Synthesis and Characterization of Polyaniline/Ignimbrite Nano-Composite Material

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Abstract

In this study, Polyaniline-ignimbrite (PAN-IB) which is a novel nanocomposite material consisting of electrically conductive Polyaniline (PAn) polymer and Ignimbrite (IB) natural insulating material was synthesized chemically using KIO3 as a radical initiator in aqueous media with conventional radical polymerization method. The synthesized nanocomposites including ignimbrite with various monomer-ignimbrite percentages were monitored with scanning electron microscopy (SEM) and structural characterizations were examined with FTIR spectroscopy. Thermogravimetric analysis (TGA), particle size analysis with dynamic light scattering, magnetic susceptibility and conductivity measurements were also examined for all synthesized composites. With making a composite with aniline, the conductivity of ignimbrite (3 × 10⁻⁷ Scm⁻¹) reached to 2.7 × 10⁻⁵ Scm⁻¹. However increasing the ratio of monomer which is added to ignimbrite did not make a significant change on conductivity of the resulting composite.

Keywords: Nanocomposites; Polyaniline; Ignimbrite; Magnetic susceptibility

Introduction

Nowadays, polymeric nano-composite materials have been gaining substantially growing importance in industrial field. Fascinating features of these polymers such as solidity, lightness, flexibility, plasticity, having high chemical and corrosion resistance, thermal stability when combined with adding a filling substance to the ultimate material exhibit mechanical features like flame resistance or thermal stability and give rise to wide range of products. Sports equipment, rocket parts and the applications in the automobile industry are some examples of the use of these materials.

There is an aroused interest in nanotechnology in composite applications because of new superior features that the use of nanotechnology offers. Due to the reason that the filling substance is in nanoscale; there might be some features that cannot be observed in macro scale and only be realized in nanoscale. This phenomenon can be explained with the increased surface area of the substance in nanoscale with respect to its initial state when it is in macro scale. Increased surface area differentiates the interactions between nano particles; and as a result of that there might be a change in the material weight, stiffness, chemical and thermal features [1]. Furthermore, as the size of the particles decreases, the bonds between atoms and molecules in particles differentiates, the number of atoms and molecules on the surface of the particles increases; and consequently these facts explain why particles in nanoscale demonstrate different behavior [2]. In addition, polymer nanocomposites are the materials that are used as matrix polymers. Polymer nanocomposites exhibit different behaviors depending upon some configuration properties such as; the ratio of polymer and filling substances they include, their chemical properties, and the crystallinity of polymer matrix.

In general, ceramic matrix composites are manufactured to improve crack resistance. As distinct from ceramic matrix composites, in the materials derived from polymer matrix composites; either endurance and solidity or flexibility and processability are the concepts that are worked on. For example, in polymer matrix composites, material features such as elasticity and thermal expansion are dependent on the filler’s structure; however the strength of the composite will vary depending on the particle size of the filling substance. One of the first studies on this subject is, polymer nanocomposite material which is conducted in Toyota Central Research Laboratories in the early 1990s [3]. As the little amount of filling material added to polymer, the positive changes on thermal and mechanical properties of the product have been observed in the research.

Conductive polymers have been the subject of many studies in recent years due to their electrical conductivity, mechanical strength, corrosion resistance, and ability to be synthesized both chemically and electrochemically. Among conducting polymers; polyaniline (PAN) is a unique substance due to its excellent electrical, magnetic, and optical properties. It is thought to have a high potential in commercial applications regarding conductive polymers because of its low cost of synthesis and raw material. Its insolubility in many commonly used solvents limits its processability with solution process or melting process methods [4,5]. Improvement in the processability of polyaniline can be achieved by preparing copolymer, composite or blends with other polymers or inorganic materials [6-9].

Conductive polymers have a wide range of application areas such as; conductive coloring [10], optical devices [11], membranes [12], biomedical applications [13], the removal of heavy metals [14,15], and solar cells [16]. In present study, a natural rock ignimbrite that widely spreads around Cappadocia region in Turkey is milled and turned into a composite inside polyaniline matrix, there by obtaining both conductive and light material with high mechanical strength.

Ignimbrite is a natural insulating material that widely spreads around Cappadocia region in Turkey. It is a light and easily processable rock
which is the deposit of a pyroclastic density current and traditionally used in the construction and chemical industries. It is made of a very poorly sorted mixture of volcanic ash (or tuff when lithified) and pumice lapilli, whose color may be white, grey, pink, beige, brown or black depending on composition and density. Due to its lightness it can be used in insulation and siding applications of buildings.

In the present study ignimbrite is mechancially milled up to nanometer scale, defused to a polyaniline matrix during polymerization process and a semiconducting Pan-IB nanocomposite material have been produced. Thermal, morphological, electrical and magnetic characterizations have been examined and this new material has been offered as a suitable material for conducting polymer technology applications.

Materials and Methods

Materials

Ignimbrite was supplied from Nevşehir province’s natural area and ball milled up to nanometer scale before used. KIO₃ (99.995%), diethyl ether and HCl were purchased from Sigma Aldrich and used without purification. Aniline (≥99.5%) was purchased from Sigma Aldrich and vacuum distilled before used, then stored at -18°C.

Characterization

For the characterizing of electrical conductivity of composites the four point probe technique was used with a Nippon NP-900 multimeter (Osaka, Japan). Fourier transform infrared (FT-IR) spectra were recorded with a Spectrum 100 model spectrophotometer (Perkin Elmer, USA) to had structural characterization. Magnetic susceptibility measurements were carried out with a Sherwood Scientific model MKI Gouy scale with a procedure reported elsewhere [17]. The physical morphologies of the composites were monitored by Zeiss LS-10 field emission SEM instrument equipped with an Inca Energy 330 X-Max spectrometer (Oxford Instruments). Samples were sputter-coated with Au (60%) and Pd (40%) alloy using a Q150R instrument (Quorum Technologies). Images were obtained at 3 × 10⁻⁶ Pa working pressure and 15 keV accelerating voltage using In Lens detection mode (2 mm working distance). Dynamic light scattering analyses were performed at room temperature using a 90Plus Nanoparticle Size Analyzer (Brookhaven Instruments, Holtsville, NY). Thermogravimetric analysis was performed with a Setaram SETSYS thermal analyzer at temperature range of 25-1200°C at a heating rate of 10°C min⁻¹. FTIR results

A certain amount of aniline monomer was dissolved in 0.5M HCl solution and bubbled with N₂ 15 minutes with stirring at 5°C. Then the KIO₃ solution was added dropwise to the medium under N₂ and the solution was stirred. 1 hour later, 1 gram of ignimbrite dispersed in HCl solution and added dropwise to the reaction mixture. The reaction was continued under nitrogen atmosphere for 24 h. Then the composite was collected and washed with 1.5 M HCl, water, and diethyl ether, respectively. We synthesized the PAN/ignimbrite composites, including ignimbrite at different percentages, by varying the amount of aniline monomer at a constant n_aniline/n_ig proportion. Reaction conditions and amount of components were given in Table 1.

Results and Discussions

Electrical conductivity

The electrical conductivity of composites was measured on pressed pellets of composite powders. The average thickness of the compressed pellets was 1.0 mm. As is known the most common green polyaniline emeraldine salt has conductivity on a semiconductor level of the order of 10⁻⁵ Scm⁻¹ [18]. In this study addition of Ignimbrite, decreased the conductivity and conductivities of composites ranged from 2.64 × 10⁻⁵ to 2.70 × 10⁻⁷ Scm⁻¹ and were close to each other as it can be seen from the Table 2.

Magnetic susceptibility

The measurement of magnetic properties of conducting polymer is important to know what the charge carrier is and how the electrical conduction occurs. Of these properties, magnetic susceptibility is a significant factor in determining the type of magnetism and density of states at Fermi level [19]. Magnetic susceptibility data of ignimbrite and Pan-IB nanocomposites were measured. As seen in Table 2, magnetic susceptibility values were all positive and range from 1.73 × 10⁻⁴ to 10.25 × 10⁻⁵. The positive values of Gouy scale measurements reveal that the conductivity mechanisms of Pan-IB composites are polaron in nature [20].

Dynamic light scattering measurements

Average particle size of ignimbrite was measured to be 34.7 and PAN-IB composites were changed between 47.5 ≥ d₁₀,₅ ≥61.3 nm (Table 2).

FTIR results

Figure 1 displays the FTIR spectrum of ignimbrite (a), aniline (b) and PAN-IB (K3) (c) nanocomposite. There is about 70% SiO₂ component in the chemical composition of ignimbrite stone. Characteristic peaks at 1028 cm⁻¹ and 911 cm⁻¹ were assigned to the stretching and bending vibration of O-Si-O bonds respectively. Aniline and polyaniline showed the main characteristics bands about 3351 cm⁻¹-3686 cm⁻¹ attributed to the stretching from amine groups. Two broad bands at 3351 cm⁻¹ and 3360 cm⁻¹, indicated the NH₂ groups of aniline. It was observed that these peaks of aniline were shifted to 3686 cm⁻¹ on the spectrum of PAN-IB. This sharp and single bond indicate the secondary N-H groups of polyaniline. And also by comparing the peaks of aniline and PAn-IB, it was observed that peaks from amine groups were shifted due to the presence of SiO₂ particles in polymer matrix.

TGA analysis

The amount of weight loss and the thermal stability of PAN-IB composites were determined using TGA at temperature range of 25-1200°C at a heating rate of 10°C min⁻¹ under argon atmosphere with a gas flow rate of 20 ml min⁻¹. TGA curves of Pan-IB (K3) are shown in Figure 2. As can be seen from TGA curves, nanocomposite shows decomposition with two steps. The first step weight loss at 105°C indicates the loss of small units such as solvents and monomers in the composites. The second weight loss at 557°C shows degradation of the polymer [21].
| Sample Coding | Conductivity (σ, S cm⁻¹) \(\times 10^{-5}\) | Magnetic Susceptibility \((X_{gi}, \text{ cm} \text{g}^{-1})\) \(\times 10^{-6}\) | Average Particle Size \(d_{0.5}\), nm |
|---------------|---------------------------------------------|-----------------------------------------------|----------------|
| IB            | 0.03                                       | +1.73                                         | 34.7          |
| K1            | 2.64                                       | +4.72                                         | 50.3          |
| K2            | 2.66                                       | +7.58                                         | 61.3          |
| K3            | 2.67                                       | +7.90                                         | 50.8          |
| K4            | 2.70                                       | +10.26                                        | 47.5          |

Table 2: Conductivity, magnetic susceptibility and dynamic light scattering data of ignimbrite and PAn-IB nanocomposites.

SEM analysis

Figures 3a-3f shows the SEM micrographs of PAn-IB nanocomposites and pure ignimbrite powder. All composites reveal granular, nonporous, aggregated surface morphologies with diverse sizes. As shown in Figures 3a-3d, percentage of composites doesn't affect the morphological image considerably. But it is obvious that ignimbrite and Pan-IB nanocomposites exhibit different view in a closer look. As shown in Figures 3e and 3f pure ignimbrite powder exhibits sharp, layered and rod like structure and transforms granular and bulk structure when polymerized with aniline.

Conclusions

In this study, a novel nanocomposite material synthesis and structural, electrical, magnetic and morphological characterizations are present. Pan-IB nanocomposites at 52 nm average particle diameter with \(2.7 \times 10^{-5}\) S cm⁻¹ electrical conductivity were synthesized. All magnetic susceptibility measurements were obtained as positive and this situation indicated that the conductivity mechanisms were polaronic. According to the FTIR spectra existence of Si-O and N-H bonds in the same spectrum implied that the formation of PAn-IB composite. It was appeared that thermal stability of composite was observed up to 557°C that showed the degradation of the polymer from TGA curves. Scanning Electron Microscopy (SEM) was used for microstructures analysis. Finally it was concluded that the Pan-IB semiconducting nanocomposite is a novel material and suitable for many future applications on science and technology.
Figure 3d: SEM images of PAN-IB nanocomposites K4.

Figure 3e: SEM images of PAN-IB nanocomposites IB at 5Kx zoom.

Figure 3f: SEM images of PAN-IB nanocomposites K1 at 20Kx zoom.

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