

**FABRICATION OF 2D CROSS-LINKED GRAPHENE OXIDE
BASED POLYMER COMPOSITES FOR IMPROVED
MECHANICAL AND THERMAL STABILITY**

SUBMITTED BY

STEPHEN DON SARKAR

STUDENT ID: 1015033202

SESSION: OCTOBER 2015

MASTER OF PHILOSOPHY IN CHEMISTRY



DEPARTMENT OF CHEMISTRY
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

YEAR OF DEFENSE 2018

The thesis entitled 'Fabrication of 2D Crosslinked Graphene Oxide Based Polymer Composites for Improved Mechanical and Thermal Stability' submitted by Stephen Don Sarkar, Roll No.:1015033202, Session: October 2015, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Philosophy in Chemistry on October 22, 2018.

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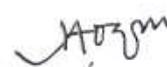
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Stephen Don Sarkar

Dedicated to
My Beloved Family
&
Honorable Supervisor

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List of Abbreviations of Technical Symbols and Terms

1. Graphene oxide (GO)
2. Oxidized graphene oxide (OGO)
3. 2-Aminoethyl methacrylate hydrochloride (AEM)
4. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC)
5. N-Hydroxysuccinimide (NHS)
6. Potassium persulfate (KPS)
7. Acrylic functionalized graphene oxide (AFGO)
8. Graphene oxide based 2D cross-linker (GOBC)
9. N,N'-Methylene bis(acrylamide) (BIS)
10. Acrylic acid (AA)
11. Poly(acrylic acid) (PAA)

Acknowledgement

At the very beginning, I humbly acknowledge my deepest gratitude to the Almighty, the most gracious, benevolent and merciful creator for his infinite mercy bestowed on me in completing the research work presented in the dissertation.

It is a immense pleasure for me to acknowledge my honest sense of gratitude, sincere appreciation, heartfelt indebtedness and solemn regards to my reverend teacher and supervisor Dr. Md. Shafiul Azam, Assistant Professor, Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), for his kind supervision, indispensable guidance, valuable and constructive suggestions, liberal help and continuous encouragement during the whole period. In fact, I am quite lucky to be a part of his ambitious research team.

It is also my great honor to convey my sincere gratitude to my respected teacher Professor Dr. Md. Abdur Rashid, honorable Head of the Department of Chemistry, BUET for giving me his wonderful support to move through the academic processes during this M.Phil. program. I would like to convey my deepest gratitude to Dr. Abu Bin Imran, Dr. Chanchal Kumar Roy and Nahida Akter for their valuable suggestions, comments and guidance during the research period. I am thankful to all other respected teachers of the Department of Chemistry, BUET, for their time to time support. I would also like to thank all of the officers and staffs of the Department of Chemistry, BUET for their continuous help during my study period.

I am highly grateful to all members of the board of examiners for their valuable suggestions and resourceful comments.

I am expressing my sincere appreciation to my dear colleagues and all the members of Azam Research Group for their friendly cooperation and lovely encouragement throughout my research period.

I am exceedingly gratified to the authority of BUET and The World Academy of Sciences (TWAS) for providing financial support for this research work.

It is a great pleasure to offer my humble thankfulness to the honorable Principal, Dr. Fr. Hemanto Pius Rozario, CSC for providing me the opportunity to carry on my research and high appreciation to all my respectable colleagues of Department of Chemistry, Notre Dame College, Dhaka for supporting to achieve the goal efficiently.

Finally, I would like to express my heartfelt indebtedness and profound gratitude to my beloved father, mother and my wife for their continuous inspiration and immeasurable sacrifices throughout the period of my study.

October, 2018

Stephen Don Sarkar

Abstract

Graphene oxide (GO) has extraordinary physical and chemical characteristics such as high mechanical and thermal stability, super adsorption property, excellent bio-sensing, electrical capacity etc. GO containing polymers especially hydrogels of poly(acrylic acid) adopt these characteristics which enhance acceptance and usability of hydrogels. In this study, acrylate functionalized graphene oxide (AFGO) is fabricated through a common EDC coupling reaction of GO and amine containing double bonded compound and this AFGO is employed as graphene oxide based cross-linker (GOBC) containing a large number of active sites on its 2D surface. It is well-established that the cross-linked polymers using traditional cross-linkers show enhanced mechanical properties but the increase of cross-linker density in hydrogel leads to immobility of molecular chain, hardness and brittleness which limits the fields of its applications. But here, polymers composites prepared by very small weight percent of GOBC overcome the drawbacks of the traditionally cross-linked counterparts by enhancing the mechanical and thermal stability of the polymer composites.

CHAPTER-1

Introduction

1.1 Composite:

A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure, differentiating composites from mixtures and solid solutions. More recently, researchers have also begun to actively include sensing, actuation, computation and communication into composites. [1] Typical engineered composite materials include:

- Reinforced concrete and masonry
- Composite wood such as plywood
- Reinforced plastics, such as fiber-reinforced polymer or fiberglass
- Ceramic matrix composites
- Metal matrix composites
- Other Advanced composite materials

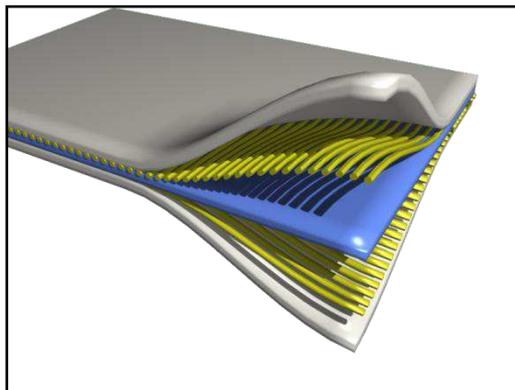


Fig. 1.1: Composite material

1.2 Polymer:

Polymers are abundant in nature, found in all living systems, and materials such as wood, paper, leather, natural fibers have found extensive use. While natural polymers retain their intrinsic importance, today synthetic materials are mostly used. The first man-made polymers, formed by chemical modification of natural materials, were

produced in the second half of the nineteenth century. Fully synthetic polymers were developed in the twentieth century, most in the period 1950–1970s driven by chemical industry expansion. These are the so-called plastics of modern society. The feedstock for polymerization processes is petro-chemical, and environmental concerns have led to more recent developments of polymers from renewable resources. [2] Polymers have a wide range of physical and mechanical properties which suit a large number of technical applications. Chemical structure, average relative molar mass and distribution, chain conformation, morphology, additives and reinforcing fillers give a pallet of controls to define individual material properties envelope and allow sophisticated tailoring of material to specific applications. Polymer process technology is mature and it is relatively easy to produce complex shapes from most materials in a cost-effective way. As most polymers are low density materials, they have specific service advantage in transport situations and substitution for metal has become important. Use of polymer membranes and media in battery and fuel cell applications has grown. Polymeric materials dominate packaging applications and environmental pressures will ensure that recycling and reuse of waste material will continue to be important development area. Healthcare equipment, medical devices, and drug delivery systems have seen significant use and development of polymeric materials, particularly bio-absorbable systems. Development of biomimetic polymers and analysis of structured molecular architectures has grown as the understanding of natural polymers increased.

1.3 Cross-linked Polymer:

In chemistry and biology a cross-link is a bond that links one polymer chain to another. These links may take the form of covalent bonds or ionic bonds and the polymers can be either synthetic polymers or natural polymers (such as proteins). In polymer chemistry, when a synthetic polymer is said to be "cross-linked", it usually means that the entire bulk of the polymer has been exposed to the cross-linking method. The resulting modification of mechanical properties depends strongly on the cross-link density. Low cross-link densities decrease the viscosities of polymer melts. Intermediate cross-link densities transform gummy polymers into materials that

have elastomeric properties and potentially high strengths. Very high cross-link densities can cause materials to become very rigid or glassy, such as phenol-formaldehyde materials. Cross-links can be formed by chemical reactions that are initiated by heat, pressure, change in pH, or radiation.

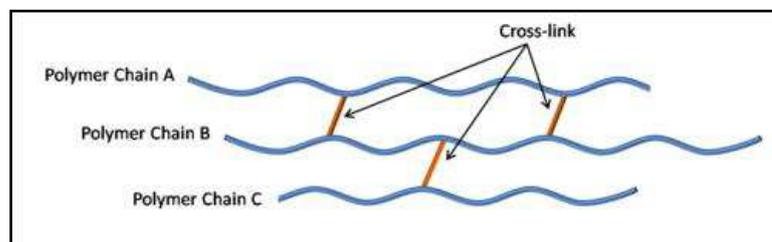


Fig. 1.2: Cross-linked polymer

1.4 Hydrogel:

Hydrogels are hydrophilic, highly cross-linked polymeric networks capable of absorbing large amount of water. Hydrogels contain water solubility groups such as $-OH$, $-COOH$, $-NH_2$, $-CONH_2$ and $-SO_3H$. They are insoluble in water and are available in dry or hydrated sheet or gel. It is highly stimuli-responsive such as pH [4], temperature [5], electric field and magnetic field. So it is called smart hydrogel. Temperature sensitive hydrogels are also called as thermogels. These stimuli-sensitive hydrogels can display changes in their swelling behaviour of the network structure according to the external environments. Hydrogels are also generally highly biocompatible, which may be attributed to the high water content of hydrogels. Hydrogels are gels in which the liquid phase is water. Cross-linking can render these gels insoluble and provide additional mechanical strength. Such gels swell by imbibing small to large quantities of water. These gels are biocompatible. It became soft when absorb water. Hydrogels are generally synthesized by free radical polymerization. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains. Many materials, both naturally occurring and synthetic, fit the definition of hydrogels. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the

polymeric backbone, while their resistance to dissolution arises from cross-links between network chains. It is a polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water.

1.4.1 Synthesis of Hydrogels:

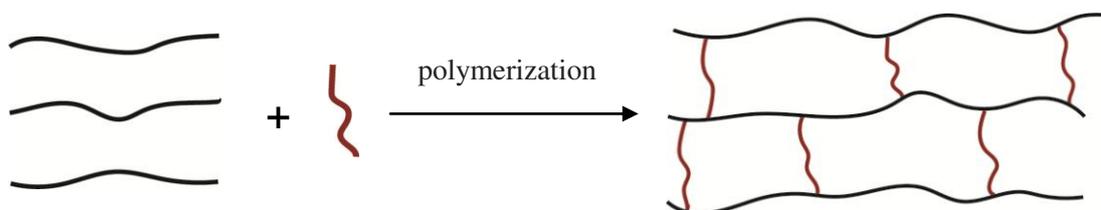


Fig. 1.3: Schematic illustration of synthesis of hydrogel

Hydrogels can be synthesized by different polymerization methods using two different cross-linking routes. They are:

1.4.1.1 Chemically Cross-linked Hydrogel:

This type hydrogels are synthesized by chain growth polymerization, addition and condensation polymerization and gamma and electron beam polymerization.

Chain-growth polymerization includes free radical polymerization, controlled free radical polymerization, anionic and cationic polymerization. It is done by three process viz., initiation, propagation, and termination. After initiation, a free radical active site is generated which adds monomers in a chain link-like fashion.

Addition and condensation polymerization involves stepwise addition of poly functional cross-linking agents with monomer functional groups. Water soluble monomers can be converted into hydrogels using cross-linking. Polymer chains may be cross-linked in the presence of water to form a hydrogel. Water occupies voids in the network, giving the hydrogel its characteristic surface properties. Polyurethanes,

polyesters, or nylon polymers are most commonly synthesized for hydrogel applications [3].

Gamma and electron beam polymerization involves high energy electromagnetic irradiation as cross-linker. These high energy radiations can cross-link water-soluble monomer or polymer chain ends without the addition of a cross-linker. During irradiation, using a gamma or electron beam, aqueous solutions of monomers are polymerized to form a hydrogel. Gamma and electron beam polymerizations also involves the initiation, propagation, and termination steps as in the free radical polymerization.

The chemical cross-linking involves forming covalent bonds between polymer chains during polymerization of monomers with low molecular weight or cross-linking of polymer precursors. The most widely used methods for the fabrication of chemically cross-linked hydrogels are to employ heterogeneous polymerization reactions in the presence of bifunctional or multifunctional cross-linkers [4]. Cross-linking of natural and synthetic polymers can be attained by reaction of some functional groups such as hydroxyl, carboxylic, and amine groups with cross-linkers such as aldehydes [4].

1.4.1.2 Physically Cross-linked Hydrogel:

Physically Cross-linked Hydrogel hydrogels are synthesized by ionic interaction, crystallization, stereo complex formation, hydrophobized polysaccharides, protein interaction and hydrogen bond.

In ionic interactions, hydrogels can be cross-linked under mild conditions, at room temperature and physiological pH. This process of cross-linking does not require presence of ionic groups in the polymer.

For stereocomplex formation, a hydrogel is formed through cross-linking that is formed between lactic acid oligomers of opposite chirality [3]. Hydrophobic interactions results in the polymer to swell and uptake water that forms the hydrogel. Polysaccharides such as chitosan, dextran, pullulan and carboxymethyl curdlan [3] are reported in literature for the preparation of physically cross-linked hydrogels by hydrophobic modification.

Protein interaction involves block copolymers that contains repetition of silk-like and elastine-like blocks called ProLastins [3]. These ProLastins are fluid solutions in water and can undergo a transformation from solution to gel under physiological conditions because of the crystallization of the silk-like domains [3].

Poly Acrylic Acid (PAA) and Poly Methacrylic Acid (PMA) form complexes with Poly Ethylene Glycol (PEG) from the hydrogen bonds between the oxygen of the PEG and carboxylic group of PMA [3]. This interaction allows for the complex to absorb liquids and swell at low pH which transforms the system into a gel.

Crystallization involves freezing-thawing process and creates a strong and highly elastic gel [5]. PVA hydrogels can be formed by physically cross-linking through repeated freezing/thawing methods, or chemically cross-linked with glutaraldehyde or epichlorohydrin.

1.4.2 Properties of Hydrogel:

Hydrophilic gels called hydrogels receive considerable attention for their use in the field of pharmaceutical and biomedical engineering. This material can be used as a carrier for drug and other therapeutic bio-molecule only if it is biodegradable, biocompatible and non-toxic. Thus once the biomaterials are prepared one must evaluate the characteristic properties like swelling behavior, mechanical properties and toxicity studies etc so that the hydrogel could be used successfully in the concerned biomedical field.

1.4.2.1 Swelling Property:

All polymer chains in hydrogels are cross linked to each other either physically or chemically and thus, considered as one molecule regardless of its size. For this reason, there is no concept of molecular weight of hydrogels and therefore, sometimes called infinitely large molecules or super macromolecules. A small change in environmental condition may trigger fast and reversible changes in hydrogel. The alteration in environmental parameters like pH, temperature, electric signal, presence of enzyme or other ionic species may lead to a change

in physical texture of the hydrogel. These changes may occur at macroscopic level as precipitate formation, changes in size and water content of hydrogels. The difference in concentration of mobile ions in the hydrogel interior relative to external solution (osmotic pressure), changes in solvent pH, drives the volume change. Hydrogels with acidic or basic functional groups respond to the fluctuations in the external environmental pH. Degree of ionization of the functional groups dictates its swelling profile and hence the volume change. Poly(acrylic) acid is such type of pH sensitive hydrogel where swelling ratio changes due to the ionization of carboxyl groups on the polymer chain. Swelling ratio is determined by the following equation [6]:

$$\text{Swelling ratio} = \frac{m_s - m_d}{m_d} \times 100$$

where, m_s is the mass of swollen hydrogel in equilibrium at a given temperature and m_d is the dry mass of sample.

1.4.2.2 Mechanical Property:

Mechanical properties of hydrogels are very important from the pharmaceutical and biomedical point of view. The evaluation of mechanical property is essential in various biomedical applications viz. ligament and tendon repair, wound dressing material, matrix for drug delivery, tissue engineering and as cartilage replacement material. The mechanical properties of hydrogels should be such that it can maintain its physical texture during the delivery of therapeutic moieties for the predetermined period of time. Changing the degree of cross-linking the desired mechanical property of the hydrogel could be achieved. Increasing the degree of cross-linking a stronger hydrogel could be achieved though the higher degree of cross-linking decreases the % elongation of the hydrogels creates a more brittle structure. Hence there is an optimum degree of cross-linking to achieve a relatively strong and yet elastic hydrogel. Copolymerization with co-monomer, may result into hydrogen bonding within the hydrogel which has also been utilized by many researchers to achieve desired mechanical properties.

1.4.2.3 Biocompatibility:

It is important for the hydrogels to be biocompatible and nontoxic in order to make it applicable in biomedical field. Most polymers used for this purpose must pass cytotoxicity and in-vivo toxicity tests. Biocompatibility is the ability of a material to perform with an appropriate host response in a specific application. Biocompatibility consists basically of two elements: (a) bio-safety i.e. appropriate host response not only systemic but also local (the surrounding tissue), the absence of cytotoxicity, mutagenesis, and/or carcinogenesis and (b) bio-functionality i.e. the ability of material to perform the specific task for which it is intended.

1.4.3 Applications of Hydrogels:

Common applications of hydrogels include:

- Scaffolds in tissue engineering. When used as scaffolds, hydrogels may contain human cells to repair tissue. They mimic 3D microenvironment of cells. [7]
- Hydrogel-coated wells have been used for cell culture. [8]
- Environmentally sensitive hydrogels (also known as 'Smart Gels' or 'Intelligent Gels'). These hydrogels have the ability to sense changes of pH, temperature, or the concentration of metabolite and release their load as result of such a change. [9]
- Sustained-release drug delivery systems.
- Providing absorption, desloughing and debriding of necrotic and fibrotic tissue
- Hydrogels that are responsive to specific molecules, such as glucose or antigens, can be used as biosensors, as well as in DDS. [10]
- Disposable diapers where they absorb urine, or in sanitary napkins. [11]
- Contact lenses (silicone hydrogels, polyacrylamides, polyacon).

- EEG and ECG medical electrodes using hydrogels composed of cross-linked polymers (polyethylene oxide, polyAMPS and polyvinylpyrrolidone).
- Water gel explosives.
- Encapsulation of quantum dots.
- Breast implants.
- Granules for holding soil moisture in arid areas.
- Dressings for healing of burn or other hard-to-heal wounds. Wound gels are excellent for helping to create or maintain a moist environment.
- Reservoirs in topical drug delivery; particularly ionic drugs, delivered by iontophoresis (see ion exchange resin).
- Materials mimicking animal mucosal tissues to be used for testing mucoadhesive properties of drug delivery systems. [12]

1.5 Graphene:

‘Graphene’ is a combination of ‘graphite’ and the suffix -ene, named by Hanns-Peter Boehm and colleagues, [13] who produced and observed single-layer carbon foils in 1962. [14] It is an allotrope (form) of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice which is the basic structural element of many other allotropes of carbon, such as graphite, diamond, charcoal, carbon nanotubes and fullerenes. [15]

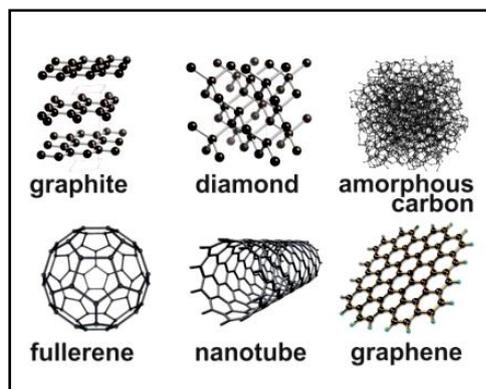


Fig. 1.4: Allotropes of carbon

Its carbon atoms are packed densely in a regular atomic-scale chicken wire (hexagonal) pattern. [15] Each atom has four bonds: one σ bond with each of its three neighbors and one π -bond that is oriented out of plane. The atoms are about 1.42 Å apart. [15] Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was successfully used to calculate the band structure for a single graphite layer using a tight-binding approximation. [15] Graphene's stability is due to its tightly packed carbon atoms and a sp^2 orbital hybridization – a combination of orbitals s , p_x and p_y that constitute the σ -bond. The final p_z electron makes up the π -bond. The π -bonds hybridize together to form the π -band and π^* -bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons. [15]

Ever since its discovery in 2004, graphene has been making a profound impact in many areas of science and technology due to its remarkable physicochemical properties. These include a high specific surface area (theoretically 2630m²/g for single-layer graphene), extraordinary electronic properties and electron transport capabilities, strong mechanical strength and excellent thermal and electrical conductivities. Graphene is the strongest material ever tested with an intrinsic tensile strength of 130.5 GPa and a Young's modulus of 1 TPa (150000000 psi). [16]

1.5.1 Applications of Graphene:

Potential graphene applications include incredibly lightweight, thin, flexible electric/photonic circuits, solar cells, and various medical, chemical and industrial processes enhanced or enabled by the use of new graphene materials. Famous applications of graphene are:

- Tissue engineering
- Polymerase chain reaction
- Drug delivery
- Transistors
- Quantum dots preparation
- Organic electronics
- Photodetector

- Energy Generation & Storage
- Biosensing
- Water filtration & Contaminant removal
- Plasmonics and metamaterials
- Lubricant
- Waterproof coating
- Coolant additive
- Adhesive fabrication

1.6 Graphene Oxide (GO):

Graphite oxide, formerly called graphitic oxide or graphitic acid, is a compound of carbon, oxygen, and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers. The maximally oxidized bulk product is a yellow solid with C:O ratio between 2.1 and 2.9, that retains the layer structure of graphite but with a much larger and irregular spacing. Graphite oxide was first prepared by Oxford chemist Benjamin C. Brodie in 1859, by treating graphite with a mixture of potassium chlorate and fuming nitric acid. He reported synthesis of "paper-like foils" with 0.05 mm thickness. In 1957 Hummers and Offeman developed a safer, quicker, and more efficient process called Hummers' method, using a mixture of sulfuric acid H_2SO_4 , sodium nitrate $NaNO_3$, and potassium permanganate $KMnO_4$, which is still widely used, often with some modifications. [17] Largest monolayer GO with highly intact carbon framework and minimal residual impurity concentrations can be synthesized in inert containers using highly pure reactants and solvents. [18]

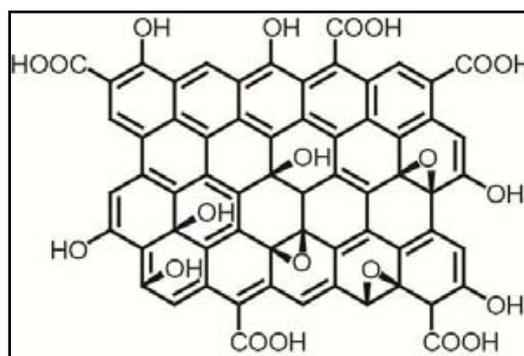


Fig. 1.5: Graphene Oxide

The structure and properties of graphite oxide depend on particular synthesis method and degree of oxidation. [19] It typically preserves the layer structure of the parent graphite, but the layers are buckled and the interlayer spacing is about two times larger (~0.7 nm) than that of graphite. Strictly speaking "oxide" is an incorrect but historically established name. Besides oxygen epoxide groups, other functional groups experimentally found are: [19] carbonyl (C=O), hydroxyl (-OH), phenol, for graphite oxides prepared using sulphuric acid (e.g. Hummers method) also some impurity of sulphur is often found, for example in a form of organosulphate groups . [20] [21] [21] There is evidence of "buckling" (deviation from planarity), folding and cracking [22] of graphene oxide sheets upon deposition of the layers on a choice of substrate. The detailed structure is still not understood due to the strong disorder and irregular packing of the layers.

Graphite oxide is hydrophilic and easily hydrated when exposed to water vapor or immersed in liquid water, resulting in a distinct increase of the inter-planar distance (up to 1.2 nm in saturated state). Additional water is also incorporated into interlayer space due to high pressure induced effects. [23] Maximal hydration state of graphite oxide in liquid water corresponds to insertion of 2-3 water monolayers, cooling the graphite oxide/H₂O samples results in "pseudo-negative thermal expansion" and below freezing point of water media results in de-insertion of one water monolayer and lattice contraction. [24] Complete removal of water from the structure seems difficult since heating at 60–80 °C results in partial decomposition and degradation of the material. Graphite oxide exfoliates and decomposes when rapidly heated at moderately high temperatures (~280–300 °C) with formation of finely dispersed amorphous carbon, somewhat similar to activated carbon. [25]

One of the advantages of GO is its easy dispersability in water and other organic solvents, as well as in different matrixes, because of the presence of oxygen functionalities. This remains a very important property when mixing the material with ceramic or polymer matrixes when trying to improve their electrical and mechanical properties. However, in terms of electrical conductivity, GO is often described as an electrical insulator because of the disruption of its sp² bonding networks. To recover the honeycomb hexagonal lattice, and with it the electrical conductivity, the reduction of GO has to be achieved. Functionalization of GO can fundamentally change the

properties of GO. The resulting chemically modified graphenes could then potentially become much more adaptable for many applications. There are many ways in which GO can be functionalized, depending on the desired application. For optoelectronics, biodevices, or as a drug-delivery material, it is possible to substitute amines for the organic covalent functionalization of graphene to increase the dispersability of chemically modified graphenes in organic solvents. It has also been proven that porphyrin-functionalized primary amines and fullerene-functionalized secondary amines could be attached to GO platelets, ultimately increasing nonlinear optical performance. For GO to be usable as an intermediary in the creation of monolayer or fewlayer graphene sheets, it is important to develop an oxidization and reduction process that is able to separate individual carbon layers and then isolate them without modifying their structure. So far, although the chemical reduction of GO is currently seen as the most suitable method of mass production of graphene, it has been difficult for scientists to complete the task of producing graphene sheets of the same quality as mechanical exfoliation but on a much larger scale. Once this issue is overcome, we can expect to see graphene become much more widely used in commercial and industrial applications.

1.6.1 Applications of Graphene Oxide:

Famous applications of Graphene oxide (GO) are as follows:

1.6.1.1 Electronics Devices:

Several electronic devices have been fabricated using GO as a starting material for at least one of the components. One such device is a graphene-based field effect transistor (FET) (Su, 2010; Wang, S. et al., 2010). Liu et al. (2010) studied the electrochemical glucose sensor using GO functionalized with glucose oxidase after being deposited on an electrode. One of the major areas where GO can be expected to be used is in the production of transparent conductive films after being deposited on any substrate. Such coatings could be used in flexible electronics, solar cells, liquid crystal devices, chemical sensors, and touch screen devices.

1.6.1.2 Energy Devices:

GO have an extremely high surface area; therefore, these materials are considered for usage as electrode materials in batteries and double-layered capacitors, as well as fuel cells and solar cells (Zhu et al., 2010). Production of GO can be easily scaled-up compared with other graphene materials, and therefore it may soon be used for energy-related purposes. Its ability to store hydrogen may, in the future, prove very useful for the storage of hydrogen fuel in hybrid cars. Nanocomposites of GO/rGO can also be used for high-capacity energy storage in lithium ion batteries.

1.6.1.3 Biosensors:

GO is a fluorescent material that could be used for biosensing applications, for early disease detection, and even for assisting in finding cures for cancer and detecting biologically relevant molecules. GO has been successfully used in fluorescent-based biosensors for the detection of DNA and proteins with a promise of better diagnostics for HIV. GO has been used as a fluorescence quenching material in biosensors that utilize the fluorescence resonance energy transfer (FRET) effect. Wang, Y. et al. (2010) used the FRET effect in a fluorescein-labeled ATP aptamer to sense ATP as low as 10 μ M. Lu et al. (2009) used single-stranded DNA with a fluorescence tag and found that it bound noncovalently to GO with subsequent quenching of the fluorescence of the tag. Addition of a complementary DNA removed the tagged DNA from the GO surface and restored the fluorescence. Song et al. (2011) used folic acid-functionalized GO to detect human cervical cancer and human breast cancer cells.

1.6.1.4 Biomedical Applications:

GO is used in the biomedical field, particularly in drug-delivery systems. GO is likely superior to many other anticancer drugs because it does not target healthy cells, only tumors, and has a low toxicity (Yang et al., 2011). Functionalized nano-GO (nGO) has been used in several studies on targeted delivery of anticancer drugs.

1.6.1.5 Water Purification:

Permeation of water through the membrane was attributed to swelling of GO structures, which enables a water penetration path between individual GO layers. The interlayer distance of dried Hummers graphite oxide was reported as 6.35 Å, but in liquid water it increased to 11.6 Å. The permeation rate of the membranes for the water is 0.1 mg/min/cm², and the diffusion rate of water is 1 cm/h. GO membranes were also actively studied in the 1960s for application in water desalination, but they were never used for practical applications (Joshi, 2014). Retention rates more than 90% were reported in this study for NaCl solutions using stabilized GO membranes in a reverse osmosis setup. GO membranes could be used for the filtration of sea water. GO film is super thin (just one single atom thick), so the water simply “pops through the very, very small holes that are in the graphene and leaves the salt behind.”

1.6.1.6 Coating Technology:

GO membranes were also actively studied in the 1960s for application in water desalination. Retention rates more than 90% were reported in this study for NaCl solutions using stabilized GO membranes in a reverse osmosis setup. GO membranes could be used for the filtration of sea water. GO film is super thin (just one single atom thick), so the water simply “pops through the very, very small holes that are in the graphene and leaves the salt behind.”

1.6.1.7 GO Composite & Paper-like Materials:

GO mixes readily with many polymers, forming nanocomposites, and greatly enhances the properties of the original polymer, including elastic modulus, tensile strength, electrical conductivity, and thermal stability. In its solid form, GO flakes tend to attach to one another, forming thin and extremely stable paper-like structures that can be folded, wrinkled, and stretched. Such free-standing GO films are considered for applications including hydrogen storage applications, ion conductors, and nanofiltration membranes.

1.7 Graphene Containing Polymer Hydrogel:

Polymer hydrogel is a soft 3D reticular material, which can absorb and store a large amount of water, but cannot dissolve in water. Due to its good biocompatibility, the hydrogel can be applied in bioengineering, such as biologic tissues, drug delivery, and artificial cartilage. [26] [27] In addition, various kinds of functional monomers and macromeres enlarge the application of hydrogels with enhanced mechanical, biological, and physicochemical properties. [28] [29] However, most hydrogels have high moisture content, low mechanical properties, which limit their practical applications. In the early reports, graphene based hydrogels have been reviewed wherein the graphene is the major component in the hydrogels [30] [31] [32] [33] [34] In the polymer based hydrogel category, graphene as additive is introduced into polymer hydrogel matrix and introduction of graphene could enable the composite hydrogel with excellent properties in various respects, including mechanics, electricity, optics, heat conduction, and bio-technology. For example, GO containing oxygen group (including carboxyl, hydroxyl, carbonyl and epoxy group) can improve the interactions between GO and polymers, thus increase their mechanics properties. [35]

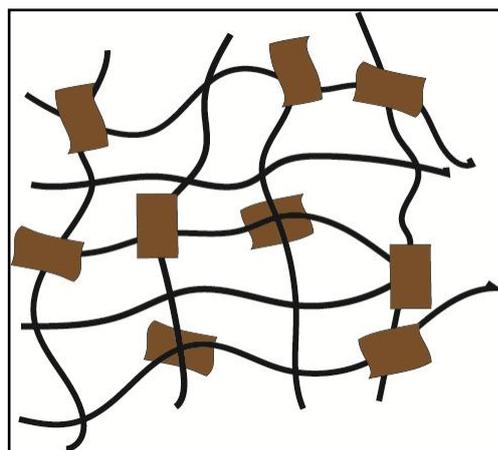


Fig. 1.6: GO containing polymer hydrogel

1.7.1 Preparatory Methods of GO Containing Hydrogel:

1.7.1.1 Simple Solution Mixing:

The simple method to prepare polymer–graphene hydrogel is by blending graphene dispersion with preformed polymer hydrogels. This method demands the polymers soluble in water. First, it requires dissolving a certain amount of polymer into a large quantity of water, followed by addition of graphene dispersion with sonication. Then, an appropriate increase of temperature leads to the evaporation of water and formation of polymer–graphene composite hydrogels. Several water soluble polymers could be applied with this method, such as polyvinyl alcohol (PVA), [36] poly(acrylic acid) (PAA), [37] and chitosan (CS). [38]

1.7.1.2 Freezing-Thawing Method:

The freezing–thawing method is a cheap and simple technique to prepare hydrogels. First, the polymer is dissolved into water by stirring to ensure the dissolution of polymer and the formation of a homogeneous solution. Then the polymer solution and the GO dispersions are thoroughly mixed by ultrasonication. Finally, hydrogels are obtained by directional freezing–thawing of the mixed solutions after several cycles.

1.7.1.3 Shaking and Sonication:

When polymer and GO are dispersed into water, hydrogels can also be obtained by simple shaking. For example, Lee and co-worker [34] reported that PVA–GO hydrogel was obtained by addition of GO dispersion into PVA solution and followed by shaking the mixtures for 3s. Xu and co-workers [35] also fabricated PVA–GO hydrogel by a similar method, where the mixtures were shaken violently for 50 s and further treated by sonication for 20 min. Although this method is very simple, GO may not be well distributed in the mixed systems and the resulted composite hydrogels behave poor mechanical properties.

1.7.1.4 *In-situ* Polymerization:

In situ polymerizations can generally be divided into two categories: thermal-initiated *in situ* polymerization and radiation-initiated in premix of the monomer and GO aqueous dispersion, making the monomer insert into the GO sheets, and then the polymer–graphene hydrogels could be obtained by addition of peroxide initiators such as ammonium persulfate and potassium persulfate (KPS) under heating. Compared to thermal-initiated polymerization, radiation-initiated polymerization requires radiation such as γ -ray [39] [40] and UV radiation [41] [42] as thermal source instead of heating. This method is especially important for some high purity of materials because of no any initiator needed in the system.

1.7.1.5 Addition of Chemical Cross-linkers:

Recently, to obtain good mechanical properties of the hydrogels, addition of chemical cross-linker was also used during synthesis of hydrogels. Compared to that of hydrogel by physical interaction, the mechanical strength of the chemical cross-linked hydrogels is highly enhanced. MBA is the most used chemical cross-linker. For example, Yang and co-workers [43] fabricated PAM–GO hydrogel. AM and MBA were first dissolved into water and then GO dispersion was added into the solution. Subsequently, ammonium persulfate was added into the mixture as an initiator. The mixture was transferred into mold and heated at 60°C for 2h in a vacuum oven. Finally, the resulting PAM–GO hydrogel was peeled off from the mold. By addition of chemical cross-linker, the mechanical properties can be increased obviously. There are many reports to demonstrate polymer graphene hydrogels such as PAM–GO hydrogel, [43] PAA–GO, [44] [45] and PNIPAM–GO hydrogel [46] by using chemical cross-linkers.

1.7.1.6 Addition of Metal-ion:

During the preparation of hydrogels, addition of metal ions or hydrophobic monomer into the system could also increase the interaction between GO sheets and polymer

matrix and result in the formation of composite hydrogels. As example, Xie and co-workers [47] fabricated PAA–GO hydrogels by addition of Fe^{3+} .

1.7.2 Properties & Application of Graphene Containing Polymer Hydrogels:

1.7.2.1 High Mechanical Properties:

Due to high water content, hydrogels exhibit low mechanical properties, which limit their applications. Traditional chemical cross-linking is used to increase the strength of hydrogels by increasing the cross-link density. However, the increased cross-linking density causes the mobility reduction of molecular chains, and therefore leads to the brittleness and hardness, which are restrictions on the application in various fields. GO with several functional groups on the surface (including carboxyl, oxhydryl, carbonyl, epoxy group, etc.) could increase the tensile strength of the polymer hydrogels to some extent. To improve the mechanical properties of hydrogels, introduction of chemical cross-linker is an efficient method. MBA (also abbreviated BIS) is a commonly used chemical cross-linker. For example, Ye and co-workers [45] introduced MBA into the PAA–GO physical cross-linked hydrogel. PAA–MBA–GO hydrogel exhibits good mechanical property with tensile strength of about 27 kPa at elongation of about 300%. Compared to that of hydrogel without GO, the PAA–MBA hydrogel readily breaks at low deformation in elongation and its elongation at break is close to 70%. For polymer graphene hydrogels, the fabrication process is very simple and there are various approaches to fabricate polymer hydrogels containing graphene as discussed in the synthesis section. In addition, introduction of graphene could not only provide the polymer hydrogel with enhanced mechanical properties but also enable the composite polymer hydrogel with special properties, such as electricity, optics, heat conduction, and biotechnology.

1.7.2.2 Self-Healing Property:

During the process of application, lots of tiny cracks will appear in the hydrogels. With the crack growth, the overall network structure of the hydrogel can be destroyed, therefore impairing its mechanical properties and shortening its service life. In order

to overcome this limitation, self-healing or self-healable hydrogels have attracted much attention, which can regain the lost functions or rebuild the destroyed structures. In terms of the healing mechanism, self-healing hydrogel can be classified into physical and chemical self-healing hydrogel. [48] Either physical or chemical cross-linking hydrogel keeps the dynamic balance of the network of hydrogel under the self-healing process involving physical interactions or dissociation and reconstruction of chemical bonds. GO can efficiently improve the mechanical properties of hydrogel mainly because oxygen-containing groups on the surface of GO sheets can form cross-linking network with polymers through a large amount of hydrogen bonds. This kind of reversible physical cross-linking enables the realization of the self-healing property of polymer–GO nanocomposite hydrogel. [49]

1.7.2.3 Stimuli-Responsive Properties:

Since the pioneer work of Tanaka, who found that PNIPAM hydrogel was responsive to temperature, [50] stimuli-responsive hydrogels have received much attention due to their multi-applications. The driving process of hydrogel actuator is generally realized by the swelling or deswelling guided by the response to the environment changes, including temperature, pH, light and electric field, etc. Because graphene has been proved to have the ability of high photo-thermal conversion efficiency, light-responsive graphene containing hydrogels have been widely reported. [51] [52] These properties can contribute to the potential application such as artificial sensing material. Additionally, GO has the ability to transfer solar energy into heat energy, which can be used to prepare photo-thermal hydrogel for the application of photo-materials. [53]

1.7.2.4 Shape Memory Properties:

Shape memory hydrogels are a special kind of stimuli-responsive soft material, which can recover the initial permanent shape from temporary shapes triggered by external stimulus. In some previous research shows small amount of GO in the hydrogels ($\leq 1.5 \text{ mg mL}^{-1}$) played a key role in NIR energy absorption and transformation into

thermal energy. The hydrogel without GO showed nonresponse to the NIR irradiation and cannot recover to its permanent shape by NIR irradiation.

1.7.2.5 Other Properties:

Graphene can make great contribution to the improvement of the mechanical property, self-healing property, stimuli-response property, and absorbability of polymer–graphene nanocomposite hydrogel. Additionally, due to its high surface area and electrical conductivity, graphene could also be incorporated into conductive polymer hydrogels used for electrical device (e.g., super capacitor). Several conductive polymers including poly-aniline, [54, 55] polypyrrole, [56] and polyhydroquinone[57] have been used for this application. Additionally, graphene-containing polymer hydrogel due to its biocompatibility can be used as biosensor, imaging agent, drug delivery carrier, etc. [58] [59] [60] In particular, GO is an effective component in the composite hydrogel for the adjustment of cell behaviors and biological sequences due to its special surface properties.

1.8 Literature Review:

Polymers and polymer composites are ubiquitous in our daily lives. Improvement of mechanical and thermal properties of polymeric materials along with self-healing and stimuli-responsiveness is one of the key attentions nowadays in this field. One of the major ways to introduce new properties or enhance the available properties of polymers is by the incorporation of suitable fillers into the polymer matrices. Silica, titania, noble metal nanoparticles, graphene or graphene oxide (GO) and carbon nanotubes are commonly used fillers. Among these nanomaterials, GO has extraordinary physical and chemical characteristics [62][63] such as high mechanical and thermal stability [64], super adsorption property, excellent bio-sensing and electrical capacity [65][66] etc. GO containing polymers especially hydrogels of poly(acrylic acid) adopt these characteristics and enhance acceptance and usability of the hydrogel [67][68]. However, in most of these works, GO is present in the polymers as additive materials or fillers [69][70][71].

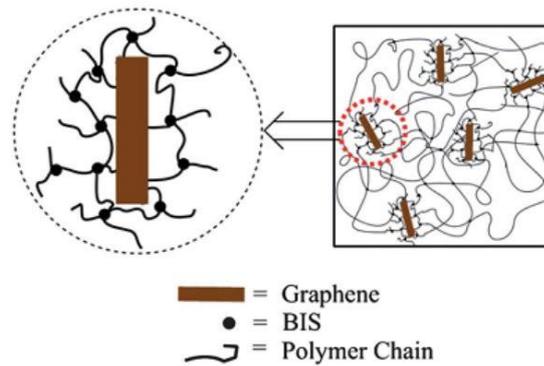


Fig. 1.7: Illustration of the microstructure that related to the specific combination of GO sheets and BIS [45]

Hydrogels	Tensile strength [kPa]	Elongation at break [%]	Elastic modulus [kPa]	Toughness [MJ m ⁻³]
PAM-GO	385	3435	28.5	4.74
PAA-MBA-GO	27	300	-	-
PNIPAM-MBA-GO	180	1500	14.8	-
PAM-SDBS-GO	155	2869	36.6	-
MeTro-GO	18	203	19.3	-
PAM-Ca ²⁺ -GO	143	1100	31.6	-
PAACA-Ca ²⁺ -GO	65.8	1190	-	-
PAA-Fe ³⁺ -GO	777	2980	50.7	11.9
PAM-GPO	650	3500	52	-
PAA-HB-GO	251	745	265	-
Clay-PDMAA-GO	184	1890	-	-

Table 1.1: Comparison of the tensile mechanical properties of various hydrogels[61]

But in the proposed research, core aim is to fabricate a cross-linked polymer composite where acrylic functionalized graphene oxide will be employed as a cross-linker containing a large number of active sites. It is well-established that the cross-linked polymers using traditional cross-linkers show enhanced mechanical properties but the increase of cross-linker density in polymers may leads to immobility of molecular chain, hardness and brittleness which limits the fields of its application. Therefore, a graphene-cross-linked polymers, as described in this

proposal, are expected to overcome the drawbacks of the traditionally cross-linked counterparts by enhancing the mechanical and thermal stability of the polymers.

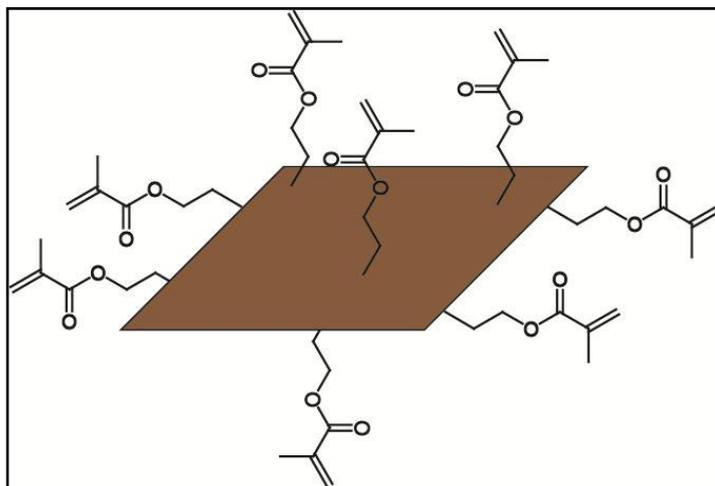


Fig. 1.8: Graphene oxide based 2D cross-linker (GOBC)

1.8.1 Aims of Current Research:

The core aim of the research is to fabricate graphene-cross-linked polymers for improved mechanical and thermal properties. Acrylic functionalized graphene oxide will be synthesized and consequently used as a 2D cross-linker in *in-situ* polymerization of acrylic acid. The aims of this research are:

- to synthesis a novel acrylic functionalized graphene oxide (AFGO) which is employed as graphene oxide based 2D cross-linker (GOBC)
- to synthesis of graphene oxide based polymer composite (GOPC) by cross-linking poly(acrylic acid) (PAA) using AFGO and to characterize the composite material by performing FTIR, UV, SEM, EDS
- to investigate of mechanical strength and thermal behaviour of GOPC by employing UTM and TGA/DSC.

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CHAPTER-2

Experimental

2.1 Materials & Instruments:

2.1.1 Chemicals & Reagents:

- 1) Graphite powder (Sigma Aldrich Chemical Co.)
- 2) Sulfuric acid (Merck, Germany)
- 3) Nitric acid (Merck, Germany)
- 4) Sodium nitrate (Merck, Germany)
- 5) Potassium permanganate (Merck, Germany)
- 6) Hydrogen peroxide (Sigma Aldrich Chemical Co.)
- 7) Hydrochloric acid (Merck, Germany)
- 8) N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (Sigma Aldrich Chemical Co.)
- 9) N-Hydroxysuccinimide (NHS) (Sigma Aldrich Chemical Co.)
- 10) 2-Aminoethyl methacrylate hydrochloride (AEM)
- 11) Acrylic acid (Sigma Aldrich Chemical Co.)
- 12) Potassium persulfate (KPS) (BDH)
- 13) N,N'-Methylene bis(acrylamide) (BIS) (Sigma Aldrich Chemical Co.)

2.1.2 Instruments:

Synthesis, characterization and data analysis were performed by using following instruments:

- 1) Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400)
- 2) UV/Visible spectrophotometer (Shimadzu-1800)
- 3) Field emission scanning electron microscope (JSM-7600F, Tokyo, Japan)
- 4) Energy-dispersive x-ray spectroscope (JSM-7600F, Tokyo, Japan)
- 5) Thermo-gravimetric analyzer (Netzsch, 449F3)
- 6) Differential scanning calorimeter (Netzsch, 449F3)

- 7) Universal testing machine (Testresourses, 100P250-12 System)
- 8) Centrifuge machine (Hettich, Universal 16A)
- 9) Freeze dryer (Heto FD3)
- 10) Oven (Lab Tech, LDO-030E)
- 11) Vacuum drying oven (HYSC, VO-27)
- 12) Ultrasonicator (Powersonic 603)
- 13) Shaker machine (Stuart, Orbital shaker, SSL1)
- 14) Digital Balance (AB 265/S/SACT METTLER, Toieto, Switzerland)
- 15) Hot plate & magnetic stirrer (Snidjers, 34532)

2.2 Method of Preparation:

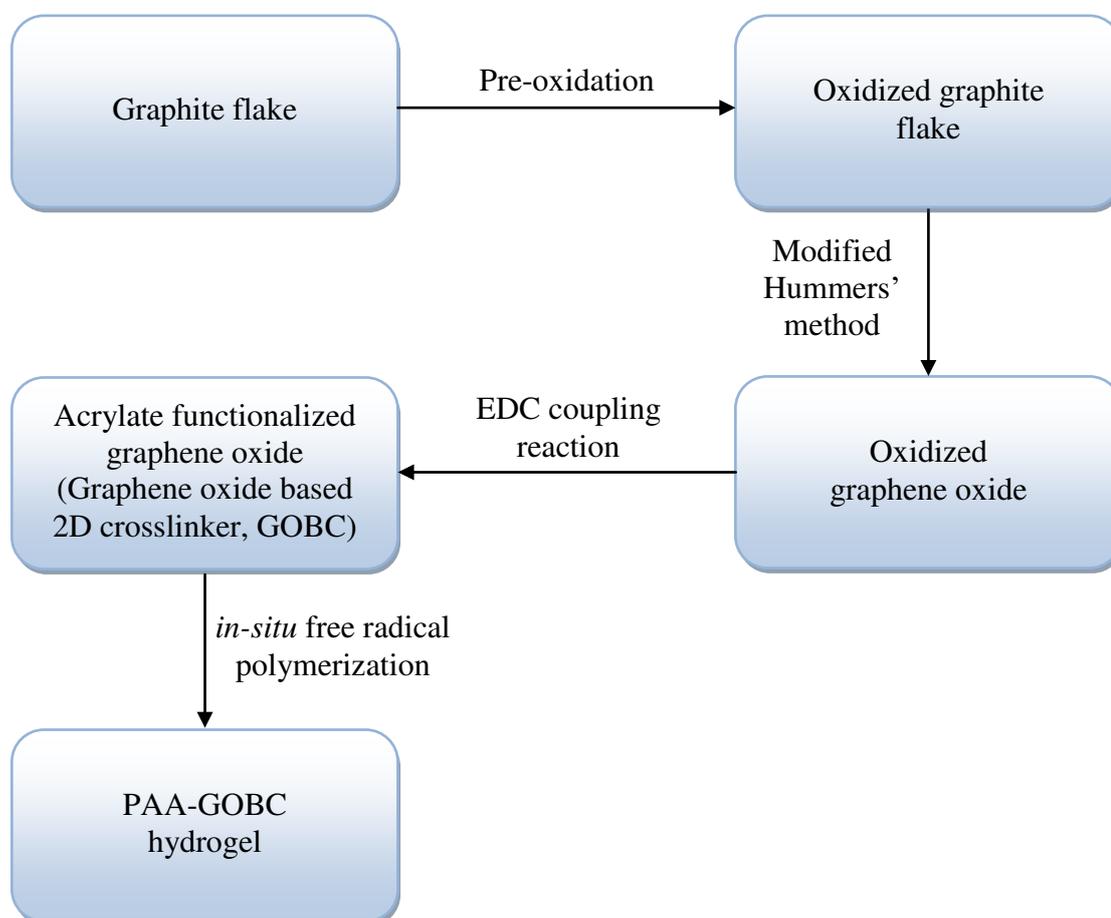


Fig 2.1: Schematic illustration of preparation of PAA-GOBC hydrogel

2.2.1 Preparation of Oxidized Graphene Oxide (OGO):

Oxidized graphene oxide (OGO) was synthesized from synthetic graphite powder according to the modified Hummers' method. 2g of graphite powder was put into a solution of concentrated H_2SO_4 (12mL) and HNO_3 (8mL) at 80°C . The mixture was kept at 80°C for 8h using a water-bath. After cooling to room temperature, the mixture was diluted with 0.5L of de-ionized (DI) water and left overnight. Then, the mixture was filtered and washed with DI water using to remove the residual acid. The product was dried under ambient condition overnight. This pre-oxidized graphite was then subjected to oxidation by Hummers' method described as follows: pretreated graphite powder (1g), NaNO_3 (1.03g), and concentrated H_2SO_4 (62g) were placed in a flask. Then, 4.5g of KMnO_4 was slowly added under stirring and the temperature of the mixture was kept to below 20°C for 2h. After further vigorous stirring for 2days at room temperature, the reaction was terminated by the addition of DI water (140mL) and 30% H_2O_2 solution (2.5mL).



Fig 2.2: Schematic illustration of preparation of graphene oxide (GO)

The mixture was filtered and washed by repeated centrifugation and filtration, first with 1M HCl aqueous solution and then with DI water. DI water (50mL) was added to the final product, which was subjected to ultrasonication. The obtained mixture was

dialyzed through semi-permeable membranes for one week to remove the remaining metal species. Finally, the resulting solid was dried in air and diluted to make an OGO dispersion (0.1mg/mL). The resulting homogeneous yellow-brown dispersion was tested to be stable for several months and used for further functionalization. [1]

2.2.2 Preparation of GO Based 2D Cross-linker:

The preparation of GO based 2D cross-linker (GOBC) which is named as acrylic functionalized graphene oxide (AFGO) was similar to that used in some previous studies of amidation method. [2] 10mg of GO was sonicated in 10mL distilled water for 1h, and then 22mg of EDC and 10mg of NHS were added to the GO solution, which was stirred for 2h at 0°C. Finally, 24mg of 2-aminoethylmethacrylate hydrochloride (AEM) was added and stirred at room temperature overnight. The product AFGO was washed several times with H₂O to ensure that the excess AEM was completely removed. [3]

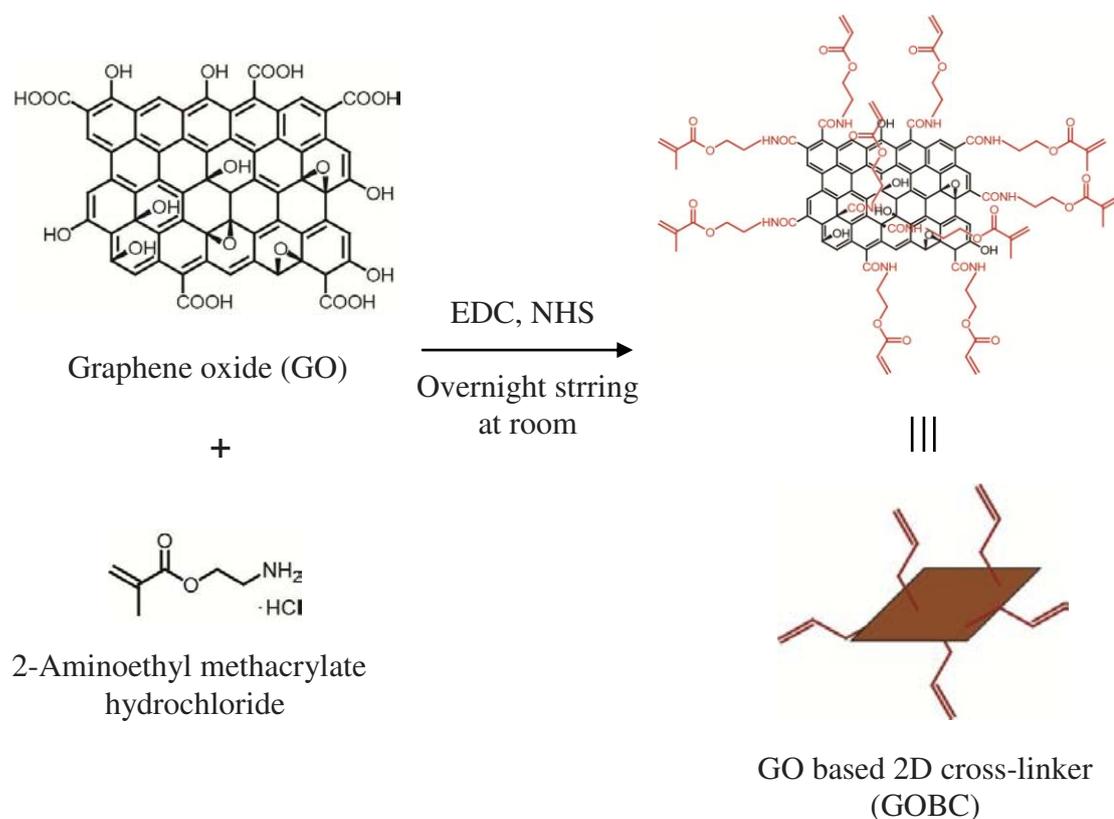


Fig 2.3: Schematic illustration of preparation of GO based 2D cross-linker

2.2.3 Preparation of 2D Cross-linked Poly(acrylic acid):

Cross-linked poly(acrylic acid) (PAA) hydrogels were prepared using initial solutions consisting of monomer (AA), cross-linker (GOBC/BIS) and initiator (KPS). In all cases, the initial solution contained 2times as much H₂O as monomer by weight. The water–polymer ratio in the resulting hydrogels was fixed at 2:1 (w/w). At first, AA (2g) was added to 1mL H₂O in a glass tube (interior size: 10mm diameter and 4inches length) with stirring at 55°C temperature. Next, 1mg GOBC (0.05wt% of monomer), 10mg KPS and 1mL H₂O were taken in a glass vial and ultrasonicated for 10minutes. Hydrogels were synthesized following a *in-situ* free radical polymerization of AA by adding the sonicated GOBC solution drop-wisely using a dropper to AA solution in the glass tube. The reaction is continued for 4hours at 55°C temperature.

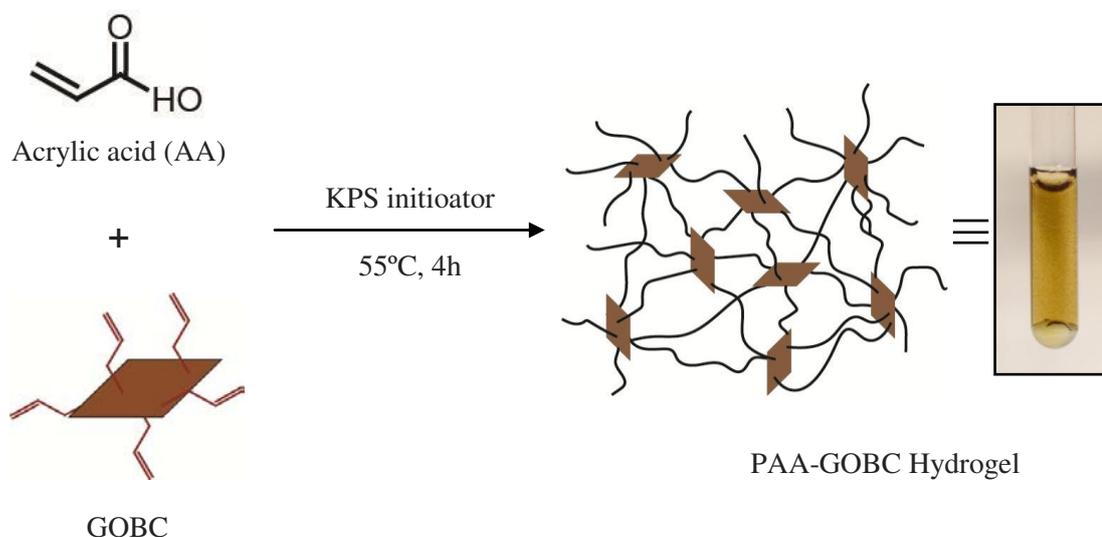


Fig 2.4: Schematic illustration of preparation of 2D cross-linked poly(acrylic acid) hydrogel (PAA-GOBC)

PAA-GOBC hydrogels of different GOBC contents (0.025 wt% and 0.01 wt%) were also prepared for different characterizations and analysis. Moreover, PAA hydrogels cross-linked with N,N'-Methylenebis(acrylamide) (BIS) of same cross-linker concentration (0.05 wt%, 0.025wt% and 0.01wt%) were also prepared for comparing the physical and thermal characteristics with PAA- GOBC.

2.3 Sample Characterizations:

2.3.1 Fourier Transform Infrared (FTIR) Analysis:

The infrared spectra of graphene oxide (GO), acrylate functionalized graphene oxide (AFGO) were investigated in FTIR spectrophotometer in the region of 4000-1000 cm^{-1} . After preparation, all of the samples were oven dried at 60 $^{\circ}\text{C}$ and small portion of samples were taken into vials. GO flakes were mechanically very strong, so it was grinded into a mortar with a pestle to get GO powder. Rests of the samples were not grinded because they were physically granule and powder after complete drying. FTIR spectra of the solid samples were frequently obtained by mixing and grinding a small amount of materials with dry and pure KBr crystals. The mixing and grinding were done in a mortar by a pestle. The powder mixture was then compressed in a metal holder under a pressure of 8–10tons to make a pellet. The pellet was then placed in the path of IR beam for measurements.

2.3.2 UV/Vis Absorption Analysis:

The UV/Vis absorption spectra of the aqueous suspensions GO and GOBC were measured on a double beam ultraviolet and visible spectrophotometer using quartz cells in the wavelength range of 200–800nm. The concentration of aqueous suspensions of GO and GOBC were 0.1mg/mL. The aqueous suspensions were ultrasonic treated for about 30min to make them stable.

2.3.3 Field Emission Scanning Electron Microscopy (SEM) & Energy-Dispersive X-ray Spectroscopy (EDS):

The surface morphology of the synthesized GOBC and PAA-GOBC (0.05wt %) were conducted using Field Emission Scanning Electron Microscopy (FE-SEM). The completely air dried samples were glued on a conducting carbon strip. The sample loaded strip was then mounted to a chamber that evacuated to $\sim 10^{-3}$ to 10^{-4} torr and then a very thin platinum layer (\sim few nanometers thick) were sputtered on the sample to ensure the conductivity of the sample surface. The sample was then placed in the

main SEM chamber to view its surface. The microscope was operated at an accelerating voltage of 5.0kV. Energy dispersive x-ray spectroscopy (EDS) of GOBC and PAA- GOBC (0.05wt %) were also done by the same instrument at that time.

2.3.4 Thermogravimetric Analysis (TGA):

The thermal stability of PAA-GOBC (0.05wt%) and PAA-BIS (0.05wt%) were studied by a thermo-gravimetric analyzer (TGA) in a nitrogen atmosphere. Approximately 3-10mg freeze dried samples taken into an aluminum cell and heated from 27 to 800°C at a heating rate of 10°C/min under a nitrogen flow of 10mL/min. Before the data acquisition segment, the sample was equilibrated at 25°C for 5 min to obtain an isothermal condition.

2.3.5 Differential Scanning Calorimetry (DSC):

Differential scanning calorimetry (DSC) is a technique used to investigate the response of polymers to heating. The aim of this experiment is to find glass transition temperature (T_g) and melting temperature (T_m) as well of the latent heats of crystallization and melting for the specimens. The DSC set-up is composed of a measurement chamber and a computer. Two pans are heated in the measurement chamber. The sample pan contains the material being investigated. A second pan, which is typically empty, is used as a reference. The computer is used to monitor the temperature and regulate the rate at which the temperature of the pans changes. A typical heating rate is around 10°C/min.

The T_g , T_c , and T_m of neat PAA-GOBC (0.05 wt%) and PAA-BIS (0.05 wt%) were recorded by a DSC in a nitrogen atmosphere. Approximately 3-10 mg freeze dried samples taken into an aluminum pan and heated from 30 to 800°C at a heating rate of 10°C/min under a nitrogen flow of 10mL/min.

2.3.6 Study of Swelling Kinetics of PAA-GOBC Hydrogel:

0.075 g of freeze-dried hydrogel was placed in a 250 ml beaker and 150ml distilled water was added. The swollen sample were removed from water and weighed after blotting off the remaining water on the sample surface with a filter paper. The swelling ratio was defined as the weight ratio of the net liquid uptake to the dried hydrogel. Swelling ratio was determined by the following equation:

$$\text{Swelling ratio} = \frac{m_s - m_d}{m_d} \times 100$$

Where, m_s is the mass of swollen hydrogel in equilibrium at a given temperature and m_d is the dry mass of sample.

2.3.7 Mechanical Properties Analysis:

All hydrogels were prepared in cylindrical shapes with 10mm diameter and 4inch length before the uniaxial tensile measurement was conducted. The tensile measurement was conducted on a Test Resources universal testing machine (UTM) at ambient temperature, with the crosshead speed of 100mm/min, and initial jaws of 10 mm. The stress (from the initial cross-section ($A=\pi r^2$) of 74.58mm²) and strain were recorded. The stress (σ) was calculated according to the equation,

$$\sigma = F/\pi r^2$$

Where, F is the recorded load and r is the original radius of the specimen.

The strain (ε) was calculated from the change of the fracture length (l) to the initial gauge length (l_0) of the measured sample, and was calculated by the equation,

$$\varepsilon = \frac{l}{l_0} \times 100$$

The initial modulus was calculated as the initial slope of the stress-strain curve. The fracture toughness was calculated by integrating the area underneath the stress-strain curve of each sample.

References:

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CHAPTER-3

Result & Discussion

0.1 Synthesis of GO Based 2D Cross-linker (GOBC):

Functionalization of GO can fundamentally change the properties of GO. The resulting chemically modified graphene could then potentially become much more adaptable for many applications. There are many ways in which GO can be functionalized, depending on the desired application. NHS is used to prepare amine-reactive esters of carboxylate groups for chemical labeling, cross-linking and solid-phase immobilization applications. Carboxylates (-COOH) may be reacted to NHS in the presence of a carbodiimide such as EDC, resulting in a semi-stable NHS ester, which may then be reacted with primary amines (-NH₂) to form amide cross-links (Fig. 3.1). Although NHS is not required for carbodiimide reactions, their use greatly enhances coupling efficiency.

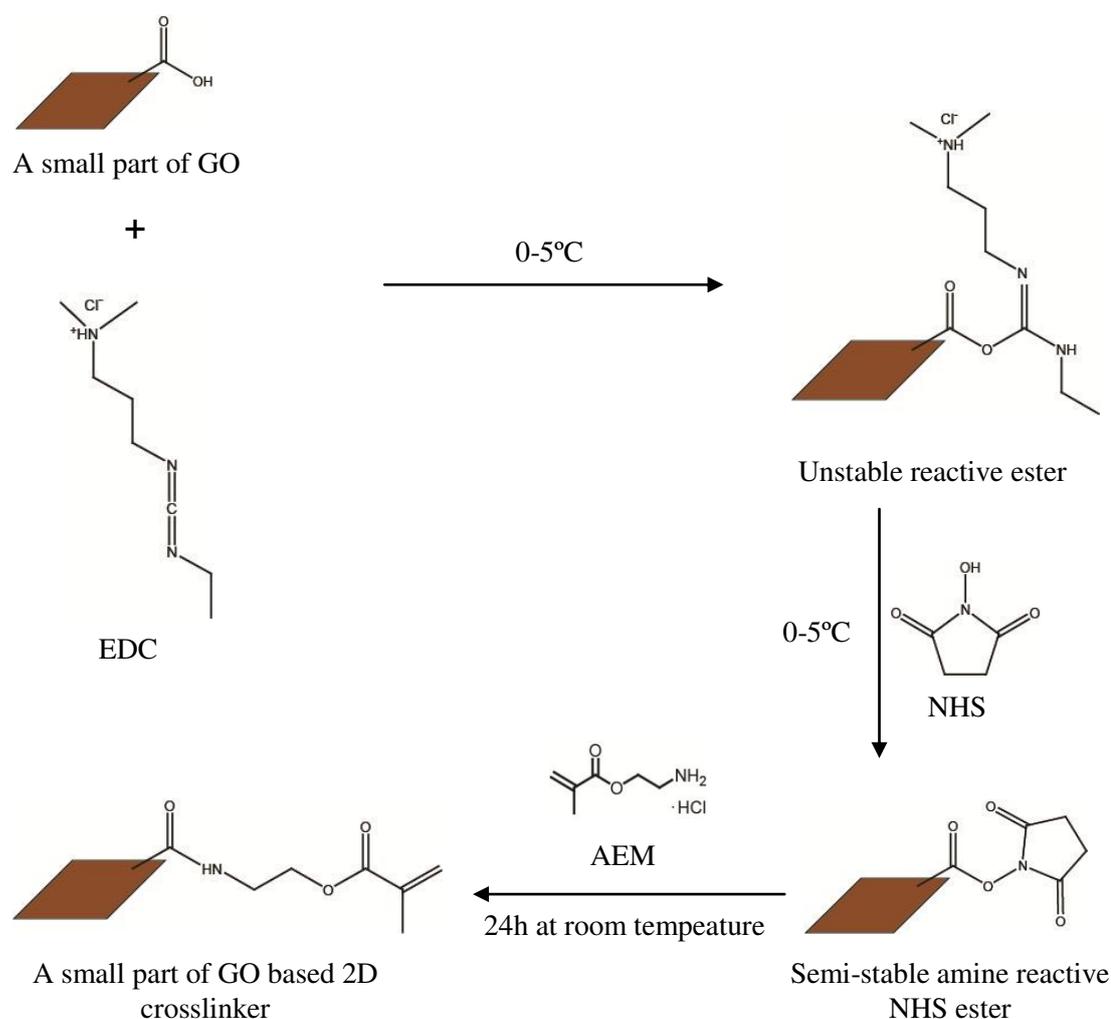


Fig. 3.1: Schematic illustration of synthesis of GO based 2D cross-linker

0.1.1 Functional Group Investigation by Fourier Transform Infrared Spectroscopy (FTIR):

Evidence of successful functionalization of GO can be provided by FTIR spectra (Fig. 3.2). In the FTIR spectrum of GO, FTIR absorption peaks at 3453, 1742, 1630, 1400, 1232, and 1061 cm^{-1} are assigned to O-H stretching mode, C=O in carboxylic acid and carbonyl groups, C=C skeleton vibrations of unoxidized graphitic domains, C-H in-plane stretching, epoxy C-O-C stretching, and alkoxy C-O stretching, respectively. [1]

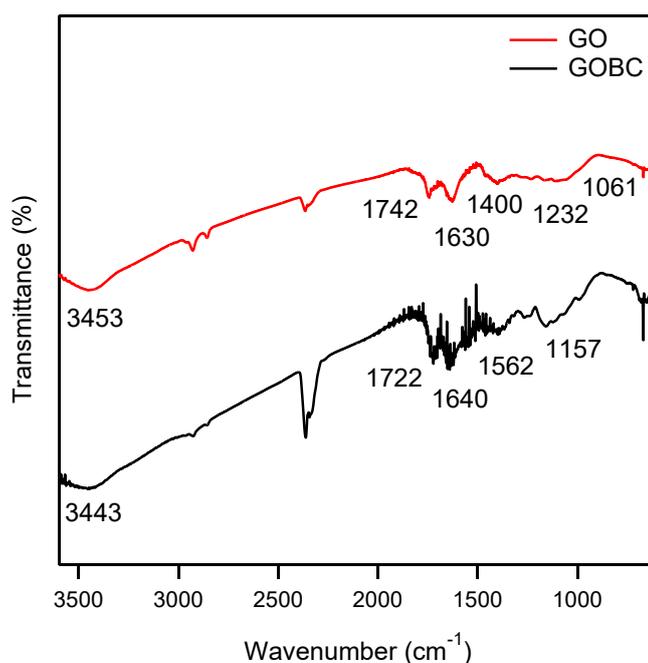


Fig. 3.2: FTIR spectra of GO & GOBC

In the case of GO based 2D cross-linker (GOBC), a peak at 3443 cm^{-1} attributed to N-H stretching, which overlapped with a broad peak arisen from carboxylic acid stretching, can be seen. Other outstanding differences are observed in the appearance of the two peaks at 1562 and 1157 cm^{-1} attributed to N-H bending and C-N stretching. A remarkable peak at 1640 cm^{-1} corresponds to stretching of NHCO bond. Hence, FTIR analysis confirms the covalent functionalization of GO by 2-Aminoethyl methacrylate hydrochloride is done successfully. [2] [3] [4] [5]

Table 3.1: Characteristic peaks and interpretations correspond to GO & GOBC

Wavenumber (cm^{-1})	Interpretations correspond to GO	Wavenumber (cm^{-1})	Interpretations correspond to GO
3453	O-H stretching	3443	N-H stretching
1742	C=O of carboxylic	1722	C=O of methacrylate
1630	aromatic C=C	1640	-NHCO- stretching
1400	C-H in-plane stretching	1562	N-H bending
1232	epoxy C-O-C stretching	1157	C-N stretching
1061	alkoxy C-O stretching		

0.1.2 UV/Vis Absorption Spectra Analysis:

Fig. 3.3 shows the UV/Vis spectra of stable aqueous suspensions of GO and GOBC. The curve of GO dispersion exhibits a maximum at 230nm and a tiny shoulder at 300nm, which are attributed to $\pi-\pi^*$ transitions of aromatic C-C bonds and $n-\pi^*$ transitions of C=O bonds, respectively. [1] [6] [7] Amino functionalization causes a clear bathochromic red-shift of the GO. Due to the formation C-N bond, an $n-\pi^*$ transitions occurs which corresponds at 211nm in the spectra. [8] [3]

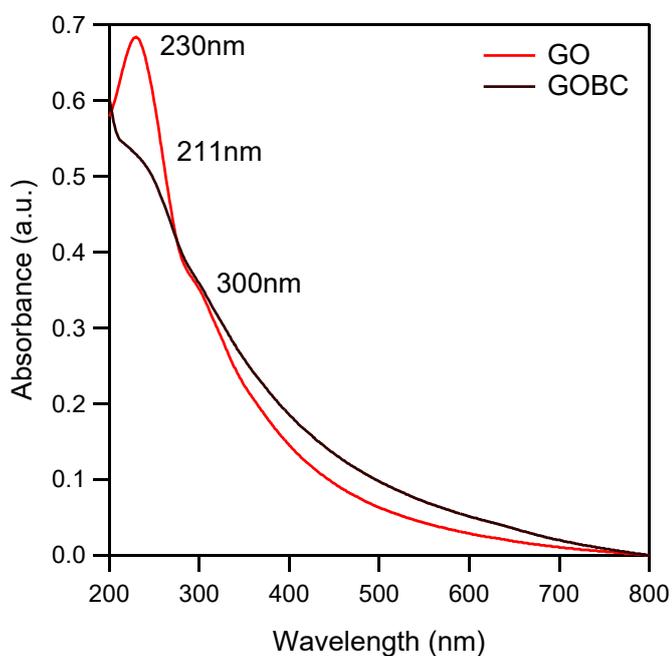


Fig. 3.3: UV/Vis spectra of GO & GOBC

0.1.3 Study of Surface Morphology of GOBC Using Field Emission Scanning Electron Microscopy (SEM):

Surface morphology of prepared GOBC is further studied from the SEM analysis. The SEM images of GOBC are shown in Fig. 3.4 a) and b) respectively. GOBC sheets are informally folded on each other with many ripples and seem to form the tangled patches. Between the crosswise edges of the multi-layer of GOBC a porous network with a size ranging from 100 to 500 nm, is clearly observable. These specifications could be related to the hydrogen bending of amino surface functional groups. [2] [9] [10]

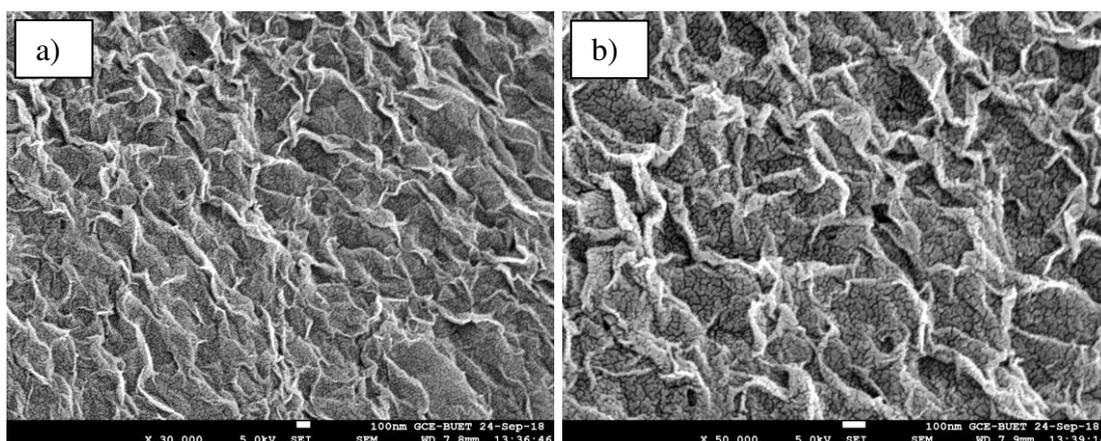


Fig. 3.4: SEM image of a) GOBC with magnification $\times 30,000$ and b) GOBC with magnification $\times 50,000$

0.1.4 Energy-Dispersive X-ray Spectroscopy (EDS/EDX) Analysis of GOBC:

The EDS elemental mapping (Fig. 3.5) of carbon, oxygen and nitrogen of a large area of GOBC dispersed powder illustrate distribution of N functionalities on the graphene structure. The EDS elemental analysis, which is given in Table 3.2, reveals 58.61, 11.20, 30.18 mass % and 64.50, 10.70, 24.93 atom% for C, N and O respectively. This analysis confirms the presence of nitrogen containing functional group on the surface of graphene oxide. [2] [9]

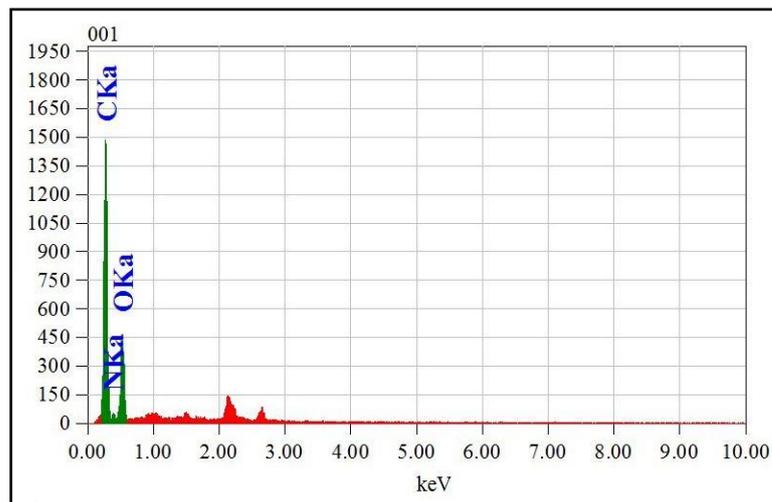


Fig. 3.5: EDS spectra of GOBC

Element	(keV)	mass %	atom %
C	0.277	58.61	64.50
N	0.392	11.20	10.70
O	0.525	30.18	24.93

Table 3.2: EDS elemental analysis of GOBC

0.2 Synthesis of GO Based 2D Cross-linked Poly(acrylic acid) (PAA-GOBC):

To prepare polymer composite, the *in situ* polymerization technique is attractive since it enables control over both the polymer architecture and the final structure of the composites. The key point of this approach relies on good dispersion of cross-linker in solvent, followed by *in situ* polymerization initiated by heat. Since cross-linker can be thoroughly exfoliated in water, it is very suitable to be used in preparation of hydrogel composites. In this research, GO based 2D cross-linked polymer composite is prepared through an *in situ* polymerization technique between acrylic acid (AA) monomer and GO based 2D cross-linker (GOBC) in presence of potassium persulfate

(KPS) at 55°C temperature. The schematic illustration of preparation of 2D cross-linked poly(acrylic acid) is given below:

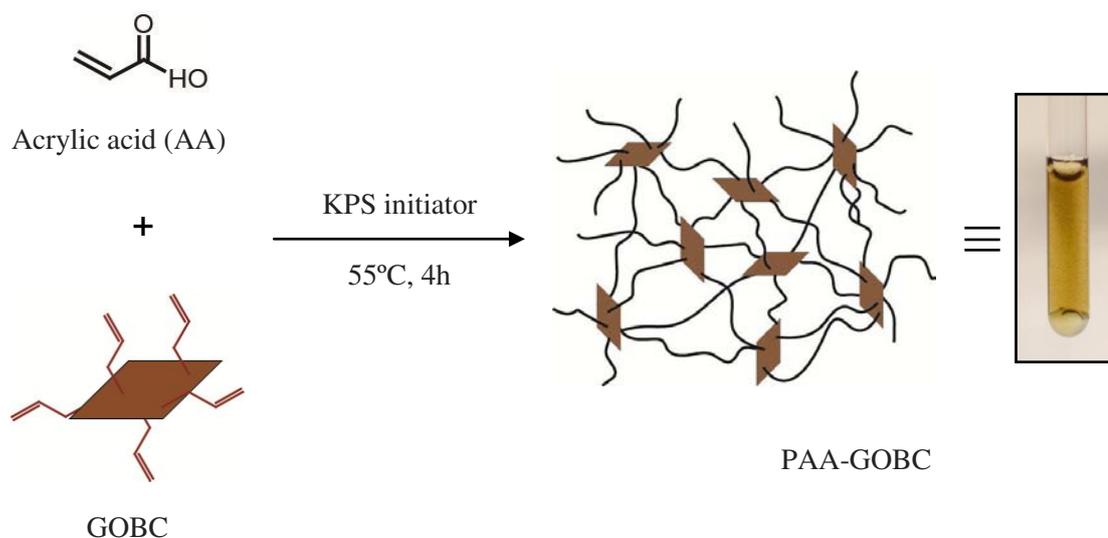


Fig 3.6: Schematic illustration of preparation of 2D cross-linked poly(acrylic acid) hydrogel (PAA-GOBC)

0.2.1 Study of Surface Morphology of PAA-GOBC Using Field Emission Scanning Electron Microscopy (SEM):

Morphological characterization on PAA-GOBC hydrogels was done through SEM. It can be seen that the morphology of the hydrogel is quite uniform in large scale (Fig. 3.7a). The image shows the presence of small sheets of GOBC uniformly dispersed in the polymer matrix of PAA-GOBC. Closer observation (Fig. 3.7b) shows that the hydrogels exhibit a three-dimensional network of randomly oriented sheet-like structures with wrinkled texture. The SEM images suggest that the GOBC sheets indeed behaved as a cross-linker. The covalent bonds of GOBC took part in the radical polymerization of AA. The bonding of multiple sites on the surface of GOBC sheets hence led to cross-link reactions during the polymerization. In other words, the GOBC sheets are like chemical cross-linkers leading to the successful formation of hydrogels. SEM images of the freeze-dried supramolecular hydrogels demonstrated that both supramolecular native and hybrid hydrogels exhibited a loose sponge-like

structure indicating the leakage or removal of the trapped water molecules during freeze-drying. [11] [12]

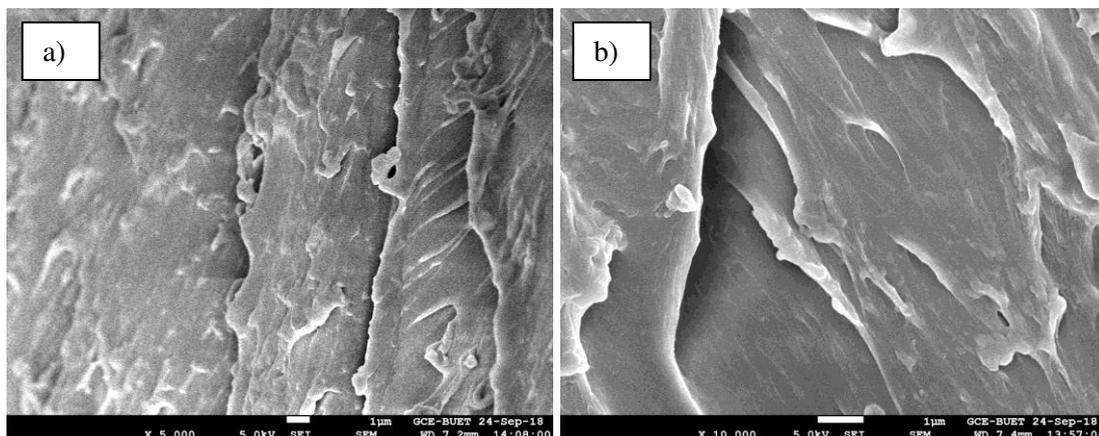


Fig. 3.7: SEM image of a) PAA-GOBC with magnification \times 5,000 and b) PAA-GOBC with magnification \times 10,000

0.2.2 Energy-Dispersive X-ray Spectroscopy (EDS/EDX) Analysis of PAA-GOBC:

Elemental analysis of carbon, oxygen and nitrogen in a large area of PAA-GOBC which is given in Table 3.3, reveals 62.23, 11.46, 26.32 mass% and 67.75, 10.73, 21.52 atom% for C, N and O respectively.

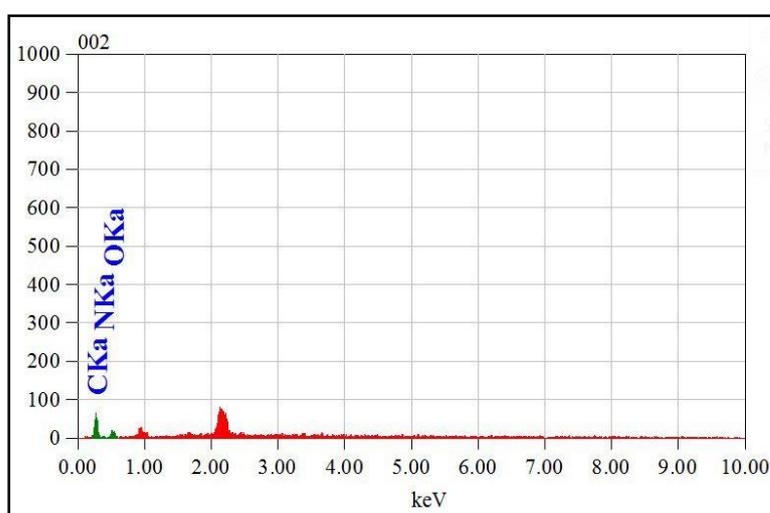


Fig. 3.8: EDS spectra of PAA-GOBC-0.05%

Element	(keV)	mass %	atom %
C	0.277	57.28	63.21
N	0.392	11.81	11.17
O	0.525	30.92	25.62

Table 3.3: EDS elemental analysis of PAA-GOBC-0.05%

0.2.3 Thermogravimetric Analysis (TGA) of PAA-GOBC hydrogel:

A thermogravimetric analysis of the PAA-GOBC-0.05% hydrogel and PAA-BIS-0.05% hydrogel was carried out provided some useful information on thermal properties of these materials. Fig. 3.9 illustrates the TGA curves of PAA-GOBC-0.05% hydrogel and PAA-BIS-0.05% hydrogel and the data are summarized in Table 3.4. A small first loss of mass is observed in the range of 100-200°C temperature and is attributed to the removal of water molecules trapped inside the hydrogel structure. The first obvious weight loss for both hydrogels were observed in the range of 200-300°C, indicating that the pyrolysis of oxygen containing functional groups of hydrogels. Another major degradation observed in 300-450°C temperature range corresponds to decomposition of cross-linked polymer networks. TGA analysis of PAA-GOBC-0.05% and PAA-BIS-0.05% is confirmed that both hydrogels have similar thermal stability. [12] [13]

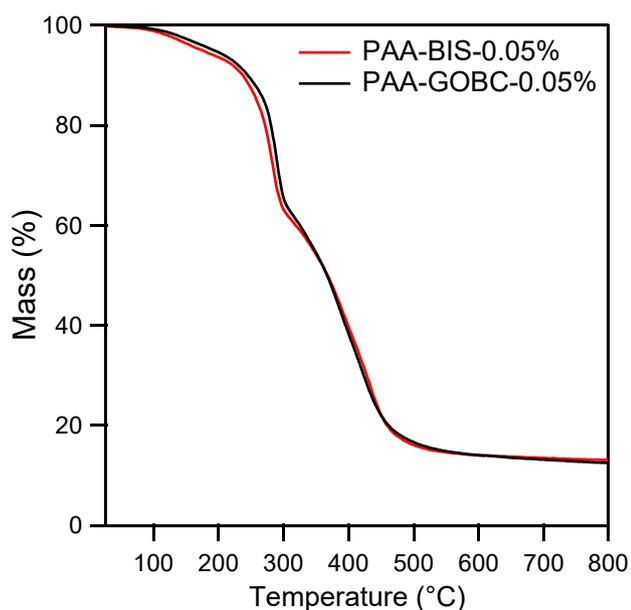


Fig. 3.9: TGA analysis of PAA-GOBC-0.05% & PAA-BIS-0.05%

Hydrogel	loss of weight (%) at temperature (°C)				
	200	300	400	500	600
PAA-GOBC-0.05%	5.39	34.55	61.72	83.34	85.96
PAA-BIS-0.05%	6.37	36.82	60.23	83.92	86.01

Table 3.4: Thermogravimetric data of PAA-GOBC-0.05% & PAA-BIS-0.05%

0.2.4 Differential Scanning Calorimetric Analysis of PAA-GOBC:

But DSC heating thermograms of PAA-GOBC-0.05% and PAA-BIS-0.05% are summarized in the Fig. 3.10. The curve of PAA-GOBC hydrogel exhibits higher T_g and T_m than PAA-BIS which is attributed to the presence of greater intermolecular force and cross-linking in PAA-GOBC hydrogel. So the DSC graphical representations are clearly illustrated better thermal stability of PAA-GOBC over PAA-BIS.

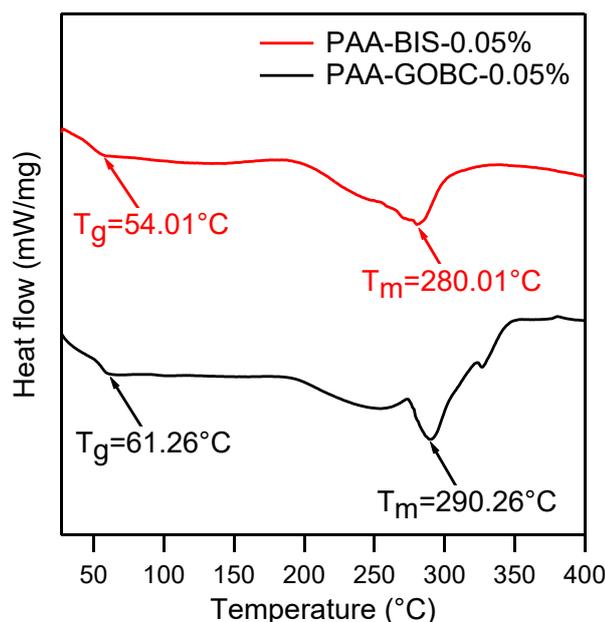


Fig. 3.10: DSC thermograms of PAA-GOBC-0.05% & PAA-BIS-0.05%

0.2.5 Study of Swelling Kinetics of PAA-GOBC Hydrogel

The swelling behavior is one of the important characteristic parameters for any hydrogel and is depending on the nature of the polymers and the environmental conditions (pH, temperature etc. of the medium). When a polymer network is in contact with an aqueous solution, the network starts to swell due to the thermodynamic compatibility of the polymer chains and water. Fig. 3.11 shows the swelling ratio (SR) as a function of time for the PAA-GOBC composite hydrogels in distilled water at 25°C. Initially the rates of swelling increased rapidly. The swelling ratio increased to 192.56 within initial 24h and then it approaches swelling equilibrium around 32h.

We continuously observed the hydrogel swelling behavior for more than 2 days and it was found that there is no apparent dissolving phenomenon; this result could be used to conclude that there is some kind of force maintaining the hydrogel network integrity. Because of chemical cross-linking agent is used during the hydrogel preparation process, the entanglement of polymer chains constructed the hydrogel network and the GOBC could be regarded as the ‘analogous cross-linking points’.

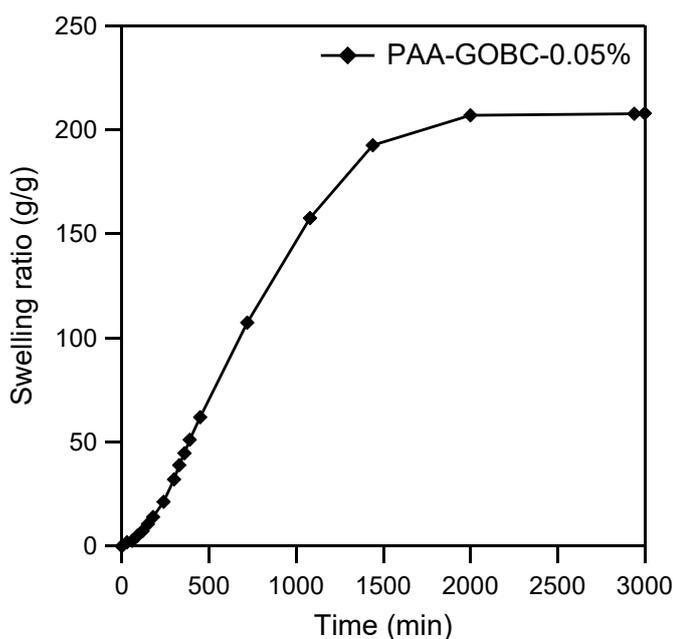


Fig. 3.11: Swelling kinetic curve of PAA-GOBC hydrogel

0.2.6 Mechanical Properties of PAA hydrogels:

PAA-GOBC-gels and PAA-BIS-gels are differed markedly with regard to their mechanical properties. Typical strain–stress curves for different weight (%) of cross-linker are given in Fig. 3.12. As can be clearly seen, the tensile strength and modulus of PAA-GOBC are very low compared with the mechanically toughened PAA-BIS. But PAA-BIS readily breaks at lower deformation in elongation and its elongation at break are in the range of 141% to 474%. On the other hand PAA-GOBC hydrogels show totally different tensile behaviour from those of PAA-BIS hydrogels, suggesting that a strong interaction exists among GO sheets and polymer matrix even in such a water-abundant hydrogel. The PAA-BIS hydrogels exhibit a brittle fraction, on the other hand, PAA-GOBC hydrogel exhibit rubber-like behaviour. Elongations of PAA-GOBC hydrogels are much higher (1492% to 1919%) than those of PAA-BIS hydrogels. As shown in Fig. 3.13, at constant water content, the elongations at break of PAA-GOBC hydrogels are completely dependent on GOBC content, while strength, modulus and elongation of PAA-GOBC hydrogels change with increasing GOBC content. At constant AA and water content content, the elongations at break of PAA-GOBC-0.025% was found the highest but the tensile strength and modulus of

this hydrogel were found comparatively lower than other two compositions. That means PAA-GOBC fracture readily on elongation increases with increase of GOBC content which indicates that higher content of cross-linker increases brittleness of hydrogel. Such a simultaneous improvement in elongation for polymer composites with a low amount of GO sheets is most likely caused by the strong interaction between GOBC sheets and PAA matrix. It may be attributed to the different network nature between the two types of hydrogels. [11]

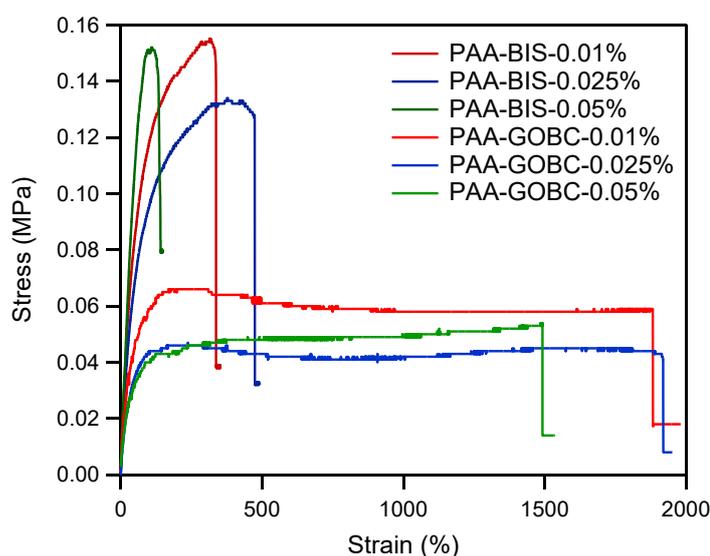


Fig. 3.12: Stress-strain curves of PAA-GOBC-0.05% & PAA-BIS-0.05%

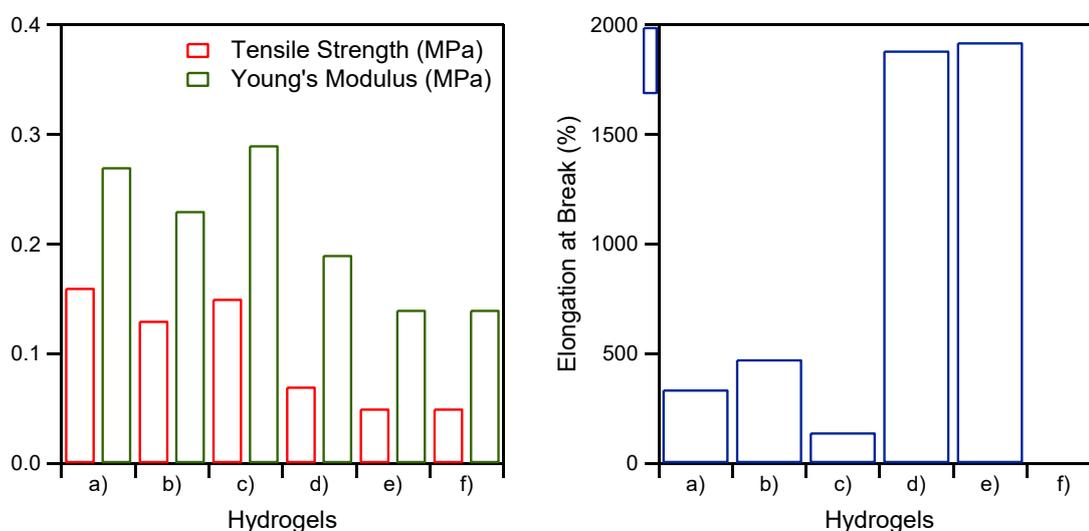


Fig. 3.13: Comparison of mechanical properties of PAA-GOBC & PAA-BIS hydrogels

Hydrogel Composite	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
a) PAA-BIS-0.01%	0.155	0.274	337
b) PAA-BIS-0.025%	0.134	0.226	474
c) PAA-BIS-0.05%	0.152	0.289	141
d) PAA-GOBC-0.01%	0.066	0.192	1882
e) PAA-GOBC-0.025%	0.046	0.138	1919
f) PAA-GOBC-0.05%	0.054	0.139	1492

Table 3.5: Table of mechanical properties of PAA-GOBC & PAA-BIS hydrogels

Since PAA-GOBC hydrogels show extraordinarily large deformation, and the polymer chains in the swollen state at ambient temperature could be regarded as flexible polymer chains just like those in the rubbery state of a solid polymer, the effective cross-link chain density of PAA-GOBC hydrogels can be evaluated by the kinetic theory. The polymer chains in PAA-BIS hydrogels have a broad distribution in length between the cross-link points and are restricted due to the random nature of cross-link reaction. Moreover, the friction between the chains is small in PAA-BIS hydrogel. These two factors result in the inhomogeneous distribution of tension among the polymers. The scission of the polymer chains occurs when the sample is under tension. However, the situation is different in the PAA-GOBC hydrogels. The network of the PAA-GOBC hydrogels is composed of rigid GO sheets and flexible polymer chains, which increases the friction between the chains by sliding of rigid GO sheets under the external tensile force. The rigid GO sheets are not only able to orient along the direction of tension, but also prevent effectively crack propagation by suppressing the stress concentration during the tensile measurement.

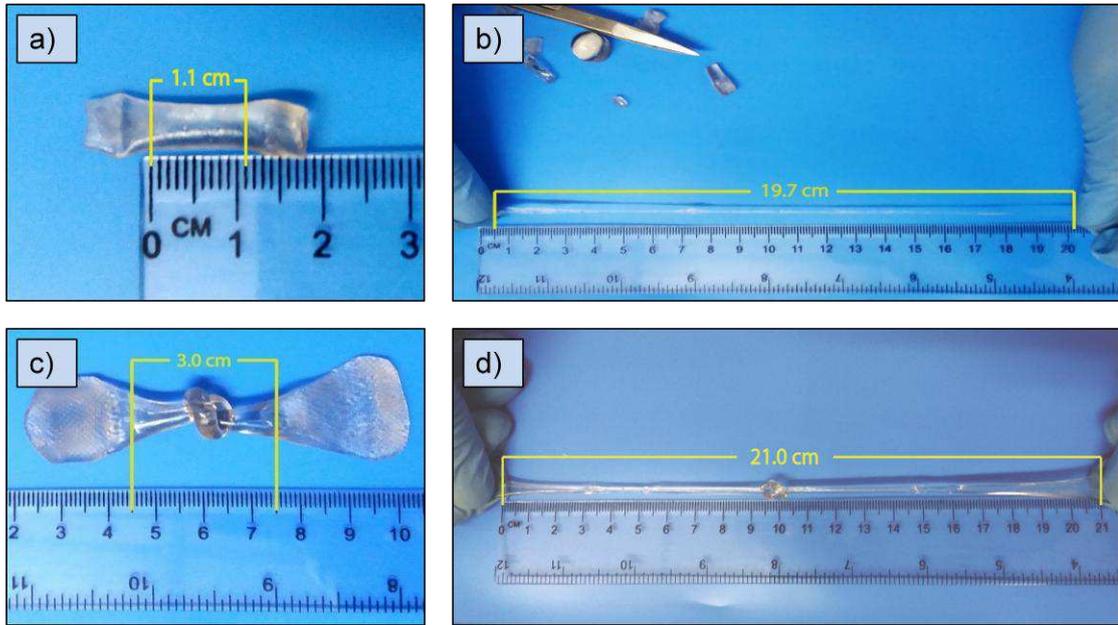


Fig. 3.14: a) photographs of the PAA-GOBC-0.01% hydrogel, b) highly stretched PAA-GOBC-0.01% hydrogel, c) knotted PAA-GOBC-0.01% hydrogel, d) highly stretched PAA-GOBC-0.01% hydrogel even with a knot

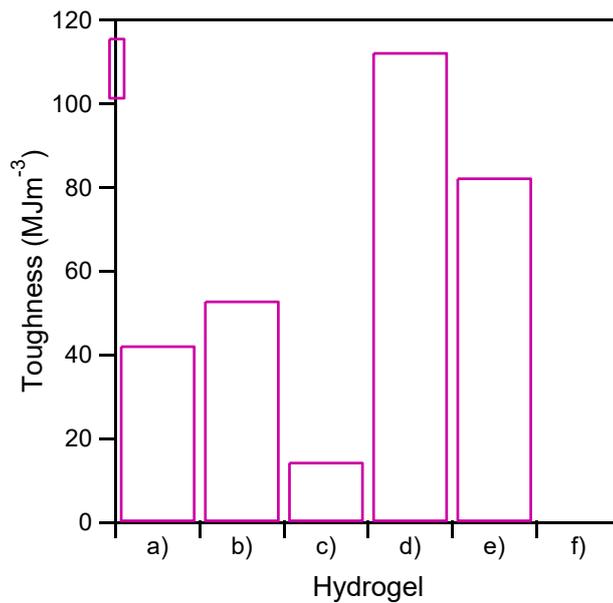


Fig.3.15: Comparison of toughness of PAA-GOBC & PAA-BIS hydrogels

Hydrogel Composite	Toughness (MJm ⁻³)
a) PAA-BIS-0.01%	4.23
b) PAA-BIS-0.025%	5.30
c) PAA-BIS-0.05%	1.65
d) PAA-GOBC-0.01%	13.46
e) PAA-GOBC-0.025%	9.87
f) PAA-GOBC-0.05%	7.17

Table 3.6: Table of toughness of PAA-GOBC & PAA-BIS hydrogels

The stress, strain and toughness of the PAA gels increase when the cross-linker content is lower, and decrease when the cross-linker content is higher (Fig. 3.16 and 3.17). It perhaps results from the interplay between the covalent cross-linking and the molecular weight of the PAA network chains among the adjacent cross-linking points. Under deformation, the covalently cross-linked network remains intact to absorb and redistribute the applied stress and thus delay the crack propagation via the PAA network chains within the covalent cross-linking, consequently maintaining the original configuration. A higher cross-linker content means more cross-linking, and it can effectively absorb and redistribute more applied stress. However, further increasing cross-linker content may induce degraded mechanical properties. The degraded stress, toughness and stretchability of the PAA hydrogels at high cross-linker content are attributed to a highly dense covalently cross-linked network within homogeneous cross-linking points and short network chains of the polymer. [14]

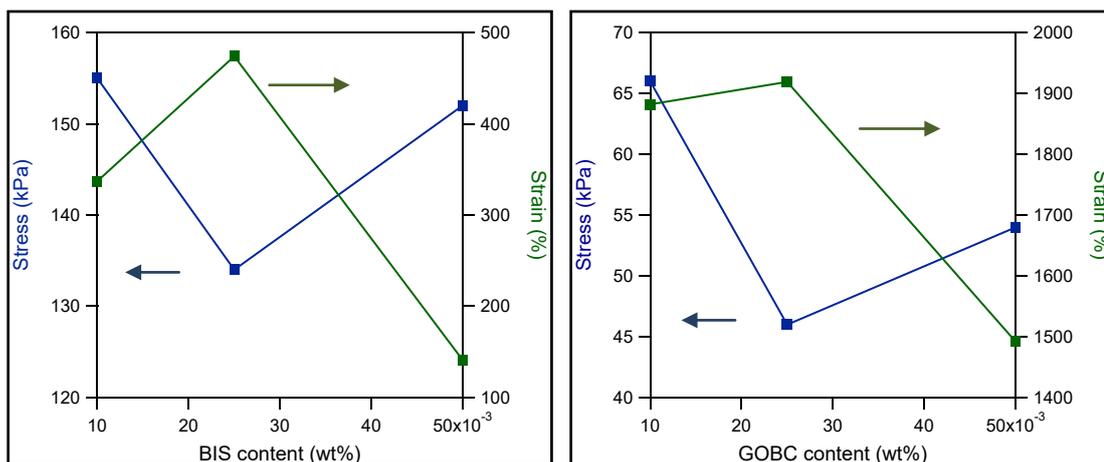


Fig. 3.16: Stress-strain curves of PAA-BIS & PAA-GOBC hydrogels

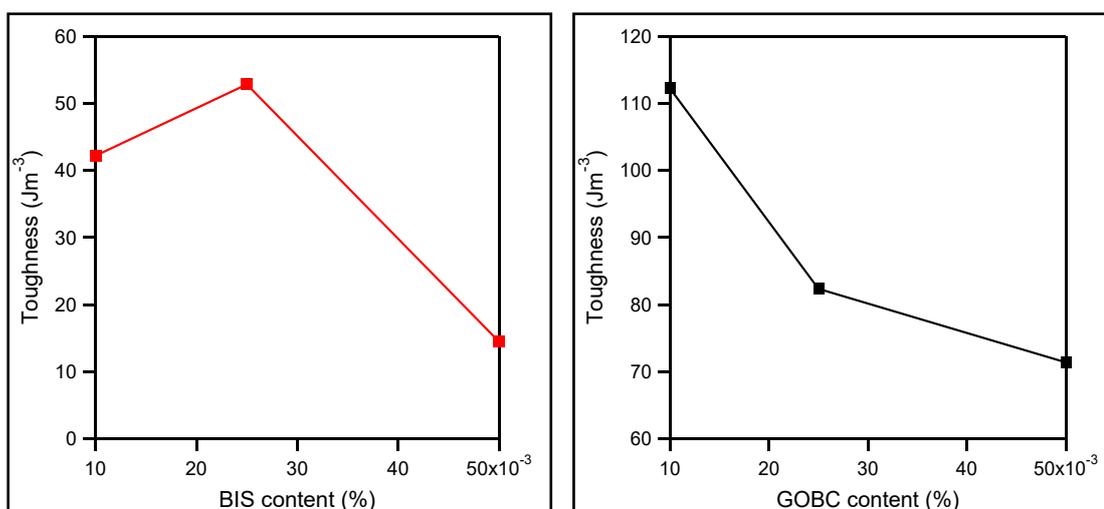


Fig. 3.17: Toughness curves PAA-BIS & PAA-GOBC hydrogels

0.3 Conclusion:

In this research, oxidized graphene oxide with a good no. of $-\text{COOH}$ functional group is synthesized following modified Hummers' method and then it is successfully functionalized by 2-aminoethylmethacrylate to prepare acrylate functionalized graphene oxide (AFGO) following EDC coupling reaction process. Formation of acrylate functionalized graphene oxide (AFGO) is confirmed by FT-IR and UV/Vis spectra analysis. Surface morphology of prepared AFGO is studied from SEM analysis and presence of N containing functional group is confirmed by EDS analysis.

Poly(acrylic) acid hydrogel cross-linked by graphene oxide based 2D cross-linker (acrylate functionalized graphene oxide) and N,N-methylenebisacrylamide (BIS) were prepared successfully through *in-situ* free radical polymerization. Surface morphology of prepared PAA-GOBC hydrogel is studied from SEM analysis and presence of N containing functional group is confirmed by EDS analysis. Thermal stability of PAA-GOBC and PAA-BIS hydrogels were studied by TGA and DSC analysis which confirmed better thermal stability of PAA-GOBC over PAA-BIS. Remarkable elongation, ductility and toughness of PAA-GOBC hydrogel were found in the study of mechanical properties using UTM. Elongation at break (%) of PAA-GOBC-0.025 (wt%) was 1919% where PAA-BIS-0.025 (wt%) can be stretched only 474%. So, it can be summarized as fabricated PAA-GOBC hydrogel is highly stretchable, ductile and tough hydrogel.

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