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Investigation of Irradiation Effects on Conducting Composite of Polypyrole/Bentonite

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Abstract: In the present study, polypyrrole/bentonite (PPy/Bnt) composite was synthesized into the Bnt interlayers by chemical oxidation polymerization. The irradiation process was carried out in air in a conventional gamma chamber, which uses a ^{60}Co source, and the composite was exposed to a dose of 40 kGy. Effects of irradiation on the composite were investigated by means of FTIR, UV-visible absorption, TGA, XRD, SEM and temperature dependent electrical conductivity in the temperature range of 290-410 K. The initial decomposition temperature of pristine PPy/Bnt composite was found higher than irradiated PPy/Bnt composite. The XRD patterns revealed that the intensity of the peaks changed with irradiation. It was found from temperature dependent conductivity measurements that the radiation significantly influenced the conductivity of PPy/Bnt composite. The conductivity results show that dominant conduction mechanisms were hopping for both PPy/Bnt composite and irradiated samples due to wide range of localized states present near the Fermi level.

Key words: Polypyrrole, bentonite, conducting composite, gamma irradiation.

Polipirol/Bentonit İletken Kompozitine Radyasyon Etkilerinin Araştırılması

Özet: Bu çalışmada, polipirol/bentonit (PPy/Bnt) kompoziti, Bnt tabakaları arasında kimyasal oksidasyon polimerizasyonu yoluyla sentezlendi. Radyasyon uygulaması ^{60}Co kaynağının kullanıldığı bir gama çemberi içerisinde hava ortamında gerçekleştirildi ve kompozite 40 kGy doz uygulandı. Kompozite radyasyon etkileri, FTIR, UV, TGA, XRD, SEM ve 290-410 K sıcaklık aralığında sıcaklığa bağlı elektriksel iletkenlik ölçümleri ile incelendi. Saf PPy/Bnt kompozitinin başlangıç bozunma sıcaklığı radyasyona uğramış PPy/Bnt kompozitinden daha yüksek olduğu bulundu. XRD desenlerine ait pik yoğunluğunun radyasyon ile değiştiği görüldü. Sıcaklığa bağlı iletkenlik ölçümlerinden radyasyonlanma sonucunda, PPy/Bnt kompozitin iletkenliğinin önemli ölçüde etkilediği gözlendi. İletkenlik sonuçları, hem saf PPy/Bnt hem de radyasyona uğramış kompozitlerde baskın iletim mekanizmasının Fermi seviyesi civarındaki seviyeler arasında hoplama yolu ile olduğu göstermiştir.

Anahtar kelimeler: Polipirol, bentonit, iletken kompozit, gama radyasyonu.

1. Introduction

In recent years, polypyrrole has attracted much attention due to its unique electrical and optical properties as well as its good thermal stability. These characteristics have led to a large number of potential applications such as rechargeable batteries, semiconductor photoanode production, in light-emitting, etc. However, the poor mechanical properties of the material along with its inherently poor solubility in common solvents constitute major obstacles to an extensive application in many areas [1].

Composite materials derived from conducting polymers such as polypyrrole (PPy) and polyaniline (PAni), associated with layered inorganic solids, is a line of investigation of increasing interest, not only for producing improved structural materials, but also for the preparation of new functional materials [2]. Among this group of materials, those incorporating electroactive polymers in diverse layered solids have been extensively studied due to their electrical conductivity properties of interest for applications in different electrochemical devices [3].

The combination of conducting polymers with clays having different characteristics opens a way to new hybrid materials showing novel properties. Also, conformation of polymer chains in the interlayer spaces may enable to further characterize the polymer structure. Clays among other hosts are natural, abundant and inexpensive minerals which have unique layered structure, high mechanical strength, smaller particle size as well as application of reinforcement of various materials with polymers. The synthesis of polypyrrole/clay composites is currently carried out by intercalation of the monomer followed by the polymerization in the clay interlayer [4]. Kim and co-workers have synthesized polyaniline–montmorillonite nanocomposite using an emulsion intercalation method [5].

Gamma irradiation of polymers causes structural and chemical variations, which leads to variation in physical properties of the material. The reduction in the average molecular weight or degradation, the generation of free radicals or the decrease in the mechanical strength are some of these effects. Low cost, high mechanical strength and resistance, flexibility, light and cheap shielding and low weight (approximately 6 g/m, which is one third of the weight of glass fibers) are the advantages of using polymers instead of crystal materials in optical experiments. The effects of gamma irradiation on polymers have been first discussed by Charlesby (1960) and Chapiro (1962). The previous authors used interferometric and other tools to study the effects of gamma irradiation on polymers [6].

In order to modify the transport, optical and mechanical properties of materials for certain applications, impurities were introduced into the host materials. In the chemical doping, solute or dopant agent can be added directly to the materials. The drawbacks of this method are segregation and solubility of the dopant in the host material. Doping via ion irradiation is an expanding field of material research in order to modify polymers and semi-conducting materials. This technique is simply the launching of atoms onto the surface of the material by bombardment of the solid with energetic ions in the keV to MeV energy ranges. When an energetic ion enters a solid, it loses energy by elastic or inelastic collisions then gives up their energy to the host atoms and finally comes to rest. During this process, ion beams introduce electrically active defects. One advantage of this technique is that the doping atoms can be implanted in different concentrations, independent of their solubility in the target material [7]. This technique is widely used in the inorganic semi-conductor technology, but, so far, little attention was paid to modify conducting polymers [8, 9, 10]. Ion implantation leads to substantial changes in their chemical, optical, electrical, mechanical and other properties because irradiation induces changes in molecular structure in polymers [9]. For example, it was found that ion irradiation causes the decrease in the resistivity by many orders of magnitudes in some polymers [11].

In the present study, polypyrrole/bentonite (PPy/Bnt) composite was synthesized by the chemical oxidation polymerization of pyrrole in the presence of bentonite in acidic solution containing an oxidant. The effect of radiation on PPy/Bnt composite was investigated by means of FTIR, UV-visible absorption, TGA, XRD, SEM and temperature dependent electrical conductivity in the temperature range of 290-410 K.

2. Experimental

2.1. Materials

Polypyyrole, monomer was obtained from Aldrich and it was distilled prior to use. Iron III chloride, $FeCl_3$ was obtained from E. Merck and used as oxidant. Bentonite Clay K-10 (Bnt) was obtained from Acros. Cetyltrimethylammonium (CTAB), cationic surfactant was purchased from Sigma. Before using, Bnt was treated with surfactant to expand the interlayer spaces of Bnt clay. N-methyl pyrrolidone (NMP) was obtained from Aldrich to UV-visible absorption spectrum and used without any purification. All the other chemicals were provided by E. Merck with analytical grade and used as received.

2.2. Synthesis of PPy/Bnt composite

PPy was synthesized by chemical oxidation polymerization method [12]. At first, Bnt was suspended for 2 h with 0.001 g CTAB to intercalate between clay layers in 1M HCl solution, and then polypyrrole ($n_{\mathrm{initiator}}/n_{\mathrm{monomer}} = 2.5$) was added into this suspension, which was stirred magnetically for 30 min under reflux at 0-5 ^{o}C temperature. Thereafter, a known amount of $FeCl_3$ solution which was dissolved in 1M HCl, was added dropwise to this suspension at the same temperature. Reaction was carried out under $N_{2\ (g)}$ atmosphere and the suspension was stirred for 14–16 h. Ambient temperature was kept between 0-5 ^{o}C during the reaction. The precipitated composite was strained and washed with 1M HCl and distilled water and then dried at 50 ^{o}C. The black colour composite was symbolized by PPy(75%)/Bnt (25%) and named as 2.

2.3. Irradiation of PPy/Bnt composite

The obtained black powders were converted into pellets of 20 mm in diameter and approximately 2 mm thickness and were pressed at room temperature under same pressure and time using hydraulic press. The PPy/Bnt composite was exposed to gamma radiation from a ^{60}Co source (rate of 7.5 kGy/h) at dose of 40 kGy in the presence of air and at room temperature. Irradiated PPy/Bnt composite was named as D2.

2.4. Characterization

The characterization of chemical structure for the samples was performed by FTIR spectrometer. The FTIR spectra of the pristine and irradiated composites were collected with Shimadzu IRPrestige-21 FTIR Spectrophotometer using a scanning range from 400 to 4000 cm^{-1}. The KBr disc technique was used for samples preparation. The electronic structure of pristine PPy/Bnt and irradiated PPy/Bnt composite was determined from UV–vis absorption spectra in NMP solutions on a Perkin Elmer (model Lambda 20) spectrophotometer. The thermal stability of non-irradiated and irradiated samples was performed using a Perkin–Elmer model TG/DTA system at a heating rate of 10 °$Cmin^{-1}$ under $N_{2\,(g)}$ atmosphere from room temperature to 900 °C. X-Ray diffraction was used to determine crystalline region in the composite structure [13]. XRD patterns for the samples were carried out using a computer-interfaced Bruker AXS D8, advanced by diffractometer operating in Bragg–Brentano [14] geometry (Cu-Kα radiation, graphite monochromator, 40 kV and 40 mA). Morphology of the composites was examined using a Jeol JSM-6360 LV model scanning electron microscope.

For the electrical measurements, typical sample dimension and thickness were 5x5 mm^2 and 100µm, respectively. Ohmic contacts for electrical measurements were made by evaporation of indium in a vacuum of 10^{-5} Torr using suitable masks, and electrodes were attached to the contact regions with silver paint. The ohmic behaviour of the contacts in the studied temperature region was confirmed by the linear variations of the I-V characteristics, which are independent from the reversal of the applied currents. The temperature-dependent conductivity measurements in the temperature range of 290-410 K were carried out by using a Keithley 2400 source measure unit. The samples were placed onto cold finger of a Janis liquid nitrogen cryostat and the temperature was accurately monitored with a Lake-Shore 320 temperature controller.

3. Results and Discussion

3.1. FTIR spectra measurements

The synthesis of PPy/Bnt composite was monitored by FTIR spectrometry (Figure 1). IR spectra of the composite were identical to those reported: for PPy, stretching vibration (3040 cm^{-1}) and bending vibration (1540 cm^{-1}) of N–H bond, stretching vibration (2900 cm^{-1}) of C–H bond, stretching vibration (1539 cm^{-1}) and bending vibration (1440 cm^{-1}) of C=C bond, stretching vibration (1190 cm^{-1}) of C–N bond, stretching vibration (1295 cm^{-1}) of C–C bond, and band (1400 cm^{-1}) of the pyrrole ring; for Bnt, stretching vibrations (3120 cm^{-1}, broad band) of structural -OH groups of Bnt, stretching vibrations (1040 cm^{-1}) of Si–O, stretching vibrations (920 cm^{-1}) of Al–O and bending vibrations (760 cm^{-1}) of Si–O.

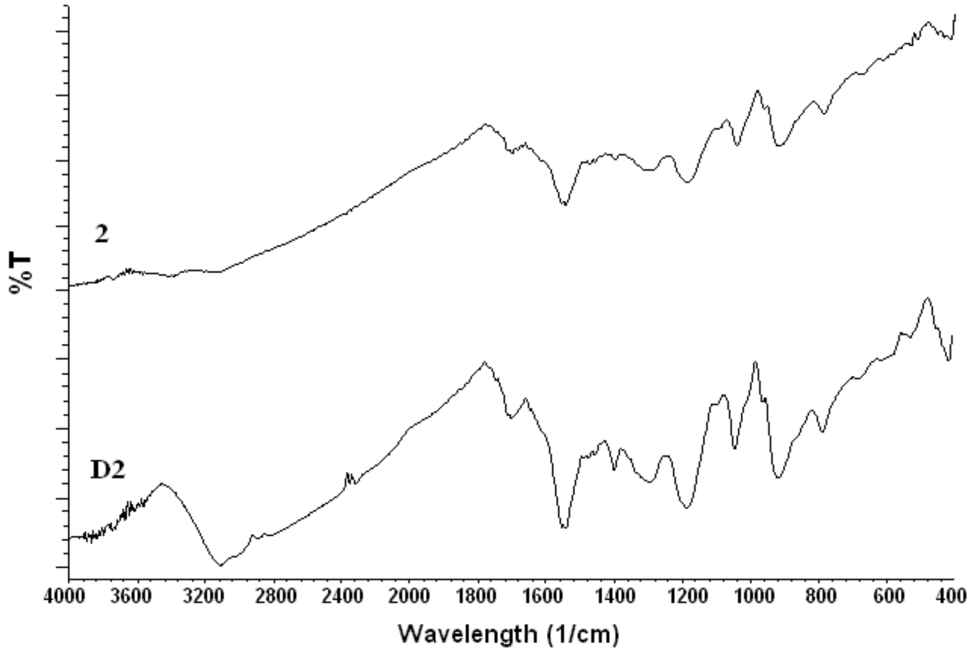

Figure 1. FTIR results of pristine and irradiated PPy/Bnt composites

3.2. Optical absorbance

The UV–visible absorption spectra of pristine and irradiated composites were carried out in NMP solution (Figure 2). The absorption peaks at 275 nm and 370 nm assign the characteristic π-π* transition on the polypyrrole and the formation of polybenzoid salt (PB) form of PPy, respectively [15]. These two peaks are attributed to transitions of the valence to polaron and bipolaron/polaron states. As it is seen from Figures 2 and 3, remarkable changes were observed in the UV-visible absorption spectra of the 2 upon irradiation. The intensities of prominent bands of 2 increased substantially after irradiation.

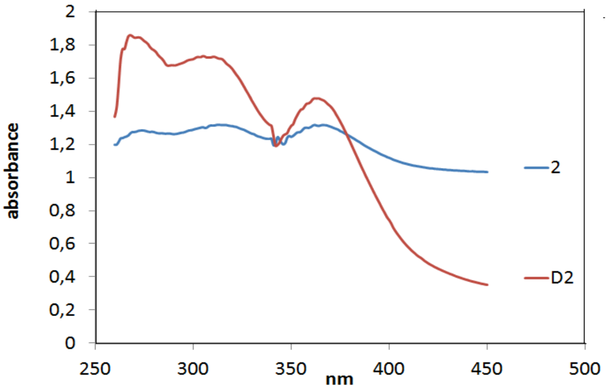

Figure 2. UV- visible absorption spectra of pristine and irradiated PPy/Bnt composites

The effect of radiation on the band structure of the PPy/Bnt composite was investigated by means of the room temperature absorption measurements. In Figure 3a and Figure

3b, the spectra of the samples in the spectral range 300–800 nm are presented. In general, the absorption coefficient of the semiconductors obeys the Eq. (1);

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (1)$$

where A is a constant, E_g is the band gap, and n is a parameter which can be assumed to have values of ½ and 2 depending on the nature of electronic transition responsible for the absorption: $n = 1/2$ for a direct-allowed transition and $n = 2$ for an indirect-allowed transition. Therefore, the dependence of $(\alpha h\nu)^n$ on photon energy ($h\nu$) was plotted of $n = 2$ for direct transitions in Figure 3a and Figure 3b. Hence a straight line graph can be plotted between $(\alpha h\nu)^2$ and $h\nu$. The intercept to the $h\nu$ axis gives the direct energy band gap of the PPy/Bnt composite. The direct band gaps have been determined as 2.95 and 3.05 eV for the samples named as 2 and D2, respectively. It is seen that a shift in the absorption peak towards higher photon energies was found indicating an increase in the energy band gap of the PPy/Bnt composite after irradiation. The shift of absorption maxima to smaller wavelengths may be explained by a larger contribution to absorption from the amorphous regions along crystalline domains. Similar results have been reported for the polypyrrole irradiated with 100 MeV silver ions [9]. We also note that a sharp decrease in the absorption spectrum may be due to irradiated PPy/Bnt and may not retain its properties as that of unirradiated sample.

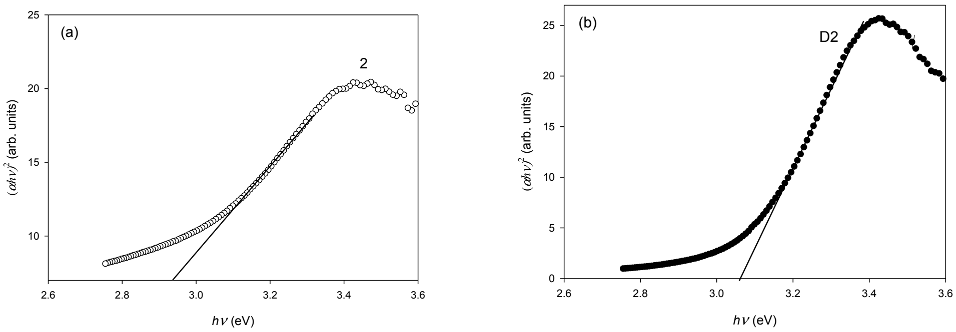

Figure 3. Absorption spectra of a) 2 and b) D2.

3.3. Thermal analysis

The thermal stabilities of the samples were investigated by thermogravimetric analysis (TGA), as shown in Figure 4 and a summary of TGA results is also given in Table 1. From the TGA curves of the pristine and irradiated PPy/Bnt composites, similar weight loss steps are observed. The weight loss below 100 °C is associated with remaining water molecules. The pyrolysis of the organic matter occurs in two steps in the 120–600 °C temperature range and it is associated with different endothermic peaks depending on the nature of both PPy and Bnt [3]. At first step, initial degradation started at 130 °C and 120 °C, which is removal of dopant anion, and this degradation continues to 270 °C and 240°C, respectively. The second degradation step started at 560 °C and 465 °C, which is degradation of polymer chains, and this step continued to 645 °C and 610 °C, respectively. Similar results were observed for polypyrrole composites in the literature [16]. The initial decomposition temperatures showed that after the irradiation of the composite, thermal stability of the composite decreased. The amount of resude from pristine and irradiated PPy/Bnt composite at 900 °C was observed as 52% and 47%, respectively.

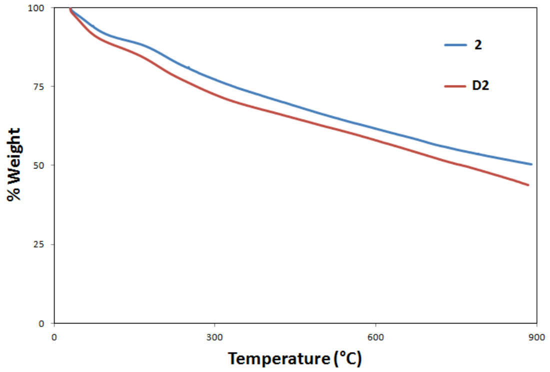

Figure 4. TGA results of pristine and irradiated PPy/Bnt composites.

Table 1. Thermal degradation temperatures of the samples (T_i, initial degradation temperature; T_m, maximum degradation temperature; T_f, final degradation temperature.)

Samples	T_i	T_m	T_f	**% Resude at 900** °C
Pristine PPy/Bnt	130	175	270	52
	560	610	645	
Irradiated PPy/Bnt	120	150	240	47
	465	540	610	

3.4. XRD analysis

In Figure 5, we have presented the XRD patterns of the pristine and irradiated PPy/Bnt composites. The XRD pattern of Bnt shows a characteristic diffraction peak at 2θ = 7.51°, which is *d*-spacing of 8.3 Å (taken from the data obtained with the XRD apparatus) [17]. The XRD pattern of PPy/Bnt composite after polymerization indicates an interlayer distance at 12.4 Å, which corresponds to a 4.1 Å expansion from the 8.3 Å of the pure bentonite [4, 18]. This peak shifts to a lower angle of 2θ = 5.65° for the PPy/Bnt composite. These results show the composite is of intercalated structure and would be expected to be in agreement with the observation that PPy chains in the layers of the Bnt as reported by Yoshimoto and co-workers [19].

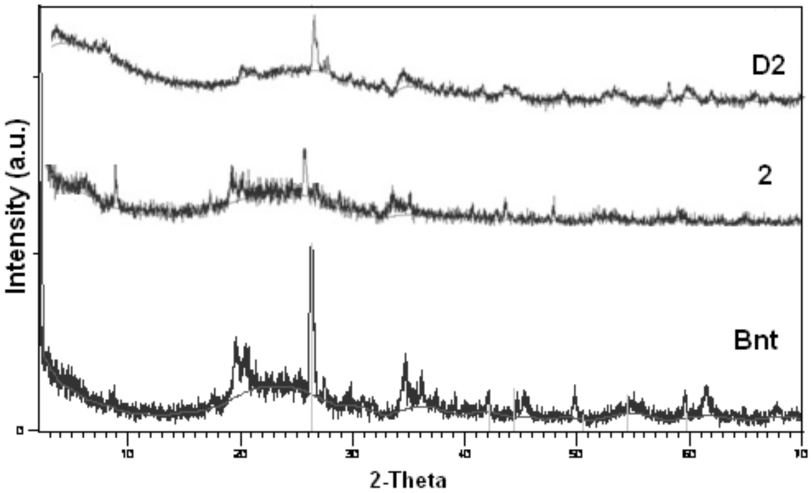

Figure 5. XRD results of Bnt, pristine PPy/Bnt and irradiated PPy/Bnt composites.

On the other hand, pristine PPy/Bnt composite exhibits sharp peaks between at $2\theta = 8°$-$40°$, which indicates some crystalline areas. The peaks of the irradiated PPy/Bnt composite agree with pristine PPy/Bnt composite. However, the intensity of the peaks changed with irradiation. This may be due to breaking of the polymer chain, which induces more amorphous regions in the polymer structure.

3.5. SEM analysis

The morphologies of unirradiated and irradiated PPy/Bnt composites were investigated using a scanning electron microscope. The microstructure of pristine surface was shown in Figure 6. Unirradiated sample exhibited tightly composite particles and a more homogenous surface. Microstructure of the irradiated sample was also shown in Figure 6. The SEM micrographs of D2 demonstrated a different morphology from the 2. The irradiated sample has more sparsely distributed particles [20]. Average diameter of the particles was found approximately 2 μm. SEM analysis clearly shows that gamma radiation influences the PPy/Bnt composite surface morphology.

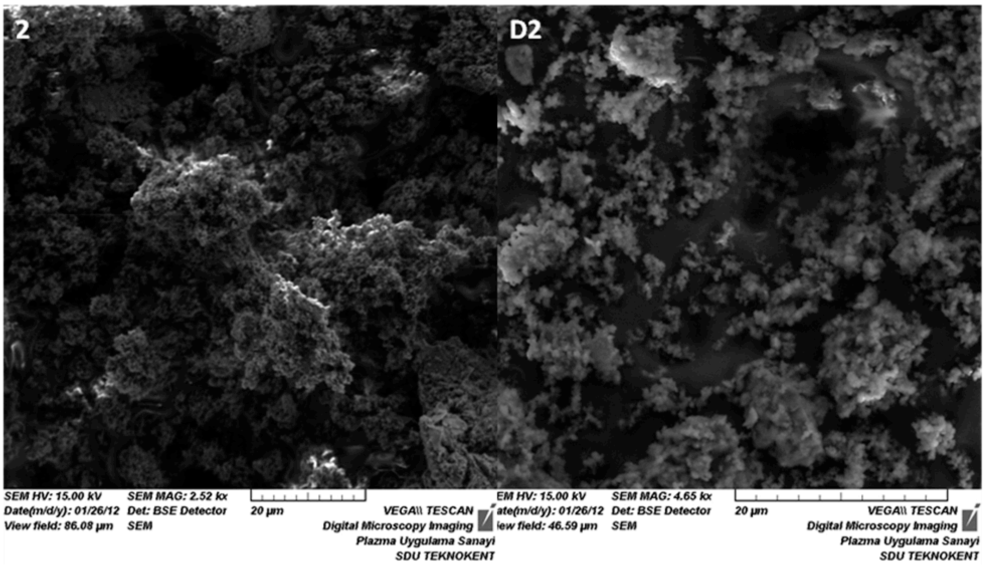

Figure 6. SEM micrographs of 2 and D2.

3.6. Electrical conductivity

The dc conductivity measurements have been carried out in the temperature 290–420 K to study the effect of irradiation on the basic mechanism of charge transport. In Figure 7, the temperature-dependent electrical conductivities of 2 and D2 samples are presented. Because of the high resistivity, reliable data could not be recorded for the unirradiated and irradiated pure polypyrrole samples. The addition of bentonite to polypyrrole caused an increase in conductivity. The conductivities of 2 and D2 were $6.29\text{x}10^{-7}$ and $3.59\text{x}10^{-7}$ $(\Omega\ \text{cm})^{-1}$ at 300 K, respectively. The conductivity of D2 was relatively lower than that of 2 at both low and high temperatures. Measured samples were exhibiting semi-conducting behavior in the specified temperature interval. In general, in a disordered semi-conducting system, the temperature-dependent resistivity follows the Mott variable range hopping model. Therefore, the possible charge transfer mechanism is thermally activated hopping, in which charge carriers jump from one localized center in the band gap to another center, with the emission or absorption of a phonon [21]. The Mott model defines the relation between conductivity and temperature as below;

$$\sigma = \sigma_o \exp\left[-(T_o / T)^{1/4}\right] \qquad (2)$$

In Eq. (2); σ_o and T_o are the conductivity at infinite temperatures and degree of disorder, respectively. Therefore, to determine the dominant conduction mechanism, the temperature-dependent electrical conductivity was plotted by constructing Lnσ versus $T^{1/4}$ in Figure 7. A linear variation for 2 and D2 was obtained for nearly full-investigated temperature range. This indicates that the 3D charge-transport mechanism was the suitable conduction mechanism for the investigated samples. From the slopes and the intercepts of these linear plots, Mott's parameters, i.e. T_o, $N(E_F)$ and average hopping range (R) were calculated by using the expressions given by Paul and Mitra and listed in Table 2 [22]. The variable range hopping is always to be expected when W>kT and αR>1 with the degree of disorder $T_0>10^3$. Thus, variable range hopping (VRH) mechanism provides the conduction of carrier in these samples. As seen from Figure 7, the conductivity of the PPy/Bnt composite decreased after irradiation process. The decreasing of conductivity is in agreement with the XRD, SEM and absorption results. Thus, a shift in the absorption peak towards higher energies was found indicating an increase in the energy band gap of the polymer after irradiation, which gives rise to the decrease in dc conductivity of PPy/Bnt composite. It is reported that the shift in the band gap causes the change in the electrical conductivity [23]. The decrease in conductivity may be due to the incident of huge amount of energy flux during irradiation at the highest dose. The decrease in activation energy between the localized states observed in the irradiated sample as shown in Table 2 may be due to an increase in the extrinsic trapping states, which decreases their conductivity. This can be explained by the increased scattering of charge carriers following decreased mobility depending on irradiation.

Table 2. Summary of the electrical parameters and activation energies of pristine and irradiated PPy/Bnt composites.

Sample	σ_{300K} $(\Omega\text{-cm})^{-1}$	W (meV)	To (K)	R (cm)	αR	$N(E_f)$ $(cm^{-3}V^{-1})$
2	6.29×10^{-7}	12196	1.73×10^{7}	$6.58\times10\text{-}^{6}$	5.81	6.98×10^{15}
D2	3.59×10^{-7}		7.58×10^{6}	$2.35\times10\text{-}^{6}$	4.76	1.92×10^{17}

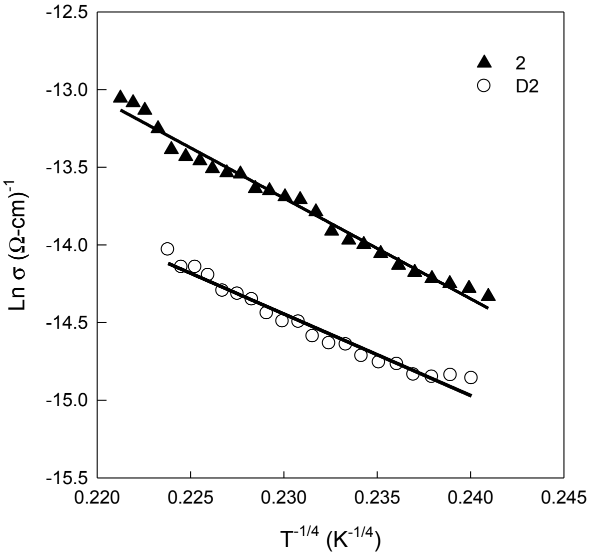

Figure 7. Ln σ - $T^{-1/4}$ variations for pristine and irradiated PPy/Bnt composites.

4. Conclusions

The results of FTIR, UV-visible, TGA, XRD and SEM analyses showed that PPy/Bnt composite was successfully synthesized by chemical oxidation polymerization. Thermal analysis results showed that the thermal stability of composite decreased with irradiation. XRD patterns showed that the intensity of the peaks which is an indication of crystallinity of structure changed with irradiation. Surface morphology of the composite was affected by gamma radiation as seen in SEM analysis.

As results of measurements, it was observed that there are clear differences in the structural, optical and electrical properties of irradiated sample when compared with pristine sample. The optical studies indicate that the absorption mechanism is due to direct allowed transition and the band edge is shifted towards higher photon energies after irradiation, which gives rise to the decrease in dc conductivity of PPy/Bnt composite. This shift in the absorption may be produced in creation of free radicals or ions. The conductivity result shows that the conduction takes place through hopping process due to wide range of localized states present near the Fermi level.

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