To Study Surface Morphology of Mechanically Cleaved Mica Layers on Oxidized Silicon

M.Phil in Applied Physics

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Maria Zafar

Dedication

To my beloved dearest Parents, my Charming Brothers (Saad, Fahad)

and my

Maternal Uncle Ata-ur-Rahman Junaid

Table of Contents

List of Figures

List of Tables

Abstract

Layered materials are solids with strong intra planar bonds and weak inter planar van der waal bonds. So these materials can be peeled off easily, peeling process is named as, exfoliation yielding 2D materials. 2D materials e.g. WS_2, MoS_2, graphene etc. are of unique importance owing to their specific properties, and they use for fabrication of new class of electronic devices, flexible electronics, super capacitors and spintronics. Apart from conducting and semiconducting materials, microelectronic industry also needs insulators which can use as substrates, dielectrics and electron tunneling barriers. Mica a dielectric material with high dielectric strength: is important, due to it its high resistance to water, heat and chemical agents, to its mechanical properties. Mica as bendable material used in fabrication of bendable devices. Mica as 2D material has remarkable characteristics; used as coating substance in paints and pigments, as filler it enhances the properties of polymer nanocomposites. Mica is successfully exfoliated by mechanical and by liquid phase exfoliation. Exfoliation is confirmed by XRD, Optical microscope and FTIR analysis. Mica solution as a filler is used in fabrication of PVC nanocomposites for enhancing mechanical properties of PVC composites. PVC composites are fabricated using different ratios of mica solution, by solution blending method. The structural and mechanical properties of these nanocomposites were analyzed by XRD, FTIR and UTM. These techniques confirmed the dispersion and mixing of filler in PVC. UTM analysis investigates that tensile strength increased with mica loading and hence, mechanical properties are increased. This increase suggests the efficient filler matrix reinforcement. Mica/PVC nanocomposites have applications in food packaging, flooring, and sheets in pool construction, smoke resistance and repairing cracks.

Chapter 1

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

2D materials are of unique importance owing to their specific physical properties which are due to quantum size effect and nano size thickness. [1-3] 2D materials have thickness comparable to one atom, they can use for fabrication of new class of electronic devices, flexible electronics, super capacitors etc. 2D materials start from discovery of Graphene and after that research for fabrication of 2D materials begins.

Among 2D materials, muscovite mica gained enough attention due to its structure, smooth surface, dielectric behaviour and remarkable properties as compared to graphene and other 2D materials. [4] Mica belongs to phyllosilicate which has layered structure. All members of mica group have layered structure, so they can transform in thin layers. Micas have almost perfect cleavage which is most important property of micas. The crystal of muscovite mica is negatively charged. In Each 2:1 layer, between every two tetrahedral silica layers an octahedral alumina layer is sandwiched. [5] Exfoliation and dispersion of layered materials into 2D nanostructures is adapted to increase the bulk properties like thermal stability, electric conductivity and mechanical strength, etc. [6] As muscovite mica is relatively soft, easily available and has industrial importance than other micas so it is preferred. The value of modulus of elasticity of muscovite is 1400-2100 $Kgfcm^2 \times 10^{-3}$. Shear Strength of muscovite is 220-270 MN/m^2.Value of Tensile strength for muscovite is 175 MN/m^2. [7] In rubber industry, mica uses as filler and mold lubricant for manufacturing molded rubber items, inclusive tires. [8] The well-defined and smooth surface of mica is used as substrate for surface force measurements.

2D materials exfoliated by different methods but liquid phase exfoliation is best among all. Exfoliation by ultrasonication is efficient because nanosheets separated in ultrasonic bath are crystalline in nature and having size in nanometer range. [1]

In Polymer nanocomposites, 2D fillers play remarkable part because properties of polymers like, strength, fire retardant, electrical, chemical and optical properties can be enhanced by addition of 2D fillers. Mica is efficient filler because its interaction with polymer matrix is strong. [7]

Present work focuses the enhancement of mechanical properties of polymers by addition of 2D mica filler. 2D mica was exfoliated first by liquid phase exfoliation method and then it was used as filler in Polyvinylchloride (PVC) to fabricate PVC-mica nanocomposites. This project includes the mica based PVC nanocomposites preparation and analysis of their mechanical properties as well as dispersion of mica in PVC. PVC nanocomposites have applications in food packaging, sheets in pool construction, smoke resistance and repairing cracks.

This thesis includes following chapters:

Chapter 2 deals with the experimental part which explains micromechanical exfoliation of mica, liquid phase exfoliation of muscovite mica and also solution blending method for preparation of mica/PVC nanocomposites. And brief detail of all characterization techniques we used to for analysis of our samples.

Chapter 3 is about results and discussion; results from all characterizations are well explained here. Results confirm; successful exfoliation of mica by both methods, successful fabrication of our samples and mechanical studies are also included.

Chapter 4 tells about the conclusions of our project as well as applications and future work related to 2D mica and PVC/mica nanocomposites.

1.2 History of Mica

Mica mineral has valuable history in industrial applications. To long before, 2000 BC, the ancient Hindus were confident that results of mica in curing are mysterious. In old Hindu system Abraka Bhasma (obtained by purification and processing of mica) used for

respiratory and digestive diseases. In old age, mica was used in cave painting, decoration, paper and paint industry and electronics and military applications. [7]

In ancient times, mica was used in decorating ornaments, mirrors, stove windows, and shock-resistant materials in early military applications to its more high-tech applications. [7]

1.3 What is Mica?

The "mica" word is originated from the Latin word "micare", meaning "to shine" or "glitter". Now a day this generic word applies to a large group of aluminosilicate minerals that have sheet-like structure. [7]

The mica group comprises of more common and most widely used mica species such as muscovite, paragonite, biotite, lepidolite and phlogopite. Paragonite is commonly called as muscovite. Muscovite is the most common of all the micas, holding a chemical formula $KAl_2 (OH)_2 (AlSi_3O_{10})$. Composition of paragonite is similar to muscovite the only difference is that the potassium in muscovite is replaced by sodium in paragonite. [7]

1.4 History of Two Dimensional (2D) Materials

Landau and Peierls claimed factually 70 years before, that two dimensional (2D) materials are thermodynamically not stable and therefore have no existence.[2,3] Their theory explained that divergently presence of thermic variations in low dimensional materials must show similar movements of atoms which can be compared with interatomic distance at a specific value of temperature.[9]

The justification was further explained by Mermin [10] and fully assisted by all experimental measurements. Naturally, melting point of thin films quickly decreases with decrease in thickness value, and thin film show instability at certain thickness of dozens layers of atoms. [11,12] That is why monolayers are known as a vital portion of 3D structure, when epitaxially grown top surface of monocrystal layers that matches with crystal lattice.[13] Discovery of 2D materials would never happen in absence of this 3D bottom support. In 2004, graphene was experimentally discovered [14] then other 2D materials are discovered

including 2D BN and bismuth strontium calcium copper oxide (BSCCO) [15] and discovery of these continues till now. [16]

1.4.1 Uniqueness of 2D materials

2D materials are of unique importance owing to their specific physical properties which are due to quantum size effect and nano size thickness. [17]

2D materials have thickness comparable to one atom, they can use for fabrication of new class of electronic devices. 2D materials have direct approach towards charge carriers and very high mobility both at room temperature and low value of temperature and very large value of thermal conductivity. Moreover, 2D materials have very close conduction band and valance even touching each other, giving only few states to exist at Fermi level therefore, 2D materials are called as zero band gap semimetals or semimetals.2D are outstanding materials for high gain photo detectors due to large mobility owing to charge carriers. [18]

Furthermore, small thickness value of 2D materials is permission for field effect behavior in conduction and it's very significant for applications in sensors and optoelectronics. [1]

1.5 Mica Minerals

"Mica" group almost contains 37 phyllosilicate minerals all have layered structure and they can transfer in thin layers. Micas have almost perfect cleavage which is most important property of micas.

Micas are 2:1 phyllosilicate that are firmly bounded and non-hydrated minerals. According to the Clay Minerals Society (CMS) Nomenclature Report, [19] the negative charge on mica minerals is due to isomorphous substitution variable ranging from $x = 0.5$ to $x = 1.0$ because of [O10 (OH)2] anion. [20]

The positive charge of interlayer cations must compensate the negative layer charge (x) to get whole charge neutrality of structure. This neutrality, in micas, is achieved by introduction of K^+ in crystal and other non-hydrated monovalent positive ions. Micas may occur naturally with excellent uniformity in crystal structure and composition as mono crystal. [21,22]

The most familiar micas from mica group are:

- Muscovite, a potassium based mica
- Phlogopite, a magnesium based mica
- Vermiculite, a hydrated biotite mica
- Lepidolite, a lithium based mica
- Zinnwaldite, a lithium/iron based mica
- Biotite, a magnesium/iron based black mica
- Roscoelite, a vanadium/potassium/magnesium mica [7]

1.5.1 Muscovite Mica

Muscovite mica has most unique market applications and easily available. The chemical formula for muscovite mica is $KAl_2(OH)_2(AlSi_3O_{10})$. Composition of muscovite mica is 4.5% H_2O, 38.5% Al_2O_3, 45.2% SiO_2, and 11.8% K_2O. Muscovite mica is lighter and used in color-sensitive applications. [7]

1.5.2 Phlogopite Mica

Phlogopite, the name originated from Greek word "phlogopos", means "fire-like". It ranks second in commercial value and is sought for its thermal and reinforcing properties. It has the inherent ability to delaminate easily. The chemical formula for phlogopite $KMg_3(OH)_2(AlSi_3O_{10})$ and the estimated composition of 11% K_2O, 43% SiO_2, 16% Al_2O_3, and 29% MgO. [7]

1.5.3 Biotite Mica

Chemical notation for biotite is similar to phlogopite with iron substituted by magnesium, $K(Mg,Fe)_3Al\ Si_3O_{10}(OH)_2$. The more iron loading, gives dark colors, and due to black color biotite cannot be used in industrial applications. But biotite is rich mineral found in granitic rocks, pegmatites and schists. [7]

1.5.4 Lepidolite Mica

Lepidolite mica is lithium dependent mica with chemical notation $KLi_2Al(OH)_2(AlSi_3O_{10})$. It is found in granitic pegmatites associated with lithium bearing minerals i.e. tourmaline, beryl and spodumene. [7]

1.6 Applications of Muscovite Mica

Muscovite mica is used for manufacturing of capacitor and some other optical instruments. Muscovite mica due to its light weight and platy structure promotes suspension and used as pigment extender, in paint industry. Muscovite mica lowers chalking and checking it hinders sheering and shrinkage of paint films, it imparts water resistance, weathering and burnishes the tone of pigment colour. Mica used as underlying substrate in fabrication of different devices like gas sensors, strain sensors, bendable devices and photodetectors. In rubber industry, mica uses as filler and mold lubricant for manufacturing molded rubber items, inclusive tires. [23,24]

As Muscovite mica has famous commercial and industrial applications therefore, my project is about exfoliation of mica and its applications. Muscovite mica is used for fundamental research due to its smooth surface as calculated in chapter 3. The well-defined and smooth surface of mica is used as substrate in many applications.

1.7 Muscovite Mica's Structure

Muscovite mica is a tri-layer phyllosilicate has 25% percent of the silicon atoms. The crystal of muscovite has negatively charged 2:1 aluminosilicate layers. Every 2:1 sheet has one octahedral alumina sheet sandwiched between two tetrahedral silica layers. Each layer is negatively charged due to substitution of silicon atoms out of four with aluminum atoms producing a localized negative charge. [25] The negative layer charges are counterbalanced by K^+ cations (or sometimes sodium ions, non-hydrated monovalent cations in the interlayer) which are firmly bounded with nearby layers. All the layers are firmly bonded by Coulomb's force produced due to "electrostatic cement" of cations placed between basal planes of oxygen in adjacent sheets. Because of strong electrostatic force, polar molecules such as H_2O

and other polar molecules cannot penetrate in interlayer spacing which makes members of mica family nonexpendable. [20]

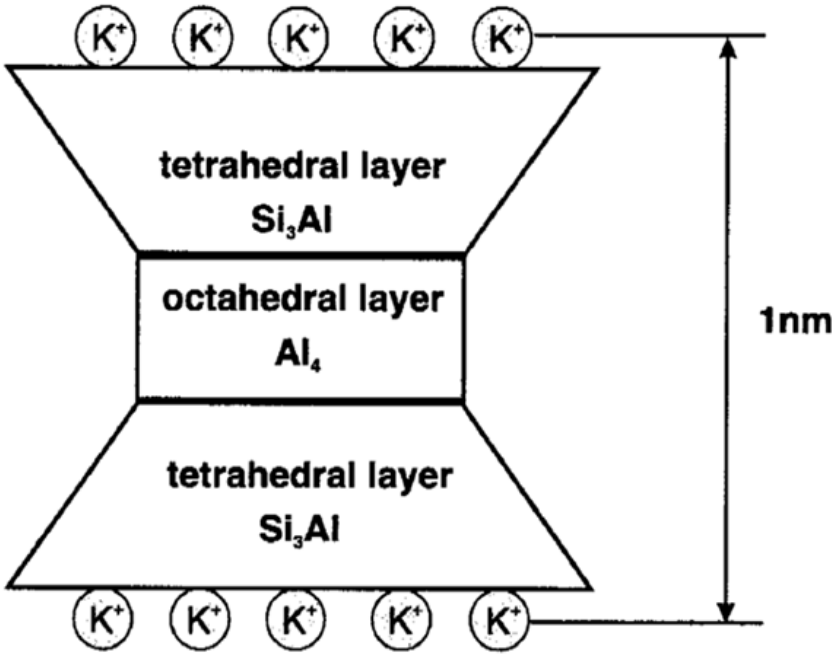

Figure 1.1: The layer structure of muscovite mica [25]

The ionic bonds between those interlayers are weak as compared to strong covalent bonds between intralayer. It is because of that structure mica sheets are easily cleaved along the potassium rich basal plane layer, thus easily producing atomically thin flat surfaces over an extended range having a regular lattice structure. The cleaved sheets are hydrophilic and negatively charged in pure water. It is important to note that freshly cleaved mica surface is not chemically homogeneous. [25]

1.8 Properties of Muscovite Mica

1.8.1 Physical Properties

Muscovite is formed from the alteration of topaz, feldspar, and kyanite. It is famous for perfect basal cleavage (001) plane. The muscovite is usually present as white, grey, green, silverery, or transparent. It follows monoclinic crystal system. The specific gravity is around

2.76 g/cm3 to 3 g/cm3. It is an anisotropic material with high birefringence. The refractive index for muscovite is: n_γ=1.56-1.57, n_α=1.553-1.563, and n_β=1.559-1.569. [7]

1.8.2 Mechanical Properties

Hardness of muscovite is 2-2.5 mohs which is relatively low so others micas as biotite (2.5-3), lepidolite (2.5-4), phlogopite (2-3). As muscovite mica is relatively soft from other micas so it is preferred mostly. The value of modulus of elasticity of muscovite is 1400-2100 $Kgfcm^2 \times 10^{-3}$. Shear Strength of muscovite is 220-270 MN/m^2.Value of Tensile strength for muscovite is 175 MN/m^2. [7]

1.8.3 Electrical Properties

Specific heat of muscovite is 0.21. Break down voltage for muscovite is 120-200 KV/mm. [7] Value of thermal conductivity is approximately 0.0013 $Gm.cal/sec/cm^2/°C/cm$.

1.9 Exfoliation methods of Muscovite Mica

As described in 1.7 that mica interlayer bonds are weak as compared to intra layer covalent bonds therefore mica can be exfoliated into thin layers easily by different exfoliation methods. Exfoliation methods of mica described here.

1.9.1 Micromechanical exfoliation using scotch tape

Mechanical exfoliation is used for fabrication of 2D or few layered thick sheets. This procedure was first utilized by Grim and his colleagues to fabricate single layer graphene. [1]

1.9.2 Mechanism

Communally reachable bulk material or thick flakes are peeled off on scotch tape. Scotch tape having some bulk flake is repeatedly folded to get mono layers and multiple thin and thick layers due to weakening of van der waal forces between different layers. The tape with flakes is transferred on pre-cleaned Si/SiO_2 substrate. Flakes on Si/SiO_2 substrate can be identified and confirmed by optical microscope and atomic force microscopy respectively. This procedure was used to get monolayers of WS_2 MoS_2, h-BN, $NbSe_2$, $Bi_2Sr_2CaCu_2O_x$ and mica from it's the bulk material. [1]

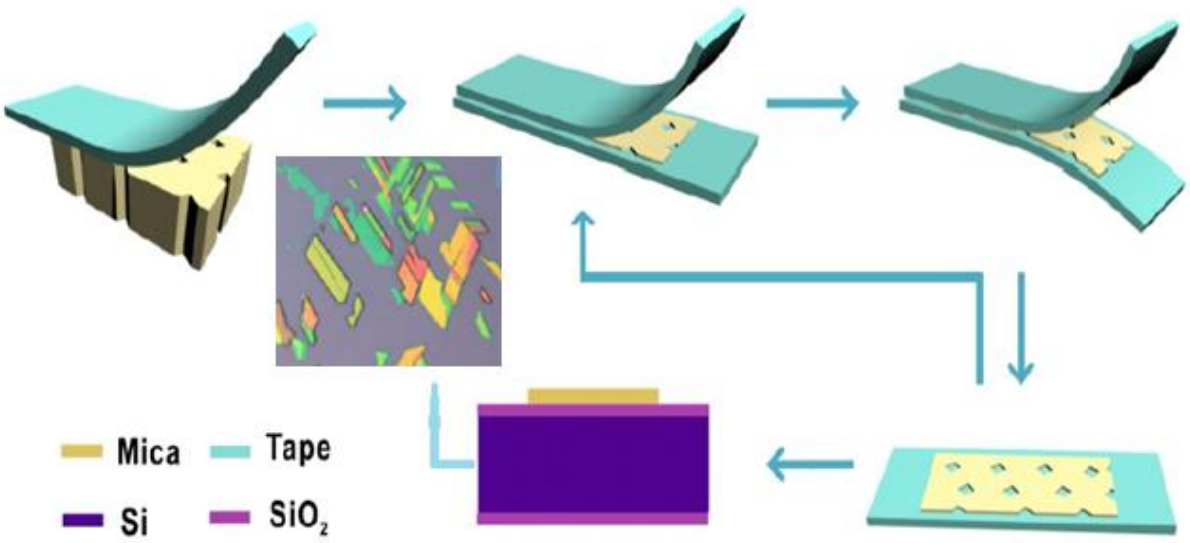

Fig 1.2: Schematic illustration of mechanical exfoliation of mica bulk material and transfer of isolated mica nano flakes onto silicon substrate. [26]

1.9.3 Benefits

This method is comparatively simple, fast and cheap than other methods. [1]

No any special chemicals are required for this method and only based on the very small force applied during the transfer of tape on substrate, so, original crystal structure does not disturb, and crystalline nature is retained.

1.9.4 Drawbacks

The monolayer production by this process is very small.

This method is only suitable for studies in laboratories for research projects and cannot be utilized for mass production at large scale. [1]

1.10 Liquid Phase exfoliation of Mica

The preparation of 2D muscovite by liquid phase exfoliation is given below [27]

As tetrahedral and octahedral layers are very close to each other, exfoliation means to increase size between different layers and minimize adhesion energy. K^+ is firmly bounded in the interlayers to compensate the charge deficiency of muscovite layers. [27]

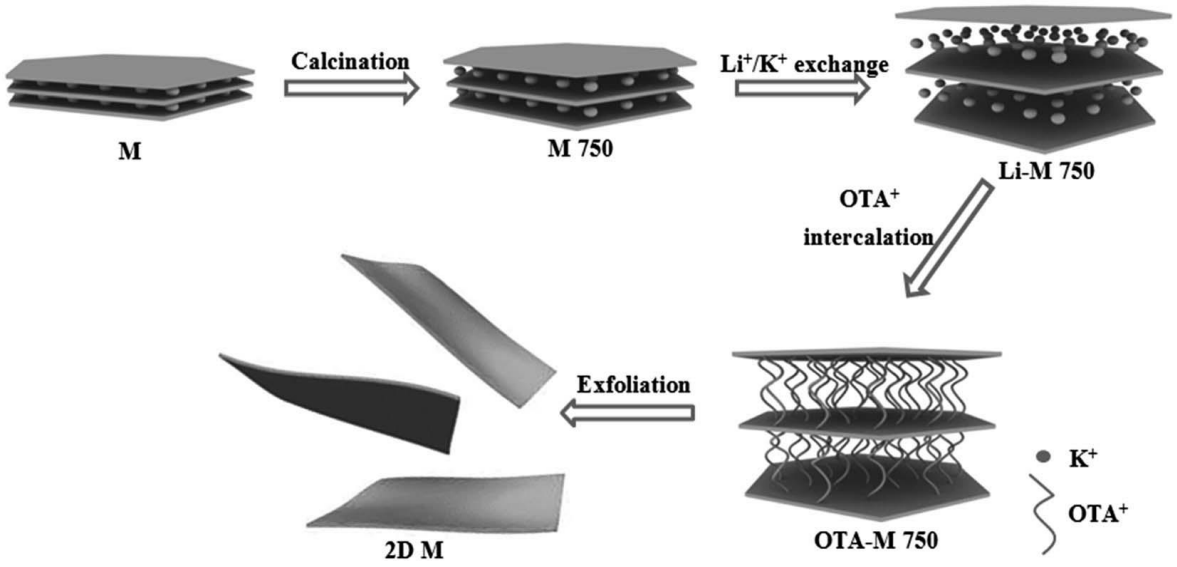

Figure 1.3: Schematic for 2D muscovite preparation. M, M750, Li-M750, OTA-M750 and 2D M are original muscovite; muscovite calcined at 750 °C, M750 after K^+ was exchanged by Li^+, Li-M750 after intercalation of OTA+ and exfoliated muscovite, respectively. [27]

1.10.1 Mechanism

The main three steps of liquid phase exfoliation are: (a) ion exchange (b) intercalation (c) ultrasonic exfoliation. [27] Muscovite is calcined at 750 °C to decrease force of attraction between K^+ and interlayers.

(a) Ion Exchange

$LiNO_3$ is selected to remove K^+ from muscovite. Li^+ is so small that it can enter between vacant tetrahedral and octahedral vacancies to cancel the charge. Now, the layers charge lowered and attraction force between different layers become weak, so interlayer spacing enhanced.

(b) Intercalation

To further increase interlayer distance, long-chain of OTA^+ (octadecyltrimethyl ammonium ion) is intercalated in muscovite mica. The heat therapy and ion exchange minimizes attraction force between the aluminosilicate layers and expands the distance between muscovite sheets.

(c) Ultrasonic Exfoliation

Ultrasound-facilitated exfoliation is then applied to bring about a complete removal of the lamellae from each other.

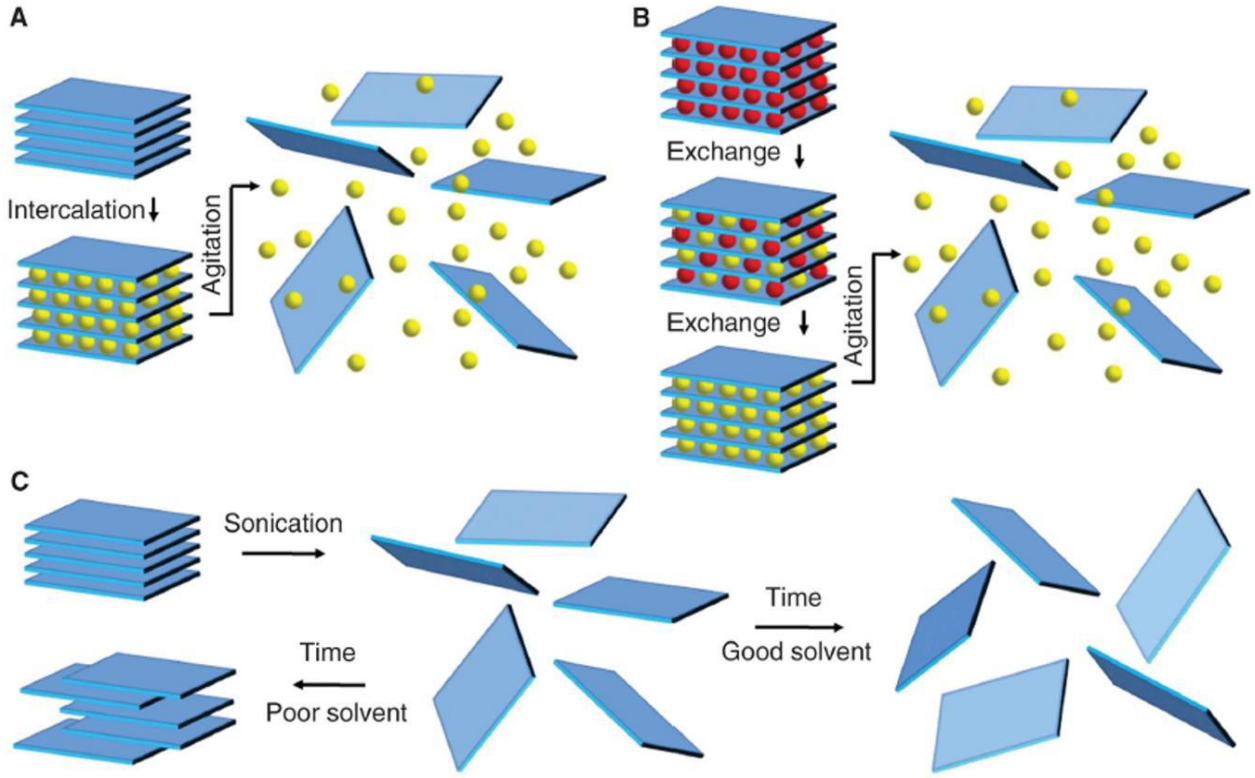

Figure 1.4: Schematic representation of variation in liquid exfoliation process: (a) intercalation, (b) ion exchange and (c) ultrasonic exfoliation [28]

1.10.2 Precautionary Measurements

We should be very careful for selection of suitable solvent. Solvent having surface tension value similar or very near to bulk material; which has to be exfoliated prohibits the restacking of exfoliated layers but also lowers the cost of exfoliation process. [28, 29, 30] Layered materials with low reduction potential are perfect for liquid phase exfoliation. [1]

1.10.3 Benefits of liquid phase exfoliation

Solvent with surface tension value near to surface energy of particular material not only reduces cost of exfoliation but also hinders the restacking of nanosheets. Nanosheets produced after processing from ultrasonic bath are crystalline in nature and has size of micrometer range.

1.10.4 Drawbacks

Against the mass production by this method, mechanical cleavage is choice for materials due to less destructive nature and mono layers of size 10μm are peeled on different kind of suitable substrates. [1]

1.11 Solvothermal process

Few layered to single layer thin mica nanosheets can be made from communally reachable mica using microwave irradiated expansion followed by solvothermal process figure 1.5 given below. [31]

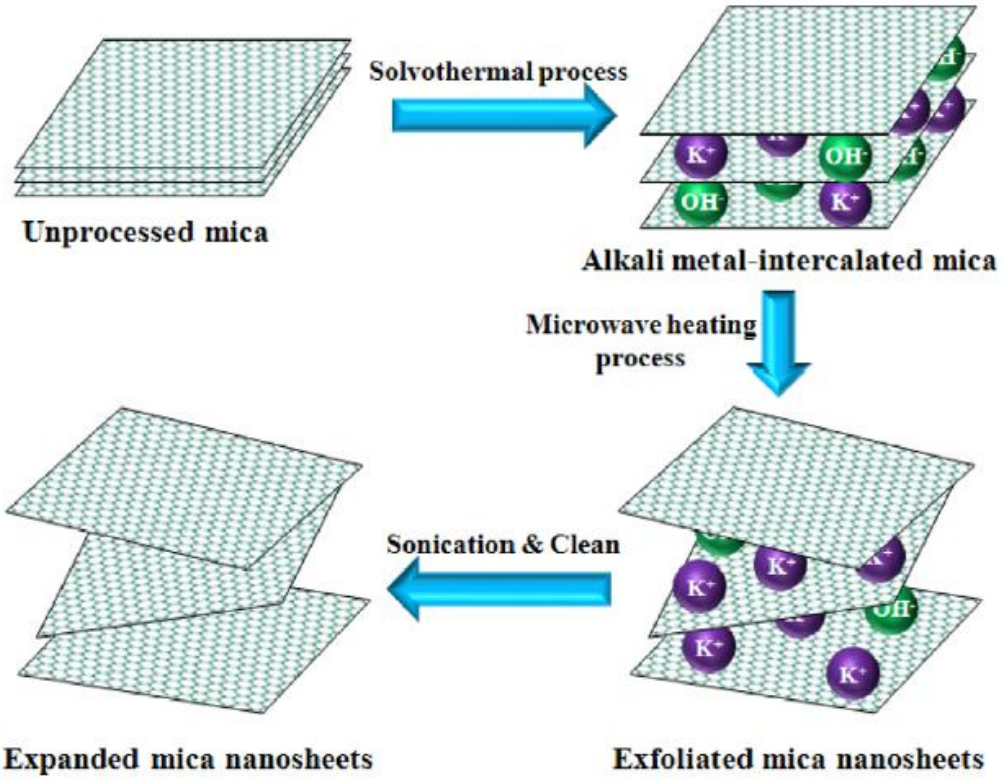

Figure 1.5: Sketch showing preparation of few layer mica nanosheets based on solvothermal and microwave method [31]

1.11.1 Mechanism

Firstly, organic solution is made with help of 5g of potassium hydroxide (KOH) in 50 ml tetrahydrofuran (organic solvent), prepared solution is stirred at room temperature for 24 hours. [31]

Secondly, 1 g mica powder is mixed into aforementioned organic solution; this mixture is then placed in Teflon-lined autoclave for 72 hours at 250 °C. During this whole process mixture is continuously stirred using Teflon magnetic stirrer. During this process the dissolved K^+ ions form a suspension between layers of mica.

Lastly, reacted products are irradiated for 5-8 minutes using rapid microwave heating at 60 Hz and 1000 W.

Hence, exfoliated mica sheets are obtained through irradiation.

Exfoliated nanosheets again dissolved in 1% solution of HCl and sonicated at small value for 7 to 10 hours afterwards solution is continuously cleaned with distilled water till pH of 7 is achieved.

To get uniform mica sheets, exfoliated sheets are centrifuged at slow speed for 5 minutes at 2000 rpm to remove remained thick sheets.

Supernatant is further centrifuged for 30 minutes at 6000 rpm to remove mica specimens and byproducts which were dissolved in water. [31]

Lastly, sheets are again dissolved in de-ionized water and sonicated at small value to form a uniform solution of exfoliated mica sheets.

Exfoliated mica solution has wide range of applications. It can use for designing gas sensors, gas barriers, strain sensors. Exfoliated solution can be used as filler in polymers to form composites and to enhance properties of composites.

Chapter 2

EXPERIMENTAL WORK

2.1 Exfoliation of Muscovite Mica

As we have explained earlier that there are different methods to exfoliate muscovite mica. And we used two methods to exfoliate mica; **(1)** Micromechanical Cleavage **(2)** Liquid phase exfoliation.

2.1.1 Micromechanical cleavage of Muscovite using scotch tape

290nm Si/SiO_2 was used as a substrate. There was a protective resist coating over the substrate, which must be cleaned before transferring flakes onto substrate.

Cleaning of substrate is important for smooth fabrication of 2D materials, to remove impurities and to remove resist layer.For cleaning purpose standard cleaning process for substrate cleaning was used as shown figure 2.1. Silicon substrate of 270nm is used because it gives best contrast of flakes, when observed optically.

Muscovite mica is a layered phyllosilicate mineral consisting of aluminum and potassium with chemical notation $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$.Atomically thin layers of muscovite were fabricated following mechanical exfoliation method. The process is given below:

- Communally convenient muscovite thick flake was transferred on scotch tape.
- Successive folding and peeling of tape provides dispersion of muscovite flakes on whole tape surface area including monolayer, bi-layer, tri-layer and thick layers, due to weakening of weak van dar Waal forces between layers. We have to transfer these flakes onto pre cleaned Si/SiO_2 substrate.
- For transferring, scotch tape with dispersed muscovite flakes was placed over the pre-cleaned Si/SiO_2 substrate.
- Then, tape was slightly pressed with thumb to make close contact between substrate and muscovite tape, so that flakes may transfer on Si/SiO_2 substrate.

- Now, substrate with scotch was placed into acetone for 5 minutes to remove tape.
- When tape leave the substrate, put the sample in fresh acetone placed at hot plate (ARE heating magnetic stirrer, VELP SCIENTIFICA) at 60 ºC for 5 minutes.
- Instantly, placed it in IPA (Isopropyl alcohol) placed at hotplate at 60 ºC for 3-5 minutes.
- Now, sample was blow dried with nitrogen (N_2) gas.
- Finally, sample was baked on hot plate (ARE heating magnetic stirrer, VELP SCIENTIFICA) for 20 minutes at 120 ºC.
- Lastly, one last peeling with fresh tape was conducted, which removes some thick layers from substrate. Now sample was saved in sample box and flakes were observed by optical microscopy.

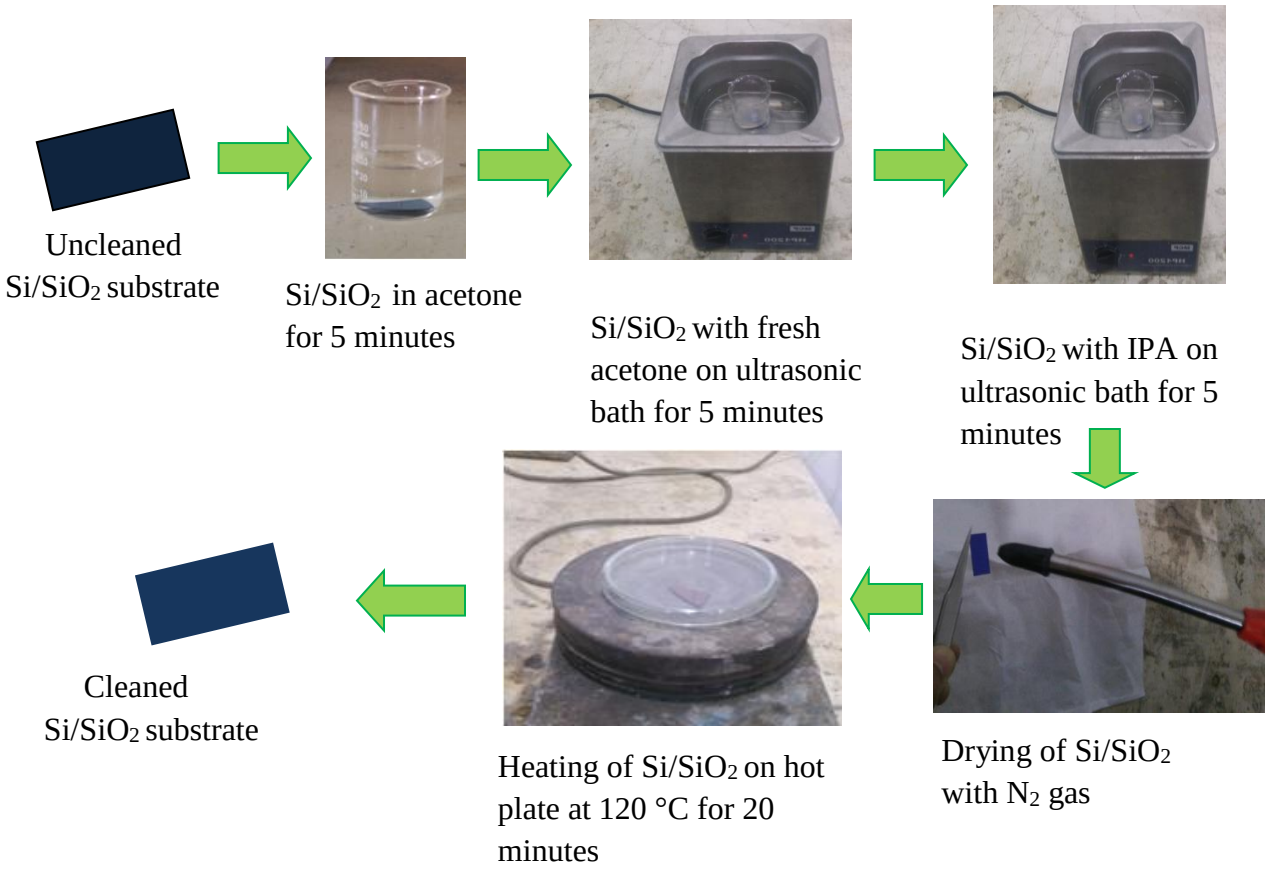

Figure 2.1: Cleaning of 290nm Si/SiO_2 substrate

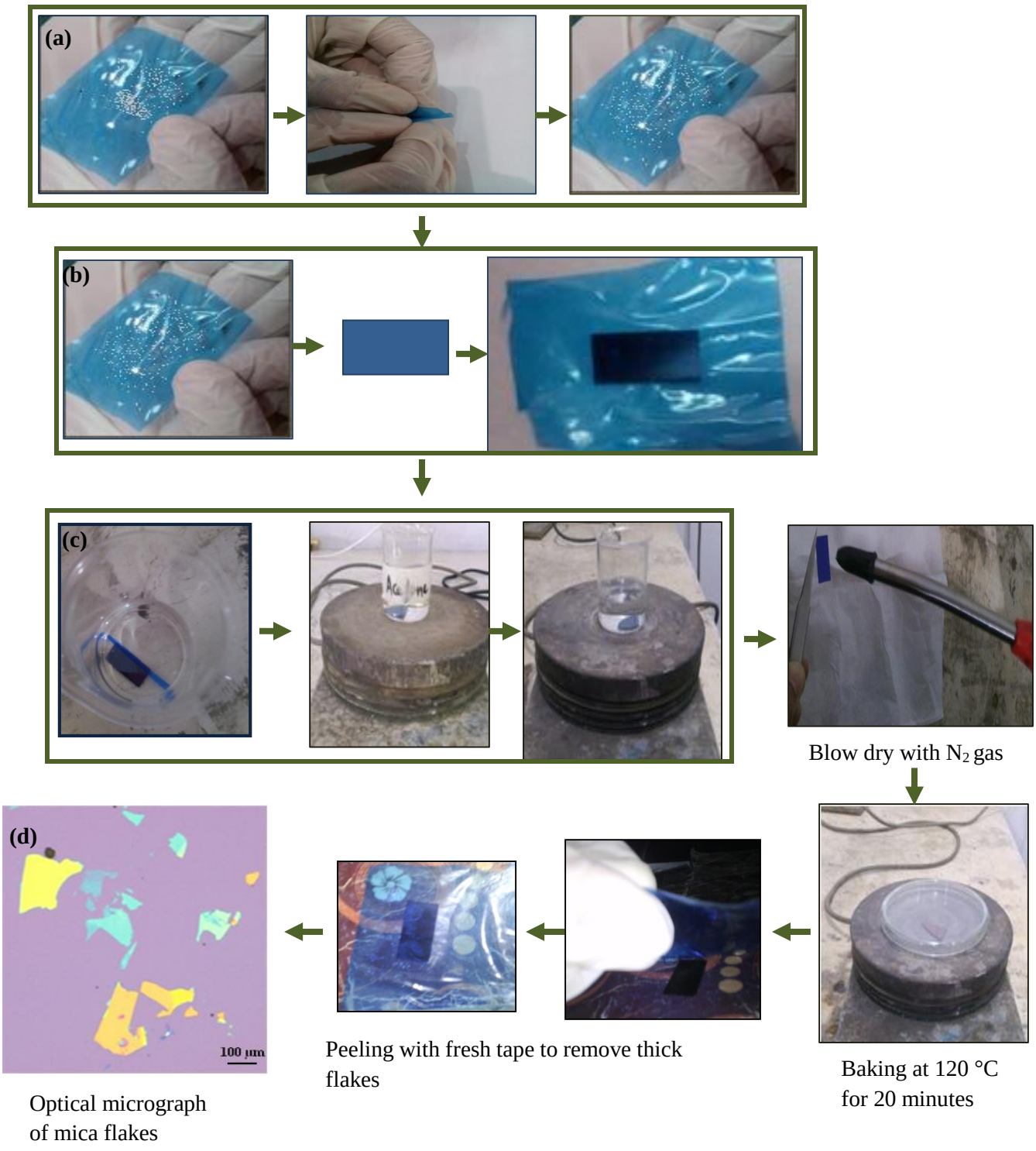

Figure 2.2: Mica exfoliation by scotch tape method (a) micromechanical cleavage, (b) deposition of flakes on Si/SiO_2 (c) removal of tape (d) optical micrograph of mica flakes is also shown

2.1.2 Liquid phase exfoliation of Muscovite Mica

Communally reachable muscovite mica powder $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$, purchased from Sigma-Aldrich and DMF (dimethylformamide) from Sigma-Aldrich.DMF is selected for exfoliation of muscovite because surface tension value of mica matches with it.

- Muscovite powder was added in DMF as a ratio of 1mg/10 ml. The ratio used for solution was i.e.10mg of muscovite powder in 100ml of DMF and sonicated for 6 hours in sonication bath (DSA100-SK).
- Then Sonicated solution was centrifuged in centrifugation machine (LABCEN6O) for 15 minutes at 6000 rpm. The supernatant part is exfoliated muscovite.

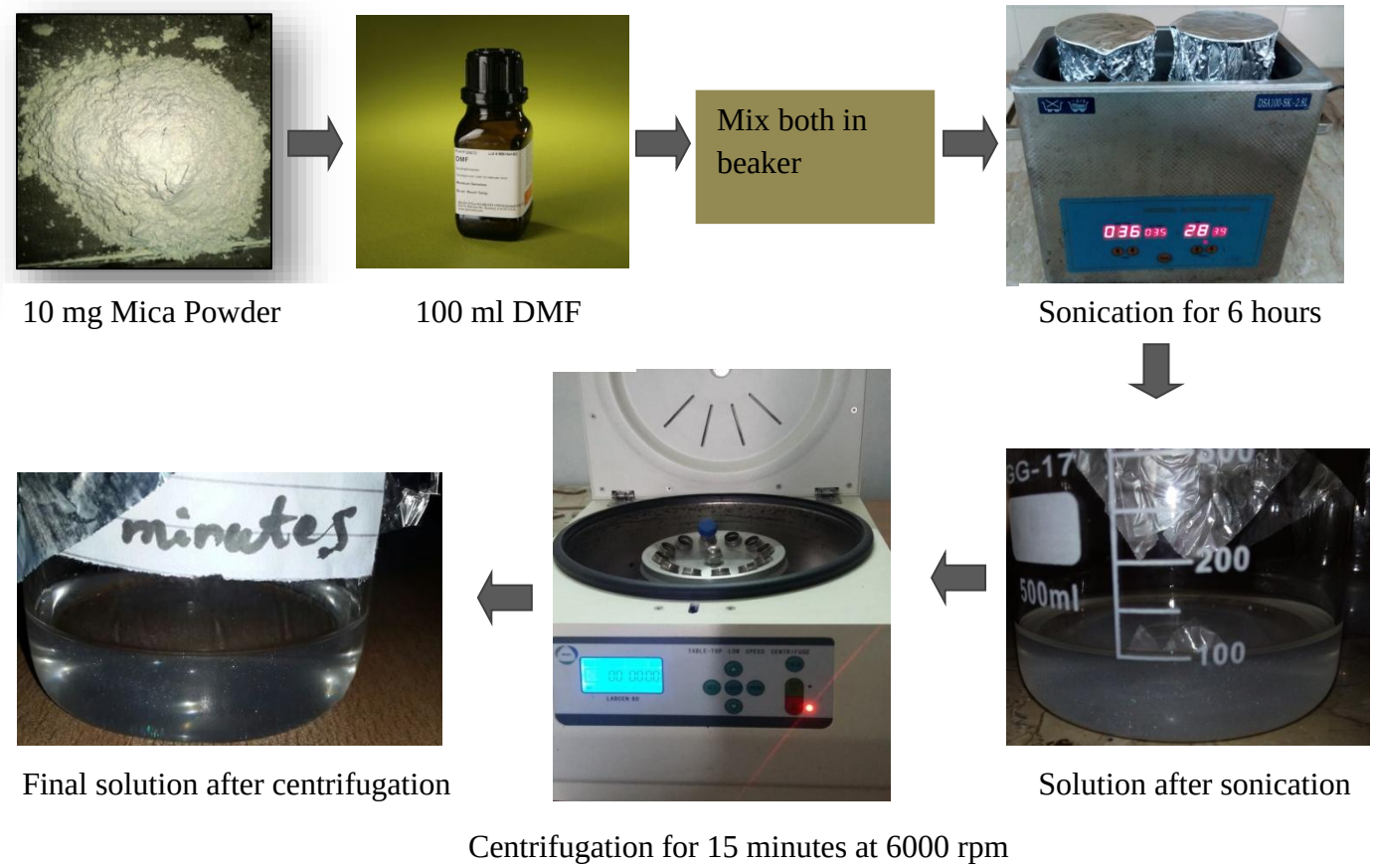

Figure 2.3: Liquid phase exfoliation of muscovite mica powder

Exfoliated mica solution can be used as nano filler in polymers. So, exfoliated solution was used for fabrication of polyvinylchloride (PVC) nanocomposites

Mica filled composites reveal meaningful reinforcement in dielectric characteristics of plastics. [32] Mica based polymer nanocomposites with advanced electrical characteristics are useful in insulating applications of electric appliances on large scale. [33]

Mica composites with thermoplastic elastomers used in fabrication of automobile parts such as sprockets and gears. [34] Composites with mica as filler also have applications in high strength applications and shock damping applications. [35]

In this thesis mica filled PVC composites with different concentrations of mica are fabricated by solution blending method and their mechanical properties are studied.

2.2 PVC nanocomposites with muscovite solution

The efficiency of polymer composites is analyzed on the base of filler added and polymer used. Here, effect of mica solution as filler with different concentrations (1 weight percent to 10 weight percent) on mechanical properties of polyvinylchloride (PVC) composites is studied. PVC is very commonly used polymer in different applications i.e. domestic products, various industrial products and applications and in piping wiring. It can be made non-flammable, non-toxic, strain resistant, light resistant and mechanically stronger by proper establishments. Because of characteristic applications and widely usage PVC is selected for composite formation.

Mica has been broadly used as strengthening agent (filler) in different polymers because of its impact on the electrical, physical, and mechanical characterizations. So, here exfoliated muscovite is added as filler in PVC matrix. Muscovite is added in weight percent i.e. 1wt. %, 2wt. %, 4wt. %, 6wt. %, 8wt. % and 10wt. %.

Polymer composites can be made by melt mixing method, solution blending method and insitupolymerization process. We fabricated PVC composites by solution blending method as follows:

- For polymer solution formation, 50 g of PVC is mixed in 500 ml of dimethylformamide DMF according to ratio: 10g PVC powder in 100ml (DMF). This mixture was stirred for 24 hours at 60 ºC.
- For muscovite mica based PVC composites, different concentrations of exfoliated solution were added in above prepared polymer solution.
- Every concentration of exfoliated muscovite solution is added in PVC prepared solution and sonicated for 1 hour to obtain smooth polymer solution.
- Sonictaed solution is then, poured in Petri dishes and dried in drying oven for 22-24 hours at 60 ºC.

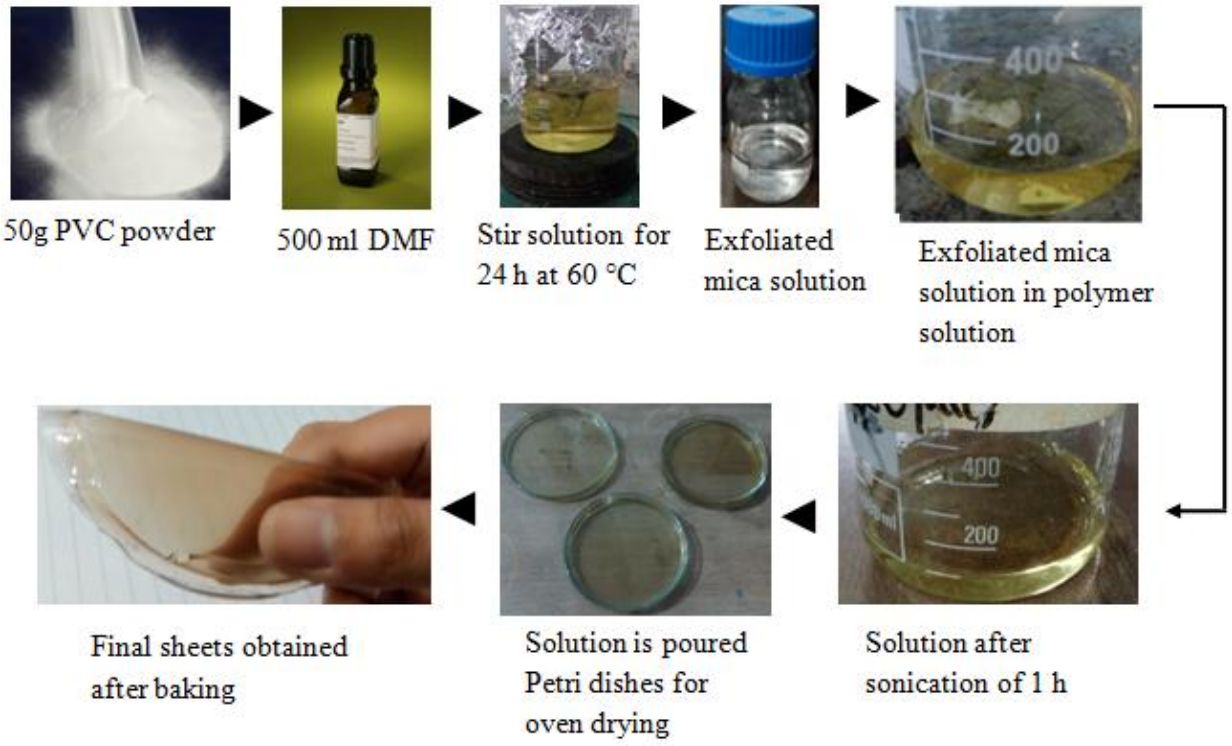

Figure 2.4: Fabrication of mica-PVC nano composites by solution blending process

2.3 Characterization Techniques

Mechanical exfoliation of mica is identified by optical microscope. Liquid phase exfoliation of mica is justified by X-ray diffraction (XRD), optical microscopy and Fourier transform infrared spectroscopy (FTIR). Composites of Polyvinyl chloride (PVC) with exfoliated mica as filler are analyzed by FTIR; the spectral lines by FTIR tell about corresponding to specific structural feature that was modified after exfoliation and UTM (universal testing machine) analysis for mechanical properties.

All characterization techniques mentioned above are described below:

2.3.1 The Optical Microscope

This microscope is generally referred as light microscope; it uses ordinary light and lenses to enlarge the tiny objects.

The compound microscope is a device (optical) which operates at ordinary light yielding magnified micrographs. In optical microscope image obtains by manipulation of light. The word compound refers to two lenses: objective lens and eyepiece, combine functioning of lenses yield the end magnification M of the image i.e.

$$M\,final\; = Mobj\; \times M\,oc$$

The two main components of microscope have demanding significance for image formation: 1st, the lens closes to the object that receives the diffracted light from the object i.e. **objective lens**, which forms a real image of object in interior of microscope. That image is then magnified by another lens or a group of lenses i.e. eyepiece. Eyepiece works as simple magnifier in compound microscope. The 2nd lens i.e. **condenser lens,** it is placed beneath the sample stage, its function is to focuses light from the illuminator on little portion of object.[36]

The arrangement of these and other components is shown in Figure below:

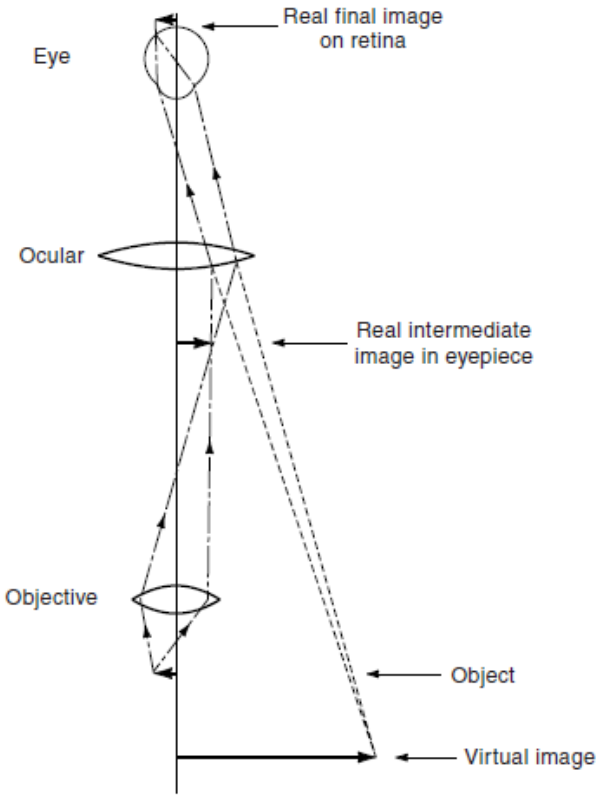

Figure 2.5: Perception of a magnified virtual image of a specimen in the microscope [36]

Looking through compound microscope, the ocular works with cornea and lenses that produces a second real inverted micrograph on retina, w is then sent to brain for translation.

2.3.2 Atomic Force Microscope

This microscope is known as a scanning probe microscope (SPM) and sensing appliance. It is suitable device for physical and chemical analysis. AFM in its fundamental arrangement, measures minuscule surface profile of any specimen by scanning mechanically with a tiny probe. The probe hikes up and hikes down corresponding to surface pattern. When the probe moves over the surface, its place (point) is noticed and recorded on computer. That captured topogram is visualized as photograph which is similar to optical micrograph.AFM gives 3D image and there is no need of sample preparation and vacuum is not required for scanning of sample.

2.3.2.1 Working of AFM

An atomic force Microscope contains a Sharp tip of about 10^{-10} m in diameter fitted at the edge of soft cantilever spring. The tip with cantilever spring can made direct mechanical contact with the specimen. Deflection of the spring is determined via a laser beam reflecting from the cantilever and onto a position-sensitive photodiode. [37]

The specimen can be moved in three directions (x,y,z) using piezoelectric electric effect scanner.

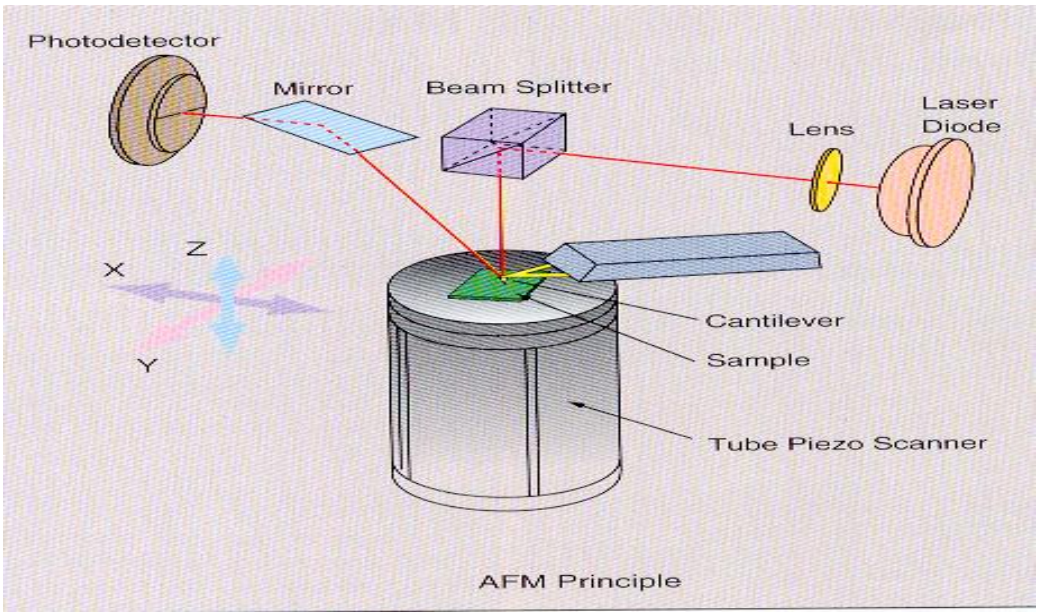

Figure 2.6: Working of AFM [37]

2.3.2.2 Modes of AFM

AFM works in two modes:

1. Contact mode of AFM
2. Dynamic mode of AFM

1. Contact Mode of AFM

In contact mode the cantilever makes mechanical contact with sample and cantilever height is kept constant.

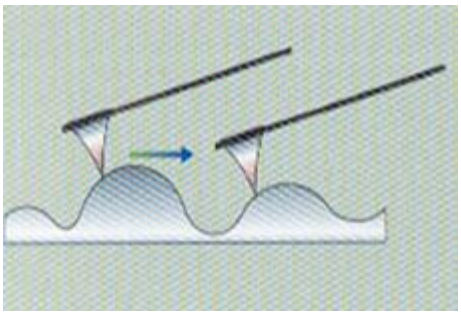

Figure 2.7: Movement of cantilever tip in contact mode on surface hill [38]

2. Dynamic Mode of AFM

In dynamic mode cantilever vibrates with resonant frequency and height of cantilever varies with height of sample.

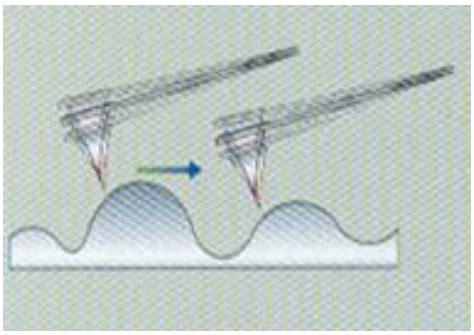

Figure 2.8: Cantilever vibration in dynamic mode on surface hill [38]

2.3.3 X-ray Diffraction

Diffractometer investigates structure of a substrate using x-rays interaction.

X-ray diffraction provides information about identity of crystalline solids, cell dimensions and bond angle. XRD is non-destructive diagnostic technique.

X- Ray diffractometer provides spectra of specimen when x-rays of specified wavelength falls on the specimen, it moves the detector and substrate which enables the machine to calculate the intensity of the diffracted beam as a relation of sample dimensions and beam angle. X- Ray diffractometer can analyze solids samples from 2-200 nm. [39]

Condition for Diffraction:

The x-rays which are incident to sample must have wavelength (λ) comparable to atomic spacing of sample. The path difference between two waves going through interference should be integral multiple of wavelength (λ).

Working:

During diffraction, x-ray beams are incident on sample and scattered off the parallel atomic layers within a material at different diffraction angles. As the x-rays have certain wavelength, for a given d-spacing so, x-rays would be in phase only at certain angles which are then detected by detector creating a peak on diffractogram. The diffraction of x-rays is described by Bragg's Law.

$$2dsin\theta = n\lambda \text{ [39]}$$

Where "d" distance between layers of atoms, "n" the order of diffraction, "θ" is diffraction angle, and "λ" is wavelength of incident x-rays.

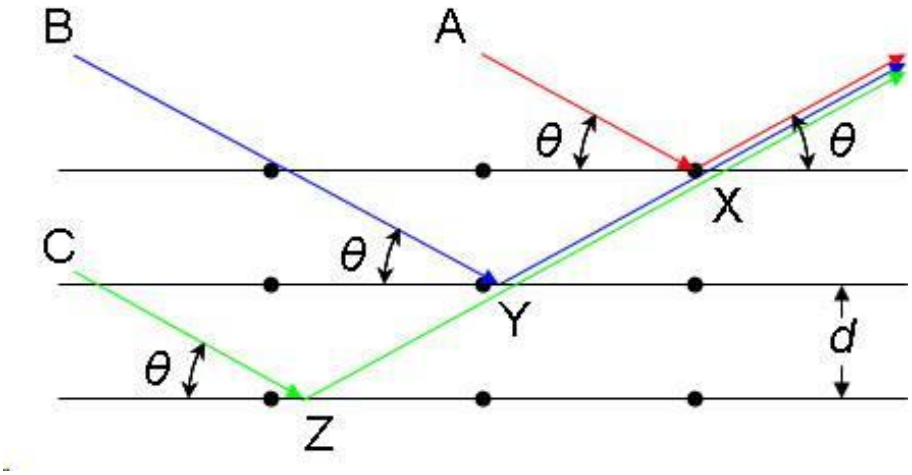

Figure 2.9: Bragg's diffraction [40]

2.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

It is a spectroscopic tool which gives inter-ferogram by interference of two light beams. Then a signal is yielded after altering path-length of the beams. Schematic of FTIR spectrometer is

shown in figure 2.10 below. The radiation after emitting from source passed from an interferometer then passed from sample and at the end moved towards detector. When signal is amplified and high-frequency is filtered out, by using analog to digital converter data is converted to digits and moved to the computer considering Fourier-transformation. [41]

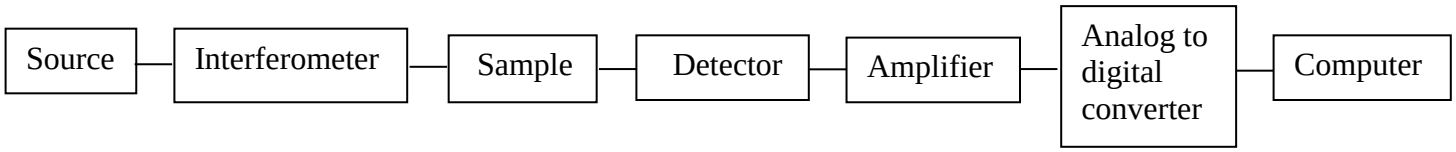

Figure 2.10: Basic components of an FTIR spectrometer [42]

2.3.4.1 Michelson Interferometers

Michelson interferometer is most commonly used for FTIR spectroscopy, in which mirrors are perpendicular to the plane, one mirror move to the plane perpendicularly as in figure 2.11. Beam-splitter is a semi-reflecting film that splits the planes of mirrors. The beam-splitter is a material selected in accordance with the region we want to examine. For the mid- or near-infrared regions, iron oxide or Ge are laminated onto infrared substrate (transparent) to form beam splitters. For the far-infrared region, thin films of PET (poly-ethylene terephthalate) are used. After collimation, having wavelength λ (cm), monochromatic beam is moved toward beam-splitter, ratio of transmittance and reflectance between two mirrors is 50:50. Mirrors reflect two beams to the beam-splitter where recombination and interference occur. Transmitted beam is the beam emits at 90° to the input beam and FTIR spectrometry detects this beam. [43]

Optical path difference is produced by two moving mirrors. Interference in path differences of two beams $(n + 1/2)\ \lambda$ is destructive in transmittance of beam and constructive in reflection.

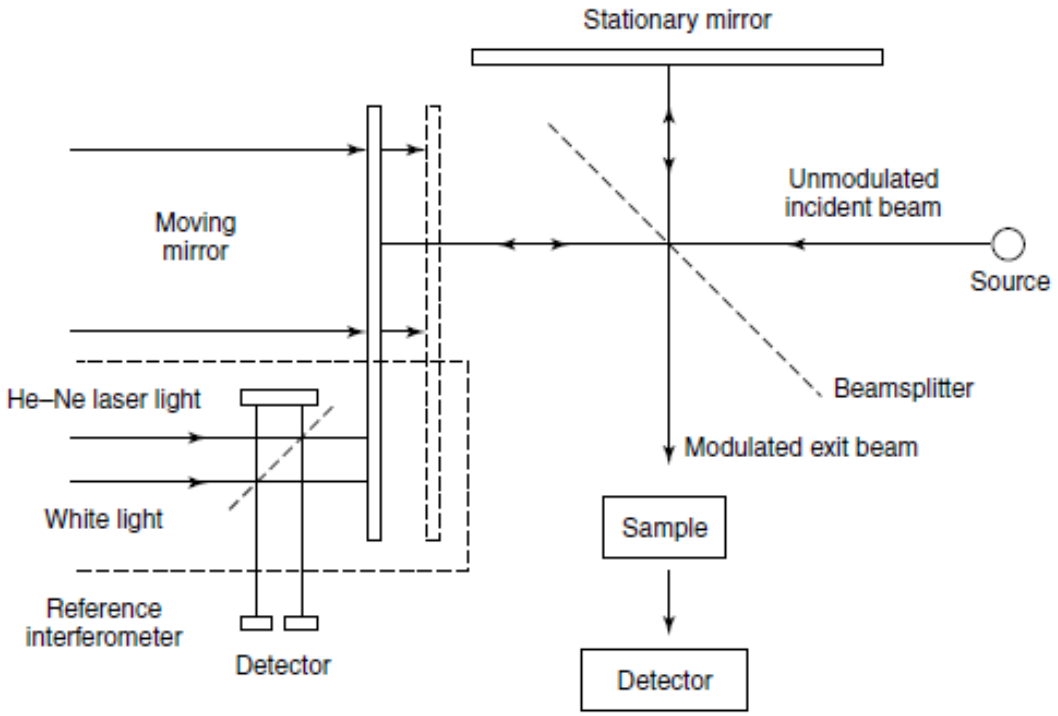

Figure 2.11: Schematic of Michelson interferometer. (Stuart, B., Modern Infrared Spectroscopy, ACOL Series, Wiley, Chichester, UK. 1996. University of Greenwich and reproduced by permission of the University of Greenwich.) [42]

2.3.5 Universal testing machine (UTM)

Tensile elongation test is most significant demonstration of strength in materials and generally, it gives detailed information about properties of plastics. Basically, tensile test of a material is the capability of material to resist the load that forced it to pull away and to find the limit to which material can be extended without breaking.

Different kinds of plastics are often analyzed on base of their tensile strength, elongation (strain) and young's modulus. But some plastics show very delicate behavior towards strain and environment. So, the details attained from UTM can't be recognized as logical technique for strain and tensile modulus. [44]

2.3.5.1 Sample selection and conditions for testing

Samples for UTM are prepared by different methods. Commonly, samples are prepared by compression molding or injection molding. Sometimes, samples are prepared by cutting from machine in different shapes e.g. in sheet, plate, slab form. Cutting of samples and conditions for analysis totally depends upon our project specifications and upon ASTM standards.
For example, according to ASTM D638 the sample of Type 1 for tensile test measurements is in dog bone shape.
As tensile properties of some plastics varies with changes in temperature changes thus, tensile tests must be performed at 50 ± 5°C relative humidity and laboratory temperature of 23 ± 2 °C. [44]

2.3.5.2 Tensile Strength

The cross head speed depends upon test conditions and material details. Five different cross head speeds can be used while following ASTM D638. Most commonly, cross head speed of 0.2in./min is used. It is best if speed according to details and descriptions of material in used. But if cross head speed is not mentioned in literature, then that convenient speed is used that breaks the sample in a maximum duration of 5 minute. The sample must be clamped vertically in UTM. The sample must be clamped tightly to avoid any slippage. The cross head speed is properly set before the machine is turned on. As the sample stretches, resistance of specimen increases and detected by load cell. That load value of load i.e. force is note down from machine. The maximum value of peak obtained by sample is also recorded. The elongation of sample continues until sample breaks. Value of force at breakage of sample is recorded.
The tensile strength is calculated by:

Tensile Strength = Force / cross section area [44]

2.3.5.3Stress-Strain Curve

The stress applied on a material in proportional to strain and elastic deformation yielded. Stress is proportional to strain by Hooke's law:

$$\sigma = E\epsilon[45]$$

Where "E" is modulus of elasticity or Young's modulus of a material. In simple words it's the resistance for elastic deformation. Young's modulus is directly proportional to the stiffer of material. Elastic deformation is not permanent deformation as material regains its earlier shape after removal of applied stress. But stress is applied beyond elastic zone material deforms permanently it's called plastic deformation and the area is called plastic zone. Basically, plastic deformation occurs due to breaking of bonds and movement of atoms from their original position, atoms arrange themselves in a new arrangement and do not turn back to their positions even when stress is removed. The point at which plastic deformation starts is called as yield point. After yielding zone plastic deformation starts and when stress reaches to its maximum value beyond the bear limit of material, breaking occurs and material fractures. The maximum stress that the material can withstand before breaking is called tensile strength.

The most meaningful details provided by UTM are tensile modulus, young's modulus and yield strength. The slope in initial elastic zone is young's modulus. Yield strength is maximum resistance of material against stress after this material is plastically deformed.

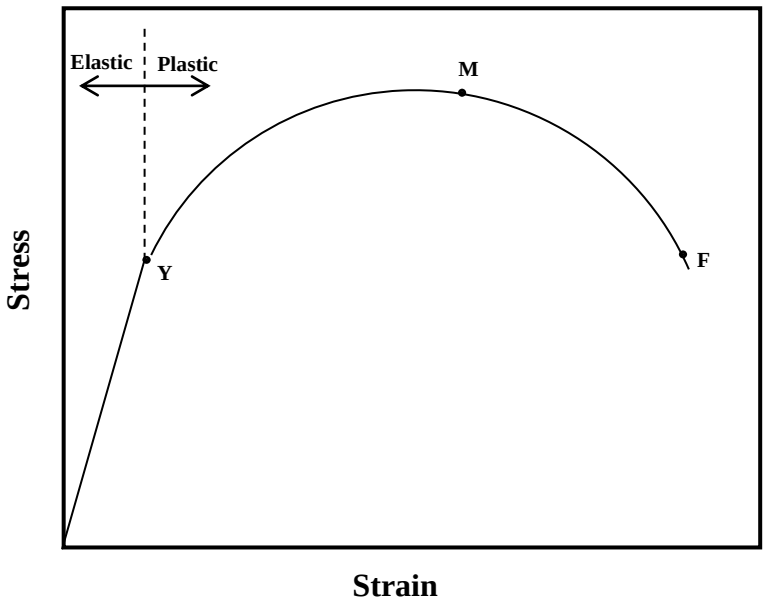

Figure 2.12: Stress strain behavior with elastic and plastic zones: yield point 'Y', maximum stress point 'M', fracture point 'F' having stress value known as yield strength, tensile strength and fracture strength respectively [45]

Chapter 3

RESULTS AND DISCUSSION

Results and discussions of this project consist of three portions.

3.1 Identification of Mechanically Cleaved Muscovite Mica Flakes

3.1.1 Optical Microscopy

Mechanically cleaved muscovite mica flakes were identified by optical microscope (OLYMPUS, MM6C-AF-2) in reflection mode at three different magnifications i.e. 20x, 50x and 100x. To get best contrast, flakes were fabricated on 290 nm Si/SiO_2 substrate.

Flakes were fabricated on two Si/SiO_2 substrates and both were analyzed at three different magnifications i.e. 20x, 50x and 100x. Single layers are highlighted in circle while bilayer and bulk flakes can be observed by contrast on Si/SiO_2 substrate.

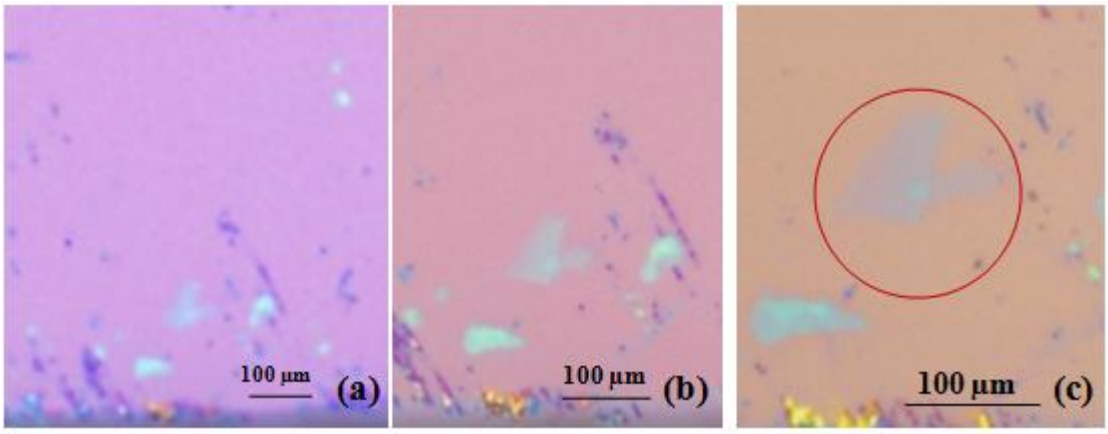

Figure 3.1: Optical images of muscovite flakes on Si/SiO_2 substrate (a) 20x (b) 50x (c) 100x

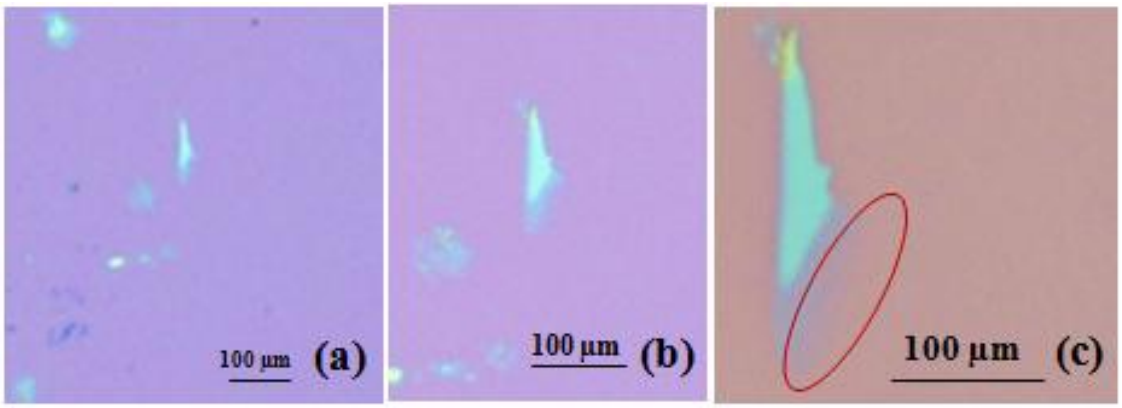

Figure 3.2: Optical images of muscovite flakes on Si/SiO_2 substrate (a) 20x (b) 50x (c) 100x

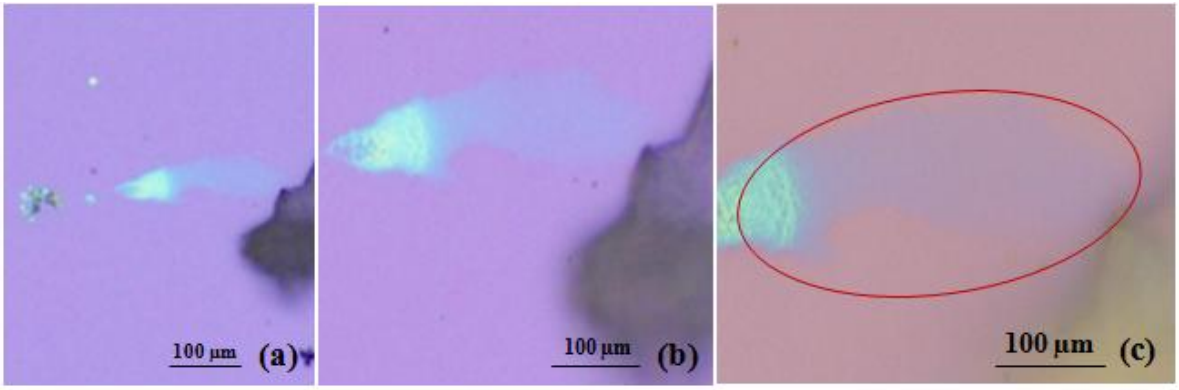

Figure 3.3: Optical images of muscovite flakes on Si/SiO_2 substrate (a) 20x (b) 50x (c) 100x

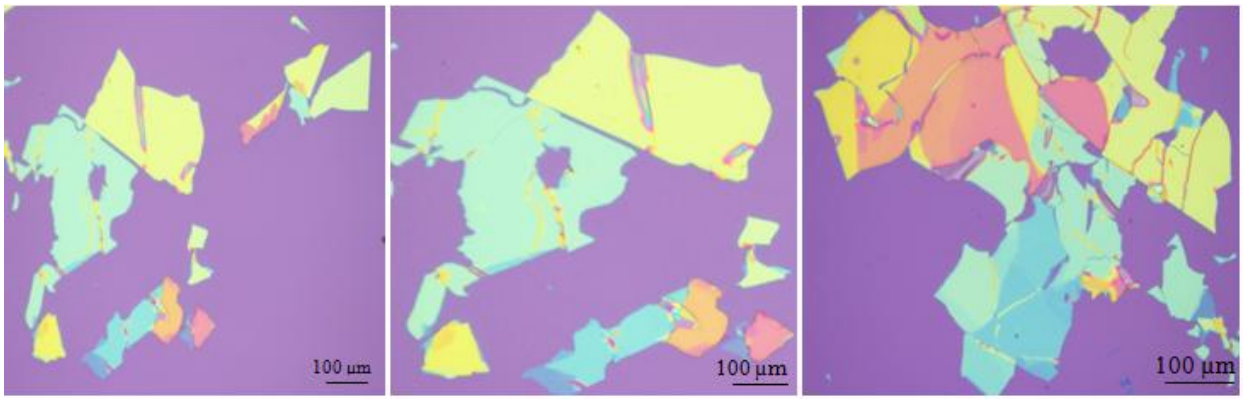

Figure 3.4: Optical images of muscovite flakes on Si/SiO_2 substrate (a) 20x (b) 50x (c) 100x

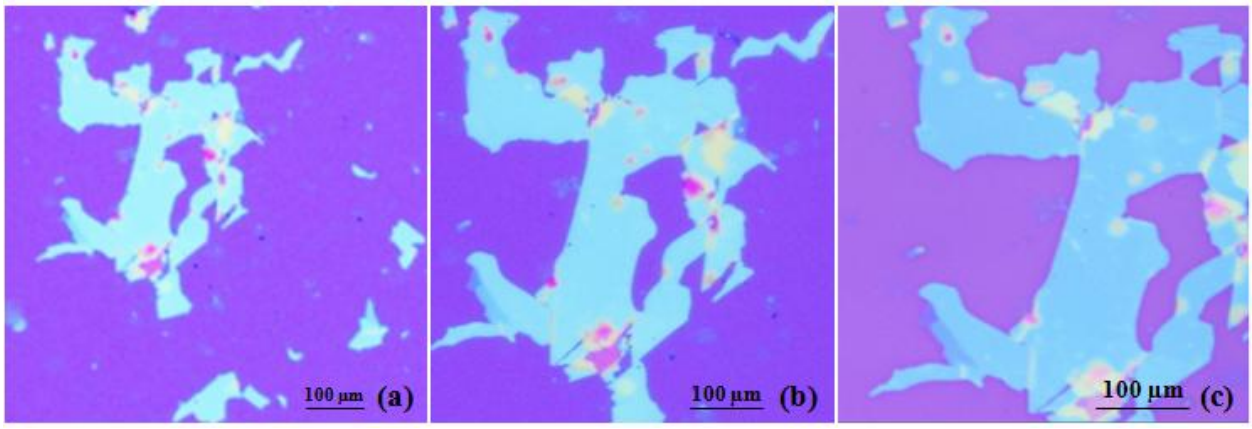

Figure 3.5: Optical images of muscovite flakes on Si/SiO_2 substrate with blue filter(a) 20x (b) 50x (c) 100x

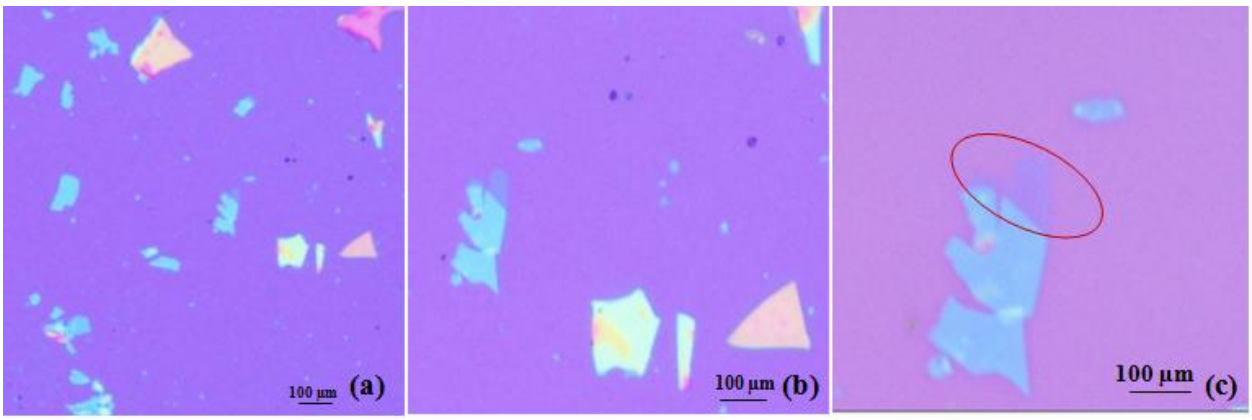

Figure 3.6: Optical images of muscovite flakes on Si/SiO_2 substrate with blue filter (a) 20x (b) 50x (c) 100x

3. 2 Atomic force Microscopy (AFM)

To check smoothness of mica substrate, roughness of mica substrate is calculated by AFM. Roughness of mica substrate is 0.067 nm in figure 3.7 (b). Roughness of mica is compared with SiO_2 substrate. Roughness of SiO_2 substrate is 0.151 nm 3.7 (a). It means that mica is more smooth material than SiO_2. Now, graphene flakes are transferred onto both substrates. RMS roughness of graphene on SiO_2 is 0.151 nm figure 3.8(a) and RMS roughness value for graphene on mica substrate is 0.078 nm figure 3.8 (b). It is concluded from our analysis that mica remains smooth even after transfer of graphene. So, mica substrate is smooth than SiO_2 substrate.

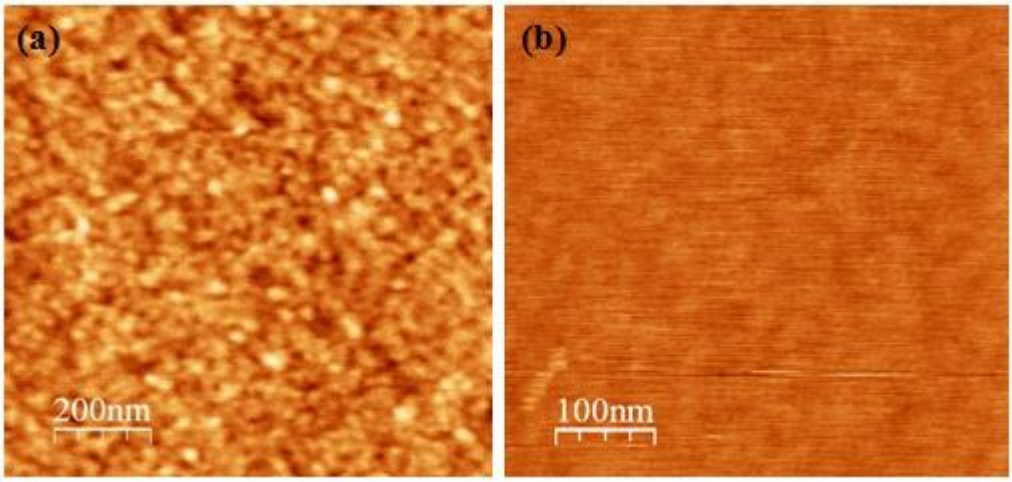

Figure 3.7: (a) AFM image of SiO_2 substrate, rms roughness 0.151 nm. (b) AFM image of mica substrate rms roughness 0.067 nm

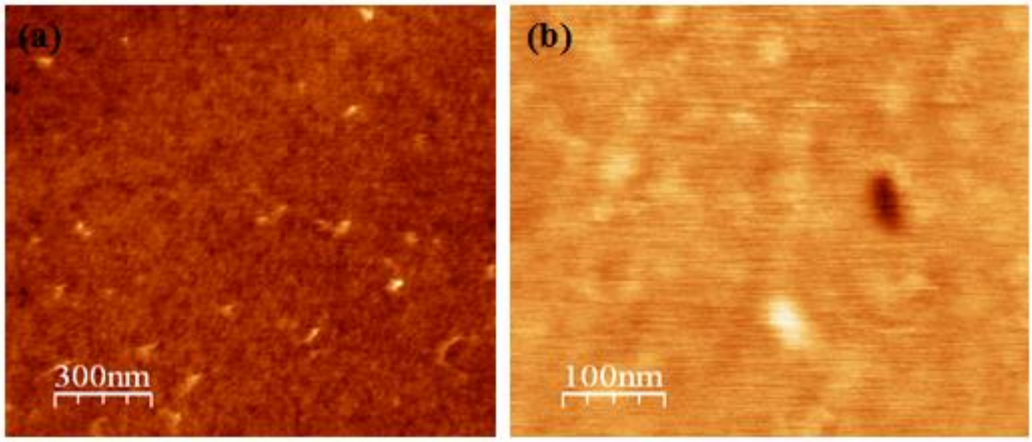

Figure 3.8: (a) AFM image of SiO_2 substrate, rms roughness 0.151 nm. (b) AFM image of mica substrate rms roughness 0.078 nm

Mica due to its smoothness used as underlying substrate in various devices e.g. in gas sensors, strain sensors, photo detectors, bendable devices. Mica due to its smoothness preferred in gas sensing applications instead of silicon. Mica used for smooth mixing and dispersion of paints and pigments.

3.3 Characterizations of Exfoliated Mica solution

Exfoliated mica solution was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and optical microscopy.

3.3.1 Optical Microscopy

Few drops of exfoliated muscovite solution were dropped on pre-cleaned glass slide and it was allowed to dry completely for 2-3 days. This glass slide was observed under optical microscope (OLYMPUS, MM6C-AF-2) at a magnification of 50x. The films (images) obtained from optical microscope show that the muscovite solution is perfectly exfoliated and drops were perfectly dispersed on glass slide.

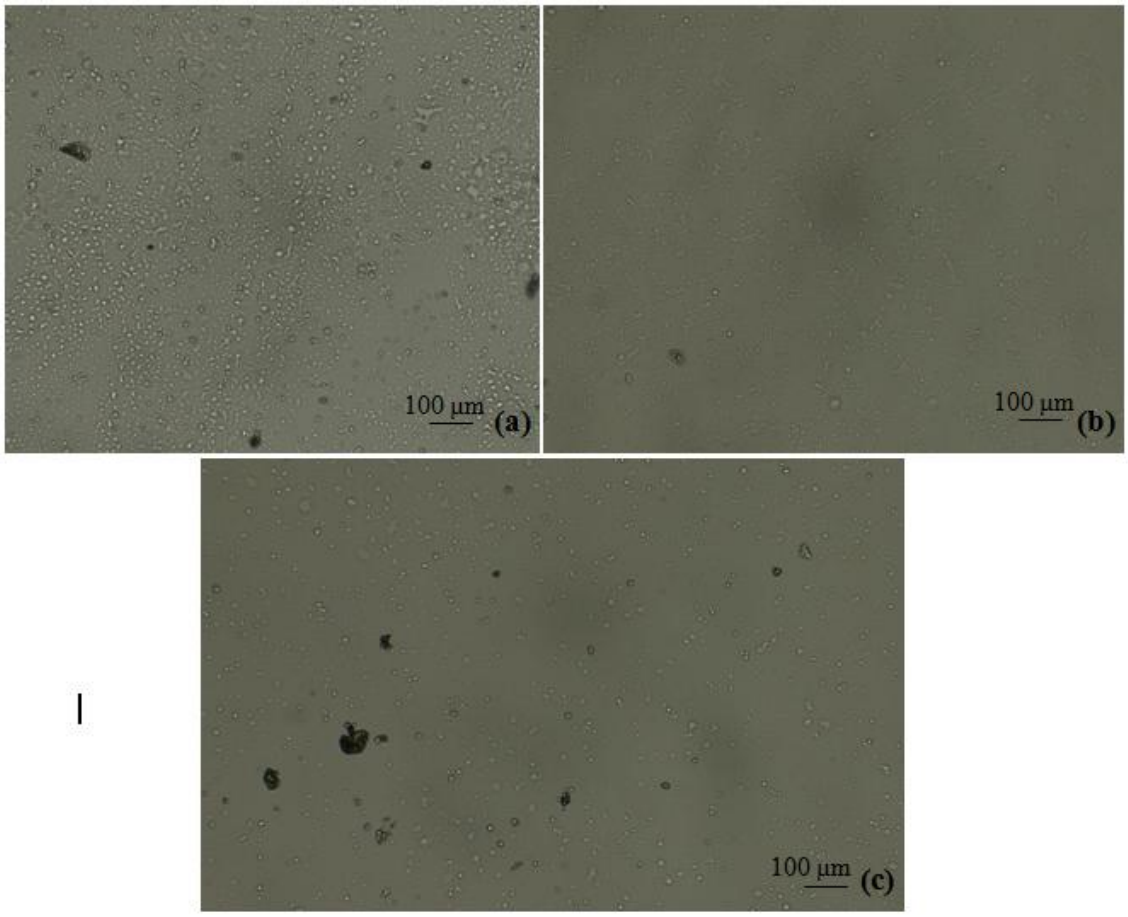

Figure 3.9: Optical image of exfoliated muscovite solution on glass slide, exfoliated at 6000 rpm (a), (b) and (c) at 50x

3.3.2 X-ray Diffraction (XRD)

For XRD testing some drops of exfoliated mica solution were dropped on 290 nm Si/SiO_2 substrate and on glass slide, and then both substrates are dried.

Figure 3.10 shows the comparison of XRD peaks of pure muscovite mica powder and exfoliated solution. Exfoliation does not disturb crystal structure of muscovite. XRD spectra reveal that two extra peaks appeared in solution after exfoliation circling in black colour. The absence of peaks means that mica powder is properly exfoliated. Peaks after exfoliation in solution are, indicating an increase between layers of muscovite mica structure, it means that solution is exfoliated.[27]

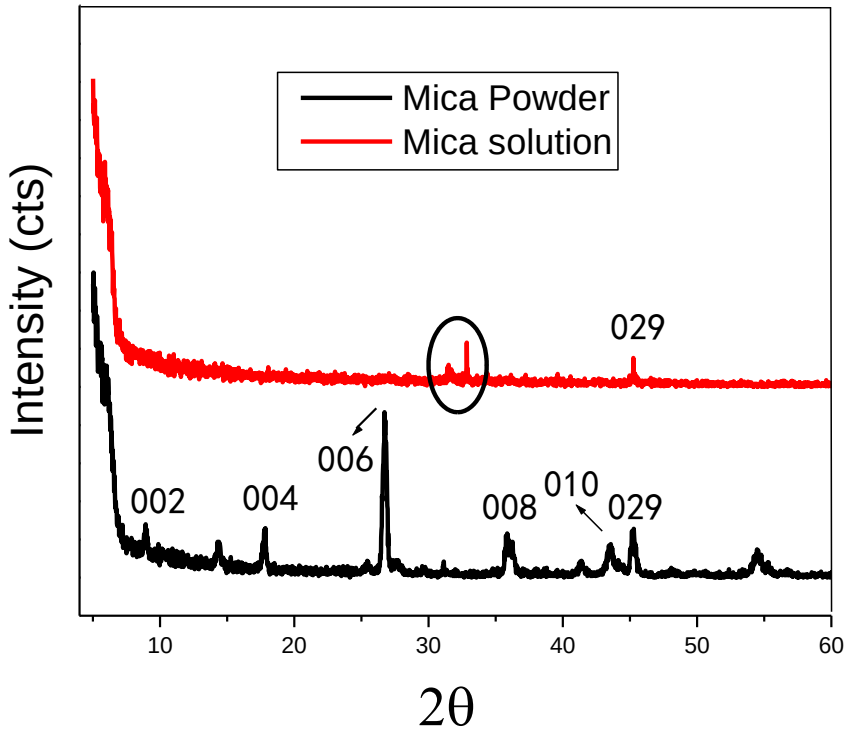

Figure 3.10: Comparison of XRD graph of muscovite powder and exfoliated muscovite solution at 6000 rpm on Si/SiO_2 substrate

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Comparison of FTIR spectra of bulk Mica Powder and Exfoliated Mica solution is shown in figure 3.11. After exfoliation appearance of extra peaks and shifting of some peaks confirm exfoliation. The peaks of 2932 cm^{-1}, 2872 cm^{-1} and 1497 cm^{-1} appeared after exfoliation. First two peaks 2932 cm^{-1} and 2872 cm^{-1}appeared due to C-H stretching of alkanes. The peak at 1497 $cm^{-1}$is due to N-H bend.[41]

The other peaks that are present in FTIR spectrum of muscovite solution are slightly shifted. The peak at 3426 cm^{-1} is shifted to 3432 cm^{-1} after exfoliation. Peak of 1651 cm^{-1}, 1061 cm^{-1} and 712 cm^{-1} are shifted to 1669 cm^{-1}, 1069 cm^{-1} and 660 cm^{-1} respectively after exfoliation. The shifting of peaks indicates that spacing between layers of muscovite is increased and muscovite solution is perfectly exfoliated.[27]

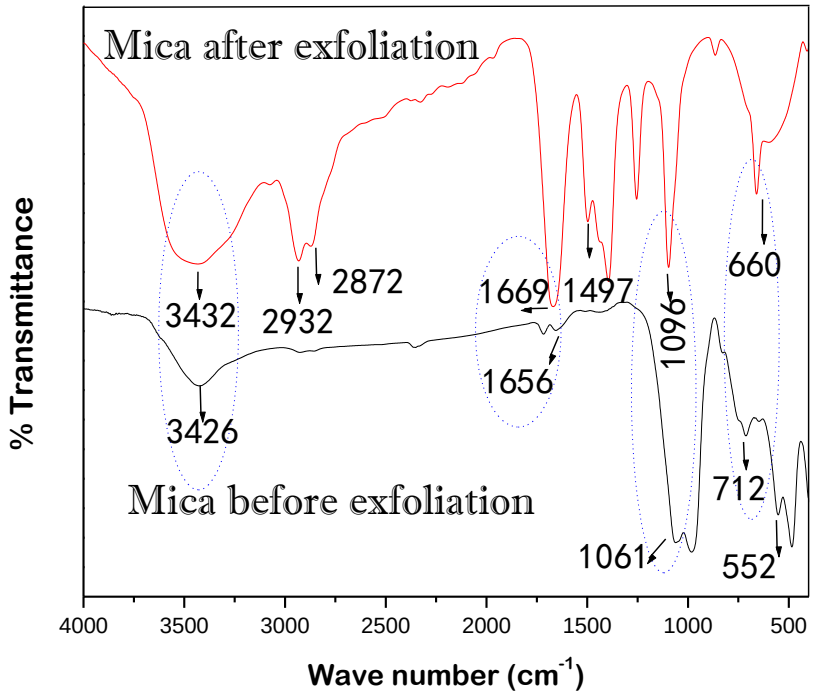

Figure 3.11: Comparison of FTIR of muscovite powder and exfoliated muscovite solution

The muscovite mica solution which is exfoliated by liquid phase exfoliation; accurate exfoliation is justified by optical microscopy, XRD and FTIR analysis. Exfoliated muscovite

solution can be used in various applications i.e. in gas sensors, strain sensing devices and as filler for fabrication of nanocomposites.

Nanocomposites is one of major and novel application of muscovite exfoliated solution therefore, here muscovite mica filled PVC nanocomposites are fabricated. Successful fabrication of nanocomposites is tested and their mechanical properties are also tested.

3.4 Characterizations of Mica filled PVC nanocomposites

Mica filled PVC composites are characterized by FTIR to analyze correct and precise mixing and formation of PVC composites. PVC composites are tested by UTM (universal testing machine) to analyze mechanical properties of composites.

3.4.1 Fourier Transform Infrared Spectroscopy

Figure 3.12 explains FTIR graphs of pure PVC sheets and different mica filled PVC nano composites. The peak at 2924 cm^{-1} is due to C-H stretching of alkanes, 1677 cm^{-1} is due to C=C bond. The peaks of 1251 cm^{-1} and 1097 cm^{-1} are due to C-O bond. The peak at 962 cm^{-1} is due to out of plane bend and the peak of 623 cm^{-1} is due to C-X while X represents chloride.[47]

From FTIR results it has concluded that some peaks of pure PVC 2924 cm^{-1}, 1667 cm^{-1}, 1097 cm^{-1} and 623 cm^{-1} are very close to peaks of exfoliated solution 2932 cm^{-1}, 1669 cm^{-1}, 1096 cm^{-1} and 660 cm^{-1} therefore, it's difficult to explain that either the peaks in nanocomposites are the original peaks of PVC matrix or appeared due to incorporated solution.

But slightly shifting in peaks of nanocomposites is observed. Shifting of peaks reveal that mica filler is incorporated into PVC matrix. The peaks of 2924 cm^{-1}, 1425cm^{-1}, 1097 cm^{-1} and 961 cm^{-1} have shifting value of 1 cm^{-1} while 623 cm^{-1} has shifting of 3cm^{-1}. From figure 3.13 it can also have concluded that no extra peak of filler (mica) in composites is observed. It means that filler is satisfactorily dispersed in PVC matrix and filler (mica) is not disturbing crystalline structure of PVC matrix, it just incorporate precisely into PVC matrix.[48]

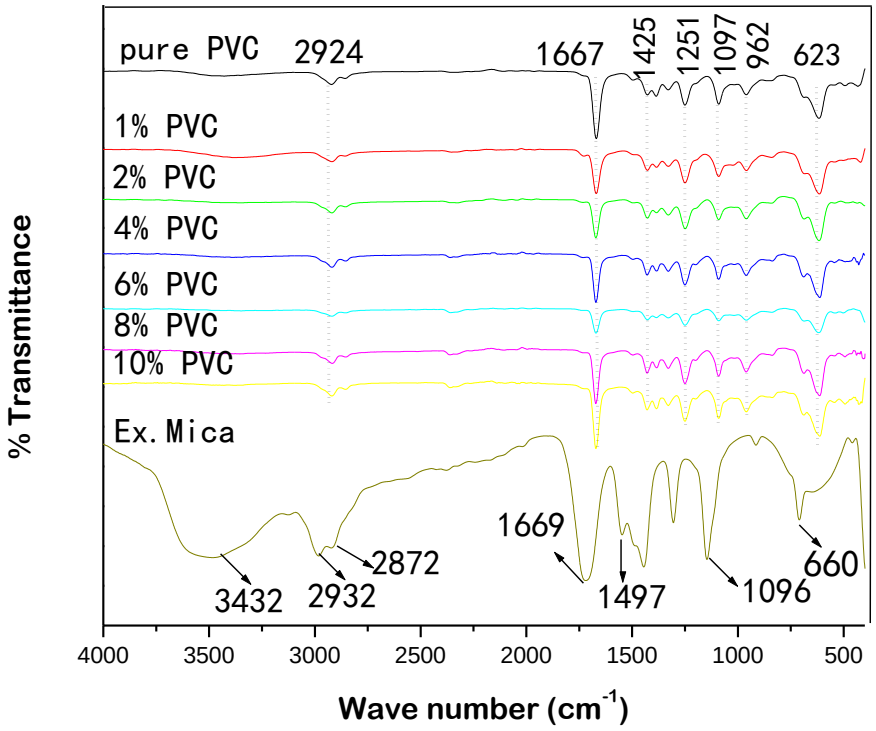

Figure 3.12: Comparison of FTIR graphs of pure PVC with muscovite mica filled PVC and exfoliated muscovite solution

3.4.2 Mechanical properties of mica filled PVC nanocomposites

The mechanical properties of mica filled PVC nanocomposites were tested using UTM (Universal testing Machine) with crosshead speed of 50mm/min following ASTM D-638 to measure Young's modulus and tensile strength. Following ASTM D-638 samples were cut in the form of straight strips. Three sets of each concentration were made to conduct mechanical test. [49]

Figure 3.13 shows change in tensile strength on addition of different concentrations of mica in PVC. Curves of graph show variation in tensile strength with increase in mica content.

The value of tensile strength first decreases at low concentration of filler from PVC 1 – PVC 2. The lowering of tensile strength of mica filled composites may be due to frail interfacial bonds between mica solution, the filler and PVC matrix interface and aggregation of exfoliated solution into PVC matrix. [50]Aggregation of filler is liable for minimization of

mechanical properties. Addition of mica solution offsets the movement of polymer chains so, the filler cannot disperse precisely into matrix, and it's the reason of weakening of interfacial bonds between filler and matrix. [50]

At an intermediate concentration of filler i.e. PVC 4 the tensile strength increases to maximum value of 37 MPa. This increase in mechanical strength is due to good dispersion and mixing of filler into whole matrix area and strong adhesion between filler and matrix. [45] At very high concentration of filler PVC 5 – PVC 6 the tensile strength again decreases to 18 MPa. This again decrease is due to poor dispersion of filler at very high content also filler molecules in larger concentrations cannot interact properly with matrix chains. [51] Filler at very high concentration agglomerates into matrix and deteriorates the mechanical properties of nanocomposites.

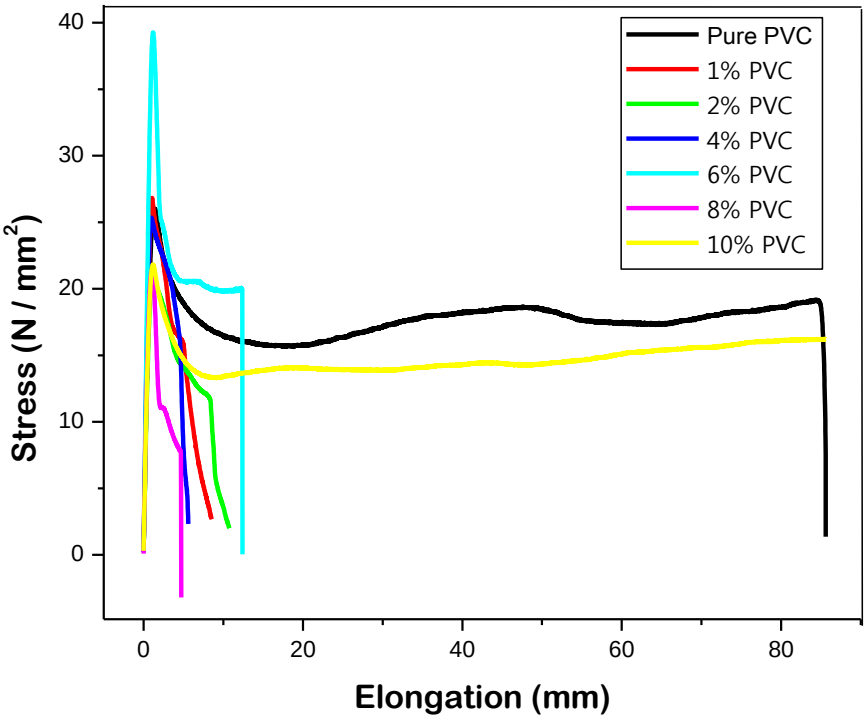

Figure 3.13: UTM analyses of pure PVC and its nanocomposites

The young's modulus also follows the same pattern at low concentration of filler it decreases to 23 MPa and at intermediate concentration it increases to 39 MPa and then at very high concentration it again reduces to 20 MPa. Table 3.1 below briefs all calculations.

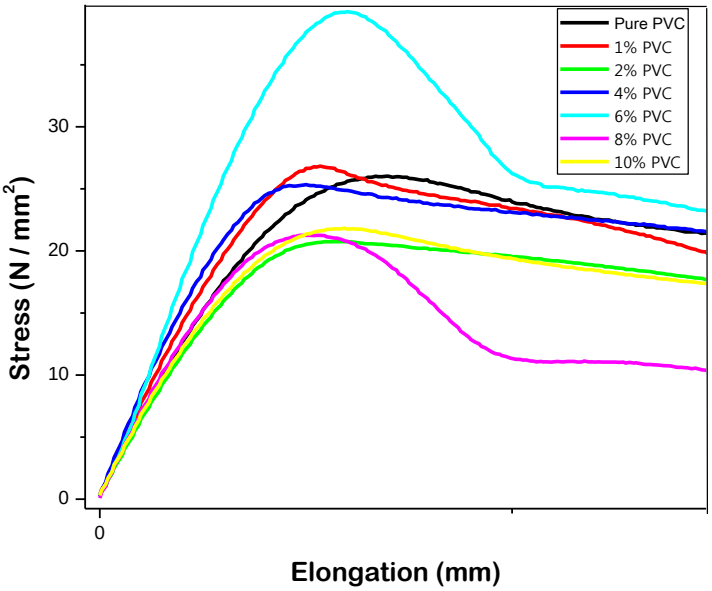

Figure 3.14: UTM analyses of pure PVC and its nanocomposites enlarged view

Table 3.1: Tensile calculations of mica filled PVC composites

Samples	Filler Content (wt %)	Tensile strength (N/mm^2)	Young's modulus (GPa)	Elongation at break (mm)
Pure PVC	0	25.06	1.33	85
PVC 1	1	25.72	1.18	8.5
PVC 2	2	19.57	1.26	10.7
PVC 4	4	24.05	1.44	5.5
PVC 6	6	37.55	1.95	12.3
PVC 8	8	19.41	1.47	4.6
PVC 10	10	18.15	1.04	125

Chapter 4

CONCLUSIONS, APPLICATIONS AND FUTURE WORK

4.1 Conclusion

Firstly, muscovite mica is mechanically exfoliated and muscovite mica flakes are identified by optical microscope. And roughness of mica is measured by atomic force microscope. From AFM micrographs it is concluded that mica is smooth substrate than silicon so mica is better to use in gas sensing application and other applications than silicon.

Secondly, liquid phase exfoliation of mica powder is justified by optical microscope which confirms smooth dispersion of exfoliated mica solution. Solution exfoliation is further supported by XRD analyses and FTIR analysis. Comparison of XRD and FTIR peaks with pure powder tell about perfect exfoliation of mica solution. Shifting of peaks and appearance of some extra peaks in both XRD and FTIR spectrum confirm exfoliation of mica solution.

Exfoliated mica solution as filler is used in polymer to enhance their properties and here in this project mica solution is used for reinforcement of mechanical properties of polyvinyl chloride (PVC) nano composites.

Mica filled PVC composites are fabricated by solution blending method. Mica filled PVC composites are fabricated in sheet form with six different concentrations of mica solution (1 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt %). The mica based PVC composites are cut into straight bar shape following ASTM D-638 for mechanical testing of samples. FTIR analysis confirms the incorporation and mixing of filler into PVC matrix. Shifting of peaks of composites in FTIR graphs assures that filler is properly mixed into polymer matrix. Mechanical analysis of composites is tested by UTM at cross head of 50 mm/minute. The tensile strength of composites is increased to maximum value of 37.55 N/mm^2 from 25.6 N/mm^2 with addition of mica solution. The maximum increase in tensile strength is 49%.

4.2 Applications

Mica filled PVC nano composites can be used in following applications:

PVC is most broadly utilized polymer because it's cheap, easily approachable and durable. It is weather resistant. PVC is good insulator and resistant to corrosion and weather. PVC nanocomposites have much more applications. PVC in non-hygroscopic polymer means it does not absorb water. Due to its hygroscopic natures PVC composites can use for preservation of products. [52]

- PVC composites used for packaging of food products, it does not affect taste.
- Insulation of roof, and floors and membrane fabrication for lakes and ponds.[52]
- PVC pipes, which are more durable, low cost and fewer chances of breakage.[52]
- PVC composites used for fabrication of window frames. With addition of filler durability and strength of composites is increased.
- Mica filled PVC composite is used in electrical insulation of cables and it can withstand high voltage. [53]
- The composites fabricated can be used to repair crack in materials. Fabricated composites can be used for designing sensors.
- Fabricated composites used in construction and pipe industry and the products have improved mechanical and thermal properties.

Figure 4.1: Shielded membrane of mica/PVC composite in construction of ponds [52]

4.3 Future Work

As in this project mechanical property of mica filled PVC nano composites are measured. In future other properties of mica based PVC composites can also b measured.

- For example, thermal properties can be studied in future as different mica loading may affect thermal stability of composites. [54]
- As mica is dielectric material so in future we can extend our work by measuring dielectric properties of mica based PVC composites. [54]
- Mica can be used as filler in other polymer matrixes i.e. polyethylene, polyester, epoxy resin and organosilicon polymers, then we can measure tensile properties thermal properties etc of that composites.

Inorganic fillers prevent the penetration of gas molecules. [54] Therefore, incorporation of inorganic filler i.e. mica into PVC matrix can improve barrier properties by providing gas molecules a complicated path so that they can diffuse into material and stops the process. The layered silicates fillers also reduce the penetration of gas into material. Mica filled PVC nano composites can also be used in gas barrier applications. [54]

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