Poly (ε-caprolactone)/TOPAS blend for packaging application

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Certificate

This is to certify that work in this thesis has been carried out by **Miss. Ayesha Iftikhar** and completed under my supervision in polymer laboratory, School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

I would like to dedicate my work to my beloved parents, friends 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.

ACKNOWLEDGEMENTS

Abstract

In this research, two bio-degradable polymers Poly (ε-caprolactone) PCL and TOPAS have been blended together to study their morphology, structure, Thermal, Thermo-mechanical, Biodegradation behavior and antimicrobial activity for bio-degradable packaging applications. Blend of PCL/TOPAS have been prepared with different concentrations (5, 10, 15, 20, 30, 50 wt.%) by solvent-casting. Morphology and structural properties were studied by X-ray diffraction (XRD), Scanning electron Microscopy (SEM) and Fourier Transform infrared spectroscopy (FTIR). X-ray Diffraction (XRD) showed increased crystallization with increasing fraction of PCL in PCL/TOPAS blends. No significant intermolecular interactions proved immiscibility between PCL/TOPAS blends observed by FTIR. SEM clearly shows as two phase morphology with the PCL particles coarsely dispersed in the continuous matrix of TOPAS. High interfacial tension was observed results in immiscibility of blends. Thermal and thermo mechanical properties of PCL/TOPAS blend were studied by means of differential scanning calorimetry (DSC) and Dynamic mechanical thermal analysis (DMTA). DSC revealed the decrease in Melting and crystallization temperatures of PCL with the fraction of TOPAS in blends indicate the dominating amorphous component of TOPAS inhibits the structural organization of minority PCL component. DMTA revealed the increase in modulus of blend at 10% concentration indicate high stiffness as it is confirmed by swelling test. Anti-bacterial resistance was studied by using ASTM-G21. Blend of PCL and TOPAS showed resistance against all bacterial and fungal strains used in this study.

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List of Abbreviation

O2	Oxygen
H_2O	Water
CO2	Carbon dioxide
PLA	poly lactic acid
PHA	poly hydroxy acid
PVC	poly vinyl chloride
LDPE	low density poly ethylene
PC	polycarbonate
HDPE	high density poly ethylene
PMMA	poly(methylemthacrylate)
PDMS	polydimethylsiloxane
PP	poly propylene
PS	poly styrene
PE	poly ethylene
HCL	hydro chloric acid
HDT	high heat deflection temperature
COPs	cyclic olefin polymer
COCs	cyclic olefin copolymer
PCL	poly caprolactone
PDLA	poly d,lactide
PGA	poly glycolide
CL	ε-caprolactone
Tg	glass transition temperature
Tm	melting temperature
Tc	cooling temperature
ΔHm	melting enthalpy
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
SEM	scanning electron microscopy
DSC	differential scanning calorimetry

DMTA   **dynamic mechanical thermal analysis**

E.Coli   **Escherichia Coli**

PDA   **potatodextrose agar**

MPa   **mega pascal**

Conc   **concentration**

+ive   **positive**

-ive   **negative**

CHAPTER 1
INTRODUCTION

For more than fifty years, plastic polymers have been the most realistic and inexpensive solution for packaging applications because of their low cost, easy obtainability, exceptional optical, mechanical, and barrier properties, heat resistance and heat seal ability compared to grease and water.

Even with these benefits, ecologists have been supported the substitute of plastic through materials from renewable reserves because plastic films neither completely degrade nor recyclable and can cause severe ecological and waste discarding issues.

Even though, high progress costs and limitation of assessable alternate products limited the development in that direction, current bangs in prices of petroleum goods have carried this issue in the frontline again, accentuating the restricted nature of crude oil resources and assumed that a convincing economic motivation for investigation of renewable options based upon biomaterials[1].

Certainly, those changes in the opposition prospect make it both crucial and profitable to focus the research on renewable biomaterials, concentrate on developing new methods and techniques that could get explicit advantages of exceptional and discrete features convenient bio-polymers.

Growing this challenge, several industrial companies and research groups are developing innovative eco-friendly solution of packaging to develop ecological advantages of bio-polymers in the field such as "food packaging".

Previous decade have realized fast development of novel materials from renewable biopolymers take out from biomass (e.g. lipids, proteins and polysaccharides) or from micro-organisms (e.g. polyhydroxyalkonates) and also developed by some classical chemical synthesis (e.g. polylactic acid) used to expand novel structures for biomedical applications such as tissue engineering, organ transplant or for controlled drug delivery in pharmaceutics[1].

Natural and synthetic polymers stand at the conflicting directions by means of their properties. Polyolefins are hydrophobic hydrocarbons resistant to hydrolysis, per-oxidation and biodegradation which are their major attributes in packaging applications. By introducing pro oxidant additives promotes oxo biodegradation through making low molecular mass bio compounds which can replicate from micro-organisms makes polyolefins biodegradable.

Natural polymers like cellulose and starch are hydrophilic in nature. They show water wetting and swelling properties and therefore biodegradable. In food packaging these natural polymers are not technically useful where hydrophobic properties are required. In the middle of these two extremes, hydro-biodegradable aliphatic polyesters such as polyhydroxy acid(PHA) and poly lactic acid (PLA)[1].
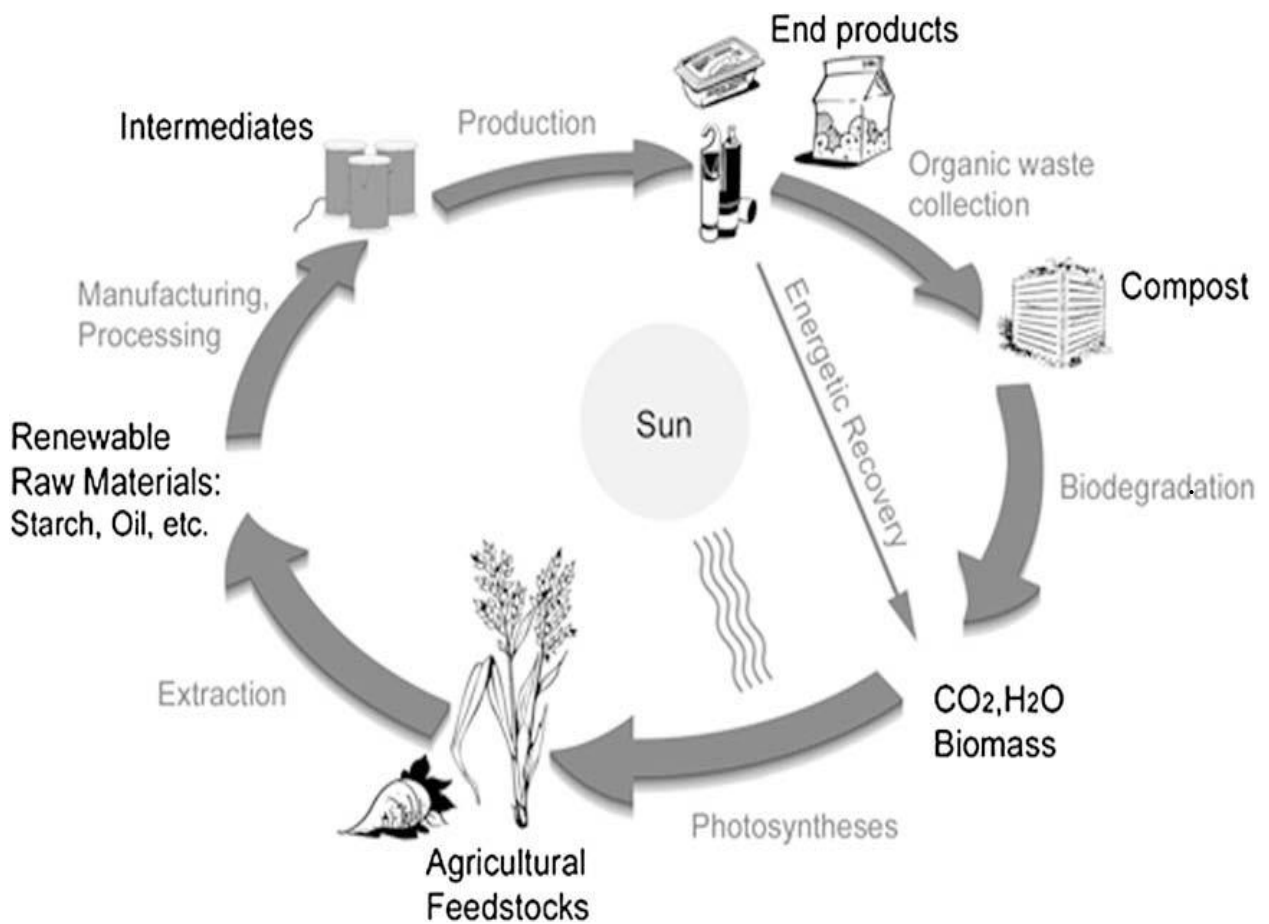
Figure 1. Life cycle

Life cycle of biodegradable polymer is shown in figure 1 which comprises conservation of water, fossil resources and production of carbon dioxide. Degradation rate of polymers depends upon temperature (50-70°C), humidity and microbe's nature.

Progress in food packaging applications by using biopolymers have lagged medical materials because of low strength, high cost and poor water resistance.

To overcome these restraining factors involved blending natural and synthetic polymers or blending two synthetic polymers together.

Unlike conventional packaging, bio-based packaging serves numerous vital functions including protection of food and containment, communicating information to consumers and preserves its sensory quality and safety.

1.2 Polymer blends

Use of natural polymers as biodegradable films for packaging applications are limited because of weak mechanical properties and poor barrier properties. Because of this limitation, natural polymers are being blended with other synthetic polymers to expand their applications[2].

Blending in limiting amount of expensive polymer in an inexpensive polymer matrix is a useful and productive way to enhance the material properties. But it is difficult to recycle the single polymer as layered material. Blends properties will fall between these two components which are mixed together, but in some cases, improved properties are obtained through those blends.

A major objective of blending is to recover lacking properties while preserving as much as possible desired properties of major component. Barrier properties are strongly influenced by morphology of polymer blends and aimed to develop favorable structures to maximize the unevenness of diffusion path.

The blend morphology takes place as result of complex interaction among processing conditions, chemical and physical characteristics of polymer components.

A lot of compounds are competent of enhancing interaction and adhesion between polymer phases when compatibilizers were added.

It is already been investigated that improved morphology of polymer blends can enhance barrier properties in polymer blends[3].

CHAPTER 2

LITERATURE REVIEW

2.1 General Introduction

2.1.1 Polymer

Polymer is something that made of many small units. These units are called "monomers" consists of small molecules that typically contain ten or less than ten atoms in a row. Most conmen atoms in monomer are hydrogen and carbon but fluorine, chlorine, nitrogen and oxygen may also be present in it. we can think polymer as a chain in which monomers are linked together to form a long chain monomer of at least 1000 atoms in a row. Because of those large features Polymers exhibit special properties.
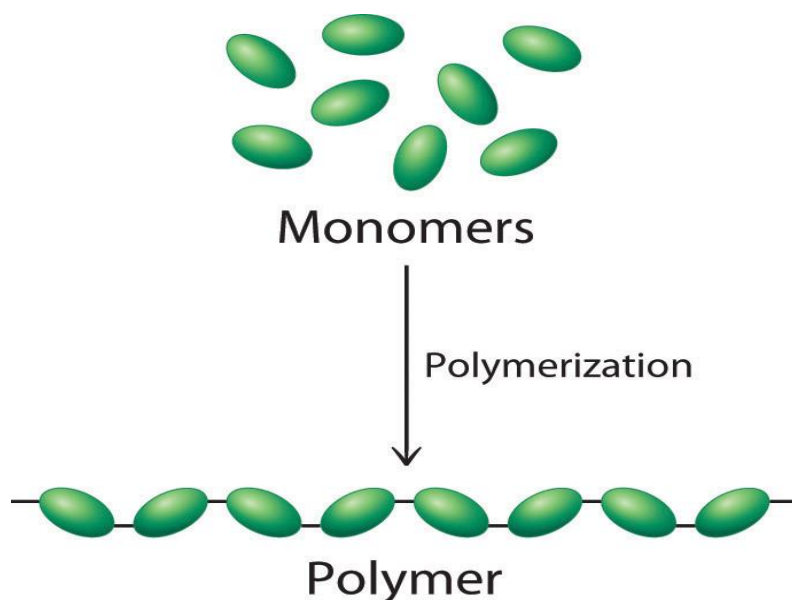
Figure 2.1 Scheme of polymer formation

Polymers or macromolecules are generally found in human body, plants, animals, manufactured product and minerals. Following substances contains polymers like glass, diamond, DNA, tires, concrete, cotton hairs, and paints etc. Macro-molecules could have dissimilar end units, chain branches, and different monomer sequences, repetition of monomers in the same chain leads to large number of natural and manufactured polymers.

Figure 2.1 shows polymerization reaction during which large number of small units called "monomers" connected by covalent bonds to form a long single molecule called a polymer.

2.1.2 Classification of polymers

There are different classifications of polymers shown in figure 2.2 below;
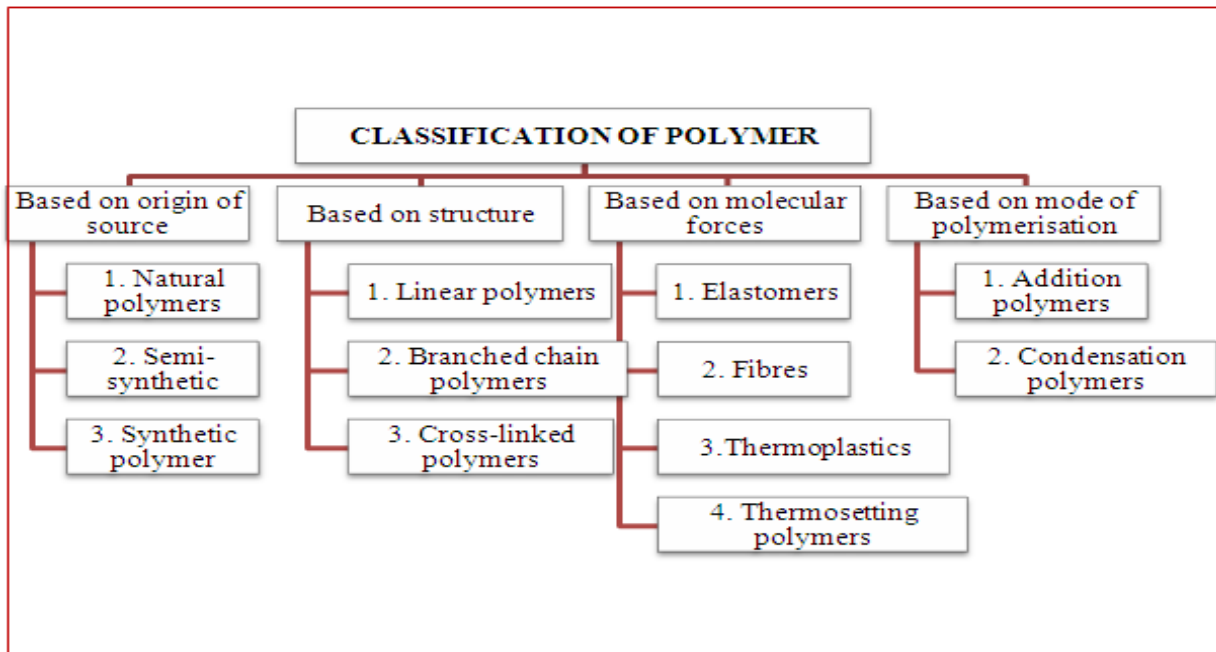
Figure 2.2 Classifications of Polymers

- **Classification by origin**

➢ Natural polymers

Polymers which are isolated from natural polymers known as natural polymers.

e.g. Wool, Silk, Cellulose, Proteins and natural Rubbers etc.

- Semi-synthetic polymers

Polymers obtained by chemical treatment of natural polymers that improves its physical properties like tensile strength and lustrous nature known as semi-synthetic polymers.

e.g. Cellulose nitrate, Cellulose acetate
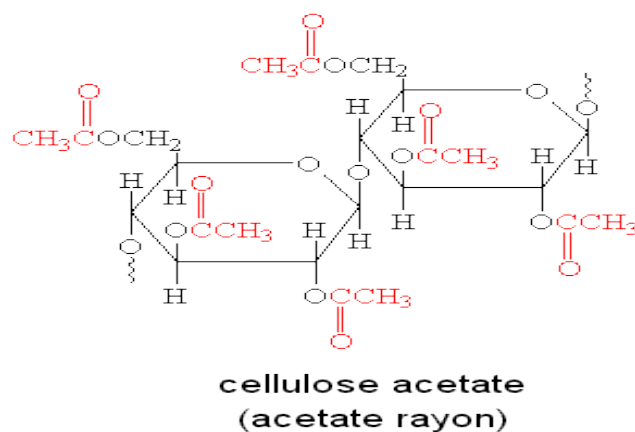
Figure 1.3 structure of Cellulose Acetate

> Synthetic Polymer

Polymers which are synthesized in the laboratory from compounds that have lower molecular weight are known as synthetic polymers.

e.g. Terylene, polystyrene, synthetic rubber, PVC, Teflon, Nylon etc.

- **Classification by monomer**
> Homopolymers

Polymer which consists of identical monomers known as homo-polymers.

e.g. polypropylene, PVC, polyethylene

> Co-polymers

Polymer which consists of monomer having different chemical structure called copolymer.

e.g. nylon 6,6

- **Classification by structure**
> Linear polymers

Monomers linked together and form long straight chain structure called linear polymers. They have no side chains. Molecules of linear polymers formed packed and possess high density, melting temperature and tensile strength.

e.g. nylon, HDPE

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-
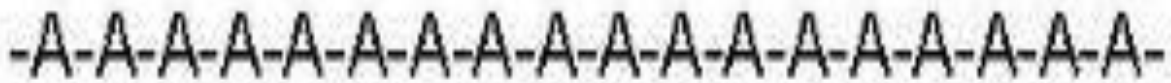
Figure 2.4 linear polymer Chain

> Branched polymers

Monomer linked together form long chains but also linked some side chains along. Molecules of branched chains are irregularly attached and have low density and tensile strength.

e. g. LLDPE. LDPE
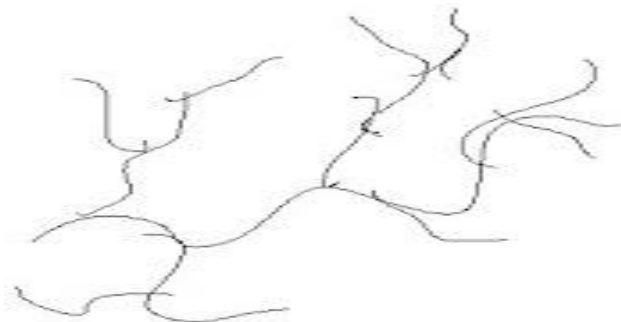
Figure 2.5 Branched polymer Chains

➢ Cross linked polymers

Monomers are cross linked together to form 3D network. Due to strong cross linking, these polymers are brittle, rigid. e.g. Formaldehyde resins, vulcanized rubber, Bakelite.

Figure 2.6 Cross linked Structure of Bakelite

- **Classification by molecular forces**
➢ Fibers

If polymers are strained into long filament like structure whose length is 100 times higher than its diameter than it is said to be a fiber. They show high tensile strength because they have hydrogen bonding in the inter- molecular structure and called as highly crystalline structures. e.g. Terylene and Nylon etc.

➢ Thermoplastic polymers

They could easily be molded in desired shape on heating and cooling at room temperature.They are hard on cooling and soft on heating. They could have branched and linear chains. e.g. PVC, PP, PS, PE etc

➢ Elastomers

They show solid nature with rubber like properties because of cross linking between their chains.they have weak intermolecular interactions show highly amorphous nature.weak binding forces permits them to stretch. e.g. BUNA-N, BUNA-S, Natural rubber and vulcanised rubber.

➢ Thermosetting polymers

These polymers are hard and have high degree of crosslinking.they cannot be reused and not remolded. e.g. Polyester resin, Poly urathane and Bakelite

- **Classification by mode of polymerization**

It is a process which connect the monomers togather and create large molecules of various sizes and shapes.

- o Addition polymerization

Polymers are formed repeatedly without elimination of byproducts known as addition polymers. They have molecular weight equal to integral multiple of all monomer units.

e.g. poly-propylene, Teflon, PVC

- o Condensation polymerization

Combination of two monomers are formed by elimination of molecules loke water, alcohol or NH3. Easter and amide linkages are present in their structure.

e.g. polyesters(PET), polyamides

$$n\ H_2N\ (CH_2)_6\ NH_2 + n\ HOOC\ (CH_2)_4\ COOH$$
$$\longrightarrow -\!\!\left[NH\ (CH_2)_6\ NHCO(CH_2)_4CO\right]_n + n\ H_2O$$

Nylon 6, 6
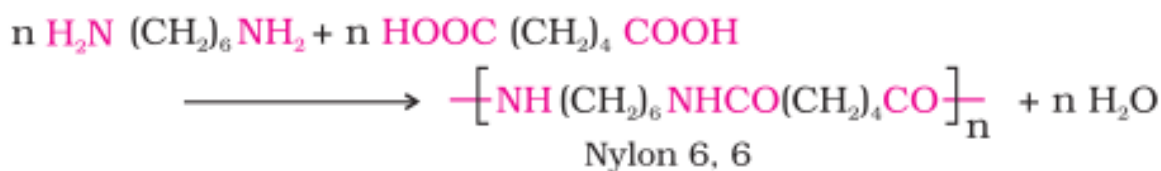
Figure 2.2 Process reaction for condensation polymerization

The Table 1 below shows just a few manufactured polymers that are made from the monomer on the right.

Table 1:Examples of manufactured polymers

Polymer	Repeating Units	Monomer
Polyethylene	$-CH_2-CH_2-$	$CH_2\!\!=\!\!CH_2$
Poly(vinyl chloride)	$-CH_2-CH-$ with Cl	$CH_2\!\!=\!\!CH$ with Cl
Polypropylene	$-CH_2-CH-$ with CH_3	$CH_2\!\!=\!\!CH$ with CH_3
Polystyrene	$-CH_2-CH-$ (phenyl)	$CH_2\!\!=\!\!CH$ (phenyl)

2.2 Introduction to TOPAS

(Thermoplastic olefins polymer of amorphous structure)

Metallocene is a catalyst, development and discovery of it opened immense opportunities to the synthesis of large variety of polymer with selected structures.

Cyclic olefin copolymer can be synthesized through addition polymerization except ring opening metathesis. Figure 2.8 shows the monomer of cyclic olefin synthesis by metallocene catalyst via addition polymerization.

Cyclic olefin monomers include cyclobutene, cyclo-pentene and norbornene provide exceptional variety of polymeric materials have interesting properties.
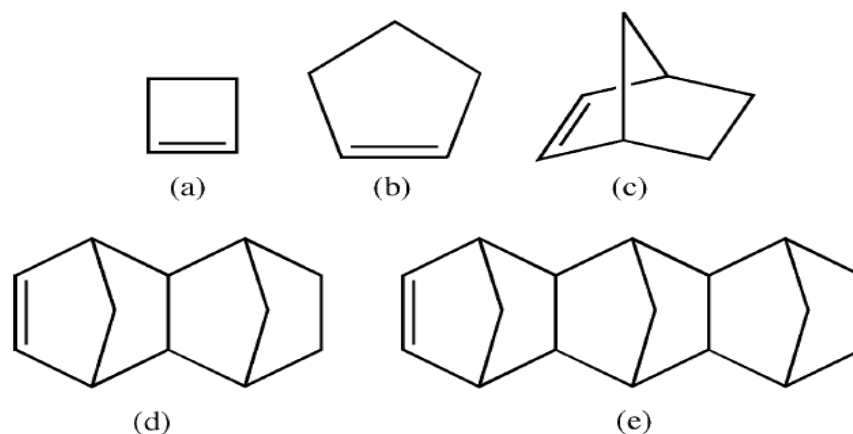
Figure 2.3 COCs polymerized by metallocene catalysts via addition: (a) cyclobutene (b)cyclo-pentene (c) norbornene (d) 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphtalene (DMON) (e)1,4,5,8,9,10-trimethano1,2,3,4,4a,5,8,8a,9,9a,10,10a-do

Each route directs to specific polymer nature which is much dissimilar in properties and structure from other two monomers. The best monomer from these three is known as norbornene which synthesis via ring-opening polymerization. Polymer thus obtained still has double bond in the backbone of polymer.

Because of this double bond polymer chains can be cross linked i.e. vulcanized. This vulcanized material of poly norbornene was used as an vulcanizable elastomeric material for sound damping and vibrations. It also has further application in flexible coupling, shock proof bumpers and engine mounts.

Porous poly norbornene was also used for soaking material for oil spills and they have absorbance capacity up to 400% to their own oil and mass. Many publications are based on norbornene polymerization via ring opening metathesis. RuCl3/ HCl catalyst in butanol used in commercial polymerization.

Vinyl polymerization of cyclic olefins may also have termed as "Addition polymerization". For norbornene it is not much developed. Product made by vinyl polymerization does not contain double bonds. It takes place as homo or as copolymerization.

Copolymerization of cyclic olefins with ethane results in cyclic olefin copolymers. This polymerization could be carried out with half sandwich/MAO catalyst and metallocene. COC can be synthesis via melt processing method. [4]

COCs chemical structure tells about its nature and copolymer group attached to it. Figure 9 shows two type of ring structures integrated in polymer chain. Cyclic olefin copolymer synthesized from ethylene, norbornene group which are randomly attached to the main carbon chain.

This Ring structure gives material more stiffness and size of molecule prevented it to crystallize. It shows ductile nature at elevated temperature so we cannot stretch COCs at low temperatures.

2.2.1 Role of Ethylene and Norbornene
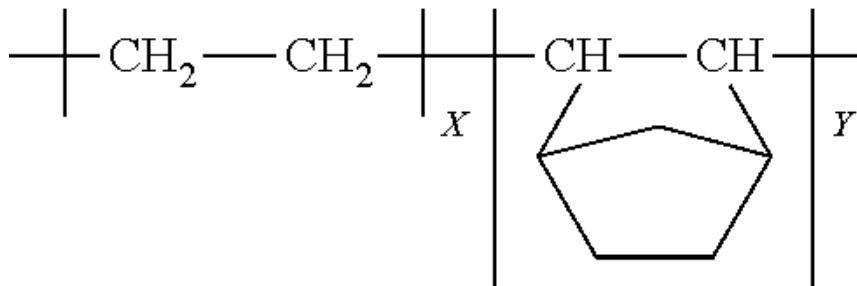
Figure 2.4 Chemical structure of TOPAS

2.2.2 Properties of TOPAS

Extensive range of properties can be realized by controlling chemical structure of cyclic olefins copolymers.

- It shows amorphous nature with broad range of glass transition temperatures Tg from (room temperature to 220 ^{o}C). It can be the result of stiffening of chains and large size of norbornene group. Change in molecular weight exhibit rheological properties.

- Its transparent nature and lack of chromophores results in both glass like and water white. They show high transparency, high refractive index, high chemical resistance and good process ability. Because of these properties of norbornene makes it suitable for optical applications i.e. coatings, blisters, CDs and DVDs, lenses and packaging material[5].

- Norbornene vinyl polymer made films having excellent transparent nature, heat resistance and viscoelastic nature, electric nature at high temperatures properties. This film could be used as insulator[4].

- COCs also possesses superior mechanical properties like strong, stiff, brittle, like PS and PVC. Low moisture absorption, high transparency with high thermal stability and

high glass transition temperatures, low moisture absorption gives it good barrier properties.

- Thermal and their mechanical properties make them as an alternative of poly olefins.
- It can also be used in non-optical applications like powder coating, gears, housing etc.[6].
- COCs have low density if we compare it with PMMA and PC because of their high heat deflection temperatures(HDT)[7].
- COCs show high resistance to polar and aqueous acids because aliphatic and aromatic ring react with them. These properties make it useful for packaging, optical and engineering applications [8].
- Different Grades of TOPAS show different deflection temperatures like Grade 8007 show 75°C deflection temperature. This grade is good fo packaging applications because of high barrier properties and have low water absorption capacity. It has longer elongation and low coefficient of elasticity as compared to their grades of cyclic olefin copolymer[9].
- It shows good resistive chemical properties. Chemical resistance of TOPAS can be seen below[10].

Table 2: Range of 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/m²/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/m²	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,: mm²/n	6×10^{-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

2.2.3 Fabrication methods

These are some methods to fabricate cyclic olefin copolymers. These methods could be low cost but not most sufficient way for fast prototyping.

Cyclic olefins can be purchased either in solution form (Nano imprinting) or in pellet form (injection molding) or sheets (hot embossing)[11].

- **Melt processing**

This technique widely used for processing methods. In this technique polymer become liquid at certain temperatures and extruded into films, fibers and tubes of different shapes. Shapes can also manipulate by molecular confirmations and phase morphology that have important role in performance of final product.

- **Injection Molding**

It consists of a hollow mold imparts the material into its final shape. Thermosets and thermoplastics are processes by compression, transfer and blow molding. Molding machine is very sophisticated capable of turning out high number of molded articles with no operating attention.

There are some parameters that directly effects on COC reproduction.

- Structure depth
- Mold wall temperature
- Injection speed
- High temperatures
- Pressure allocation in the interior of the mold[11].

Figure 2.10 Injection Molding machine

2.2.4 COC Grades

COC shows large range of Grades on basis of heat deflection temperatures (HDT) mechanical properties[9] listed in table 3 below.

Table 3: basic grade characteristic of COC

Grades	Basic grade characteristics
8007	Heat deflection temperature (HDT/B) = 75°C Water adsorption is small and barrier properties are exceedingly good, making this grade particularly suitable for package applications for products that dislike moisture. Grade 8007 has lower coefficient of elasticity and larger elongation compared with other TOPAS grades.
6013	Heat deflection temperature (HDT/B) = 130°C Due to its high transparency, low levels of eluates, superior chemical resistance, and high heat deflection temperature, this grade is suitable for products such as pharmaceutical packaging and diagnostic equipment.
6015	A similar grade to 6013. However, heat deflection temperature (HDT/B) = 150°C This is a temperature that cannot be achieved with many other amorphous polymers.
5013	Heat deflection temperature (HDT/B) = 127°C This grade is characterized by its high flowability and superior optical properties. It is suitable for optical components such as lenses and light guide panels where high molded precision is indispensable.
6017	Heat deflection temperature (HDT/B) = 170°C Possesses the highest heat resistance among cyclic olefin-type resins.

2.3 Introduction of Poly ε-caprolactone(PCL)

Polycaprolactone is semi-crystalline aliphatic polyester synthesized by Carothers group on early 90s. It is sensitive to microorganisms and degrade easily[12].

It is semi-crystalline, hydrophobic polymer and its crystallinity decrease with increasing molecular weight. It has low glass transition and melting temperature (-60 - 60 °C) respectively makes it soluble in other solvents and gives it exceptional blend compatibility with other polymers that could be used further in different applications in biomedical and packaging fields.

A lot of work has been published on poly caprolactone in various applications.
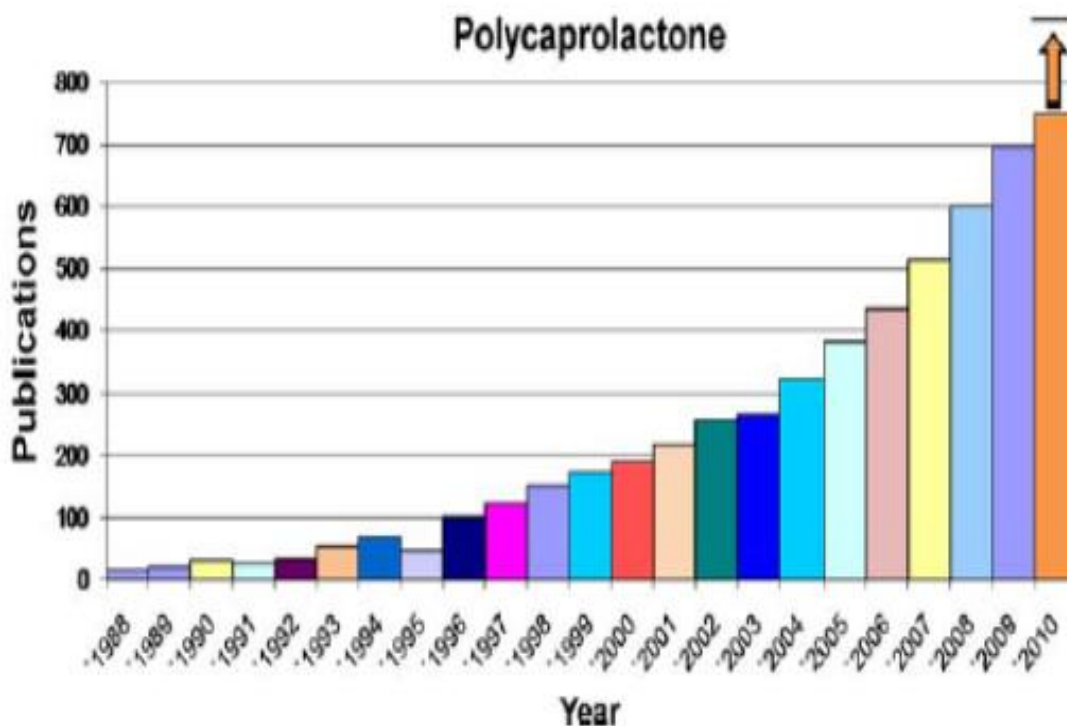
Figure 2.11 Publication using PCL

PCL could be used in drug delivery because of following properties:

- o Tailor able degradation kinetics
- o Mechanical properties
- o Variable pore size

Addition of functional group could make it more hydrophilic and biocompatible[13].

PCL degrades slower as compared to Poly d,lactide(PDLA) and poly-glycolide (PGA) used in drug delivery and also in suture materials.

Poly caprolactone is most widely used bio-degradable polymer due to its easy possibility (low melting temperature and high solubility) and high compatibility to form blend with wide range of other polymers like poly vinyl chloride (PVC), poly carbonate (PC) and poly vinyl methyl ether. It is derived from ε-caprolactone (CL) which exhibit properties like low cost, and high polymerizable [13].

Applications of PCL could be limited because of low degradation rates connected to its crystallinity and hydrophobicity. It is confirmed that bio degradability of PCL starts from its amorphous region where it experiences high degradation as compared to crystalline region. To attenuate the crystallinity of PCL could refine its degradation behavior [13].

2.3.1 Synthesis and Physiochemical properties of PCL

Poly ε-caprolactone (PCL) was synthesis by ring opening polymerization of cyclic monomer (ε-caprolactone). Stannous octate catalyst used to catalyze polymerization and to control molecular weight, alcohols of low molecular weight has been used[12].

It show high toughness but It possesses high toughness but comparatively low strength gives it rubber like nature [14].
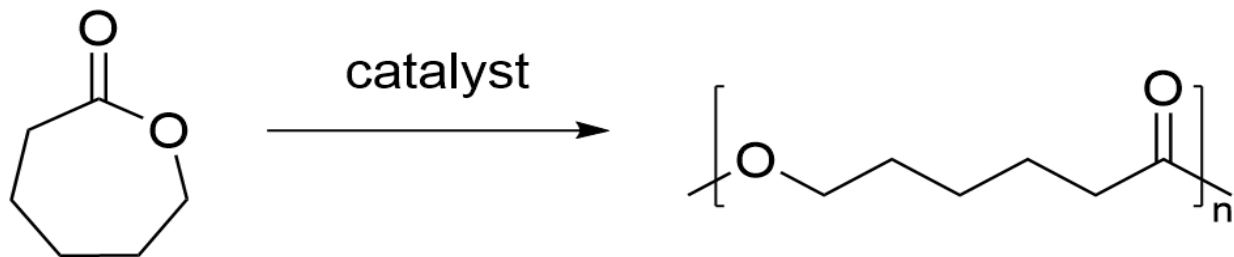
Figure 2.12 Structure of PCL

Different mechanisms can affect the polymerization of poly (ε-caprolactone) and these are cationic, coordination, anionic and radical. All these mechanisms effect the resulting molecular weight, end group composition, chemical structure of copolymer and molecular weight distribution [5].

2.3.2 Properties of PCL

Semi crystalline PCL possess low melting temperature leads to easy formability. Average molecular weight of PCL generally ranges from 3000 to 80,000g/mole and can be graded according to its molecular weight[12].

It is easily soluble in chloroform, carbon tetrachloride, dichloromethane, toluene and benzene at room temperatures. It is insoluble in petroleum ether, alcohols and diethyl ether.

Poly caprolactone(PCL) be able to blended with other polymers to enhance stress crack resistance, adhesion, dye ability and have been used with polymers like cellulose acetate butyrate, polylactic acid to manipulate the drug release rate for micro-capsules[15].

It has already been studied that PCL blends exhibits three types of blending.

- o Exhibit only single Tg
- o Exhibit Tg of each component but improved mechanical properties of phase separated material.
- o Incompatible with enhanced phase separated properties

PCL compatibility with other polymers generally exhibit better control on permeability in drug delivery and packaging systems[16].

2.3.3 Polymer Blends Literature

Interaction of the components and physical properties of blend of PP/COC has been studied in 2010 where immiscibility of both polymers was investigated. Melting temperature and crystallization of the PP component slightly decrease with the portion of COC in blends, in the range of 56–47%. Shifts in Glass transition temperatures were investigated by DMTA also indicate the immiscibility of PP/COC blends [17].

Poly ε-caprolactone (PCL)/polystyrene blend was investigated in 2007 showed enhanced thermal stability evidenced by DSC results in which melting temperatures and crystallization temperatures were slightly decreased as compared to Pure PCL indicate slight miscibility in PCL/PS blends. Two glass transition temperatures in the blends showed Immiscibility. FT-IR showed some n-π interaction between PCL and PS polymer blend[18].

Coalescence effect was studied in PCL/PLLA blend. Increased radiation dose results in high lamellar structure of PCL indicate high cross linking in PCL. Radiation dose also change the morphology of PCL/PLLA blend showed immiscibility[19].

Poly (vinyl)phenol blends with Poly ε-caprolactone and poly (β-propiolactone) experienced the strong inter molecular interactions between PVPh blends because of alkyl groups presents in blended polymers. Strong hydrogen bonding was observed in Ft-IR between the hydroxyl group of PVPh and carbonyl and ether oxygen moieties in blended polymers showed compatibility between polymer blends[20].

Conductivity properties of PVC/PMMA polymer blend was observed in 1999 in which they investigated that by increasing concentration of PMMA in PVC/PMMA blend electrolyte enhanced the conductivity[21].

The effect of blending chitosan with poly(ε-caprolactone) (PCL) on their biomechanical properties was studied.50:50 blends when processed at 55 °C in an oven showed significant improvement in mechanical properties as well as support for cellular activity relative to chitosan [22].

2.4 Objectives of the research work

Main objective of this research work is to prepare a novel blend membranes of PCL/TOPAS through solvent casting method and successfully characterization of these membranes.

- This study is carried out to investigate the thermo-mechanical properties of PCL/TOPAS blend membrane.
- Main goal of this research work is to Investigate anti-microbial activity of blend for packaging application.
- We will also investigate structural and thermal properties of PCL/TOPAS blend.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

These following materials were used for preparation of PCL/TOPAS Films.

Table 4. Materials

Materials	Manufacturer and Specifications
Cyclic olefin copolymer (TOPAS)	TICONA GmbH, Germany, TOPAS(Grade-8007)
Poly ε-caprolactone (PCL)	Solvay chemicals, Belgium PCL molecular weight $=2000$gmol^{-1}
Chloroform	Sigma Aldrich Co, USA (Lab grade)

3.1.1 PCL/TOPAS Blend preparation

The blend of PCL/TOPAS was prepared by solution casting method. Different weight percent of PCL and TOPAS are listed below in Table 5.

Table 5. PCL/TOPAS blends of different weight %

Weight % of TOPAS	Weight % of PCL
100	0
95	5
90	10
85	15

80	20
70	30
50	50

Different weight percent of TOPAS and PCL was dissolved in 20ml of solvent named chloroform separately. Samples was Stirred for 24 hours at 40°C temperature until they homogeneously dissolved in Chloroform. Then mixed these two polymers together and stirred vigorously for 24 hours.
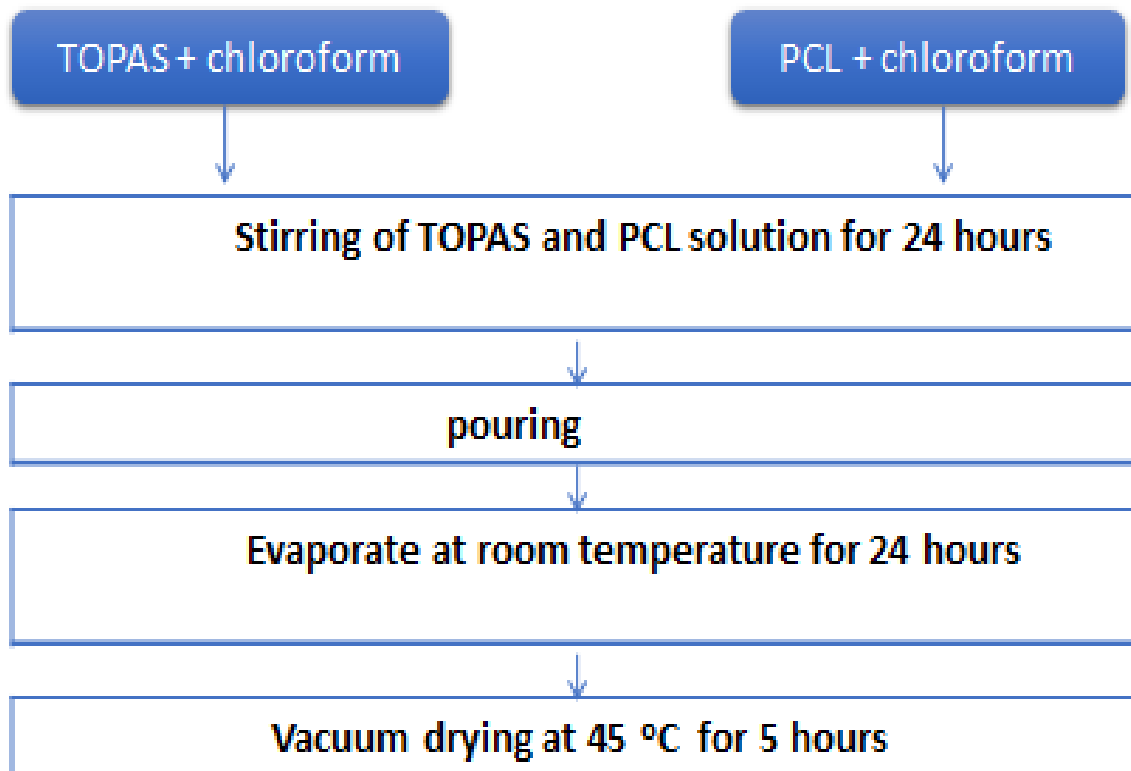
Figure 3.1 Flow chart of preparation of PCL/TOPAS blend films

Homogeneously dissolved solvents of PCL/TOPAS then poured in Petri dishes. These films were kept at room temperature for next 24 hours for drying and then vacuum dried at 40°C for complete solvent evaporation.

3.2 Testing and analysis

3.2.1 X-Ray Diffraction (XRD)

X-ray diffraction patterns were measured at room temperature by using theta-theta instrument Siemens D5005, STOE-Germany with a Cu Kα radiations ($\lambda = 0.15418$ nm) using an operating

voltage and current of 40kV and 40mA, respectively. The scanning rate was $2°/min$ over the range of $2\% = 5° - 65°$.

3.2.2 Fourier Transform infrared spectroscopy (FTIR)

FTIR is a technique used to detect the inter-molecular interactions between two polymers. Immiscibility of PCL/TOPAS blends thin films was confirmed by FTIR spectra because specific interactions affect the local electron density and related frequency shifts can be observed.

3.2.3 Scanning Electron Microscopy (SEM)

Morphology and Microstructure of Cryo-fractured surface of PCL/TOPAS blend film created by using liquid nitrogen was investigated by FE-SEM JEOL JSM-7200F. Samples were coated with Gold Layer of about $250A°$ by using a JOEL JFC-1500 ion sputtering machine. Samples were mounted on aluminum stubs for examination.

3.2.4 Differential Scanning Calorimetry (DSC)

DSC analysis were undertaken in Perkin Elmer 6000. All samples were weighted between 5-7mg and then sealed in an aluminum sample pan. During DSC analysis, all samples were subjected to a heating rate of $10°C/min$ from $-50-120°C$ to determine the change in glass transition temperature, Crystallization temperatures, Melting temperatures and heat of Fusion. Effect of processing history was removed by heating, cooling and reheating the samples again at same rate ($10°C/min$). Percentage Crystallinity of all samples was calculated by using melting endotherm and divided by reference endotherm value.

3.2.5 Dynamic Mechanical and Thermal analysis (DMTA)

Dynamic mechanical and thermal analysis was carried out to investigate viscoelastic behavior of PCL/TOPAS blends as a function of temperature and deformation frequency.

DMTA test was carried out through (Dynamic Mechanical Analysis ASTM D4065). Rectangular samples of (length = 20mm, R width = 8.7mm and thickness = 0.1mm) were investigated. Samples PCL/TOPAS blends were heated from $-20°C$ to $100°C$ at $5°C/min$ with constant frequency of 1.0Hz**.** Tan∂, Loss modulus E", and Storage Modulus E' was investigated.

3.2.6 Swelling Test

Samples were prepared of 20mm diameter and 1mm thickness and placed in Eppendorf tubes which were filled with 1ml distilled water.

Equilibrium swelling weight was investigated after 24 hours by using sensitive weigh balance. Swelling Ratio was calculated by dividing wet weight of each with dry weight of each sample and then taken % value by multiplying with 100. 3 replicates were used for each concentration.

3.2.7 Biodegradability Test

For biodegradability test, Samples of PCL/TOPAS blends at concentration (10%, 20%, 30%, 50%, Pure TOPAS) was cut with the same dimensions as per used for swelling test. Samples were first placed in the Eppendorf tubes and dried them in freeze dryer.

Original weight of each sample was measured first. Then we add the solution of 1ml of 2.5 U/ml collagenase type II on every sample. Then we incubated these samples at $370^{o}C$ at the speed of 130rpm in a shaker and examined their degradation after different time periods (8, 24, 32, 40, 48). DPBS was used for the soaking of enzyme solution. Then we obtained the weight of dried sample after freeze dried them again. By dividing weight of dried samples after enzymatic degradation with original weight, remaining % mass was calculated. Number of replicates of each sample concentration was 4.

3.2.8 Anti-microbial activity

3.2.8.1 Anti-bacterial test

Anti-bacterial test for PCL/TOPAS films was investigated by using standard "AATCC 147(modified – antibacterial activity assessment of textile material: parallel streak method).

First prepared Muller Hinton ager media by dissolving the media in distilled water and then autoclaved at 120psi for 15 min. Then we poured ager into the plates and incubate them for overnight. After that, we Streaked the bacterial strains (Escherichia coli) and (Acinetobacter jhonsonii) on prepared muller Hinton ager plates with sterile cotton swab. Sample disks were placed with the help of sterile forceps on the surface of plates.

Anti-biotic disc (ciprofloxacin) was used as positive control and Pure TOPAS Disc used as negative control in anti-bacterial disc diffusion method.

Testing parameters for Antibacterial activity

- Agar plate test

- Size: 1 x 1 cm

- Incubation time: 24 hours

- Incubation temperature: $37^{o}C$

3.2.8.2 <u>Anti-fungal test</u>

Resistance of polymeric blend films against fungus was investigated by using standard **<u>ASTM G 21-96.</u>** First, we prepared PDA ager and then poured it on plates. Then two selected fungal strains which are (Tricoderma Harzarium and Aspergillus Niger) streaked on prepared ager with sterile cotton swab. Then discs of samples were placed on the plates with the help of forceps. Those were the most common strains present in atmosphere.

Testing parameters for Antifungal activity

- Agar plate test

- Size: 1 x 1 cm

- Incubation Duration: 15 days

- Incubation temperature: 27 $^{\circ}$C

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. X-Ray Diffraction (XRD)

Fig 4.1 shows wide angle X-ray diffraction traces for pure TOPAS, pure PCL and PCL/TOPAS blends with varying content of PCL. Pure TOPAS is amorphous polymer so it only shows wide hump in diffraction pattern.
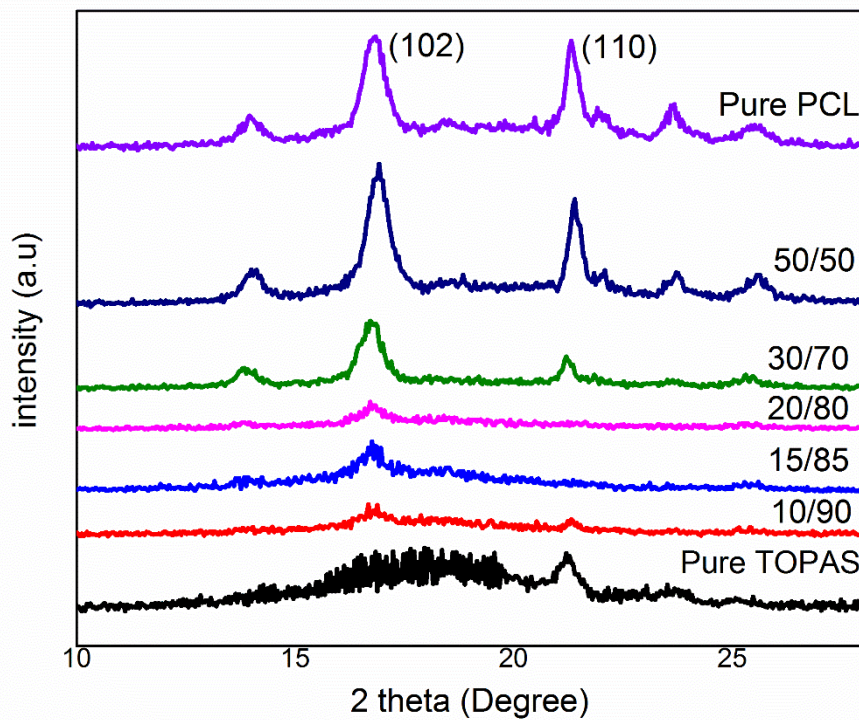

Figure 4.1 XRD spectrum of Pure TOPAS, Pure PCL and PCL/TOPAS Blends

A small peak was also observed at 22° indicate small localized ordering of chains in rigid structure of TOPAS.

Pure PCL is a semi crystalline polymer with two diffraction peaks around $2\Theta = 17.1°$ for (102) and $2\Theta = 21.3°$ at (110) [23]. Furthermore, peaks were sharp and distinct. With increasing

concentration of PCL in TOPAS up to 20%, Diffraction peaks were obtained with very low intensity indicating the less content of PCL.

Afterwards, with increasing content of PCL i.e. 30%, 50% indicates distinct sharp diffraction peaks like pure PCL. It can be concluded that gradually increase in semi-crystalline polymer content in blend material represents high crystallinity due to arrangement of chains.

4.2. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy; a powerful technique was used to identify any peak shifts in PCL/TOPAS blend. It detects the intermolecular interaction between two polymers gives evidence whether polymers are miscible or immiscible.

Figure 4.2 show the FTIR spectra of Pure TOPAS, Pure PCL and PCL/TOPAS blends in the wavelength ranges from 500-4000cm^{-1}.

Band occurring in the region of 1715-1725 cm^{-1} corresponds to the carbonyl group(C=O) of Pure PCL. The band occurring at 1240 cm^{-1} is assigned to asymmetric C-O-C stretching modes of crystalline state and the band appearing at 1158 cm^{-1} is attributed to C-O-C stretching band of components of amorphous part of PCL. Two peaks appeared at 2864-2940 cm^{-1} assigned to C-H stretching of Semi-crystalline PCL and a peak appeared at 1464 attributed to C-H bending of PCL.

A peak appeared at 1461 cm^{-1} indicates the C-H bending of TOPAS[24]. Two peaks at 2849 cm^{-1} and 2917 cm^{-1} indicate the C-H stretching of pure TOPAS. At 1639 cm^{-1} TOPAS show a characteristic peak corresponds to norbornene group in it. C-H group appears for both PCL and TOPAS. But carbonyl peak is corresponding to semi-crystalline PCL. TOPAS does not show carbonyl peak because of no (C=O) group. All blends of varying concentration of PCL in TOPAS show carbonyl peaks indicate the presence of both polymers in one matrix.

No prominent peak shifting was observed in PCL/TOPAS blend indicate no hydrogen bonding is occurring so we might say PCL/TOPAS blends are immiscible. Decreases in peak intensities of PCL/TOPAS blend as compared to Pure PCL indicate some weak interaction between two polymers. This might be the response of dipole interactions between carbonyl group of PCL and norbornene group of TOPAS.
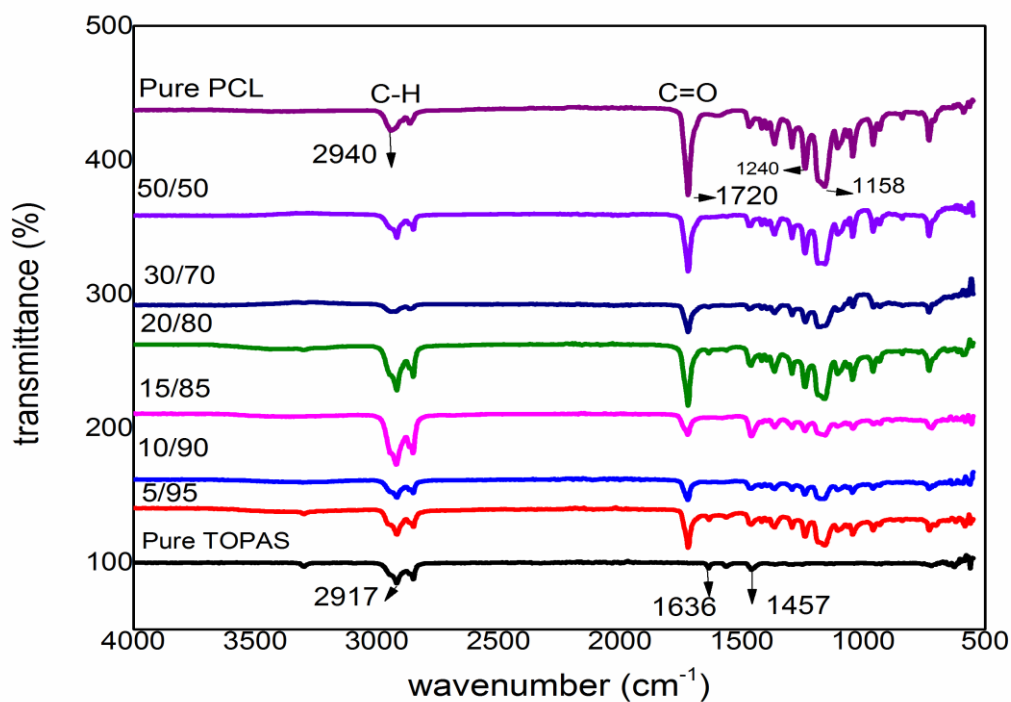
Figure 4.2. FTIR spectra of Pure TOPAS, Pure PCL and PCL/TOPAS blends.

4.3. Scanning Electron microscopy (SEM)

Figure 4.3 shows the SEM micrograph of fractured surface of Pure TOPAS (A) and 20%PCL/TOPAS blend. Pure TOPAS shows the plan morphology because of its amorphous nature. When we added PCL in TOPAS matrix, appears clearly as two phase morphology with the PCL particles coarsely dispersed in the continuous matrix of TOPAS. It shows interfacial boundaries very clear means the high interfacial tension might be attributed to weak adhesion at phase boundaries. This is demonstration of incompatibility of polymer components indicate immiscibility. All immiscible blends show this behavior[25].
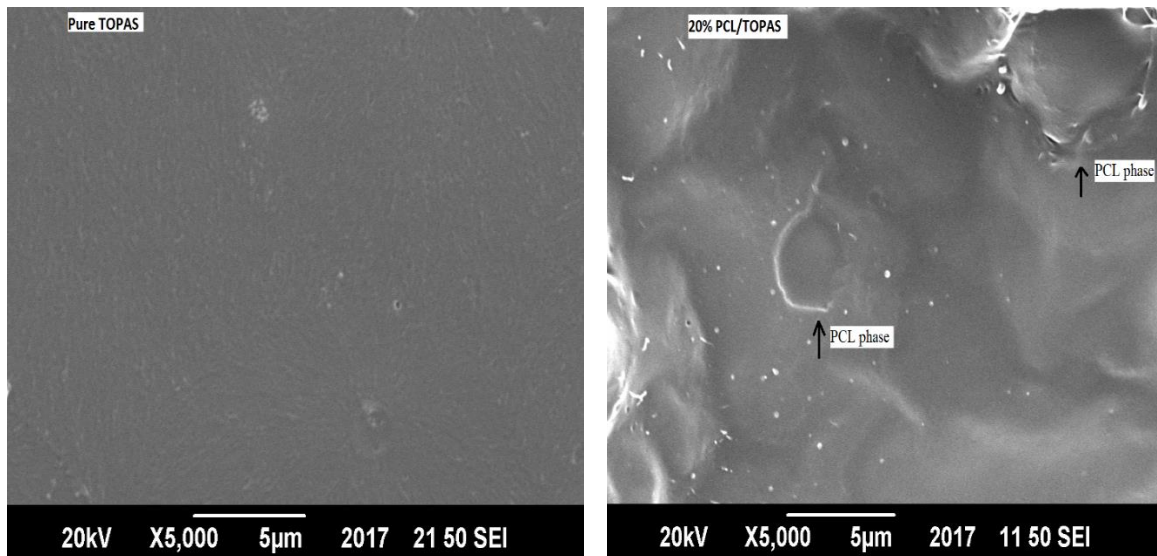
Figure 4.3 showes SEM micrographs of fractured surface of (A) PURE TOPAS (B)20%PCL/TOPAS

4.4 Differential Scanning Calorimetry (DSC)

Thermal history of the samples was determined by PerkinElmer DSC 6000. Figure 4.4 shows the DSC traces of Pure PCL, Pure TOPAS and its blends with cooling and followed heating scans. Obtained calorimetric values are mentioned in Table 6.

First heat thermo-grams were neglected to erase the thermal history. DSC traces of second heat are shown in figure 4.4 shows the endothermic peaks of Pure TOPAS, Pure PCL and different concentration of PCL/TOPAS blends respectively. Table 6 represents glass transition temperatures of pure TOPAS and pure PCL i.e. 30.1°C and -60°C respectively. Blends of PCL/TOPAS shows slight shift in Tg indicates that TOPAS matrix does not perceptibly influenced by the addition of PCL.
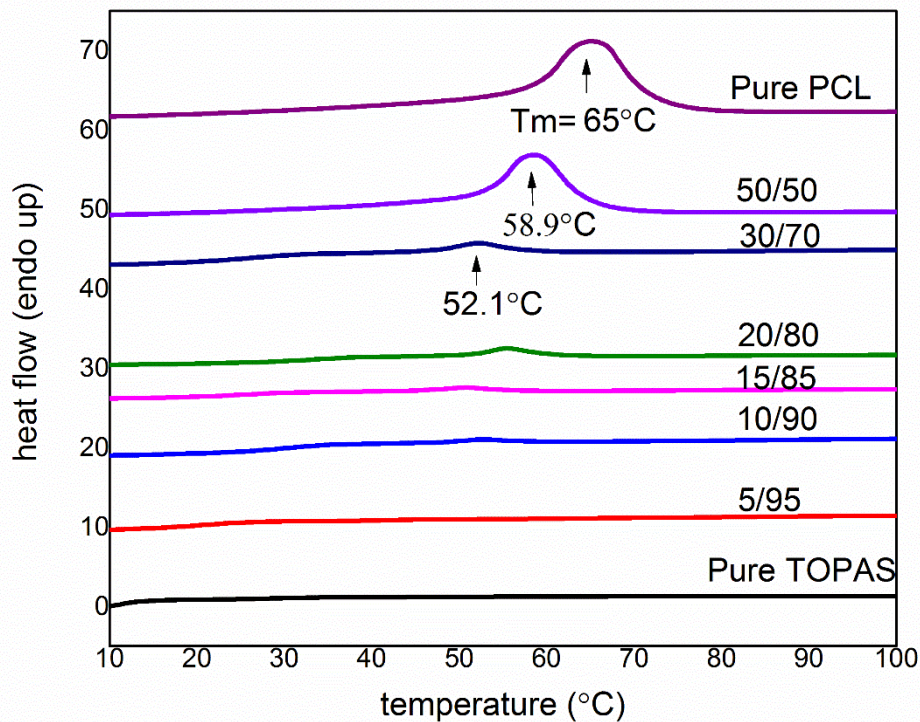
Figure 4.4 DSC Thermo-grams of Pure TOPAS, Pure PCL and its blends.

Poly ε-caprolactone (PCL) is semi-crystalline aliphatic polyester showed prominent melting and crystallization peaks at 60.8 °C and 24.1 °C in figure 4.4 and figure 4.5. Neat TOPAS is an amorphous polymer did not show melting and crystallization temperatures. Melting temperature slightly decrease with increasing fraction of TOPAS in the matrix as it is shown by Figure 4.4 and listed in the Table 6.

Decrease in crystallization temperature with decreasing content of PCL in TOPAS matrix was observed shown in Figure 4. Crystallization temperature of 50/50 blend of PCL/TOPAS blend in the cooling scan is higher to some extent than pure PCL may show a little nucleating effect of TOPAS similar with the previous work observed for PP/COC blends[17].
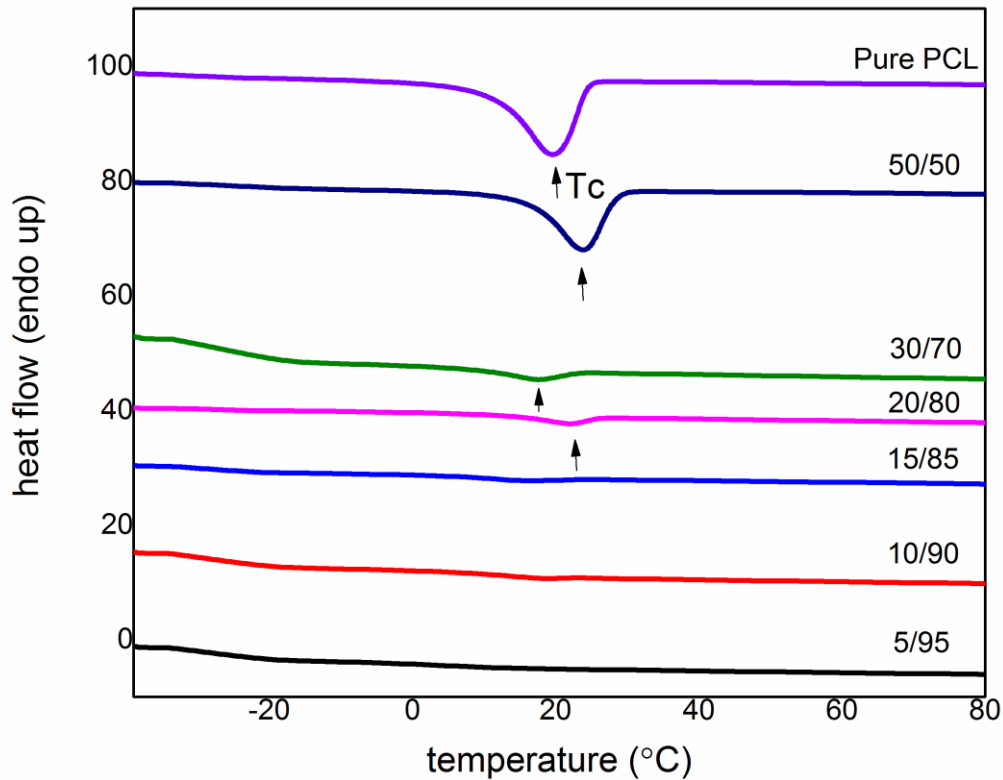
Figure 4.5 DSC Exotherms of Pure TOPAS, Pure PCL and its blends

The continuous decrease in crystallization temperature, crystallinity figure 4.5 and melting temperature for 30/50, 20/80, 15/85, with increasing TOPAS concentration indicate the dominating amorphous component of TOPAS inhibits the structural organization of minority PCL component.

In fastidious, the changing morphology of PCL in TOPAS matrix is obviously by an enlargement in peak of crystallization and decrease in crystallization temperature Tc.

Moreover, a shoulder at 24.07°C confirms the existence of fractioned crystallization figure 4.5. This phenomena also observed recently in heterogeneous blends such as poly styrene, polypropylene or COC, where minority component present a delayed crystallization at larger under cooling due to decrease in particle size[13].

% crystallinity of PCL/TOPAS blends was observed by formula mentioned below:

$$\chi_{DSC} = \frac{\Delta H_m}{\Delta H_m^o} \times 100$$

Figure 4.6 in showed % crystallinity graph Vs concentrations of PCL in PCL/TOPAS blends. It revealed that percent crystallinity is increased by increasing content of PCL but less than pure PCL because pure PCL have favorable environment to crystalline.
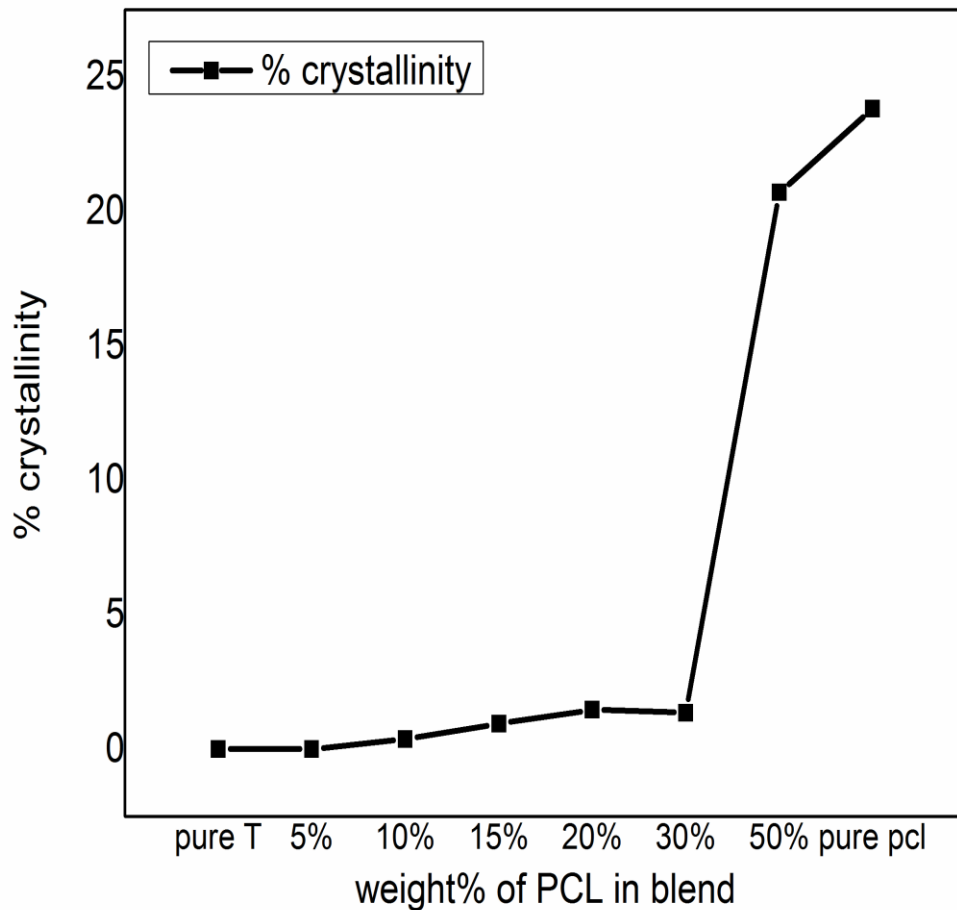

Figure 4.6 %crystallinity of PCL/TOPAS blends at various concentrations

But in PCL/TOPAS blends, PCL crystallization must have influenced by the amorphous TOPAS matrix that could hinder its crystallization and resulting coarsening of crystals. That might be the reason of less crystallinity in PCL/TOPAS blends as compared to pure PCL.

Table 6: Shows enthalpy ΔHm (J/g), melting temperature Tm ºC and crystallization temperature Tc (ºC) of PCL/TOPAS blend.

Sample Concentrations	ΔHm (J/g)	Tm ºC	Tc (ºC)
Pure TOPAS	-	-	-
5%	-	-	-
10%	0.5040	52.601202	-
15%	1.2892	50.83376	-
20%	1.9950	55.51111	21.83739
30%	1.8428	52.36512	17.49398
50%	28.1760	58.55725	20.03044
Pure PCL	32.389	60.83964	24.07842

4.5 Dynamic Mechanical and Thermal analysis (DMTA)

DMTA studies tell about visco-elastic behavior of the materials. Sample was exposed to the stress, temperature, frequency. For known stress, sample will deform a certain amount. Moreover, it also gives an idea about storage Modulus and damping behavior $\tan delta$. DMTA results give us idea about blend behavior and phase morphology. Storage modulus shows the change in stiffness of material. Effect of temperature on different PCL/TOPAS blend concentrations at frequency of 1Hz is shown in Figure 4.7.

At start, Pure TOPAS shows the storage modulus at 2.37 GPa. In case of semi-crystalline nature of Pure PCL, its regular chain remains intact with each other till it reaches to melting temperature. Only amorphous part will undergo segmental motion. But when we added PCL into the TOPAS matrix of about 10% PCL, observed high storage modulus i.e. 3.9Gpa that

might be due to interaction of semi-crystalline material that hinder the segmental motion of TOPAS and that makes it more stiff [26]. We can say, by adding PCL in TOPAS matrix, PCL acts as stress concentration sites at low temperatures expected to absorb more energy than pure TOPAS. Load is transferring from one phase to another because of micro-phase separation present between polymer blend. At higher concentrations of PCL i.e. above 20%, load is not transferring from one phase to another. This could be due to the presence of macro phase separation having no damping behavior.
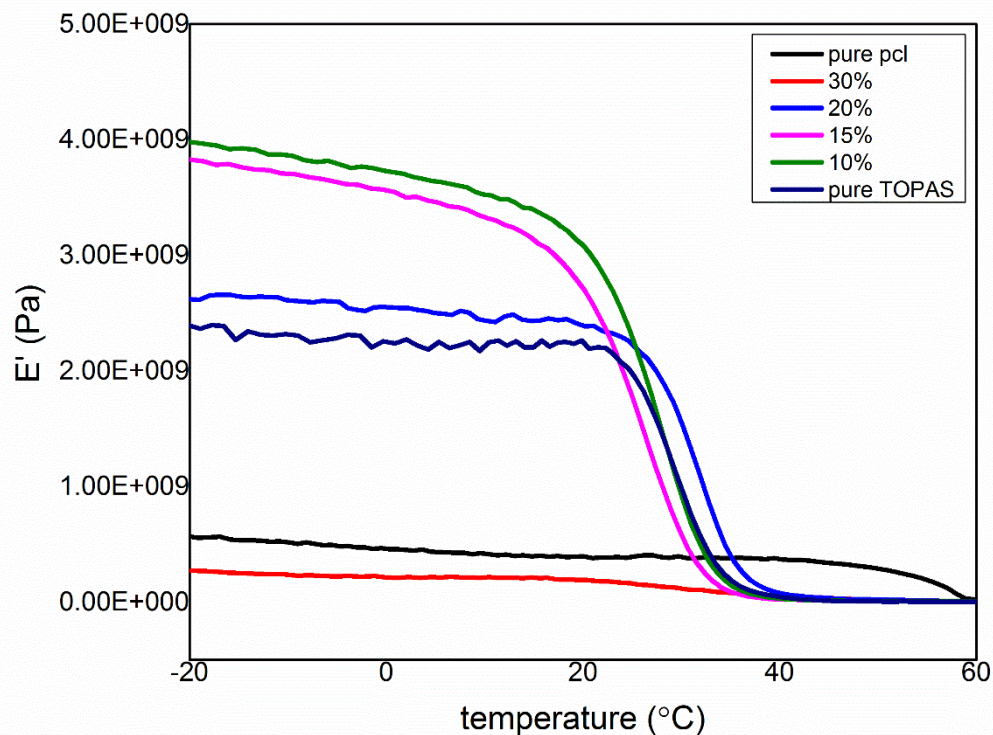

Figure 4.7 DMTA graph of storage modulus Vs temperature of Pure TOPAS and PCL/TOPAS blends.

Figure 4.8 also giving evidence of increased storage modulus at 10% and 20% PCL content and high stiffness.
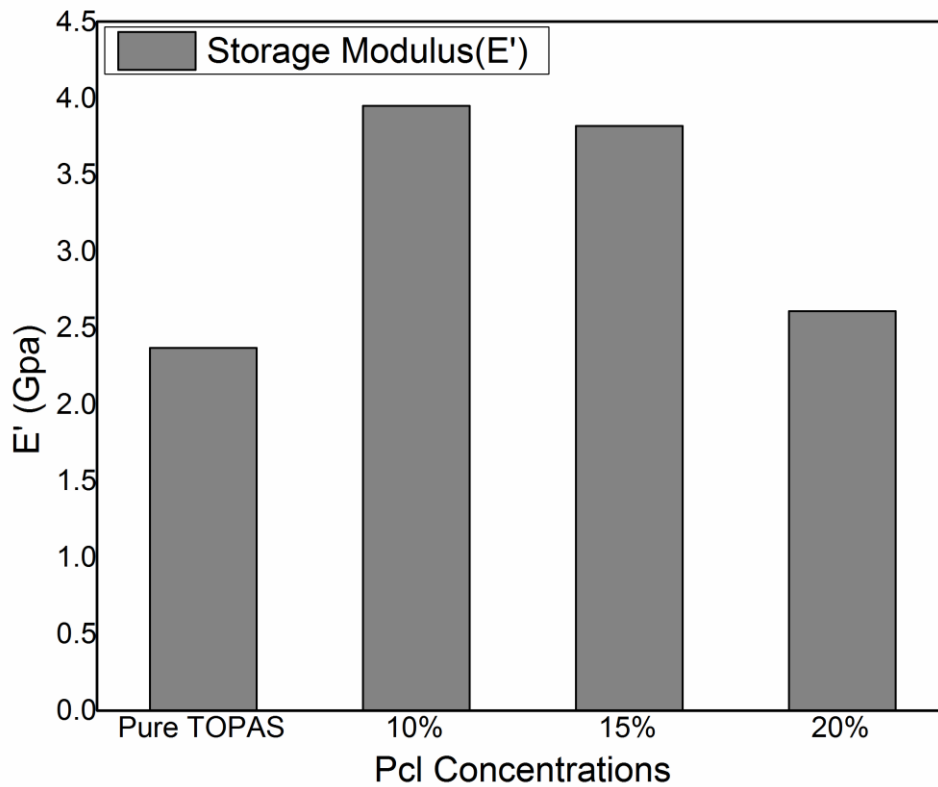
Figure 4.8 shows Modulus Vs Concentration graph of PCL/TOPAS blends.

Figure 4.9 shows the tan delta behavior of Pure TOPAS and PCL/TOPAS blend. As we know tan delta values indicate the viscous behavior of polymers.it tells about how much energy is needed to activate the sample. In PCL/TOPAS blends, high intensity and width was appeared in 10 % and 20% blend is indication of high chain mobility and low interaction between two polymers. It also show lo glass transition temperature Tg at these concentrations. Width and intensity of tan delta curves appeared to be decreasing with increasing concentrations of PCL upto 20%, indicate reduction in chain segmental mobility and show high Tg i.e. 38°C as compared to pure TOPAS i.e. 36°C.

Above 20%, peak diminished indicate macro phase separation with no molecular interaction.
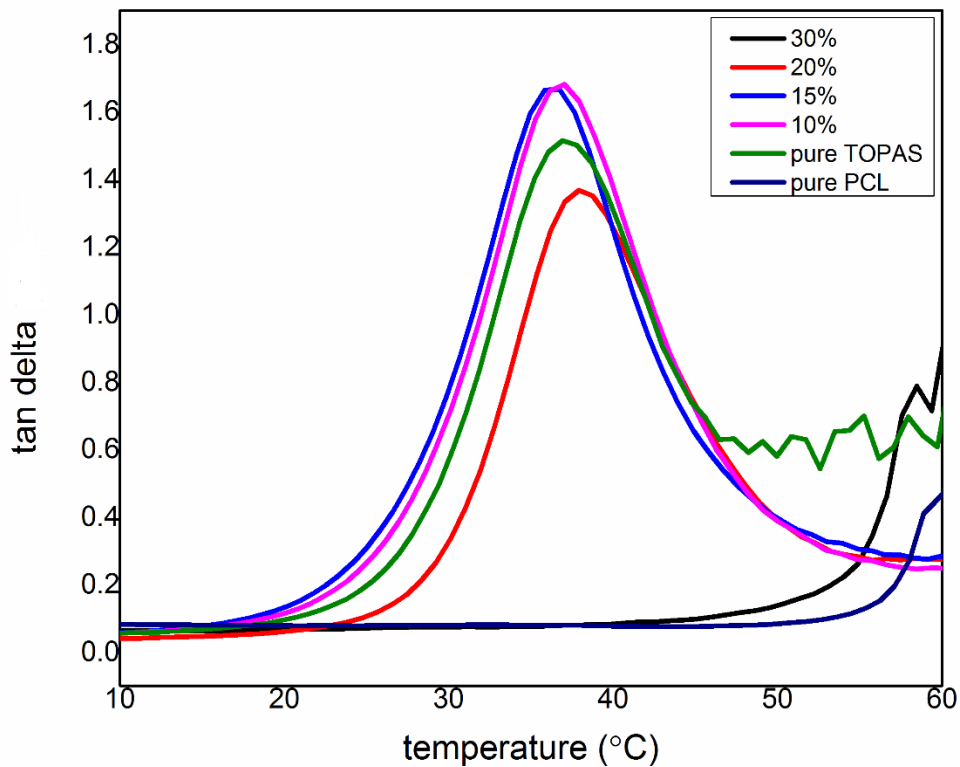
Figure 4.9 DMTA tan delta graph Vs temperature of Pure TOPAS and PCL/TOPAS blends.

Figure 4.10 shows glass transition Vs temperature graph. Glass transition temperature is not much influenced at low concentration of PCL. Little decrease in glass transition in 10% and 15% is because of less amount of semi-crystalline material in TOPAS matrix. Transition will start at low temperatures 33.2°C as most of the part in matrix is amorphous and show rigid behavior.

With increasing amount of PCL, segmental motion is restricted by crystalline portion results in transition observed at high temperature 38°C in 20% blend. We can say material is more elastic as compared to 10% and 15 % PCL/TOPAS blend.
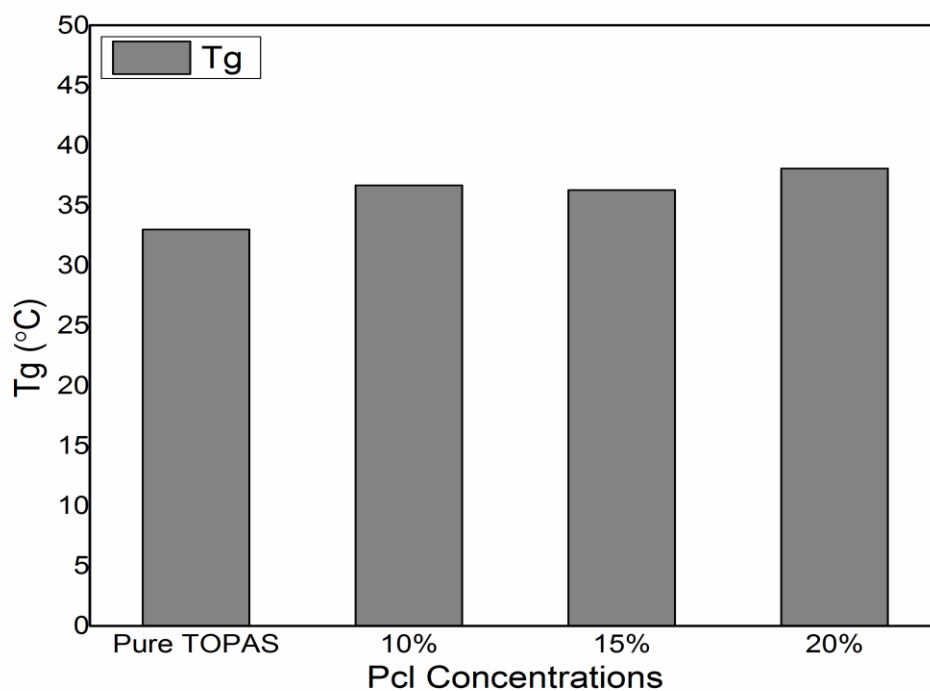
Figure 4.10 show Tg Vs Concentration graph of Pure TOPAS and PCL/TOPAS blends.

4.6 Degradability Test

Figure 4.11 shows the degradation characteristic of Pure TOPAS and its blends with PCL at various concentrations. Degradation behavior tells about the rate of disappearing of blend film under enzymatic activity. Degradation behavior was determined using collagenase which is a natural enzyme which degrades both polymer and collagen.

Pure TOPAS and PCL/TOPAS blend show approximately same degradation behavior with respect to time. Pure and all blends show slight degradation at exposure of 8h. Whereas, after 28 hours 65% mass of the samples was still intact.

Figure 4.11 shows enzymatic degradation behavior of pure TOPAS and PCL/TOPAS blends.

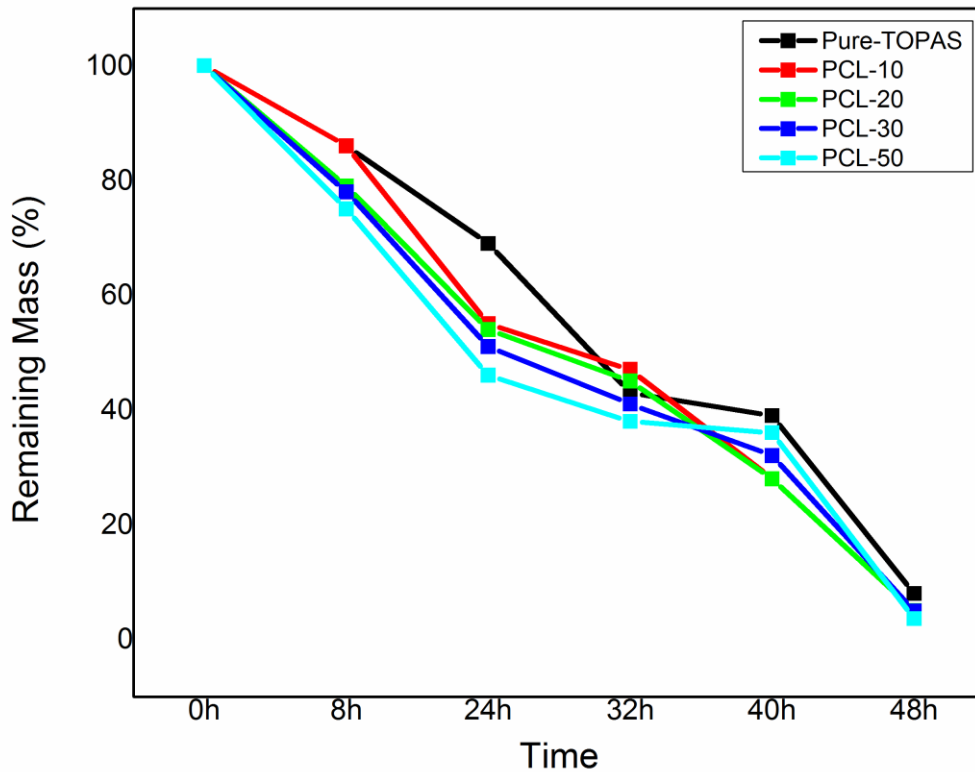All samples included Pure TOPAS and PCL/TOPAS blends were fully degrade by exposure of 48 hours. Without changing degradation behavior of TOPAS and PCL/TOPAS blends, Material become more stiff and strong. Because of this additional property we can use it in tissue engineering applications as an implant[24].

4.7 Swelling Test

Figure 4.12 shows the swelling behavior in distilled water of Pure TOPAS and PCL/TOPAS blends of various concentrations. Swelling behavior of a material is important and reveals the solute diffusion, surface and mechanical properties. Swelling ratio was low in 10%, 20%, and 30% blend as compared to pure TOPAS.

Pure TOPAS show high swelling rates because of its amorphous nature containing large spaces in their randomly oriented chains which can contain water molecule. Significant decrease in

swelling rates in 10% and 20% could be due to alignment of TOPAS chains with incorporation of PCL decrease the spaces between amorphous chains.
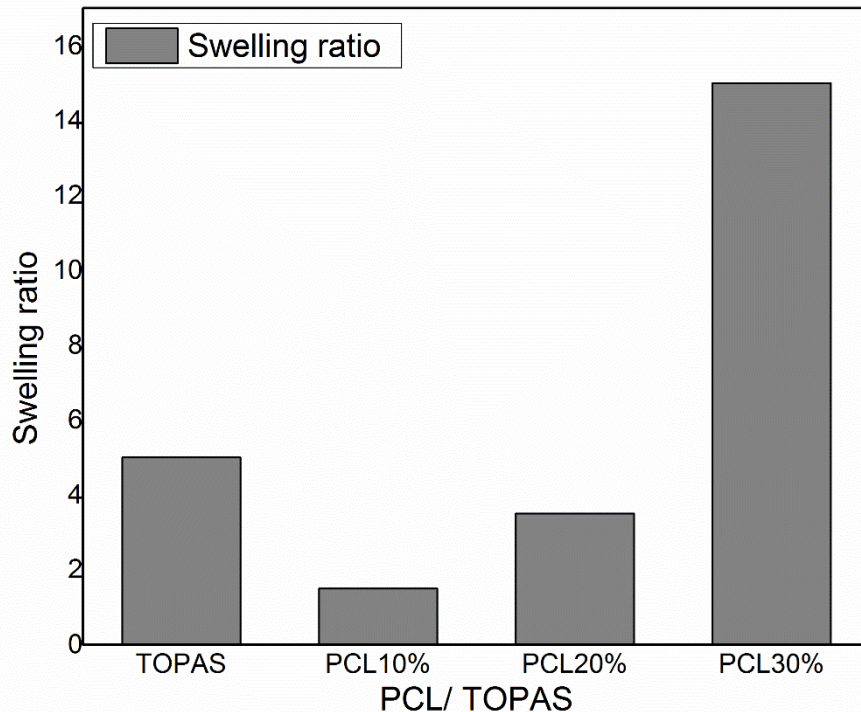

Figure 4.12 indicates the swelling ratios of Pure TOPAS and PCL/TOPAS blends

Diffusion of distilled water must follow the long-aligned path of chains is the reason of reduced swelling. We can also relate it with DMA modulus result with high modulus at 10% blend show improved mechanical properties as discussed earlier.

4.8 Anti-microbial test

Anti-bacterial and anti-microbial test was studied in which total 4 strains were used.

- ➢ (Acinetobacter jhonsonii, Escherichia coli) strains were used for anti-bacterial activity.
- ➢ (Tricoderma harzariumand, Aspergillus Niger) strains were used for anti-fungal activity.

4.8.1 Anti-bacterial test

All concentrations of PCL/TOPAS blends and Pure TOPAS showed resistance against two bacterial strains which are mentioned below in Table 7. Anti-biotic "Ciprofloxacin" has been used as positive and Pure TOPAS film used as negative control.

Table 7. Bacterial strains used in anti-bacterial activity

Bacterial strains	nomenclature	Specie	Results
E. coli	Escherichia coli	Gram + ive	Resistance
A. jhonsonii	Acinetobacter jhonsonii	Gram – ive	Resistance

Figure 4.13 showed no growth of bacteria belong to E. Coli specie. No growth was observed around and beneath the positive control. Disks of PCL/TOPAS blends also showed resistance against E. coli strain as it is shown in the figure 4.13. Although there is no inhibition zone appeared around the blend disc because of non-leaching nature but we experienced no bacterial growth on the surface and beneath the blend disk.

We might say our blend show contact inhibition and can called bacterio-static because bacterio-static films does not kill the microorganisms but only stop its growth on the film. Trend was the same for the other bacterial specie (A. jhonsonii).
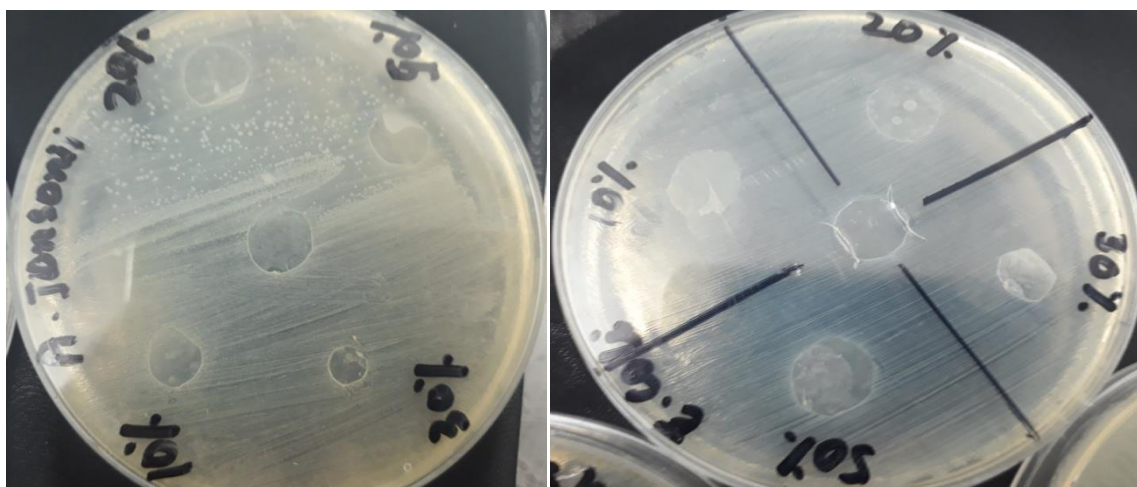

Figure 4.13 showed anti-bacterial activity with (A) A. jhonsonii (B) Escherichia coli

4.7.2 Anti-Fungal test

Table 8 mentioned the fungal species used in anti-fungal test and the results. Pure TOPAS was used as negative control. All blend films showed resistance against all used strains. Results were observed on 5th, 10th, 15th day of incubation.

Table 8.Fungal strains used in anti-fungal activity

S. No.	strains	Specie name	Results
1.	F1	Tricoderma harzarium	Resistance
2.	F4	Aspergillus Niger	Resistance

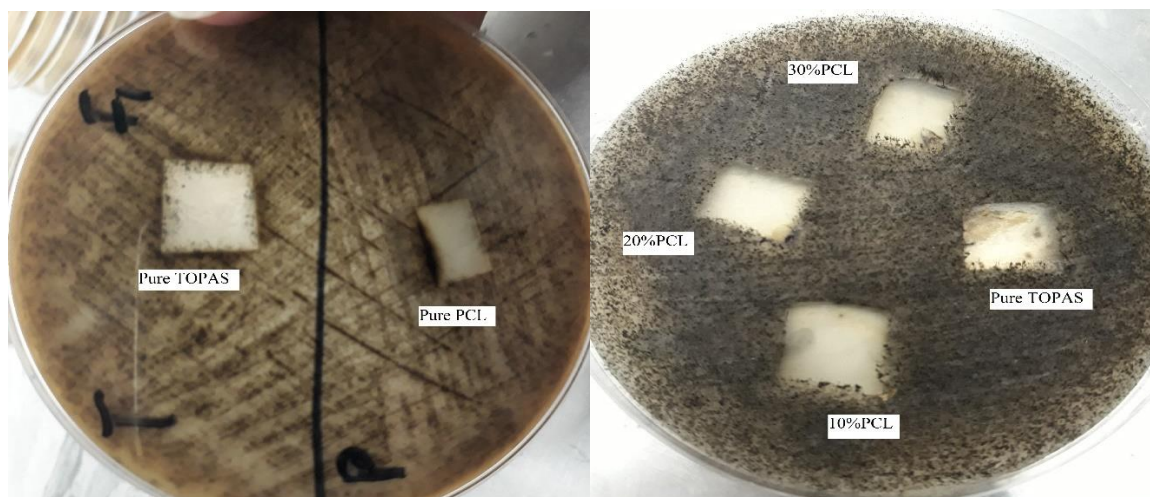**Figure 4.14 Anti-fungal activity of Pure TOPAS and blend films against Tricoderma harzarium strain.**

Pure TOPAS does show some fungal growth on the surface of the film but when we added PCL into the TOPAS matrix, no fungal growth was observed on and under the surface of the blend films as it is shown in figure 4.14 and 4.15.
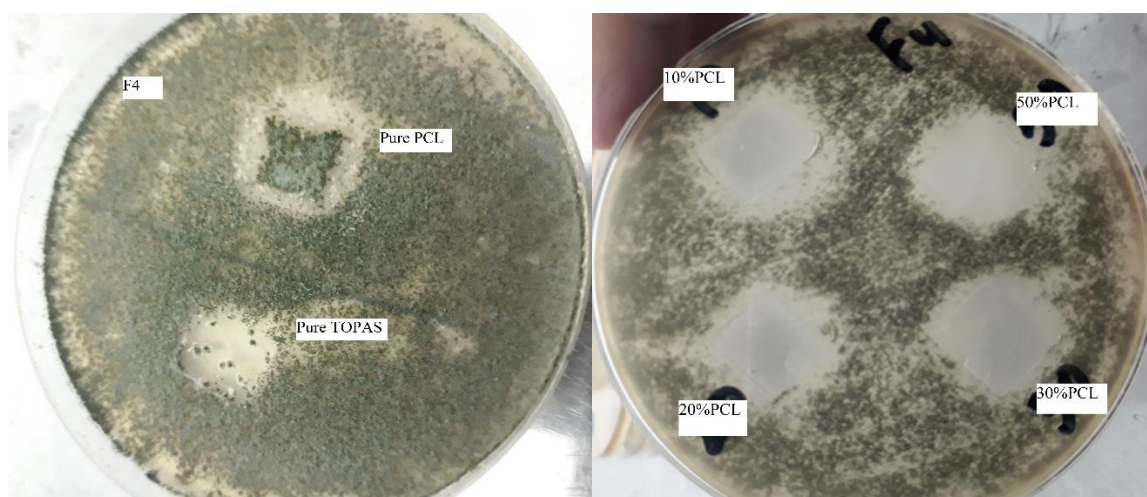
Figure 4.15 Anti-fungal activity of Pure TOPAS and blend films against Aspergillus Niger strain.

Blend films showed anti-bacterial resistance in disc-diffusion method because of non-leaching nature of films. But in anti-fungal test, fungal needs light, CO_2 and moisture to grow. No material came out from the film to facilitate the fungus growth that could be the reason for the blend films to show anti-fungal resistance. Below mentioned figure 4.16 show the mechanism behind the contact inhibition.

Figure 4.16 Mechanism behind contact inhibition

Conclusions

A Novel PCL/TOPAS blend is prepared by varying concentrations of PCL from 5 to 50 wt.% for packaging applications. PCL was blended in TOPAS by solution casting method. SEM indicates the phase segregation among two polymers at higher concentrations of PCL. It clearly shows two phase morphology with the PCL particles coarsely dispersed in the continuous matrix of TOPAS. High interfacial tension was observed results in immiscibility of blends.
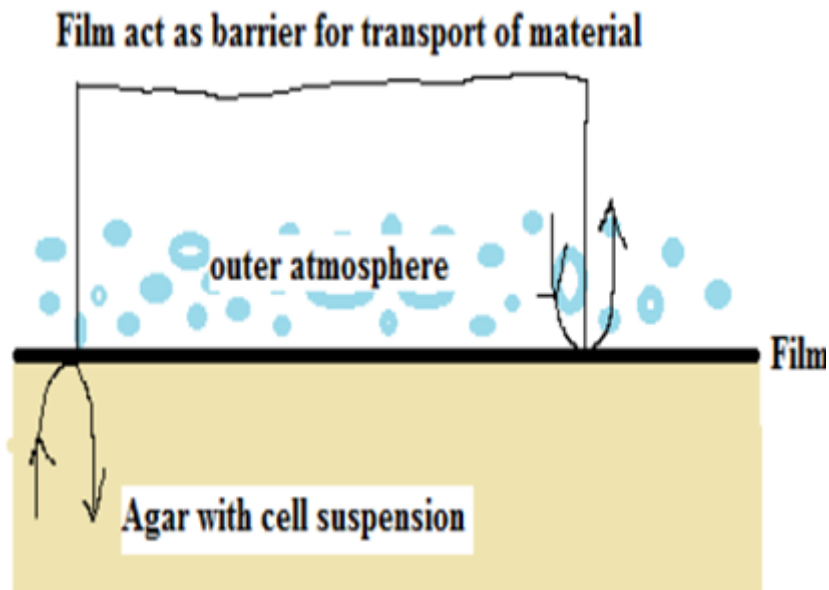
FTIR analysis proves this phase separation as no hydrogen bonding is present in the blends show immiscibility between PCL and TOPAS.

Overall melting, Crystallization temperature and % crystallinity was reduced as compared to Pure PCL indicates the dominating amorphous component of TOPAS inhibits the structural organization of minority PCL component.

% crystallinity of blend is significantly increased from 5% PCL to 50% PCL in TOPAS matrix indicate the presence of crystalline part in amorphous matrix and this phenomenon was also revealed in XRD analysis.

Overall storage modulus was enhanced in 10% and 15% of PCL/TOPAS blends indicate stiffness of the material but it decreased by further addition of PCL due to phase segregation. Slight decrease in Tg ^{o}C was observed in 10 and 15 wt.% PCL from tan∂ values because of small size of chains that show early glass transitions. But with 20% PCL, glass transition temperature was increased by 2°C might be due to long chains of PCL incorporated in TOPAS matrix.

Swelling test also confirmed that 10% and 15% PCL/TOPAS blend with high Storage modulus show stiff behavior as they showed less swelling ratios.

Degradation Test of PCL/TOPAS blend show approximately same behavior as compared to pure TOPAS concluded that degradation rates were remain unaffected by loadings of PCL in TOPAS blends.

Anti-bacterial resistance was studied by using ASTM-G21. Blend of PCL and TOPAS showed resistance against all bacterial and fungal strains used in this study.

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