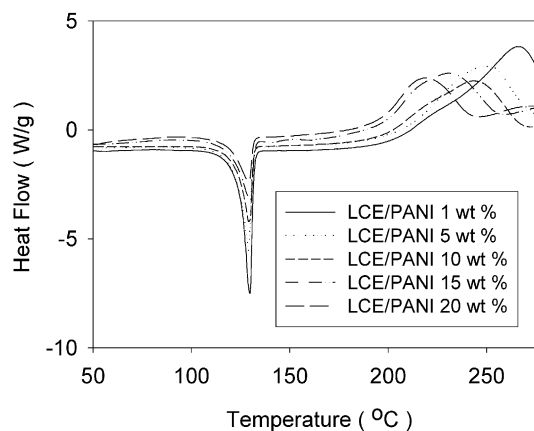
nucleophile-electrophile complexes with epoxide group in LCE molecules. On the ground that the effect of PANI nanorod composition on heat of cure and activation energy is more dominant than any other factors such as steric factor and filler property, it was clear that the incorporated PANI nanorods showed characteristics of curing agent.

The isothermal DSC curves for LCE/PANI nanorod (25 wt% PANI) system were illustrated in Fig. 9. The maximum heat flow associated with maximum cure rate increased with increasing cure temperature. This fact demonstrated that the PANI nanorods as a curing agent did not show any diffusion-barrier effect. To obtain the extent of cure, the DSC curves were integrated and the partial areas as a function of time were normalized with respect to H_{com} (heat for complete cure) and presented in Table 4. It has been revealed that the extent of cure (α), calculated from the heat of cure was almost independent of cure temperature at a given curing agent composition in LCE/PANI nanorod system. The extent of cure was 0.59–0.69 at a fixed PANI nanorod composition (25 wt%). In addition, the maximum cure rate tends to approach to an asymptotic value at higher temperatures. Isothermal kinetic parameters were evaluated from the Kamal equation [41]:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n$$

where k_1 and k_2 are the kinetic rate constants, and m and n are kinetic exponents. This equation is valid for the autocatalyzed reaction. Generally, m is related with the maximum cure rate and n with the post-cure reaction. In epoxy/amine system, the overall reaction order is known as

Table 2
The peak temperature (T_p), heat for cure, and activation energy of (E_a) LCE/PANI nanorod nanocomposite as a function of heating rate

Nanocomposite	Scan rate (°C/min)	20	10	5	2.5
LCE/PANI nanorod (30 nm)	T_p (°C)	212.9	200.1	192.7	182.3
	Heat of cure (kJ/mol epoxide) E_a (kcal/mol)	129.1	126.4	127.3	125.4
		116.6			

Table 3
The peak temperature (T_p), degree of cure, and heat for cure of LCE/PANI nanorod nanocomposite as a function of PANI nanorod composition

PANI composition (wt%)	Heat of cure (kJ/mol epoxide)	Degree of cure	T_p (°C)
1	75.4	0.50	267.0
5	81.2	0.53	249.8
10	90.5	0.58	243.1
15	97.9	0.62	230.3
20	104.1	0.67	218.4

Table 4
Degree of conversion as a function of cure temperature in LCE/PANI nanorod nanocomposite

Temperature (°C)	Conversion (α) at 40 min
160	0.59
170	0.62
180	0.64
190	0.66
200	0.69

Weight ratio of PANI to LCE is 25 wt%.

2 [42]. In the case of LCE/PANI nanorod system, m and n values calculated from Kamal equation was 1.276 and 0.689, respectively at 180 °C. The value of $m+n$ was 1.965, and it was reasonable value in epoxy/amine system. This fact also showed that the cure reaction of LCE/PANI nanorod was an auto-catalyzed reaction, where PANI nanorods initiated curing reaction as curing agent in the early stage and promoted the curing reaction as catalyst throughout the curing process. Considering all the facts, it was obvious that the cure behavior of curing agent free LCE/PANI nanorod system displayed typical characteristics of cure reaction of epoxy/amine system.

Thermal resistivity of cured LCE/PANI nanorod system was examined by thermogravimetric analysis (TGA). Fig. 10 represents the TGA thermograms for LCE/PANI nanocomposite with variable amount of PANI nanorod. As the concentration of PANI nanorod increased, the initial degradation temperature of the nanocomposite was elevated and the residual mass was proportional to the amount of PANI nanorod. Above 10 wt%, the increment in initial degradation temperature was not remarkable because the extent of cure was nearly constant. We have found that simple mixing of inorganic fillers did not elevate the thermal stability of resulting composites. For LCE/carbon nanotube (CNT) system, the initial degradation temperature was independent of carbon nanotube content [14]. It means that physical interfacial interaction between epoxy molecules and filler cannot improve the thermal resistivity of cured materials. Therefore, it is important to form interfacial
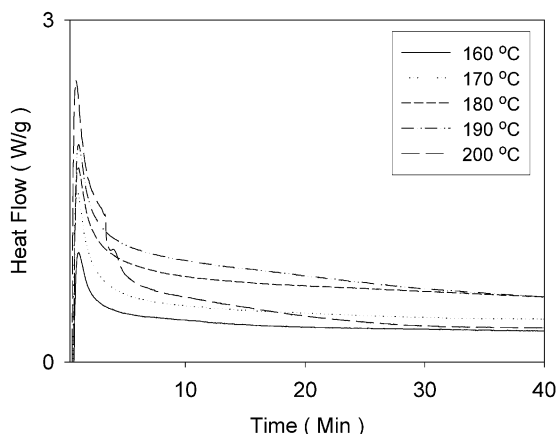
covalent bonds between the epoxide and filler to improve thermal properties of prepared composites. When the PANI nanorod concentration increased, the number of amine groups forming chemical bonds with LCE matrix increased. Consequently, the thermal stability of nanocomposite could be enhanced. The polar interaction combined with nanoscale structural architect promotes the efficient and homogeneous incorporation of PANI nanorods into LCE matrix during cure reaction. Judging from these facts, it is clear that PANI nanorods showed a characteristic of nanoscale reinforcement filler.

The electrical conductivity of the LCE/PANI nanorod was illustrated in Fig. 11. The electrical conductivity of LCE/PANI nanorod was quite low below 5 wt% of PANI, whereas it rose quickly above 10 wt%. This fact indicated that the electrical conductivity of LCE/PANI nanorod rose quickly at about 5–10 wt%, which is observed in percolation threshold behavior [43]. It means that more electrical paths were created with increasing the amount of PANI nanorods. PANI nanorod can be minutely dispersed in the polymer matrix owing to the nanoscale architect, and chemical bond formation with LCE molecules can restrict the aggregation of PANI nanorods in LCE matrix. In addition, high aspect ratio of PANI nanorods induced the effect of directional ordering when incorporated in epoxy matrix. That is how the electrical conductivity of LCE/PANI nanorod can be enhanced compared with conventional epoxy composite (10^{-4} S/cm).

Fig. 12 demonstrates that the fracture surface of cured

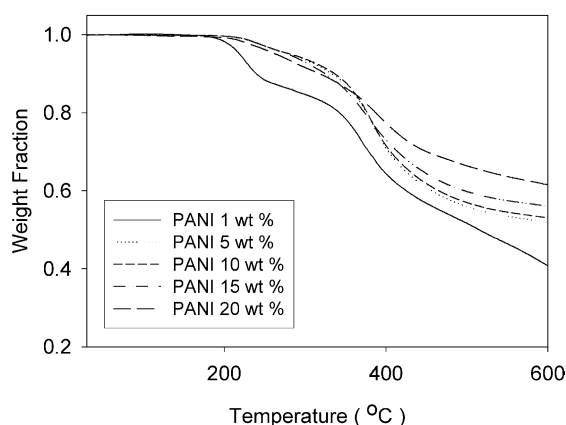Fig. 9. Isothermal DSC thermograms of LCE/PANI nanorod system.

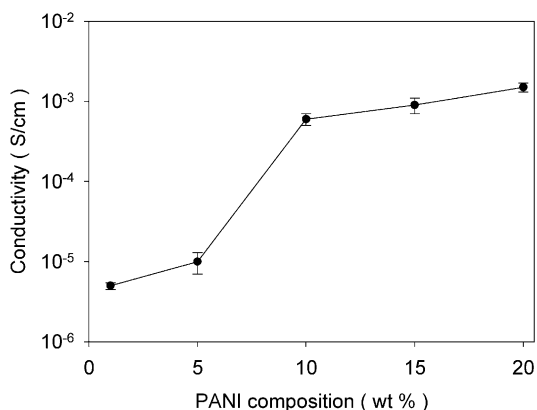Fig. 10. TGA curve of cured LCE/PANI nanorod nanocomposites.

Fig. 11. Electrical conductivity of LCE/PANI as a function of PANI composition.

LCE/PANI nanorod composite was flat and homogeneous regardless of PANI nanorod composition. To prepare high performance LCE composites, homogeneous incorporation of filler into matrix is very important. PANI nanorods have surface amine groups, which can form covalent bonds with LCE molecules. This covalent bond promoted dispersion of PANI nanomaterials into LCE matrix thus prevented macrophase separation. Therefore, phase separation was not observed in the fracture surface of the composite. This SEM image also confirmed the homogeneous mixing of LCE resin with filler, PANI nanorods.

4. Conclusions

We have demonstrated a dispersion polymerization for the mass production of PANI nanorods. The PANI nanorods with the diameter of 20–50 nm and the length of 0.2–1 μm were fabricated in multi-gram scale quantity (approximately 10 g) and high yield ($>$95%) without undesired morphology. The synthesized PANI nanorods was successfully incorporated as curing agent owing to the amine functional group and nanofiller due to the high conductivity and stability. Dynamic and isothermal DSC revealed that cure behavior of LCE/PANI nanorods system showed characteristics of conventional epoxy resin. In addition, the cured LCE/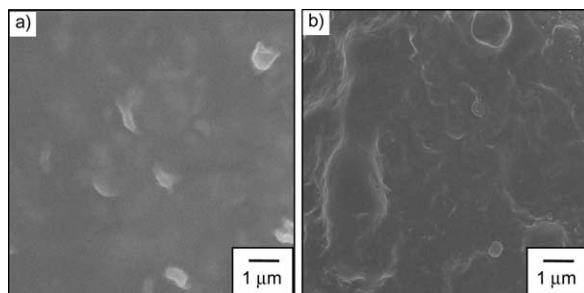PANI nanocomposites showed an enhanced thermal stability and electrical conductivity owing to the introduction of nanoscale PANI rods as conducting and reinforcing filler. The LCE/PANI nanocomposites can be used as conducting adhesives, highly conductive composites, and coating materials.

Acknowledgements

References

[1] Tans SJ, Verschueren ARM, Dekker C. Nature 1998;393:49.
[2] Long RQ, Yang RT. J Am Chem Soc 2001;123:2058.
[3] Wang Z, Chen M, Li HL. Mater Sci Eng A 2002;328:33.
[4] Wei Z, Zhang Z, Wan M. Langmuir 2002;18:917.
[5] Stejskal J, Špírková M, Riede A, Helmstedt M, Mokreva P, Prokeš J. Polymer 1999;40:2487.
[6] Covolan VL, D'Antone S, Ruggeri G, Chiellini E. Macromolecules 2000;33:6685.
[7] Curran SA, Ajayan PM, Blau WJ, Carroll DL, Coleman JN, Dalton AB, et al. Adv Mater 1998;10:1091.
[8] Woo HS, Czerw R, Webster S, Carroll DL, Ballato J, Strevens AE, et al. Appl Phys Lett 2000;77:1393.
[9] Lee YH, Kim DH, Kim H, Ju BK. J Appl Phys 2000;88:4181.
[10] Haggenmueller R, Gommans HH, Rinzler AG, Winey KI, Fischer JE. Chem Phys Lett 2000;330:219.
[11] Milo SP, Windle AH. Adv Mater 1999;11:937.
[12] Gangopadhyay R, De A. Chem Mater 2000;12:608.
[13] Bae J, Jang J, Yoon SH. Macromol Chem Phys 2002;203:2196.
[14] Jang J, Bae J, Yoon SH. J Mater Chem 2003;13:676.
[15] Punchaipetch P, Ambrogi V, Giamberini M, Brostow W, Carfagna C, D'Souza NA. Polymer 2001;42:2067.
[16] Mormann W, Bröcher M. Polymer 1998;39:6597.
[17] Reesink JB, Picken SJ, Witteveen AJ, Mijs WJ. Macromol Chem Phys 1996;197:1031.
[18] Farren C, Akatsuka M, Takezawa Y, Itoh Y. Polymer 2001;42:1507.
[19] Osada S, Yano S, Tsunashima K, Inoue T. Polymer 1996;37:1925.
[20] Rivera D, Serra A, Mantecon A. Polymer 2003;44:2621.
[21] Chin HC, Chang FC. Polymer 1997;38:2947.
[22] Sadagopan K, Ratna D, Samui AB. J Polym Sci A: Polym Chem 2003; 41:3375.
[23] Barclay GG, McNamee SG, Ober CK, Papathomas KI, Wang DW. J Polym Sci A: Polym Chem 1992;30:1845.
[24] Shiota A, Ober CK. Polymer 1997;38:5857.
[25] Sreedhar B, Palaniappan S, Narayanan S. Polym Adv Technol 2002; 13:459.
[26] Sue HJ, Earls JD, Hefner RE. J Mater Sci 1997;32:4031.
[27] Sue HJ, Earls JD, Hefner RE. J Mater Sci 1997;32:4039.
[28] Earls JD, Hefner Jr RE, Puckett PM. US Patent 5,463,091; 1995.
[29] Sue HJ, Earls JD, Hefner RE, Villarreal MI, Garcia-Meitin EI, Yang PC, et al. Polymer 1998;39:4707.
[30] Lee KJ. Master Thesis. Laboratory-scale mass production of polyaniline nanorods using dispersion polymerization. Seoul National University (Korea); 2004.
[31] Wei Z, Wan M. Adv Mater 2002;14:1314.
[32] Zhang L, Wan M. Adv Funct Mater 2003;13:815.
[33] Kumar S, Naqvi AZ, Kabir-ud-Din. Langmuir 2000;16:5252.

Fig. 12. SEM images of fracture surface of LCE/PANI nanorod composites. The weight ratios of PANI was (a) 1 and (b) 25 wt%.

[34] Jang J, Bae J. Angew Chem, Int Ed 2004;43:3803.

[35] He C, Tan Y, Li Y. J Appl Polym Sci 2002;87:1537.

[36] Mu JH, Li GZ, Jia XL, Wang HX, Zhang GY. J Phys Chem B 2002; 106:11685.

[37] Jang J, Oh JH, Stucky GD. Angew Chem, Int Ed 2002;41:4016.

[38] Mazerolles L, Folch S, Colomban P. Macromolecules 1999;32:8504.

[39] Ozawa T. Bull Chem Sci (Japan) 1965;38:1881.

[40] Ozawa T. J Therm Anal 1970;2:301.

[41] Kamal MR, Sorour S, Ryan M. Soc Plast Eng Technol Pap 1973;19: 187.

[42] Ishida H, Rodriguez Y. The preprints of the 35th IUPAC international symposium on macromolecules, Akron, OH, USA 1994. p. 634.

[43] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. Polymer 1999;40:5967.