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Synthesis of Graphene oxide (GO) Produced by Hummers Method Doped with Poly (Vinyl Alcohol) (PVA) and Investigation of Its Structural/Thermal Properties

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In this study, effects of graphene oxide (GO) additive produced by Hummers method on polyvinyl alcohol (PVA), a water soluble synthetic polymer, were observed. PVA was doped with GO while it was solution state to increase the nanofiber properties of the composite. The PVA-GO ratio was determined to be 100: 1 and nano-composite material was produced from the prepared solution. Thermal characterization of the produced material was made by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), surface characterization was made by scanning electron microscopy (SEM), structural characterization was made by Fourier Transform Infrared (FT-IR) Spectrometer and compared with each other. The distribution of the elements constituting the material was also determined by energy disperse X-Ray analysis (EDX). Experimental results showed that the addition of GO to the polyvinyl alcohol matrix improves the structural properties of the polymer. According to all these results, the covalent bonding self-healing GO/PVA composites could be used for smart materials and structural materials.

Keywords: Poly (vinyl alcohol), Polymer Based Composite, Thermal and Structural Analysis, GO/PVA.

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1. Introduction

Graphene and graphene derivatives have attracted considerable attention since their discovery because of their unusual physical and chemical properties. Graphene is 30 times stronger than steel and consists of a single layer of graphite. Considering that graphene is only 0.42 nm thick, it is quite impressive. The electron transport properties of graphene are unique. One of these properties is a high carrier concentration and mobility, which allows an electrical current to flow at close to the speed of light. In other words, by the movement of electrons in the material at speeds close to the speed of light, the electric current is transmitted more rapidly than other materials. As a result, faster computers and high-performance electronic devices can be produced. Researchers from the Columbia Nanotechnology Center have discovered that electrons can be transported through graphene with their very low effective masses at room temperature, similar to conduction of relativistic particles such as photons. This discovery proved the unusual quantum hall effect due to the occurrence of such an event at high temperatures, rather than the quantum hall effect, which describes the movement of electrons through strong magnetic fields at low temperatures. At room temperature, electrons can move over long distances without any scattering in graphene. Therefore, graphene shows better electrical properties than most materials [1].

Graphene with these superior properties is used as reinforcement for composite materials. Graphene used as reinforcement for polymer matrix composites and its derivatives, have been preferred in many important applications. Over the past few years, researchers have taken successful steps for graphene oxide and graphene-based polymer composites, similar to CNT (carbon nanotube)-based polymer composites. 2-D graphene has better electrical, thermal and mechanical properties. It also has a wider surface area than some backing materials such as

CNT carbon fibers. Graphene doped composites can provide excellent properties for electronic field, space, automotive and green energy applications. Due to recent developments about synthesis of graphene and graphene oxide, these structures have been incorporated into various polymer matrices. However, there are many problems that need to be solved:

- Functioning of graphene layers,
- Homogeneous distribution of materials with minimal clustering,
- Effective mixture of graphene oxide and graphene with polymers,
- Understand the structure and properties of intermediate products,
- Control of folding, creasing and bending of graphene material [1].

Some of the methods of synthesizing polymer matrix composites are solution blending, melt mixing and in situ polymerization. The solution blending technique is widely used in the production of polymer-based composites. This technique allows the polymer to be easily dissolved in water and organic solvents such as acetone, dimethylformamide, chloroform and toluene. In this technique, the polymer is dissolved in a suitable solvent. Then, the polymer is mixed with a dispersed solution of graphene in solution. Polar polymers such as PMMA, PAA, PAN and polyesters have been successfully mixed using this technique with isocyanate, alkyl amine, etc. and functionalized graphene oxide to improve dispersion in organic solutions. For example, esterified graphite was mixed with dissolved PVA in oxide DMSO to produce the PVA-GO composite [2]. Various polymer composites such as graphene-PVA [3], graphene-PVC [4] and PVDF-thermally reduced graphene [5] were prepared using this technique. In the melt mixing technique, shear force is used to increase the dispersion in high temperature and matrix polymer. It must have been avoid the use of toxic solvents during the procedure. The high temperature facilitates the liquefaction of the polymer phase and the distribution between the GO layers. The melt mixing method is less efficient than the solution blending method due to its high viscosity that occurs due to the charging of graphene plates. This process can be applied to both polar and apolar polymers. Furthermore, this technique is a very practical method in the production of large-scale thermoplastics. Graphite doped composites such as exfoliated graphite-PMMA [6], graphene-polypropylene (PP), GO-polyethylene-2,6-naphthalate (PEN) [7] and graphene-polycarbonate [8] are prepared by this method. The low efficiency of chemically reduced graphene limits the use of graphene in this technique. Furthermore, graphene production by thermal reduction may be suitable for industrial production. Removal of functional groups by thermal reduction may prevent homogeneous dispersion in polymeric matrices, particularly in the apolar polymers. The technique of in situ polymerization begins with the dispersion of GO and reduced graphene oxide (RGO) in the monomers of the polymerization. Non-covalently bonded composites such as PMMA-GO [9], PP-GO [10] and PE-graphite [11] can be prepared by this technique.

In this study GO was prepared by hummers method and PVA was produced by chemical precipitation method. Polymer matrix composite (GO/PVA) was synthesized by solution blending method. Thermal and structural analysis of polymer matrix composite material was performed and compared with the literature.

2. Experimental details

Primarily for GO synthesis, 1 g of powdered graphite and 1 g of sodium nitrate ($NaNO_3$) were mixed in 48 mL of 98% sulfuric acid (H_2SO_4) for 1 hour. 6 g of potassium permanganate ($KMnO_4$) was added gradually to the obtained mixture. The mixture was stirred in an ice bath for 90 minutes, then 2 hours at 35 °C. Then, 40 mL of deionized water was added dropwise to the mixture and stirring was continued for 1 hour. After adding 100 mL of deionized water-10mL hydrogen peroxide (H_2O_2-30%) solution to the mixture, the temperature was raised to 90 °C and stirred for 90 minutes. Graphene oxide was collected by centrifugation. The mixture was washed with solution of HCl (37%) - deionized water (ratio of 1: 10) until pH = 7. Then, the remaining material was dried in the oven at 50 °C for 24 hours to obtain GO as a powder.

In the second step, a mixture of 8% by mass of powder PVA and pure water was prepared. The mixture was stirred at 100 °C in a magnetic stirrer for 4 hours. The pH value of the mixture was adjusted to 4 with hydrochloric acid solution (HCl). The mixture was continued to stir at room temperature for 4 hours after the addition 1mL of glutaraldehyde compound. GO: PVA solution in a 1: 100 ratio was stirred with ultrasonic stirrer at room temperature for 4 hours. The mixture was placed in a petri dish and dried at room temperature for 24 hours. After 1 day, a PVA sample doped 1% GO was formed.

3. Results and discussion:

FT-IR spectra were analyzed to identify the interaction between the PVA chains and the GO sheets. It was reported that the existence of hydrogen bonding would influence the stretching ands of oxygen-containing groups [12]. FT-IR spectra of GO/PVA composite film with 1 wt.% GO and two counterparts (PVA, GO) are shown in Fig. 1. There are three typical peaks of GO at 1064, 1620 and 3402 cm^{-1}, suggesting the existence of epoxy, carboxyl, and hydroxyl groups, respectively. Pure PVA shows a very strong peak at 1082 cm^{-1}, which can be ascribed to C-OH stretching. While in the GO/PVA composite, the C–O stretching peak (~1100 cm^{-1}) becomes very weak compared to that of pure PVA, indicating the existence of hydrogen bonding between the PVA matrix and the GO [13, 14].

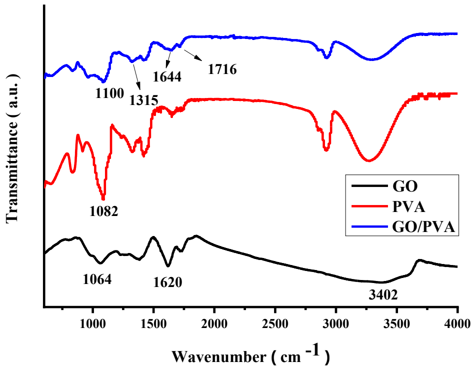

Figure 1. FTIR spectra of GO, PVA and GO/PVA composite film with 1 wt.% GO.

SEM images of GO/PVA material at 500X and 1.00KX magnification are given in Fig.2. It is concluded that the structure has become layered with GO added to PVA polymer which generally has a smooth surface. In other words, only a few GO sheets were observed to be dispersed in PVA matrix. In Fig.3, the energy dispersive X-Ray analysis (EDX) result of the produced GO/PVA is given. 56.09 wt% carbon atom, 41.62 wt% oxygen atom and 2.28 wt% nitrogen atom were detected in the material as expected.

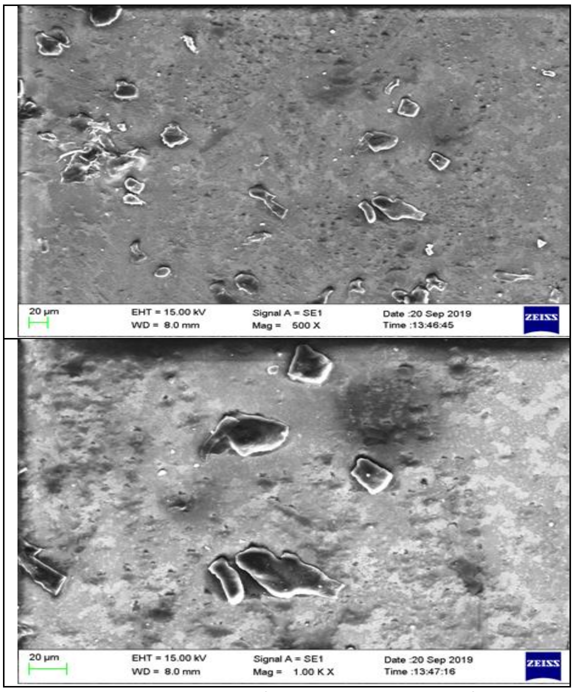

Figure 2. SEM images of GO/PVA composite film with varied GO contents 1wt.%.

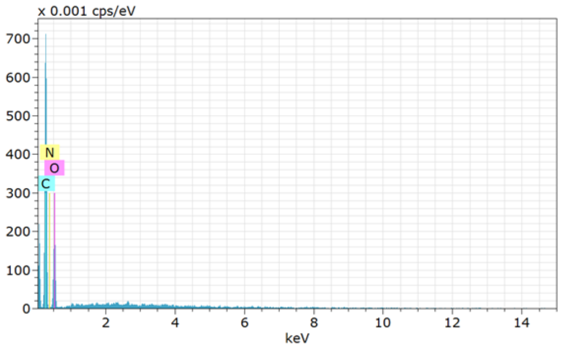

Figure 3. EDX analysis of GO/PVA composite film with varied GO contents 1wt.%.

3.35 mg of GO/PVA sample was taken and the thermogram in Fig.4 is given. When the TGA thermogram of the GO/PVA sample is examined, the first mass loss is caused by the removal of moisture in the composite structure. The first mass loss is approximately 70-141 °C and 10%. The second mass loss seen in the decomposition curve is 27% between 142 °C and 351 °C. The third major mass loss is 52%, between 352 °C and 500 °C. The PVA-GO sample remaining as a result of all degradation after 500 °C is 0.36mg (91.524% mass loss).

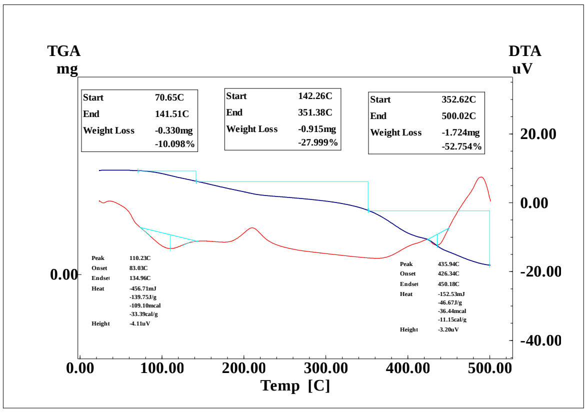

Figure 4. TGA-DTA curve of PVA-GO sample.

The thermal strength of the PVA and GO/PVA samples that we produced is given in Fig.5 by TGA thermogram. It is seen that the decomposition of the poly (vinyl alcohol) polymer by heat effect starts at about 165 °C temperature. Due to the GO contribution, the density of cross-linking of the sample was increased and chain movements were restricted. So the thermal decomposition temperature increased to about 297 °C. It has been observed that GO additive increases the thermal resistance properties of PVA material.

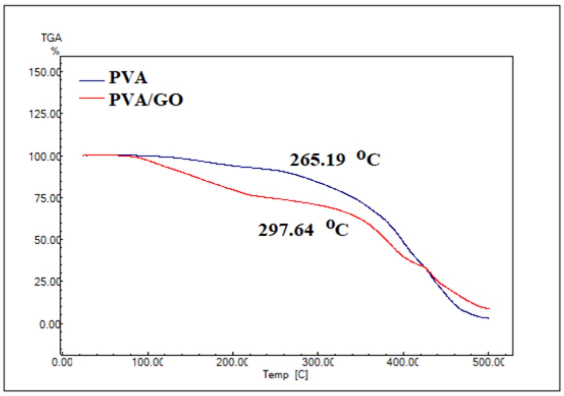

Figure 5. TGA curves of PVA and PVA / GO samples.

Differential scanning calorimetry (DSC) was used to investigate the thermal properties of GO/PVA nano composite obtained by solution blending technique. DSC analysis result is given in Fig.6. When the DSC curve is examined, three endothermic peaks are observed. The first endothermic peak gives the glass transition temperature (T_g) of the polymeric composite. The second peak indicates the crystallization temperature (T_c), which is about 102 °C. The final endothermic peak shows the melting temperature (T_m) associated with the melting of the crystallized regions formed in the sample during DSC analysis. This value is about 239 °C. According to DSC analysis, the peak corresponding to the glass transition temperature was formed at a temperature of about 64 °C.

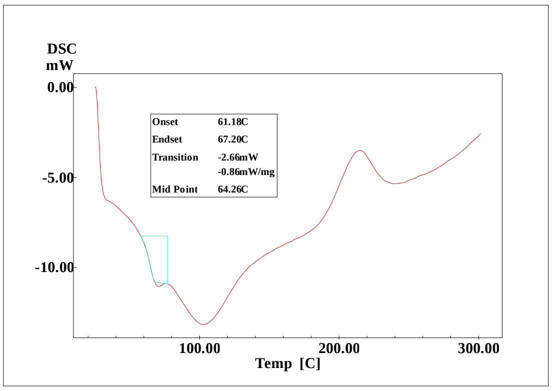

Figure 6. DSC curve of PVA-GO sample.

Conclusions:

The aim of this study was to produce 1% graphene oxide doped PVA (polymer based material) nanocomposite. It was concluded that obtained material as a result of thermal and structural analyzes were usable in many fields, especially technological and industrial areas. When the FT-IR spectrum is examined, in addition to the functional groups in the GO/PVA sample, the tensile band of the C = O group at 1716 cm^{-1}, the tensile band of the C = C (aromatic) group at 1644 cm^{-1}, the CO at 1315 cm^{-1} (epoxy) group and 1100 cm^{-1} of the CO (alkoxy) group was seen. The appearance of these tensile bands indicates that the GO is added into the structure. In SEM imagines, only a few GO sheets were observed to be dispersed in PVA matrix. According to EDX result of the produced GO/PVA, 56.09 wt% carbon atom, 41.62 wt% oxygen atom and 2.28 wt% nitrogen atom were detected in the material as expected. The thermal properties of GO/PVA composite were investigated by TGA-DTA and DSC analysis. According to TGA-DTA analysis, that GO additive increases the thermal resistance properties of PVA material. According to all these structural and thermal analysis results, it can be said that produced polymer based composite material is compatible with literature.

References:

[1] E. Erikli, .A Hasanoğlu, Grafen Oksit/Aramid ve Grafen/Aramid Kompozitlerinin Geliştirilmesi, Ç.Ü Fen ve Mühendislik Bilimleri Dergisi Yıl 2018 Cilt: 35-6.

[2] Salavagıone, H.J., Gomez, Mn.A, Martınez, G., 2009. Polymeric modification of graphene through esterification of graphite oxide and poly(vinyl alcohol). Macromolecules, 42, 6331.

[3] JIANG, L., SHEN, X.P., WU, J.L., SHEN, K.C., 2010. Preparation and characterization of graphene/poly(vinyl alcohol) nanocomposites, J.Appl Polym Sci, 118, 275.

[4] VADUKUMPULLY, S., PAUL, J., MAHANTA, N., VALIYAVEETTIL, S., 2011. Flexible conductive graphene/poly(vinyl chloride) composite thin films with high mechanical strength and thermal stability. Carbon, 49, 198.

[5] ANSARI, S., GIANNELIS, E.P., 2009. Functionalized graphene sheet-poly(vinylidene fluoride) conductive nanocomposites. J Polym Sci Part B - Polym Phys, 47, 888.

[6] KALAITZIDOU, K., FUKUSHIMA, H., DRZAL, L.T., 2007. A new compounding method for exfoliated graphite–polypropylene nanocomposites with enhanced flexural properties and lower percolation threshold. Compos Sci Technol, 67, 2045.

[7] KIM, H., MACOSKO, C.W., 2008. Morphology and properties of polyester/exfoliated graphite nanocomposites. Macromolecules, 41, 3317.

[8] KIM, H., MACOSKO, C.W., 2009. Processing-property relationships of polycarbonate/graphene composites. Polymer, 50, 3797.

[9] JANG, J.Y., KIM, M.S., JEONG, H.M., SHIN, C.M., 2009. Graphite oxide/poly(methyl methacrylate) nanocomposites prepared by a novel method utilizing macroazoinitiator. Compos Sci Technol, 69, 186.

[10] HUANG, Y., QIN, Y., ZHOU, Y., NIU, H., YU, Z.Z., DONG, J.Y., 2010 Polypropylene/graphene oxide nanocomposites prepared by in situ Ziegler–Natta polymerization. Chem Mater, 22, 4096.

[11] FIM, FD.C., GUTERRES, J.M., BASSO, N.R.S., GALLAND, G.B., 2010. Polyethylene/graphite nanocomposites obtained by in situ polymerization. J Polym Sci Part A - Polym Chem, 48, 692.

[12] Xiaoming Yang, Liang Li, Songmin Shang, Xiao-ming Tao, Synthesis and characterization of layer-aligned poly(vinyl alcohol)/ graphene nanocomposites, Polymer, 2010, 51, 3431-3435.

[13] Nina I. Kovtyukhova, Patricia J. Ollivier, Benjamin R. Martin, Thomas E. Mallouk, Sergey A. Chizhik, Eugenia V. Buzaneva, and Alexandr D. Gorchinskiy. Layerby- Layer Assembly of Ultrathin Composite Films from Micron- Sized Graphite Oxide Sheets and Polycations, Chem. Mater. 1999, 11, 771-778.

[14] Yuxi Xu, Wenjing Hong, Hua Bai, Chun Li, Gaoquan Shi, Strong and ductile poly(vinyl alcohol)/ graphene oxide composite films with a layered structure, Carbon, 2009, 3538-3543.