



Synthesis, Characterization and Investigation of Electrical Conductivity of Poly(2-Oxo-2-Phenyl Ethyl -2-Amino Benzoate)/Bentonite Nanocomposite

Tolga Acar YEŞİL^{*1}, Ömer DİLEK², Tahir TİLKİ³, Mustafa YAVUZ³

¹*Sinop University, Türkeli Vocational School, Department of Property Protection and Security, 57900, Sinop, Turkey*

²*Isparta University of Applied Science, Central Research Laboratory Application and Research Center, 32200, Isparta, Turkey*

³*Suleyman Demirel University, Faculty of Art and Science, Department of Chemistry, 32260, Isparta, Turkey*

**corresponding author e-mail: tyesil@sinop.edu.tr*

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Abstract: This study was carried out in two stages. In the first stage; 2-oxo-2-phenylethyl-2-aminobenzoate (OPA) compound, which was an aniline derivative, was synthesized by starting the appropriate components. Then, poly(OPA) was obtained via chemical polymerization of the OPA in the presence of ammonium peroxydisulfate (APS) as the initiator and DMF as the solvent. Poly(OPA)/Bentonite (BNT) nanocomposite was synthesized by effectively dispersing the inorganic nanolayers of BNT in poly(OPA) matrix by means of intercalation method. In the second stage; the characterization of the synthesized OPA, poly(OPA) and poly(OPA)/BNT nanocomposite was investigated. The OPA was characterized by liquid chromatography mass spectrometry (LC/TOF-MS). The structures of the poly(OPA) and nanocomposite(OPA) were characterized by using Fourier Transform Infrared Spectroscopy (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). In addition, the conductivity of poly(OPA)/BNT nanocomposite was investigated and change in electrical conductivity was examined.

Key words: Polyaniline derivatives, Bentonite, Nanocomposite, Conductivity

Poli(2-Okso-2-Feniletıl -2-Amino Benzoat)/Bentonit Nanokompozitinin Sentezi, Karakterizasyonu ve Elektrik İletkenliğinin İncelenmesi

Öz: Bu çalışma iki aşamada gerçekleştirilmiştir. İlk aşamada; bir anilin türevi olan 2-okso-2-feniletıl-2-aminobenzoat (OPA) bileşiği uygun bileşenlerden başlanarak sentezlenmiştir. Daha sonra OPA'nın başlatıcı olarak amonyum peroksidisülfat (APS) ve çözücü olarak DMF varlığında kimyasal polimerleşmesi sonucu poli (OPA) elde edilmiştir. Poli(OPA)/Bentonit (BNT), BNT'in inorganik tabakalarının poli(OPA) matrisinde interkalasyon yöntemi ile etkin bir şekilde dağıtılmasıyla sentezlenmiştir. İkinci aşamada ise sentezlenen OPA, poli(OPA) ve poli(OPA)/BNT nanokompozitin karakterizasyonu incelenmiştir. OPA, sıvı kromatografi kütle spektrometresi (LC/TOF-MS) kullanılarak karakterize edilmiştir. Poli(OPA) ve poli(OPA)/BNT nanokompozitin yapıları Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), termal gravimetrik analiz (TGA) ve taramalı elektron mikroskobu (SEM) kullanılarak karakterize edilmiştir. Ayrıca poli(OPA)/BNT nanokompozitin iletkenliği araştırılmış ve elektriksel iletkenliğindeki değişim incelenmiştir.

Anahtar Kelimeler: Polianilin türevleri, Bentonit, Nanokompozit, İletkenlik

1. Introduction

In recent years, as a result of the increase in the usage areas of polymers, studies in polymer science and technology have accelerated and scientists have started to work on synthesizing new polymers and improving the properties of synthesized polymers. Among these, controlling the conductivity of conductive polymers by changing the synthesis conditions and synthesis methods is the most important. In studies conducted for this purpose, many conductive polymers have been synthesized by chemical and electrochemical methods [1]. Conducting polymers are currently used in scientific studies for rechargeable batteries. It is widely used in the construction of sensors, diodes, transistors and microelectronic devices, modified electrode productions, electronic display panels and biochemical analyzes [2-8]. Polyaniline and its derivatives are one of the most promising conducting polymers that have been studied extensively because of their environmental stability, electrical and optical properties, high conductivity [9]. The thermal analysis of conducting polymers is very important to determine their performance in application processes of these materials [10]. Therefore, thermal analysis of conducting polymers provides significant information about the effect of morphological structure. Different methods are applied to improve the conductivity, mechanical and physical properties of conductive polymers. One of these methods is chemical methods in which the properties of conductive polymers are improved by preparing copolymers [11] or composites [12]. Polymer systems are very popular in composite industry because of their low cost and performance. Recently, a great number of studies have been performed to obtain nanomaterials with better chemical and physical properties than the pure polymer systems [13]. A common approach to synthesize polymer nanocomposites is to employ intercalation of layered solids. Thus, polymer is thrown in the interlayer space. Among layered solids, clay minerals have been commonly used and justified to be very impressive due to their structure and properties. Polymer/clay nanocomposites provide enhanced mechanical and thermal properties compared with conventional composites. BNT, one of the most important clay structures, is a special clay belonging to the smectite clay group. BNT has a layered structure which consists of both tetrahedral silicate sheets and octahedral alumina sheets. BNT has totally negative charge and can easily take in positive charges with cationic surfactants [14].

In this paper, we synthesized aniline derivative OPA as monomer and chemical polymerization of OPA was carried out. Then, we prepared poly(OPA)/BNT nanocomposite material by effectively dispersing the inorganic nanolayers of BNT sample in poly(OPA) matrix. The effect of BNT on the thermal properties of poly(OPA) was investigated. The synthesized monomer which was known in the literature [15], was characterized by FTIR, melting point, LC/TOF-MS technique. Poly(OPA)/BNT nanocomposite materials were characterized by FTIR spectroscopy. The thermal stabilities of poly(OPA) and poly(OPA)/BNT nanocomposite were also studied by TGA. Surface structures of BNT, poly(OPA), poly(OPA)/BNT nanocomposite were examined by SEM. Also, the electrical conductivity of poly(OPA) and poly(OPA)/BNT nanocomposite was measured using the standard four-probe technique. Furthermore, temperature-dependent on electrical conductivity of poly(OPA)/BNT nanocomposite was investigated.

2. Material and Method

2.1 Materials

Anthranilic acid ($C_6H_4NH_2COOH$), BNT [$Al_4Si_8O_{20}(OH)_4 \cdot nH_2O$], cetyltrimethylammonium bromide (CTAB), bromo-2-acetophenone (C_8H_7BrO) and ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) were purchased from Aldrich (Germany). All solvents and reagents were used without any other purification.

2.2 Synthesis of OPA (3)

Anthranilic acid (**1**, 205.7 mg; 1.5 mmol; 1.0 equiv.) and K_2CO_3 (207.3 mg; 1.5 mmol; 1.0 equiv.) was heated to 90 °C in 10 mL DMF:H₂O (1:1). After 2 h, the mixture was cooled down to ambient temperature and bromo-2-acetophenone (**2**, 298.6 mg; 1.5 mmol; 1.0 equiv.) was slowly added into the mixture. Then, mixture was stirred at ambient temperature for 2 h. The conversion was followed by TLC (silica gel; Hexane/EtOAc, 8:2). After the conversion was completed, 10 mL of distilled water added and cooled in refrigerator for 24 h. The product was filtered, dried and recrystallization with ethanol afforded 367 mg (**3**, 1.44 mmol, 96%) of the title compound. **Melting point:** 123-124 °C (Lit [15]:122.5-124 °C). **TLC:** $R_f = 0.6$ (silica gel; Hexane/EtOAc, 8:2) **FTIR (KBr):** $\tilde{\nu}_{max}$ (cm^{-1}) = 3360, 3520 (N-H stretching), 3060, 3070 (aromatic -CH stretching), 1680 (C=O groups), 1400-1600 (aromatic C=C), 1300 (-CH bending), 1240 (ester groups), 1180 (C-C stretching), 1130 (C-N stretching), 680, 760 (aromatic -CH bending). **LC/TOF-MS m/z :** $[M+H]^+$ Calcd for $C_{15}H_{14}NO_3$, 256.1; Found: 256.1, $[M+Na]^+$ Calcd for $C_{15}H_{13}NO_3Na$, 278.1; Found: 278.1. The scheme of synthesis is demonstrated in Fig. 1, LC/TOF-MS chromatogram is demonstrated in Fig. 2.

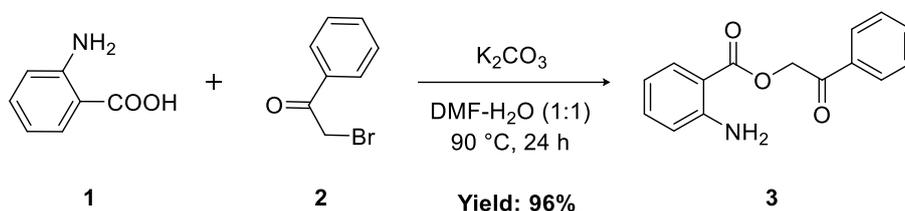


Figure 1. Synthesis route of OPA

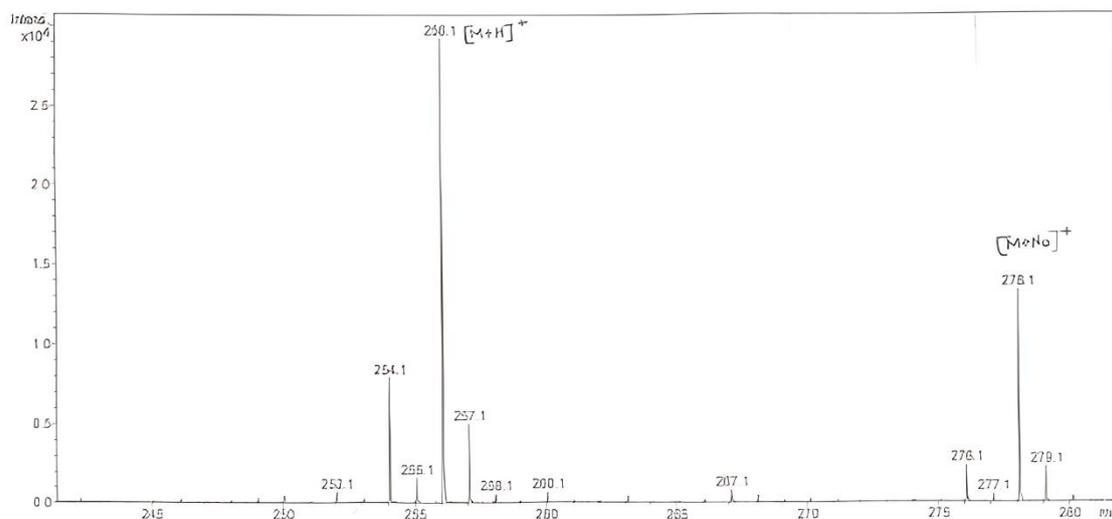


Figure 2. LC/TOF-MS chromatogram of OPA

2.3 Synthesis of poly(OPA) (4)

OPA (3, 0.5 g) and 10 mL DMF were added into the 100 mL two necked flask. The polymerization of OPA was initiated by the drop wise addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (6.1 g) solution in 10 mL 1.0 M HCl as oxidizing agent at ambient temperature under nitrogen. The molar ratio of initiator/OPA was chosen as 2.5. Temperature of the reaction mixture was set to 60 °C via oil bath and the mixture was stirred at this temperature overnight. Then, precipitated product (4) was filtered, washed with distilled water and dried. Yield was 75 %.

FTIR(KBr): $\tilde{\nu}_{\text{max}}$ (cm^{-1}) = 3350, 3500 (N-H stretching), 3060, 3070 (aromatic -CH stretching), 1680 (C=O groups), 1400-1600 (aromatic C=C), 1300 (-CH bending), 1240 (ester groups), 1180 (C-C stretching), 1130 (C-N stretching), 680, 760 (aromatic -CH bending). The synthesis is demonstrated in Fig. 3.

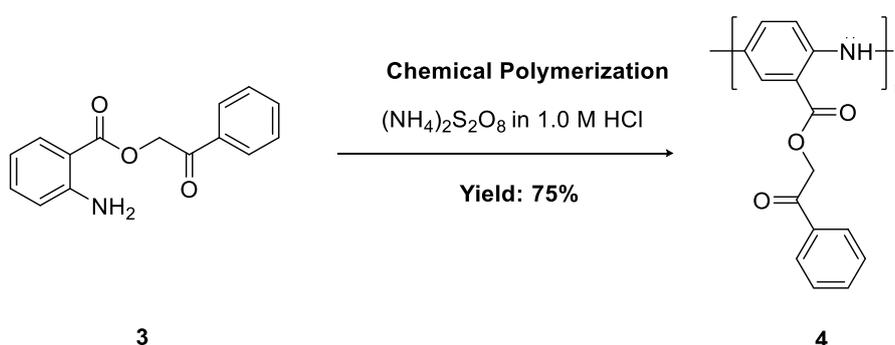


Figure 3. Synthesis route of poly (OPA)

2.4 Synthesis of poly(OPA)/BNT nanocomposites

Bentonite (4 g), cetyltrimethylammonium bromide (0.1 g) (CTAB) as cationic surfactant and DMF (40 mL) were added into the three necked round 100 mL flask that was equipped with magnetic stirring bar. Then, OPA (1 g) was added into the flask and temperature of the reaction mixture was set to 60 °C via oil bath and the mixture was stirred at this temperature for 1 h. After 1 h, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (9.82 g) solution in HCl (20 mL, 1 M) was added dropwise into the flask. The mixture was stirred overnight at 60 °C under N_2 . Then, precipitated product was filtered, washed with distilled water and dried. Route of synthesis is demonstrated in Fig. 4.

FTIR(KBr): $\tilde{\nu}_{\text{max}}$ (cm^{-1}) = 3350, 3500 (N-H stretching), 3060, 3070 (aromatic -CH stretching), 1680 (C=O groups), 1400-1600 (aromatic C=C), 1300 (-CH bending), 1240 (ester groups), 1180 (C-C stretching), 1130 (C-N stretching), 680, 760 (aromatic -CH bending).

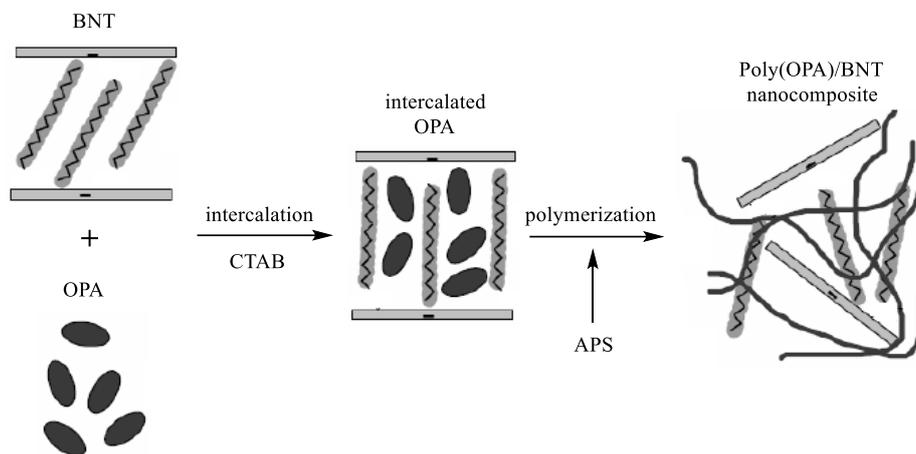


Figure 4. Schematic demonstrate of poly(OPA)/BNT nanocomposite

2.5 Instrumentation

FTIR spectra were determined, as KBr disks, by use of a Shimadzu IR Prestige-21 FTIR spectrophotometer (Japan). TGA was taken by using Perkin Elmer Model (USA) device that is working between 25 °C and 900 °C under air atmosphere. Electrical conductivity was measured by using a standard four-probe method. The variation of the resistances of the polymers between the temperatures of 80-400 K with 5 K temperature intervals was investigated. For measurement, samples were placed in a Janis nitrogen-cooled cryostat with a four-point strip contact. Temperature control and heating processes are provided by Lake shore 331 (USA) temperature control unit. Electrical measurements were made with the help of Keithley-2400 (USA) source meter, which is a constant current-voltage source. The Philips XL-30 S FEG (Netherlands) device was used while taking SEM images. LC/TOF-MS measurement was taken by preparing the solution of the sample in CHCl_3 with the Bruker microTOF-Q (Germany) device.

3. Results

Poly(OPA) spectrum has stretches of -NH, aromatic -CH, C=O, aromatic C=C, ester groups, C-C and C-N at 3500, 3350, 3060, 3070, 1680, 1600, 1400, 1240, 1180 and 1130 cm^{-1} , respectively. FTIR analysis can be used to determining of poly(OPA)/BNT nanocomposite formation. As a result of interactions between polymer matrix and BNT, some additional peaks and shifts can occur in spectrum when compared with pure polymer [15]. After addition of BNT into polymer matrix, the -NH peak shifted from 3500 to 3700 and 3350 to 3470 cm^{-1} . The band of C=O stretching shifted from 1680 to 1700 cm^{-1} .

Fig. 5 shows the TGA thermogram of poly(OPA) and poly(OPA)/BNT nanocomposite. The first weight loss of 5-10% observed up to 100 °C is due to loss of water from the poly(OPA)/BNT nanocomposite. As regards the thermal behavior of poly(OPA)/BNT nanocomposite, between 25-900 °C, it was observed degradation of approximately 75% of poly(OPA) and 15% of poly(OPA)/BNT nanocomposite. Thereby forming nanocomposite, thermal stability of polymer was increased because of the presence of BNT [16].

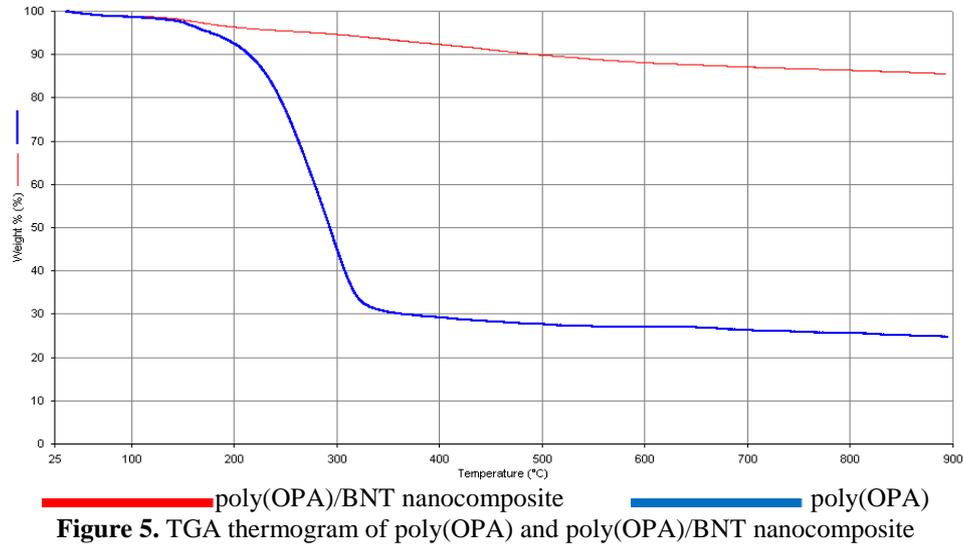


Fig. 6 shows SEM images of BNT (a), poly(OPA) (b) poly(OPA)/BNT nanocomposite (c), respectively. As seen from SEM image Fig. 6 (a), the morphology of the BNT, it was observed that it consist of a large, non-porous, layered and granular structure of different sizes. According to SEM image of Fig. 6 (b), surface of the polymer structure were observed large and small intergranular spaces. When SEM morphology of poly(OPA)/BNT nanocomposite (Fig 6 (c)) was examined, similar to the surface structure of BNT were observed homogeneous and non-porous structures.

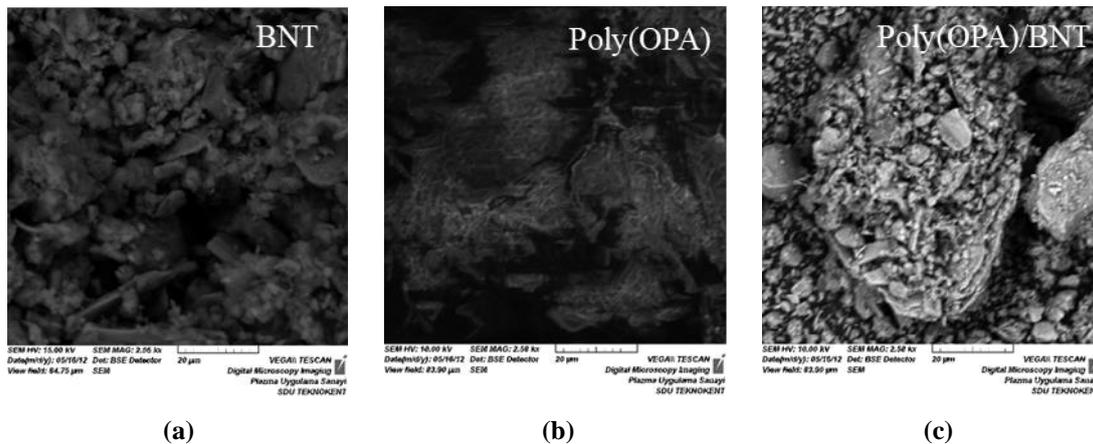


Figure 6. SEM images of BNT (a), poly(OPA) (b) and poly(OPA)/BNT nanocomposite (c)

The electrical conductivity of poly(OPA) and poly(OPA)/BNT nanocomposite were measured using the standard four-probe technique. Conductivity values were decreased by the addition of BNT. Electrical conductivity of the poly(OPA)/BNT nanocomposite (1.85×10^{-7} S/cm) was less than the conductivity of the poly(OPA) (2.1×10^{-7} S/cm). This was because of the reducing effect of BNT which had no electrical conductivity [17]. Thermal stability of the poly(OPA) was less than the thermal stability of the poly(OPA)/BNT nanocomposite. The result supported conductivity measurements.

Fig. 7 shows temperature-resistivity diagram of poly(OPA)/BNT nanocomposite. It was observed that, resistivity decreased as linear with increasing temperature. At room temperature (300 K), it was measured that the resistivity of sample was 5.4×10^6 (Ω -cm), the conductivity of sample was 1.85×10^{-7} (S/cm).

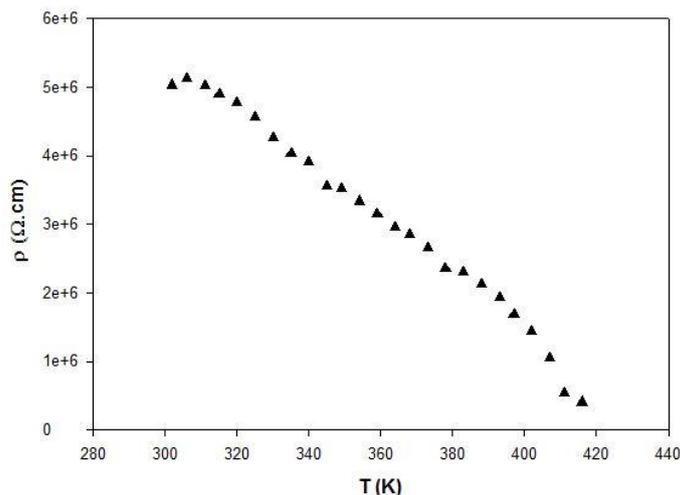


Figure 7. Temperature-resistivity diagram of poly(OPA)/BNT nanocomposite

Fig. 8 shows temperature-activation energy diagram of poly(OPA)/BNT nanocomposite. Also, as shown in the graph, poly(OPA)/BNT had two different slopes, and hence there was two activation energy. In low temperature region (296-360K), the temperature dependence of conductivity was weak and in this region the activation energy was measured 78 meV. In high temperature region (364-402K), conductivity showed a rapid increase with temperature and in this region the activation energy was measured 229 meV. As a result of these calculations, it was observed that poly(OPA)/BNT nanocomposite was a semiconductor [16].

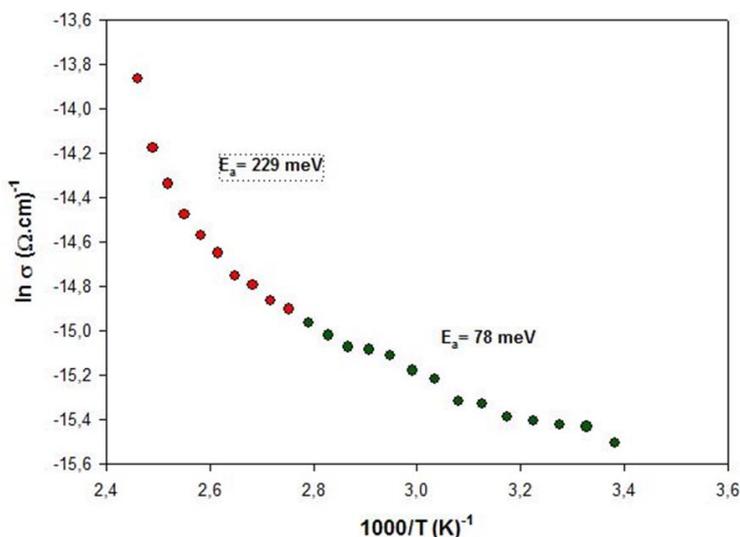


Figure 8. Temperature-activation energy diagram of poly(OPA)/BNT nanocomposite

4. Conclusion and Comment

In this study, firstly OPA was successfully synthesized by the reaction of anthranilic acid and bromo-2-acetophenone and the crude product was purified crystallization technique by using absolute ethanol as a solvent (Yield: 96%). OPA monomer was characterized with FTIR and LC/TOF-MS. In the second step, synthesis of conducting poly(OPA) was performed by chemical polymerization using an initiator (APS) and DMF as a solvent

(Yield: 75%). Then, poly(OPA)/BNT nanocomposite was synthesized by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator and CTAB as a surfactant in HCl medium of the OPA monomer with BNT which had inorganic structure. The synthesized poly(OPA) and poly(OPA)/BNT nanocomposite structures were characterized by spectroscopic methods, such as FTIR, TGA, SEM. Thermal stability of poly(OPA) and poly(OPA)/BNT were investigated via TGA analysis. Thermal stability of poly(OPA)/BNT nanocomposite was found to be higher than the thermal stability of poly(OPA). Surface structures of BNT, poly(OPA) and poly(OPA)/BNT nanocomposite were characterized by SEM. Surface morphology of poly(OPA)/BNT nanocomposite was observed to be different from BNT and poly(OPA). Conductivity of poly(OPA) and poly(OPA)/BNT were measured by four-probe technique. Electrical conductivity of the poly(OPA)/BNT nanocomposite was found to be lower than the conductivity of the poly(OPA). Changes in depend on temperature of electrical conductivity of the poly(OPA)/BNT nanocomposite was examined and poly(OPA)/BNT nanocomposite had two different slopes, so there were two activation energy. (In low temperature; 78 meV; In high temperature: 228 meV). As a result, it was observed that poly(OPA)/BNT nanocomposite was a semiconductor.

Author Statement

Tolga Acar YEŞİL: Investigation, Validation, Original Draft Writing.

Ömer DİLEK: Investigation, Validation, Visualization.

Tahir TİLKİ: Resource/Material/Instrument Supply.

Mustafa YAVUZ: Resource/Material/Instrument Supply.

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

References

- [1] H. Randriamahazaka, V. Noel, S. Guillerez, and C. Chevrot, "Interpenetrating Organic Conducting Polymer Composites Based on Polyaniline and Poly(3,4- ethylenedioxythiophene) from Sequential Electropolymerization," *J. Electroanal. Chem.*, 585, 157-166, 2005.
- [2] M. S. Rahmanifar, M. S. Mousavi, M. Shamsipur, and M. Ghaemi, "What is the Limiting Factor of the Cycle-Life of Zn-Polyaniline Rechargeable Batteries," *J. Power Sources*, 132, 296-301, 2004.
- [3] K. Luo, X. Guo, N. Shi, and C. Sun, "Synthesis and Characterization of CoreShell Nanocomposites of Polyaniline and Carbon Black," *Synth. Met.*, 151, 293-296, 2005.
- [4] W. Pan, S. L. Yang, G. Li, and J. M. Jiang, "Electrical and Structural Analysis of Conductive Polyaniline/Polyacrylonitrile Composites," *Eur. Polym. J.*, 41, 2127-2133, 2005.
- [5] A. S. Chen, K. R. Chuang, C. I. Chao, and H. T. Lee, "White Light Emission from Electroluminescence Diode with Polyaniline As the Emitting Layer," *Synth. Met.*, 82, 207-210, 1996.
- [6] P. Topart, and P. Hourquebie, "Infrared Switching Electroemissive Devices Based on Highly Conducting Polymers," *Thin Solid Films*, 352, 243-248, 1999.

- [7] A. A. Athawale, S. V. Bhagwat, and P. P. Katre, "Nanocomposite of Pd-polyaniline As a Selective Methanol Sensor," *Sens. Actuators, B.*, 114, 263-267, 2006.
- [8] M. M. Ayad, N. Salahuddin, and M. A. Shenashin, "The Optimum HCl Concentration for the In Situ Polyaniline Film Formation," *Synth. Met.*, 142, 101-106, 2003.
- [9] W. F. Alves, E. C. Venancio, F. L. Leite, D. H. F. Kanda, L. F. Malmonge, J. A. Malmonge, and L. H. C. Mattoso, "Thermo-analyses of polyaniline and its derivatives," *Thermochim. Acta.*, 502, 43-46, 2010.
- [10] S. Wang, Z. Tan, Y. Li, L. Sun, and T. Zhang, "Synthesis, characterization and thermal analysis of polyaniline/ZrO₂ composites," *Thermochim. Acta.*, 441, 191-194, 2006.
- [11] Z. Hu, X. Shang, Y. Yang, C. Kong, and H. Wu, "The Electrochemical Synthesis of Polyaniline/Polysulfone Composite Films and Electrocatalytic Activity for Ascorbic Acid Oxidation," *Electrochimica Acta*, 51, 3351-3355, 2006.
- [12] V. N. Bliznyuk, A. Baig, S. Singamaneni, A. A. Pud, Y. K. Fatyeyeva, and G. S. Shapoval, "Effects of Surface and Volume Modification of Poly(vinylidene fluoride) by Polyaniline on the Structure and Electrical Properties of Their Composites," *Polymer*, 46, 11728-11736, 2005.
- [13] A. O. F. Rossetto, D. S. Vicentini, C. H. Costa, S. P. Melegari, and W. G. Matias, "Synthesis, characterization and toxicological evaluation of a core-shell copper oxide/polyaniline nanocomposite," *Chemosphere*, 108, 107-114, 2014.
- [14] M. Cabuk, Y. Alan, E. İ. Unal, "Enhanced electrokinetic properties and antimicrobial activities of biodegradable chitosan/organo-bentonite composites," *Carbohydr. Polym.*, 161, 71-81, 2017.
- [15] S. S. Gandhi, K. L. Bell, and M. S. Gibson, "Synthetic Routes to 1,5-Dihydro-5-oxo-4,1-benzoxazepines and to 5-Oxooxazolo[3,2-a]quinolines," *Tetrahedron*, 51, 13301-13308, 1995.
- [16] M. Cabuk, T. A. Yesil, M. Yavuz, H. I. Unal, "Colloidal and Electrorheological Properties of Conducting Polyaniline/Bentonite Composite in Silicone Oil Medium," *Curr. Smart Mat.*, 2, 4-11, 2017.
- [17] P. Eaksuwanchai, M. Promsawat, S. Jiansirisomboon, A. Watcharapasorn, "Fabrication, Phase, Microstructure and Electrical Properties of BNT-doped (Sr,La)TiO₃ Ceramics," *J. Korean Phys. Soc.*, 65, 3, 377-381, 2014.