Fabrication of cellular structures in thermoplastic polyurethane matrix using carbonaceous nanofillers

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Abstract. In the present study, we have synthesized, graphene oxide (GO) by using modified Hummer’s method and reduced graphene oxide(rGO) by using hydrazine hydrate as reducing agent. Since GO and rGO have high surface area and modification of surface is easier, they produce drastic changes in the matrix properties at a very low loading volume. Oxygen functionalities further allow increased interaction with polar polymer composites. Modified hummers method is the most commonly and widely used method of chemical reduction to synthesis graphene oxide as it is rapid and safe. Unlike other method, it is less hazardous and requires less reaction time. Sulfuric acid was used to disperse graphite and NaNO\textsubscript{3} and KMNO\textsubscript{4} as oxidizing agent. The use of KMNO\textsubscript{4} instead of KClO\textsubscript{3} reduced the chances of ClO\textsubscript{2} explosion and also accelerated the reaction. Characterization of graphene oxide and reduced graphene oxide was done using XRD, SEM, FTIR, Raman spectroscopy and TGA. The synthesized GO and rGO were used as nanofillers for the synthesis of polyurethane nanocomposite. Thermoplastic polyurethane is biodegradable and thus polyurethane nanocomposites have wide application. PU nanocomposites were prepared using thermo-chemical solvent mixing method and their microstructures were investigated using various characterization techniques.

Keywords – nanofillers, nanocomposites, hummers method, solvent mixing

1. Introduction

Intense interest from researchers have been generated towards the study of polyurethane(PU) due to its versatile application in various industries and unique properties. PU are semicrystalline thermoplastic copolymer alternately consisting of hard and soft segment in its domain. Diisocyanate constitutes the hard segment contributing to hardness of the polymer. Soft segment is attributed to polyols, either polyester or polyether, part which influence the elasticity of polymer. The unique property of PU arises due to incompatibility and heterogeneity of both phases which leads to microphase separation. Crystallization of either or both of these segments contribute to microphase separation\textsuperscript{[1]}. Nature and size of segments, synthesis condition and manufacturing process affect microphase separation of PU. The chemical structure of polyol, diisocyanate and chain extenders affect the physical and thermal properties of PU\textsuperscript{[2]}. Extensive study on the structural\textsuperscript{[3]}, mechanical\textsuperscript{[4]}, thermal\textsuperscript{[5]} and rheological\textsuperscript{[6]} properties of PU has been done by researchers. It has been investigated that crosslinking density also broadly affect properties\textsuperscript{[7]}. PU is a prominent candidate for fibers, coating, adhesives, biomedical items, manufacturing elastomers, binder resin etc. Versatile application of PU can be owed to its excellent flexibility, elasticity, damping ability, good stress-strain recovery, thermo-plasticity\textsuperscript{[8]}, biocompatibility and biodegradation. The use of PU for
industrial application has been limited due to its low stiffness, low tensile strength, easy combustibility[9], weak barrier properties, low water and gas permeability and deformability. Incorporation of nanofillers can significantly impact the properties of nanocomposites due to high interfacial interaction between nanofillers and polymer, fiber–matrix adhesion and high aspect ratio. It has been reported that nanocomposites have higher thermal stability[10][11], mechanical properties[10] and electrical property[12] as compared to pure matrix material. As compared to micro-composites, interest in nanocomposites has escalated due to low percolation threshold, reduced distance between particles and particle–particle correlation at low volume. Moreover, significant enhancement in property is achieved at very low dispersion loading in nanocomposites. Polyurethane nanocomposites with nano-clay as fillers have attracted a lot of researchers due to improved thermal stability, biodegradability (5-10-fold), tensile strength (2-5 times) and scratch hardness. Due to this PU/nano-clay nanocomposite can be used in biomaterials.[13][14] But the addition of inorganic fillers decreased elongation at break[11]. Moreover, researchers tend to use fillers which does not deteriorate with time easily.

Apart from inorganic fillers carbonaceous fillers such as graphene, CNT, fullerenes due to its reinforcing effect and good compatibility with polymer[10] are prominently used as fillers in nanocomposites. Graphene nanoplatelets can cause increase in crystallization temperature which can improve the thermal properties. While at the same time functionalized graphene sheets usually hinder crystallization of soft segment[12]. Among carbon nanofillers a widespread research is being done using graphene oxide and rGO as nanofillers in composites[15]. Since they have high surface area and modification of surface is easier, they produce drastic changes in the matrix properties at a very low loading volume. Graphene oxide is highly stable and thus has wide range of applicability. Among the various synthesis method developed such as Brodie’s method and Staudenmaier method, Hummer’s method is the safest method considering the reduced risk of explosion as compared to other method. GO is an insulator due to the disruption of sp² carbon and its conductivity depends on the oxidation level. It is hydrophilic in nature and can be easily dispersed in water as well as other polar solvent like Dimethyl formaldehyde (DMF), ethylene glycol, Tetrahydrofuran (THF) etc. They are used as a membrane to measure osmotic pressure and membrane potential. Due to the attached functional groups, graphene oxide shows strong oxidizing properties. When functionalized with aromatic aliphatic amino acids by condensation reaction and nucleophilic substitution it shows stable dispersion in water and other organic solvents. Due to its high stability and the ability to control its properties according to its functionalities, they are used in nanocomposites. The zeta potential/surface charge measurement of graphene oxide shows negative charges on the surface when dispersed with water which suggests its high stability. The addition of graphene in composite can change transition temperature, chemical and physical properties of matrix. High dispersion ability of functionalized graphene helps in the synthesis of economically viable nanocomposites. Oxygen functionalities further allow increased interaction with polar polymer composites. Graphene polymer nanocomposites are widely being used to produce low weight, high strength material. Intense interest has escalated among researches on PU nanocomposites due to improved Payne effect, shape memory effect[16][17], self-healing effect, light absorption, improved gas barriers, biodegradability. These properties attributes to its versatile application in biomedical devices, thermo responsive shape memory, actuators. Particle size of nanofillers[18], method of synthesis and dispersion of nanofillers affects its property significantly. PU/graphene nanocomposites formed by film blowing has been reported by Russo et al[19]. Park et al[20] investigated that allyl isocyanate modified GO in PU matrix act as light actuators, nucleating agent and multifunctional cross-linkers. The increased near infrared absorption of PU/GO nanocomposites enabled light induced shape recovery which makes them suitable candidate for actuators. 10-fold increase in tensile stiffness and 90% decrease in nitrogen
permeability by the addition of 3 wt.% graphene reported by Kim shows high impact of nanofiller addition[21]. Influence of rGO content on moisture permeability was also reported[22]. Reduced nitrogen permeability was observed with increased graphene oxide content. By addition of modified GO in PU increased light absorption has been observed. This increased light absorption contributes to self-healing of polymer by accelerated thermal diffusion[23]. PU/graphene nanocomposites formed by film blowing have been reported by Russo et al.[17]. Thus, PU nanocomposites can be tailored to meet the highly diversified demands of modern technology.

Nanocomposite synthesis can be done by various synthesis methods such as in situ polymerization, solvent method or extrusion. Whatever may be the chosen method for synthesis, good dispersion of nanofillers in polymer is critical to achieve high performance of nanocomposites. Solution mixing method is the most feasible method wherein good dispersion is attained by sonicating in a low viscous solution. The solvent used for the synthesis can easily penetrate in between nanofillers and hence agglomeratio nt tendency is reduced and exfoliation is enhanced. The removal of solvent does not affect the exfoliated structure. Thus, this method is most suitable to attain polymer nanocomposites with high dispersion and low agglomeration. In this study authors have used solvent mixing method for synthesis. XRD, Raman spectroscopy, FTIR and SEM were used to chemically and structurally characterize nanocomposites. Authors believe that the improved property of nanocomposites can widen its application in industries[24].

2. Experimental

Graphene oxide (GO) synthesis[25]: For the synthesis of graphene oxide by modified hummer’s method 3gm graphite was added to 75ml H2SO4. Further NaNO3 was added and the temperature was maintained at 0°C by using an ice bath. This mixture was stirred for 2hrs while the temperature was constantly maintained at 0°C. Further 9gm of potassium permanganate (KMNO4) was added very slowly to ensure homogenous mixture. While addition of KMNO4 temperature was maintained below 15°C, this mixture was continuously stirred for 1hr at 35°C. After 1hr, cooling bath was removed and mixture was left at room temperature. Once the temperature came down to room temperature 100mL deionized water (DI) was added. The beaker was put in an oil bath and heated up to 90°C. After the reaction reaches 90°C, 300mL DI water was further added and this was stirred continuously for 1 ½ hour. This was treated with 30mL of 30% H2O2 and 3L of hot water addition for diluting. The mixture was left overnight to settle down and then acid wash was done. Next day sample was decanted and to the residue again 2L water was added. Further decant the sample next day and place in vacuum oven at 85°C for 2-3 hours. After drying, sample was collected and weighed.
3gm graphite and 1.5gm NaNO3 added to 75ml conc. H2SO4

Cool this mixture at 0°C in ice bath

Stirr for 2hrs

Add 9gm KMNO4 in the mixture slowly, T<15°C through the mixture

Stirr for 1hr keeping the mixture at 35°C

Add 100mL DI water slowly

Put in oil bath and heat upto 90°C

After T=90°C add 300mL DI water and stirr for 1 1/2 hrs

Treat this mixture with 30mL 30% H2O2 and 3L hot water

Put this mixture overnight to settle down

Decant the sample and again add 2L DI water

Nextday decant the sample and keep in vaccum oven at T=85°C for 2-3 hrs

Collecting and weighing the sample

**Reduced Graphene Oxide synthesis (rGO)**[26]: 250mg synthesized GO was added to 200mL DI water and sonicated for 3hr. To this dispersed GO solution 20mL hydrazine hydrate solution (10mL hydrazine hydrate added to 10mL DI) was added. Homogenization was done for 2hr at 80°C. Further it was cooled down and NaOH (1M) wash was done for several times to neutralize. The treated solution was the centrifuged at 5000rpm and heated in oven at 60°C.
Nanocomposite synthesis\cite{27}:
GO and rGO fillers in varying concentration (0.5wt\%, 1wt\%, 5wt\%) was added to 10mL dimethylformamide (DMF) and sonicated. This solution was centrifuged and redispersed in DMF. After complete dispersion the solution was heated to 90\C and added to hot polyurethane which was homogenized in 100mL DMF at 20mg/mL concentration. Further homogenization after solvent mixing was done for 1hr and then it was quenched to 30\C when precipitation starts to form. DMF solvent was removed by decantation. The gel formed where then soaked in ethanol and further heated in vacuum oven at 30\C to evaporate the solvent.
Results and discussions

**XRD:**
XRD was used to confirm the synthesis of GO and rGO. The graphite showed an intense peak at 26.34° and a broad peak at 54.47°. The disappearance of peak at 26.34° and appearance of peak in GO [Fig. 1 (b)] confirms the complete oxidation of graphite[28]. The reduction of GO to rGO was confirmed by the presence of two prominent peak, one at 24.32° and other less intense peak at 42.77°[29].
Fig. 1: XRD of nanofillers of (a) graphite powder (GT); (b) graphene oxide (GO) and (c) reduced graphene oxide (rGO)

**Scanning electron microscopy:**
Morphological analysis of nanofillers was done by using scanning electron microscopy (Fig 2). Both GO and rGO shows inhomogeneous and shows the presence of stacked layers. The presence of folds on the surface indicate that fillers are in the form of flakes. The flakes provide high surface area which makes modification easier hence these fillers can be modified according to applications. The nanofillers appear to be in the range of few to 10nm.
Fig. 2: SEM images of nanofillers of graphite powder (a-c); graphene oxide (d-f) and reduced graphene oxide (g-i) at varying magnification

Microstructural analysis of the synthesized nanocomposites was also done at different magnification. It can be observed that nanocomposites with low loading showed higher dispersion and the nanofillers are embedded in the matrix indicating compatibility of polymer with nanofillers. The clear appearance of interface morphology at higher weight percentage suggests lower matrix-polymer interaction while at 0.5wt.% and 1wt.% higher interface interaction observed. The formation of agglomerate at higher loading results in collapse of pores. At low loading [Fig.3(c) and (f)] porous cellular structure formation is observed. The porosity of PU nanocomposite makes it a suitable candidate for various application such as water filtration membrane.
Fig. 3: SEM images of PU nanocomposites with various loading of rGO (0.5 wt% rGO (a-c), 1 wt% rGO (d-f) and 5 wt% rGO (g-i)) at different magnification

Raman spectroscopy:
The nanofillers were characterized by using Raman spectroscopy. In graphite (GT) two prominent peaks are visible, one at 1571 cm\(^{-1}\) and 2708 cm\(^{-1}\). While in GO peaks at 1358.79 cm\(^{-1}\) and 1599.2 cm\(^{-1}\) each corresponding to D band and G band. The disordered D band is due to in plane vibrations of sp\(^3\) carbon while G band is due to out of plane vibration of sp\(^2\) carbon. Broadening of G band and narrowing of peak at D is indicative of reduction of GO into rGO.
The Raman spectroscopy shown in Fig. 5 depicting the Raman shift in neat polyurethane (NPU)[Fig. 5a]; the nanocomposites of PU incorporated with graphite powder (GT)[Fig. 5b], (c) graphene oxide (GO)[Fig. 5c] and reduced graphene oxide (rGO)[Fig. 5d].

The D-band (disorder-induced phonon mode), which corresponds to mode of the boundaries in the Brillouin zone and also having the high sensitivity to disordered of the structures in the carbon materials usually comes in the in the region of 1250–1450 cm\(^{-1}\) in the Raman spectroscopy; the G band is at the vicinity of 1580 cm\(^{-1}\) [30, 31].
Fig. 5: Raman spectroscopy of (a) Neat polyurethane (NPU, black color); nanocomposites of PU reinforced by 1wt% fillers of (b) graphite powder (GT, red color), (c) graphene oxide (GO, black color) and (d) reduced graphene oxide (rGO, pink color).

The Raman spectra of the fabricated nanocomposites showed significant changes due to the incorporation of graphite powder, GO and rGO to the PU matrix. The Raman bands related to phenol group (1616 cm$^{-1}$) and to urethane group (1537 cm$^{-1}$) of the PU are not visible due to the low intensities compared with the peaks of graphite powder, GO and rGO[32]. The above observation in Raman spectra of graphite powder, GO and rGO incorporated into the PU matrix were probably due to the π-π interaction between the functional groups (hydroxy and urethane group) of PU chains and the added fillers [33].

FTIR:

FTIR spectroscopy [Fig.6] was done to study the functional groups present in nanocomposite and to analyze changes that occurred after nanofiller addition. FTIR of neat PU shows broad peak at 3362 cm$^{-1}$ and 1715 cm$^{-1}$ corresponding to urethane N–H stretching and C=O stretching. The two peaks at 1553 and 1238 cm$^{-1}$ are attributed to the N–H in-plane and C–N bond stretching. The characteristic peaks of neat PU are present in PU nanocomposites as well which indicate that no change in the functional group has taken place. A slight decrease in the absorption peak intensity was observed at the 3313-3362 cm$^{-1}$ as compared to neat PU. This decrease indicated the H-bond formation between nanofillers and N-H group of polyurethane. The H-bond formation provides stability to the PU nanocomposite structure. As seen in PU with rGO[Fig.6(b)] with increasing weight percentage transmittance decreases due to the hydrogen bonding between the functional group of rGO and urethane group present in the hard segments of the PU. The distribution and dispersion of rGO is also better than GO due to its lower size which in turns increase the interfacial strength because of the hydrogen bonding.
Conclusions:
The synthesis of graphene oxide by modified Hummer’s method and rGO by using hydrazine hydrate as reducing agent was carried out. The structural and microstructural changes that occur after synthesis of GO and rGO was showed in SEM images. The formation of GO and rGO was confirmed from the intensity of D-band and G-band in Raman analysis. Thus, modified Hummer’s method and reduction by hydrazine hydrate was concluded to be feasible method for GO and rGO synthesis. Porous structure of polyurethane (PU) was obtained at low weight percentage i.e at 0.5wt% and 1wt% while agglomerate formation of nanofillers was observed at higher loadings i.e. 5wt%. FTIR confirmed that the nanofillers are bonded to PU by H-bonding and no other chemical change was found after the addition. Thethermo-chemical solvent mixing method yields stable nanocomposites with good nanofillers dispersion throughout at lower weight percentage of nanofillers. Thus, it can be adapted as a successful and reliable method for the preparation of PU nanocomposites with better dispersion than other reported method like melt mixing.

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