

Synthesis and Characterization of Cd_xZn_{1-x}O Nanoparticles-Doped Aryl Poly Ether Ether Ketone for Novel Application Potentials

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ABSTRACT: The influence of polymer on the structure, optical, electrical, and thermal properties of nanoscale fillers is a crucial clue to introduce these novel nanocomposites to service life applications. In the present work, different compositions of cadmium-doped zinc oxide (Cd_xZn_{1-x}O) nanopowders, $x = 0.1, 0.3,$ and $0.5,$ with a uniform particle size of around 8 nm have been synthesized. A fixed amount, 1 wt %, of the prepared nanopowders was blended with aryl poly ether ether ketone (PEEK) by solution mixing to prepare PEEK/Cd_xZn_{1-x}O nanocomposite films. The structure and morphology of Cd_xZn_{1-x}O nanopowders and PEEK/Cd_xZn_{1-x}O nanocomposite films have been characterized using transmission electron microscopy and X-ray diffraction. The results showed that the particle size of nanoscale filler decreases from 10 nm to 5–7 nm when mixed with PEEK and these nanocomposites have amorphous structure. The thermog-

gravitational analysis results show that a small amount of Cd_xZn_{1-x}O nanopowders (1 wt %) without surface modification can greatly improve the thermal stability of PEEK. The UV–vis spectra showed that there is absorption peak at 284 nm due to interband $\pi-\pi^*$ electronic transition. This absorption peak gets shifted toward the longer wavelength region as the concentration of cadmium ions increase in the PEEK matrix. This red shift results in a decrease of the band energy gap. The electrical conductivity of PEEK/Cd_xZn_{1-x}O nanocomposite films was increased as the cadmium ion increases. The results showed that PEEK/Cd_xZn_{1-x}O nanocomposite films can be used in thermostat and/or fire alarm devices. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 339–343, 2012

Key words: nanocomposites; thermal stability; electrical properties; optical Properties

INTRODUCTION

ZnO is an important and attractive semiconducting material. It has drawn enormous research attention due to its distinguished properties from optics, photonics and electronics.¹ Its wide bandgap energy (3.4 eV) at room temperature is ideal for short-wavelength optoelectronic applications. It is possible to modify the physical properties of ZnO upon mixing with CdO. Most of the recent works have been focused on the preparation of Cd_xZn_{1-x}O alloys.^{2,3} Cd_xZn_{1-x}O alloy would be a good candidate because of the small direct band gap of CdO which shows a red shift of the luminescence peak with respect to that of ZnO.⁴ It is also much more resistant to radiation damage. Moreover, Cd_xZn_{1-x}O can be simply obtained through wet chemistry, which offers it a potential viable route to achieve uniform dispersion in polymer matrices through solution mixing. As the size decreases to the regime in

between the bulk and isolated molecules, the properties of the semiconductor nanopowders may have mechanical, optical, electric, and thermal properties quite different from the bulk, known as the quantum size effect.⁵ Aryl poly ether ether ketone (PEEK) is a semicrystalline polymer which has a glass transition temperature (T_g) of 143°C, a melting point (T_m) of 343°C and an onset of decomposition temperature between 575 and 580°C.⁶ Its excellent thermal, chemical, and mechanical properties have allowed for its use in a variety of high-performance applications. PEEK's excellent thermal properties are attributed to the stability of the aromatic backbone comprising the bulk of the monomer unit. To date, no work has been published on the influence of dielectric medium on the structure and physical properties of nanoscale filler. In this study, we examine the introduction of 1 wt % of Cd_xZn_{1-x}O nanopowders, at different $x = 0.1, 0.3,$ and 0.5 into PEEK.

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EXPERIMENTAL DETAILS

Preparation of Cd_xZn_{1-x}O and PEEK/Cd_xZn_{1-x}O nanocomposite films

The PEEK/Cd_xZn_{1-x}O nanocomposites are prepared via a simple solution-mixing method. First,

$\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders have been prepared typically as indicated in our previous works.⁷ One weight percent of the prepared $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders ($x = 0.1, 0.3, \text{ and } 0.5$) are redispersed in methanol for the preparation of PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposites. In second step, PEEK ($M_w = 100,000 \text{ g mol}^{-1}$, Fluka) is dissolved in tetrahydrofuran (THF) at first, and then the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ /methanol and PEEK/THF are mixed during stirring. The solution mixture is clear throughout, indicating a homogeneous dispersion of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders in the solution. In final, the nanocomposite solution is cast on a Petri dish and the solvents are evaporated under vacuum to obtain the film sample. The thicknesses of all prepared films were controlled to around 0.5 mm by adjusting the concentration and amount of solution utilized.

Characterization

High-resolution transmission electron microscopy (HR-TEM) of PEEK/ $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{O}$ nanocomposites was carried out using a JEOL 2010 high-resolution transmission electron microscope operated at 200 kV. To prepare the HR-TEM samples, purified $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders were first redispersed in methanol and diluted, followed by placing a droplet of the solution onto a 400-mesh carbon-coated copper grid. The grid was then dried in a desiccator for one day before imaging. The PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite samples for HR-TEM were prepared by using ultramicrotomy. The nanocomposite films were embedded into epoxy resin before thin sectioning. A Reichert-Jung Ultra cut-E microtome was utilized to prepare thin sections with thicknesses of around 70–100 nm for HRTEM imaging. The X-ray measurements were performed using Philips X'pert diffractometer supplied with copper X-ray tube ($\lambda_{\text{CuK}\alpha} = 1.5406 \text{ \AA}$), nickel filter, graphite crystal monochromator, proportional counter detector, divergence slit 1° and 0.1-mm receiving slit. The working conditions were 40 kV and 30 mA for the X-ray tube, scan speed 0.05° and 2 s measuring time per step. For each measurement, a complete scan was made between 10° and 70° (2θ). To calibrate the measured Bragg 2θ -angles, a standard reference material (SRM 640a) of pure Si powder was used. The thermal stability of pure PEEK and PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ was investigated by nonisothermal thermogravimetric analysis (TG) using Shimadzu calorimeter with an accuracy of $\pm 0.1 \text{ K}$ and sensitivity $\pm 10 \mu\text{W}$ under air flow at a flow rate of 50 mL min^{-1} . Ten micrograms of sample is being placed in a standard aluminum pans and scanned by using a differential scanning calorimeter (DSC) over a wider temperature range at constant heating rates of $20^\circ\text{C min}^{-1}$. UV-vis spectra were recorded on JASCO-V570 Spec-

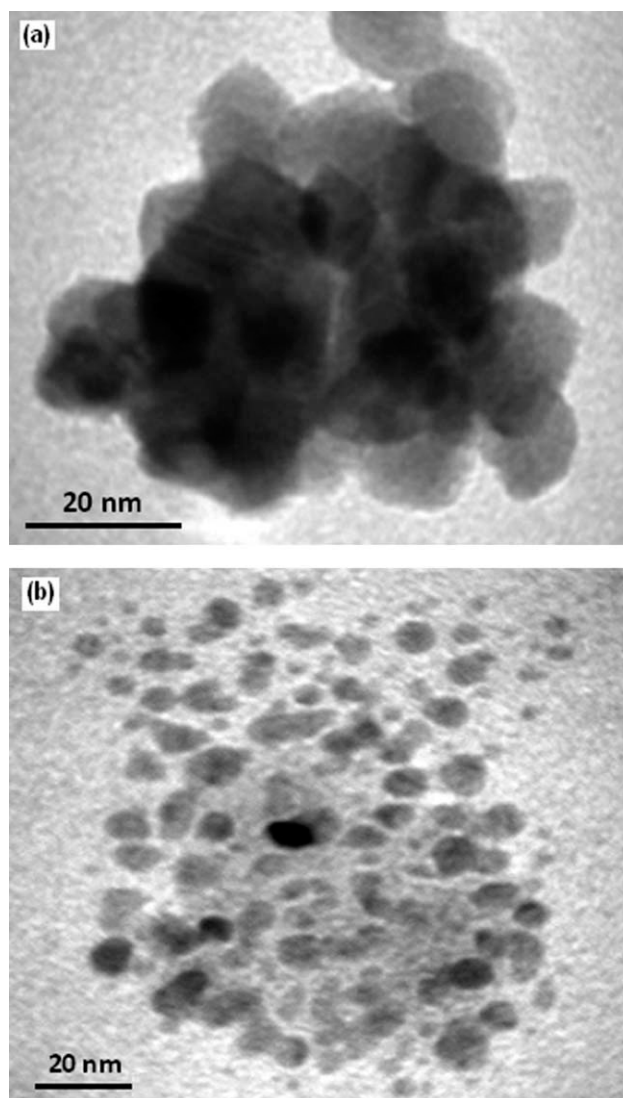


Figure 1 TEM image of (a) $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{O}$ nanopowder and (b) $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{O}$ into PEEK.

trometer to measure the transmittance of PEEK and PEEK/PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films from 200 to 800 nm. For electrical measurements the samples were made in the form of discs with 2-mm thick and 1-cm diameter. Silver paste was painted to the parallel faces of the samples as electrodes. In electrical measurements a digital electrometer (616 Keithly, USA) was used. A regulated noninductive furnace cell connected to a temperature controller (Digi-Sense, IL 60,010) was used to vary sample temperature from 30 to 100°C with constant rate of 2°C/min .

RESULTS AND DISCUSSION

TEM images of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanoparticles and PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films

Figure 1(a) shows the TEM image of one of the prepared $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders as an example. It is

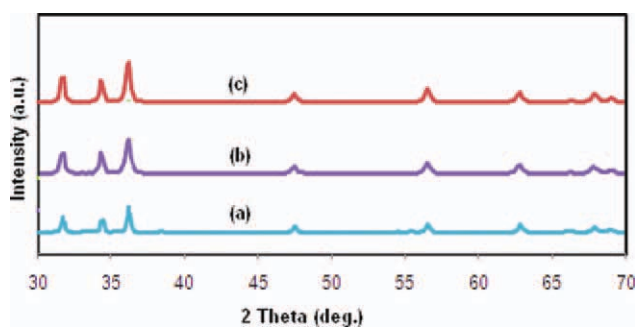


Figure 2 XRD patterns of as-prepared $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ nanopowders at different concentration of Cd, (a) $x = 0.1$, (b) 0.3 , and (c) 0.5 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

clear $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{O}$ nanopowder has a spherical shape with average particle size around 8 ± 2 nm. Figure 1(b) shows the distribution of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{O}$ into PEEK. One can notice that, the nanopowder tends to disperse into the PEEK matrix. The spherical shape of the nanopowders is conserved but there is a reduction in the average particle size of the nanopowder. The average size of nanopowder is 7.8 ± 2 nm.

XRD of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanoparticles and PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films

Figure 2(a–c) shows XRD patterns of as-prepared $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ nanopowders at different concentration of Cd, $x = 0.1$, 0.3 , and 0.5 . The diffraction peaks in the XRD spectra indicated the all powders had typical hexagonal wurtzite structures. For $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, no diffraction peaks of Cd or other impurity phases were found in prepared samples, suggesting that Cd^{2+} ions would uniformly substitute into the Zn^{2+} sites or interstitial sites in ZnO lattice. Moreover, the major diffraction peaks shift slightly toward smaller diffraction angle compared to the standard card of ZnO (JCPDS 79-2205, $a = 0.325$ nm and $c = 0.522$ nm).^{3,4} The lattice parameters c calculated from the (0 0 2) peak of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ samples are alter between 0.523 and 0.525 nm, which is approximately the same as ZnO . This is due to the ionic radius of Cd^{2+} (0.74 Å) is close to that of Zn^{2+} (0.60 Å), so the wurtzite phase, which is a stable phase of ZnO , is conserved when Cd is alloyed.⁷ Also it is clear from Figure 2 that the peak intensity very low and broad width which implied that Cd^{2+} -doped ZnO nanopowders with a smaller average diameter were synthesized.

Figure 3(a) depicts the XRD pattern of neat PEEK. It is clear that there is a broad peak around $2\theta = 20^\circ$ which indicates the semicrystallinity of PEEK. Figure 3(b–d) shows XRD patterns of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ /PEEK nanocomposites. These nanocomposites are amor-

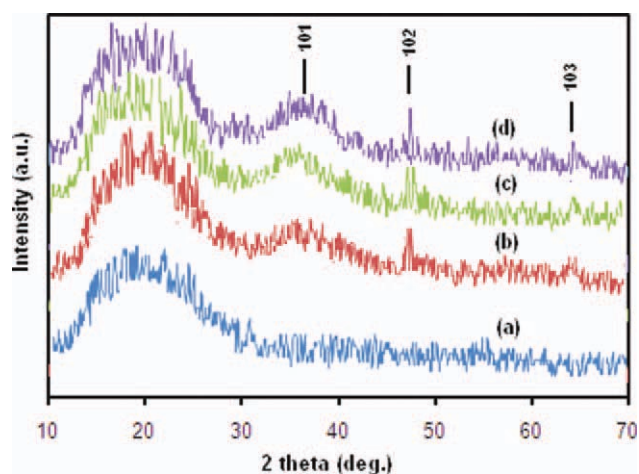


Figure 3 XRD patterns of (a) neat PEEK and $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ /PEEK nanocomposites at different concentration of Cd, (b) $x = 0.1$, (c) 0.3 , and (d) 0.5 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phous and just three broad peaks appear at angles 36.5 , 47.2 and 64° which corresponding to [101], [102], and [103] plans of reflections.

Thermal stability of PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films

The thermal decomposition profiles of the neat PEEK and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ /PEEK nanocomposite films are given in Figure 4. There is much higher thermal stability of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ /PEEK nanocomposite films than the neat polymer film, and the more cadmium ions concentration; the nanocomposite film shows the higher thermal stability.

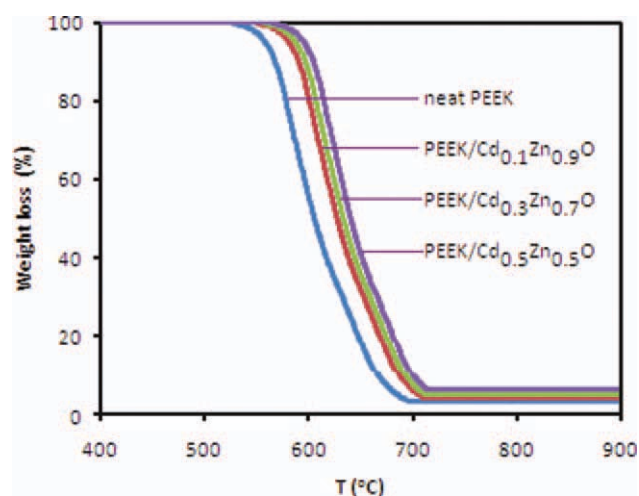


Figure 4 The thermal decomposition profiles of the neat PEEK and PEEK/ $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films under air flow at heating rates $15^\circ\text{C min}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Thermal Stability Parameters of
PEEK/Cd_xZn_{1-x}O Nanocomposites

Sample	Critical temperature (°C)	Activation energy, E _g (eV)
Neat PEEK	58	0.11
Cd _{0.1} Zn _{0.9} O/PEEK	40	0.071
Cd _{0.3} Zn _{0.7} O/PEEK	31	0.063
Cd _{0.5} Zn _{0.5} O/PEEK	–	0.052

To quantify the improvement of thermal stability, two characteristic parameters of the TGA curves, i.e., the onset decomposition temperature (T_{onset}) and the temperature at 50% weight loss ($T_{50\%}$), are extracted and shown in Table I.

These results also suggest that Cd_xZn_{1-x}O nanopowders retard the thermal degradation of PEEK. Usually, the properties of the polymer composites containing inorganic spherical particles depend on many factors, such as the size and dispersion of the particles, the interaction between the particles and the polymer chains, and the properties of the polymer matrix and the particles.⁸⁻¹⁰ In this study, the particle size of the Cd_xZn_{1-x}O nanopowders is about 8 nm as shown in Figure 1(b). They have a much larger surface area. At the nanoscale, the surface atoms contribute significantly to the free energy of the materials.¹¹ The massive free energy created by the extremely small Cd_xZn_{1-x}O nanopowders requires the surrounding polymer chains to strongly interact with them to reduce the surface free energy and to avoid significant aggregation. This could be one of the main reasons why only a small amount of Cd_xZn_{1-x}O nanopowders (1 wt %) can significantly improve the thermal stability of PEEK observed here. Another reason resulting in the great improvement of thermal stability by incorporating only a small amount of Cd_xZn_{1-x}O nanopowders could be due to the use of pristine Cd_xZn_{1-x}O nanopowders, which may ensure the polymer chains to directly interact with the surface of Cd_xZn_{1-x}O nanopowders, thus allowing the free radicals generated in PEEK during heating to be more effectively quenched by the unmodified Cd_xZn_{1-x}O nanopowders.

Optical properties

The analysis of optical absorption spectra is one of the most productive tools for understanding and developing the band structure and energy band gap, E_g , of structure. Figure 5 shows the dependence of absorption on the wavelength λ in the spectral range 200–800 nm for nanocomposite films.

From such figure it is clear that, there is absorption peak at 284 nm due to interband π - π^* electronic transition. This absorption peak shifts toward the

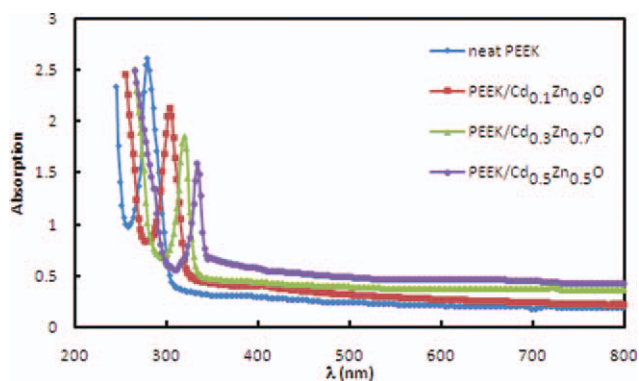


Figure 5 Absorption spectrum of Cd_xZn_{1-x}O/PEEK nanocomposite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

longer wavelength region as the concentration of cadmium ions increase in the PEEK matrix. This red shift results from a decrease of the band energy gap. The band-gap value could be obtained from the optical absorption spectra by using Tauc's relation¹²;

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^n \quad (1)$$

where α is the absorption coefficient, $(h\nu)$ is the photon energy, A is a constant, and n assumes the values 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. Now for allowed direct type of transitions

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

Figure 6 shows the variation of $(\alpha h\nu)^2$ versus $(h\nu)$ for the nanocomposite films. The straight line nature of the plots over a wide range of photon energy

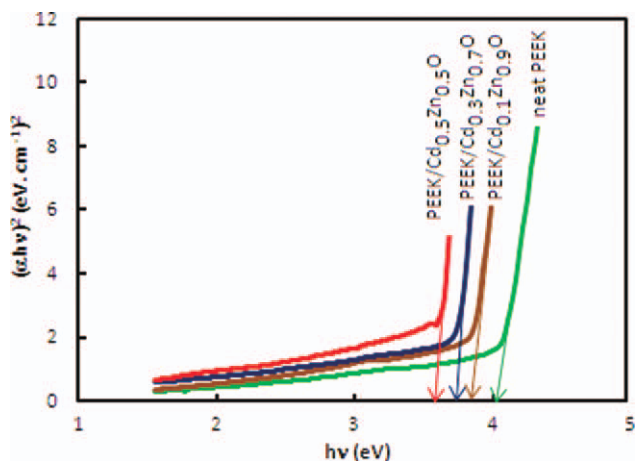


Figure 6 The variation of $(\alpha h\nu)^2$ versus $(h\nu)$ for Cd_xZn_{1-x}O/PEEK nanocomposite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicates the direct type of transition. The optical gap has then been determined by the extrapolation of the linear region on the energy axis as shown in Figure 6. The optical gap for neat PEEK and $\text{Cd}_x\text{Zn}_{1-x}\text{O}/\text{PEEK}$ nanocomposite films at $x = 0.1, 0.3,$ and 0.5 is 4.07, 3.85, 3.73, 3.62 eV, respectively. This reduction is due to the increase of cadmium ions concentration into $\text{Cd}_x\text{Zn}_{1-x}\text{O}$.¹³

Electrical properties

Figure 7 represents the relation between $(\ln \sigma)$ and $(1/T)$ for neat PEEK and $\text{Cd}_x\text{Zn}_{1-x}\text{O}/\text{PEEK}$ nanocomposite films at $x = 0.1, 0.3,$ and 0.5 . In fact the conductivity-temperature plot has two regions, one at low temperature and the other at high temperature. At low-temperature range, there is a decrease in conductivity against temperature.

This decrease may be due to the thermal expansion of PEEK which results in an increase in the hopping path of electrons and in turn reduction of conductivity. This decrease continues until certain temperature (critical temperature). This critical temperature shifts toward low temperature as the x value of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ increase as indicated in Table II. This is due to the enhancement of the thermal stability of PEEK, which results in a reduction of its thermal expansion and/or the increase of Cd/Zn ratio into $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ reduce the hopping path of electrons, which leads to an increase of the conductivity. After such critical temperature, a thermal activation takes place which causes a progressive increase in conductivity against temperature. These results indicate that the prepared nanocomposites can be used in thermostat and fire alarm devices.

The temperature dependence of conductivity can be interpreted on the basis of Arrhenius equation at high temperature region.¹⁴ The activation energy values E_a for nanocomposite films have been calculated and presented in Table II. It is clear that the activation energy decreases as the amount of cadmium ions increase.

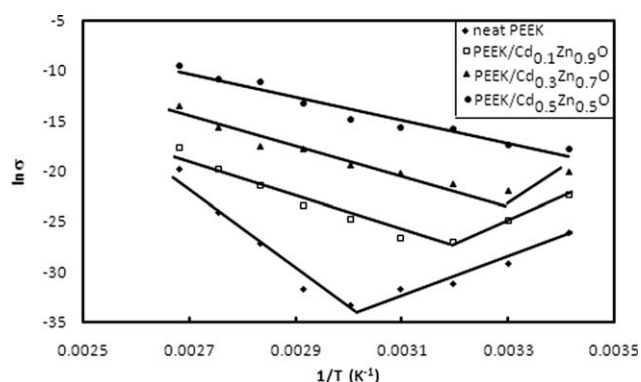


Figure 7 Plot of $(\ln \sigma)$ versus $(1/T)$ for neat PEEK and $\text{Cd}_x\text{Zn}_{1-x}\text{O}/\text{PEEK}$ nanocomposite films.

TABLE II
Critical Temperature and Activation Energy of $\text{PEEK}/\text{Cd}_x\text{Zn}_{1-x}\text{O}$ Nanocomposites

Sample	Onset temperature (°C)	Temperature at 50% weight loss (°C)
Neat PEEK	358.9	604.8
$\text{Cd}_{0.1}\text{Zn}_{0.9}\text{O}/\text{PEEK}$	571.4	626.5
$\text{Cd}_{0.3}\text{Zn}_{0.7}\text{O}/\text{PEEK}$	584.6	635.9
$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{O}/\text{PEEK}$	591.8	641.1

CONCLUSION

$\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders, at different $x = 0.1, 0.3,$ and 0.5 , without surface modification were incorporated into PEEK via a simple solution mixing method. TEM image shows that the particle size of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders is around 8 nm and for $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ embedded into PEEK is around 8 nm. The onset of the UV absorption from the $\text{PEEK}/\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films exhibit red shifting as the x value of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ concentration increases. The TGA results demonstrate that only a small amount of unmodified $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanopowders (1 wt %) can greatly improve the thermal stability of PEEK. The conductivity-temperature plot showed negative temperature coefficient of conductivity (NTCC) until certain temperature and then exhibited positive temperature coefficient of conductivity (PTCC). The activation energy of the $\text{PEEK}/\text{Cd}_x\text{Zn}_{1-x}\text{O}$ nanocomposite films was decreased as the x value increases.

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