Highly Stiff, Strong and Super Tough Nanocomposite, Blends and Hybrids of TOPAS with Few Layer Graphene and Cellulose Acetate for Degradable Packaging

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DEDICATION

I would like to dedicate my work to my beloved parents, my husband, my daughter and my supervisor. I couldn't be able to achieve this milestone without them. It is their love, support and guidance which keep me motivated and ambitious to fulfill my dreams. I am nothing without them. This work is sign of my love to them.

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"Truly my prayer and my service of sacrifice, my life and my death, are (all) for ALLAH, the Rabb (Only God, Cherisher and Sustainer) of the Worlds". **(QURAN 6:162)**

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ABSTRACT

In this study the nanocomposite, blends and hybrid of TOPAS with cellulose acetate (CA) and few layer graphene (FLGs) has been prepared successfully by solution casting method using chloroform as a mutual solvent. All the samples are characterized by using X-ray diffraction, scanning electron microscopy, universal tensile testing machine and antimicrobial resistance test techniques. For TOPAS/CA Blend system, XRD peaks showed no change as TOPAS and CA both are amorphous in nature. However, by adding FLGs into the TOPAS and TOPAS/CA blends, characteristic peak of graphitic structure appears at 26.5^{o} and the intensity of the peak increases with increasing FLG concentration. SEM micrograph showed that CA and FLGs are dispersed uniformly in TOPAS matrix. Tensile strength and tensile modulus are enhanced significantly as compared to pure TOPAS. For TOPAS/FLG nanocomposite, TOPAS/CA blends and TOPAS/CA/FLG hybrids, maximum tensile strength is increased upto 160%, 150% and 150% respectively while enhancement in modulus was achieved upto 84%, 90% and 17%, respectively. Also due to chains alignment elongation at break was improved which was increased upto 110, 80 and 118 times respectively making the system super-tough with enhanced strength and stiffness. Anti-bacterial resistance is determined by using AATCC-147 (modified) standard while anti-fungal resistance is determined by using ASTM G-21. Nanocomposites, Blends and Hybrid of TOPAS showed resistance against all strains of bacteria and fungus used in study making it a promising system for packaging.

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LIST OF ABREVIATION

O_2 Oxygen

CO_2 Carbon dioxide

PLA   poly lactic acid

PC   polycarbonate

PMMA   poly(methylemthacrylate)

PDMS   polydimethylsiloxane

COPs   cyclic olefin polymer

COCs   cyclic olefin copolymer

HDT   heat deflection temperature

PP   Poly propylene

THz   tera hertz

PS   Polystyrene

HDPE   high density polyethylene

PEEK   polyetheretherketone

PNCs   polymer nanocomposites

WAXD   Wide angle X-ray diffraction

SAXS   small angle X-ray scattering

SEM   scanning electron microscope

TEM   transmission electron microscope

STM   Scanning tunnelling microscope(

SPM   scanning probe microscope

AFM   atomic force microscope

DSC	**differential scanning calorimeter**
TGA	**thermo gravimetric analysis**
DMA	**dynamic mechanical analyzer**
CF	**Carbon fiber**
FLGs	**few layer graphene**
CA	**cellulose acetate**
Wt	**weight**
MRSA	**Staphylococcus Aureus**
S. Typhi	**Salmonella Typhi**
E.Coli	**Escherichia Coli,**
AB- 10	**Acineto Bacter**
PA-10	**Pseudomonase Aeruginosa**
L.B	**liquid broth**
PDA	**potatodextrose agar**
MPa	**mega pascal**
xGNP	**graphene nanoplatelets**
S-S	**Stress-Strain**
T.S	**Tensile strength**
E	**elastic /young/ tensile modulus**
Conc	**concentration**
+ive	**positive**
-ive	**negative**
ATPs	**adenosine triphosphates**

Chapter 1

1.   Introduction

The fundamental function of packaging is to maintain the quality and safety of the product. Its main and most important function is to increase shelf life of the product. It act as a barrier in order to save the product packed inside from harsh condition prevailed outside. It provide physical protection and create physiochemical condition to protect the product so that shelf life increase[1]. These packaging are also self-sterilized[2].

1.1 Properties of packaging material

There are certain properties that an excellent packaging material must be fulfill or demonstrate (shown in figure 1)[1].
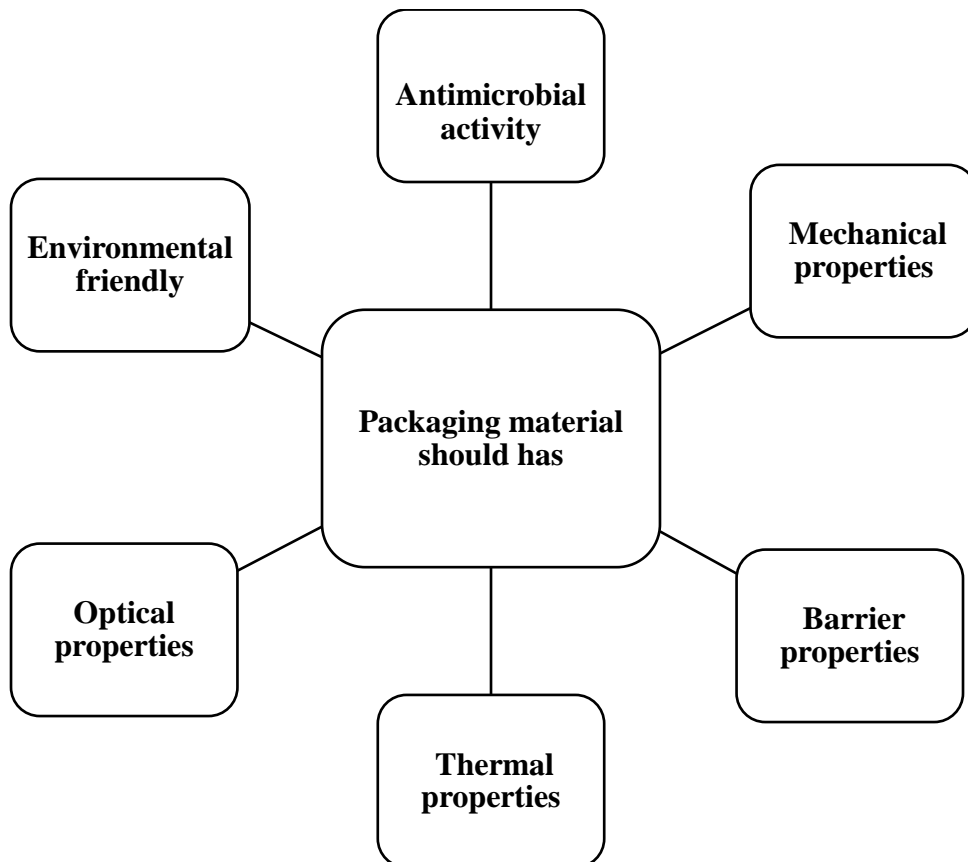
Figure 1: General properties of packaging material

Permeation is the mass transport process in which material move from interior to the exterior and vice versa through diffusion. Permeation depends on the following factors (shown in figure 2). The internal and external environment at the surface of the polymer is consist on atmospheric gases, vacuum, liquid and solid. So the external boundary condition have a very pronounced effect on the permeability of the surface(figure 2)[3]
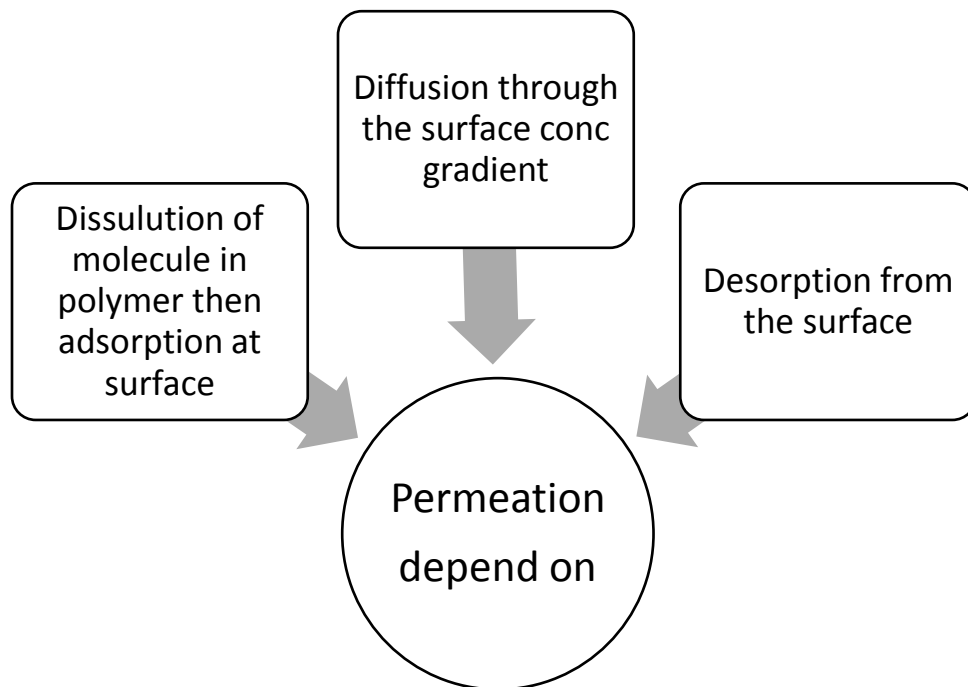
Figure 2: Factor that effect permeation

Anti-microbial packaging can act in two ways, number one to bind an antimicrobial agent to the package surface and it should be large enough that it interact with the bacterial cell while still attached with the surface. And second one is, it release some anti-microbial agent on surface of packed material.   To add antimicrobial effect into packaging to stop growth of microbes result in reduce transparency of the film which is physical limitation of packaging material [4].

1.2   Packaging material

All three classes' ceramic, metal and polymer are extensively used in packaging. The popular packaging materials are paper and paper product, plastic, glass and metal and metal

alloys. Out of these up to forty percent packaging is done by polymer half of which is considered as food packaging[1].

All of these packaging material derived from petroleum based nonrenewable resources since the mid of the twentieth century. Because these are cost effective and easy to process[1].

1.2.1 Synthetic polymer

Synthetic polymers are widely used in packaging. They have replaced paper, glass and even metals. Because they showed better
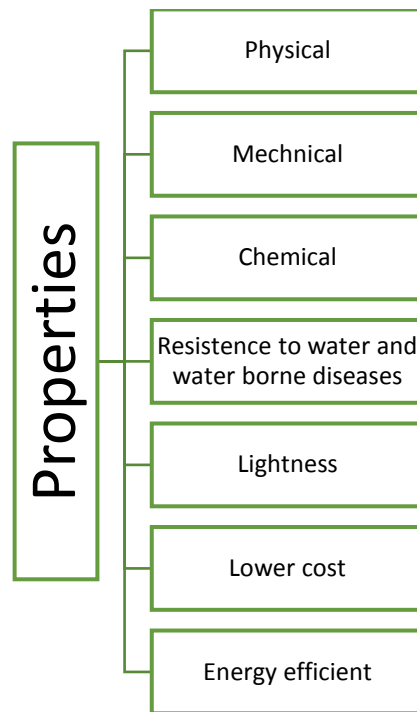
Figure 3: General properties of polymer

In spite of all these properties the major limitation with synthetic polymer is that their waste accumulate in the environment after its useful use as a lither. Waste generated by synthetic polymer is considered as major environmental solid waste pollutant. The major difficulty in managing solid waste generated by synthetic polymer is variability of material and resources.

Due to environmental pollution and eco degradation, the demand for eco-friendly products has been increased day by day. Environmental awareness and new rules and regulation forced industries to focus on eco-friendly product. As a result attempt has been made to add biodegradability into polymer to use them in daily life by slight change in their structure [5, 6].

Now bio based polymer materials have been widely used and has gained much attention due to concern of global environment and as an alternative to petroleum based polymeric material.

1.2.2 Biopolymer

Now a day the ideal packaging material is the biodegradable material also called biomaterial and polymer derived from these material are called biopolymer. These polymers are derived from renewable resources. These polymers should have excellent mechanical, barrier, antimicrobial and thermal properties. Also they must degrade at the end of their useful life without polluting environment so no waste generated. These polymer are the substitute for the non-degradable packaging polymeric material[1].

The natural polymer chitosan, most abundant biopolymer second to cellulose, is nontoxic, edible and biodegradable polymer. It has been used as a packaging material due to its ability to form film without additives. It has good mechanical properties, antimicrobial activity against bacteria, fungus and yeast. It shows good permeability against oxygen (O_2) and carbon dioxide ($CO_{2)}$. It is used in edible coating and films to extend shelf life of fruits, seafood and meat etc. in spite of all these there is a major drawback to use chitosan in packaging due to its high affinity to absorb moisture. To overcome this problem chitosan blended with poly lactic acid(PLA) but result showed that mechanical properties was compromised[7].

1.3 Active packaging

One of the new concepts in packaging is active packaging, as common traditional packaging is limited in its ability to increase the shelf life of product. Active packaging concept is defined as it is packaging that change the condition of the packaging while increasing shelf life of the product as well as improve safety and sensory condition with maintaining quality[2].

One type of active packaging is oxygen scavenger technology in which material cannot allow oxygen to permeate in or absorb extra oxygen so save product from deterioration due to oxygen. The CO_2 scavenger and emitter cannot allow carbon dioxide to destroy the packed food. CO_2 is produced due to respiration and deterioration of food. So to save the food it is essential to remove it from inside atmosphere. Some product destroy by moisture so the active moisture barrier packaging play role and stop moisture to get inside also active packaging absorb moisture from inside of the packaging material.

For example Ethylene act as a hormone in many plant species it help in ripening and soften. It also cause yellowing of the fruit and vegetable so ethylene scavenger packaging help to overcome this problem. Some product such as fish, meat, fruit, vegetable, poultry, bread, cheese and butter need to protect from microbes. Antimicrobial substances must be incorporated in the packaging films or coated on the packaging material so that microbes cannot get attack on the substance. Antioxidant packaging concept also very widely used in order to stabilize lipid oxidation to increase shelf life of the product. Absorption and adsorption of food flavor through polymeric films cause the reduction in flavor as well as in taste. Usually flavor scalping is not good for food. But it is used in positive way i.e. it used to reduce bitterness in grapefruit juices. To respond to bitterness an active cellulose acetate thin film is used inside the packaging material [2].

Chapter 2

2   Literature review

In the field of polymer science the biodegradable polymers are newly emerging field of current research. During the last two decades biodegradable polymers are widely used as bio stable biomaterials are replaced by biodegradable materials for so many applications. A large number of biodegradable polymer materials are synthesized rapidly and there are many microorganism which are capable to degrade these material. Biodegradation is a natural process by which complex organic molecule converted into their simpler forms[5, 8].

Due to environmental pollution and eco-degradation, the demand for eco-friendly products has been increased day by day. Environmental awareness and new rules and regulation forced industries to focus on eco-friendly product. As a result attempt has been made to add biodegradability into polymer to use them in daily life by slight change in their structures [2, 3]. Now bio based polymer materials have been widely used and has gained much attention due to concern of global environment and as an alternative to petroleum based polymeric material. It is a substitute for none biodegradable polymer whose waste is difficult to manage [5, 9, 10].

Over the last two decades the field of Nano science blossomed. The importance of Nano technology increased in areas such as computing, sensors, biomedical and many other fields. The synthesis of nanoparticle of various sizes, shapes and of many materials shows the advancement in these fields. The change from micro particle to nanoparticle yields significant changes in physical properties. For the same volume the Nano scale has more surface area as compared to micro scale [11-13].

The opaque material may become transparent just like a copper, stable material may be combustible like aluminium, insulator become conductor such as silicone and solid become liquid at room temperature when reduced to nanoscale. For fibre and particle the surface area per unit volume is inversely proportional to their diameter, so smaller the diameter larger will be the active surface area.

In the recent era the nanomaterials have wide range of application. But the material scientists and engineers still searched the material with improved physiochemical properties for a

particular application [9]. The Nano composite play an important role in upgrading the structural and functional properties of polymer matrix[14].

Now a day the organic and inorganic filler is used frequent in polymer system. Polymer composites are used for various industrial and diverse applications such as sporting goods, aerospace and medical equipment. In the last two decades the emphasis on polymer nanocomposite has increased where one of the dimensions of material is in nanometer scale. The search in the nanotechnology is facilitated by the invention of scanning tunneling microscope and scanning probe microscope. With these tools scientist are able to see the nature of surface structure with atomic resolution. With the rapid increase in the computer technology now it is possible to characterise and predict the properties at nanoscale with simulation modelling[15].

Nature gives the idea of nanocomposite. Late in 1998 the article "Nano sandwiches" published, which state that nature is a master chemist with incredible talent. With polymer such as carbohydrate, lipid, and protein nature make strong composite of bones, shells and wood by using natural reagent. In early 1990s the Toyota central research laboratory in japan has published a report on nylon6 nanocomposite for which very small nano filler result in enhanced in mechanical and thermal properties. After that the world of nanoscience blossomed very fast[16].

There are many polymeric materials such as polycarbonate (PC), poly(methylemthacrylate) (PMMA), polydimethylsiloxane(PDMS), cyclic olefin polymer (COPs) and cyclic olefin copolymer (COCs). All these polymers are amorphous, thermoplastic as well as transparent polymer and are important engineering material for various applications [12]. All these polymer have different physical and chemical properties and from these polymer COCs are of special interest because they possess unique properties when compared to other polymer such as PMMA and PC[13].

COPs are commercially available under different brand name such as Apel, Arton, Topas, Zeonex and Zeonor. Out of these Apel and Topas are made from more than one monomer unit so called cyclic olefin copolymers (COPs) [14]. COCs are transparent like a glass. They have low density as compared to PMMA and PC. Their heat deflection temperature (HDT) is very high. They show excellent electrical properties. They have high chemical resistance to aqueous acids, bases and polar organic chemicals. Aliphatic and aromatic hydrocarbons react with them. Also exposure to toluene, hexane, certain oils and fats must be avoided. Table 1 also depict these properties[17]. They show high tensile modulus and high rigidity. Also show low elongation at break and good surface hardness. Along all these properties they are highly pure and show excellent water barrier and low moisture absorption properties[17]. The glass transition temperature of different cyclic olefin grades varies between 80°C-160°C. COCs are copolymer of ethylene and a ring shaped norbornene group usually derived from dicyclopantadiene. The chemical structure of COPs show its nature and copolymer group (Fig: 4), two different ring structures incorporated in polymer chain. This ring structure gives the polymer its stiffness while its size prevent the molecule to be crystalize [16]. The stretching of COCs at low temperature is not possible while at elevated temperature it is ductile [16].
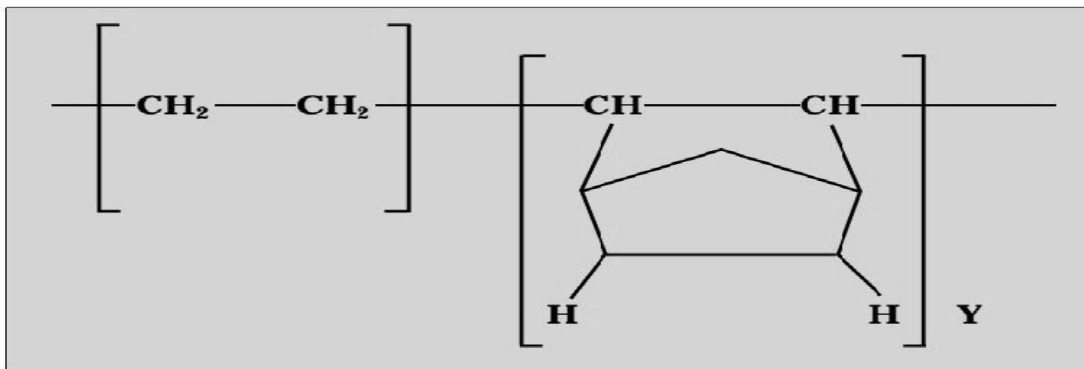
Figure 4: Structure of COC

COCs are synthesised from ethylene and norbornene groups. Norbornene incorporated randomly in carbon main chain (Source [15]).

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Table 1: Properties of COC

Range of properties of commercial COCs*

Physical/Mechanical properties	Value
Density, g/cc	1.02
Water absorption, %	<0.01
Water vapor permeability @ 23°C, 85% R.H., g/m^2/day	0.02 to 0.04
Tensile strength, psi	9570
Elongation @ break, %	3 to 10
Tensile modulus, kpsi	377 to 464
Charpy impact, kJ/m2	13 to 20
Notched charpy impact, kJ/m^2	1.7 to 2.6
HDT at 66 psi, °C (°F)	75 (167) to 170 (338)
Glass transition temperature °C (°F)	80 (176) to 185 (365)
Melt flow index at 260°C, g/10 min.	4 to 56, depending on T_g
Mold shrinkage, %	0.6 to 0.7

Optical properties	
Luminous transmission, %	92
Refractive index @587.6 nm	1.533
Abbe number	56
Photoelasticity,: mm^2/n	6x10^{-7}
Haze, %	1 or below, depending on grade
Birefringence	Low

Electrical properties	
Dielectric const. @ 60 Hz	2.35
Comparative tracking index, volts	>600
Volume resistivity, ohm-cm	>10^{16}
Dielectric breakdown	30 kV/mm
Dielectric loss at 60 Hz	< 0.02 %

Data encompass Ticona's Topas COC grades 8007, 5013, 6013, 6015, 6017

2.2   Applications

Poly propylene (PP) film has already been used for sensors and other actuator applications. But these films are not good at elevated temperature they perform well only in the 60^0C to 80^0C range. Now COCs perform well even at elevated temperature [16].

Topas has high abbe number and low chromatic abration. "The change of refractive index with wavelength is known as abbe number" and this value is high for COCs which show low chromatic abration[17]. Due to very low absorption of Topas, it has applications in tera hertz (THz) wave guiding. Cunningham *et al* (2011) have found that topas is an ideal material for broadband THz optical component such as
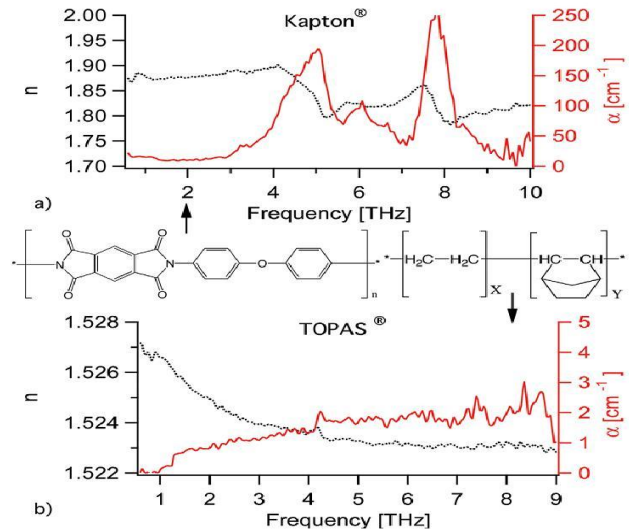
Figure 5: Refractive index and absorbtion cofficient

waveguide and window materials. As it is resistant to several acids and bases so it is a good choice for substrate material broad band THz spectroscopy[17].

The refractive index dotted and absorption coefficient solid kapton and topas. Chemical structure also shown in (fig: 5) shows the refractive index dotted and absorption coefficient solid kapton and topas. Fine scale for the topas shows its precision in measurement and has nearly constant value of the index for topas in THz band[17].

The use of microfluidic devices in life science has become very popular due to its ability to analyse minute quantities of sample high throughout sample capability. Initially glass is used as a substrate material for microfluidic device due to its transparancy, thermal stability, biocompatibility, chemical resistivity and surface properties. The major drawback of glass as a substrate material is its brittleness, time consumption, cost and use of hazardous chemical such as hydrofluoric acid during manufacturing. The interest in transparent polymer for disposable microchip is growing and now COCs are used for substrate for microfluidic devices [13].

Interest in plastic and polymer based micro fluidic devices has been increased due to demand of disposable product in medical and genetic field. Producing devices from plastic has significant advantage over glass and silicone in manufacturing as well as in cost. For any use material must possess certain properties. It must be machinable, optically transparent and resistant to external and internal chemical environment. It must has acceptable thermal and electrical propertied according to application. Also has ability to bond when sealed [18]. Table: 2 shows the comparison of properties of COCs with other clear plastics

Polymer such as PMMA, PS (polystyrene), and PC are easily moulded and machined. But for packaging purpose it is necessary to understand the physical properties of the system. For packaging purpose the most important property of material and its packaging is its inertness to chemical environment and show resistance towards acid, bases and solvents [18].

PMMA is colourless, amorphous, durable thermoplastic, has good abrasion resistance, has UV resistance and good optical clarity but has poor solvent resistance. PS has similar properties but has poor chemical resistance. PC is widely used in medical devices due to its good sterilisability and good dimensional stability. But it also show poor chemical resistance [18].

Polymer such as high density polyethylene (HDPE) and polyetheretherketone (PEEK) show excellent chemical stability. But both of these are opaque and so less desirable and attractive. So new material such as COCs have excellent optical, chemical and physical properties and has a wide range of application in optical devices, medical equipment and packaging industry [18].

Table 2: Comparison of COC with other clear plastic

Property	COC	PS	PC	PMMA
General				
Density, g/cm^3	1.02	1.05	1.2	1.2
Flexural modulus, Msi	0.5	0.45 - 0.5	0.34	0.45
Tensile strength, ksi	9	6.4 - 8.2	9	10
Elongation, %	3 - 10	2 - 4	80	5
Notched Izod, ft-lb/in.	0.4	0.4	5 - 16	0.3
Heat distortion temperature, °C (°F)	75 - 170 (167 - 338)	75 - 94 (167 - 201)	142 (288)	92 (198)
Shore D	89	75 - 84	85	100
Water absorption, %	0.01	0.1 - 0.3	0.04	0.1
Optical				
Luminous transmission, %	92	91	88	92
Haze, %	1	3	1	1
Index of refraction	1.53	1.59	1.586	1.491
Abbé Number	56	31	34	61
Birefringence	Low	Variable	Variable	Low
Stress-optical coeff., 10^{12} Pa/s	4.0	4.8	68	–4.6

*Data for plastics other than for COC is from literature sources.

2.3 Characterization techniques for Nanocomposite

Characterisation tools are very important to understand the physical and chemical properties of

polymer nanocomposites (PNCs). Various techniques have been used to characterise the PNCs. Wide angle X-ray diffraction(WAXD), small angle X-ray scattering(SAXS), scanning electron microscope(SEM) and transmission electron microscope(TEM) are powerful characterisation techniques[15].

The SEM provides the information about surface topography. Scanning tunnelling microscope (STM) and scanning probe microscope(SPM) also used extensively in nanotechnology research. In STM the probe tip bring sufficiently close to the surface. After the invention of STM the atomic force microscope (AFM) is invented in which tip make contact with the sample. Raman spectroscopy is also a powerful tool for carbon based material characterization [15].

WAXD is most commonly used technique due to its easiness of use. But it cannot tell about the formation of nanocomposite and their structure. So the transmission electron microscope is the best option for characterisation of PNCs. It tell about the qualitative understanding of the internal structure, spatial distribution of the various phases present in the system, and the defective structure if present in the system by direct visualisation. SAXS is used to visualize the structure of larger object of $10A^0$ or larger. All these techniques are compulsory to study composite[15].

To study the thermal characteristic and curing behaviour (for thermoset) the most commonly used techniques are differential scanning calorimeter(DSC), thermogravimetric analysis (TGA), dynamic mechanical analyser (DMA) and rheometer [15].

2.4   Polymer/Graphene nanocomposite

Several approaches have been made to prepare nanoparticle/polymer nanocomposite. Conventionally polymerization process and nanoparticle formation done separately, then they are mixed mechanically to form composite[18]. In order to meet the demand of various application several strategies have been used i.e. polymer blending and inculcation of nanoparticle into elastomeric polymer for reinforcement purposes[19]. Carbon fibre (CF) as a reinforcement in polymer matrix has been used for commercial purposes since 1960s. CF are preferred for composite material due to its high specific strength and stiffness, performance to weight ratio, thermal stability, high conductivity, self-lubrication and resistance to corrosion[20].

Diamond, graphite, fullerences, carbon nanotubes and newly discovered graphene are all allotropes of carbon. In 2004 the Geim and coworker has identified single layer of graphene after that there are countless number of research has been carried out on this material[21]. Graphene is a basic building block of all form of graphitic material. It consist of one atom thick sp^2 hybridized carbon atom arranged in a structure known as honeycomb structure[15]. Graphene as a novel two dimensional nanomaterial has excellent mechanical, electrical and thermal properties. Therefore it is used for polymer modification to improve its properties. Great effort has been made to find out preparation method, structure and properties of polymer/ graphene nano composite[22]. Kalaitzidou et al., Miloaga et al. and Pinto et al investigated that graphene is a reinforcement filler for various polymers[23].
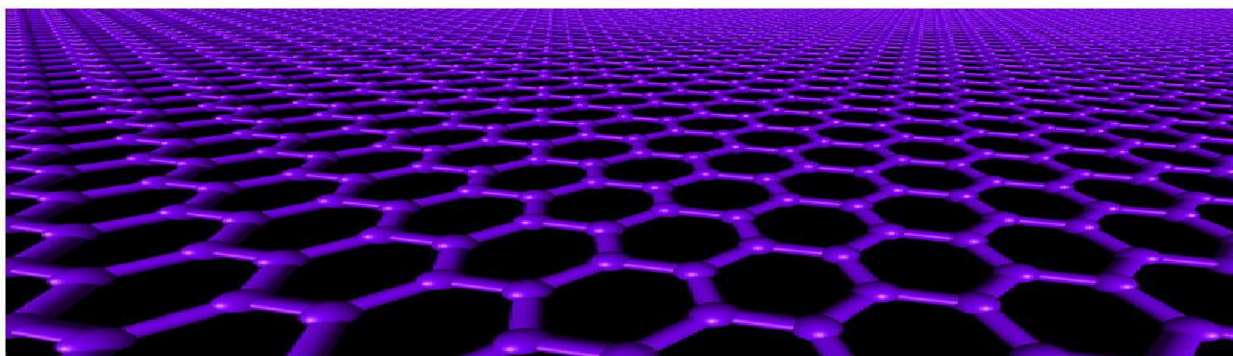
Figure 6:Molecular modal of single layer graphene.

2.5   Synthesis of Graphene

There are four methods to prepare graphene these are

1. Chemical vapour deposition or epitaxial growth.
2. Exfoliation of graphite by micromechanical method.
3. Epitaxial growth on insulating substance.
4. Reduction of graphene oxide in solution.

2.6   Surface modification of graphene

Due to the agglomeration behavior of graphene in bulk polymer chains, different approaches have been used to modify graphene to get better properties. These approaches are

Figure 7: Approaches to modify Graphene

2.7 Synthesis of graphene/ polymer Nano composite

There are three common method which are used frequently for the preparation of Nano composite of graphene and polymer. These three method are given below (fig: 7)

Figure 8: Method to prepare composite of polymer with graphene

2.7.1 Solution mixing

For preparation point of view the most simple and easy method for the preparation of nanocomposite of polymer with Graphene is solution mixing method. There are three steps involved in this method.
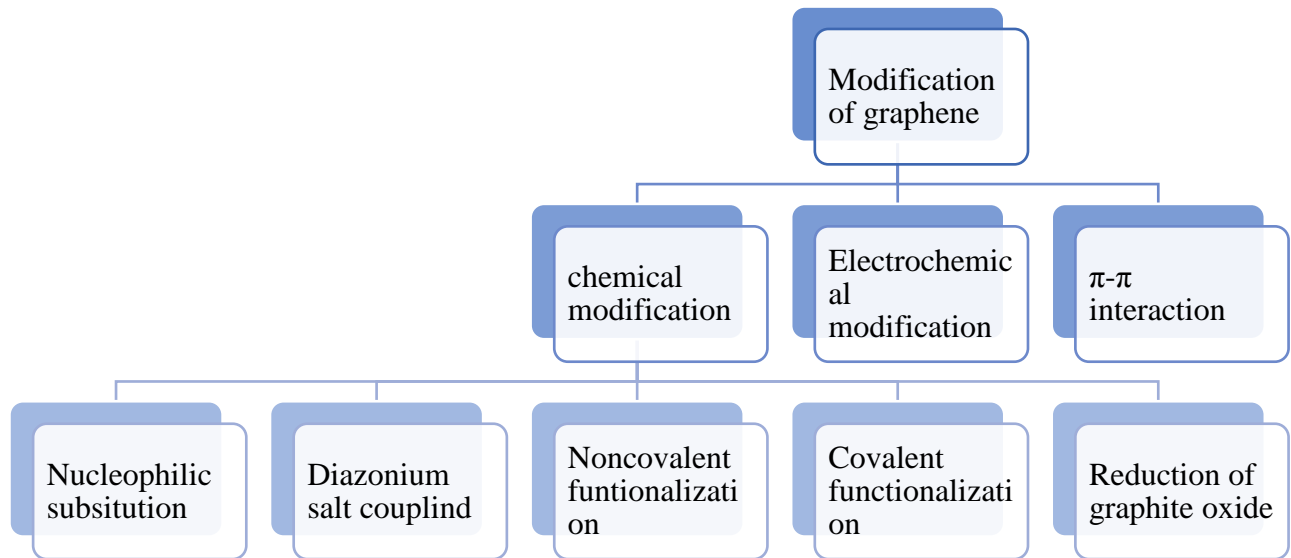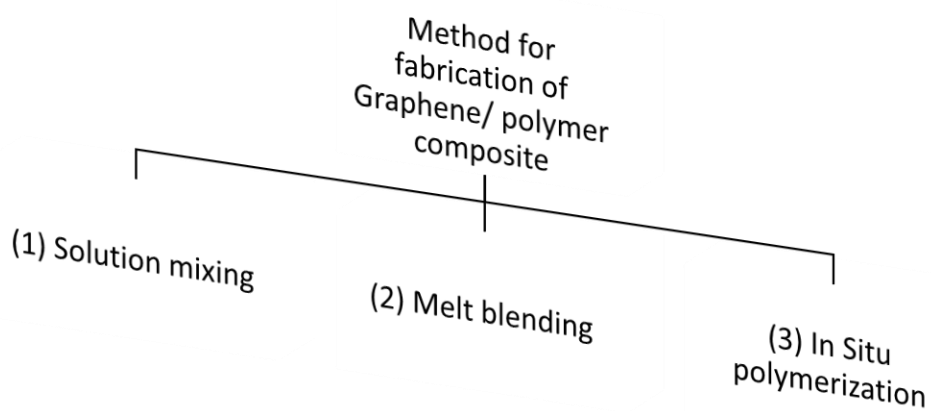
- Dispersion of filler in suitable solvent i.e ultrasonication etc.
- Mixing with polymer
- Evaporation of solvent

2.7.2 Melt blending

Special technique for making nano composite of thermoplastic polymer is melts blending. It is nifty and more useful approach. It require

- High temperature (to soft the polymer) and,
- Shear force (to disperse filler into matrix)

This technique does not involve any toxic solvent. But this technique has several limitations for dispersing G. It cannot properly disperse graphene due to high viscosity of polymer, also it cause rolling and breaking of graphene sheets. It also causes buckling of sheets.

2.7.3 In Situ polymerization

This is another method for making conmposite of polymer with graphene. In this process graphene is dispersed in liquid monomer then appropriate initiator is added to start polymerization. This is an effective method but as polymerization proceed the viscosity increase which is major limitation also evaporation of solvent is a problematic [14, 24, 25].

2.8 Graphene/ polymer composites

The use of organic and inorganic filler in polymeric system is ubiquitous. Carbon-fibers have been used as reinforcement for polymer matrix since 1960s. The study of graphene in material science is one of the most interesting topics and it can be used in various applications[20, 25].

Based on all type of carbon filler many composite system has been reported. But still there is aneed to investigate a composite system with outstanding properties. Given below were the system already studied.
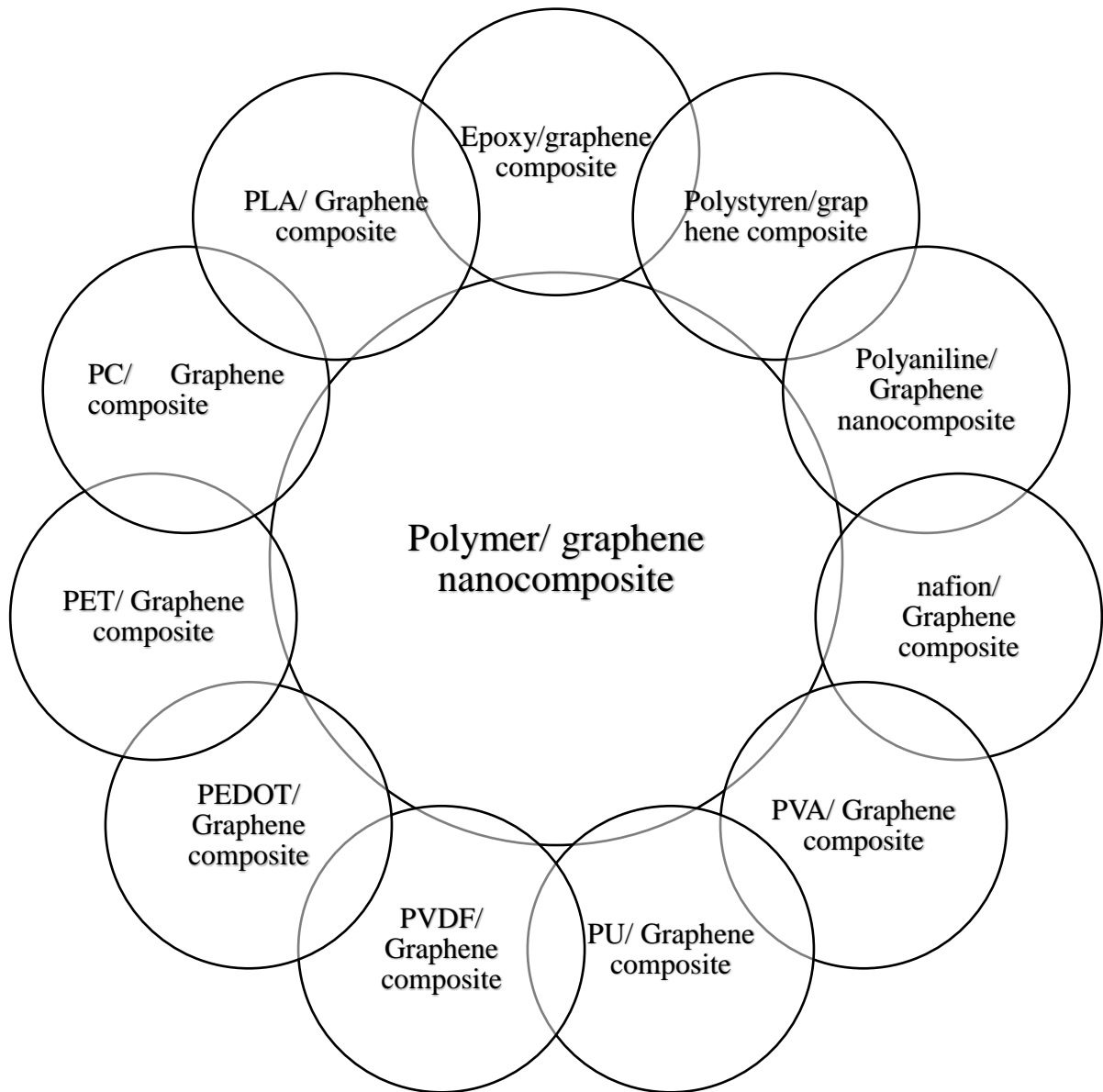
Figure 9: nanocomposite of graphene with different polymer

There are number of reasons for making graphene based nanocomposite. The most obvious reason is that the filler with such marvellous mechanical properties would lead to the improvement in the mechanical properties of the matrix. The change in mechanical properties also cause change in functional properties such as electrical, thermal and barrier properties[15]. Graphene based polymer nanocomposite attract the attention of both scientific and academic society because it cause the enhancement in the properties at very low filler rate. Furthermore the graphene is much cheaper than single wall carbon nanotube and multiwall carbon nanotubes[23]. Table 3 showed the composite of COCs already made with different fillers.

There is no work has been done on TOPAS / Graphene nanocomposite yet. A. Kasgoz *et al.,* have studied in detaile "Effect of different types of carbon fillers on mechanical and rheological properties of cyclic olefin copolymer (COC) composites". The SEM study of his work showed that the microstructure of sample varied depending upon the geometric feature of the fillers but all these sample show week interfacial adhesion due to lake of compatibilizer or interfacial agent[26].

S.Fu *et al*., have studied the composite of COCs with short Kevlar fiber. In his work he used MA-g-PP as a compatibilizer for better adhesion between filler matrix interface [19]. Similarly C.OU and M. Hsu studied the COCs composite enforced by silica nanoparticle without compatibilizer. And this composite showed enhancement in mechanical properties, glass transition temperature and even barrier properties of composite are much batter then only COCs film[27].

2.9   Interface modification

The properties of nano composite depend not only on their parents properties but also on their morphology and interfacial characteristic[15]. Several chemical treatments frequently used to make good interface bonding by activating functional group of fiber to greatly improve the interfacial strength of fiber and polymer. However these treatments destroy the fiber structure, involved toxic chemical, are time consuming and are not cost effective. S. Fu *et al.,* were selected hydrolysing and polydopamine coating on Kevlar short fiber before incorporating in polymer matrix[19].

Many researcher has been focused to investigate the physiochemical relation between fiber and matrix interface. For better composite performance the strong interfacial adhesion is necessary. It means the sufficient amount of forces i.e vander waals and hydrogen bonding between fiber and matrix are required. Also the interfacial adhesion energy must be higher than the cohesion forces of matrix[20]

Chapter 3

3. Experimental

3.1 Materials

The following table gives us the specification of material that was used to carry out experimentation.

Specification of materials used for experimentation

Table 3: Specification of material used for experimentation

S NO	Material	Manufacturer and Specification
1.	TOPAS (COC)	TICONA GmbH, Germany
2.	Few Layer Graphene	Janowska
3.	Chloroform	Sigma aldrich Co, USA (Lab grade)
4.	Cellulose acetate	Sigma Aldrich CO, USA (LAB GRADE)
5.	Di choloro ethane	Sigma Aldrich CO, USA(LAB GRADE)
6.	Cyclohaxane	Sigma Aldrich CO, USA(LAB GRADE)

3.2 Procedure

3.2.1 Selection of mutual solvent

TOPAS was dissolved in 10 ml of each of three different solvents namely Chloroform, Di choloro ethane, and Cyclohexane. These samples were stirred until topas was dissolved completely in the solvent. In di choloroethane topas was not dissolved. Better solvents for topas were cyclo hexane and chloroform. These two solvent were further tested for dissolution of cellulose acetate (CA) and FLGs dispersion. Chloroform was choosed as a matual solvent. As the dispersion of FLGs is better in choloroform and this is also confirmed from literature[28].
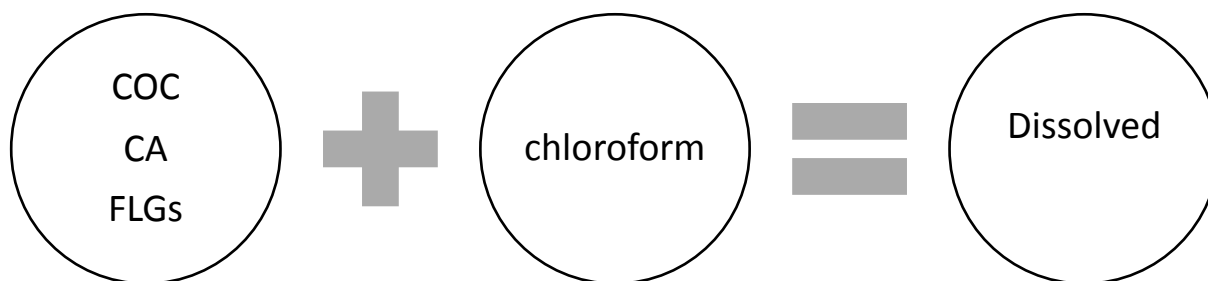
3.2.2 Preparation of TOPAS/ CA Blend

The blend of cellulose acetate and COC were prepared by using solution casting method. The table given below shows the weight percentages of CA in COC matrix

Table 4: concentration of CA in COC matrix

S no	Weight(wt) % of coc	Wt % of CA
1.	100% COC	0% CA
2.	0% COC	100% CA
3.	99% COC	1 % CA
4.	90 %COC	10% CA
5.	80% COC	20% CA
6.	70% COC	30% CA

These concentration were prepared by solution mixing method. First COC dissolved in 15 ml of chloroform stirred by magnetic stirrer and stirring plate until the solution was completely homogenized. Then CA was added in this solution and stirred vigorously for 24 hours.

Figure 10: Mixing and stirring of COC/CA

3.2.3 Preparation of COC/CA films

The above made solution was poured in patri dish. These films were kept at $30^{o}C$ for seven days for drying. After drying at room temperature these films were put in vacuum oven for three days at $60^{o}C$[28].

Figure 11: a.Pouring of solution, b. covring with foil, c. dry film

3.2.4 Preparation of COC/FLGs films

The table given below gave the concentration of FLGs in COC matrix.

Table 5: Concentration of FLGs in COC

S NO.	Wt % of COC	Wt % of FLGs
1.	99.9%	0.1%
2.	99.7%	0.3%
3.	99.5%	0.5%
4.	99.0%	1%

COC was dissolved by the same method mentioned above. FLGs were dissolved separately in 5 ml of chloroform. In 5 ml of solution varying % of FLGs were dissolved by stirring at stirring plate with magnetic stirrer until FLGs were completely dispersed. After dissolution of FLGs the solution was sonication using ultra probe sonication (probe sonication equipment manufactured by labsonic® M Type: BBI-5835027) having power output of 230 watts) for 5-10 minutes in order to get homogenised solution. Ultra probe sonication was operated at 0.5 Hz and 40% amplitude for this purpose. Then the FLGs solution slowly added into polymer solution and continuously stirred for 2 hour. Then this solution was sonicate with a probe sonication for 15 minutes and then stirred for 24 hours prior to pouring into petri dish. The film was dried by the same procedure mentioned above.
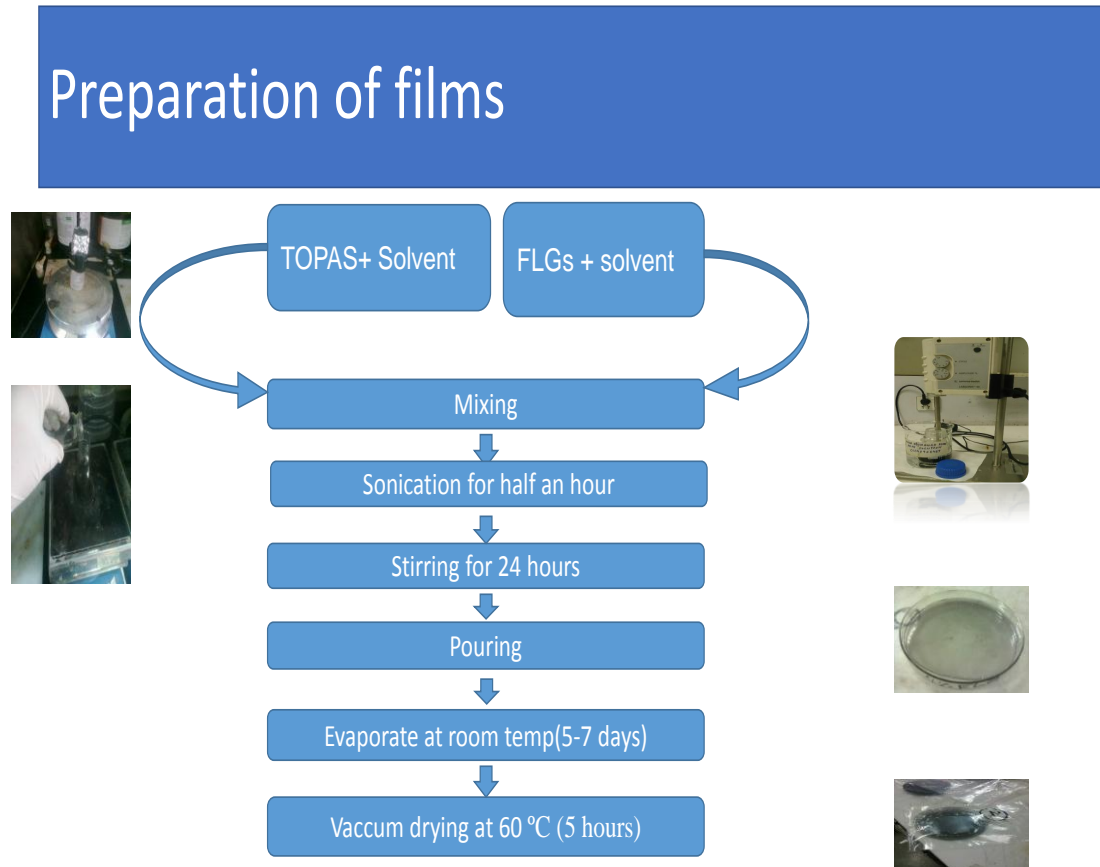
Table 6: Steps for preparation of polymer blend

Preparation of films

TOPAS+ Solvent → FLGs + solvent

Mixing

↓

Sonication for half an hour

↓

Stirring for 24 hours

↓

Pouring

↓

Evaporate at room temp(5-7 days)

↓

Vaccum drying at 60 ℃ (5 hours)

Figure 12: Melting of COC, dispersion of FLGs, sonication of FLGs, mixing of FLGs and COC

3.2.5 Preparation of COC/CA/FLGs films

COC, CA and FLGs dissolved by the same method as mentioned above. On the basis of mechanical result the 10 wt% concentration (conc) of CA was fixed for three component system. Here first COC and CA mixed and stirred vigorously. Then this solution was mixed into (already dispersed and sonicate) FLGs solution slowly. The table given below showed the concentration of the samples of three component system.

Table 7: Variation of FLGs in COC/10CA blend

S No	Wt% of COC	Wt % of CA	Wt % of FLGs
1.	89.9%	10%	0.1%
2.	89.7%	10%	0.3%
3.	89.5%	10%	0.5%
4.	89%	10%	1%

3.3   Characterization of specimen

3.3.1 Scanning electron microscope (SEM)

Morphology of COC/CA/FLGs films was investigated by using a JEOL JSM-6490A Analytical scanning electron microscope. A cryogenic crack was produced in the polymeric films using liquid nitrogen. These samples were frozen in liquid nitrogen where they became brittle and easily broken to generate fresh surface. Furthermore these samples were coated with gold (layer of gold is 250A approximately) by using a JOEL JFC-1500 Ion sputtering method device. For examination these samples were mounted on aluminum stubs.

3.3.2 Tensile testing

Tensile properties of COC/CA/FLGs were determined by using TRAPEZIUM-X Universal Testing machine (AG- 20KNXD Plus) manufactured by Shimadzu Corporation at a cross head speed of 5mm per minute (ASTM D 882). The samples used in tensile test were cut into 10x 90 mm2 (WIDTH X LENGTH) with a gauge length of 20mm. these samples were cut by using hand cutter (ASTM D 6287). The samples were cut carefully in order to ensure the perfect smooth surface without notches or imperfect edges. All samples were tested at room temperature. At least five samples were tested to obtain an average value.

3.3.3 Anti-microbial test

3.3.3.1 Antibacterial test

Antibacterial test for the COC/CA/FLGs conducted using the standard "AATCC 147(modified)-Antibacterial activity assessment of textile material: Parallel streak method". This is specified test for non- porous and non-leaching surfaces. This standard was selected as the disc diffusion method was fail to show result which is the most commonly used method to check antibacterial activity; because the disc diffusion method was for leaching nanomaterial. In this method nutrient ager surface was inoculated with cell suspension. Lawn of bacterial was used instead of parallel streaks. 20cm x 20 cm samples were cut and placed on surface of the inoculated agar. These petri plates were covered and wrapped with food wrap then incubated at 370C for 24 hours.

Six bacterial strains had been used to study antibacterial resistance. These strains are, Shigella, Staphylococcus Aureus (MRSA), S. Typhi, Escherichia Coli, Acineto Bacter (AB- 10) and Pseudomonase Aeruginosa (PA 10). Before using these strains fresh culture had been prepared in liquid broth (L.B) media(in 9 ml of L.B 1 ml of cell suspension added in test tube then placed this test tube for shaking overnight but not more than 24 hour). Now 1ml of freshly prepared culture was spread on the agar with the help of spreader. Test piece was placed on the agar to check anti-bacterial resistance.

In order to form nutrient ager media 14 g of nutrient agar was added in 500ml of distilled water and auto clave for two hour. Then 25 ml of this agar was drop in each petriplate and let it to solidify. When solidify put in incubation for 24 hours to ensure that there was no contamination in plates.

3.3.3.2 Antifungal test

For assessing antifungal resistance of non-porous polymeric film standard "ASTM G 21-96" was used[5]. This is agar plate test and the rate of growth on film was visually assessed. This test shows the resistance of synthetic polymer to the fungus. Three species of fungi Aspergillus Flavus, Aspergillus Niger and mixed culture of Aspergillus Flavus, Aspergillus Niger and Penicillium Commune were used to study anti-fungal resistance. These are the most common strains present in atmosphere.

For the growth of fungi potatodextrose agar (PDA) was used. Agar plate was prepared and incubates for 24 hours. Each plate was checked to make sure that there was no contamination. Then fungal spores spread on the agar with the help of spreader. 20mm x 20mm test piece was cut and placed on the aagar surface. Each plate was tighten with parafilm to create anarobic condition for fungal growth. Plates were placed in incubation at 25 ^{0}C for 28

Chapter 4

4. Results and Discussions

4.1 Morphology of Nanocomposites, Blends and Hybrid of TOPAS

4.1.1 Wide angle X-Ray differaction

4.1.1.1 XRD of nanocomposites of TOPAS

Wide angle X-Ray diffraction patterns for pure TOPAS (COC), pristine FLGs and TOPAS/ FLG Nanocomposite at varying concentration of FLGs is showing in figure 12. A hump in XRD pattern of pure TOPAS represents amorphous plateau of TOPAS. The graphitic peak was observed at $2\theta=26.5^o$ in the TOPAS/ FLGs nanocomposites samples. This peak was observed to be increase by increasing the filler loading in TOPAS matrix. This peak was very small for FLGs loading of 0.1% and 0.3%, which indicate good dispersion of FLGs in TOPAS matrix. The increase in graphitic peak at increasing filler loading represents more staking of FLGs layers. The sharping of TOPAS amorphous plateau was also observed which is due to possible ordering of TOPAS chains in the presence of FLGs.
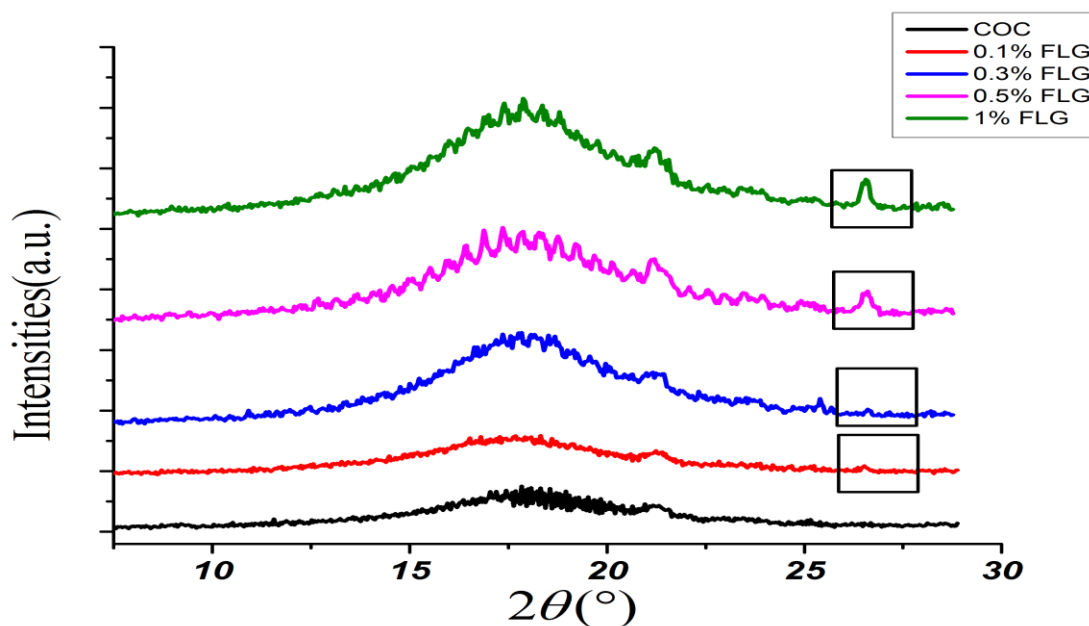

Figure 13: WAXD patterns of pure TOPAS, pristine FLGs and TOPAS/ FLGs nanocomposite at varying FLGs concentration.

4.1.1.2 XRD of Blend of TOPAS

Wide aangle X-ray diffraction of pure TOPAS, CA and TOPAS/ CA blend at varying concentration of CA was shown in figure 13. The amorphous plateau region of TOPAS remains unchanged by the addition of CA indicating that all blends remain amorphous.
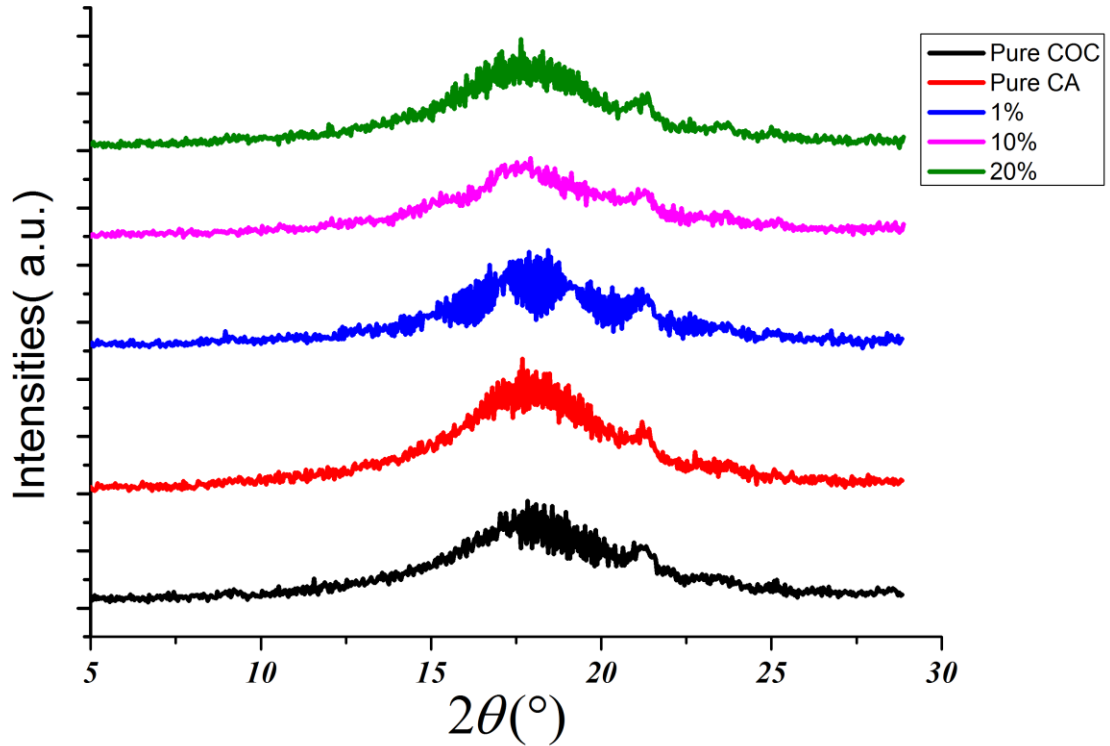

Figure 14: WAXD pattern of pure TOPAS, pure CA and TOPAS/CA blend at varying concentration of CA.

4.1.2.3 XRD of hybrid of TOPAS

Wide angle X-ray diffraction of pure TOPAS, CA and hybrid of TOPAS at varying concentrations of FLGs shown in figure 14. A hump in pure TOPAS and pure CA was representing amorphous plateau. A graphitic peak was observed gratually by increasing concentration of FLGs. No graphitic peak was observed at 0.1% FLG concentration which indicates good dispersion. Also very small graphitic peak was observed at 0.3%FLG and 0.5% FLG loading. The increase in graphitic peak at 1% FLGs loading indicate stacking of FLGs layers. Sharpening of amorphous hump of TOPAS at all concentration of FLGs was observed

which indicate good level of chain alignment or chain ordering. But this sharpening was reduce at 1% FLG loading which is may be due to stacking of FLGs with each other.
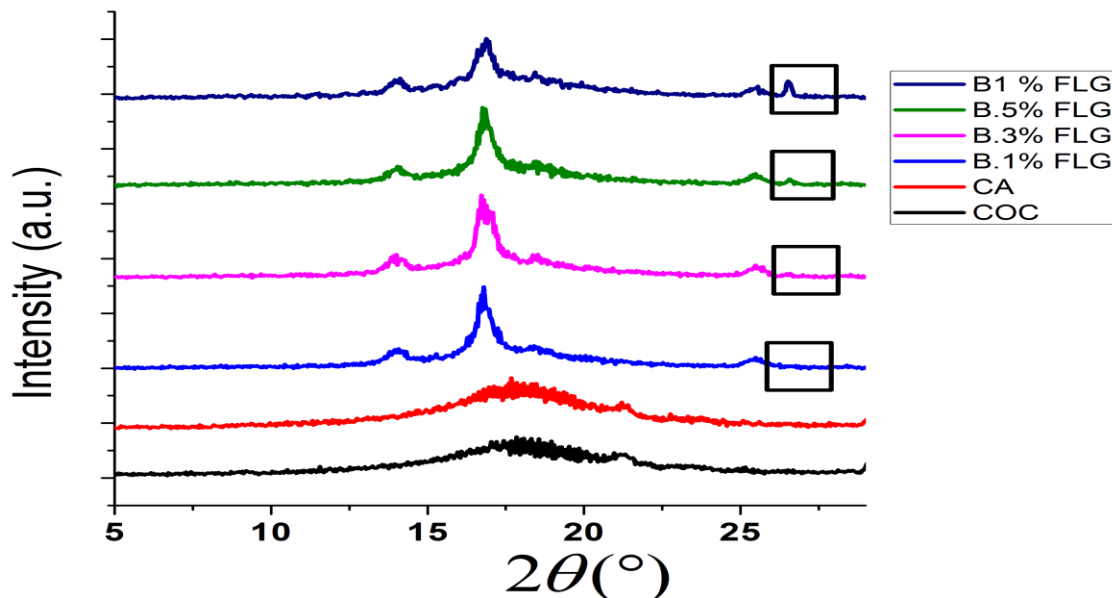

Figure 15: WAXD pattern of pure TOPAS, pure CA and TOPAS/CA/ FLG (Hybrid) at varying concentration of FLG.

4.1.2 Scanning electron microscopy

Morphology of COC, COC/FLGs, COC/CA and COC/10%CA/FLGs was observed by SEM.

4.1.2.1 SEM images of nanocomposites

Fracture surface of the composite was study by the scanning electron microscope, to investigate morphological properties. It was seen from the micrograph (figure 15) that at filler loading of .3wt% the dispersion is fairly good, and no filler pullout at this loading from the matrix. The dispersion of filler at 0.3wt% was uniform and homogeneous therefore better tensile properties were achieved as shown in table 8. It could be seen from micrograph that there was a stretching of filler which showed strong interfacial adhesion of filler and matrix. This was clear from elongation at break. The homogeneous dispersion of FLGs may be due to fact may be during solution mixing FLGs retain its stability or may be the chains of COC prevent FLGs to stack together. Further increase of filler loading from 0.3wt% to 1wt% the agglomeration of FLGs started and FLG-FLG interaction started. There were more filler competence for matrix. So this was result in weaker tensile properties. Similar result was also reported by [10, 28].
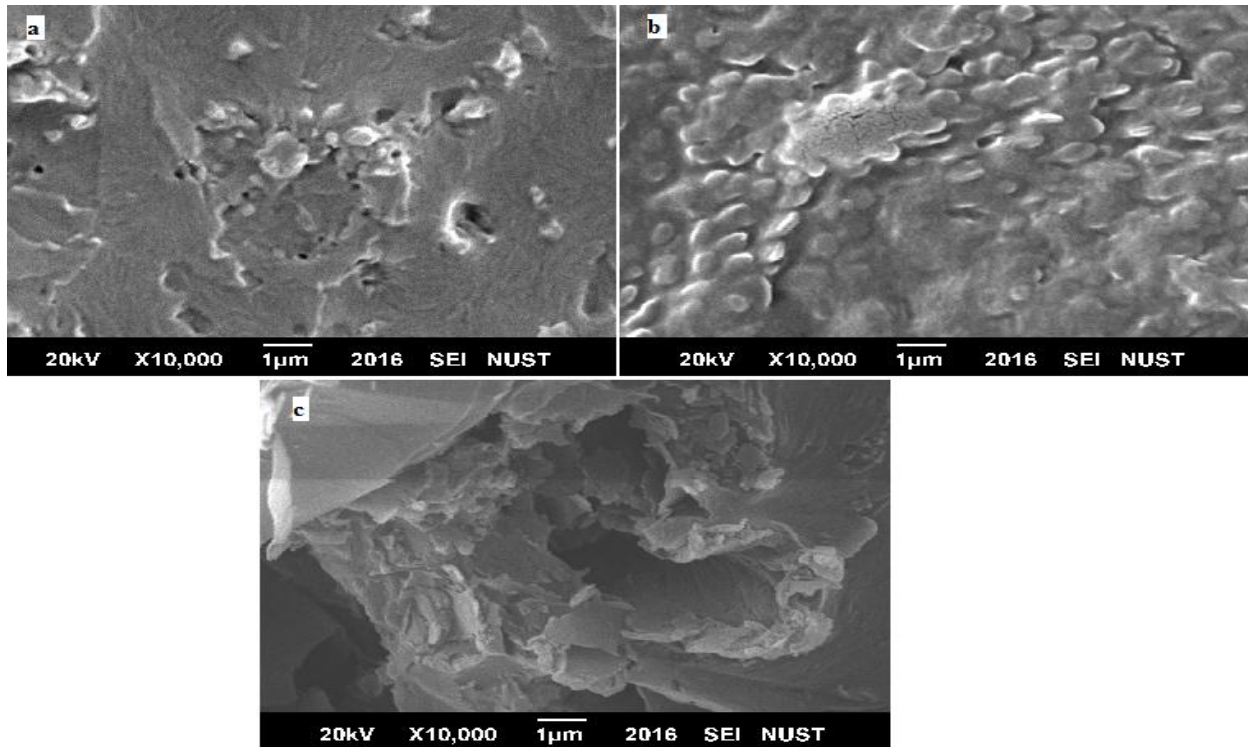
Figure 16:SEM micrograph of COC/.1% FLG(a), COC/.3% FLG(b), COC/1% FLG(c)

4.1.2.2 SEM images of blends

From the SEM micrograph it was clearly seen (figure 16), that varying concentration of CA, has obvious effect on dispersion and homogeneity of the film, effect of which can be seen in tensile mechanical properties. By adding 1% CA in COC it was seen that COC phase was apparent in first image figure 16(a), the dark phase was the matrix. Figure 16(b) showed that at 10% CA conc the dispersion was quite good. But it was better at CA conc of 20% figure 16(c). At this conc the COC was completely miscible with CA. dispersion was homogeneous and the fracture surface was smooth. Further increase in CA conc, in COC matrix, result in the formation of voids and agglomeration of CA phase, which could be clearly seen in figure 16(d) and (e). These result was also compatible with mechanical result of these samples. Similar result was also reported by Ou *et al* they prepared the composite of COC with silica nanoparticle [26].
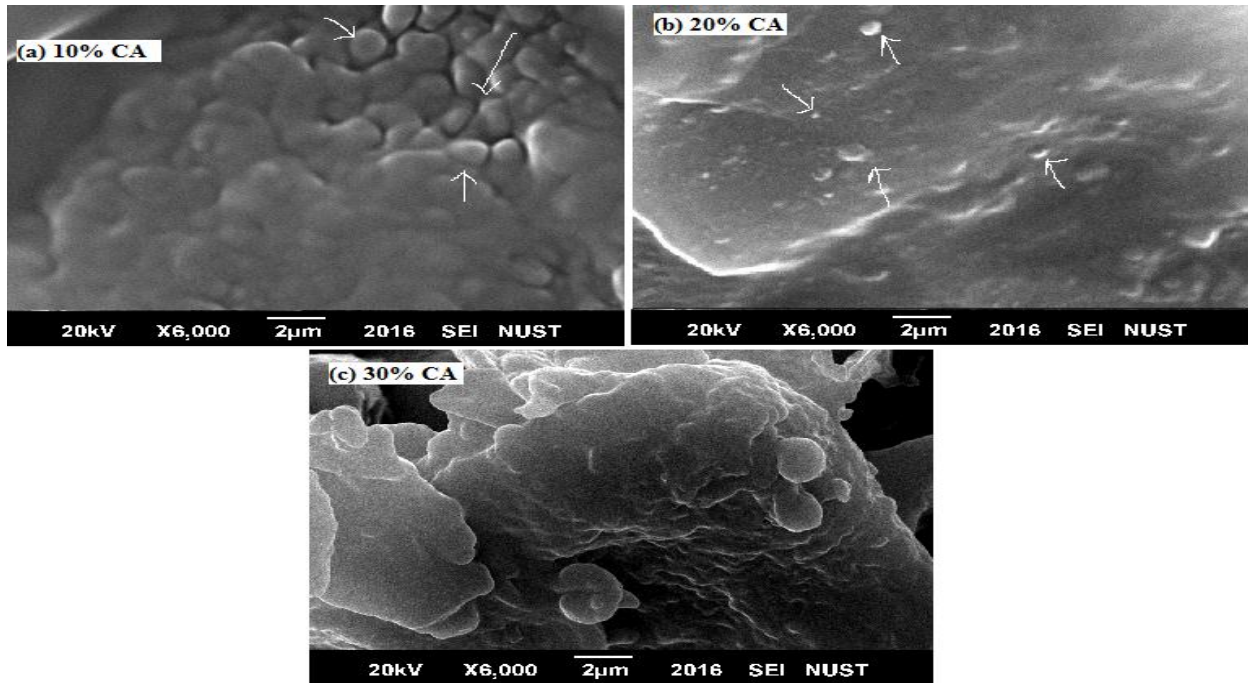
Figure 17: SEM micrograph of COC/10% CA(a), COC/20% CA (b), COC/30% CA(d).

4.1.2.3 SEM micrograph of HYBRID

In the hybrid system it was seen that dispersion of FLGs upto 0.5 wt% showed good dispersion. The dispersion of filler was uniform shown by SEM micrograph. Stretching of FLGs also shown very clearly in 0.5 wt % FLGs concentration shown in figure 17 b. This effect can further demonstrated in elongation at break property of mechanical test. Further increase in filler result in agglomeration of FLGs with each other which result in decrease in mechanical properties. Figure 17 c showed 1% FLGs, stacking of graphene sheets was clearly seen in this figure. Fractured surface was rough and pullout of FLGs seen.
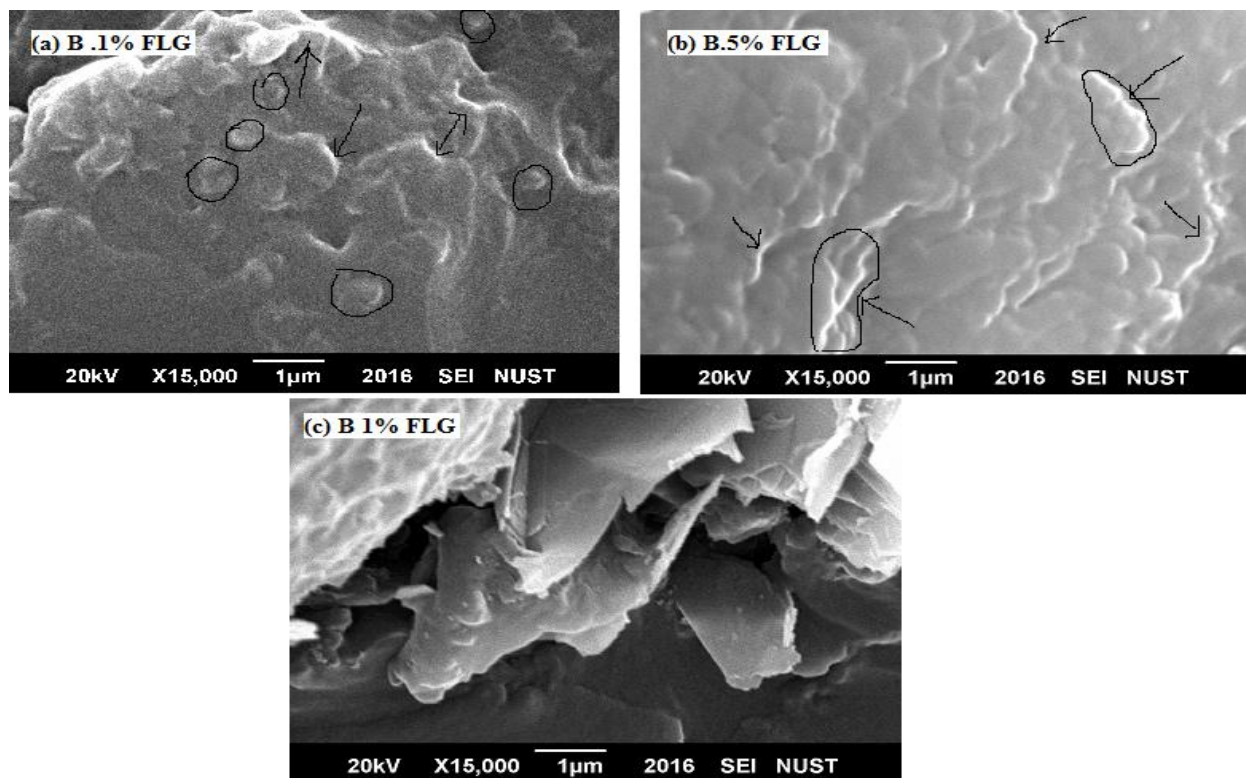
Figure 18: SEM micrograph of HYBRID system

4.2   Tensile mechanical testing

Tensile mechanical properties of pure COC, COC/CA, COC/ FLGs and COC/CA/FLGs films and stress strain(S & S) curves are shown below.

4.2.1   Nanocomposites of TOPAS

Tensile properties of COC/FLGs containing various FLG content were examined at room temperature. Stress strain curve of nano composites shown in figure 18 shows the effect of addition of FLGs on mechanical properties. By the addition of FLGs in blend system mechanical properties enhanced. The stress strain curve of the hybrid system showed the effect of the filler on the hybrid system. S-S curve showed the super strong as well as super tough behavior of the system. This is because as the stiffness and elongation at break both were increased which gave hybrid super strong and super tough property.

Figure 19 showed the tensile strength of nanocomposite of TOPAS. By the addition of FLGs the tensile strength of COC enhanced. By the addition of only 0.1wt% FLG the strength reaches to more than double then pure polymer that is 25.4182MPa. Tensile strength reached to

maximum at filler loading of 0.3wt% which is 31.7287 MPa. After that further addition of filler the mechanical strength reduce, at 0.5 wt% it is20.0549 MPa. At 1wt% of filler tensile strength reach 13.7849 MPa.

FLGs are added in order to enhance the mechanical properties of the matrix. The enhancement of mechanical properties depends on the homogeneity/ dispersion, orientation of filler and interfacial interaction between matrix and filler. The Tensile strength of COC increases by the addition of FLGs and reach to maximum at filler loading of 0.3wt%. At 0.1 wt% of FLGs loading the reinforcement effect is not very much pronounced due to the low density of the FLGs so no percolated network is formed due to insufficient density of the filler. 0.3 wt% is the critical loading rate of filler in COC matrix. At this loading rate the tensile strength reach to maximum which reveals that at this loading percolation reached. At this loading distribution, orientation and dispersion all are properly improved which result in the formation of percolation network.

After the formation of percolation network two type of interaction FLG-FLG interaction and FLG-matrix interaction develop. The FLG-FLG interaction is weaker while FLG- matrix interaction is stronger but when the distance between two FLGs is so small they try to stack with each other due to wander walls interaction rather than to make bonding with matrix. This phenomenon result in decrease in mechanical properties on filler loading rate >0.5 wt%. Similar trend was observed by Cheing et al for PLA/ xGNP (graphene nanoplatelets)nano composite [10, 28].

Figure 20 shows the tensile modulus of the COC/ FLGs nanocomposites. Term tensile modulus is used to measure the stiffness of the material. The stiffest material has the highest modulus. This term is use to characterize the material. When the material has higher modulus it means the more stress is required in order to produce given amount of strain. The trend for tensile modulus is similar as for tensile strength. The highest tensile modulus was observed for filler loading of 0.3wt% after that the modulus decrease. At critical loading due to percolation network more stress is required to produce given amount of strain. This is direct reinforcement effect of the filler that make the polymer stiffer at critical loading value as compared to the pure COC.

Figure 21 show the elongation at break of the COC enhanced by FLGs. The elongation at break increases by 531% order of magnitude at FLGs loading of 0.3wt% after that the decline in elongation at break was observed which reach to 253.795% order of magnitude at filler loading

of 1wt% which showed that system became more brittle. The decline in elongation at break may be due to the two reason one is higher aspect ratio of the filler and second is the restriction of polymer chain due to FLGs and matrix interaction[23].

Table 8: Mechanical properties of COC/FLGs system

Conc of FLGs (%)	Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at break (%)
COC	12.2283	468.425	4.7689
0.1%	25.4183	636.273	250.988
0.3%	31.7287	855.259	531.735
0.5%	20.0549	455.028	331.77
1%	13.7849	360.471	253.795
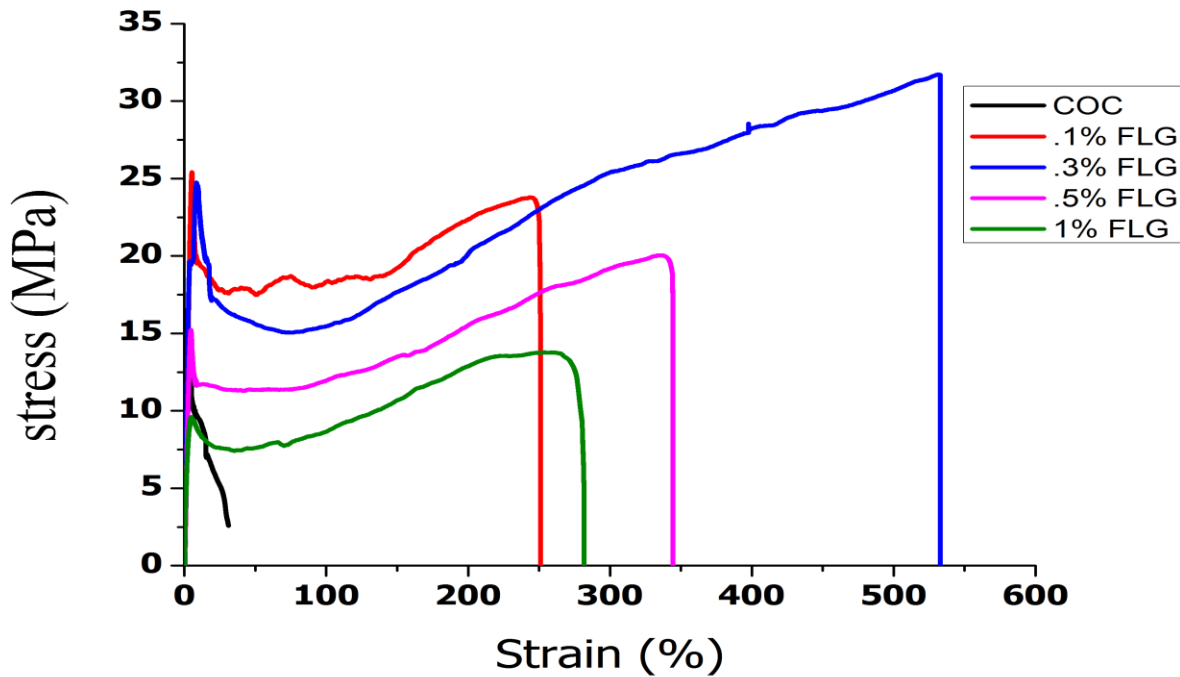
Figure 19: S-S curve of nanocomposite of TOPAS
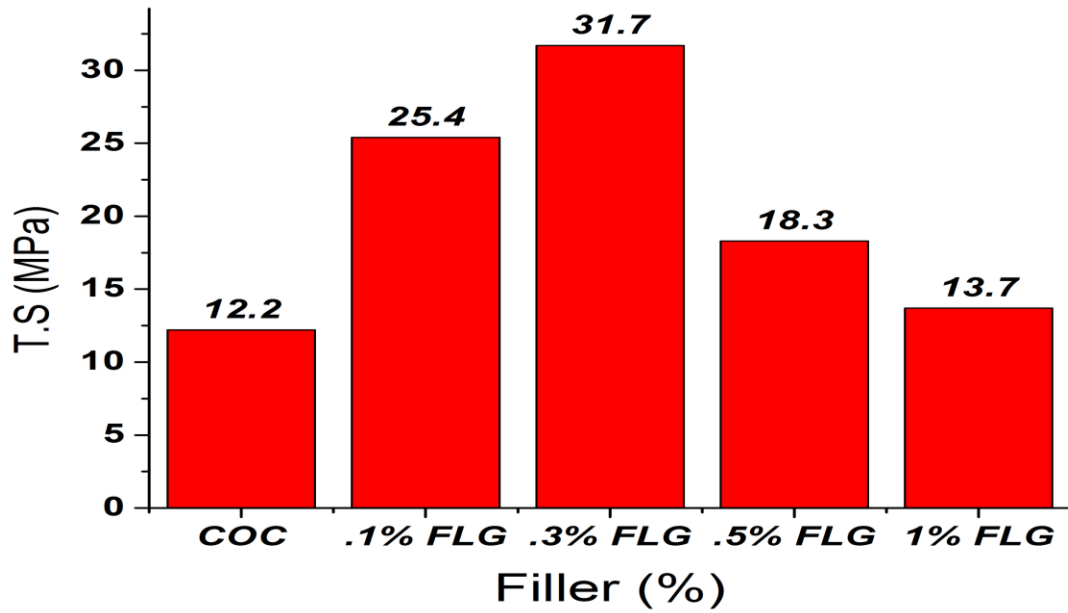
Figure 20: Tensile strength of Nanocomposite of TOPAS
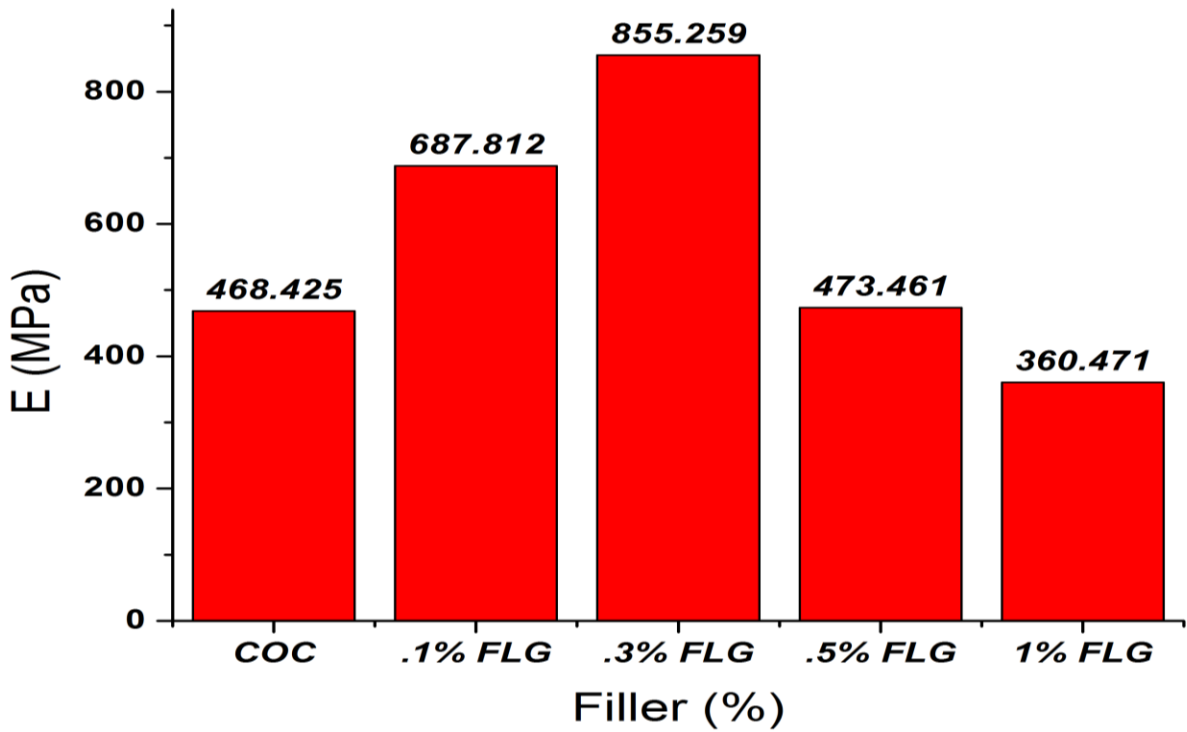
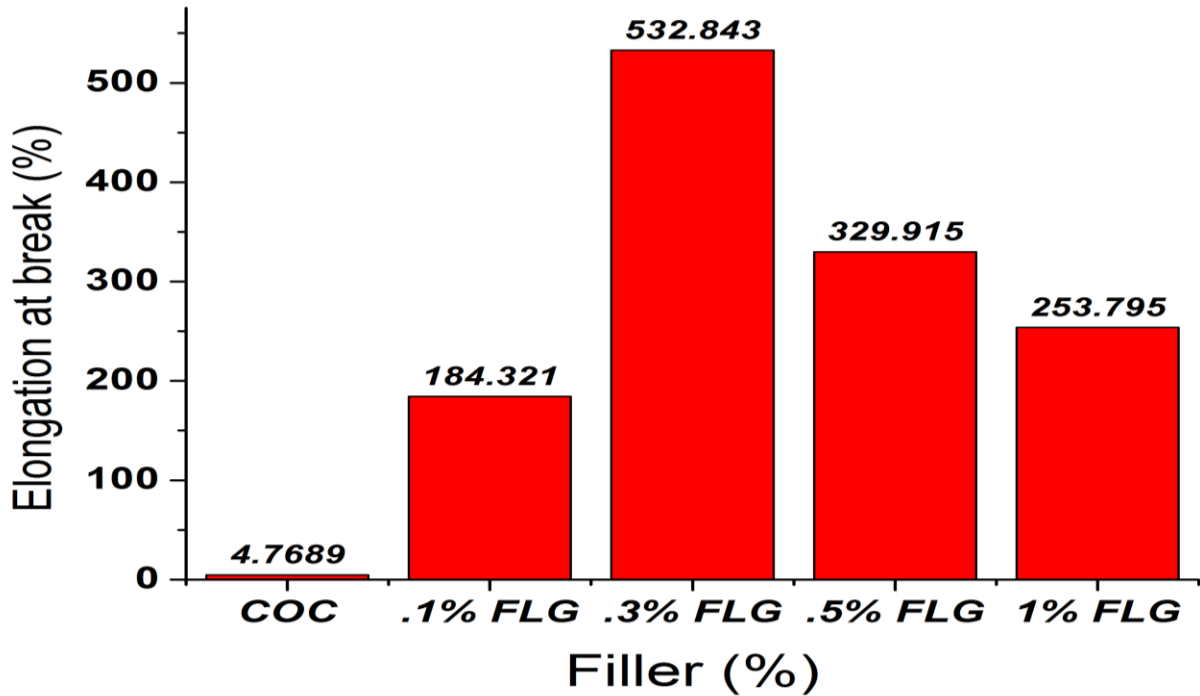**Figure 21: Tensile modulus of nanocomposite of TOPAS**

Figure 22: Elongation at break of nanocomposites of TOPAS

4.2.2 Blend OF TOPAS

Table 9 and figure 22 showed the mechanical properties of COC/ CA blend system. By the addition of FLGs in blend system mechanical properties enhanced. The stress strain curve of the blend system showed the effect of the filler on the hybrid system. S-S curve showed the super strong as well as super tough behavior of the system. this is because as the stiffness and elongation at break both were increased which gave hybrid super strong and super tough property.

It was observed that by the addition of CA in COC the mechanical strength of system increased (figure 23). The tensile strength reached to its maximum value (that is 30.3540MPa) at critical loading which in the case of CA was 20%. At low loading of CA i.e. 1% and 10 % the enhancement in tensile strength is limited. This was probably due to the low concentration of the CA. At these concentration no percolated network was formed. 20 % CA loading was the critical loading for the COC. At 20% loading COC and CA both were compatible with each other and secondary bonding between them was sufficient to support the system. Further increase in CA result in eventually decrease in tensile strength, which is 25.9453 MPa at CA loading of 30%. The strengthening in mechanical properties by the addition of CA was due to the secondary

forces of attraction between COC and CA. in the case of COC/CA blend this force of attraction may be the hydrogen bonding. As COC has ethylene group and CA has hydroxyl functional group in its structure. So these groups may be involved in secondary bonding (most probably hydrogen bonding). After the critical loading CA chains try to coil around each other and making separate phase which could be seen in SEM images. So tensile strength at 30% CA was reduce. Figure 19(a) showed the strengthen mechanism. When CA was added in low amount the CA chains spread randomly in COC matrix. So this low concentration of CA could not effectively enhanced the properties. But at 20% conc the CA phase completely disperse in COC matrix see figure 26(b). So percolation network formed. At CA concentration above critical conc the CA is making the separate phase rather than making bonding with COC so mechanical strength reduce(figure 26(c)).

Similar trend was observed for tensile modulus. Figure 24 showed tensile modulus of COC/CA system. The modulus increase by addition of CA. This due to the formation of secondary bonding. The bonding between COC and CA make it stiff. The maximum stiffness was achieved at 20%CA loading. At this loading all the COC chains were bonded with CA chains which could be seen in the form of higher modulus. After this limit modulus reduced due to the segregation in COC and CA figure 26(c) illustrate the phenomenon.

Figure 25 showed the elongation at break of COC/CA system. The elongation at break was increased by adding CA. it reached to its maximum value (387.420%) at critical loading. After that it decrease at 30% CA loading. The extensive secondary bonding make the system stiff and so the elongation at break was reduced.

Table 9: Tensile mechanical properties of COC/CA blend

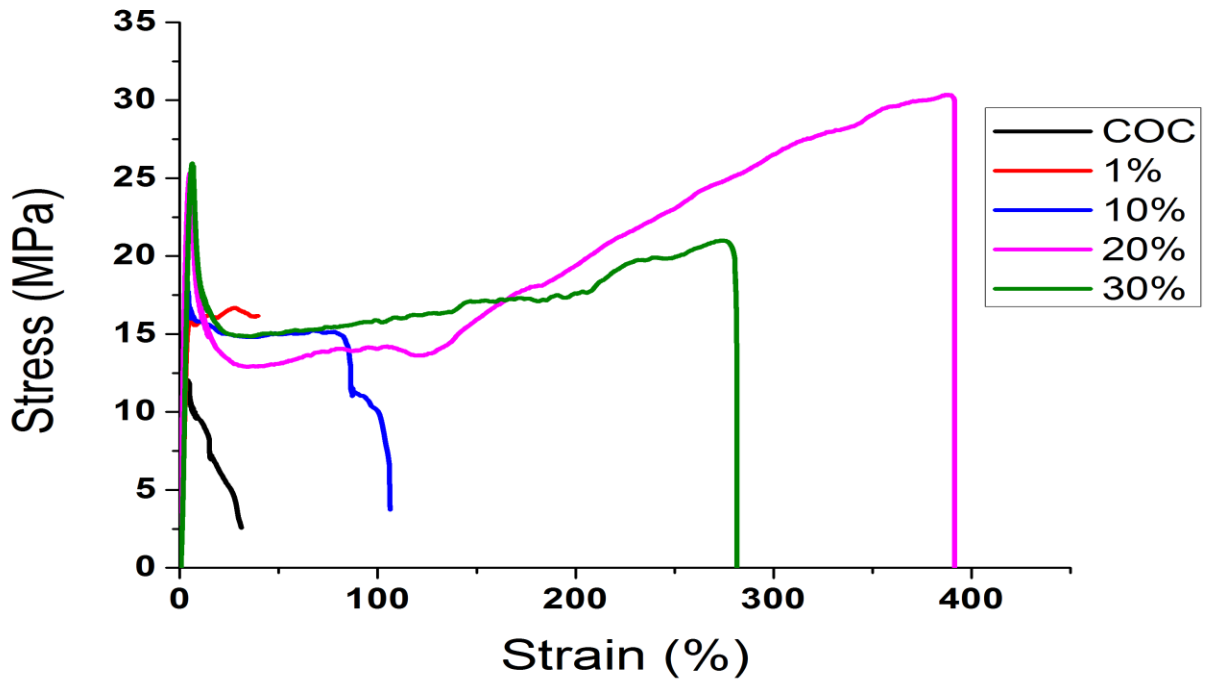| Conc of CA (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
Pure COC	12.2242	468.425	4.7689
1% CA	16.6830	551.471	27.7688
10%CA	18.3297	672.6	80.129
20%CA	30.3540	884.667	387.420
30%CA	25.9453	714.605	280.2895

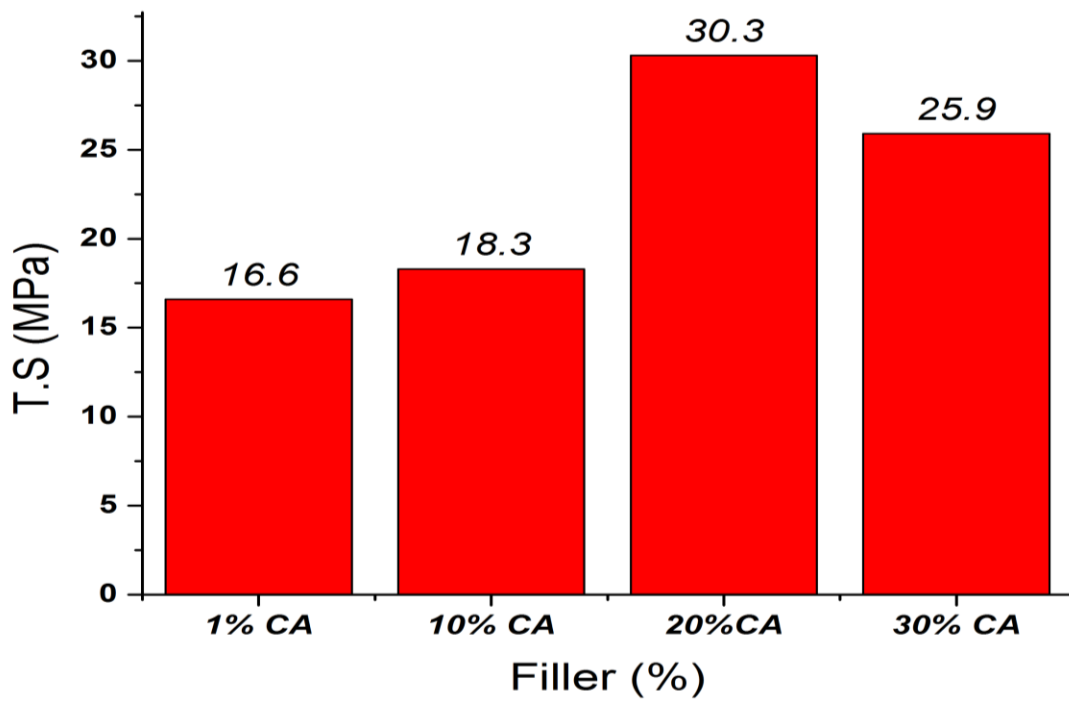**Figure 23: S-S curves of blend of TOPAS**

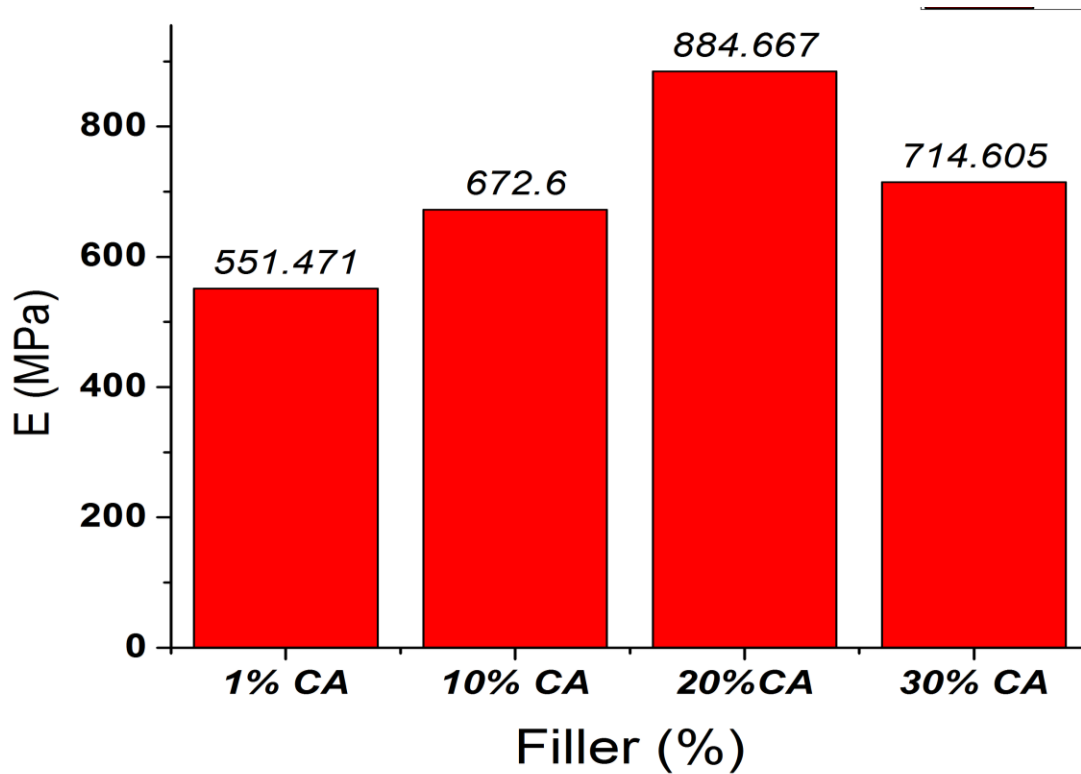**Figure 24: Tensile strength of Blend of TOPAS**

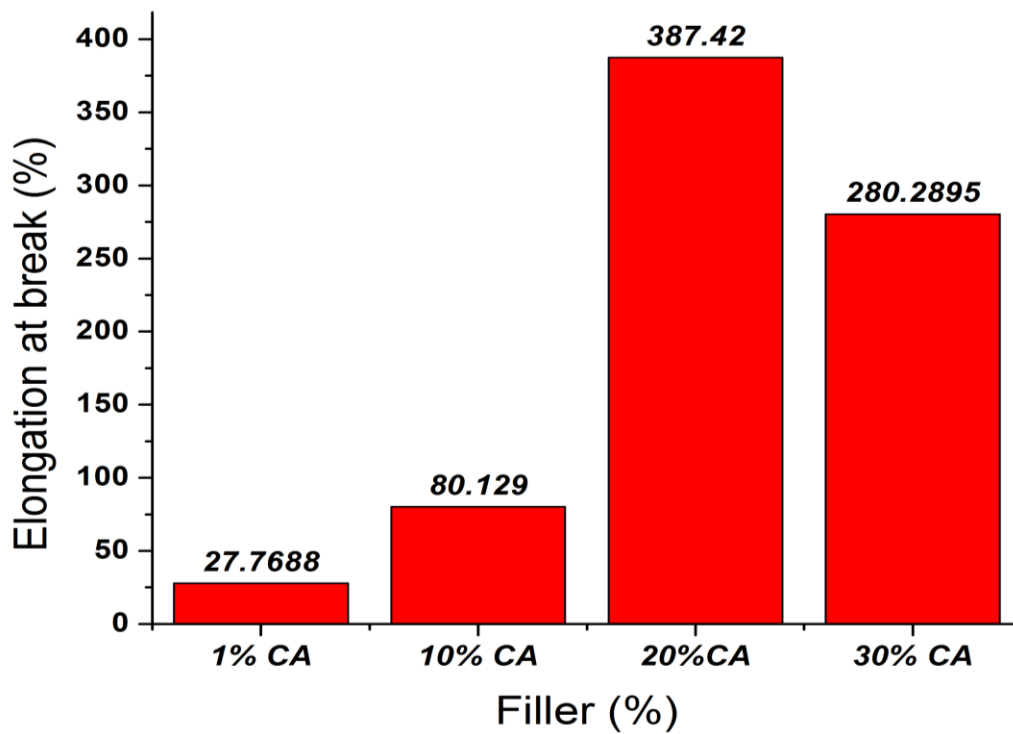**Figure 25: Tensile modulus of blend of TOPAS**

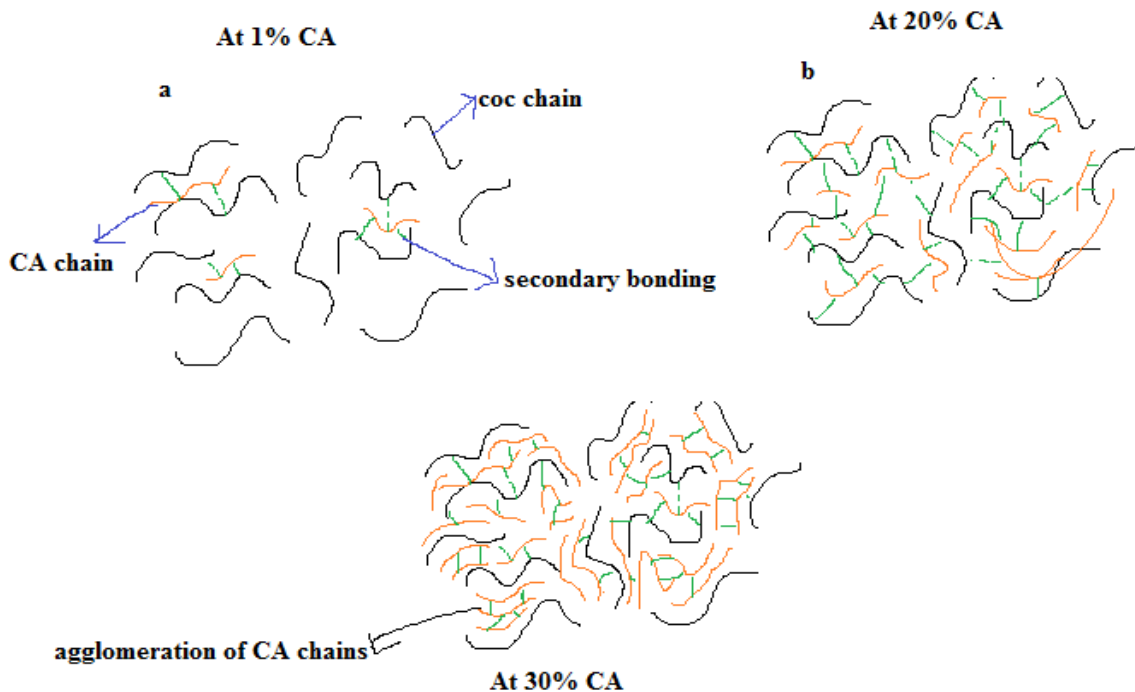**Figure 26: Elongation at break of blend of TOPAS**

Figure 27: Bonding in COC/CA blend

4.2.2.1 Comparison between COC/FLGs and COC/CA blends

Comparison of properties of COC/FLG and COC/CA given in table

Table 10: comparision between COC blends

Mechanical property	COC/FLG	COC/CA
Maximum Tensile strength (MPa)	31.7287	30.3540
Maximum Tensile modulus (MPa)	855.259	884.667
Maximum Elongation at break (%)	531.735	387.420

The comparison between two blend of COC showed in the table 10. It was clear from the table that maximum tensile strength was achieved by the addition of FLGs and also it give maximum elongation at break. The maximum elongation at break was less for CA blend but it gave better modulus.

Usually it was observed that when tensile strength and tensile modulus increased the elongation at break was reduced. But for COC with both blend it was observed that tensile strength and modulus improved and so the elongation at break. From the literature it was found that some

time it happened, by the addition of filler the alignment of polymer chain achieved, and when polymer chain align between the filler, now they have some space to move over each other and so elongate.

4.2.3 Hybrid of TOPAS

Figure 27 and table 11 showed the mechanical properties of the hybrid of the TOPAS. By the addition of FLGs in hybrid system mechanical properties enhanced. The stress strain curve of the hybrid system showed the effect of the filler on the hybrid system. S-S curve showed the super strong as well as super tough behavior of the system. This is because as the stiffness and elongation at break both were increased which gave hybrid super strong and super tough property.

Figure 28 showed the tensile strength of the hybrid system. The tensile strength increased upto 150% at filler loading of 0.5%. Further increase in the filler reduce the tensile strength. Maximum tensile strength was achieved 30.6 MPa at 0.5 wt % which reduce to 19.4 MPa at filler loading of 1%. This reduction in tensile strength was may be due to agglomeration of filler.

Figure 29 showed the tensile modulus of the hybrid system. By the addition of filler the modulus increase upto certain limit and maximum modulus was achieved at filler loading of 0.3 wt % after this limit modulus reduce and % age reduction was 17% at filler loading of 0.5%. Then again modulus was increased which is may be due to the rigid filler which make the material stiff.

Figure 30 represented the elongation at break of the hybrid system. By the addition of FLGs the elongation at break was increased. The increase in elongation at break was achieved upto 118 times at filler loading of 0.5%. Maximum elongation at break was 571.278 % at filler loading of 0.5 %. Further increase in the amount of filler reduce the elongation at break which was 363.037 at filler loading of 1%. This is may be due to the rigid behavior of the filler which increased the stiffness while reduce elongation at break at 1% filler loading.

Table 11: Mechanical properties of the hybrid system

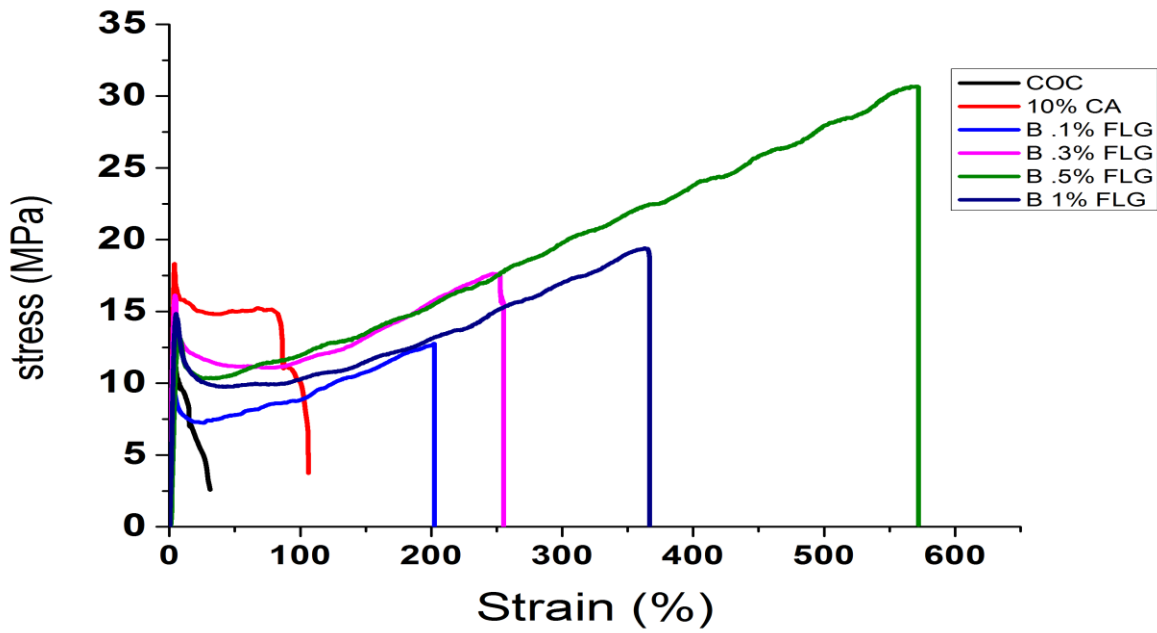| Conc of FLGs(%)	T.S(MPa)	E(MPa)	Elongation at break(%)
COC	12.2	468.4	4.7
B +0.1	14.7	486.786	218.854
B +0.3	17.6	569.31	247.057
B +0.5	30.6	332.86	571.278
B +1	19.4	486.29	363.037

Figure 28: S-S Curve of Hybrid of TOPAS
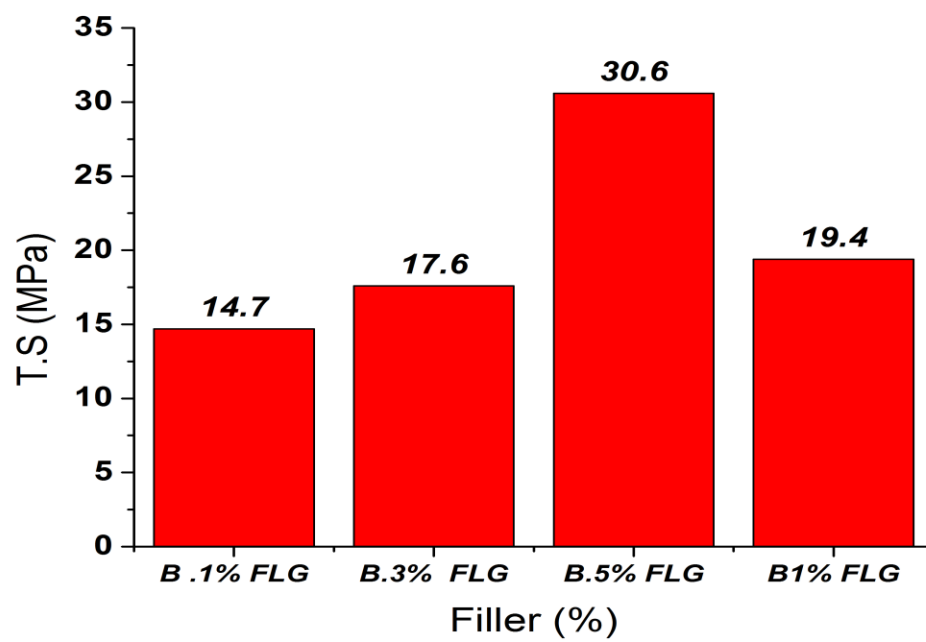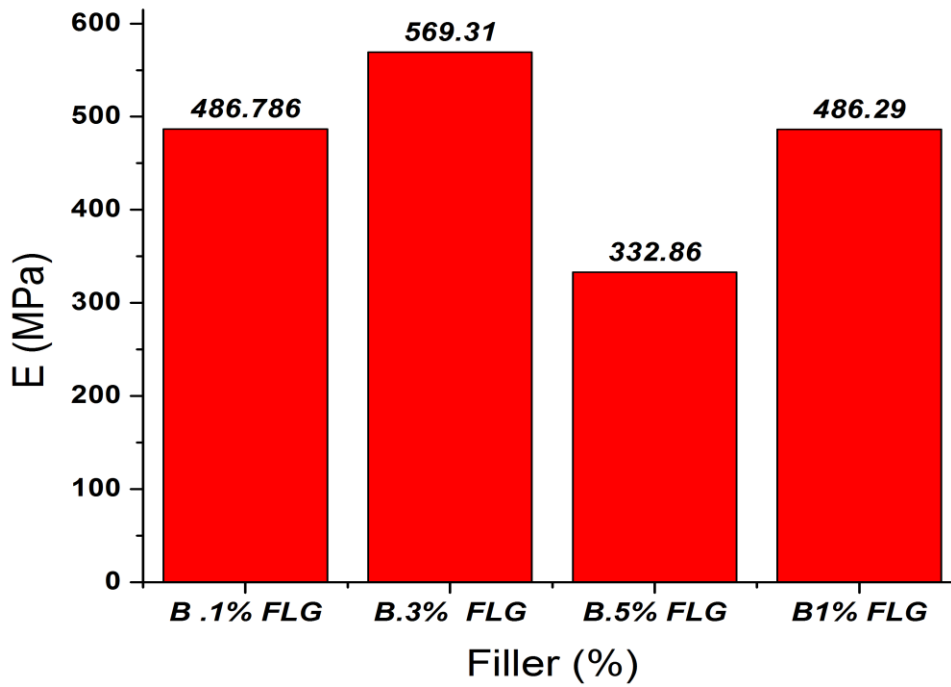
Figure 29: Tensile strength of Hybrid of TOPAS

Figure 30: Tensile modulus of Hybrid of TOPAS
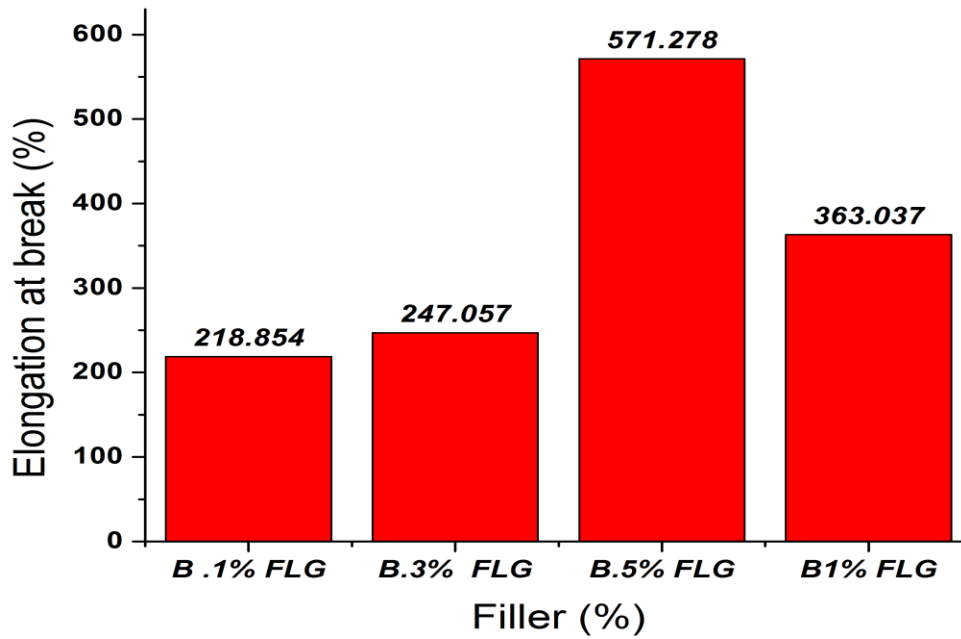

Figure 31: Elongation at break of Hybrid of TOPAS

4.3   Antimicrobial activity

In antimicrobial activity the antibacterial resistance and antifungal resistence was study. For antibacterial resistance six strains have been used against which resistance was checked. For antifungal resistance three strains have been used.

4.3.1   Antibacterial resistence

It is found that pure TOPAS(COC) film, COC/FLGs films COC/CA films and COC/10%CA/FLGs films showed the resistence against all the six strains. For all the films antibiotic ceftizoxime (ZOX: 30ug) has used as a positive control. While negative control is PES film.

Table 12: Bacterial strains and their result

S.NO	STRAINS	nomenclature	Specie	RESULTS
1.	SA	Staphylococcus aureus	Gram +ive	Resistance
2.	E.Coli	Escherichia Coli	Gram -ive	Resistance
3.	Shegilla	Shegilla	Gram -ive	Resistance
4.	S.Typhi	Salmonella Typhi	Gram -ive	Resistance
5.	PA-10	Pseudomonase Aeruginosa	Gram -ive	Resistance
6.	AB-10	Acineto Bacter	Gram -ive	Resistance
7.	ZOX	Antibiotic	Positive control	Resistance
8.	PES	polyethersulfone	Negative control	Non resistant

In the figure 10 it is clearly seen that there is no growth of bacteria belonging to specie Shigella (above and below) all the films. While there was growth on the negative (-ive) control. There was no growth around and under the positive (+ive) control. Pure COC show good resistence against the shigella. May be this is one of the reason that all the system nanocomposites, blend (COC/CA and COC/FLGs) and hybrid system showed resistance against all bacteria. From figure 31-36 similar trend was observed for all bacterial species. Trend is similar no matter the specie was gram positive or gram negative. S.Aureus is gram +ive bacteria and all systems showed resistance against S.Aureus. Other five strains are gram –ive all system showed very clear zone under the films. From the study it was shown that these films not make zones of inhibition and are categorized as antibacterial reistant films by the AATCC-147(modified)

standard. These are non-leaching films having active surfaces so no microbial growth was possible on these surfaces. These films are biostatic in nature. Biostatic films are one which only stop the growth of the living organisms not kill them. These films stopped growth of the living organisms so the area under and above the films was very clear and clean.
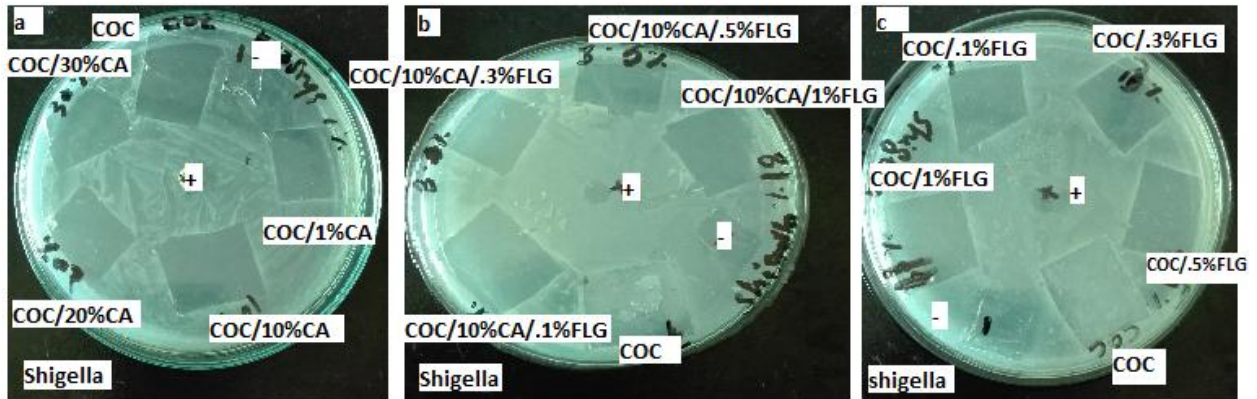

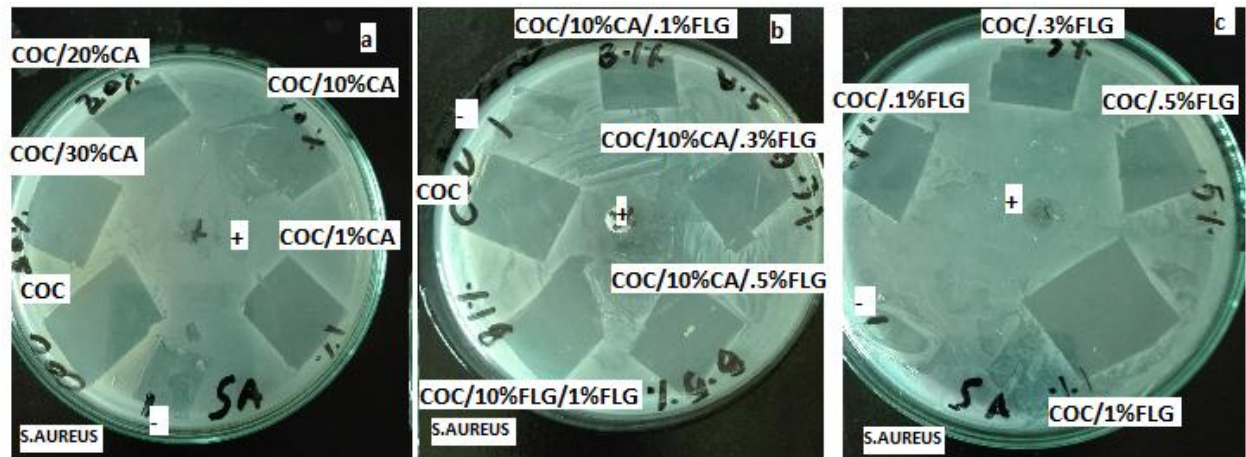**Figure 32: (a) COC/CA films, (b) COC/10%CA/FLGs films, (c) COC/FLGs films showing of resistance against shigella**

Figure 33:(a) COC/CA films, (b) COC/10%CA/FLGs films, (c) COC/FLGs films showing of resistance against S.Aureus
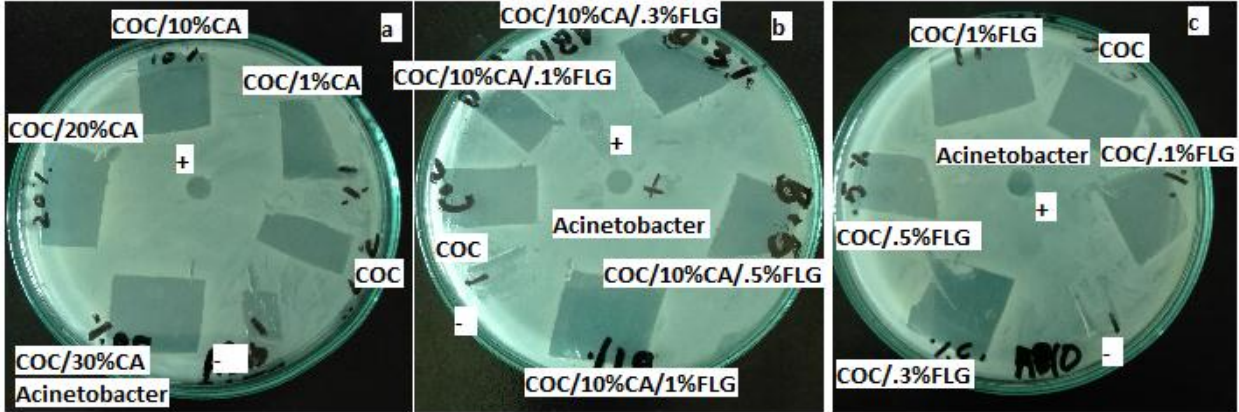
Figure 34: (a) COC/CA films, (b) COC/10%CA/FLGs films, (c) COC/FLGs films showing resistance against Acinetobacter
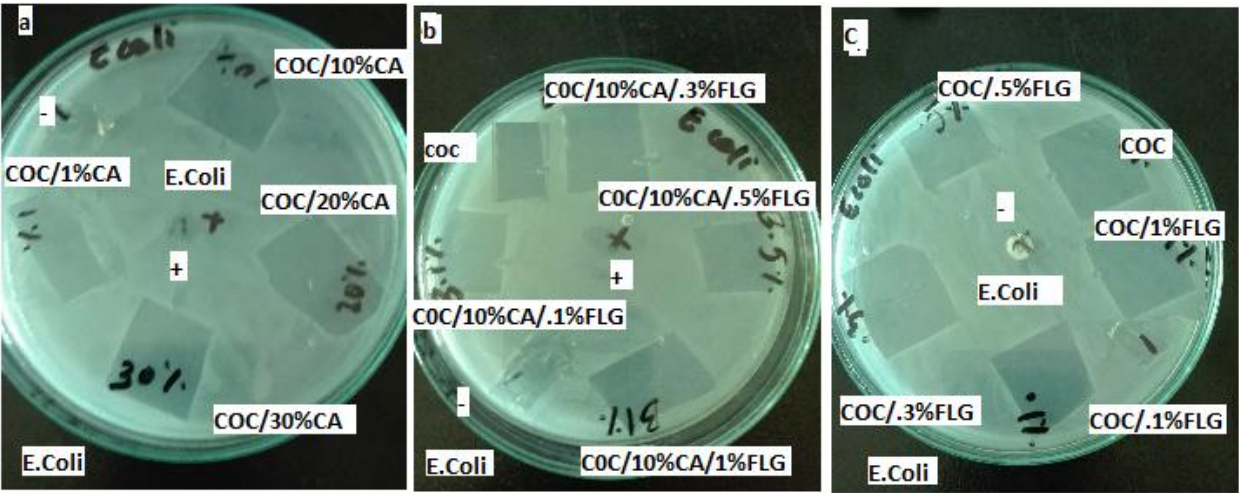

Figure 35:(a) COC/CA films, (b) COC/10%CA/FLGs films, (c) COC/FLGs films showing resistance against E.Coli
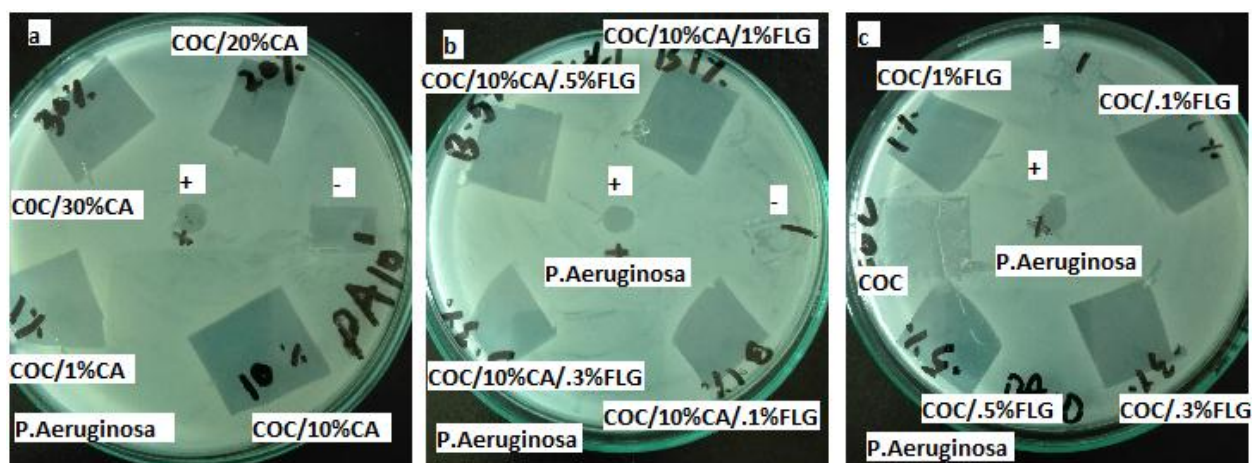
Figure 36: (a) COC/CA films, (b) COC/10%CA/FLGs films, (c) COC/FLGs films showing resistance against P.Aeruginosa
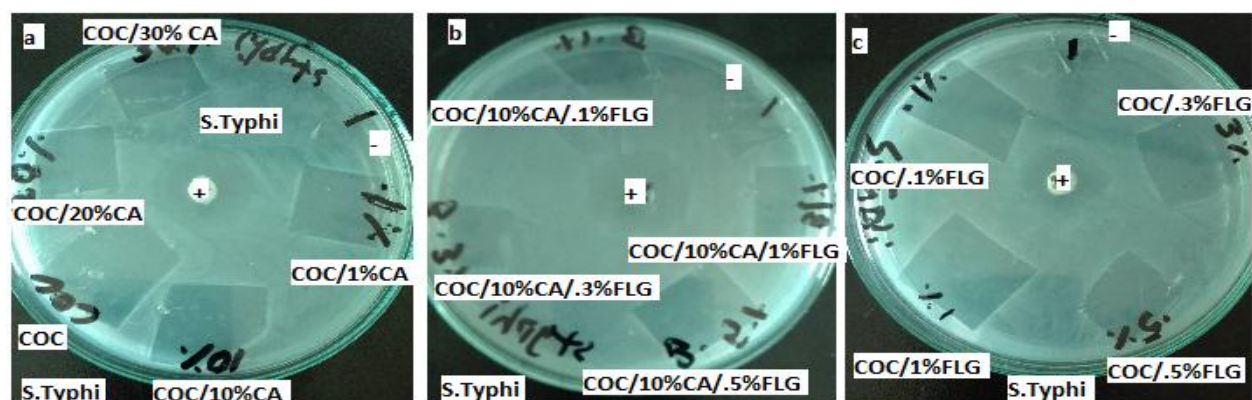

Figure 37: (a) COC/CA films, (b) COC/10%CA/FLGs films, (c) COC/FLGs films showing resistance against S.Typhi

For the respiration bacteria require acceptor of electron from extracellular environment to ensure movement of electron. So an electronic channel was developed between proteins (which are responsible for respiration) and extracellular surroundings. Disruption in this channel causes death of bacteria. Graphene has excellent tendency to accept electron while bacteria membrane has negative potential due to cell composition[29]. So it readily lose electron. There is possible reason for the death of bacteria under the films. The bacteria under the pure COC film also die this is may be due to the pie electron as it has tendency to extract electron toward itself. So bacterial membrane lose electron and also integrity of cell membrane. Which may cause the reduction in adenosine triphosphate (ATPs), cause inhibition [30]. Schematic of the process is given below in the figure 37. In the case of graphene as graphene has high effinity to accept electron may be it extract electron from the membrane and transfer to the COC and COC retain it

47

so cause deficiency of electron in the cell. As it was proved that these films are non-leaching and nothing come out from there edges (which is reason of the failure of disc diffusion method), so once electron captured by the film it cannot leach out so cause deficiency of electron for bacteria.
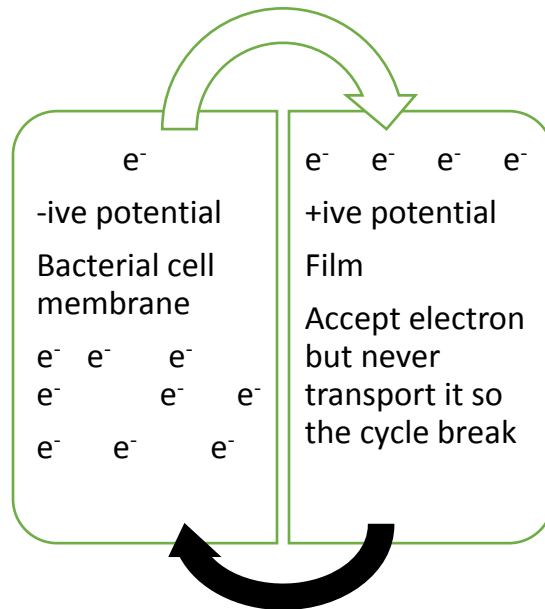

Figure 38: schematic of transport of electron from cell membrane to film

Another possibility for the microbial inhibition of bacteria, that these films were non-leaching and dense so they act as a barrier between bacteria and the surrounding environment from which bacteria get moisture and nutrient. So cut off from surrounding environment result in death of bacteria. Figure 38 explain this phenomenon.
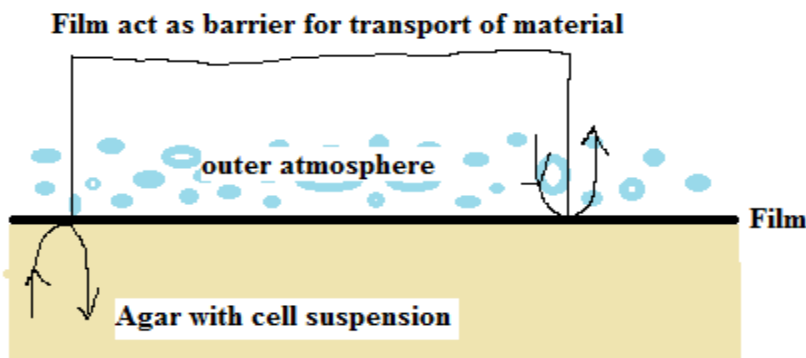

Figure 39: Schematic of the process inside the petri plate (how film act as a barrier)

4.3.2 Antifungal resistance

For antifungal resistance three strains have been used, out of which two were pure and one was mixed strain. Pure TOPAS (COC) film, nanocomposites, blends and hybrid films showed the resistance against all the three strains of fungal spores. Here pure TOPAS was used as a negative control. And resistance was analyzed against pure TOPAS film.

It was proved from disc diffusion test of all the films conducted for anti-bacterial resistance (as on the basis of failure of disc diffusion test AATCC-147(modified) was used to demonstrate antibacterial result) used under this study that these films are non-leaching. While Fungus need moisture, CO_2 and light to grow so no material came out of the films to promote the growth of the fungus. That was may be the reason for anti-fungal resistance. Figure 38 also explain the anti-fungal resistance of the films. Similar result was observed for all the films of nanocomposites, blends and hybrid. The growth was observed on 5th, 15th and 28th day of incubation. The amount of fungus spores increase and spread everywhere. Figure 39- 44 explain whole growth period.

Table 13: Strains of Fungus

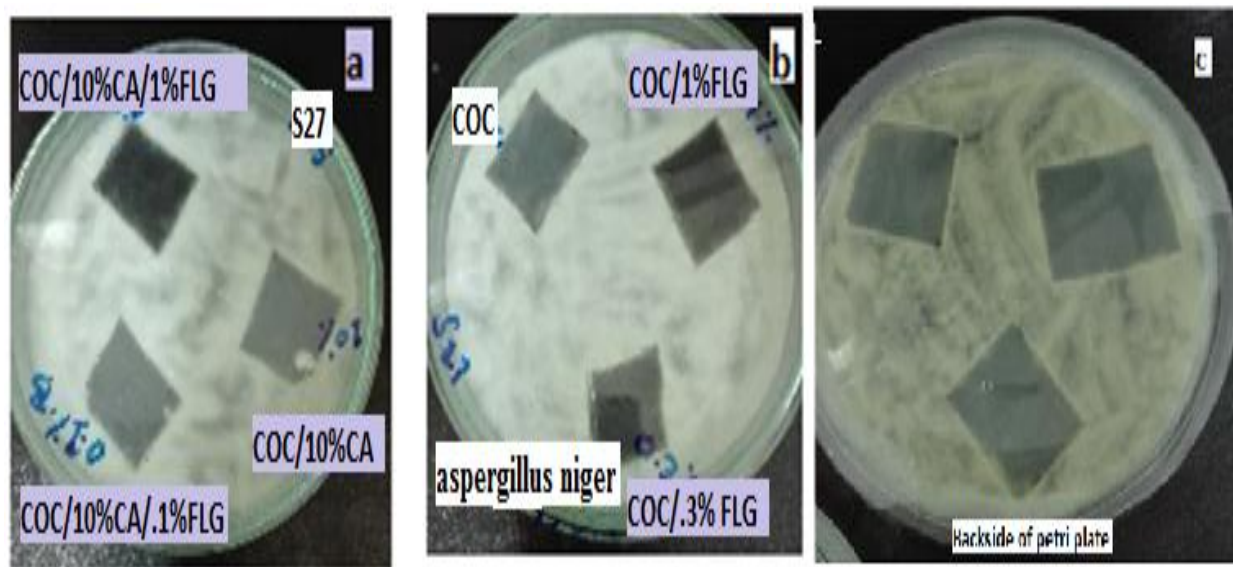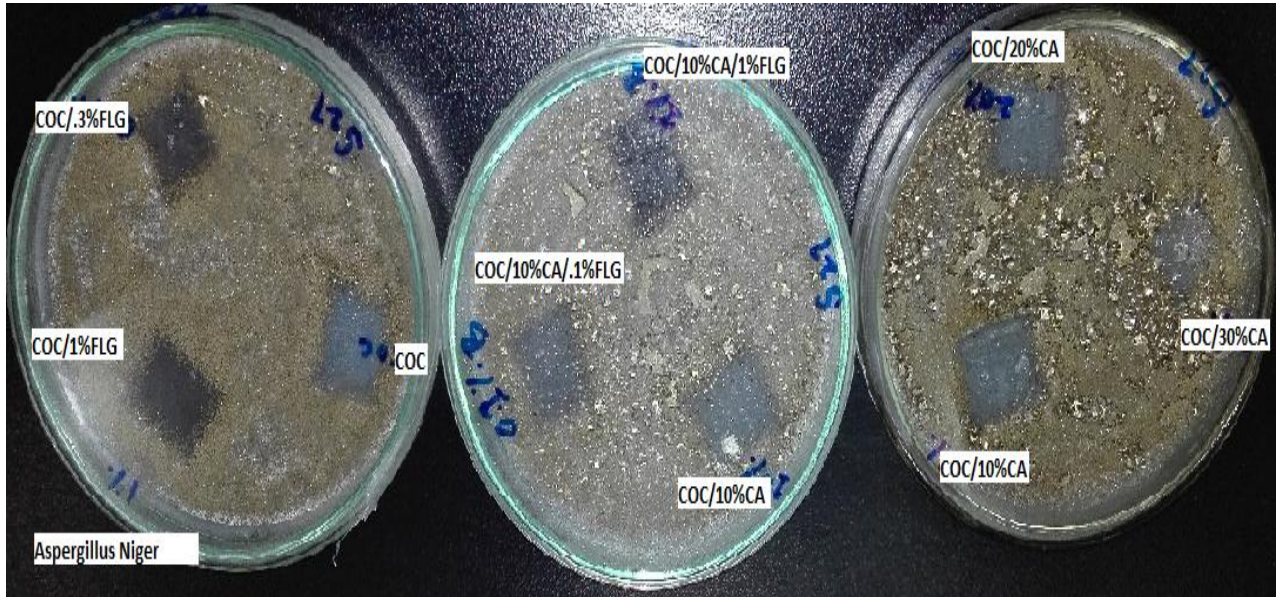| S.NO	Strains	Specie name	Results
1.	S_{25}	Aspergillus Flavus	Resistance
2.	S_{27}	Aspergillus Niger	Resistance
3.	S_{14}	Mixed culture	Resistance

Figure 40: Growth on fifth day

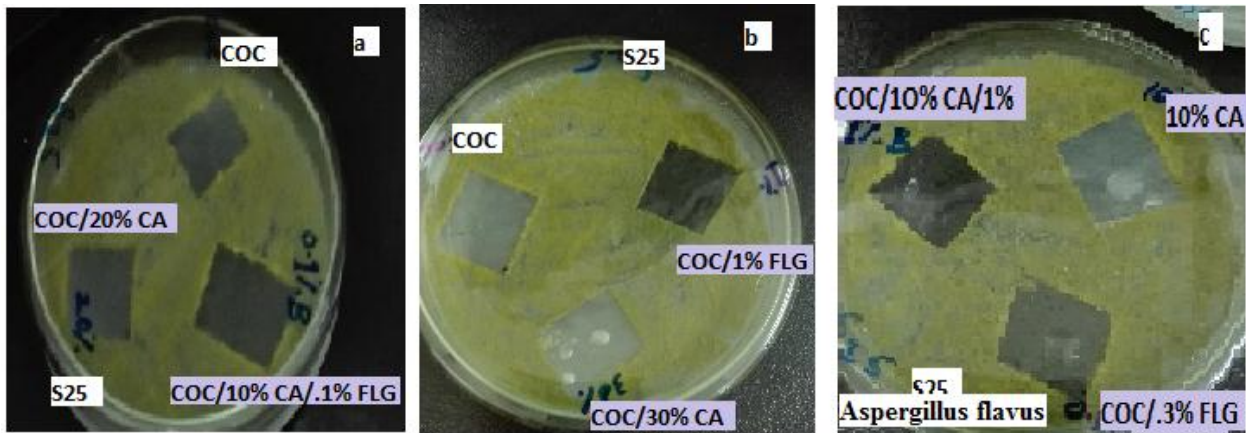**Figure 41: Growth on fifteenth day.**
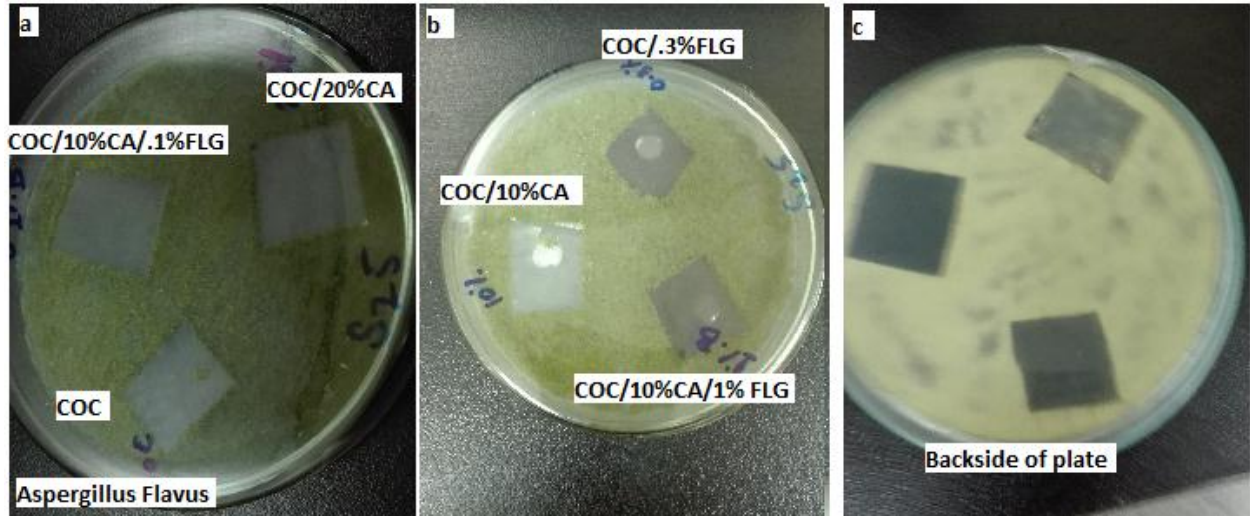

Figure 42: Growth on fifth day.

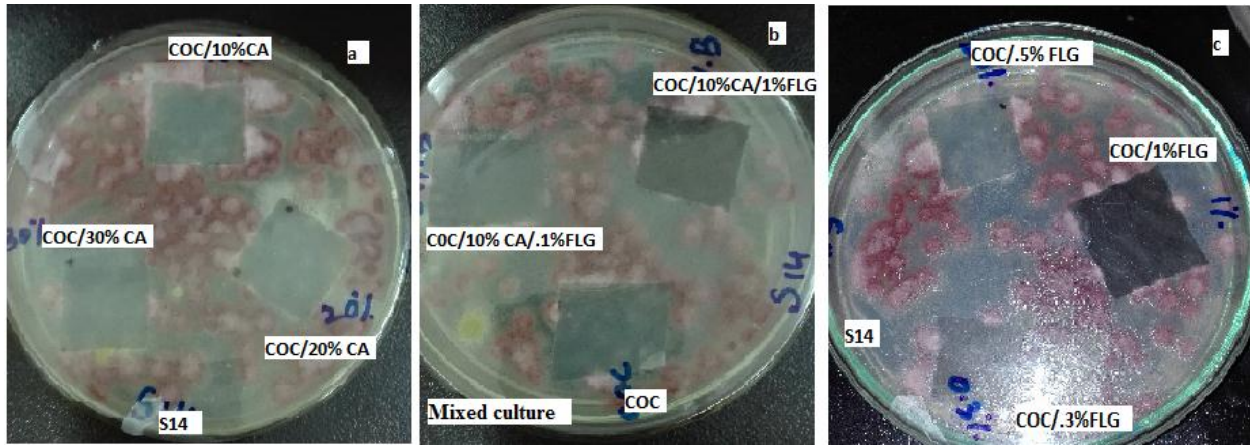**Figure 43: Growth on fifteenth day.**

Figure 44: Growth on fifth day.
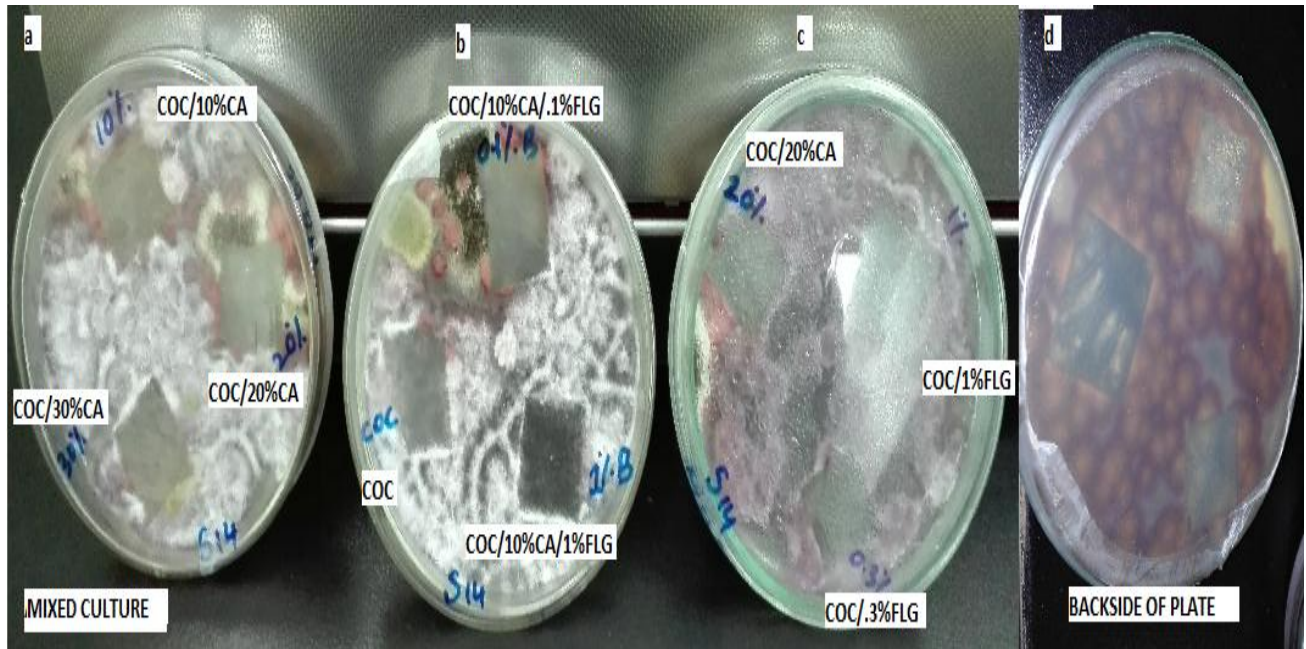
Figure 45: Growth on fifteenth day.

Figure 45 showed the growth of aspergillus Niger on pure TOPAS film. The film was completely covered and damaged by the fungal specie. While nanocomposite, blend and hybrid were showing resistance against same species. Figure 46- 48 represented the nanoconposite, blend and hybrid which gave better mechanical properties. These films also gave better anti-fungal resistance property. Aspergillus Flavus and mixed culture of fungal spiecies also showed similar results.

Figure 46: pure TOPAS film

Figure 47: nanocomposite containing 0.3% FLG

Figure 48: Blend containing 20% CA

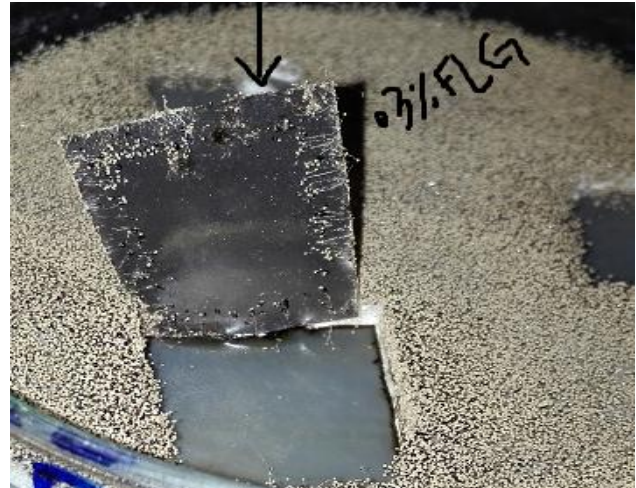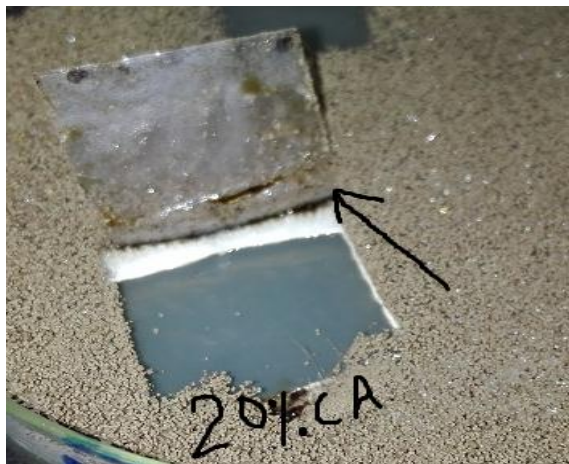**Figure 49: hybrid containg 0.5% FLG**

On the basis of visual observation it was not easy to say that which film has better antifungal resistance. There was need to test these film further by SEM or any other technique. Visually all the surfaces were clear.

CHAPTER 5

5.   Conclusions and Recommendations

From this study it was found that mechanical properties of Nanocomposites, blends and hybrid of TOPAS, CA and FLGs are enhanced. However, maximum Tensile strength and modulus are improved in TOPAS/FLG than TOPAS/CA blend and TOPAS/CA/FLG hybrids. Moreover, due to chains alignment in the vicinity of FLG, elongation at break was significantly improved in TOPAS/FLG nanocomposites which were increased upto 110 times as compared to pure COC. Percolation limit for FLG as a filler for COC was 0.3% which was critical loading limit for COC matrix. Critical loading for CA in COC matrix was 20%. After this limit properties decline. XRD and SEM micrograph showed that dispersion was good at lower concentration of the FLGs up to 0.3 wt% while at higher concentrations up to 1.0 wt%, the agglomeration started to occur in the TOPAS matrix. All films showed anti-bacterial and anti-fungal resistance against all strains used in this study.

For antimicrobial assessment and verification there is a need to investigate the properties further. On the basis of visual observation it was not easy to say that which film at which concentration has higher resistance. There was need to test these film further by SEM or any other technique. Visually all the surfaces were equally clear. There is also need to do permeability studies for these films in order to use them for gas separation and ultrafiltration membranes. There is a need to study barrier properties of these systems. There is also a potential to study thermal degradation behavior of these films. In future, one can also investigate EMI shielding properties of these systems along with the dielectric properties.

6. References

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