Original Article

Structural investigation and enhancement of optical, electrical and thermal properties of poly (vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate)/graphene oxide nanocomposites

Ahmed Y. Yassin\textsuperscript{a,b,*}, Abdel-Raouf Mohamed\textsuperscript{b}, Elmetwaly M. Abdelrazek\textsuperscript{c}, Muhamed A. Morsi\textsuperscript{d}, Amr M. Abdelghany\textsuperscript{e,*}

\textsuperscript{a} Dental Biomaterial Department, Faculty of Oral & Dental Medicine, Delta University for Science & Technology, Gamassa, Egypt
\textsuperscript{b} Physics Department, Faculty of Science, Port-Said University, Port-Said, Egypt
\textsuperscript{c} Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt
\textsuperscript{d} Engineering Basic Science Department, Faculty of Engineering, Egyptian Russian University, Cairo, Egypt
\textsuperscript{e} Spectroscopy Department, Physics Division, National Research Center, 33 Elbehouth St., Doki, Giza, Egypt

\begin{abstract}
Different concentrations of graphene oxide (GO) were successfully embedded into poly (vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (PVVH) copolymer. The composites obtained were characterized using XRD, FT-IR, SEM and UV/Vis techniques, in addition to investigating their electrical properties. XRD results showed the predominance of the amorphous phase inside the prepared samples. The main characteristic peaks of the used materials were observed in FT-IR spectra with changes in their intensities and/or their positions, confirming the successful complexation and strong interaction between GO and PVVH. A bathochromic shift in the main absorption sharp edge was detected in UV/Vis spectra. Additionally, the two peaks at 214 and 280nm were ascribed to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions, respectively. Both optical energy gap and refractive index were calculated in terms of UV/Vis absorption spectra using Mott–Davis model and Dimitrov–Sakka equation. The thermal behavior of the current samples was carefully investigated by employing TGA. Moreover, the activation energy was studied using Coats-Redfern and Broido models. The homogeneous dispersion of GO has contributed to the significant increase in the electrical conductivity as well as improving thermal stability of the PVVH-based nanocomposites. The experimental results obtained for the current system promote these nanocomposites for use in optoelectronic applications.

© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
\end{abstract}

\* Corresponding authors.
E-mails: a.yassin2200@yahoo.com (A.Y. Yassin), a.m.abdelghany@yahoo.com (A.M. Abdelghany).
https://doi.org/10.1016/j.jmrt.2018.08.005
2238-7854© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

Since discovering graphene in 2004 [1], it has significantly attracted researchers’ attention in academia and industry alike owing to its outstanding properties. It has been graded as a promising candidate, which can make a turning point in nanoscience and nanotechnology. Graphene is a monolayer of sp²-hybridized carbon-carbon bonds densely packed with a single atom in thickness, which is arranged into a two-dimensional (2D) form of honeycomb lattice [2]. It can be employed in some electrical and electronic applications such as touch screens, batteries, solar cells, fuel cells and supercapacitors [3-5].

Graphene also exhibits many interesting photonic properties due to its composition (one-atom-thick layer), making it almost transparent with negligible reflectance (< 0.1%) to visible light, in addition to its strong interaction with photons that arose owing to Van Hove singularity [6,7]. However, the zero energy band gap that is originated from the direct contact between valence and conduction bands, limits its use in some optoelectronic applications, such as: photovoltaics and photodetectors. So, this band gap should be opened up either via applying an electric field [6], deforming structure [8], or doping with chemical compounds [9], but these methods can adversely affect the other properties. Kaushik et al. [10] reported that modifications of structural, optical and electrical properties of epitaxial graphene on silicon carbide (SiC) imply that these materials may enhance the applicability of graphene in optoelectronic areas. Their work has depended on the existence of substitutional and sp² defects which might be introduced from dangling bonds reaction with environmental vapor and oxygen.

The main reason for the use of graphene and its derivatives (including graphene oxide) with polymer to form nanocomposites has stemmed from their high mechanical stability and is unique in their electrical, magnetic, thermal and optical properties [11]. However, using graphene as a nanofiller can strongly influence the structural, electrical and optical properties of the polymers. Consequently, studying the optical properties, in particular, the optical absorption and energy band gap (Eg) of graphene-based nanocomposites bring a great interest as the researchers are trying to find an answer to the puzzling question: how can these properties be changed with the polymer composition changes to pave the way for new practical applications.

Graphene oxide can be produced from the low-cost natural graphite in large scale. It is also distinguished by the presence of some functional groups such as: hydroxyl, carboxyl, epoxide and carbonyl groups on its basal plane and surface, that can considerably improve the interfacial interaction of GO with polymer matrix [12]. PVVH, which is a flexible copolymer composed of three monomers and commonly used in sensors, is characterized by its sensitivity to temperature changes. In literature, there are few reports for PVVH, which may be counted on one hand [13-16], whereas GO was studied with some polymers including: poly (vinyl alcohol) [11], poly (vinylidene fluoride) [17], polyacrylamide [18] and poly (methyl methacrylate) [19].

So, in an attempt to overcome the aforesaid obstacles and the complex experimental steps, the current work has been carried out. Another reason for selecting GO is to exploit graphene’s outstanding properties without adversely affecting other properties and without introducing new processing impurities as well as to overcome the gapless problem, as this gives GO a comparative advantage over pristine graphene. Furthermore, we spotlight on the structural, optical and electrical properties of PVVH/GO nanocomposites, where the obtained results may significantly help in tailoring and harnessing such novel nanocomposite for use in nanoelectronics and optoelectronic applications. To the best of our knowledge, this is the first report on the synthesis, characterization and investigation of graphene oxide incorporated into PVVH matrix.

2. Experimental work

2.1. Materials

In this study, the prepared nanocomposite consists of: a) PVVH copolymer, as the basic material which was purchased from Aldrich Chemicals Co. Ltd. (81 wt.% vinyl chloride; 15 wt.% 2-hydroxypropyl acrylate; 4 wt.% vinyl acetate; having average molecular weight ca. 33,000 g/mol), and b) graphene oxide that was prepared by modified Hammer’s method [20] from graphite oxide nanopowder with oxidation degree 5–10% purchased from Sigma–Aldrich. Tetrahydrofuran (THF), which is the common solvent in the current work, was bought from Fisher Scientific for chemicals, UK.

2.2. Preparation of PVVH/graphene oxide nanocomposite films

The preparation steps are shown in Fig. 1. In brief, a 3.5 g of PVVH and 0.5 g of graphene oxide were individually dissolved in 50 ml of THF, then vigorously stirred at 40 °C for 2–3 h. After incorporating GO into PVVH matrix with various concentrations (0.2, 0.4, 0.8, 1.6, 3 and 4 wt.%), the viscous solutions were sonicated for 20–30 min. Generally, there are two important aims should be achieved when dispersing nanoparticles in the polymer matrix: 1) to deagglomerate the nanoparticles to the smallest unit, and 2) to be homogeneously distributed into polymer matrix. So, after doping with GO, Ultrasonication process is used to fulfill these aims for harnessing the outstanding features of GO. The formed mixtures were slowly dropped onto cleaned glass Petri dishes and were left to dry at room temperature for 2 days in order to eliminate the residual solvent traces. Under the same conditions, the pure PVVH film was also prepared to be used as reference, which makes characterization easier through comparing the results. The final films were tightly stored in vacuum desiccators.

2.3. Measurements

The single beam Fourier transform infrared spectrometer, which is Nicolet iS10 type, USA, was used through the spectral range of 4000–400 cm⁻¹ to record FT-IR absorption spectra. X-ray diffraction patterns were obtained to investigate structural
properties using DIANO corporation - USA equipped by means of Cu-Kα radiation (λ = 1.5406 Å, 15 kV in operation, the Bragg’s angle (2θ) in the range of 5–60°. The spectrophotometer (V-570 UV/Vis-NIR, JASCO, Japan) was employed to measure Ultraviolet/visible (UV/Vis) absorption spectra in the wavelength region of 190–1000 nm. But we focused on the 190–500 regions where most changes took place. The morphological characterization was carried out by scanning electron microscope (SEM) using a JEOL JSM 6510 LV, USA, operating at 15 kV accelerating voltage with an Oxford EDAX system. Measurements of DC electrical conductivity were performed by 2-probe method using an insulating tester (Level type TM14) with accuracy ±0.3%. TGA thermograms of the samples under investigation were recorded using Shimadzu Thermogravimetric -45 H in the temperature range from room temperature to 800 °C at a heating rate of 10 °C/min such that nitrogen atmosphere has been used. The GO/PVVH nanocomposite was also studied by the density functional theory (DFT) to support the experimental results. This analysis can furnish with a deep insight into mechanistic aspects, which is not easily accessible to experiments, giving rich elucidations about the experimental results [21,22]. In the present study, the nanocomposite construction was performed by attaching the host polymer to GO on different sites as well as orientations. The best aspects of position and suggested orientation are represented in Fig. 2, where the data obtained from the optimized geometry shown in Fig. 2d was largely consistent with the experimental results.

3. Results and discussion

3.1. X-ray diffraction analysis

XRD scans of pure PVVH copolymer and PVVH filled with varying levels of GO are depicted in Fig. 3, where the main peak centered at 2θ ≈ 21.8° is ascribed to pure PVVH. Broadness of this peak has increased with a decrease in the intensity when dispersing GO in the host matrix. This is in agreement with Hodge et al. criterion [23], indicating the predominance of amorphous phase in the complexed system.

Further, the diffraction peak observed at 2θ ≈ 10.5° is attributed to GO and corresponds to (0 0 1) plane [24]. This peak has detected at lower concentrations of GO (0.2 and 0.4 wt%), then disappeared for the other samples, indicating the complete incorporation of GO into host matrix. In other words, the characteristic peak of GO has decreased gradually with increasing its concentration and completely disappeared at higher concentrations, which give a clear indication that GO sheets were efficiently exfoliated into single sheets and successfully dispersed within PVVH matrix at molecular level. Furthermore, this observation implies the compatibility between constituents of the nanocomposite obtained, confirming complexity between them.

3.2. Fourier transform infrared analysis

FT-IR absorption spectra for the described samples were carried out in the region 4000–400 cm⁻¹ at room temperature as shown in Fig. 4. The absorption band observed at about 3441 cm⁻¹ was ascribed to the stretching vibrations of hydroxyl groups (OH) stemmed from the 2-hydroxypropyl acrylate monomer in PVVH and/or OH groups on the basal plane of GO [25]. The hydrogen bonding that formed between the nanofiller and PVVH, as well as Cl⁻ ions of vinyl chloride monomer have made changes in this band, manifesting the specific interaction occurred in the polymer matrix [26].

Further, the bands corresponding to asymmetric and symmetric C–H stretching of methylene groups were detected at about 2980 cm⁻¹ and 2870 cm⁻¹, respectively. The vibrational sharp peak, representing C=O stretching of PVVH was observed at about 1731 cm⁻¹, which provides an indication of the amorphous nature of the nanocomposite. Also, it is noteworthy that the polaron and bipolarons would not find more
suitable sites than the present double bonds segments to be created [27]. More assignments for the FT-IR absorption bands' positions were summarized in Table 1.

Fig. 5 exhibits the data calculated theoretically by DFT for IR absorption spectrum of PVVH-based nanocomposite for 1.6% of GO loading. This data is largely consistent with that obtained experimentally. Thus, the experimental and theoretical results of FT-IR proved the presence of GO and PVVH in the prepared samples, and consequently the successful complexation between them.

3.3. Ultraviolet and visible analysis

Fig. 6 illustrates the absorption spectra of pristine PVVH and PVVH/GO nanocomposite at the region (190-500 nm) at room temperature. These spectra are characterized by the main absorption sharp edge at about 234 nm. The distinct decrease in the sharpness of this edge with increasing GO loading is due to the disorder in the current matrix. In other words, it is ascribed to domination of the amorphous regions inside the present samples, which confirms the findings of X-ray diffraction analysis [27].

The band observed at about 214 nm is due to $\pi \rightarrow \pi'$ transition [28], while the absorption band located at about 280 nm has resulted from $\pi \rightarrow \pi$ interaction of the polymer with GO, then became shoulder-like with increasing the dopant concentrations. Also, it has been shifted toward longer wavelengths, which in turn assures complexation between the filler and PVVH copolymer. In other words, the band at about 280 nm was ascribed to $\pi \rightarrow \pi'$ transition, which arose from unsaturated bonds, mainly; carbonyl group (C=O and/or C=C) [29], that was observed in FT-IR at 1731 cm$^{-1}$, and it is
Table 1 – Assignments of the FT-IR absorption bands’ positions for the present system.

<table>
<thead>
<tr>
<th>Vibrational freq. (cm$^{-1}$)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3441</td>
<td>O–H stretching</td>
</tr>
<tr>
<td>2980</td>
<td>Asymmetric C–H stretching</td>
</tr>
<tr>
<td>2911</td>
<td>Symmetric C–H stretching</td>
</tr>
<tr>
<td>2870</td>
<td>Symmetric C–H stretching</td>
</tr>
<tr>
<td>1731</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1432</td>
<td>C–C stretching</td>
</tr>
<tr>
<td>1371</td>
<td>CH$_2$ bending</td>
</tr>
<tr>
<td>1328</td>
<td>O–H bending</td>
</tr>
<tr>
<td>1243</td>
<td>C=OH stretching</td>
</tr>
<tr>
<td>1190</td>
<td>Epoxy ring</td>
</tr>
<tr>
<td>1173</td>
<td>C–O–C stretching</td>
</tr>
<tr>
<td>1100</td>
<td>C–O stretching of acetyl groups</td>
</tr>
<tr>
<td>1058</td>
<td>Cl–O (ion pair)</td>
</tr>
<tr>
<td>963</td>
<td>Out-of-plane rings C–H bending</td>
</tr>
<tr>
<td>840</td>
<td>C=C stretching</td>
</tr>
<tr>
<td>770</td>
<td>CH$_3$ rocking</td>
</tr>
<tr>
<td>690</td>
<td>C–Cl stretching</td>
</tr>
<tr>
<td>617</td>
<td>C–H wagging</td>
</tr>
</tbody>
</table>

3.4. Optical constants

3.4.1. Optical energy gap ($E_g$)

Generally, two types of transitions can take place at the absorption edge of materials; a) direct and b) indirect transitions. According to Mott–Davis model \[16,27,30\] and using Eqs. (1) and (2),

\[(n\alpha h\nu)^2 = B_1(h\nu - E_{gd})\]  \hspace{1cm} (1)

\[(n\alpha h\nu)^{3/2} = B_2(h\nu - E_{gi})\]  \hspace{1cm} (2)

where $h\nu$ is the photon energy, $h$ is Planck’s constant, $E_{gd}$ is the direct band gap, $E_{gi}$ is the indirect band gap, $B_1$, $B_2$ are constants, and $n$ is integer. We can plot the relation between $(n\alpha h\nu)^2$ and $(n\alpha h\nu)^{3/2}$ as functions of energy ($h\nu$) to obtain optical band gap.

Fig. 7 shows this relation for the pure PVVH and 4 wt% of GO as examples, where the two transitions are observed. The
absorption coefficient ($\alpha$) can be designated as a function of frequency in the following formula [26]:

$$\alpha (\nu) = 2.303 \times \frac{A}{d} \quad (3)$$

where $A$ is the absorbance, and $d$ is thickness of the sample under study. Optical band gaps of PVVH, before and after blending with GO (Table 2), were determined by taking the extrapolation of the straight portion to $h\nu$-axis, i.e., $(\alpha h\nu)^2 = 0$ and $(\alpha h\nu)^{1/2} = 0$ for direct and indirect transitions. It’s clear that the decrease in $E_g$ with increasing the filler content has resulted from the various polaronic and defect levels formed inside the matrix.

### 3.4.2. Refractive index ($n$)

Refractive indices of the nanocomposites were calculated via the following formula [16,31] and their values were listed in Table 2:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_g}{20}} \quad (4)$$

The increase in nanocomposite density with GO content led to a decrease in the speed of light passing through it and thereby the refractive index was increased in accordance to the relation, $(n = c/\nu)$ where, $c$ and $\nu$ is the velocity of light in free space and in the material, respectively. In other words, the reduction of the inter-atomic spacing originated from high density of the samples has resulted in an increase in the coordination number. Thus, the higher the number of non-bridging oxygen bonds (NBO), the greater the $n$ values.

The results proved that these nanocomposites possess the advantageous features that promote them as a promising candidate for use in optoelectronic applications and for designing optical devices such as high refractive index lenses, filters, and light-emitting devices.

### 3.5. DC Conductivity

The variation of electrical conductivity ($\sigma$) with temperature for the prepared samples at a fixed applied field is represented in Fig. 8. XRD results exhibited that the amorphous regions have been increased; thereby they have provided free volumes

<table>
<thead>
<tr>
<th>$W$ (wt.%)</th>
<th>$E_g$ (eV)</th>
<th>$E_{ad}$ (eV)</th>
<th>Refractive index ($n$)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region I</td>
<td>Region II</td>
<td>Region I</td>
<td>Region II</td>
</tr>
<tr>
<td>Pure PVVH</td>
<td>4.42</td>
<td>3.55</td>
<td>5.03</td>
<td>4.0</td>
</tr>
<tr>
<td>0.2</td>
<td>3.97</td>
<td>3.2</td>
<td>4.82</td>
<td>3.92</td>
</tr>
<tr>
<td>0.4</td>
<td>3.85</td>
<td>3.15</td>
<td>4.73</td>
<td>3.87</td>
</tr>
<tr>
<td>0.8</td>
<td>3.4</td>
<td>2.71</td>
<td>4.55</td>
<td>3.69</td>
</tr>
<tr>
<td>1.6</td>
<td>3.33</td>
<td>2.6</td>
<td>4.45</td>
<td>3.57</td>
</tr>
<tr>
<td>3.0</td>
<td>1.85</td>
<td>1.5</td>
<td>3.68</td>
<td>2.8</td>
</tr>
<tr>
<td>4.0</td>
<td>3.22</td>
<td>2.5</td>
<td>4.3</td>
<td>3.7</td>
</tr>
</tbody>
</table>
within the polymeric matrix. Besides, the acquired vibrational energy by polymer segments due to increasing temperature is sufficient to push against the repulsive force exerted by their neighbors, and these vibrations produced free spaces where translational motion can take place \[26\]. They also result in inter and/or intra-chain ion hopping, causing enhancement in conductivity.

From Fig. 8, the electrical conductivity has significantly increased with increasing temperature. But at a certain temperature, this increase was much lower than at low temperatures, especially for 4\% of GO loading, despite the continuous increase in charge carriers. This behavior can be explained in terms of the mobility of charge carriers, as their movement has been partially hindered at high temperatures because of their scattering or ion pairs/triplet formations, and this result is consistent with the free volume theory \[27\].

Moreover, the non-linearity observed in this figure implies that the conduction in this system obeys the Williams–Landel–Ferry (WLF) mechanism (non-Arrhenius), and it largely follows VTF relation \[27\]:

\[
\sigma = \sigma_0 T^{-1/2} \exp \left( \frac{-E_a}{K_B (T - T_a)} \right)
\]

where \(\sigma_0\) is a pre-exponential parameter related to conductivity, \(E_a\) is the activation energy required for charge carriers’ movement and \(K_B\) is the Boltzmann’s constant.

It is worthwhile to mention that the conductivity of all complexes has been improved with increasing temperature as well as the filler content. The conductivity was changed from \((3.06 \pm 1) \times 10^{-12}\) S/cm for pure PVVH recorded at room temperature to \((5.49 \pm 1.2) \times 10^{-7}\) S/cm for 4\% of GO. This value has improved by increasing temperature, so that it achieved its highest value \((3.32 \pm 0.6) \times 10^{-5}\) S/cm using only a small amount of GO. Kong et al. \[32\] reported that polydimethylsiloxane (PDMS) composites containing 4\% of graphene achieved the highest electrical conductivity \(7.89 \times 10^{-5}\) S/cm, while Zhang et al. \[33\] found that \((\sigma)\) of poly(ether sulfone) (PES)/5\% graphene composite was \(5.82 \times 10^{-6}\) S/cm. This gives our nanocomposite a comparative advantage over some composites by achieving acceptable performance at low cost and using only a small amount of GO. Activation energies of different concentrations were calculated by taking the slope of \(\log (\sigma)\) vs. \(1000/T\) plots, and their values were tabulated in Table 2. \(E_a\) values decreased with increasing GO content, where this dramatic reduction was due to the increased disorder inside the matrix, i.e., an increase in the amorphous degree.
3.6. SEM analysis

Fig. 9 demonstrates the representative micrographs of the samples under study obtained by SEM at magnification 100 times. As observed in Fig. 9a, which represents pure PVVH micrograph, the surface is clearly smooth and characterized by the presence of spherical pores that are distributed regularly. When GO is added to the host matrix, it has partially filled these pores as seen in Fig. 9b–e.

For the highest concentration in the current series (4% of GO content), the pores have become smaller than before, as most of them have been completely filled with GO nanoparticles, and the surface has changed from smooth to rough as shown at magnifications of 100 in Fig. 9f and 500 in Fig. 9g. In other words, surface morphology has been considerably affected by incorporating GO into the PVVH matrix, and this change can be referred to as the physical interaction between them. It is noteworthy that no phase separation was detected in these micrographs, which provides a clear indication about the compatibility of the PVVH matrix with GO, confirming the successful complexation between them.

3.7. Thermogravimetric analysis

The TGA thermograms of residual weight as a function of temperature for GO, pure PVVH, and their nanocomposites at a heating rate of 10 °C/min from room temperature to 800 °C are shown in Fig. 10. It is obvious from the figure that the PVVH curve exhibits three-step degradation, where the first step is in the temperature range 71–100 °C. It is worth noting that this curve is stable up to 200 °C and the initial weight loss reached 12% at 100 °C. The main weight loss detected in the range of 215–330 °C is attributed to the structural decomposition of the polymer used and represents the second step. While the step in the temperature range of 400–575 °C is assigned to the degradation of the residual carbon.

The TGA thermograms of the PVVH/GO nanocomposites exhibit three-step decomposition behavior. The first step at a temperature ranging from 75 to 150 °C may be due to evaporation of moisture or adsorbed water, which is followed by a plateau extending up to 250 °C without significant weight loss. In other words, these samples have good thermal stability up to 250 °C. While the second step is in the range 250–390 °C with a weight loss of about 30% of the total weight due to the splitting of polymer main chain. The third step shown in the range 500–625 °C is attributed to the decomposition of the polymer backbone. Therefore, the samples prepared are stable up to 625 °C and the residual weight of the obtained nanocomposite films was increased as a result of the addition of graphene oxide to the PVVH matrix.

$T_{20}$ and $T_{50}$ are the decomposition temperatures at 20% and 60% of the weight loss, respectively. For pure PVVH, these temperatures are $T_{20} = 217 °C$ and $T_{50} = 394 °C$, while for PVVH/GO nanocomposites they have increased to 290 °C and 515 °C, respectively. Thus, the highest concentration of GO has successfully achieved the highest decomposition temperature. Finally, the TGA results imply that the mobility of the polymer segments and GO at interfaces was partially suppressed by the strong hydrogen bonding interactions between them, resulting in a delay in the polymer degradation. Overall, the thermal stability of the nanocomposites has been improved compared to that of pure PVVH, confirming the positive structural changes due to blending the current polymer with GO.

3.7.1. Determination of activation energy ($E$)

Influence of GO on the thermal decomposition rate of PVVH can be modeled by two different methods. The first is the Coats-Redfern model [34,35], which is a helpful tool in obtaining activation energy that results in the thermal degradation depending on the residual mass according to the following relation:

$$\log \left[ \frac{1 - (1 - \alpha_t)^{1-n}}{T^2} \right] = \log \frac{R}{E} \left[ 1 - \frac{2RT}{E} \right] - 0.434 \frac{E}{RT} \tag{6}$$

where $T$ is the absolute temperature in Kelvin, $n$ is the order of reaction, $E$ is the activation energy in J/mol, $R$ is the universal gas constant (8.31 J/mol K) and $\alpha_t$ is the fractional weight loss corresponding to a particular stage of decomposition.

For $n \neq 1$, Eq. (9) becomes:

$$\log \left[ -\log \frac{(1 - \alpha_t)^{1-n}}{T^2} \right] = \log \frac{R}{E} \left[ 1 - \frac{2RT}{E} \right] - 0.434 \frac{E}{RT} \tag{7}$$

By plotting $\log \left[ -\log (1 - \alpha_t) \right]$ versus $\frac{1000}{T}$ for each sample, the activation energies (listed in Table 3) were calculated from slopes of the straight lines obtained using:

$$E = 2.303 R \times \text{slope} \tag{8}$$

The second method depends on Brodö model [35,36], which is an uncomplicated and accurate method introduced by A. Brodö in 1969 for calculating ($E$) according to the following equation:

$$\ln [ -\ln (1 - \alpha_t) ] = - \frac{E}{RT} + \text{const.} \tag{9}$$

In this method, plotting $\ln [ -\ln (1 - \alpha_t) ]$ versus $(1000/T)$ produced straight lines used in determining the activation energy from their slopes ($-E/R$) and the calculated values were listed in Table 3.
Table 3 – Values of (E) of the nanocomposites using Coats-Redfern and Broido methods.

<table>
<thead>
<tr>
<th>W (wt.%)</th>
<th>Activation energy, E (kJ/mol)</th>
<th>Residual (%) at 800 °C</th>
<th>T20 (° C)</th>
<th>T60 (° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coats-Redfern method</td>
<td>Broido method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure PVVH</td>
<td>12.60424</td>
<td>21.12402</td>
<td>1</td>
<td>217</td>
</tr>
<tr>
<td>0.2</td>
<td>13.50372</td>
<td>22.13535</td>
<td>2</td>
<td>230</td>
</tr>
<tr>
<td>0.4</td>
<td>13.73912</td>
<td>22.76358</td>
<td>3.8</td>
<td>230</td>
</tr>
<tr>
<td>0.8</td>
<td>13.85203</td>
<td>22.86497</td>
<td>5.5</td>
<td>243</td>
</tr>
<tr>
<td>1.6</td>
<td>14.3611</td>
<td>22.95804</td>
<td>7</td>
<td>250</td>
</tr>
<tr>
<td>3.0</td>
<td>14.92184</td>
<td>23.15083</td>
<td>12</td>
<td>270</td>
</tr>
<tr>
<td>4.0</td>
<td>15.16107</td>
<td>23.40179</td>
<td>17.5</td>
<td>290</td>
</tr>
</tbody>
</table>

From this table, it is obvious that the higher GO content, the greater the activation energies of the nanocomposites. This enhancement in activation energy is a good indication of higher thermal stability for the nanocomposite films compared to the pure PVVH. This result implies that the current nanocomposite is a suitable material for using in potential applications.

4. Conclusion

A series of PVVH-based nanocomposite with varying percentage of GO was successfully prepared via a solution mixing method. The complexation of PVVH copolymer with GO was confirmed by XRD, FT-IR and UV/Vis studies. Results of the optical measurements have clarified the existence of a well-defined π → π* transition, which commonly takes place in association with the conjugated electronic structures formation. FT-IR results showed the presence of hydroxyl, epoxide, and carbonyl functional groups, which in turn have enhanced the interfacial adhesion between PVVH matrix and GO. Furthermore, these results were verified by using DFT calculations. The homogeneous and well dispersion of GO has helped in the significant enhancement of the electrical conductivity. SEM micrographs have demonstrated that GO was regularly distributed throughout the PVVH matrix, confirming their compatibility. Even at very low GO loading, the nanocomposite has exhibited a notable amendment in thermal stability in addition to the char yield, which gives a clear indication about the good interaction between the well dispersed GO and PVVH matrix. These optical and electrical results achieved without additional reagent prove that the present nanocomposite possesses the advantageous features that suggest them as a promising candidate for using in some technological applications, especially nanoelectronics and in the optoelectronic field for interlayers or electrode support materials in photovoltaics and photodetectors.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


