EFFECT OF GRAPHENE OXIDE (GO) ON THE PROPERTIES OF ITS
NANOCOMPOSITE WITH POLY (N-VINYL CARBAZOLE) (PVK)

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Abstract

Purpose of Study--- Herein we report the preparation of poly(N-vinyl carbazole) (PVK) and graphene oxide (GO) or
nanocomposite was carried out by solution mixing process with the aid of sonication. Solutions of the GO with the PVK
were prepared using mixed solvents aided by sonication which resulted in exfoliation and disaggregation of the GO into
the PVK polymer matrix.

Methodology-- In this work, the PVK/GO was prepared from exfoliated graphite nanoplatelets using solution mixing
process with the aid of sonication in a suitable solvent like N-cyclohexyl-2- pyrrolidone (CHP). The as-prepared
nanocomposites were characterized using XRD, DSC, FTIR-KBr, UV-Vis and EIS analysis.

Main Findings-- The preparation of PVK/GO nanocomposites was carried out by solution mixing process with the aid of
sonication. Using this method in dispersing the GO both exfoliation of the GO into the PVK polymer matrix was attained.
Nanocomposite solution comprising GO wrapped within PVK polymer matrix was characterized using TGA, XRD, and
EIS analysis. FTIR-ATR spectroscopy and XRD invoked the wrapping of GO outer surfaces by PVK. The thermal
properties of PVK/GO nanocomposites were analyzed using TGA. Correlation of impedance data and XRD provided a
structural rationale for PVK/GO nanocomposites.

Application of Study-- The PVK/GO nanocomposites can be applied to various applications such as precursor polymer
for hole-transporting materials and for electronanopatterning.

Limitations-- The study is limited on the characterization of the prepared GO and PVK/GO nanocomposites. Possible
applications of the composites were not part of the study.

Originality of Study-- The findings of the study show that it is possible to prepare graphene/PVK nanocomposites using
solution mixing process.

Keywords-- graphene oxide, nanocomposite, PVK, solution-mixing

INTRODUCTION

Polymer nanocomposites based on carbon black, carbon nanotubes have been used for improved mechanical, thermal,
electrical and gas barrier properties of polymers (Spitalsky, 2010). Through the years the discovery of CNTs and graphene
with its physical, mechanical properties and the ability to be dispersed in various polymer matrices has created a new class
of polymer nanocomposites. Polymer nanocomposites containing carbon nanotubes (CNTs) and graphene have received
high interest due to its unique and robust properties, such as high electrical conductivity, thermo-mechanical
characteristics, and the ability to create new materials with improved characteristics.

Graphene has attracted a tremendous amount of attention with its novel electronic, mechanical and thermal properties have
been well documented and studied. However, just as with the newly discovered allotropes of carbon, such as carbon
nanotubes, the availability and processability have been the rate-determining steps in the evaluation of graphene
applications. Graphene is a 2-dimensional single-atom-thick sheet of hexagonally arrayed sp²-bonded carbon atoms
exhibiting high specific surface area. Graphene-based organic nanocomposites are of interest as the fundamental
properties of graphite can be tailored in these composites for different applications. An important challenge involves
achieving homogeneous colloidal suspensions of individual graphene sheets to accelerate the use of such dispersions to
various and in large scale applications. Fabrication of graphene-organic composites which comprises thin graphitic layers
requires exfoliated graphite sheets (Santos, 2012). But, the nondispersibility of graphite in aqueous medium and in organic
solvents lead to the difficulty of working with graphite. Therefore, colloidal dispersions of oxidized graphite sheets are
mostly used in various works.

One possible route to harness the excellent properties of graphene sheets for different applications is to incorporate them
into nanocomposite materials (Akhavan and Ghaderi, 2010). The manufacturing of such composites requires not only that
graphene sheets be produced on a sufficient scale but also that they can be incorporated and homogeneously distributed
into various matrices. However, graphene sheets are very hydrophobic and form agglomerates easily and irreversibly in
polar solvents in the absence of dispersing reagents as a result of strong pi-pi stacking and van der Waals interactions (Bonnacorso, 2010). Thus, various methods have been developed to stabilize graphene sheets either by
covalent or noncovalent modification by aromatic molecules, surfactants, and polymers. Among the two strategies,
noncovalent modification is favoured because it is more convenient and the electronic structure of graphene sheets can be
Stable graphene dispersion is hard to prepare under common mechanical method like stirring and sonication because of inter and intra pi-pi stacking of graphene with a mount of carbon leads to aggregation. The action of mechanical forces is beneficial in dispersing the graphene but it is not enough to control the aggregation of graphene sheets through van der waals interactions. In this work the pristine graphite is oxidized using Hummers method to produce graphene oxide (GO)(Rafiee, 2009). The GO containing oxygen functionalities, such as carboxyl, hydroxyl and epoxide easily forms GO hydrogel by another 30 minutes sonication. The PVK/GO dispersion was subjected to a high-speed centrifugation (4400 rpm, 30 minutes) and a grayish precipitate that settled at the bottom of the tube were collected as PVK/GO nanocomposites. The above precipitate was re-dispersed in CHP followed by 20 minutes of ultrasonication which furnishes a stable PVK/GO solution (Santos, 2012).

RESULTS AND DISCUSSION

Characterization of GO and R-GO

A. Oxidation of Graphene
B. Reduction of GO

Figure 1. Proposed Oxidation-reduction mechanism of graphene oxide (GO) using Hummers Method.

of 0.823 nm compared to the typical value of graphene which is 0.34 nm. The increase in the d-spacing is due to the insertion of hydroxyl and epoxy groups between the carbon sheets and the carboxyl groups along the terminal and lateral sides of the sheets as a result of the oxidation process (Rodil, 2009).

Figure 2. XRD pattern result of pristine graphite and GO.

Figure 3 shows the thermo gravimetric curve and its derivative plot for pristine graphite, GO, and R-GO. The main mass observed for graphene oxide which takes place around 200°C can be ascribed to the decomposition of labile oxygen functionalities. Comparing with the pristine graphite, GO shows much lower thermal stability, which could be due to the lowered thermal stability because of the disrupted and reduced van der Waals interaction. The lowered onset temperature is due to pyrolysis of the labile oxygen containing functional groups (Che, et. al., 2010). This behaviour can be explained through the oxidation product of graphite has a layered morphology with oxygen-containing functionality which thereby weakens the van der Waals forces between layers. This disrupt the hexagonal carbon basal planes on the interior of multi layered stacks of GO which accelerates the weight loss of the material. This decomposition disappears after the reduction process and the mass loss around 300°C is still present in R-GO. This mass loss can be attributed to loss of carboxylic groups given that the mass losses at that temperature have been confirmed to come from strong acidic carboxylic groups and hydrazine is not supposed to reduce these groups, and that they are still present in R-GO.
DSC ANALYSIS

To understand the formation of GO and R-GO, DSC analysis was also performed in this study. Figure 4 shows the DSC traces of pure NGP, GO and R-GO. For pure NGP, the melting temperature ($T_m$) was observed around 470°C. The formation of GO shows $T_g$ at around 150°C and $T_m$ at around 290°C.

FTIR-KBr

Figure 5 shows the FTIR spectra of pristine graphite, GO and R-GO. The spectrum of GO illustrates O-H (carboxyl) at 1400 cm$^{-1}$ and O-H at 3445 cm$^{-1}$ which originated from carboxylic acid group and the O-H stretching mode of intercalated water, C=O in carboxylic acid and carbonyl moieties at 1729, the C-O from the epoxy and alkoxy group at 1055 and the C=C at 1620 assigned to skeletal vibrations of unoxidized graphitic domains or the contribution from the stretching
deformation vibration of intercalated water. After the reduction of GO using hydrazine, the peaks for the oxygen functionalities disappear and that the spectrum of R-GO is similar to that of pristine graphite (Liu, 2009).

GRAPHENE OXIDE (GO) DISPERSIONS

The GO was dispersed in different organic solvents to a concentration of 1 mg/ml with the aid of sonication and the dispersions were allowed to settle for days. The Figure below shows the UV-vis spectra of all the dispersions immediately after sonication and after 30 days after sonication. For the freshly sonicated materials, it can be observed from the picture that the GO can be dispersed in most organic solvents but after 30 days of incubation most of the dispersion started to agglomerate and the most stable dispersion are those solvents like DMF, THF, water and CHP. The UV-vis spectra for these 4 most stable solvents for GO is presented in the Figure 6.

![Normalized Absorbance](image)

Figure 6. UV-vis absorption spectra of as-prepared GO dispersed in different solvents by means of sonication. The spectra were recorded for stabilized dispersion after 24 hours incubation.

UV-Vis analysis

The Figure 7 below show the UV-vis spectra of GO and R-GO dispersion in CHP. The increased in absorption for the R-GO signify that the reduction is successful and that the aromatisation is enhanced. The spectrum of GO dispersion presents a characteristic feature of π-π* which shows a shoulder at around 300 nm which is assigned to the transitions of C=O bonds (Jang, 2008).

![Absorbance](image)

Figure 7. UV-vis analysis of GO and R-GO.

PVK/GO nanocomposites

**Thermal stability study using TGA**

TGA was performed to study the decomposition pattern and thermal stability of the nanocomposites. The TGA curve of pristine graphite indicated 25% mass loss that could be attributed to the residual oxygen –containing groups. The TGA data for the PVK/GO nanocomposites indicated a three-step decomposition process. The first 2 steps are consistent with
the thermal degradation of the PVK, corresponding to the degradation of the side chains and polymer backbone. The observed third decomposition step corresponds to the oxidation and decomposition of GO.

Figure 8. TGA therograms result of PVK/GO nanocomposite, pristine graphite and GO.

**XRD of PVK/GO nanocomposites**

XRD is an effective method to evaluate the interlayer changes of graphite-related powders and crystalline properties of nanocomposite. XRD patterns of the nanocomposites further support the preparation of PVK/GO as individual graphene sheets in the nanocomposites as presented in Figure 9. After the electrochemical cross-linking of GO in PVK matrix, the XRD pattern of the PVK/GO nanocomposites shows only the diffraction peak for PVK and the peak for GO was shifted to a larger 2 theta. A similar phenomenon can also be observed for many polymer/GO nanocomposites and is considered to be a result of polymer crystallization that is induced by graphene. This result could be due to the electrostatic interaction that may contribute to the ordered arrangement of the PVK attached to GO.

Figure 9. XRD pattern of the prepared PVK/GO nanocomposite and pure PVK.

**EIS analysis**

EIS was used to investigate the change of electrochemical system and interface within PVK/GO nanocomposites. The EIS measurements for the PVK/NGP-GO nanocomposite films were performed under open circuit potential in an ac frequency range from 100,000 to 0.01 Hz with an excitation signal of 5 mV. The EIS data were analyzed using the nyquist plot which show the frequency response of the electrode/electrolyte system and are the plots of the imaginary component ($Z''$) of the impedance against the real component ($Z'$). From the nyquist plots shown in the Figure of the pure PVK, GO and PVK/GO display a small semicircle at high frequency followed by a transition to linearity at low frequency. The intercepts of the pure PVK and PVK/GO nanocomposites film with the real impedance 58.65 $\Omega$ and for PVK/GO is 35.10 $\Omega$, this result shows that the PVK/GO nanocomposite film is 23.55 less resistive than pure PVK. While this result is in agreement with a conductive contribution from the addition of GO, this decrease in resistance could also be due to the formation of between the cross-linking of GO and PVK polymer chains as presented in Figure 10A and Figure 10B.
FTIR-ATR

The FTIR-ATR spectra of PVK and PVK/GO nanocomposites are presented in the Figure 11 above. The main absorption peaks of pure PVK structure are shown at the following characteristic bands at around 700-800 cm\(^{-1}\) (out of plane \(-\text{C-H aromatic}\)), 1100-1150 cm\(^{-1}\) (in plane \(-\text{C-H aromatic}\)) and at around 1600 cm\(^{-1}\) (C=C stretching). The main peaks of pure PVK are attributed to the following vibrations at 741 (>CH\(_2\) rocking vibration due tail to tail addition), 1159 (out of plane deformation of vinylidene group and \text{C-H} in plane deformation of aromatic ring), 1226 (C-N stretching of vinyl carbazole), 1328 (>CH\(_2\) deformation of vinylidene group), 1488 (ring vibration of n-vinyl carbazole), and 1561 cm\(^{-1}\) (C=C stretching).
vibration of vinylidene group). The peaks at 749, 1255, 1328, 1597 indicate the doped PVK and shift to 1335 when GO was introduced to the composites. This could be explained to the doping of the carboxyl acid of GO to the PVK backbone and pi-pi stacking of PVK and GO.

CONCLUSIONS

The PVK/GO nanocomposites were successfully prepared via solvent mixing process. The said process disrupted the van der Waals interactions and lead to a better dispersion of GO in PVK polymer matrix. In the case of nanocomposites formed with PVK and GO, spectroscopic and microscopic investigations have identified considerable evidence of polymer wrapping interaction within GO outer most basal-plane sidewalls. ATR-FTIR demonstrated the wrapping/cross-linking interaction between the PVK and GO chains. The prepared PVK/GO nanocomposites also exhibited better thermal stability as revealed by TGA and DSC. This indicates a good dispersion of GO within PVK polymer matrix. The addition of PVK appears to help the dispersion of GO in the polymer which consequently forms a composite which leads to an improved characteristics for different applications like electropatterning, anticorrosion, etc.

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