Investigation on mechanical properties of graphene-polyurethane nanocomposites

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Abstract. Polymer nanocomposites are increasingly used in applications because of their improved mechanical properties compared to traditional polymers. Graphene has attracted considerable attraction as a reinforcing material in polymers in recent years due its extraordinary effect on enhancing mechanical properties of polyurethane. This paper presents the development and characterisation of mechanical properties of graphene based polyurethane nanocomposites. The yield of the graphene nano material was carried out by using the technique called liquid exfoliation as the use of N-Methyl-2-Pyrollidone (NMP) and Tetrahydrofuran (THF) solvent. Granules polyurethane was converted into blend polyurethane by heating at 100ºC and then graphene nano particles were fused with pure polyurethane matrix with different percentage weight of graphene (0, 0.1, 0.3, 0.5 and 0.7 wt.%). Microstructural and Mechanical characterisation of graphene/polyurethane nano-composite matrix were carried out involving Atomic Force Microscopy (AFM), X-Rays Diffraction (XRD) and Universal Testing Machine (UTM) and results were compared with pure polyurethane. The results have shown drastic improvements in mechanical properties with modulus of elasticity increasing by 320% and elongation at breaking point increased by 134% with just 0.7 wt. % of graphene concentration as compared to those of pure polyurethane sample.

1. Introduction
Materials are playing an important role in the development of mankind for decades. Physical properties of materials have great influence on their applications. Nano materials have special properties on nanoscale dimensions and a remarkable difference is examined when materials are seen from macro to nanoscale. These dimensions include large surface area, high surface free energy, and good dispersion availability [1]. In these nanomaterials, graphene has become hot topic because of its unique properties and has opened new pathways towards energy related applications. Graphene has overlapping of sp² hybrid bonds with single layer of carbon atoms. It is a thinnest and strongest material in the world having tensile stress 130 GPa and Young’s Modulus 1 TPa. Whereas, thermal conductivity of graphene is also high and surface area 2630 m²/g. These reasons have attracted physicists, chemists and engineers to enjoy the fruitful applications of graphene [2, 3].
Composites are combinations of two or more materials with varying properties to produce an end product of enhanced characteristics. To improve the properties of combining materials is a reason behind the preparation of composites. It is found out that interference of graphene in nanocomposites has resulted in enhancement of electrical conductivity and mechanical strength of composites. Graphene is considered as a wonder material and it has become a platform for the researchers to explore graphene based composites and its applications. By viewing the marvellous properties of graphene it is believed that addition of small amount of graphene will result in improvement of variety of polymeric metrics [4].

High yield and large scale production of graphene nano material is a most challenging task in the graphene nanocomposites. Several methods were used to prepare graphene but liquid phase exfoliation method is the most favourable one because of its low cost, high yield and scalable production. Keeping the advantages of liquid phase in mind, in this methodology, this paper presents the results of this experimental work for graphene synthesis and mechanical properties of graphene based polymer nanocomposites.

2. Experimental

2.1. Materials
Tetrahydrofuran (C\_4H\_8O) with a molecular weight of 72.11 g/mol was used for the dispersion of polymers like polyurethane, polystyrene, etc. and N-Methyl-1,2-Pyrrolidone (NMP) (C\_5H\_9NO) with good solubility and surface tension was purchased from Merck Schhrhardt, Germany. Graphite for the preparation of graphene nanoparticles was obtained in bulk form from DAEJUNG reagents chemical, China and polyurethane in granular form was purchased from Sigma Aldrich.

2.2. Synthesis of graphene nanoparticles
Graphene was prepared using liquid phase exfoliation method. Liquid phase exfoliation is a powerful technique consisting of four steps i.e. dispersion, sonication, centrifugation and purification. It is a costly process with low yield but graphene dimensions obtained can be from 500 – 700 nm [5]. Firstly, dispersion solution of 10 g graphite and 100 ml N-Methyl-1,2-Pyrrolidone (NMP) (C\_5H\_9NO) with good solubility and surface tension was prepared and then allowed to sonicate using a probe sonicator. For better exfoliation of graphite sonication time set for 72 hrs [6]. The purpose of sonication was to breakdown bulk graphite into nanoparticles using ultrasonic waves [7]. Secondly, the sonicated solution was centrifuged at 250 rpm for 20 mins for the removal of graphite powder from the solution. After the removal of graphite powder, presence of graphene in NMP solution was verified through XRD analysis. The next step was to remove graphene from NMP. For that purpose, the filtration was carried out in a vacuum filtration assembly using 0.22 \( \mu \)m Nylon filter paper where NMP passed through the filter paper and graphene left behind on filter paper. After filtration, heat treatment process was carried out on the filter paper at 150 °C and dried filter paper was dissolved in Tetrahydrofuran (THF) solvent for graphene extraction from filter paper where THF acted as a surfactant. Lastly, 11 mg/ml solution of graphene and THF was prepared on basis of weight difference of filter paper before and after filtration. Calculated weight difference was 59.1 mg as 41 mg results in 8 ml solution so, 59.1 mg resulted in 11 mg/ml solution.

2.3. Preparation of G/PU nanocomposites
For the preparation of G/PU nanocomposites, granular polyurethane was converted into blend by heating a 5 g granular polyurethane and 100 ml THF solution at 100 °C using magnetic stirrer. The samples of G/PU nanocomposites were prepared by mixing graphene solution and polyurethane blend according to
weight percentage as shown in Table I. The samples were further bath sonicated to 10 minutes for proper mixing of graphene and polyurethane blend. After sonication these samples were poured into petri dishes and allowed to dry for 12 hrs at room temperature. It is necessary to dry the samples so that, THF can evaporate and pure G/PU nanocomposites can left behind.

| Sample No. | Graphene Wt. % age |
|------------|--------------------|
| Sample 1   | 0                  |
| Sample 2   | 0.1                |
| Sample 3   | 0.3                |
| Sample 4   | 0.5                |
| Sample 5   | 0.7                |

2.4. Characterization

For verifying the prepared graphene solution (graphite and NMP) to be graphene X-ray diffraction test was carried out. The surface morphologies of G/PU were observed using atomic force microscopy (JEOL, JSPM 5200 AC). The mechanical testing of G/PU nanocomposites were carried using ultimate testing machine (SHIMADZU, AG-X, 100 kN) and the mechanical properties were measured at an elongation rate of 10 mm/min at room temperature. The specimens were 0.07 mm thick with dimensions of 20 mm (L) × 10 mm (W) [6]. The mechanical testing was done under following measurement conditions: deformation rate 10 mm/min, force 100 kN and room temperature. Atleast five specimens were used for mechanical testing and their average values were used.

3. Results and discussion

3.1. Microstructural characterization of G/PU nanocomposites

Atomic force microscopy was carried out for examining topography of graphene nanomaterial [8]. During the test laser tracked cantilever was used with the help of sharp AFM tip. Pure graphene sample was dipped silicon substrate’s surface and then analysed. Surface area was 440 nm$^2$ of graphene nanomaterials as shown in figure 1. The measured thickness of graphene nanomaterial was 0.757 nm. Z1 and Z2 are two reference points having values 1.05 nm and 1.81 nm respectively. The inclination between the two reference points represents angle. The angle of inclination is 0.221° which is calculated over the length of 196.3 nm. Whereas, histogram represents the bearing ratio.
Figure 1. Atomic force microscopy (AFM) analysis of specimen.

Using X-ray diffraction (XRD) peaks of constituent composite system can be recognized [9]. XRD represents a graph between intensity and two theta as shown in figure 2. Pure polyurethane is represented by black line whereas G/PU nanocomposites by wt. % (0.1, 0.3, 0.5, 0.7) are represented by red, blue, cyan and pink colour. Polyurethane has XRD peak at 21.35° [10] with plane 001 [1] and graphene has XRD peak at 25.5° with plane 002 from JCPDS 75-1621 [11]. Existence of polyurethane and graphene in the samples are confirmed by obtaining the same peak through XRD test.

Figure 2. Results of X-rays diffraction (XRD) analysis of specimens.

3.2. Mechanical properties

The mechanical properties of G/PU samples were obtained from the stress-strain curves of each sample using the Ultimate Tensile Machine (UTM). Mechanical testing is performed on five samples of G/PU
Mechanical testing was carried out for pure polyurethane and four samples of polyurethane having different concentrations of graphene. From stress-strain diagram concentration of graphene has direct co-relation with mechanical properties of polyurethane nanocomposite. As the concentration of graphene increases in polyurethane, the mechanical properties of polyurethane also increase. Stress and strain values of polyurethane nanocomposites are increasing as the concentration of graphene is increasing. Graphene a blanket to polyurethane and acted as a load bearing resistant. As graphene requires more force to deform than to polyurethane. As a result, mechanical properties of graphene is higher than it means mechanical properties of polyurethane will also rise. It means more graphene concentration means more strength to polyurethane. It can be seen in the diagram that stress value is decreasing for PU/Gr-0.3% as compared to pure polyurethane sample. It may be due to inhomogeneity of graphene in the sample. Improper mixing of graphene in polyurethane resulted in lack of homogeneity. Hence, the nanocomposite required less value of strain for deformation.

Figure 4 represents the elongation in polyurethane and its nano-composites. The graph consists of five bars where each of the bar is representing elongation with respect to the amount of graphene present in that sample. From the fig. 4 it can be clearly seen that as the amount of graphene is increasing in polyurethane, the elongation is also increasing. Addition of graphene in polyurethane is providing extra elongation to polyurethane. As the concentration of graphene is increasing, elongation in polyurethane is also increasing. It starts rising from 101.6 mm and goes up to 236.4 mm depending upon the concentration of graphene in each nanocomposite.
Figure 4. Maximum Elongation.

Figure 5 represents the modulus of elasticity in G/PU nanocomposites. The diagram verifies as the importance of graphene in polyurethane. With the increase in graphene’s concentration there is a visible change in polyurethane’s mechanical properties. Modulus of elasticity obtained for the pure sample of polyurethane is 0.02 whereas with addition of graphene there is a gradual increase in the mechanical properties of polyurethane. And the value obtained for Pu/Gr-0.7% is 0.084 which is far greater than 0.02.

Figure 5. Modulus of elasticity of G/PU nanocomposites.
## 4. Conclusion

Polyurethane nanocomposites were prepared in the presence of graphene nanoparticles. Graphene nanoparticles were extracted by liquid phase exfoliation method. Different concentrations of graphene nanoparticles are mixed with polyurethane blend to obtain Gr/PU nanocomposites. The main conclusions from this work are as follows:

1. AFM and XRD was used for microstructural characterization. It has been verified that graphene and polyurethane occurs in AFM and XRD results which shows presence of graphene peaks at angle 25º-30º and polyurethane peaks at 21.35º. Through AFM, surface area of graphene nanoparticles is obtained as 440.4 nm², with inclination angle 0.221º and length 196.3 nm.

2. Mechanical testing is performed on five samples of G/PU having different concentration of graphene in each sample. Results show that stress increases from 8.18 MPa to 24 MPa for PU/Gr-0.7%. Similarly, modulus of elasticity increases from 0.02 MPa to 0.084 MPa (by 320%), and elongation increases from 101.6 mm to 236.4 mm (by 134%) as compared to those of pure polyurethane. G/PU sample with graphene 0.7% wt. concentration showed best mechanical properties with elongation 236.4 mm and modulus of elasticity 0.084 MPa as compared to other samples and pure polyurethane.

3. Mechanical properties of polyurethane enhanced as the concentration of graphene increased. Hence, there is direct relation between mechanical properties of polyurethane and concentration of graphene nanoparticles.

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