

## Research Article

# Polyurethane Nanocomposites Containing Reduced Graphene Oxide, FTIR, Raman, and XRD Studies

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Recently, graphene and other graphene-based materials have become an essential part of composite science and technology. Their unique properties are not only restricted to graphene but also shared with derivative compounds like graphene oxide, reduced graphene oxide, functionalized graphene, and so forth. One of the most structurally important materials, graphene oxide (GO), is prepared by the oxidation of graphite. Though removal of the oxide groups can create vacancies and structural defects, reduced graphene oxide (rGO) is used in composites as effective filler similar to GO. Authors developed a new polyurethane nanocomposite using a derivative of grapheme, thermally reduced graphene oxide (rGO), to modify the matrix of polyurethane elastomers, by rGO.

## 1. Introduction

Recently, graphene itself and other graphene-based materials have become an essential part of composite science and technology. Their unique properties are not only restricted to graphene but also shared with derivative compounds like graphene oxide, reduced graphene oxide, functionalized graphene, and so forth [1–3]. One of the structurally most important materials, graphene oxide (GO), is prepared by the oxidation of graphite. Through removal of the oxide groups vacancies and structural defects are created, which changes compatibility of polymers chains to r(GO) nanofiller. Reduced graphene oxide (rGO) is much more effective filler in composites similar to GO because of additional, nanosized adhesion spots present on the flakes surface and edges [4].

Elastomer composites established some time ago have unique position amongst graphite derived, new generation nanomaterials. Graphitic and graphenic fillers in expanded form, flakes, or nanoplates have an influence on rheological, electrical, mechanical, and thermal properties of nanocomposite materials [5, 6]. For nanosized materials, which are in common interest nowadays, particle size and good dispersion are also important [7, 8]. Systematic evaluations of

composite parameters obtained using SEM, XRD, DMA, Raman, and FTIR methods show significant improvement in samples properties. Adding adequate amount of nanofiller 1–3 wt% after which stiffness quickly increases causes critically decreasing other valuable mechanical properties like elongation at break [9]. Raman and FTIR spectroscopy are used to study matrix surface morphology changes due to characteristic filler content, number of layers, and so forth. XRD technique is used for assessment of GO exfoliation, intercalation effect [7, 10–15].

Authors obtained a new polyurethane nanocomposite, using a derivative of graphene, thermally reduced graphene oxide (rGO), by modification of the polyurethane elastomers matrix [16], and also microcellular systems and flexible [16] and viscoelastic polyurethane foams. Nanocomposite materials were characterised by means of XRD, FTIR, Raman, and SEM techniques.

## 2. Experimental

Graphene oxide (GO) was synthesized from natural graphite flakes (G) according to Marciano method [15]. Reduced

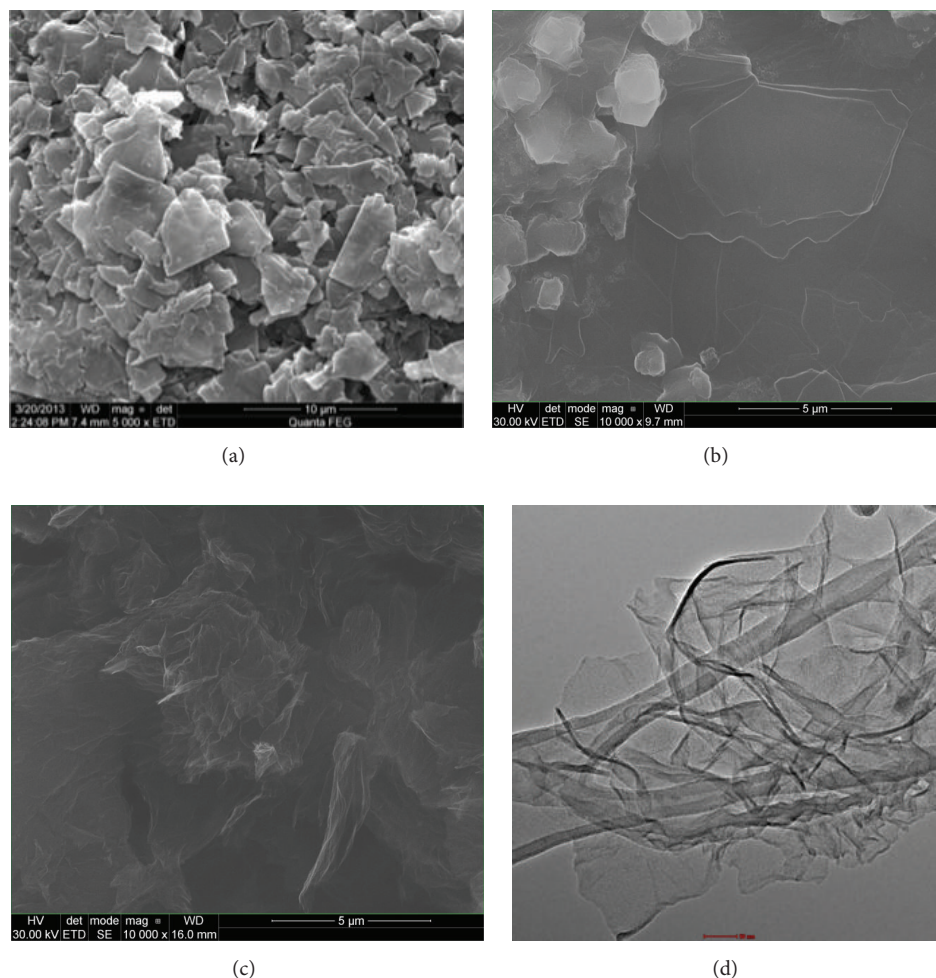


FIGURE 1: Microphotographs of graphite (a), graphene oxide (b), reduced graphene oxide (c) SEM, and reduced graphene oxide (d) TEM.

graphene oxide (rGO) was obtained by thermal reduction, at 200°C in inert argon atmosphere, during 30 minutes.

Poly(ethylene, butylene)adipate diol and 0.5–3 wt% rGO were prepared by vigorous mechanical stirring and sonication process for 60 min. In next step, a calculated amount of 4,4-methylene diisocyanate (MDI) was added to obtain a prepolymer mixture. In the last step prepolymer was mixed with butane-1,4-ol and poured into a heated (90°C) mould.

SEM microphotographs were obtained using Quanta 250 FEG apparatus (Acceleration voltage 20 kV, Detector LFD) with EDAX Apollo X-SDD EDS module. TEM analysis was performed on Transmission Electron Microscope (TEM) (FEI Europe, model Tecnai F20 X-Twin) coupled with EDX spectrometer (STEM-EDX).

Raman spectra were recorded using a Horiba Jobin Yvon Aramis confocal Raman microscope with He-Ne laser beam (633 nm) and Nd:Yag DPSS (532 nm) coupled with a CCD detector. He-Ne laser nominal output power used for investigation was 17 mV and for 532 nm it was 15 mV (75% filter). Exposed area was approximately 100 μm<sup>2</sup>; 2 accumulations were taken, 10 seconds each.

Spectroscopic results were obtained using FTIR Nicolet 8700 Spectrometer from ThermoElectron Corp. working in ATR mode.

The X-ray patterns of the nanofiller and polyurethane nanocomposites were recorded in an X'Pert Philips diffractometer (source radiation: CuK<sub>α1</sub> = 0.1546 nm, 40 kV, 30 mA) in the 5–50° (2θ range) and at scanning rate 0.25°/s.

### 3. Results and Discussion

Analysis of nanofillers morphology was conducted using SEM microscope (Figures 1(a)–1(c)). Figures 1(b) and 1(c) present GO and rGO microphotographs. Both fillers are in shape of flakes and their thickness range is between few and tens of nanometers. These results obtained for GO and rGO samples compared to much larger graphite structures results (Figure 1(a)) show great difference between form and number of layers apparent in each investigated carbon-based filler. Structures of GO and rGO are much more inhomogeneous and have a lot of folds. The most of valuable information about morphology was obtained from TEM

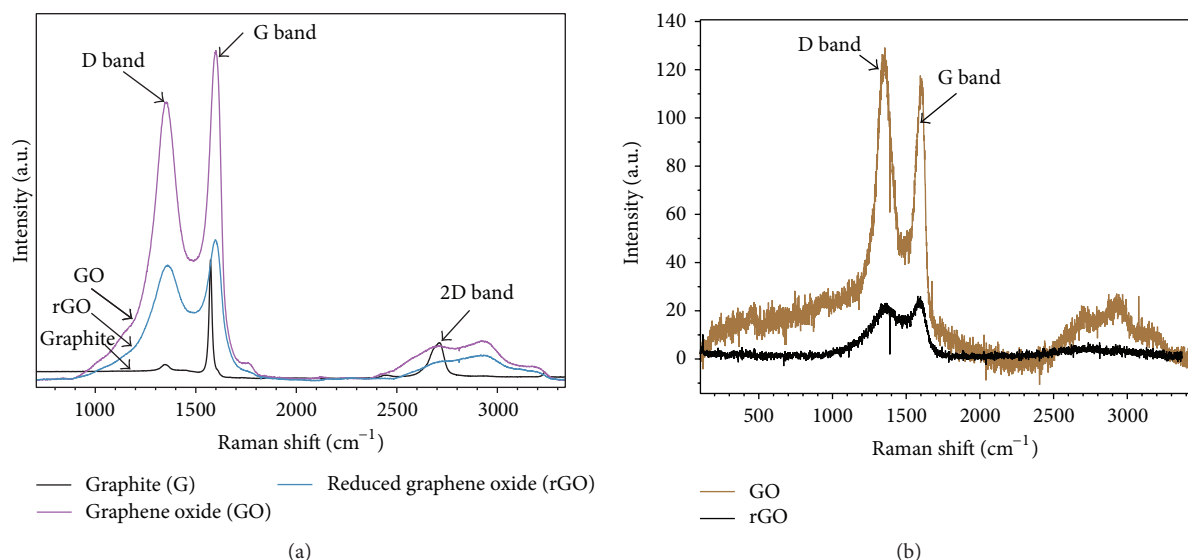


FIGURE 2: Raman spectra of graphite (G), graphene oxide (GO), and reduced graphene oxide (rGO).

analysis. Figure 1(d) presents the surface of rGO, which is highly expanded, and number of defects is not so abundant.

Figure 2 presents Raman spectra of graphite (G), graphene oxide (GO), and reduced graphene oxide (rGO). For GO, most important signals are visible as strong D and G bands at  $1350$  and  $1550\text{ cm}^{-1}$  [2, 3, 17]. Intensity of band D depends on the number of defects and oxygen atoms present on GO surface [18]. Therefore, thermal reduction of GO to rGO provided us with a material having reduced number of carboxylic acid, ether, and hydroxyl groups. This decreased D band intensity in Raman spectroscopy; however it has various effects with matrix compatibility, mostly positive [2, 8, 19].

Reduction of GO was also analysed in matter of D versus G signal intensity. ID/IG ratio (Figure 2(b)) shows the degree of disorder in this carbon-based material. It is inversely proportional to average  $\text{sp}^2$  clusters size and the higher the (rGO to GO) ratio is, the better efficiency and build-up in  $\text{sp}^2$  surface area we can get. Similar method regarding proper check of functionalization degree was performed by Oh et al. [3].

In Figure 3 typical FTIR spectra for graphite, GO, and rGO were presented. For graphite bands above  $3400\text{ cm}^{-1}$  (emerging from OH groups) are not visible as well as those from C=O and C-O-C stretch, at  $1720$  and  $1220\text{ cm}^{-1}$ . According to FTIR spectra GO shows multiple signs of oxygen-derived species; functional groups are apparent in the structure; for example, broad band between  $2500$  and  $3200\text{ cm}^{-1}$  is from carboxyl COOH groups forming hydrogen bonds. This data is in good correlation to results obtained by Yoo et al. [2, 19, 20].

That suggests significant reduction of OH band in rGO which can be clearly observed (Figure 3). That means the process has proven effective in matter of improving structure homogeneity and overall order. Carbonyl bands are still visible which leads to assumption that these kind of chemical species are one of the hardest to eliminate from

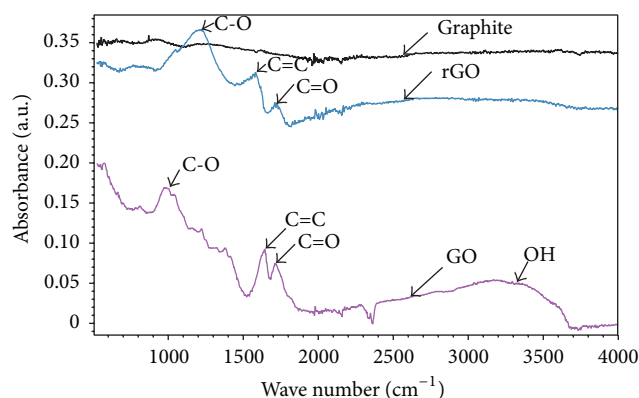


FIGURE 3: FTIR spectra of graphite (G), graphene oxide (GO), and reduced graphene oxide (rGO).

these materials. Most characteristic band at  $1220\text{ cm}^{-1}$  is emerging from C-O-C stretch epoxy bands on rGO surface [21]. C=C aromatic stretch is still well-visible what proves good, unchanged  $\text{sp}^2$  honeycomb-like graphene structure after intensive thermal reduction process [6].

The XRD spectra were measured in a range of  $2\theta$  from  $5^\circ$  to  $50^\circ$  and show (001) diffraction peak at  $2\theta = 11.0^\circ$  and  $2\theta = 25.3^\circ$  for GO and rGO, respectively, indicating the distance between graphene layers. Bragg's equation was applied to (001) reflection for estimating the distance  $d$  between graphene layers (Figure 4, Table 1). Value for GO is  $0.81\text{ nm}$  and for rGO  $0.35\text{ nm}$ . Scherrer's equation with a constant equal to  $0.9$  was applied to (001) reflection to calculate the average height of stacking layers  $H$ . The GO consist of 9 graphene layers ( $7\text{ nm}$  height), whereas the rGO consists of about 6 layers ( $2\text{ nm}$  height) in a stacking nanostructures, compared to many layers (135) observed in graphite structure (Table 1) [10]. Similar structural analysis regarding these kinds of graphene

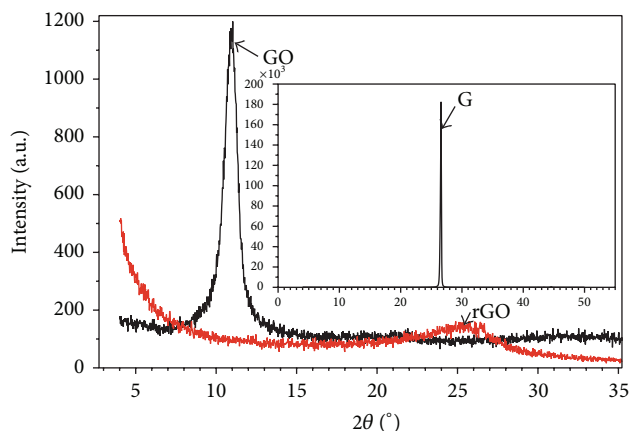


FIGURE 4: XRD spectra of graphite (G), graphene oxide (GO), and reduced graphene oxide (rGO).

TABLE 1: Comparison of structural parameters of G, GO, and rGO resulting from the XRD patterns.

| Sample | $2\theta/^\circ$ | $\Delta\nu/^\circ$ | Peak ( $d_{001}$ ) | $H/\text{nm}$ | $d/\text{nm}$ | $n$ |
|--------|------------------|--------------------|--------------------|---------------|---------------|-----|
| G      | 26.6             | 5.04               |                    | 46            | 0.34          | 135 |
| GO     | 11.0             | 1.20               |                    | 7             | 0.81          | 9   |
| rGO    | 25.3             | 0.18               |                    | 2             | 0.35          | 6   |

$H$ : average height,  $n$ : average number of graphene layers in graphene stacking nanolayers, and  $d$ : average distance between graphene layers.

nanoderivatives were performed by Pokharel et al. whose results could be successfully related to this case [19, 22].

Most prominent nanocomposite bands have been described separately on Raman (Figure 5) and FTIR spectra (Figure 6). All FTIR measurements done in reflection mode confirm that achieved polyurethane systems have their characteristic signals from existing chemical groups and additives (Figure 6). Most of apparent bands in unmodified polyurethane matrix occur also in modified GO nanocomposites. Most important fact is the lack of isocyanate band at  $2275\text{ cm}^{-1}$ , which tells us that all NCO groups from MDI have been successfully bonded together to form urethane groups containing N-H ( $3340\text{ cm}^{-1}$ ), C=O ( $1730\text{ cm}^{-1}$ ), and C-O-C ( $1140\text{--}1180\text{ cm}^{-1}$ ) with C-N ( $1240\text{ cm}^{-1}$ ) signals (Figure 6) [21, 23].

Raman technique is a complementary source of information to FTIR. Addition of graphene nanoderivatives greatly contributed to overall C=C aromatic band intensity recorded by Raman spectroscopy. Its position shifts however towards lower frequencies (from  $1613\text{ to }1580\text{ cm}^{-1}$ ) which means that interactions between conjugated double carbon bonds are more aromatic-like [21]. Meanwhile other signals like C-O or N-H also increase their intensity (Figure 5) due to changing matrix-filler interactions. Shoulder band emerging near C=C aromatic peak ( $1620\text{ cm}^{-1}$ ) shows that other forms of C=C bonds are getting more and more abundant with increasing addition of rGO.

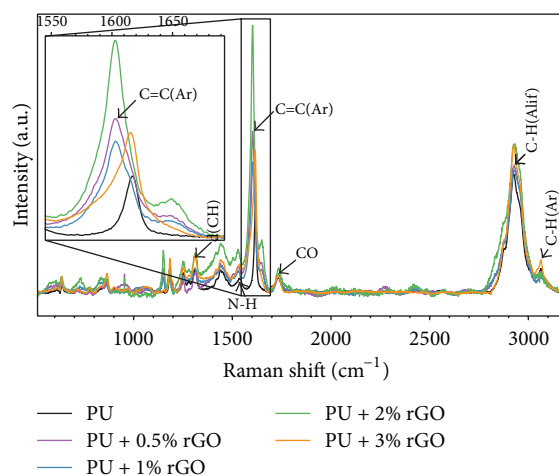


FIGURE 5: Raman spectra of PU nanocomposites.

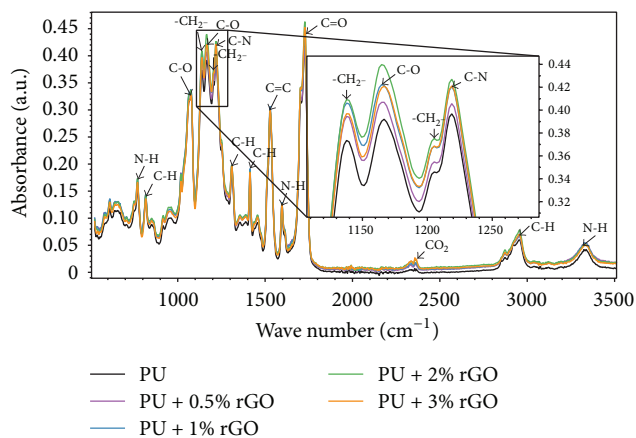


FIGURE 6: FTIR spectra of PU nanocomposites.

On the base of the recorded rGO diffractogram a broad diffraction peak can be seen at higher  $2\theta$  angles (about  $26^\circ$ ). This maximum indicates the presence of strongly delaminated nanostructures [24, 25]. XRD spectra for PU nanocomposites (Figure 7) show maximum peak at approximately  $21^\circ$ . Its intensity decreases (from 850 to 650 a.u.) with increasing nanofiller content. This leads to a conclusion that interactions between rigid segments are being more and more disrupted with rising rGO concentration giving ultimately more amorphous and disordered nanocomposite structures [26]. Noticeable difference in signal intensity between materials containing 2 wt% of rGO and higher is due to fact that the composite is overloaded with the nanofiller in which concentration exceeds critical, optimal values for this kind of PU matrix [7, 9, 16].

#### 4. Conclusions

Reduced graphene oxide nanofiller was characterised by means of Raman, FTIR, and XRD techniques. We validated structure of rGO in comparison to starting materials, graphite and graphene oxide. Obtained polyurethane nanocomposites



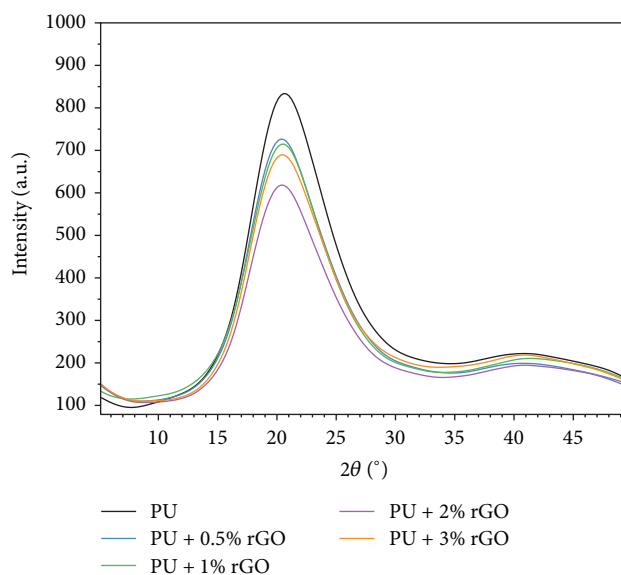


FIGURE 7: XRD spectra of PU nanocomposites.

contained 3 wt% of rGO. Reduced graphene oxide with reactive hydroxyl or epoxy groups present on its surface can interact with polyurethane matrix. For polyurethane nanocomposites modified by rGO, Raman and FTIR spectra share similar characteristics because of predominant amount of polymer materials comparing to quantity of added rGO nanofiller. Delaminated structure of polyurethane nanocomposites was successfully obtained and investigated.

## Competing Interests

The authors declare that they have no competing interests.

## Acknowledgments

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