Journal of Molecular Structure 1111 (2016) 46–54

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Determination of glass transition temperature of reduced graphene oxide-poly(vinyl alcohol) composites using temperature dependent Fourier transform infrared spectroscopy

Suman Mahendia [a, *], Heena [a], Geeta Kandhol [a], Uday P. Deshpande [b], Shyam Kumar [a]

[a] Department of Physics, K. U. Kurukshetra, 136119, India
[b] UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore, 452017, India

A R T I C L E I N F O

Article history:
Received 6 September 2015
Received in revised form
26 January 2016
Accepted 26 January 2016
Available online 29 January 2016

Keywords:
Thermal properties
Glass transitions
Fourier transform infrared spectroscopy (FTIR)
Composite materials

A B S T R A C T

In the present work, structural properties of reduced graphene oxide (RGO) synthesized using modified Hummer's method and its composites with Poly(vinyl alcohol) (PVA) fabricated using solution-cast method have been studied. The structural properties of prepared samples have been systematically studied through UV–Visible absorption, Raman, Fourier Transform Infrared (FTIR) and Differential Scanning Calorimeter (DSC) spectroscopy. Infrared spectroscopy indicates the grafting of PVA chains with graphene layer through the formation of H-bonding linkage in the composites. Temperature-dependent FTIR spectra of PVA-RGO composite films were recorded to obtain the glass transition temperature (T_g) and to study its molecular origin. From these spectra the values of T_g were obtained using two-dimensional (2D) mapping of the first derivative of the absorbance intensity with respect to temperature (dA/dT), over the space of wavenumber and temperature. The value of T_g obtained for pure PVA increases from 78 °C to 92 °C after loading 0.5 wt.% of RGO in PVA and can be attributed to the strong H–bonding interaction between polymer chains and grafted solid surface of RGO. These results are in good agreement with those obtained from DSC analysis. This clearly indicates that the thermal behavior of PVA gets modified with loading of RGO.

1. Introduction

Since the experimental discovery of Graphene in 2004 [1], it has been realized to be one of the frontiers of nanomaterials research. It is a 2-D nanomaterial composed of planar sheets of sp [2] bonded carbon atoms. Many experimental and theoretical studies related to this material have been progressed not only to explain its inherent electronic and mechanical properties [2,3] etc. but also to exploit its use for fabricating efficient devices [4,5]. An insight into its physical properties includes its quite high values of Young's modulus (~1000 GPa), elastic modulus (0.25 TPa) [6], thermal conductivity (~5000 W m^{-1} K^{-1}) [7], charge carrier mobility (~2630 m^2 g^{-1}) [8], low density and high aspect ratio. These properties open the window for the promising capabilities of graphene in many applications like in solar cells, sensors, super capacitors etc. [9–13]. Moreover, its unique properties are exploited to improve the properties of other materials like ceramics, silica, polymers etc. by making their composites [14–17].

Motivated with exceptional behavior of such composite materials, the present study is devoted to the synthesis of graphene grafted Poly(vinyl alcohol) (PVA) composites and to study their structural properties and thermal stability behavior. The choice of PVA polymer is due to its water solubility and wide applications as binder in biological as well as in other material [18,19]. PVA is one of the most important polymers due to its good mechanical and thermal properties. Its semi-crystalline nature allows us to circumvent complexities of interpreting property changes associated with crystallization versus graphite addition [20]. Further, due to their various technological applications, it is necessary to investigate the thermal properties like glass transition temperature (T_g) of such composites. However, the glass transition temperature and thermal behavior of polymer has been investigated by various methods like waveguide spectroscopy [21], ellipsometry [22], X-ray reflectometry [23]. In this paper, our emphasis is on the determination of T_g using temperature dependent Fourier transform infrared (FTIR) spectroscopy. The utility of FTIR spectroscopy for

* Corresponding author. Tel.: +91 9466095387.
E-mail address: mahendia@gmail.com (S. Mahendia).

http://dx.doi.org/10.1016/j.molstruc.2016.01.072
0022-2860/

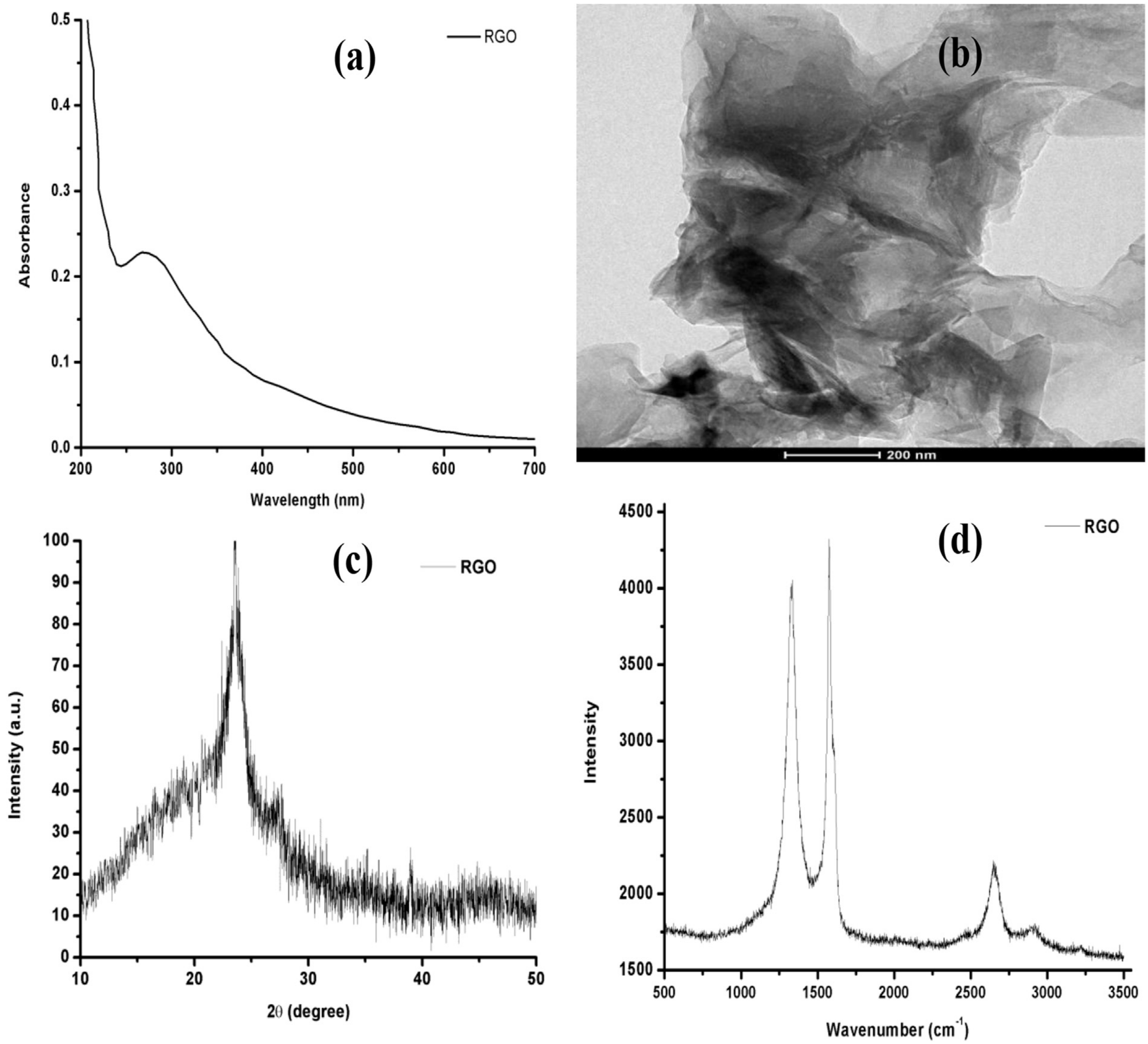

Fig. 1. **(a)** UV–Visible absorption spectra, **(b)** TEM image, **(c)** XRD spectra and **(d)** Raman spectra (λ = 514.5 nm) of as-prepared reduced graphene oxide (RGO).

determining T_g stems from the specificity of the IR probe to different sub-molecular and segmental constitutes in the polymer system, which evolve a unique capability of this method to elucidate the molecular origin of transition temperature [24]. The method simultaneously probes subtle changes of intensities of individual IR bands by monitoring the first derivative of the absorbance with respect to temperature. Therefore, by locating the position of maxima and minima at various wavenumber regions which is based on changes in molecular environment experienced by different chemical moieties associated with the IR absorption at specific wavenumbers, glass transition temperature can be estimated. Further, this method involves the construction of two-dimensional (2D) contour maps of the first derivative of the absorbance with respect to temperature over the space of temperature versus wavenumber. The proposed 2D representation approach depicts the attractive feature of the ability to directly visualize the entirety of complex spectral events occurring during a transition phenomenon. Most importantly, the 2D mapping technique exploits the selectivity of individual IR bands to allow the observer to easily and quickly draw connections between the macroscopic transition phenomenon and the molecular-scale responses [25].

To the best of our knowledge, no report is available of such kind of study for PVA-graphene composites. In the present study, we have constructed the two-dimensional (2D) contour maps of the first derivative of the absorbance of IR bands with respect to temperature over the space of temperature versus wavenumber for reduced graphene oxide (RGO) grafted PVA samples. Such contours show all changes in the band intensity, thus enabling the identification of subtle changes in the conformations of PVA as an effect of RGO loading. Further, the obtained results have been confronted in the light of the Differential Scanning Calorimeter (DSC) study.

2. Experimental section

2.1. Materials and method

A simple sol–gel chemical method was used to synthesize the graphene grafted poly(vinyl alcohol) (PVA) composite films. Graphene sample was prepared using the chemical exfoliations of graphene oxide (GO) using modified Hummer's method reported elsewhere [26]. In brief, 1 gm of graphite flakes were mixed into ice