Study the effect of solvent and nanoclay on poly (styrene-*b*-isoprene-*b*-styrene) (SIS)/ poly (styrene-*co*-methylmethacrylare) (PSMMA) polymer blends

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بسم الله الرحمن الرحيم

They said: 'Holy art Thou! No knowledge have we except what Thou hast taught us; surely, Thou art the All-Knowing, the Wise.

(Al-Quran 2-32)

Dedicated to

My beautiful land Pakistan, beloved grandparents, parents, siblings, my uncles, my aunts, teachers and friends

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CHAPTER 1 INTRODUCTION

Abbreviations and Symbols

µm	micrometer
0D	Zero-imension
1D	One-dimension
2D	Two-dimension
3D	Three-dimension
ABS	Acrylonitrile butadiene styrene
AFM	Atomic force microscopy
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
CB	Carbon black
CCVD	Combustion chemical vapor deposition
$CHCl_3$	Chloroform
CNTs	Carbon nanotubes
CTAB	Cetyltrimethylammonium bromide
DMDO-Hect	Dimethyldioctadecylammonium-hectorite
ENR	Epoxidised Natural Rubber
EPDM	Ethylene Propylene Diene Monomers
FTIR	Fourier-transform infrared spectroscopy
HDPE	High-density polyethylene
HIPS	High Impact Polystyrene
IPN	Interpenetrating polymer network
Kao-DMSO	Kaolinite clay exfoliated by dimethyl sulfoxide
LCP	Liquid-crystal polymers
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MA	Maleic anhydride

MMT clay	Montmorillonite clay
MPa	Mega Pascals
nm	nanometer
NMs	Nano-materials
NR	Natural Rubber
PA	Polyamide
PA6	Nylon 6
PA66	Polyamide 66 or Nylon-6,6
PC	Polycarbonates
PCL	Polycaprolactone
PE	Polyethylene
PEDOT	Poly (3,4-ethylene dioxythiophene)
PEEK	Polyether ether ketone
PE-g-MA	Poly (ethylene-g-maleic anhydride)
PEI	Polyethylenimine
PHE	Plate Heat Exchange
PMF	Poly (melamine-co-formaldehyde)
PMMA	Poly (methyl methacrylate)
POE-g-MA	Poly(ethylene-octene elastomer-g- maleic anhydride)
POM	Polyoxymethylene
PP	Polypropylene
PP-g-MA	Poly (propylene-g-maleic anhydride
PPO	Poly (phenylene oxide)
PPS	Polyphenylene sulfide
PS	Polystyrene
PSA	Pressure-sensitive adhesive
PSF	Polysulfones
PSMMA (PS-co-PMMA)	Poly (styrene-co-methylmethacrylate)
PSSA	Poly (styrene sulfonic acid)

PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
SAXS	Small-angle X-ray scattering
SBR	Styrene-butadiene rubber
SEBS	Styrene Ethylene Butylene Styrene
SEM	Scanning electron microscopy
SIS (PS-b-PI-PS)	Poly (styrene-b-isoprene-b-styrene)
Td	Final decomposition temperature
TEM	Transmission electron microscopy
Tg	Glass transition temperature
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
Tm	Melting temperature
TPU	Thermoplastic polyurethane
Ts	Starting degradation temperature
TVPs	Thermoviscosifying polymers
WAXS	Wide-angle X-ray scattering
Wt.	Weight
XRD	X-ray diffraction

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AMNA AKRAM

Abstract

In this study various blends of Poly (styrene-*b*-isoprene-*b*-styrene) (SIS) and Poly (styrene-*co*-methylmethacrylate) (PSMMA) copolymers along with nanoclay composites, have been first time synthesized, characterized and studied for their improved properties. The SIS copolymer is a glassy-rubbery-glassy copolymer while PSMMA is a glassy-glassy copolymer. The SIS is very elastic and bearing less stress while PSMMA bears stress but not elastic as compared to SIS. The resultant blends of SIS/PSMMA increased the bearing stress capacity of SIS by reducing the elasticity. The Kao-DMSO clay was incorporated (as nanofiller) within SIS/PSMMA blend to form the nanoclay composites. Among various prepared blends, 20/80% SIS/SMMA blend ratio had exhibited maximum stress bearing property therefore was further employed to form the nanocomposites. The FTIR confirmed the successful formation of physical blends of these two copolymers and nanocomposites. Stress-strain curves of the blends and nanocomposites have been determined by mechanical testing. Glass transition temperatures were measured by DSC thermal analysis while thermal decomposition temperatures of blends and nanocomposites were investigated by TGA. The nanoclay composites (1,3,5 % nanoclay) were prepared in different solvents like THF and $CHCl_3$ to study the effect of solvent on nanoclay composites w. These as-prepared copolymer blends-nanoclay composites have been subjected to measurement of same properties by similar techniques as been previously evaluated for pure blends. The blends have shown better properties than an individual components of the system while nanocomposites have exhibited further improved properties than blends. The SEM analysis was also carried out for the morphological studies which have corroborated that nanoclay fillers have reduced the phase separation of SIS/SMMA blends that results in improved properties.

CHAPTER 1

INTRODUCTION

1.1Polymer

The word polymer is a combination of two Greek words; poly (many) and mers (many).[1] The polymer is formed by the repetition of simple and smaller molecule units, monomer, via covalent bonding i.e., the monomer vinyl chloride CH_2=CHCl is the repeat unit (monomer) of the poly (vinyl chloride). This repetition can either be linear for the formation of chain or branched or interlinked for the formation of three-dimensional network.[2]

The numbers of repeating units/monomers in the chains are responsible for the length of the polymer chain that is known as the degree of polymerization (DP) and the product of repeat unit and DP is, in fact, the weight of the polymer.

$$\text{Weight of polymer} = \text{monomer (repeat unit)} \times \text{DP}$$

Properties of polymers are mainly affected by molecular mass and it states to the average molecular mass of the component molecules in the chain and the mass of the polymer varies from 10,000 to many millions.[3]

Polymers are classified as natural polymers (biological polymers) and synthetic polymers (nonbiological polymers).

In nature polymers are present in the form of protein, cellulose, silk, rubber, wool, skin etc. known as biological polymers and life depends on it.[4]

Synthetic polymers are prepared in industry i.e., polystyrene, polyethylene, nylon, plastics, fibers, and elastomers. Natural rubber Hevea has synthetic name polyisoprene.

Polymers, due to their high molecular weight, are important in existing technology. Polymers, in the beginning, were neglected but after 1930's polymer science started to emerge and wrapped the half of industry and also got the attention of the scientist.[5]

Today these substances are actually essential for humans i.e., for clothing, shelter, transportation, communication as well as for the eases of modem living.

As natural polymers along with the synthetic polymers were unable to fulfill all the needs of increasing population of mankind so to compete with this and meet the needs different kind of monomer units joined together in the same polymeric chain and formed the copolymer.

After 1970's it was hard to form new monomers to be polymerized to form a polymer of required properties. So this trouble was overcome by the formation of polymeric alloys, composites and blends of desired properties.[6] Polymer blends have many advantages due to its commercializing properties and low cost.

1.2 Classification of Polymeric Materials

Polymeric materials can be divided into different categories as follows:

1.2.1 On the basis of processing

i) Thermoplastics

Polymers then can be softened by heating and processed for desired properties are known as thermoplastics. By applying the heat and pressure, the thermoplastics can be reproduced and refabricated. The important example of the thermoplastics is polystyrene (PS). Other examples are polyolefins, polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC).

ii) Thermosetting

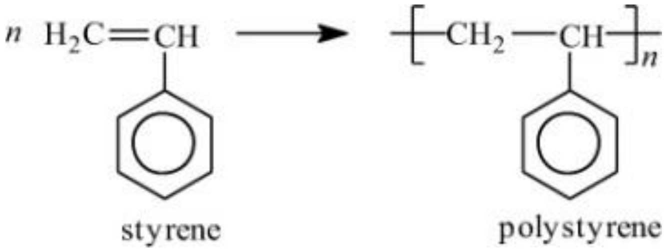
Polymers that resist solvent attacks, creep and heat-softening are thermosets. They cannot be treated thermally. They show resistance due to the presence of covalent bond. The bond forms during the fabrication either by thermal or chemical treatment.

So, they are feasible for coatings, composites and adhesives. The unsaturated polyesters, epoxy, phenol-formaldehyde resin are the major examples of the thermosets.

1.2.2 On the basis of synthesis

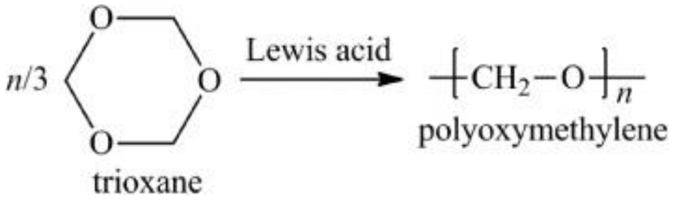
i) Addition polymers

The sequential addition of the monomers to ethylene double bond gives the addition polymers. Polystyrene formed by the addition of styrene monomer.



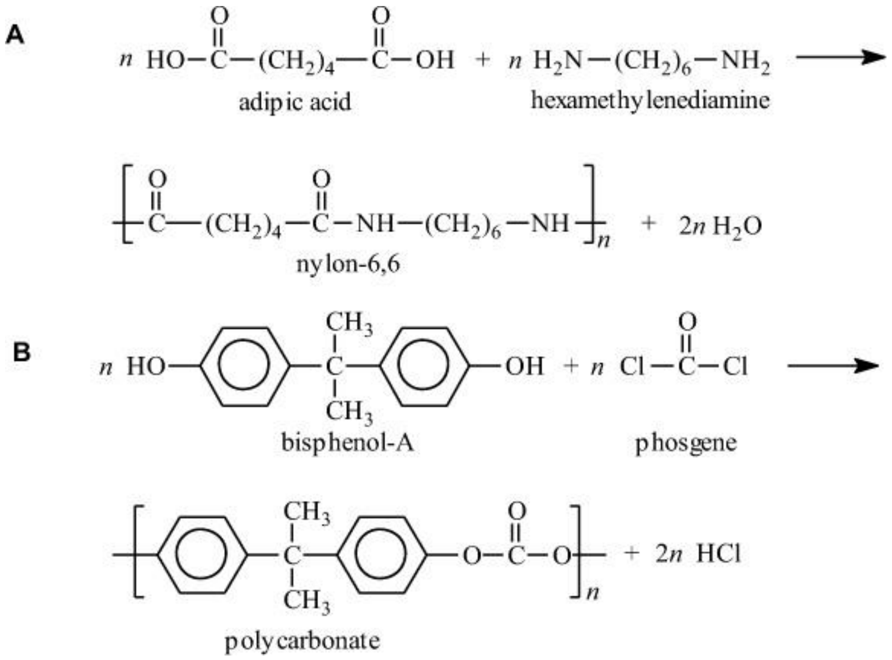
Other examples of addition polymers are poly (methyl methacrylate) (PMMA), poly (vinyl alcohol) (PVA), poly (acrylonitrile) (PAN), poly (vinyl chloride) (PVC).

Not only the addition to ethylene double bond gives addition polymers but also the ring opening polymerization of cyclic monomers give addition polymers. The example of ring-opening polymerrization is trioxane that gives polyoxymethylene (polyacetal).



ii) Condensation polymers

These are formed by the random reaction of two molecules followed by the elimination of small molecules i.e., water, salt or gas. The participating molecules of the reaction can be monomers, oligomers or high molecular weight intermediate each with corresponding functional groups; hydroxyl or carboxyl functional groups. Nylon 6, 6 (A) is a condensation polymer obtained by the condensation of adipic acid and hexamethylene diamine and liberation of two water molecules for each repeating unit. The other condensation polymer is polycarbonate (B) obtained by condensation of bisphenol-A and phosgene and two molecules of HCl are liberated.



1.2.3 On the basis of functional groups in the main chain

i) Homo-chain polymers

Homo-chain polymers are those polymers having the carbon atoms in the backbone chain of the polymer. On the basis of the single, double or triple bond, the homo chain polymers can be classified as:

Polyakylene: single bond along the backbone chain of carbon polymer. The examples are polyolefins [polyethylene (PE), polypropylene (PP)] addition type polystyrene (PS) and polyvinyl chloride (PVC).

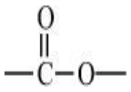
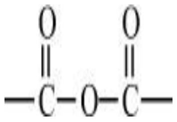
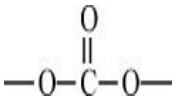
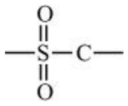
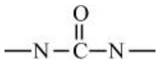
Polyalkenylene: carbon chain polymer having the double bond in the backbone of the chain. The diene elastomer is the example of polyalkenylene. Other examples are polyisoprene (PI), polybutadiene (PB) and polyacetylene that is a conductive polymer.

Polualkynylene: having the triple bond in the backbone carbon chain of the polymer.

ii) Hetero-chain polymers

In hetero-chain polymers, the backbone of the polymer chain contains more than one type of atoms. They are categorized on basis of the chemical groups and types of atoms present in the backbone chain.[2]

Table1: List of functional groups in hetero-chain polymers

Carbon-Oxygen Polymers	
• Polyethers	$-C-O-$
• Polyesters of carboxylic acids	 $-\overset{O}{\overset{\Vert}{C}}-O-$
• Polyanhydrides of carboxylic acids	 $-\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}-$
• Polycarbonates	 $-O-\overset{O}{\overset{\Vert}{C}}-O-$
Carbon-Sulfur Polymers	
• Polythioethers	$-S-C-$
• Polysulfones	 $-\underset{O}{\underset{\Vert}{\overset{O}{\overset{\Vert}{S}}}}-C-$
Carbon-Nitrogen Polymers	
• Polyamines	$-C-N-$
• Polyamides	 $-\overset{O}{\overset{\Vert}{C}}-N-$
• Polyureas	 $-N-\overset{O}{\overset{\Vert}{C}}-N-$

1.2.4 On the basis of tacticity

i) Isotactic-polymers

The properties of the polymers can be influenced by the spatial arrangement of the substituent group. If the substituent groups (R) are on the same side of the plane (formed by the long chain in backbone) then it is known as isotactic polymers. R may be methyl group in PP, a phenyl ring in PS or a chlorine atom in PVC. Commercial PP is an isotactic polymer.

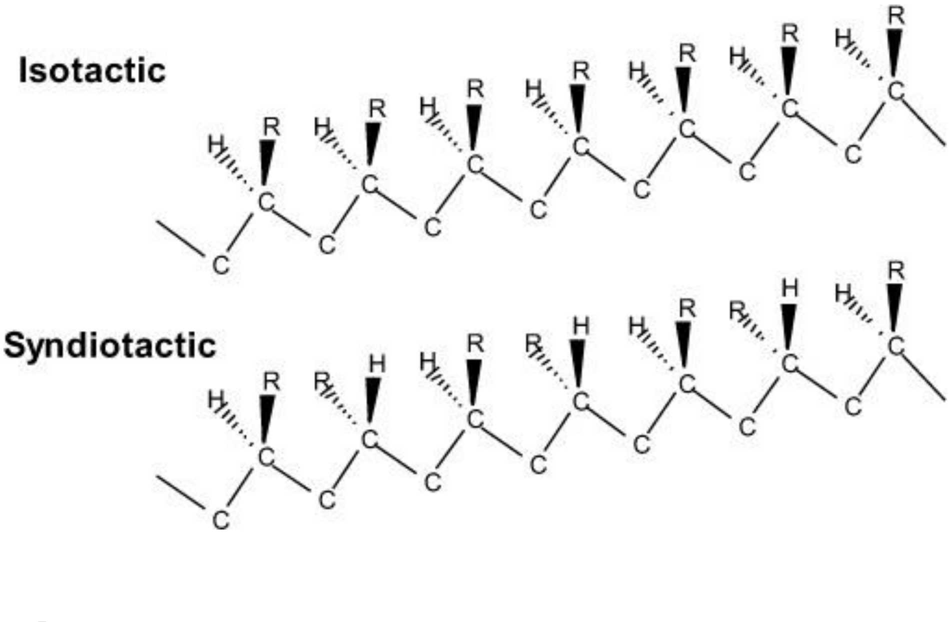
ii) Syndeotactic-polymers

If R group repeatedly alternate from one side to the other side of the plane then it is known as syndeotactic polymer.

iii) Atactic-polymer

Atactic polymers have no preferred or placement of the substituent groups. PVC is an example of the atactic polymer

Tacticity affects the mechanical and thermal properties of the polymers. Tactic polymers (isotactic and syndeotactic) are crystalline in nature while atactic polymers are amorphous. Tacticity is dependent on the conditions of polymerization like choice of solvent and temperature.[7]



1.3 Copolymers

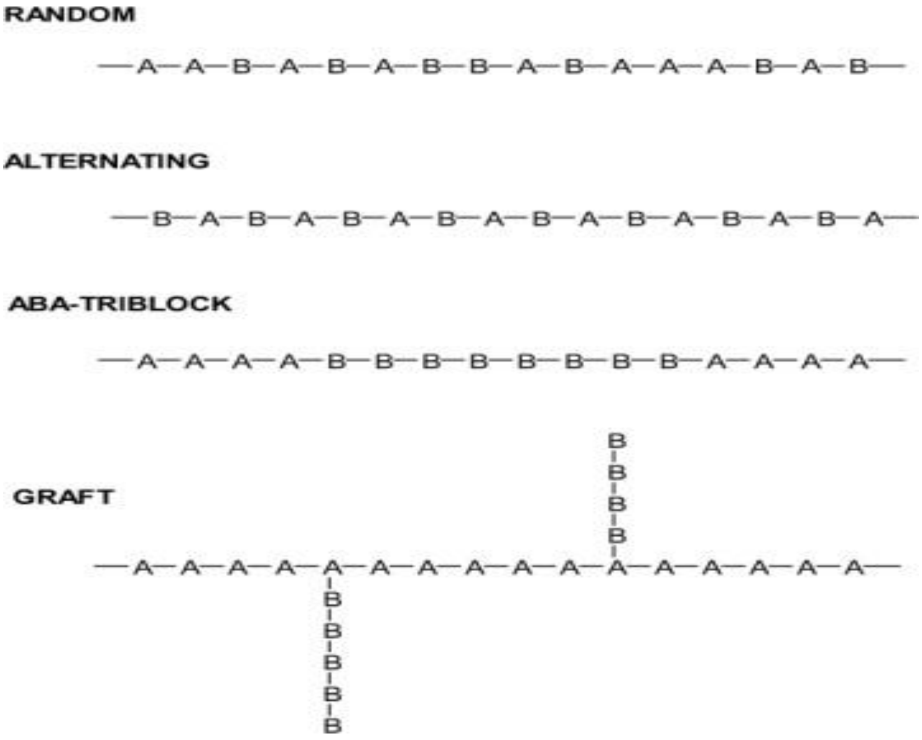
The chemical composition, the arrangement of the monomers and the chain structure influence the properties of the polymers especially in case of copolymers. By linking two or three different types of monomers during the polymerization, a polymer of desired properties can be obtained. The polymer having two different kinds of monomer units in the chain is known as a copolymer. The important copolymers are obtained from the vinyl monomer units of ethylene, styrene, vinyl chloride and acrylonitrile. If there is three different kind of monomer units in the chain that is a terpolymer.

A copolymer may be a random or alternating copolymer as the exact arrangement of the monomers in the chain can differ due to relative reactivities of individual monomer during the polymerization course.

The AB block copolymers can be prepared under special conditions in which a long block of B monomer is followed by the long block of monomer A.

A triblock copolymer has a middle B block connected by A block on the edges. The example of ABA copolymer is commercially important polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS). SBS is a thermoplastic elastomer.

Graft copolymers are as important as elastomers (SBR) and high impact polymers (high impact PS and ABS). Graft copolymers can be prepared by the polymerization of one monomer in the presence of a completely formed polymer having another monomer.[8]



1.4 Engineering polymer

This type of polymer has stable, definite and precise dimensions. It shows elevate performance and properties at a continuous temperature more than 100°C. It is a process-able polymer material having 40MPa tensile strength. Polyamide is the best example of engineering polymer. Kevlar, Trogamid and Nomea show high-temperature resistance and high tensile strength for tire cord and fire retardant fabric. Other examples are PA (Polyamide or Nylon), Polyoxymethylene or Acetal, PEST (Thermoplastic polyester), POM, PPE (Polyphenylene ether) and PC (Polycarbonate of bisphenol-A).[4]

1.5 Polymer blends

Mixing of two polymers or co- or terpolymers leads to the formation of the polymer blend. In polymer blends, the ingredient amount is more than 2-wt. %.[9] So the polymers with advanced and modified properties can be achieved by making multi-component systems; polymer blends or polyblends. The components are joined by secondary interaction (hydrogen bonding, London dispersion interactions, van der Waal's interaction, pi-pi interactions etc.) not by a covalent bond. They usually show the properties better than the individual polymers. The final properties of the blends are determined by the degree of compatibilization. There are few polyblends are compatible while many of are incompatible.[10]

1.6 History of Polymer Blends

The use of polymer blends was came into being before the making of synthetic polymers. For example, the natural products (natural polymers) like resins, cellulose and natural rubber were mixed or combined to make or get desired adhesive and coating materials. In the mid of 1800s, the very first commercialized and modified polymer blend nitrocellulose was noted. The nitrocellulose was mixed with shellac (natural resin product) to modify coating toughness.

In 1846, Parkes patented the blends of natural rubber (NR -an amorphous *cis*-1, 4-polyisoprene) with gutta-percha (GP-a semi-crystalline *trans*-1, 4-polyisoprene) partly co-dissolved in CS_2. These blends were partly cross-linked (co-vulcanized). Their rigidity was controlled by composition. These blends have many uses in tableware, picture frames, shielding of submarine cables and ear trumpets.

In the early 1900s, the phenolic thermosetting polymers were also introduced in blend technology for improved and better properties. The blends of phenolic polymers with vulcanized (cross-linked) NR presented the very first application of interpenetrating polymer networks IPNs.[11]

They were used for amended phonograph records above the brittle phenolic structures. In the 1940s, the blends of synthetic polymers i.e., butadiene acrylonitrile (nitrile natural rubber NBR) copolymer elastomers and poly (vinyl chloride) (PVC) were commercialized and they are still available.[12] The miscibility and single wide Tg was shown by this blend.[13] The permanent plasticized PVC was obtained by the addition of uncross-linked butadiene acrylonitrile elastomers to PVC. This blend is used for a number of applications like it is utilized for cable and wire jacketing, fuel how covers, gaskets, oil containment liners, printing roll covers, pollution control pond liners, conveyor belt and many other applications demanding durability of plasticization additive for the PVC.

In the late 1960s, polymer blend technology got the major interest. In 1965, The General Electric commercialized poly (2, 6-dimethyl-1,4-phenylene oxide) (PPO)/PS blends (trade name Noryl). The blends were had properties lied between the components (weight averaged) on the complete composition range. It was observed that the PPO/PS blends were miscible and increased Tg was noted (heat distortion temperature). Hence the blends showed the increased tensile strength and improved impact resistance.

At present, polymer alloys, blends, and composites consume over 80 wt. % of all plastics. The polymer blends, composites and alloys utilize above 80% of all the plastics. The part of polymer blend technology is widespread in goods of daily life. The tires consist of impact modified polymers (PVC, polypropylene, polystyrene, ABS) and elastomer blends. In electronics, appliances and automotive applications, engineering polymer blends are consumed. Polyolefin blends are used for numerous film applications.[14]

1.7 Objective of blending

The purpose of polymer blending is to make and get the commercially available products of versatile properties with lower expense. The properties of polymer blends are excellent than the constituents of homo-polymers. The blending technology offers desirable prospects for recycling and reuse of polymeric wastes. There are a number of economic advantages are obtained by blending:

- The chance of developing and improving of properties to meet up customer demands.
- The ability to reduce material expenses with or without a slight forfeit in properties.
- Allow quick growth of modified polymer materials to fulfill evolving demands by by-passing polymerization step.
- Extensive service temperature range.
- Improved toughness, increased ozone resistance and light-weight
- The capability to enhance the process-ability of materials which are then restricted in their ability to be converted into final products.
- Increased hardness and modulus and better flame retardant and barrier property.
- Better environmental and impact stress cracking resistance.
- Concisely exclusive materials are formed by blending as concerns its process-ability and or performance. The phase structure of the polymer blends can either be miscible or immiscible.

In case of miscible/homogeneous blends, the entropy of mixing of polymer components is comparatively low and thus particular interactions are required to get the blends on a molecular level.[15]

In case of immiscible blends, the complete physic-mechanical performance depends on two requiring structural parameters.[16]

1. An accurate interfacial tension directing to small phase size to permit the material as macroscopically homogeneous and
2. A strong interphase adhesion to adjust strains and stresses without disturbing the formed morphology. The gap between the elastomers and thermoplastics are covered by the rubber-plastics blends. These blends are commercialized thermoplastics elastomers (TPEs) or rubber-toughened plastics.[17]

1.8 Compatibilization

It is a process used for the variation and alternation of interface properties of immiscible polymer blends. This process leads to the better interactions between the solid-state phases, maintenance of required properties, stabilization of morphology and reduces interfacial tension. As it is mentioned earlier that compatibilization leads to the formation of polymer alloy. There are two ways of compatibilization either physical or chemical. In case of physical compatibilization, the extent of dispersion is produced followed by physical stabilization (cross-linking, co-crystallization or quenching). While in case of chemical compatibilization, compatibilizer controls the morphology along with the extent of mechanical mixing.[18]

1.8.1 Degree of compatibility

The degree of compatibility is the extent of the strength of interfacial bonding between the constituent of immiscible polymer blends or composites or nanocomposites and ability to transfer stress across the interface.[9]

Mechanical performance of blends or composites, size of phase domains or interphase diameter determine the degree of compatibility, relative to immiscible blends without compatibility.[19]

So the compatibility, in phase separated blend, can be achieved by the addition of block and graft copolymer, ternary component, by reactive compatibilization, cross-linking, interpenetrating networks, in-situ polymerization and nano-particle addition.[20]

1.9 Types of blends

1.9.1 Polymer alloy

They are obtained by the compatibilization of the immiscible polymer blends. They show the constant physical properties through the whole volume on the macroscopic level. They are immiscible compatibilized blends having modified morphology and interface. They comprise the compatible polymer blends, multiphase (phase separated domains) copolymer and the miscible polyblend. The properties of many polymers like plastics can be enhanced by alloying and blending two or more polymers. There is a slight difference between the blend and alloy that the blends are not completely compatible while alloys are completely compatible. A particular sub-class of polymer blends; high-performance engineering blends is known as the polymer alloys.[21]

1.9.2 Homologous polymer blend

Mixing of two or more portions of the same polymer all of them having different (narrow) molecular mass or weight distribution.

1.9.3 Isomorphic polymer blend

These are the blends in which two or more different partially crystalline polymers show single phase (completely miscible) in the molten and crystalline state. They show a single and composition dependent Tg and composition dependent melting point Tm.

The polymer blend of two or more different semi-crystalline polymers is miscible in the crystalline state as well as in the molten state. As it is the extremely rare case to be known.[22]

1.9.4 Compatible polymer blend

An immiscible blend having small inhomogeneity due to different phases is useful and known as a compatible blend. They show even and smooth physical properties on a macroscopic level. These uniform physical properties are due to adequately strong interactions among the constituent polymers. They seem homogenous to the eye and having improved physical properties. They can be made compatible by using or adding the compatibilizer. These are miscible over a suitable range of pressure, composition and temperature but immiscible after the specified ranges of pressure, temperature and composition. Modified compatible immiscible blends are known as alloy.[23]

1.10 Classification of Polymer blends

1.10.1 On the basis of miscibility

Basically, there are three different types of blends depending on the miscibility.

i) Miscible polymer blends

Miscibility is the tendency of a mixture for making a single phase over the specific ranges of the composition, temperature and the pressure. The presence of single phase depends on the following:

- Molar mass distribution
- Chemical structure
- Molecular architecture of components

Miscibility can be achieved by hydrogen bonding, dipole-dipole interactions, matched solubility parameters, ion-dipole interactions, Mean field approach, Association model, Light scattering, neutron and X-ray scattering techniques are used for the determination of single phase in the system.

1. Completely miscible blends have the negative free energy of mixing and ΔH m ≤ 0 due to specific interactions.

$$\Delta G_m \approx \Delta H \leq 0$$

2. They show single glass transition temperature Tg or optical clarity. These blends have single phase structure. If there is cross-linking and molecular architecture is changed then there is no longer miscibility.[24]
3. In case of miscible/homogeneous blends, the entropy of mixing of polymer components is comparatively low and thus particular interactions are required to get the blends on molecular level.[25]
4. The blends of PS/PPO is miscible in all compositions on a wide range of temperature.

   The other examples of the miscible blends are PS/PVME, PVC/PS, PAA/PEO, PP/PB and PS/PPO.[26]

ii) Partially miscible blends

In these blends, a small portion of one of the blends is dissolved in the other portion. They have reasonable properties with proper and smooth phase morphology. The phases of blends are homogeneous having their own Tg. So the both Tg's of pure blend constituent are moved towards the Tg of blend constituent. PC and SAN phase of ABS is partially dissolved in one another. So the interfacial adhesion is good and the interface is broad.[27]

iii) Immiscible polymer blend

A mixture is unable to make or form a single phase. This is known as an immiscibility. It can be confined to a specific range of composition, temperature and pressure. It depends upon the molar mass distribution, molecular architectures of the constituent and chemical structure. They show the positive value of free energy mixing.

$$\Delta G_m \approx \Delta H \geq 0$$

In these blends, two or more phases are observed. They commonly show two Tg's due to phase separation. The different Tg's are shown in correspondence of the constituent polymers. They have poor adhesion and sharp interface rough morphology. These blends are useless without compatibilization. The examples of completely immiscible blends are PA/ABS, PA/PPO, PA/EPDM, PA/PP, PMMA/PCL, PVC/PMMA, PE/PP, PS/PSAN, PVPh/PA, SIS/PVPh, PVPh/PSMMA, SIS/PA. By using appropriate compatibilizers, these blends have become commercially useful.[28]

In case of immiscible blends, the complete physic-mechanical performance depends on two requiring structural parameters.[1]

1. An accurate interfacial tension directing to small phase size to permit the material as macroscopically homogeneous and

2. A strong interphase adhesion to adjust strains and stresses without disturbing the formed morphology.

It is an ability of a single constituent either in a polymer composite or in an immiscible blend for showing a better and modified interfacial adhesion. For a miscible system, this term is not favoured to use. As is specifically used for the immiscible polymer blends.[29]

Generally, immiscible polymers are chemically different. So they show reduced mechanical reliability and frail or weak interfacial adhesion. So the conversion of such blends to beneficial polymer products with improved and required properties needs some control and manipulation of the interface. For this, a compatibilizer is used to reduce the interfacial tension and enhance the adhesion between the phases of polymer blends. A compatibilizer may be a polymer or copolymer that is added to immiscible blend system to modify the interfaces and maintain the morphology. They can stabilize morphologies of blend systems over the range of micro-meter or less.[25]

High impact PS (PS having a dispersed rubbery phase polybutadiene); Acrylonitrile, styrene and butadiene polymer (ABS) and a variety of polypropylene-poly (ethylene-*co*-propylene) blend are the compatible blends.[30]

Elias et al. conferred the use of firm and hard nanomaterials i.e., silica nanoparticles for compatibilization.[31]

1.10.2 Blends on the basis of physical state

The polymer blends can either be defined on the basis of the physical state of the components. There are three types of classes of blends on the basis of the physical state. The semi-crystalline polymers, crucial commercially, PE covers 35% of the market, PVC 14%, PP 9% and PS (noncrystalline) covers 41% of the market products.

i) Amorphous polymer blends A/A

The both components of the polymer are amorphous. Only one phase, liquid or glass, is consider with miscibility phenomenon. The amorphous polymer blends may be miscible m, partially miscible pm or immiscible im.[32]

ii) Amorphous- semi-crystalline blends A/C

In this case, the amorphous polymer A is blended with the semi-crystalline polymer C. If the processing temperature of A Tproc › Tg and melting point of C Tm ‹ Tproc, then both phase equilibrium at Tproc and crystallization on cooling would be taken into account. So at Tproc, the blend system may be m or im.

If the Tproc ‹ Tm of C, then the semi-crystalline component may super cool and crystallize. In this case, the A/C would be considered as A/A. The blend system may be m, im, or pm.[33]

The Tg of polymer composites depends on the interactions and degree of mixing. If the attractive forces between the polymer and nanofiller like silica are favourable then increased Tg is expected. This is because the silica reduces the long-range motion and increase the Tg.

There are many factors responsible for increased or decreased Tg’s. The increased Tg is due to the presence of intermolecular forces, high CED, inter-chain steric hindrance, bulky and stiff side groups. The decrease in Tg is due to flexibility in chain groups (ether linkage and double bond), flexible side groups and symmetrical substitution.

Table 2: List of semi-crystalline and amorphous polymers for blends

Semi-Crystalline Polymer	Amorphous Polymers
Polybutylene terephthalate (PBT)	Acrylonitrile butadiene styrene(ABS)
Polypropylene (PP)	Polymethylmethacrylate (PMMA)
PP	Bisphenol A Polycarbonate (PC)
PP	Polystyrene (PS)

iii) Semi-crystalline-semi-crystalline blends C/C

In case of miscible blends of two semi-crystalline polymers, three phases will form. One phase will be amorphous while two crystalline phases will be formed. Isomorphism or co-crystallization is seen rarely having a single crystalline phase. Crystallization in miscible blends depends on the Tg of the blend in comparison with the Tg's of the components. While in case of crystallization rate of the individual component will be unchanged if there is no other component nucleates crystallization of another component. Morphology will be reflected either in amorphous or crystalline phase .[34]

Table 3: List of semi-crystalline polymers for blends

Semi-crystalline polymer	Semi-crystalline polymer
Syndiotactic Polystyrene sPS	Isotactic Polypropylene iPP
Low-density polyethylene LDPE	Polyamide 6 (PA6)
Polyethylene terephthalate (PET)	High-density polyethylene HDPE
Polypropylene PP	Polybutylene terephthalate PBT

1.11 Modes of preparation of Polymer blends

The properties of the blends are greatly dependent on the methods of preparation. There are many techniques employed i.e., simple mixing of polymer powders followed by the heating and diffusion control mixing, mechanical melt and solvent mixing in addition to in-situ polymerization.

1.11.1 Solvent mixing

Polymer blend preparation is done in a mutual solvent. If the densities of the solvent-polymer blend phase are different (two layers will form) then phase separation would be observed and the blend is immiscible in the solid state. While in case of phase separation in solution, the unsettled solution will be opaque or turbid. In some cases, the polymer-solvent interactions are weaker than polymer-polymer interactions. This happens with water-soluble polymer blends i.e., poly (acrylic acid)/poly(ethylene oxide). In this case, the water solution of each constituent goes towards turbidity at lower concentration and coagulats at higher concentration. The solid-state characterization of the polymer blends is done by the solution casting followed by the evaporation of the solvent.

In this method, it is very important to remove the solvent for characterization because low levels of the solvents can affect the phase edges. If the constituent of blends, one or both, have high Tg polymer then solvent should be removed above the Tg of high Tg constituent. If the casting temperature is not above the Tg, the immiscible blend will be miscible. When Tg reaches the evaporation temperature then viscosity increases which hinder the phase separation. So to avoid the freeze-in miscibility the solvent casting above the Tg of Highest Tg constituent is important. The solvent effect is also noted in borderline miscible PVAc/PMAc blends.[35]

As phase behavior is being determined by the solvent used. Dobry-Kawenoki[36] and Slocombe[37] observed the effect of solvent on the miscibility of polymer blends. Phase separation with common solvent was studied for 35 pairs of polymer blends. The systems i.e., Nitrocellulose with PVAc, PMMA with PVAc and styrene copolymers, polystyrene with benzyl cellulose were the single phase solutions. The studies showed that most of the polymer blends pairs would be phase separated.

Schultz and Bistac studied the effect of residual amounts of many solvents like THF, $CHCl_3$, toluene and acetone on the loss factor, tan D, of PMMA films. The alpha peak in tan delta traces was decreased for all solvents but beta peak was only decreased for chloroform and increased for other solvents.[38]

Zhang et al. studied the interruption of H-bonding in nylon on the addition of solvent to the system. This concept is particular for the polymers having side groups able of H-bonding as effectively as nylon.[39]

The solvent can affect the mechanical properties of polymers and can shift the Tg to lower value. [40, 41]
Scott et al. reported the effect of 30 wt. % of imidazolium and diethylhexylphthalate ionic liquids on storage and loss modulus on cast PMMA samples. The Tg trends were not dependent on solvent but the room temperature modulus did. The Tg above the boiling points of THF and chloroform would be retained, if long chain polymer motion is allowed to escape solvent molecules.[38]

The addition of ethanol in $CHCl_3$/THF solvent mixture reduced the transition region and glassy modulus to lower value as compared to $CHCl_3$/THF. The reason for this is that ethanol shows H-bonding with MMA and it has a higher boiling point. Both of these factors act as good plasticizer for PMMA film which results as lower mechanical properties.

The ethanol in the sample could hinder the oxygen stabilization route that primarily pushed PMMA's degradation to a higher temperature than another atmosphere. As oxygen produces the radical that is thermally stable and reduces the opening of the polymer. The degradation onset would shift to the lower temperature if the process is blocked by the presence of ethanol H-bonded to the polymer.[42]

i) Freeze drying

In this method, miscible solid of single-phase solutions of immiscible polymer blends can be obtained by freeze drying. Phase separation will occur on the exposure of the sample above Tg. Immiscible PS/PMMA is an example that shows miscibility when freeze dried but above the blend Tg phase separation is observed.[43]

ii) Compositional quenching

It is the rapid devolatilization of a homogeneous solution of two immiscible polymers. It produces an initial single-phase metastable system that can further be phase separated by spinodal decomposition to form unique structures.[44]

iii) Rapid expansion of supercritical solution (RESS)

In this method, polymer blend is dissolved in a supercritical solution followed by rapid depressurized. After then mixtures of polymer powders are formed and exposed to higher temperatures to allow for diffusion mixing for the preferred blend.[44]

So the powder particle size will be the phase size for immiscible blends. The polymer chains will diffuse to form a miscible system in case of miscible blends when heated above the Tg's of both constituents. This requires the long time period and long exposure to get equilibrium.

iv) Water-based dispersion or emulsion blends

The particle will retain their intrinsic size in case of immiscible system or will diffuse slowly headed for homogeneous material in case of the miscible system when water is being evaporated.[45]

Emulsification process of in-situ polymerization with sequential polymerization is done in water borne systems. This leads to the formation of core-shell structured morphologies.[46]

1.11.2 Melt Mixing

It is one of the common techniques for the preparation of the sample and size of the polymer samples is large. A Brabender melt mixer and the miniature extruder are used to prepare the samples of the size of 30g. The gram scale mixing can be done by a small scale mixer. Improved dispersion for PP/HIPS was done by this method. Conventional laboratory extruders are used for larger sized samples (≥500g). The advantage of melt mixing is the easy preparation of large-scale samples for mechanical property studies. Injection molding or compression molding is done for the samples. Melt mixing is a solvent-free method until the blend is prepared in a solvent and devolatilized through an extrusion process. Extrusion process is used for preparation of thermoplastic polymer blends on commercial scale.[47]

1.11.3 In-situ polymerization

The polymerization of one polymer is done in the presence of the other polymer. Polyolefin blends can be prepared by sequential polymerization of compositionally different polyolefins; PP/EPR or by simultaneous polymerization of polyolefin modifications with several catalyst systems. In-situ polymerization in water-borne systems (e.g., emulsions) can be conducted with sequential polymerization, leading to structured morphologies such as core-shell structures well-noted.

1.11.4 Interpenetrating polymer networks

Two or more polymers are combined in the form of network known as interpenetrating polymer network. In this method, one polymer is prepared and/ or cross-linked in the presence of another polymer.

Different polymeric networks are prepared by either sequential polymerization; IPNs are formed by first crosslinking of the one polymer, or by simultaneous polymerization; by this two polymers are formed and cross-linked simultaneously.

The polymers used for the preparation of IPNs are polyurethane (PU), polystyrene (PS), poly (ethyl acrylate) (PEA) and polymethylmethacrylate (PMMA). Polypropylene and ethylene-propylene-diene terpolymer (EPDM) are commercialized IPN used for automotive applications.

The advantage; if in IPNs two polymers are immiscible, the phase separation will occur as monomers or monomer polymerizes. But the size of dispersed phase would be smaller 10-100 nm as compared to blends of physically mixed or a graft of two constituents or block copolymer. As the phase separation is restricted by the cross-linking process.[47]

1.11.5 Layer-by-layer Assembly

This method is used for the formation of polyelectrolyte complexes. Coating of a polymer, of different charge from diluted aqueous solution, on a charged surface (substrate) is done. From the dilute solution, a polymer is added with a different charge of the deposited polymer after rinsing the substrate.

To form the polyelectrolyte film having molecular dense layers of anionic and cationic polymer, the above mentions process is repeated many times with intermediary rinsing stages.

1.12 Applications of Polymer Blends

- Elastomeric blends have stable properties and enhanced fabrication and they are less expensive. They are used in tire components.
- To improve ozone crack resistance, the EPDM is added to the tire sidewalls. Better tread life and wear resistance gain by the addition of polybutadiene to

SBR or NR. As NR has outstanding track strength for the production of belt compounds and carcass.[48]

- For industrial and automotive applications that require oil resistance and 150°C, Polyamide/polyacrylate TPVs are used.[49]
- Thermoplastic elastomer blends with a high coefficient of friction (wet and dry) and low modulus are used in the applications of foot pads, sporting goods, hand grips, toothbrush, razor handles, power tool handles, water craft grips, knobs, handles and lawn and garden equipment.[50]
- These elastomers are shaped on hard substrates like hard metals or polymers. They include low modulus TPVs, SEBS blends with polyolefins, polyolefin/elastomer and polyolefin blends.
- Polyolefin blends show better compatibility and are very common in applications of commercial polyolefins. 30% of polyolefin products have polyolefin blends.[51] Improved environmental stress crack resistance, balance film characteristics, improved additives and filler acceptance, tear resistance and surface and toughness properties are obtained by polymer blends. For this purpose blends of ethylene copolymers i.e., ethylene-ethyl acrylate, ethylene-vinyl acetate, ethylene-acrylic acid copolymers have been added to HDPE, LLDPE, and LDPE.
- Functionalized polyolefins (introduced by Equistar, Integrate ^{TM}) are used to enhance dispersion and adhesion in mineral-filled polyolefin composites and wood fiber filled.
- Polyisobutylene added to LDPE and HDPE to enhance tear resistance, toughness and environmental stress-rupture resistance.
- The maleic anhydride (MA) grafted polyolefins like PE-g-MA and PP-g-MA are used to mend the compatibilization of polyamides with polyolefins. They are also used as coupling agents for particulate filled polyolefins composites.
- The impact polystyrene with PPO is used to increase the toughness, strength and expanded the heat distortion temperature. As PPO addition to impact PS allowed the use of low-cost flame retardants. This combination is used to get the required UL-94 flammability necessities for machines and utility for electrical applications.[52]
- Good mechanical compatibility (even the phase separation exists) is obtained by BisphenolA polycarbonate (PC)/ABS blends.

- PC/polyetherimide (PEI) blends offer a balance of chemical resistance, toughness and heat resistance (commercialized by General Electric (Ultem R _ LTX)). Applications include microwave cookware, ducts and consoles, thermoformable sheets for aircraft window housings, and fire-fighter helmets.
- PEEK (polyether ether ketone), a crystalline polymer with a Tm = 325°C, shows very good hydrolytic stability, good toughness, excellent chemical resistance, high strength and stiffness, and environmental stress crack resistance. Rigby and Cakmak reviewed the properties of PEEK.[53, 54]
- Polyamide/polyamide blends are used for fiber and food packaging applications.[55]
- PVC is widely used polymer in hard systems as pipe and plumbing applications, hous siding, ponds, pit and pool liners, and as flexible or plasticized systems in upholstery applications. PVC also shows flammability resistance and it is low cost.
- Phase separated blends of ABS/PVC and PMMA/PVC show good mechanical compatibility and can be utilized for many applications i.e., mass transit interiors, appliance housings, telecommunications equipment where flammability resistance is demanded. PMMA is partially miscible with PVC.
- PVC/ASA blends are used for weatherability applications i.e., house siding, window profiles and automotive exterior trims.
- Blends of PS and impact PS are used to get toughened versions.
- The thermoplastic/ABS blends are used in the applications of filler panels, bumper fascia, aircraft seat tracks, automotive painting, rock shields and give high toughness.[56]
- PS/PMMA blends are phase separated and are used for the decoration of the objects and in jewelry.
- Polytetrafluoroethylene (PTFE) particulate with engineering polymers (PC, PEI, PA, PSF, PPS, POM (polyamide-imide, polyimides) consists of blends prepared for explicit wear and abrasion applications.
- PTFE provides the lubricity needed for multiple traversal applications such as bushings, gears, sleeves, where a lower coefficient of friction permits for reduced wear and abrasion.

- Polyethylene/crystalline polyamide (PA66, PA6) blends are used in container and barrier film and container, presenting a compromise in oxygen and water barrier properties.[57]
- Artificial teeth are prepared from cross-linked PMMA mixed with MMA monomers and polymerization is done (sequential IPN). Commercial IPNs include sheet molding compositions (urethane/polystyrene/acrylic: Ferro chemical), vibration and sound damping compositions (vinyl phenolic).[58]
- Poly (3,4-ethylene dioxythiophene) (PEDOT) doped (complex) with poly (styrene sulfonic acid) (PSSA), is a commercially water borne conductive polymeric system, used as an anti-static coating for photographic film, conductive transparent films, solid electrolyte capacitors and a hole injection layer for polymeric light emitting diodes. Other applications proposed for utility include static-dissipation coatings for TV screens and monitors, electronics packaging, a primer for electrostatic coatings on non-conductive surfaces and clean-room equipment and packaging.
- The hydroxyl compounds (sorbitol, ethylene glycol, glycerol) in addition to the water-borne PEDOT (PSSA prior to film casting) result in up to numerous orders of magnitude increase electrical conductivity for the dried film.[59]
- PHE/TPU Phenoxy/thermoplastic polyurethane (PHE/TPU) blends have used a binder for iron oxide in magnetic tape.[60]
- PCL/ABS blends are used for Shoe construction (e.g., heel counters) and commercial for more than 30 years.

1.13 Polymer composites

Composite systems have polymer blend as a matrix. They contain fibers or inorganic particulates, carbon black, natural rubbers and organic fibers (Kevlar fibers) or fillers. Polymer blends show unique properties for the composite systems. The example of polymer blend composite is the incorporation of the conductive carbon black at the interface of phase separated polymer blends. Composite fillers are responsible for the compatibility in polymer blends.[61] Conductive carbon black is added to various polymers as semi-conductive shielding for wire cable insulation, and a polymer matrix based conductive compositions for EMI shielding and antistatic applications.[62]

Table 4: List of Polymers and fillers for composites and their advantages

Polymer A	Polymer B	Filler	Advantages
ABS	PS	Mica	Adhesion is increased by silane; burning rate decreased by mica.[63]
PS	PMMA	Organoclay	Organoclay acted as compatibilizer as domain size of the blend decreased and organoclay concentrated in PMMA and at blend interface.[48]
HIPS	LCP	Carbon black (CB)	Electrical conductivity at high shear rates was maintained by 20% LCP and 2% CB. CB network located on LCP particles.[64]
PEEK	LCP (Ekonol)	MoS2/graphite	PEEK/MoS_2-graphite composite with Ekonol lowed coefficient of friction and wear rate.[65]
NR	ENR	Clay	Epoxidized natural rubber (ENR) added as a compatibilizer; improved tear and tensile strength.[66]
PP	PP-g-MA	Clay	improved dispersion by intercalation into clay layers.[66]
PS	PA6	Carbon black (CB)	CB concentrates in the PA6 phase; continuity of the PA6 phase and gives higher conductivity.[67]
POE-g-MA	PP	Exfoliated clay	The clay resides in the POE-g-MA phase; small domain sizes observed with a good balance of ductility and hardness.[66]
PP	PP-g-MA or diisocyanate	Cellulosic fibers	PP-g-MA compatibilized the PP/cellulosic fiber composite as well as a diisocyanate. The PP-g-MA/cellulosic fiber composite was also improved with diisocyanate addition.[67]

1.14 Nanotechnology

The analysis of controlling the matter either on an atomic or molecular level falls in the category of nanotechnology. The word nano is driven from Latin word *nannus* or Greek word *νᾶνος* both means dwarf. Normally nanotechnology deals with the components and structures of sizes between 1 to 100 nm in at least one dimension. It develops, creates, or modifies the devices and materials within that length range. The formation of nanoscale dimensioned materials or particles is a basic and main concern of the nanotechnology. These materials, particles and structures are known as nanomaterials, nanoparticles and nanostructures respectively, they show exotic and unique properties that are not seen in bulk materials. Nanotechnology is a system or process to provide services and goods that are got from the matter at nanometer level 10^{-9}, i.e., from sizes in the range of one billionth of a meter. Drexler defined "Nanotechnology is the principle of manipulation of the structure of matter at the molecular level. It involves the ability to form molecule systems with atom-by-atom precision, producing a variety of nanomachines."

Nanoscience studies the essential principles of atoms/molecules and structures with at least one dimension between the range of 1 to 100nm. These structures are known as nanostructures and nanotechnology is the implementation or application of the nanostructure into beneficial nanoscale devices.[68]

1.15 Classification of Nanomaterials

The nanomaterials are classified on the basis of the number of dimensions in nano range (≤ 100 nm).

i) Zero-Dimension nanomaterials (0D NMs): All dimension within nanoscale (not larger than 100nm). The nanoparticles, hollow spheres, uniform particles arrays (quantum dots), nano lenses, heterogeneous particles arrays, onions, core-shell quantum dots and are 0D nanomaterials. These nanoparticles can be amorphous or crystalline, ceramic, metallic or polymeric. 0D NMs i.e., quantum dots have been widely studied in light emitting diodes (LEDs), solar cells, single-electron transistors, and lasers.[69]

ii) One- Dimension nanomaterials (1D NMs): One dimension in nano range. The needle-like shaped materials have one dimension in nanoscale. The Nanorods, nanoplatelets, nanosheet, nanotubes, nanowires, nanobelts, nanoclays are the examples of 1D nanomaterials. The field of 1D NMs such as nanotubes has attained a significant attention after the pioneering work by Iijima. 1D NSMs have a profound impact in nanoelectronics, nanodevices and systems, nanocomposite materials, alternative energy resources and national security.[70]

iii) Two-Dimension nanomaterials (2D NMs): Two dimensions in nano range. They include nanofibers, whiskers, nanotubes, nanowalls, nanoprisms, nanodisks, nanorods nanosheets, nanoplates. Carbon nanotubes are the best example 2D NMs.[70]

iv) Three-Dimension nanomaterials (3D NMs): All the three dimensions are out of nanorange or ≥ 100 nm. They include nanoclays, equiaxed nanoparticles, nanogranules, nanopillars, nanoflowers, nanocoils, nanoballs (dendritic structures), nanocones. The 3D NMs have higher surface area and enough absorption sites for all molecules in small space. These materials have porosity in three dimensions that can lead to better transport of the molecules.[69]

1.16 Nanocomposites

These are the composite materials have at least one dimension in the nanometer range. Nanosized filler components are added to modify or enhance the properties of resulting materials. Nanocomposites are prepared by two or more different phases or components. The components have different chemical and physical properties separated by a distinctive interface. Their exclusive properties are not shown by any of the components. The component or constituent that is commonly present in large quantity is known as matrix. The component implanted or embedded in the matrix is known as reinforcement. The reinforcement (or nanomaterial; usually nanosized filler materials) is used to enhance the mechanical properties of nanocomposites. The reinforcing material includes particles (e.g., minerals, Carbon nanotubes, metallic nanoparticles,), fibers (e.g., Electrospun nanofibers), sheets (e.g., graphene, exfoliated clay stacks).

Nanocomposites are more beneficial and useful than typical composites. The enhancement in the properties of the matrix in nanocomposites can be gained by the addition of a little amount nanofiller compared to simple composites that need a high amount of microparticles to enhance the properties.[71]

Nanocomposites are light weighted as compared to simple composites, as the amount of nanofiller material is small. Nanomaterials possess size-dependent properties enhances thermal, mechanical, chemical, magnetic, optical and electrical properties to a greater extent than composites.

Nanocomposites have high surface area to volume ratio of the reinforcing nanoparticles and their remarkably high aspect ratio compared to composites. The area of the interface between the matrix and nano-reinforcement is specifically an order of magnitude higher than the simple composites.

In 1991, the discovery and uses of carbon nanotubes in the fabrication of nanocomposites introduced a novel feature to this area. Nanocomposites are also present in nature i.e., the structure of bone and abalone shell.

1.17 Types of Nanocomposites

Nanocomposites are categorized on the basis of matrix and reinforcement materials. They can be classified into different categories i.e., Nanoclay-reinforced nanocomposites, Structurally reinforced nanocomposites, Nanofibre-reinforced nanocomposites, Inorganic particle-reinforced nanocomposites, Carbon nanotube-reinforced nanocomposites.[72]

On the basis of the matrix material, there are three types of nanocomposites.

- Metal Matrix Nanocomposites
- Ceramic Matrix Nanocomposites
- Polymer Matrix Nanocomposites

1.17.1 Metal Matrix Nanocomposites

In these nanocomposites, the matrix is an alloy or ductile metal wile nanoparticles are used as reinforcement. The chemical and mechanical properties of these materials are totally different from the matrix material. The nanoparticles are used to enhance the mechanical properties, wear resistance and damping features. The nano-level interactions of particles with dislocations have become of importance and notable betterment has been observed in mechanical properties. The nanoparticles work as barriers in dislocation movement to improve mechanical properties. The processing of these materials is done by spray pyrolysis, vapour techniques, liquid metal infiltration, chemical methods and electrodeposition, which involves sol-gel and colloidal methods. Ni/Al_2O_3, Mg/CNT, Al/CNT, $Fe\text{-}Cr/Al_2O_3$ and Fe/MgO are examples of metal-matrix nanocomposites.[73]

1.17.2 Ceramic Matrix Nanocomposites

These materials have matrix phase of oxides, silicates and oxides. They are widely used in industry. The nanoceramic composites provide excellent mechanical and electrical properties. These materials are prepared by polymer precursor route, spray pyrolysis, colloidal, sol-gel, precipitation method and template synthesis. The examples of ceramic matrix nanocomposites are Al_2O_3/SiC, Al_2O_3/SiO_2, Al_2O_3/TiO_2 and SiO_2/Ni. The carbon nanotubes (CNTs) are extensively used for the fabrication of the nanocomposites. The CNTs-ceramic matrix nanocomposites are MgO/CNT, Al_2O_3/CNT and $MgAl_2O_4$/CNT.[74]

1.17.3 Polymer matrix nanocomposites

These materials have polymer phase as matrix and nano additives as reinforcement. The additives may be nanotubes or fibers (1D), layered materials such as clay (2D) or spherical particles (3D). This field has been of great interest for academic research and industries for last twenty years, and tremendous growth has been observed over the past ten years. As the neat polymers/micro particulate filled polymers lag behind the polymer nanocomposites. Polymer nanocomposites show distinctly better properties i.e., strength, modulus, heat resistance at low concentration of inorganic material (1-10 wt. %) and impact performance. Nanocomposites are easy to handle and light weighted. So the polymer nanocomposites are can be manufactured by a direct combination of nanoscale inorganic building blocks with polymers.[74] They possess the high elastic strength and stiffness, having good barrier resistance, wear resistance, magnetic, optical, electrical properties and flame retardancy. Polyamide, a thermoplastic polymer (matrix), carbon and glass fibers are mostly used as reinforcement materials. Carbon fibers are widely used as a reinforcing phase in the aerospace industry. The reinforcement material is chosen according to the application. There is weak intermolecular forces between the polymer matrix and nanofiller, however, there may be chemical bonding in some cases. The notable enhancement in the mechanical properties can be achieved by chemical bonding between the matrix and filler. Clay minerals (hectorite, montmorillonite, kaolinite and saponite etc) are used as fillers to get better properties of materials. The layers of silicate clay show high aspect ratio. It is due to 1nm thickness and designed of platelets of around 100 nm in width. While the glass fiber has a 13µm diameter and 0.3mm length, that is 4×10^9 times size of silicate layer. [75]

Nanoclays are the nanoparticles of layered mineral silicates. Clay minerals are known as layered silicates as they belong to a major group of silicates having a layered structure. The layered silicates are natural or artificial minerals formed of fixed or ordered stacks of aluminosilicate layers having high surface area and aspect ratio. On the basis of the morphology of particle and chemical composition, nanoclays are classified as montmorillonite, kaolinite, halloysite, bentonite and hectorite. Nanoclays, hybrid organic-inorganic nanomaterials, are potentially used with polymer nanocomposites as gas absorbents, drug delivery carriers and rheological modifiers. The most common nanoclay used in material applications is Montmorillonite.[76]

Clays are nanofiller materials widely used for the preparation of polymer matrix nanocomposites. Polymer/clay nanocomposites have gained immense attention in academia and industries due to better properties as compared to simple composites. Clay is a soil fraction with a thickness in nano range; usually around 1nm and particle size of about 2µm.

Since 1985, Toyota automotive corporation developed the first polymer/clay nanocomposites and concern in their potential has been extended.[77] The addition of a minute amount of smectite clay, mostly modified with surfactants, to polymers (5 wt %) is discovered to increase barrier and mechanical properties. They also retained the processability of thermoplastics. These composites are used as biodegradable packaging, biomaterials and energy-related products.

1.18 Preparation of Polymer Nanocomposites

Polymer nanocomposites are prepared by following techniques;

- Intercalation method
- Melt intercalation method
- Sol-gel method
- In-situ polymerization
- Direct mixing of polymer and nanofillers

1.18.1 Intercalation Method

In this method, the nanomaterial (nanoplatelets) are dispersed in the polymer matrix. For example, the inclusion of the nanoclays in polymer matrix increases the bulk properties like flammability, stiffness and shrinkage.intercalation is a top-down approach. It involves surface modification of nanomaterial in a polymer matrix, for homogeneous dispersion. The polymer chains are intercalated into the silicate layers in a crystallographic regular order, in intercalated nanocomposites, irrespective of the clay to polymer ratio.

The diffusion of polymer chains in the gallery spacing of the layered structure results in intercalated morphology.[78]

1.18.2 Melt Intercalation Method

This method is widely used in industry as it is compatible with present industrial processes like injection molding and extrusion. In this method, the nanofillers (clays) are mixed with polymer matrix at molten temperatures. The mixture of polymer and nanofillers are annealed either by shearing or statically. The polymer powder or pellets are melted to form the viscous solution and nanofillers are added to polymer solution by high shear rate and high-temperature diffusion. The resulting product is fabricated by injection molding, compression molding or fiber production technique. It is useful for the polymers which are not compatible for solution intercalation or in-situ polymerization.[78]

1.18.3 Sol-gel Method

It is a two-step method forming the sol and gel. Sol-gel is a bottom-up approach. Sol is a colloidal suspension of the nanoparticle in monomeric solution while the gel is a three-dimensional interconnecting network formed between the phases. The solid nanoparticles are distributed in monomeric solution to form a suspension of solid nanoparticles and interconnecting network between the phases is formed by polymerization reaction afterward the hydrolysis process. The polymer act as nucleating agent and favors the growth of layered crystals. The nanocomposite is formed when the polymer seeps between the layer as crystals grow.[79]

1.18.4 In-Situ Polymerization Method

In this method, the nanofillers are swollen in the monomer solution. The low molecular weight monomeric solution can seep between the layers resulting swelling. The resulting mixture is polymerized either by heat, radiation, organic initiator or by initiator diffusion. The monomer is then polymerized between interlayers thus developing intercalated or exfoliated nanocomposites. The clay layers are uniformly and completely dispersed in the polymer matrix in case of exfoliated nanocomposites. The layers of clay are separated in the polymer matrix by a normal distance that usually depends on clay loading. Normally the clay layers content in an exfoliated nanocomposite is lower as compared to intercalated nanocomposites as shown in fig 1.

In-situ polymerization method involves the dissolution of the polymer matrix and clay in aqueous solution and the resulting gel is refluxed at a higher temperature. The polymeric chains are confined inside the layers of clay. At high temperature, the nucleation and growth of clay layers occur on polymeric chains. The problem of this method is the decomposition of the polymer at high temperature.[80]

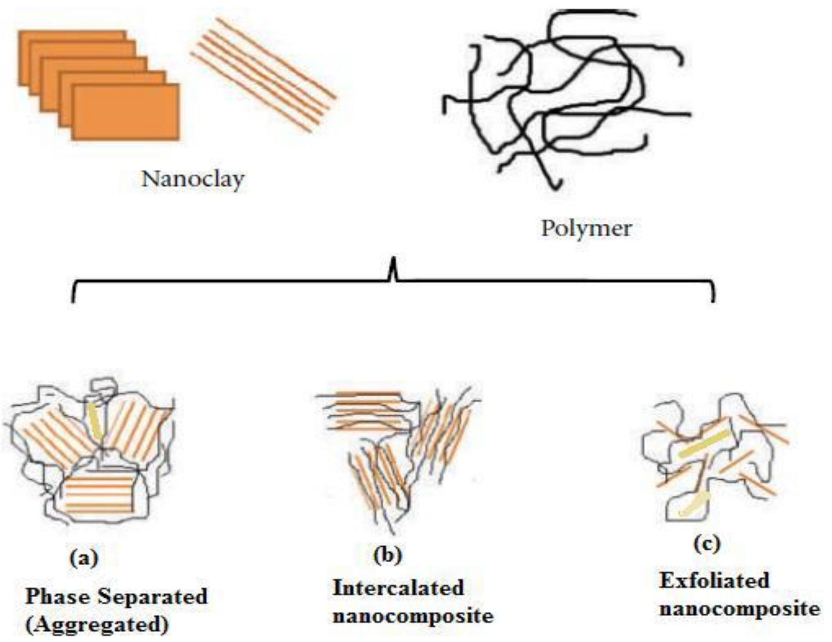


Fig. 1: Structure of modified clay.

1.18.5 Direct Mixing of Polymer and Nanofillers

This method is a top-down approach to nanocomposites production. There are two ways of mixing of the nanofillers and polymer matrix:

Melt compounding

Nanofillers are mixed with polymer matrix above the glass transition temperature, in the absence of a solvent. The shear stress (hydrodynamic force) is applied on polymer melt by viscous drag and this stress is used for breaking the nanofiller aggregates and thus raises the uniform and homogeneous dispersion of the nanofiller in polymer phase.

Solvent Method

In this method, the polymer is dissolved in a co-solvent and nanoparticles are dispersed in a solvent. The solvent is evaporated and nanocomposites are obtained.[81]

1.19 Applications of polymer nanocomposites

- Nylon 6/montmorillonite nanocomposite was synthesized by Toyota Automotive in 1985. They used it in the car for timing belt cover. This was the very first polymer-clay nanocomposite having high mechanical properties.[82]
- Conjugated polymeric nanocomposites are used as a gas and biosensors.
- Polymer nanocomposites have also been used in the solar cell to form large flexible solar panels.
- Polymer nanocomposites show a high range of scratch resistance due to high Young‘s modulus and hardness such as PP/clay nanocomposites.
- Nguyen and Diaz have described microwave absorption properties of polypyrrole nanocomposite with iron oxide, tin oxide, and titanium oxide nanofillers.[72]
- The polymer/clay nanocomposites have a wide range of applications in submarines, airplanes and vehicles, to reduce fire risk.[82]
- Rapoport et al. stated the lubricating properties of tungsten sulfide nanocomposite with epoxy; polyacetal to reduce the coefficient of friction between steel discs.[72]
- The polystyrene-clay nanocomposites have interesting commercial importance in packaging, construction, automotive, electrical materials and fuel cell.

- The commonly used clays with polystyrene are kaolinite, montmorillonite, hectorite and bentonite.[83]

1.20 Literature Review

William C. et al. used Sum frequency generation (SFG) vibrational spectroscopy for the structural analysis of PS/PS-co-PMMA blends. The ratio was 1:1 for both polymer contents. SFG study showed that components such as PS and PMMA separated on the surface of blend and copolymer before annealing though PMMA has marginally high surface tension. After annealing, PS laid on the surface of PS/PMMA more but there was no change on PS-co-PMMA surface. The flat surface of PS-co-PMMA blend was confirmed by the AFM images but rough surface (domains present) was seen for PS/PMMA blend.[84]

Sihama E. Salih et al. prepared Low-density polyethylene/polypropylene (LDPE : PP) and High-density polyethylene/polypropylene (HDPE : PP) and binary blends (10-90%) by melt mixing in an extruder. They studied their mechanical properties and analyzed the morphology by SEM. SEM results showed that both the pair of blends were incompatible. There was some interfacial adhesion domains between the 20HDPE : 80PP but there was no such adhesion for 20LDPE : 80PP. Hence HDPE/PP blends have better mechanical properties as compared to LDPE/PP blends. Tensile strength, Young modulus creep modulus, hardness and bending modulus increased for both pairs of blends by increasing PP % age in blends except elongation. The 20:80 HDPE : PP and LDPE : PP bore high load as compared to other samples of different ratios. The mechanical properties of HDPE : PP blends gave higher values compared to LDPE : PP blends.[85]

Ayesha Kausar et al. prepared blends of polyamide and PMMA. The polyamide was prepared by the condensation of 1, 4-phenylenediamine and 1, 5-diaminonaphthalene with isopthaloyl. They studied the properties of the blends like mechanical, thermal, and morphology. The high strength of 51-58MPa was calculated for these blends due to ample adhesion between the blend constituents. The morphology was also changed from ellipsoidal to circular spheres. The Tg of blends was between 67-81, lower than the pure polymer. The thermal stability increased 10% for the blends. These cylindrical/spherical nanoblends are easy to process and can be used for industrial applications.[86]

S. Shabbir et al. functionalized PS with amino groups to form amino-substituted polystyrene (APS). Then they formed the blends of PS/SEBS-g-MA and APS/SEBS-g-MA. They compared the properties of these blends. The APS showed compatibilizing effect and these blends had better and improved properties than PS/SEBS-g-MA blends. The prime properties like thermal, mechanical and morphology were observed for 20 wt% APS blends.[87]

A.Enotiadis et al. prepared the nanocomposites of SIS block copolymers with 1 and 5 wt. % addition of nano-additives of modified clay-carbon nanotubes. The catalytic chemical vapor deposition (CCVD) method was used for the preparation of nano-additives. The surface of smectite clay nanolayers was used for the growth of carbon nanotubes. The characterization techniques like FT-IR and Raman spectroscopy were used to confirm the presence of hybrid nano additive in the nanocomposites. XRD and TEM confirmed the exfoliation of the clay. The uniform dispersion and inclusion of nano-additives were verified by the viscometry measurements. These nanocomposites showed the better and modified mechanical properties. Strain at the break and tensile strength were enhanced due to good interfacial adhesion of clay-CNT hybrid of elastic rubbery polyisoprene blocks of SIS copolymer matrix.[88]

GUILLERMO JIMENEZ et al. prepared the blends of modified MMT clay with PCL [poly (e-caprolactone)] by solution mixing. The isothermal crystallization results showed that small amount of nanoclay in the blend promoted the crystallization of the PCL while the large amount reduced it due to agglomeration. The SAXS and WAXS analysis showed that silicate layers were not completely dispersed in PCL blends. So the solvent mixing method did not show good results for these blends.[89]

Xie et al. synthesized the Polystyrene/MMT nanocomposites by suspension polymerization. XRD and TEM studies confirmed the exfoliation of silicate layers and clay dispersion in polymer phase. 5 wt. % addition of clay showed improved thermal stability and 7.5 wt. % clay enhanced the mechanical property.[90]

Arlette Vega-Gonza´lez et al. precipitated biopolymers and PMMA/PCL blends by using supercritical carbon dioxide antisolvent method ($SCCO_2$), for biomedical application. This technique is used to make fibrous networks of blend components of PCL and PMMA polymers. The flow rate, liquid solution and nozzle design had an influence on the properties and morphology of the polymeric blends. The fibers having an area in the order of 100–400 m^2 g^{-1} and uneven textured surface were precipitated out. These materials can be used for tissue engineering as they showed a biomimetic approach.[91]

P. Sergio et al. studied the effect of the solvents on the morphology of HIPS/clay nanocomposites. They used the chloroform and toluene/chloroform solvents. The clay (MMT) composition was varied from 1 to 3 wt. %. The results showed that the nanocomposites prepared in toluene/chloroform (1:1) solution were more likely to be exfoliated and homogeneous than in chloroform solvent. The nanocomposites in toluene/chloroform solution had higher degradation temperature and better dispersion of the organic nanoclay. The 3 wt. % clay denied the effect of the solvent and the thermal degradation temperature (TGA analysis result) was the same for the nanocomposites prepared in different solvents. The overall experimentation proved that the use of solvent pair (toluene/chloroform) is better than the single solvent for improved properties of the blends and fine dispersion of the organoclay in polymer phase.[92]

K. Mohan Bbaul et al. prepared the nanocomposites of polyoxymethylene with cloisite organoclay. They prepared the nanocomposites by extrusion technique and used the twin extruder for the mixing of the polymer and clay (1%, 3%, 5% clay). The final product was obtained by the injection moulding process. SEM studies confirmed that the 1% clay addition showed the better mechanical properties than 3% and 5% clay content. In this case, the thermal stability was decreased by the addition of organoclay. Mechanical testing showed that the low concentration of clay had better tensile strength. This was due to the immiscibility of the polymer and clay on increased clay content and poor interfacial interaction due to agglomeration.[93]

Ş. TÜZÜNER et al. synthesized the PS-co-PMMA/Ag nanocomposites. Firstly, they prepared the Ag nanoparticles by the reduction of $AgNO_3$ through $NaBH_4$ in aqueous solution. These particles showed high crystallinity confirmed by the XRD. They also prepared the nanoparticles of Ag/CTAB. They prepared the PS/PMMA blends by solution mixing using THF. They mixed the Ag/CTAB nanoparticles in PS/PMMA blend solution. The films of nanocomposite were prepared by moulding the dispersion mixture on glass slide using the micropipette. The nanoparticle addition showed better thermal stability and fine morphology. The particles tended to stay on PMMA surface of the blend proved by the SEM studies.[94]

Z. Špitalský et al. reported the molecular dynamic study of SIS/expanded graphene nanocomposites. These composites were prepared by the solution method using toluene as a solvent. First the expanded graphene was sonicated in toluene for 20 minutes then 1 to 10% varied amount of graphene was added to SIS solution. This solution was stirred for 24 hours. Thermal analysis showed the decreased in thermal stability on the increased amount of graphene. The mechanical analysis showed the increased tensile strength for 1% graphene content. The storage modulus was increased significantly for 8% graphene addition in SIS solution. DC conductivity showed small increase in conductivity, at low concentration, without formation of continuous conducting path. The conductivity was increased by 5% graphene as the conductive path was formed. WAXS studies proved that this phenomenon can be affected by the little interactions between the polymer and filler. [95]

Botan et al. prepared the PS/kaolinite (Kao) nanocomposite by in-situ emulsion polymerization. Firstly kaolinite was modified by DMSO, a displacement method (Kao–DMSO). After then styrene monomer was intercalated in kaolinite. The nanocomposites with 1 and 3 % clay content were prepared. The results of Flame retarded test showed that the 3% clay on nanocomposites had reduced burning rate by 50% compared to pristine PS. For 3% clay content on nanocomposites, thermal degradation was started 20°C higher the temperature of initial degradation of pristine PS. [96]

George et al. used the nano kaolinite as competent reinforcing agent for PS/HDPE blends. With the addition of 2 wt. % clay, the mechanical properties were enhanced. The blends with clay showed higher storage modulus than the modulus of neat blends. Tg was increased for compatibilized nanocomposites. The fibrillar morphology due to addition of clay was identified by SEM analysis. [97]

Elbokl et al. synthesized the intercalated nanocomposites via free radical-initiated polymerization reaction of styrene and a Kao-DMSO. The one layer of PS completely substituted DMSO molecules in the interlamellar spaces of kaolinite clay. The intercalation of PS into the inter-lamellar spaces of Kaolinites clay was confirmed by the XRD analysis. The nanohybrid degraded at the temperature of 300°C in air, maximum exotherm at 370°C. [98]

Mingzhe Xu et al. prepared the PS-co-PMMA/Na-MMT composites by emulsion polymerization with reactive surfactant AMPS. The XRD analysis confirmed the exfoliation of the MMT clay and TEM results confirmed the nanostructures of the clay in copolymer. The clay content was varied from 1 wt. % to 5 wt. %. The 3 wt. % clay content showed 7% increase in decomposition temperature as compared to other samples and 30% storage modulus as compared to neat polymer. As clay has a thermal barrier property.[99]

Abdallah et al. determined that electrical properties of PS/kaolinite were affected by some procedures like electron hoping, ion diffusion and space charge polarization through composite microstructure development. The electrical and optical properties of PS/kaolinite composite with 20 wt. % clay (grain size; 63, 106, 212 and 300 µm) and pristine PS were studied. The optical absorption spectra were found in wavelength of 300-800nm. The energy tail width and optical energy gap were changed with kaolinite grain size. AC impedance measurements were used for electrical properties, at frequency of 100 kHz^{-1} MHz and different temperatures.[100]

A. Ibrahim et al. prepared the blends of PS and ABS poly (acrylonitrile-butadiene-styrene) of different compositions by melt extrusion method using a single screw extruder. They investigated the mechanical and thermal properties of blends. The blends with the ratio of 70/30, 60/40, 50/50 of blends of PS/ABS showed better mechanical properties than other blend compositions and pure polymers. DSC analysis confirmed the miscibility of the blends by showing single Tg for all compositions of blends and Tg value decreased by increasing the content of ABS polymer in the blends.[101]

Hausner et al. prepared the nanocomposites of PS and modified synthetic Na-fluorohectorite ($[Fe (bpy)3]^{2+}$ and C18) clay. These nanocomposites enhanced the fire, thermal and gas barrier properties. The improvement in the properties was due to redox and thermal properties of $[Fe (bpy)_3]^{2+}$. The good thermal stability, char forming properties and good fire activity was shown by the $[Fe (bpy)3]^{2+}$ -Hec portion of clay. The 3.0 ±0.2g residue amount was given by the PS-$[Fe (bpy)3]^{2+}$-Hec nanocomposite that justly associated the inorganic matter of nanocomposites and showed little for char creation. Comparatively high 3.8± 1.0g residue amount was shown by the PS-C18-Hec nanocomposite.[102]

Voulgaris et al. used dimethyldioctadecylammomiumhectorite (DMDO-Hect) as emulsifier, organically modified clay, for immiscible PS/PEMA polymer blends. The organoclay was absorbed on PEMA chains and intercalated structures of PEMA/DMDO-Hec were formed. In these structures, PS chains were formed as separate domains. DSC thermograms showed a single Tg value that confirmed the emulsifying action of the organoclay.[103]

L. Ferguson et al. studied the effect of solvent on the nanocomposites of SIS and PS-co-PMMA polymers with SiO_2 by solution mixing. They used the pair of solvent THF/$CHCl_3$ along with ethanol. SIS/SiO_2 and PSMMA/SiO_2 nanocomposites did not show any improvement when they were prepared in THF/$CHCl_3$ solvent. But the improvement in the properties, thermal and mechanical, of these nanocomposites was observed by the addition of 1 g of ethanol to THF/$CHCl_3$ solvent.[104]

1.21 Present work

Copolymers have controlled surface structure as compared to polymer blends. Their properties are totally different from the blends and pristine polymers. Their properties can be modified by changing the concentration of structural units. Copolymers have extensive applications in many areas; as adhesives, coatings, biosensors and lubricants. The copolymer SIS, a thermoplastic terpolymer, is an elastomer used as an adhesive sealant, pressure sensitive, hot melts. This copolymer has glassy-rubbery-glassy domains and highly flexible.

PS-co-PMMA (PSMMA) is a block copolymer and can be used as a compatibilizer. In this copolymer, both the components are glassy. This can be used for lenses, bullet-proof security barriers and skylights.

The formation of SIS/PSMMA blends is a novel approach. In the present work, the properties of individual terpolymer have been tuned up by the addition of another copolymer. The stress point of SIS has been increased by the addition of PSMMA polymer. While the toughness of PSMMA has been increased due to SIS polymer. As these blends have shown partially immiscible behaviour, so they were compatibilized by the addition of nanoclay, kaolinite, that leads to the formation of nanocomposites. These nanocomposites can be used in packaging material due to hydrophobic property of nanoclay.

The plentiful mineral of kaolin group is kaolinite, it includes halloysite, nacrite, dickite and hydrated analogs. The kaolinite, (Al_2 Si_2 O_5 $(OH)_4$, the structure is made up of Si_2O_5 sheet bound by aluminum cations that are coordinated by OH-groups. Some of the OH-groups are replaced by O_2 of Si-O sheet. These layers are held together via H-bonding, van der Waals forces and dipolar interactions. These interactions are responsible for little intrinsic inner surface reactivity. The molecular weight of kaolinite is 258.10 g/mol, having 46.55% SiO_2, 39.49% Al_2O_3 and 13.96% H_2O. The spacing of kaolinite is 0.72nm.

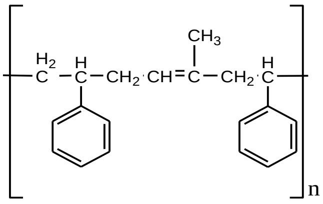
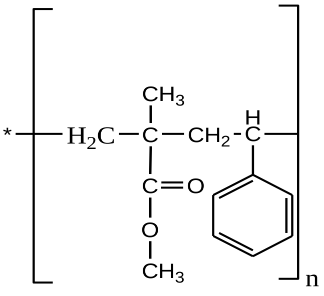
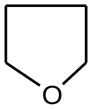
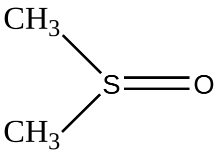
The compounds used for intercalation of kaolinite layers are formamide, urea, *n*-dodecylamine, dimethylsulfoxide (DMSO), deuterated DMSO, methanol, hydrazine, *N*-dimethylformamide (DMF) and potassium acetate. These compounds directly intercalate between the layers of kaolinite. It is used in many industrial applications such as in the ceramic industry as a whitening agent, in the paper industry as filler. It is used as a filler in cosmetics, rubber, pharmaceutical and paint applications. It has a tendency for making new nanocomposites as it is cost effective as compared to MMT clay.

CHAPTER 2

EXPERIMENTAL

Polymer blends and nanoclay composites are prepared by the solution blending method. To form the blends of SIS (terpolymer) and PSMMA (copolymer), polymers were mixed with different concentrations. After the preparation of blends, their properties were studied.

Table 5: List of chemicals is given below:

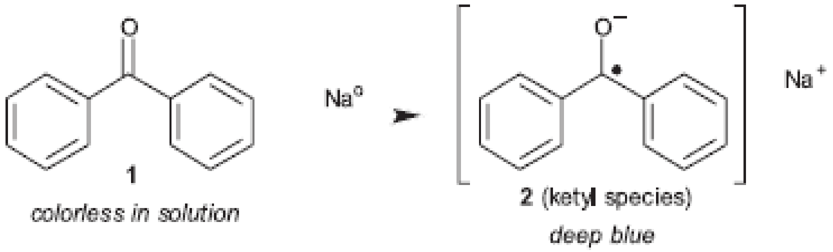
Chemical name	Abbreviation	Chemical structure	Supplier	Purity(%) or mol.wt
Polystyrene-b-polyisoprene-b-polystyrene	SIS		Aldrich	22 wt. % styrene
Polystyrene-co-polymethylmethacrylate	PSMMA		Aldrich	100,000-150,000 44 wt. % styrene
Tetrahydrofuran	THF		Merck	>99%
Dimethylsulfoxide	DMSO		Merck	99.9%
Kaolinite clay		$Al_2Si_2O_5(OH)_4$		258.16mg
Chloroform		$CHCl_3$	Merck	99%

2.1 Drying of THF solvent

It is necessary to distil or dry the THF to eliminate the impurities from it. The sodium-benzophenone is used to remove the oxygen, peroxides and moisture from organic solvents (diethyl ether and THF) especially from tetrahydrofuran (THF).

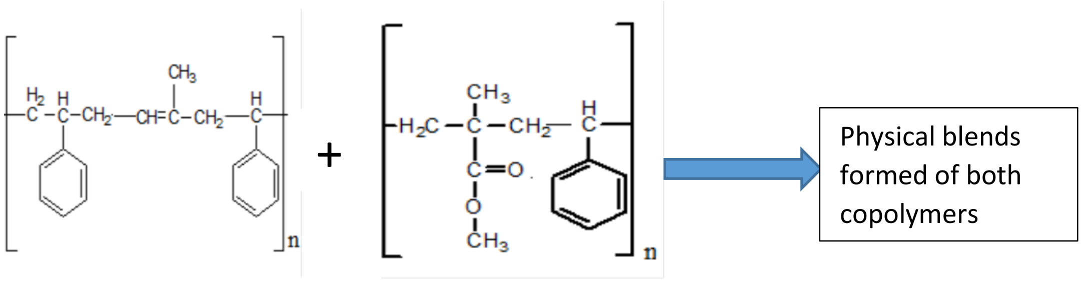
By reduction of the carbonyl with Na-metal, the benzophenone ketyls are formed as radical anions. This ketyl anion is of deep blue colou readily reacts with oxygen, water and peroxides in organic solvents. The deep blue colour is the indication of oxygen free and dry conditions.

For drying of THF 20g benzophenone (indicator), 4g Na-metal and 300ml THF were taken in three neck round bottom flask. The flask was kept in the oil bath for even heating of the contents in the flask. The temperature was 220°C. On the one neck of the flask, the collecting funnel was attached for the collection of dry THF. The collector was attached to the condenser for refluxing of THF. When solution turned deep blue, THF was collected in the collector. The whole process took 3 hours for drying. The reaction is given below:



2.2 Preparation of SIS/SMMA blends

Various blends of SIS/SMMA were prepared in different proportions, in dry THF solvent. These were mixed by continuous stirring for 72 hours at room temperature. Constant and uniform stirring is important for the proper mixing of polymers for blend preparation. Films of different concentrations of blends (0% to 100% SIS) were cast by pouring the blends in petri dishes on a leveled surface. The solvent was evaporated at room temperature. Then films were placed in a vacuum oven for 72 hours. Vacuum drying was done for the complete removal of solvent for better results of desired properties. The films of 0.16mm-0.40 mm thickness were made.



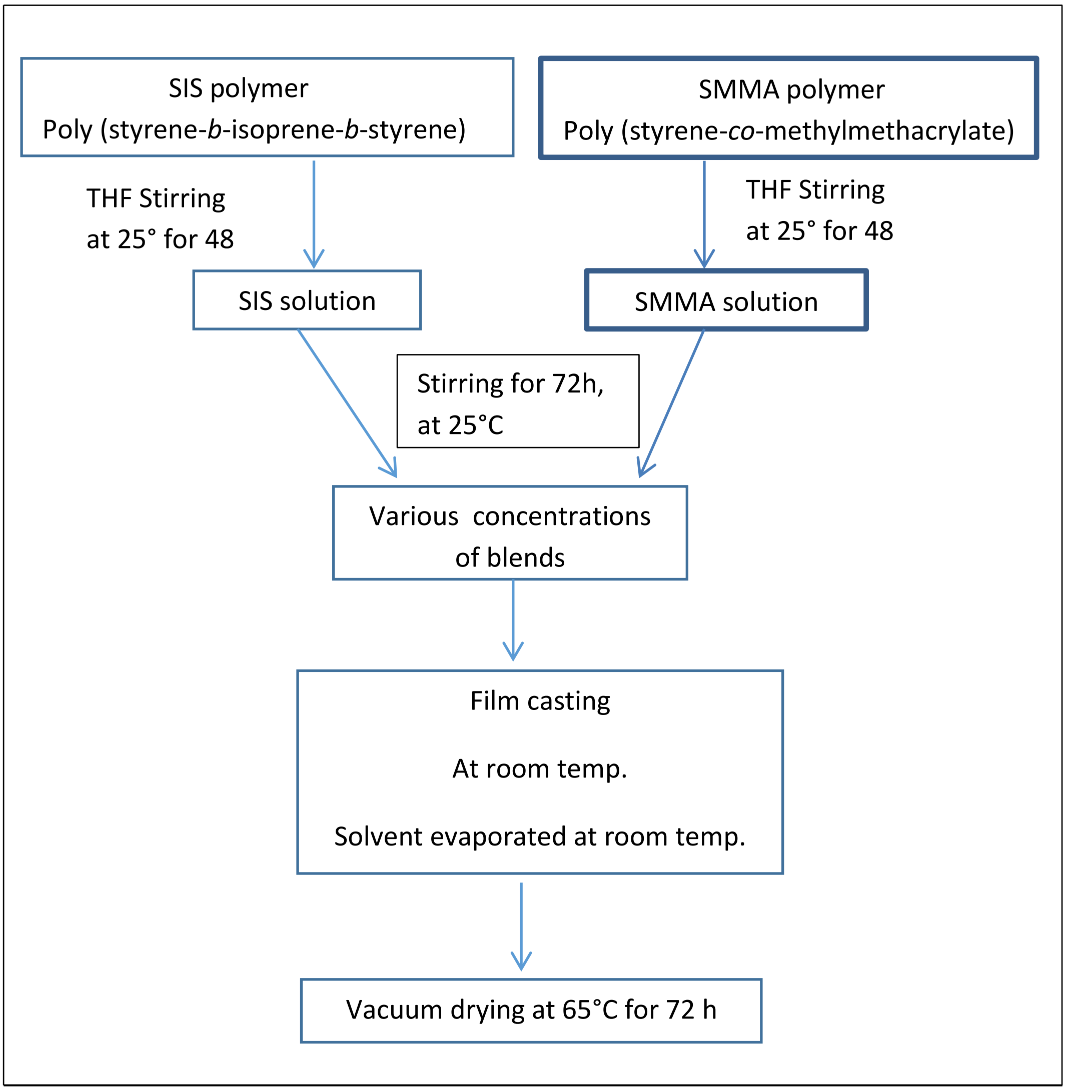


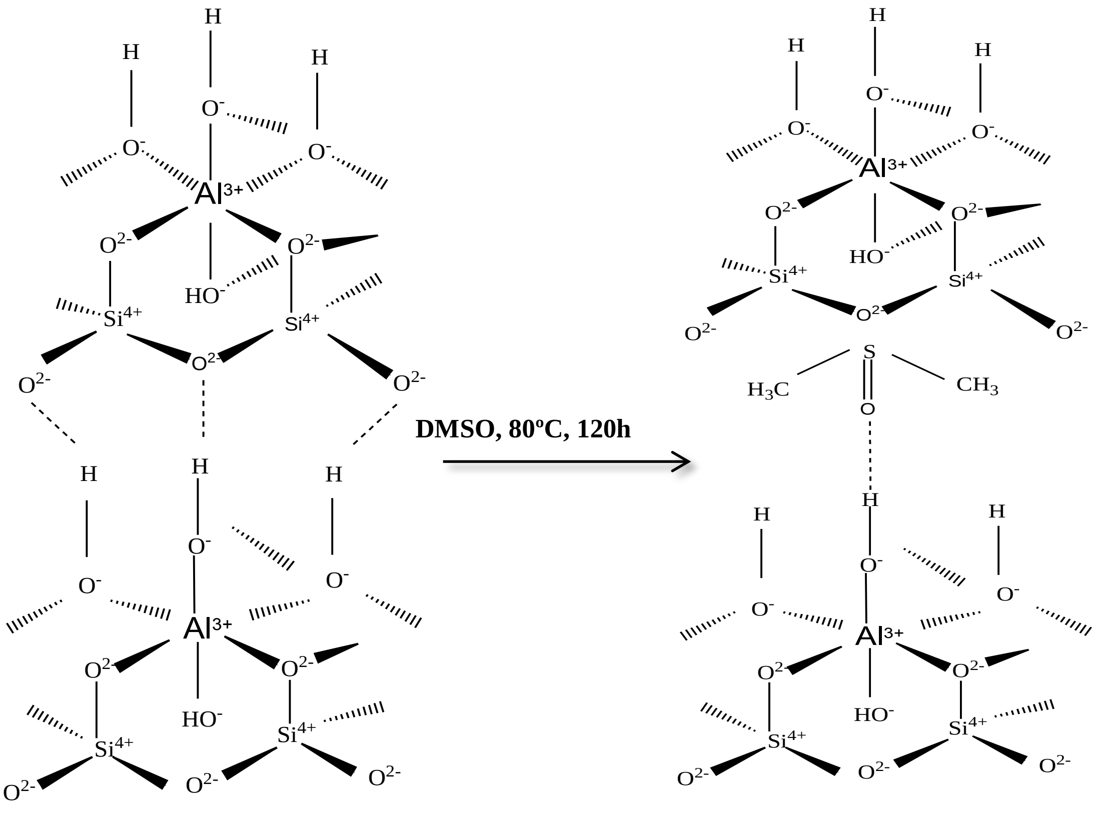
Fig. 2: Flow sheet diagram of SIS/SMMA polymer blends preparation.

2.3 Polymeric nanocomposites

Nano-composites of clay and polymer were prepared at room temperature by varying the proportion of the exfoliated clay in polymeric blend solution of fixed composition. Different solvents were employed for their preparation and solvent effect was also studied along with other properties of nanocomposites.

2.3.1 Exfoliation of the Kaolinite clay

Bulk kaolinite soaked in DMSO solvent at 80°C for 120 h. and sonicated for 30 min for better and maximum exfoliation of clay. Exfoliated clay was filtered, washed with methanol and dried at 100°C for 24 h. The resulting treated clay is known as Kao-DMSO precursor.



Kaolinite clay

Kao-DMSO (kaolinite DMSO)

Exfoliation of Kaolinite

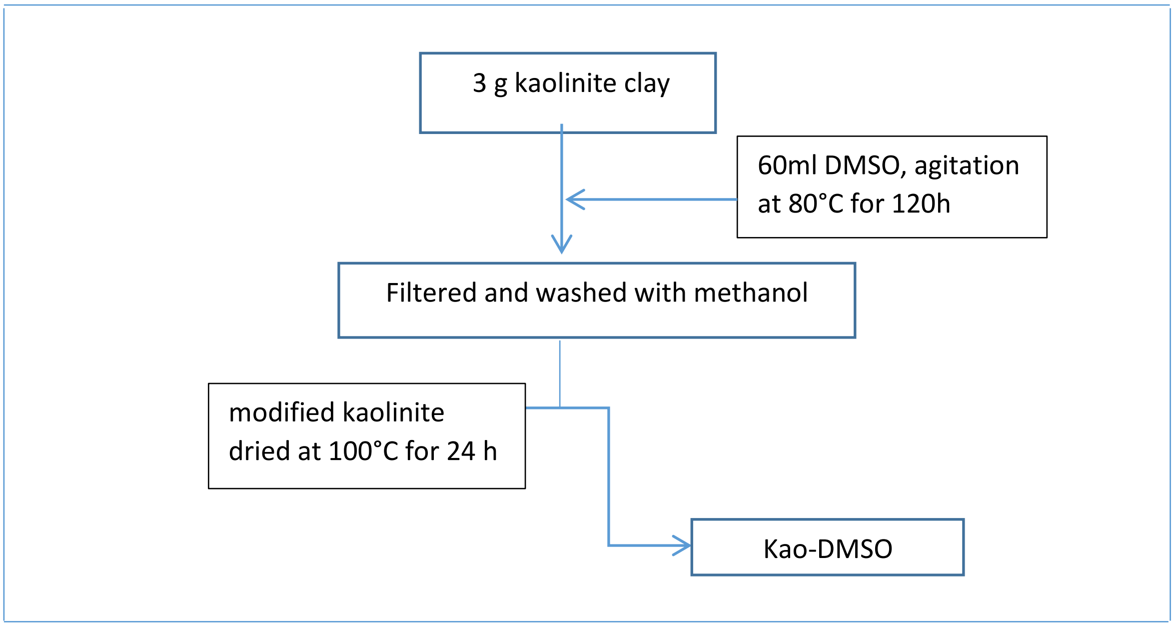


Fig. 3: Flow sheet diagram of exfoliation of kaolinite clay

2.3.2Preparation of nanoclay composites

i) In THF solvent

The ratio of SIS/SMMA (20/80%) blend that had previously exhibited good properties was further employed for the preparation of nano-clay composites by adding varying amounts of (0.01-0.05g) of exfoliated kaolinite clay while THF was used as a solvent.

Firstly, clay was sonicated for 2 h for uniform dispersion Afterward 20/80 wt. % SIS/SMMA polymers were added to the solution and uniform stirring was done at room temperature for 72 h. The solution was poured into Teflon petri dish for film casting in and the solvent was evaporated at room temp. Subsequently, films were placed in a vacuum oven at 70°C for 72 h. The dried films were used for further analysis

ii) In Chloroform

Another series of nanoclay composite blends were prepared by using the chloroform as a solvent with varying amount of clay (0.01-0.05g) added in 20/80% ratio of SIS/SMMA polymer blend. Firstly, clay was sonicated for 2 h for uniform dispersion.

Afterward 20/80 wt. % SIS/SMMA polymers were added to the solution and uniform stirring was done at room temperature for 72 h. The solution was poured into Teflon petri dish for film casting in and the solvent was evaporated at room temp. Subsequently, films were placed in a vacuum oven at 70°C for 72 h. The dried films were used for further analysis.

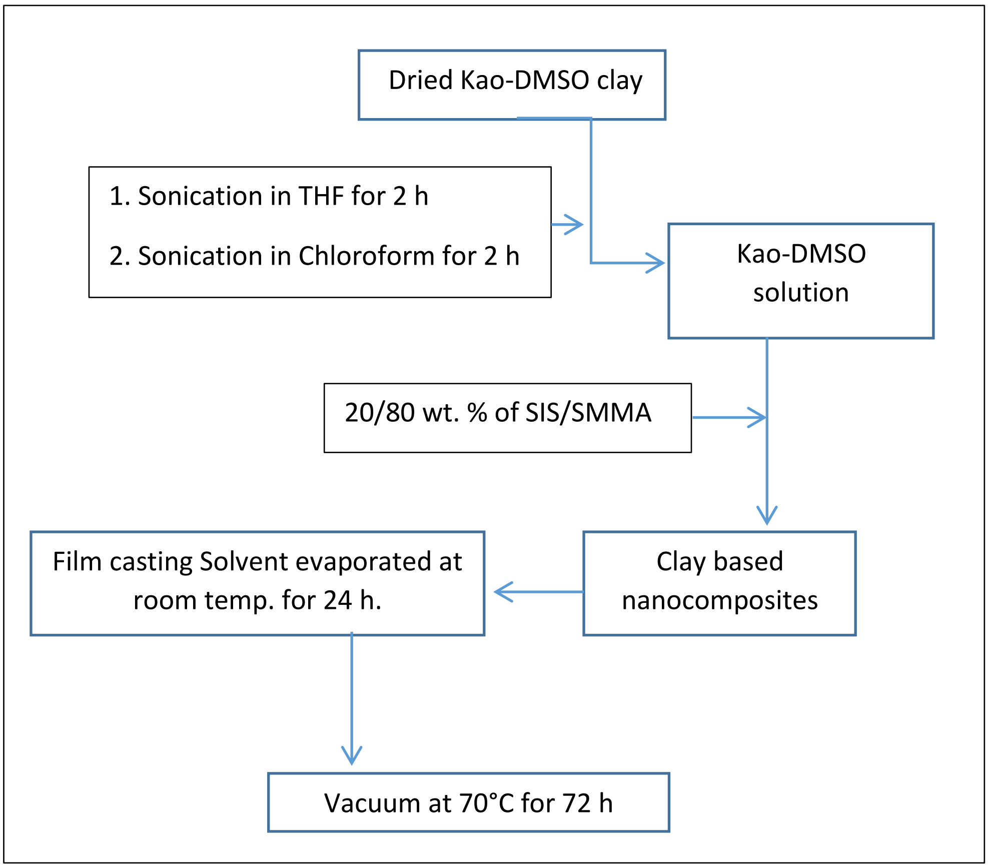


Fig. 4: Flow sheet diagram for the preparation of clay-based nanocomposites.

2.4 Characterization of Blends and Nano-composites

2.4.1 X-Ray Diffraction

X-Ray Diffraction is rapidly used the analytical technique used for the crystalline materials to identify the phase and information about unit cell dimension. The material should be finely ground and homogenized.

Bragg's Law $\mathbf{n}ʎ\mathbf{= 2}d\ \mathbf{sin}\ \boldsymbol{\theta}$ should be satisfied during the interaction of incident ray with sample and yields constructive interference and diffracted ray.

About 95% of solid material classified as crystalline. When there is an interaction between the x-rays and crystalline material, a diffraction pattern is obtained. Due to this, the diffraction pattern is the like fingerprint of the sample. So, this technique is ideal to identify and characterize the polycrystalline phases. The area under the peaks is related to the quantity of each and every phase present in the sample.

Solid matter can be classified as

- **Amorphous:** Random arrangement of the atoms like in liquid i.e., some polymers (Polystyrene-*co*-polymethylmethacrylate) and glasses.
- **Crystalline:** Regular pattern of the atoms and smallest volume element (unit cell) repeats in three-dimensional to form a crystal. Three axes a, b, c, and angles between them alpha, beta, gamma determine the dimensions of the unit cell.

XRD analysis is used for

- Identification and investigation of high/low-temperature phase, unit cells of new materials and solid solution.
- Polymer crystallinity: As a polymer can be partly amorphous or crystalline. The crystalline portion gives sharp narrow peaks and broad peak (halo) is given by the amorphous portion. The crystallinity of material is calculated by the ratio of intensities (of the crystalline and amorphous portion).
- Residual Stress: The stress remains in the material after external force.
- Texture Analysis: It is preferred arrangement of crystallites in polycrystalline aggregates.[105]

2.4.2 FT-IR Spectroscopy

A molecule possesses rotational, electronic, vibrational energy levels. These energy levels are responsible for the internal energy of the molecule. The interactions between the matter and electromagnetic waves (EM waves), in IR region, is studied by the Infrared Spectroscopy. When these waves are being absorbed by the molecules, the molecules are excited to higher vibrational state. The chances of a specific IR frequency absorption depend on the interface between the molecule and IR frequency. If the vibrational energy level of the molecule and the photon energy of the frequency match then the high frequency will be absorbed. This technique gives the fingerprint knowledge about the chemical composition of the sample in accordance with Beer-Lambert Law.

Polymeric materials are used on a large scale in many fields either the packaging industry or medical and aerospace technologies. FT-IR is used for the determining the composition of a polymeric material by measuring the infrared spectra.

FT-IR (Fourier Transform Infrared) spectroscopy in association with attenuated total reflectance (ATR) is beneficial for the analysis of polymer material. ATR is an accessory having a single reflection Zinc Selenide (ZnSe) or diamond ATR crystal used for the analysis.

ZnSe is useful for the analysis of the soft and flat polymeric material while diamond is attuned with all kind of polymer material either of irregular shape or rigid sample because it cannot be spoilt or scratched by applying high pressure on polymeric material.[105]

2.4.3 Mechanical Properties

Polymers are mostly viscoelastic materials and they come in the category between the elastic solids and viscous liquids.

Hooke’s law; stress is proportional to stain is obeyed by the ideal linear elastic material while Newton’s law; stress is proportional to the rate of change of strain is fulfilled by viscous liquids.

A polymer may act like a glass with Young’s modulus of $10^9 N/m^2$ to $10^{10} N/m^2$ at high frequency or low temperature and will break at strain higher than 5%. But at low frequency or high temperature, the very same polymer can show rubber-like behaviour having a low modulus of $10^6 N/m^2$ to $10^7 N/m^2$ and no permanent change with 100% or larger extension.

If there is intermediate frequency or temperature range then polymer will neither glassy nor rubbery having an intermediate modulus and viscoelastic and may release a significant amount of energy on being strained. Even at high temperatures, a polymer still acts like highly viscous liquid.[106]

i) Stress and Tensile Strength

During the mechanical testing, the each end of the sample is clamped in the machine and it is stretched when the machine is turned on. The amount of force (F) exerting on the sample (during stretching) is measured. So by this, stress is calculated by the force (exerting on the sample) divided by the cross-section area (A).[107]

$$\textbf{Stress = F/A}$$

Force is continuously increased and the stress on the specimen unless it breaks. The tensile strength of the material is the stress required to break the sample. The tensile stress and strength both are measured in the unit of F by a unit of A, N/cm^2. The units gigapascals (GPa) and megapascals (MPa) are used for stress and strength. As 1 MPa = $1N/mm^2$ or $100N/cm^2$ while 1 GPa = 1000 MPa or $100{,}000N/cm^2$.

ii) Strain and Elongation

Elongation or deformation is a change in the shape of the sample under applying stress. As in tensile stress, the sample elongates (longer) or deforms by stretching. Elongation is dimensionless property.

$E= \Delta L/L_o$ L_o is original length and L_f is final length

$\Delta L= L_f-L_o$

$E= (L_f-L_o)/L_o$ and $e\% = [(L_f-L_o)/L_o] \times 100$

The ratio of change in length (extended length) to the original length of the specimen is known as strain or length at rupture.

The percentage elongation (e%) is the length of polymer sample after stretching divided by the original length of the sample and multiplied by 100.

iii) Modulus

It is a mechanical property of material about resisting deformation. Strength and the ultimate elongation is required to measure the tensile modulus.

A plot of stress and strain is formed as:

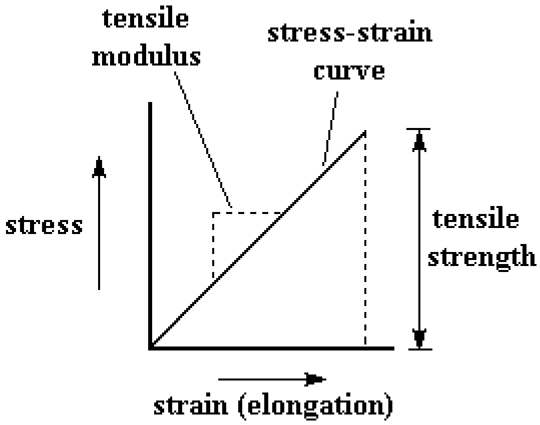


Fig. 5: A conventional stress-strain curve

This graph is known as a stress-strain curve. Strain and elongation (tensile strain) are types of deformation. Tensile strength is the height of the curve when sample breaks and the slope is the tensile modulus. The steep slope indicates the high tensile modulus (resists the deformation) and a gentle slope indicates low modulus (easily deformed).

In case of flexible plastic polymers, the stress-strain curve is not straight or slope is not constant as stress increases. The modulus (slope) changes with stress so the initial slope is taken as modulus in such condition.

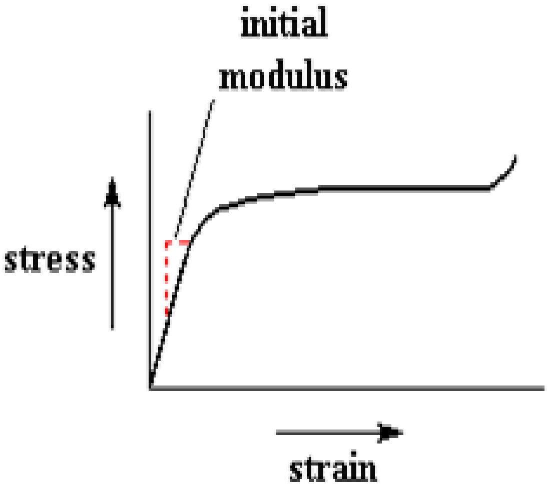


Fig. 6: A stress-strain curve for plastics

Elastomers have the lowest modulus, fibers have higher and plastics are in between the elastomers and fibers. Modulus unit is N/cm^2.

Modulus can be calculated, using the formula given below, from the initial slope of the stress-strain curve as:

E= Stress/strain to the limit of proportionality

It is also known as the stiffness of the material, the measure of interatomic bonding forces. Measuring the deformation during applied force is known as strain.

iv) Toughness

Toughness is the area under the stress-strain curve. It measures the energy being absorbed by the sample before breaking.

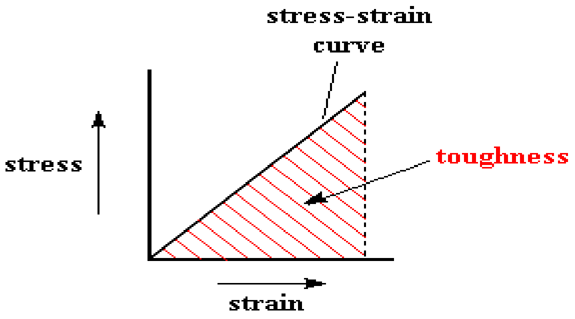


Fig. 7: Area under stress-strain curve showing toughness

Toughness is different from strength as strength tells about the force required to break the sample while toughness tells about the energy required to break the sample. It is not a rule that if the material is strong then it would be though as well.

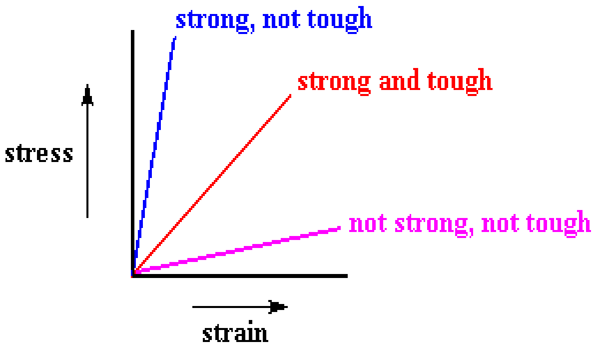


Fig. 8: Stress-strain behaviour of polymeric materials

The very 1st plot is the stress-strain curve for a strong but not tough sample. It requires a lot of force to break but not much energy due to less area under the curve. It is a brittle material.

The 2nd plot for a sample of both strong and tough. It is not as strong as the first one but absorbs a lot of energy for breakage. This sample elongates more before breaking and deformation permits a sample to disintegrate energy.[106]

Toughness is measured by integrating the area under complete stress-strain curve up to failure point by using origin software.

2.5.5ThermalAnalysis

Thermal analysis is actually having a group of analytical techniques that are used for monitoring the properties of the sample against the temperature of time and in a definite atmosphere, the temperature of the sample is set or program-controlled.

Table 6: Thermal Analysis Techniques

TA Measurement Technique	Abbre viation	Property	Unit	Phenomenon / properties study
Differential Thermal Analysis	DTA	Difference Temperature	°C or µV	Exothermic and endothermic with TGA
Differential Scanning Calorimetry	DSC	Enthalpy	W=J/sec	Melting, glass transition, crystallization, reaction (curing/ polymerization), thermal history, specific heat capacity.
Thermogravimetr Analysis	TGA	Mass	Gram	Sublimation/evaporation/dehydration, thermal decomposition, reaction (curing/polymerization)
Thermomechanical Analysis	TMA	Deformation	Meter	Glass transition, reaction (curing/polymerization), thermal history, thermal expansion/thermal shrinkage, melting, crystallization
Dynamic Mechanical Analysis	DMA	Elasticity	Pa=N/m^2	Glass transition, crystallization, reaction (curing/ polymerization), thermal history

2.5.5.1 Differential scanning calorimetry

As a function of time or temperature, the heat flow of sample is measured by DSC. It quantitatively measures the chemical reactions and the physical changes.

Glass Transition: It is a generalized Ehrenfest type 2nd order transition between the glass and a liquid that is supercooled below its melting point. It is categorized by glass transition temperature Tg. Tg seems as a step in DSC and change of specific heat capacity C_p from solid to liquid phase is being shown by it.

It is a kinetic process: measured value of Tg depends upon the cooling rate, evaluation conditions and the thermo-chemical history of the sample. Tg will be lowered if the cooling rate is lower

It is a reversible transition happens when an amorphous material is heated or cooled in a specific temperature range. On cooling the brittle material is obtained like a glass (less flexible) and soft on heating.[108]

Plastics, organic polymers, glasses, semi-crystalline even the completely amorphous solids or polymers exhibit the glass transition.

Following physical properties change happen at Tg temperature

- Dielectric constant
- Coefficient of thermal expansion CTE (can also be measured by TMA)
- Mechanical modulus
- Specific heat capacity C_P

2.5.5.2 Thermogravimetry Analysis

This technique is being used for the measurement of the mass of sample when it is heated, kept isothermally or cooled in a specified atmosphere. It is a quantitative analysis. The mass loss step is related to the loss of volatile components (solvent, monomer, moisture) combustion of carbon black, decomposition of polymer and final residues (ash, glass fibers, filler) is shown by the TGA curve.

DTG curve is the 1st derivation of TGA curve with respect to the time and it is proportional to the rate of decomposition of the sample.

So, the chemical bonds break and polymers or intricate (complex) compounds decompose, in a decomposition process, to form water, hydrocarbons or carbon dioxide (gaseous products). If the condition is inert (non-oxidizing) then the organic material can also be degraded by forming the carbon black. TGA with FT-IR or MS (mass spectrometry) can be used to identify volatile decomposition products.[108]

2.5.6 Scanning Electron Microscopy (SEM)

The particle size, its distribution and the fractured surfaces are being examined by the SEM. It consists of electron gun as a source of electrons having an energy range of 1 to 40 keV. A small focused beam, produced by electron lenses that reduce the diameter of the electron beam, is placed on the specimen. During the interaction of the beam with the surface region or fractured surface of the sample (to the depth of 1-micron meter) the generated signals are used to form the image. If the beam size is small then the resolution of the image would be better and less current is required for a clear picture.

Fine tuning of the SEM is required for optimization of the picture with better resolution. In SEM vacuum is needed to avoid retarded resolution as beam interacts with the glass molecules. Most of the polymers are non-conductive so they may have changes in surface potential causing instabilities, astigmatism and false x-ray signals. Not only these but also a condition is known as charging in which charge gathers on the surface of the non-conducting sample resulting extreme brightness and gives bad quality images. To avoid such problems, the non-conducting samples are sputtered with fine layer of gold, copper or palladium.[109]

CHAPTER 3

RESULTS and DISCUSSIONS

3.1 XRD Analysis

The exfoliation of the clay was confirmed by XRD analysis. The Rigaku X-ray diffractometer was used, radiation source was Cu-Kα having the wavelength of 0.154 nm along with graphite monochromator in the 2θ range of 5°-40° with 0.05 step at a time count of 1 second. The diffraction analysis was done at room temperature under persistent conditions. The exfoliation of the clay is confirmed by the XRD result. The 001 is the characteristic peak for clay. The d-spacing of pure clay is 0.72 nm at 12° 2θ. When the clay is treated with DMSO solvent for exfoliation, the d-spacing was increased from 0.72 to 1.1063 nm. That 2θ value for 1.1603nm d-spacing is 7.98°. There was a little shift in 2θ and d-spacing when nanoclay composites were formed. The d-spacing for the nanocomposites is 1.09 nm and 2θ is 8.08°. The average crystallite size of nanoclay is 1nm while the particle size is 48.95 nm.

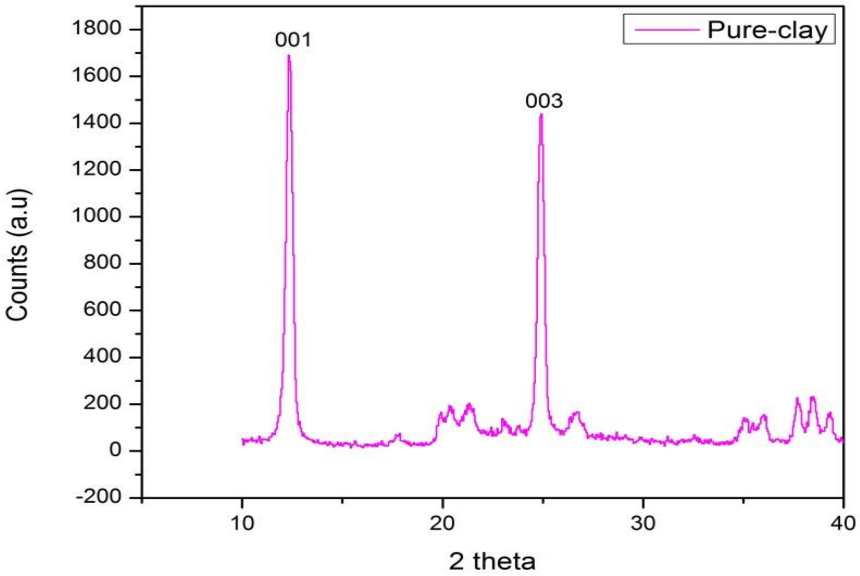


Fig. 9: XRD of pure Kaolinite clay

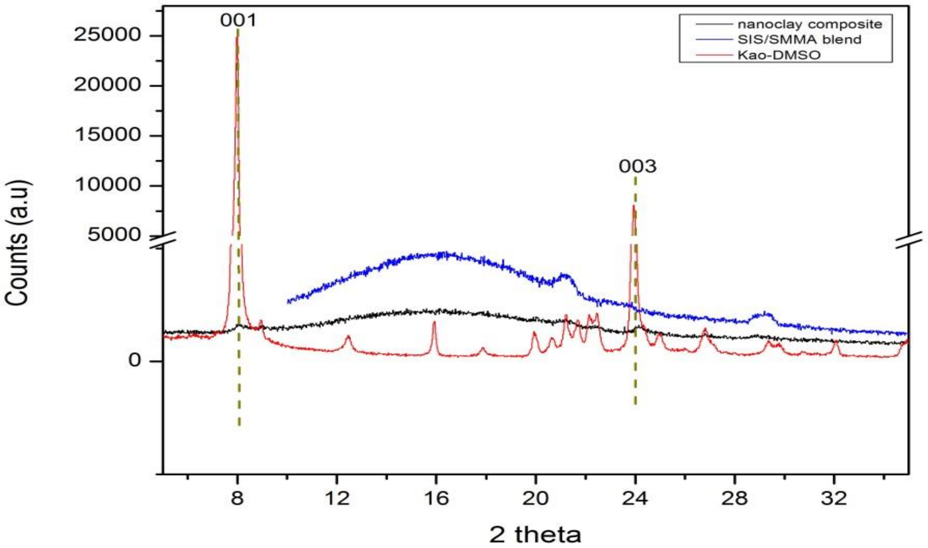


Fig. 10: XRD analysis of blend, exfoliated clay and nano-clay composite

3.2 FTIR Analysis

FTIR analysis was performed by using Alpha (BRUKER) Spectrophotometer in the range of 4000 cm^{-1} to 500 cm^{-1}. ATR technique provides useful surface information of a sample. The IR spectrum of pure polymeric films and blends were obtained. The IR spectrum confirmed the presence of the functional groups in pure polymeric films and in blends.

3.2.1 IR spectrum of PS-*co*-PMMA (SMM or SMMA)

The C-H stretch from H atom on aromatic ring was observed at 3030 cm^{-1}. The band at 2945 cm^{-1} confirmed the stretching of C-H from alkyl groups. The band at 1728cm^{-1} was observed due to C=O. C-O of ester and methyl groups were observed at stretch 1130 cm^{-1} and 1195 cm^{-1} respectively. The band at 1451 cm^{-1} confirmed the methyl group attached to the ester group. The band at 1600 cm^{-1} was due to carbons, C=C, in the aromatic ring. The band at 797 cm^{-1} was due to aromatic C-H bend.

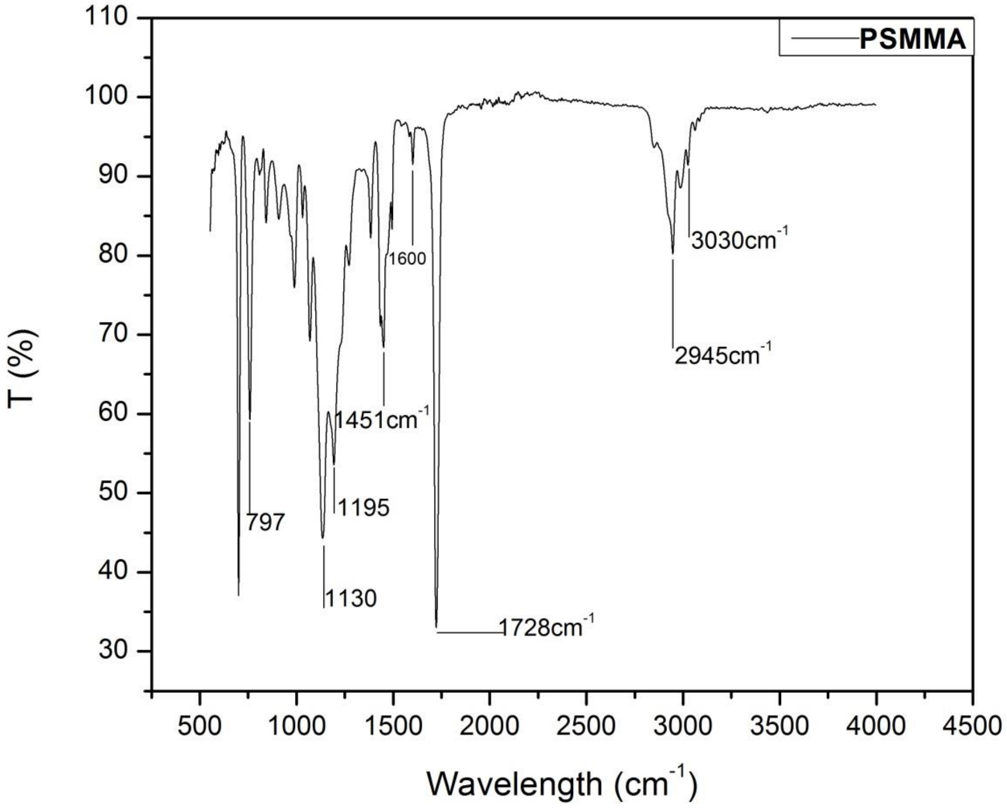


Fig. 11: IR spectrum of pure polystyrene-co-polymethylmethacrylate (PSMMA)

3.2.2 IR spectrum of SIS polymer

The band at 3030 cm^{-1} corresponded to the aromatic ring of polystyrene (PS) in SIS polymer. The bands appeared at 2977 cm^{-1} and 2916 cm^{-1} are assigned to C-H symmetrical and C-H asymmetrical stretching in aromatic ring respectively. The band at 2855 cm^{-1} was corresponding to C-H stretching vibration in aliphatic chain of SIS copolymer. Bands appeared at 1648, 1595 and 1441 cm^{-1} are assigned to C=C stretching in the aromatic ring, C=C stretching in alkenes and C-H bending in aliphatic chain of SIS copolymer respectively. The C-H in-plane and C-H out-of-plane stretching vibrations were observed at 1373 and 1014 cm^{-1} respectively. The band at 834 cm-1 was assigned C=CH$_2$ stretching vibration in SIS copolymer.

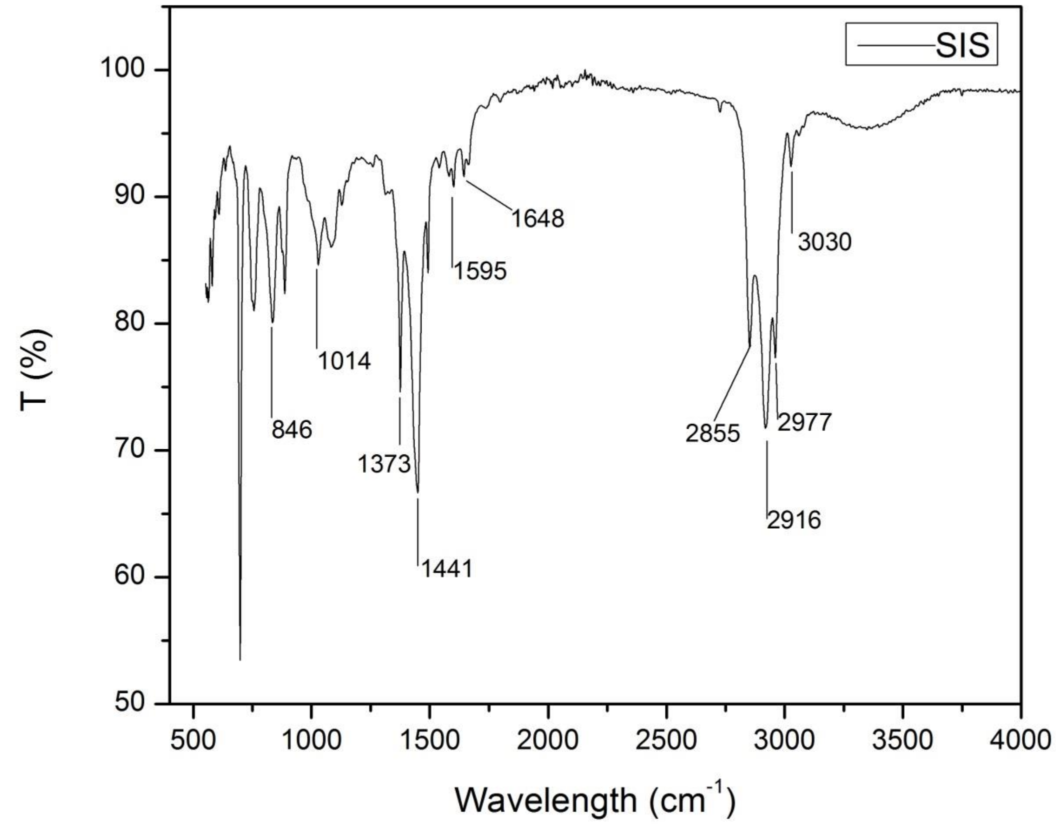


Fig. 12: IR spectrum of pure poly (styrene-b-isoprene-b-styrene) (SIS)

3.2.3 IR spectrum for blends

IR spectrum of the blends confirmed the presence of all the functional groups (mention above) present in individual polymers. The spectrum confirmed the physical mixing of polymers and formation of the blends.

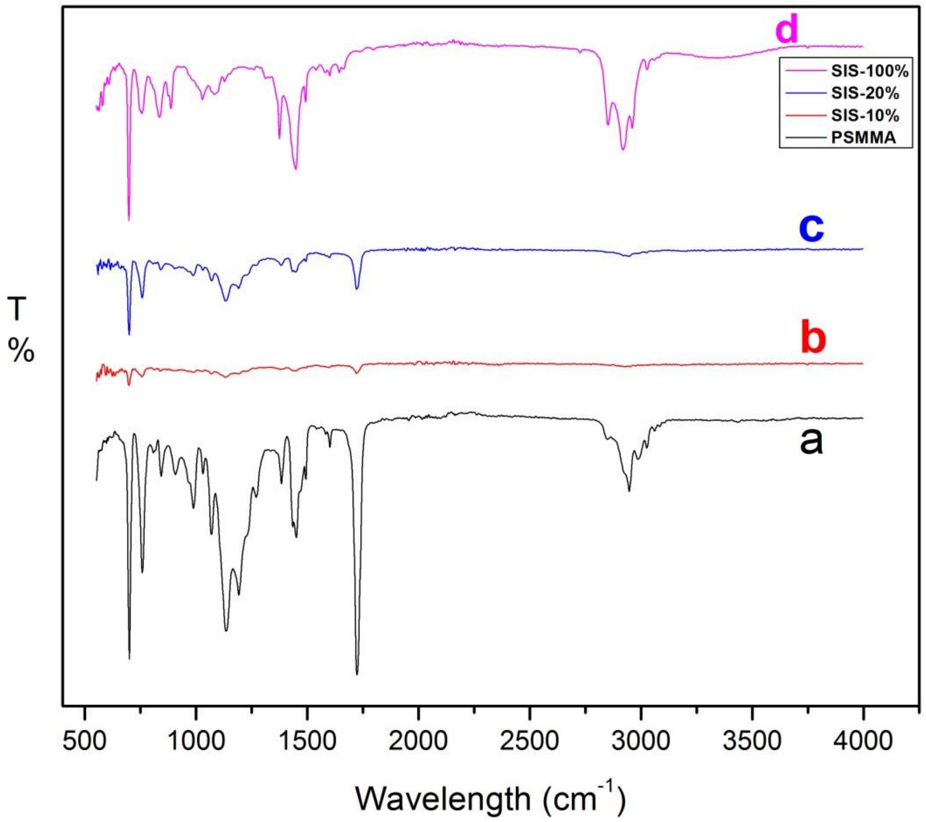


Fig. 13: IR spectrum of pure polymer (a=PSMMA, d=SIS) and SIS/SMM blend (b=10%SIS, c=20%SIS)

3.2.4 IR spectrum of Kao-DMSO clay

The IR spectrum of Kao-DMSO clay confirmed the presence of functional groups present in the clay. The bands at 3695, 3668, 3622 and 3539 cm^{-1} were due to interlayer stretching of –OH groups. The band at 1323 cm^{-1} was due to Al-O as –Si cage. The bands at 1120 and 1010 cm^{-1} confirmed the presence of Si-O stretching. The band of Al-OH bend was observed at 907 cm^{-1}. The bands at 760 and 677 corresponded to C-Si-C symmetric and C-Si-C asymmetric stretching respectively. The band position at 612 cm^{-1} was due to Si-O-Al stretching.

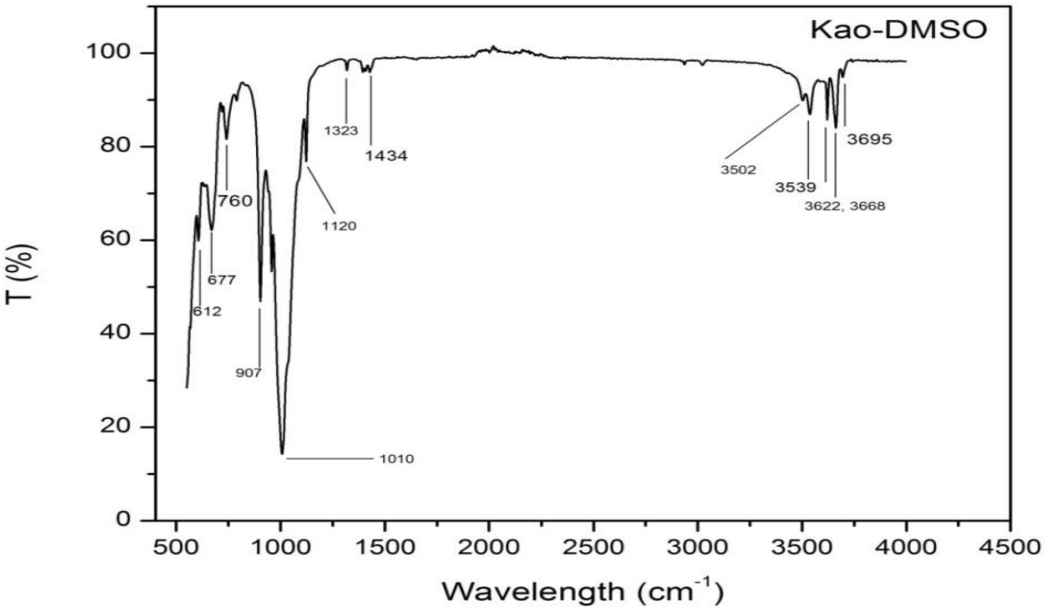


Fig. 14: IR spectrum of exfoliated Kaolinite clay (Kao-DMSO)

3.2.5 IR spectrum of nanoclay composites

The IR spectrum of nanocomposites showed bands of all the functional groups present in polymers and in nanoclay. There was no chemical reaction was observed as blends and nanocomposites were prepared by the physical method. Hence, physical interactions can be present among the blends and nanocomposites.

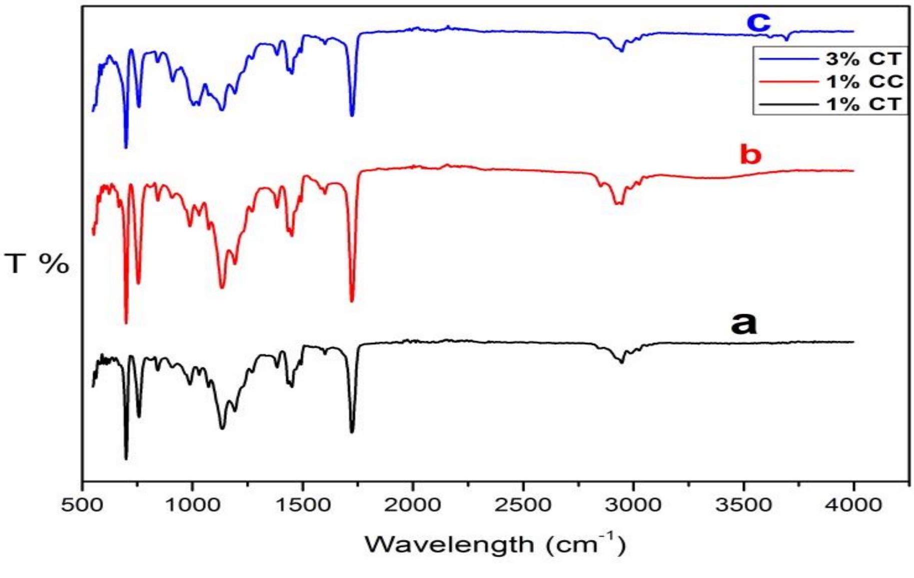


Fig. 15: IR spectrum of nanoclay composites(a=b=c=SIS/SMMA/Kao-DMSO nanocomposites)

3.3 Mechanical Testing of SIS/SMMA blends

To measure the mechanical properties of the blends the tensile testing was done for each blend and pure polymers. This test was carried out according to ASTM D882 by using SHIMADZU tensile testing machine available at SCME mechanical testing lab, NUST, at a strain rate of 5mm/min. The pristine SIS copolymer has Young's modulus of 34 MPa, strain 996.15% bearing the stress of 325 MPa. The area under the curve indicates the amount of energy required to break the film. For SIS copolymer, the area under the curve is 1046.95 that shows it requires a lot of energy to break the film but bears less stress. While the pristine SMMA copolymer has Young's modulus of 117 MPa, strain 5.99% bearing the stress of 19.56. This shows that SMMA is not very elastic but bears a large amount of stress as compared to SIS copolymer. The SIS copolymer on the addition of PSMMA polymer showed increased stress bearing property and reduction in the elongation (strain). The maximum stress was tolerated by the blend having the composition of 20% SIS copolymer and 80% SMMA copolymer. It tolerated the stress of 1148 MPa with strain 3.38% and having Young's modulus of 400 MPa. The stress-strain graph is given below. The table shows the values of stress, strain, elongation and Young's modulus.

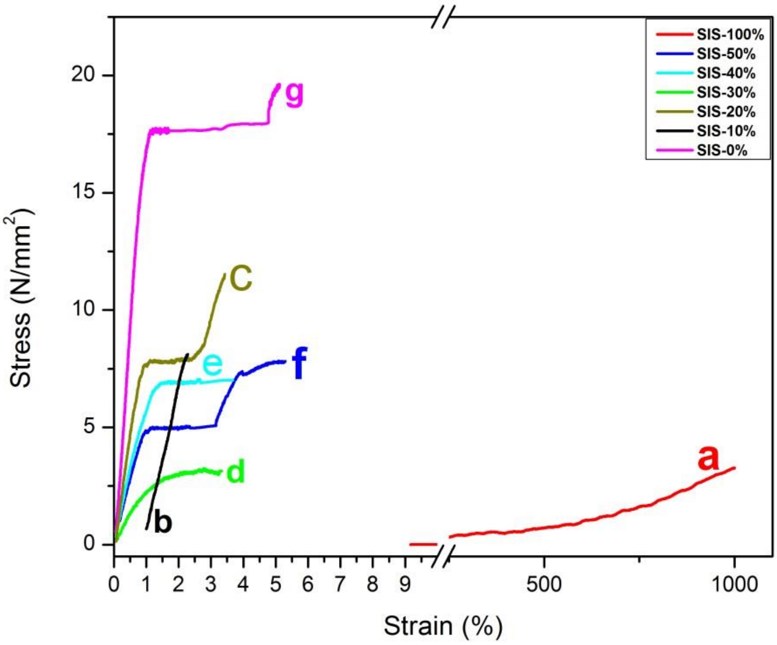


Fig. 16: Stress-strain curves for SIS/SMMA polymer blends (a=100%, b=10%, c=20%, d=30%, e=40%, f=50%, g=0% SIS)

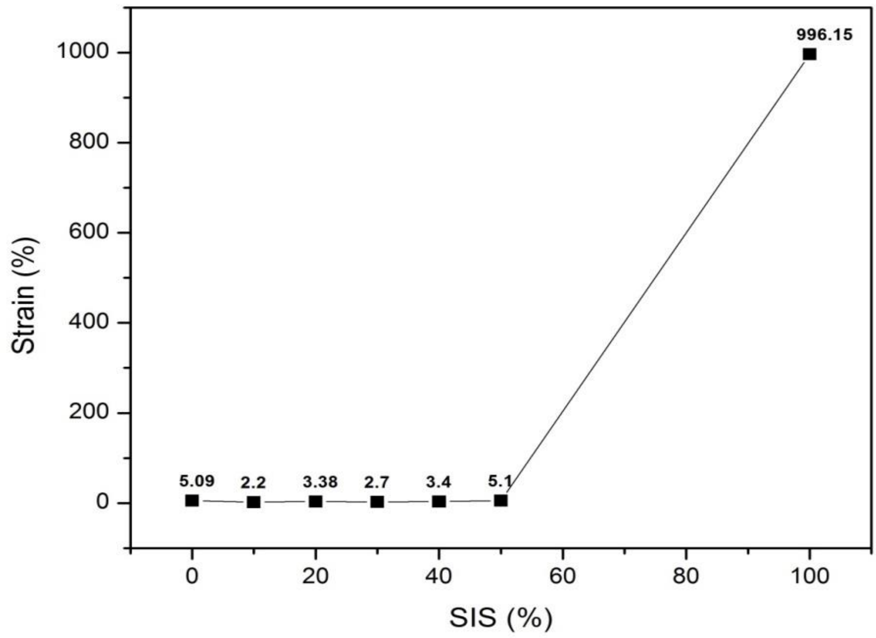


Fig. 17: Strain Vs % of SIS polymer in SIS/SMMA blends

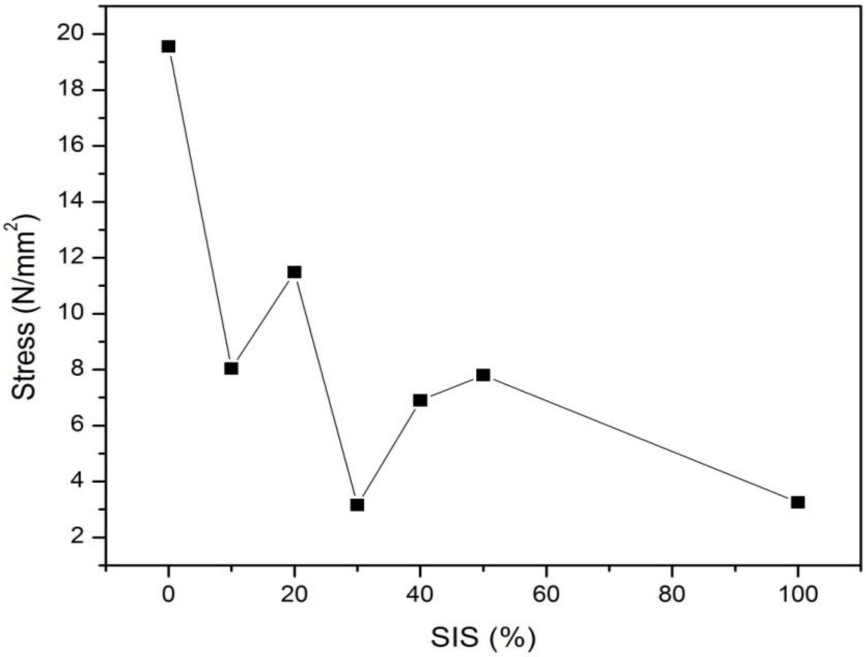


Fig. 18: Stress Vs % of SIS polymer in SIS/SMMA blends

Table 7: Mechanical properties of SIS/SMMA blends

% of SIS copolymer in blends	Stress (MPa)	Strain (%)	Toughness (MPa)	Modulus (MPa)
0%	5.09	19.56	82.57	117
10%	8.04	2.2	6.025	600
20%	11.49	3.38	24.91	400
30%	3.15	2.7	8.035	70
40%	6.9	3.4	21.41	130
50%	7.8	5.9	27.148	100.8
100%	3.25	996.15	1046.95	34

3.3.1 Mechanical testing of nanocomposites (using THF solvent)

The clay nanocomposites were prepared by the solvent method. The nanoclay content was varied from 1 to 5% in SIS/SMMA blends. The nanocomposites having 5% clay showed the brittle behavior due to agglomeration. It has Young's modulus of 450 MPa, bearing 650 MPa stress and strain was 0.9. It showed brittle behavior. The nanocomposites with 1 and 3 % of nanoclay have Young's modulus of 120 and 310 respectively. The 1% clay in nanocomposite showed ductile behavior as compared to 3 and 5% clay content in nanocomposites. The table shows all the values calculated for tensile testing.

Table 8: Mechanical properties of nanocomposites (THF solvent)

% of clay	Stress (MPa)	Strain (%)	Toughness (MPa)	Modulus (MPa)
0	11.49	3.4	24.91	400
1	9.3	5.8	39.88	120
3	8.6	1.6	44.35	310
5	6.5	0.9	4.7	450

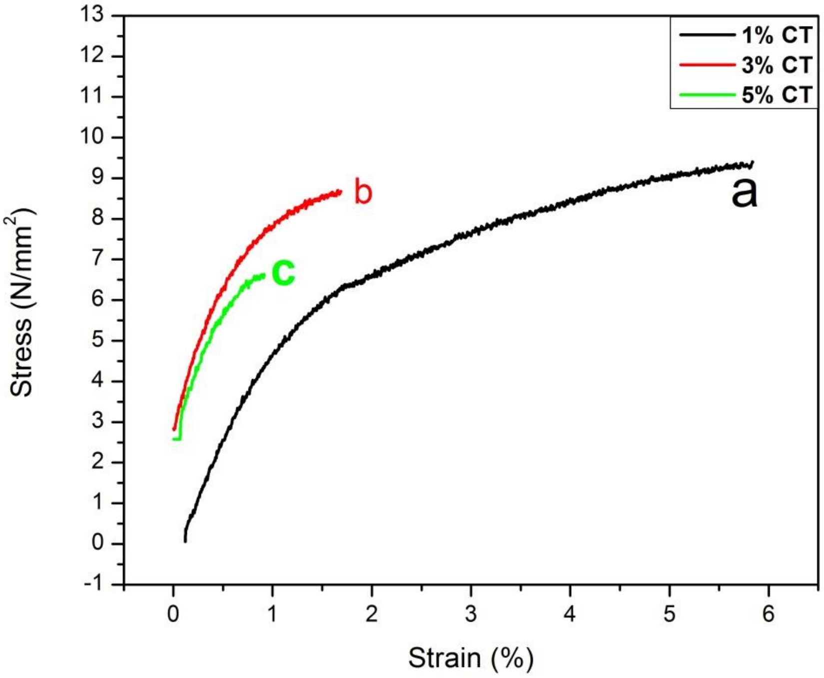


Fig. 19: Stress-strain curves for SIS/SMMA/Kao-DMSO nanocomposites using THF solvent. (a=1% ,b=3%, c=5% clay nanocomposites prepared in THF solvent)

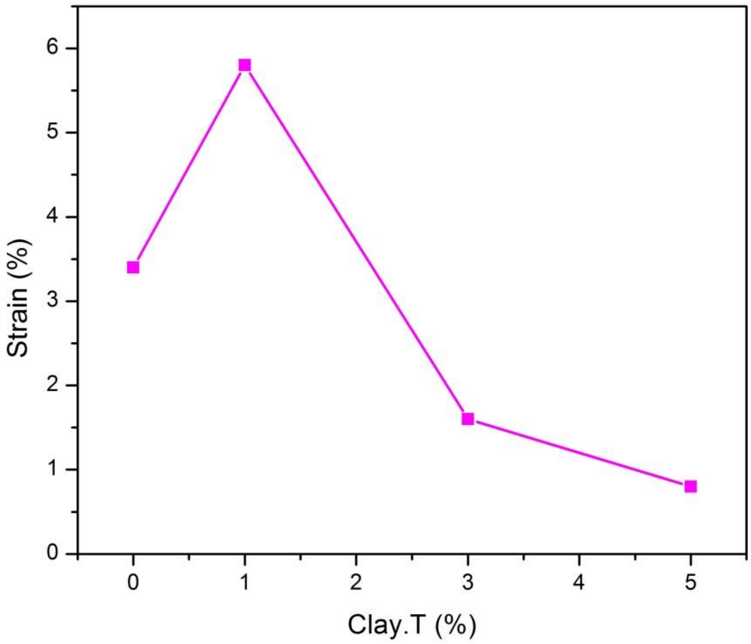


Fig. 20: Maximum strain Vs % of clay content in nanocomposites (THF solvent)

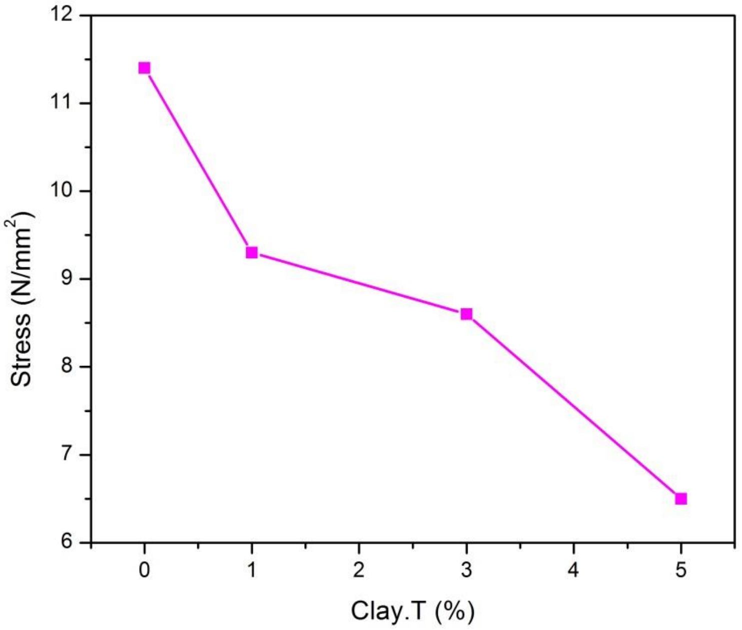


Fig. 21: Maximum stress Vs % of clay content in nanocomposites. (THF solvent)

3.3.2 Mechanical testing of nanocomposites (using Chloroform Solvent)

The nanocomposites prepared in chloroform solvent showed ductile behavior as compared to nanocomposites prepared in THF solvent. The maximum stress tolerated by 5% clay content in nanocomposites. The Young’s modulus for 5% clay in nanocomposites was 150 MPa, bearing stress 1156 MPa and strain 5.8%. The table shows all tensile testing values for nanocomposites prepared in chloroform solvent. The solvent affected the mechanical properties of the nanocomposites. As it is observed that chloroform has a better effect on nanocomposites and good for the fine and even distribution of the clay content in nanocomposites.

Table 9: Mechanical properties of nanocomposites (Chloroform solvent)

% of clay	Stress (MPa)	Strain (%)	Toughness (MPa)	Modulus (MPa)
0	7.9	6.02	37.01	103
1	9.2	9.9	67.40	67
3	9.9	10.11	76.60	76
5	11.56	5.8	51.54	150

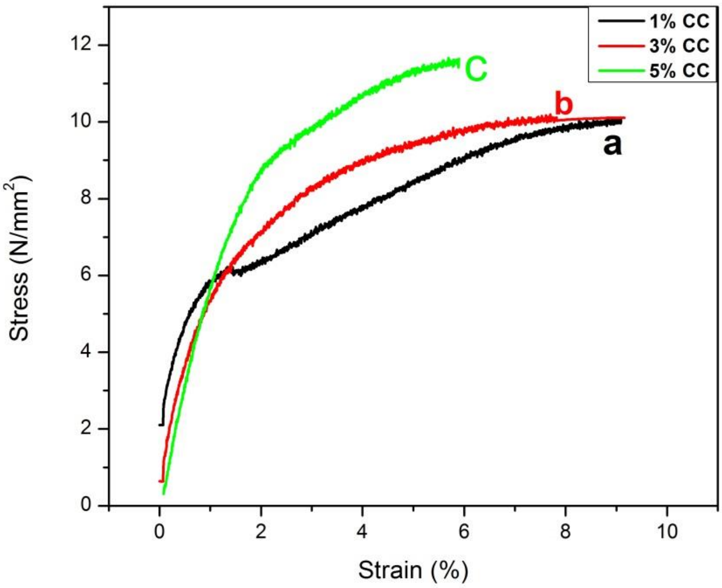


Fig. 22: Stress-strain curves for SIS/SMM/Kao-DMSO nanocomposites. a=1%, b=3%, c=5% clay nanocomposites in chloroform solvent)

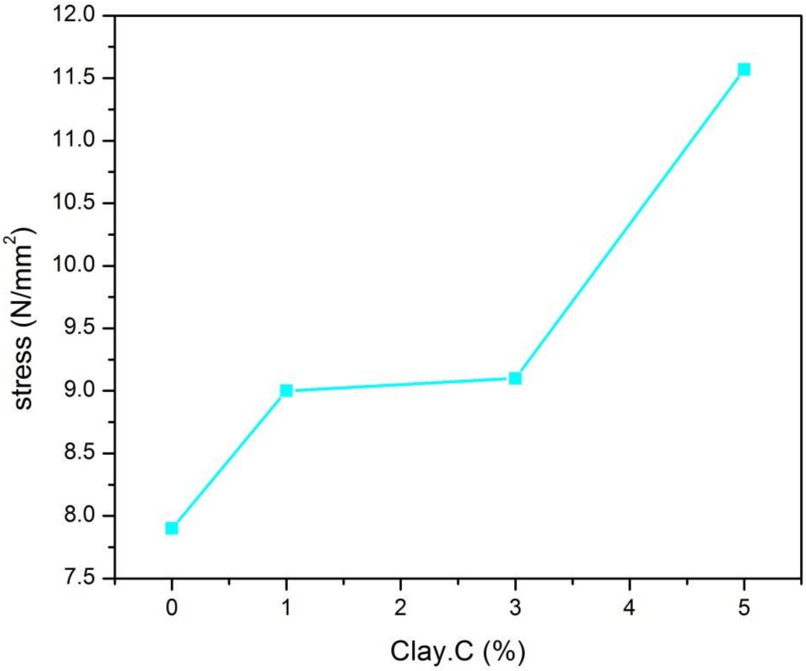


Fig. 23: Maximum stress Vs % of clay content in nanocomposites (chloroform solvent)

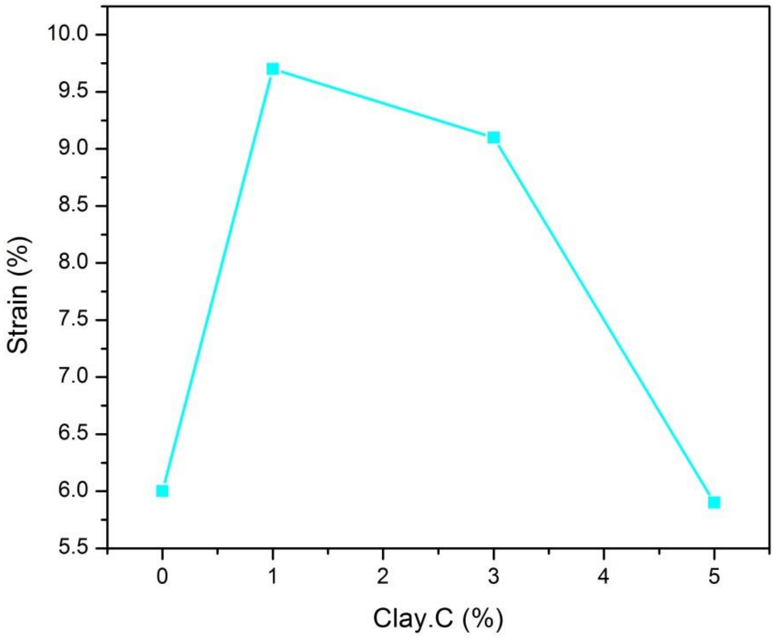


Fig. 24: Maximum strain Vs % of clay content in nanocomposites (chloroform solvent)

3.4 Thermal analysis of SIS/SMMA blend and nanocomposites

3.4.1 DSC measurements

DSC measurement was done at the temperature range of -30 to 200°C in a nitrogen environment at a heating rate of 10°C/min and first heat run. The Tg values for pure SIS and SMMA copolymer are 95°C and 111°C respectively. The 20/80 SIS/SMMA blend has Tg of 55.51°C in THF solvent and 60.63°C in chloroform solvent. The increased Tg is due to increased intermolecular forces developed between the SIS/SMMA/Kao-DMSO nanocomposites. The Tg was increased for the nanocomposites, in THF solvent as well as in chloroform solvent, as compared to the blend. The increased Tg of nanocomposites in chloroform solvent showed the better interaction of components of the system. The decreased Tg in case of THF solvent based nanocomposites was due to less interaction of solvent with components of the system. As there is a strong physical interaction (H-bonding) between the –Cl of solvent and –H of the polymers. While weak van der Waals forces are developed, when THF is used. The heat flow and Tg graphs are given below. The details of Tg with respect to solvent are given in the table.

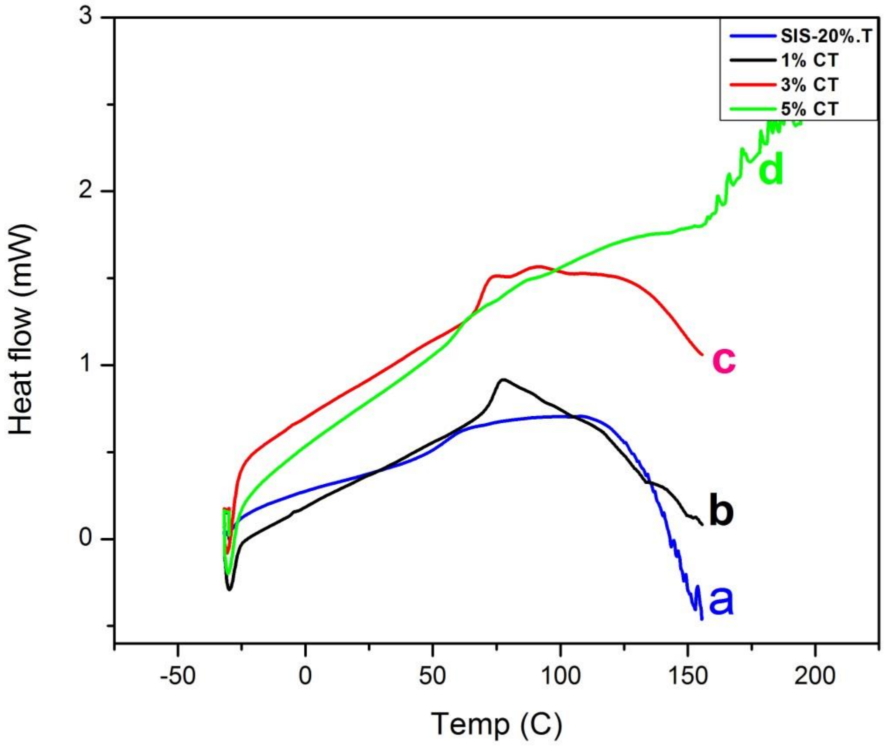


Fig. 25: DSC curves for blend (a=20% SIS) and nanocoposites (b=1%, c=3% and d=5% clay in nanocomposites using THF solvent) CT=clay nanocomposites prepared in THF solvent

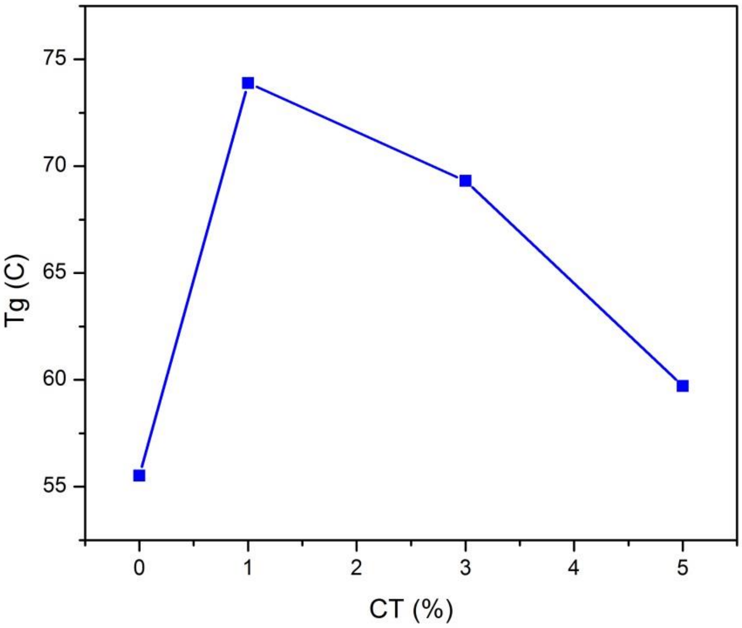


Fig. 26: Tg values for the blend and nanocomposites (CT; THF solvent)

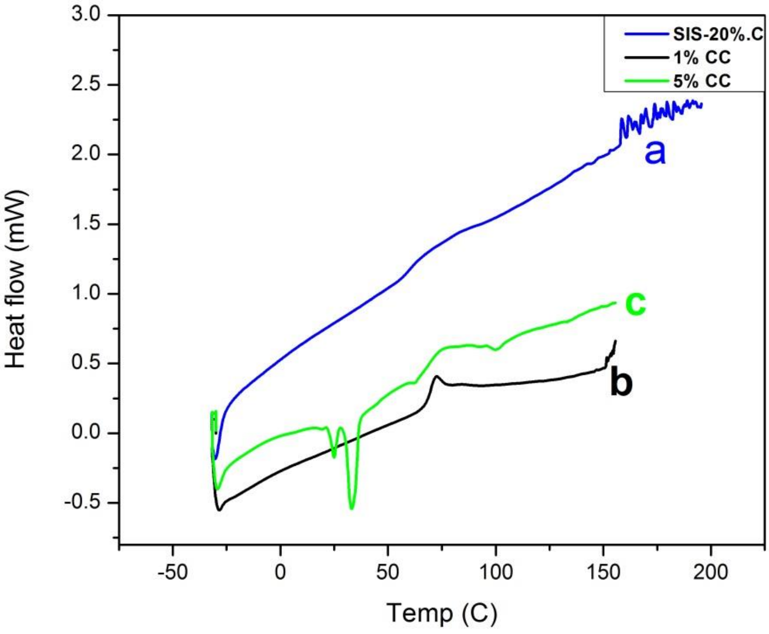


Fig. 27: DSC curves for blend (a= 20% SIS) and nanocomposites (b=1% and c=5% clay in nanocmposites using chloroform solvent) CC= clay nanocomposites prepared in chloroform solvent

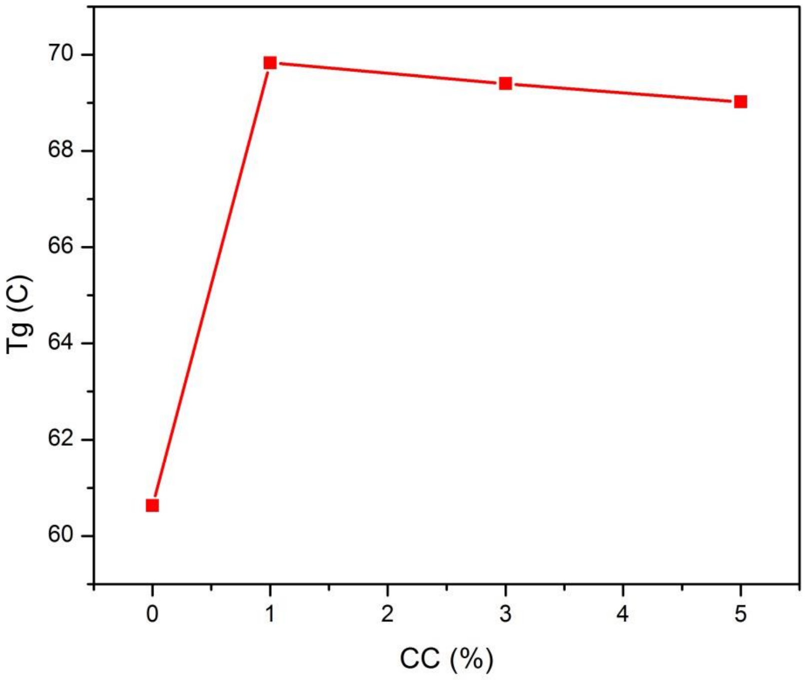


Fig. 28: Tg values for blend and nanocomposites. (CC; chloroform solvent)

Table 10: DSC analysis of pure polymers, blends and nanocomposites

Blends and nanocomposites	**Tg (°C)**
SIS	94
PSMMA	111
20/80 SIS/SMMA (T)	55.51
1% nanoclay (CT)	73.89
3% nanoclay (CT)	69.31
5% nanoclay (CT)	59.71
20/80 SIS/SMMA (C)	60.63
1% nanoclay (CC)	69.83
5% nanoclay (CC)	69.02

T; THF solvent, CT; clay-based nanocomposites prepared in THF solvent), C; chloroform solvent, CC (clay-based nanocomposites prepared in chloroform solvent).

3.4.2 TGA measurements

For TGA analysis DTA-TGA-50/50H SHIMADZU machine at CAS-EN was used. TGA analysis was done at a temperature range of 25°C to 800°C by using nitrogen atmosphere. The blend 20/80 SIS/SMMA was stared to decompose at 329°C. The nanocomposites 3%, 5% clay content in nanocomposites prepared in THF and 5% nanoclay composites prepared in chloroform started to decompose at 338, 329 and 364°C. The complete degradation of blend and nanocomposites were done at 412 and 434°C respectively. The TGA results indicated that solvent was completely removed during the analysis due to very temperature. So, in this case, the solvent has minimal effect on the nanocomposites. But the addition of nanoclay increased the thermal stability by some extent shown in the table. The TGA graph is given below. The change in TGA curve before 320°C is due to the removal of the solvent.

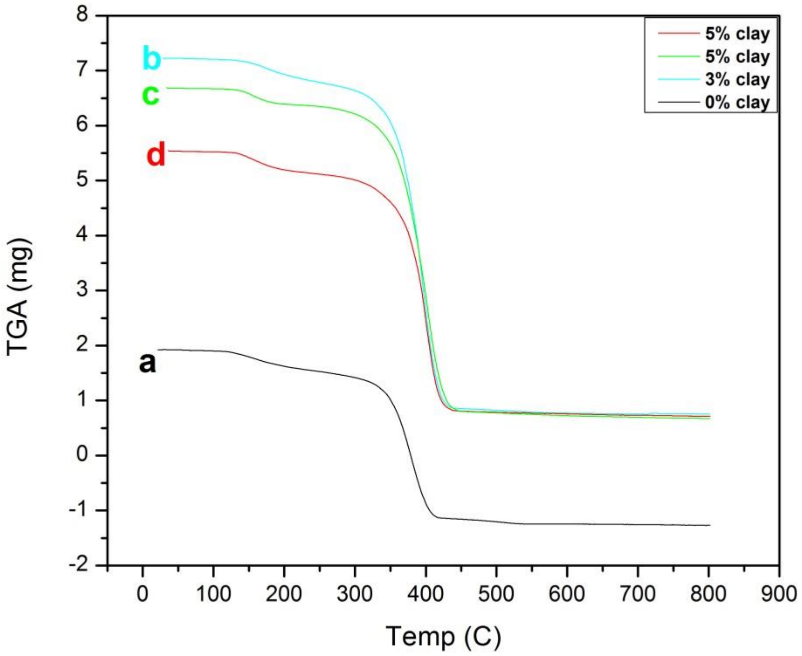


Fig. 29: TGA curves for blend and nanocomposites (a=0% clay, b=3%, c=5% clay in T, d=5% clay in C)

Table 11: TGA analysis data for SIS/SMMA blend and nanoclay composites.

Blend and nanocomposites	Ts	Td
20/80 SIS/SMMA blend	329	412
3% CT nanocomposite	338	426
5% CT nanocomposite	335	419
5% CC nanocomposite	339	434

Ts: starting decomposition temperature, Td: final decomposition temperature.

3.5 SEM analysis (morphological study)

SEM analysis was done by using instrument SEM JSM-6490 at accelerating voltage 20kV. The fractured surface of the film was used for SEM analysis, fractured in liq.N_2. The magnification from X5000 to X20000 was used. The SIS/SMMA blend showed partially immiscible behaviour, as shown in fig. 30:

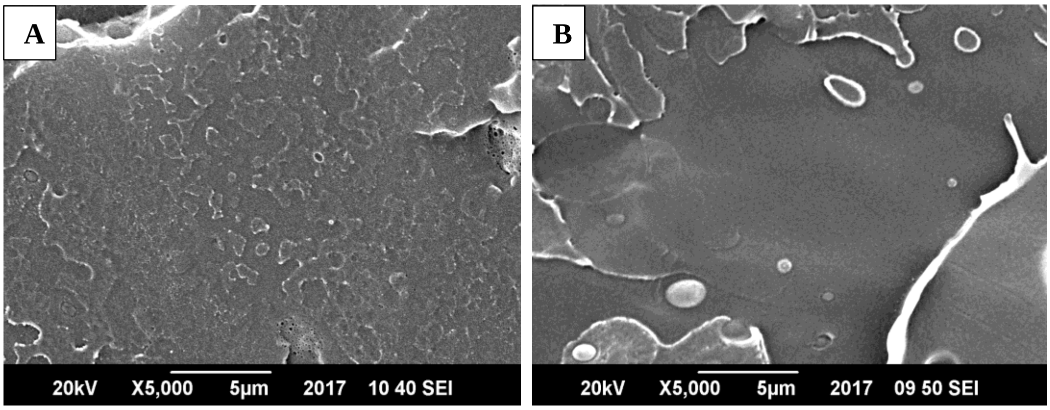


Fig. 30: SEM images of A; polymer blend (THF solvent), B: polymer blend ($CHCl_3$ solvent)

The extent of immiscibility was very low in polymer blends, prepared in different solvents. By the addition of Kao-DMSO clay, the resulting nanocomposites were miscible. Clay acted as nanofiller for blends to make them miscible and eliminated the phase separation. The nanoclay was finely dispersed in both solvents. The nanocomposites prepared in chloroform solvent have the strong physical interaction of electronegative atom –Cl with –H groups present in polymers, easily available for H-bonding interaction. As THF has no such group for better adhesion than the chloroform.

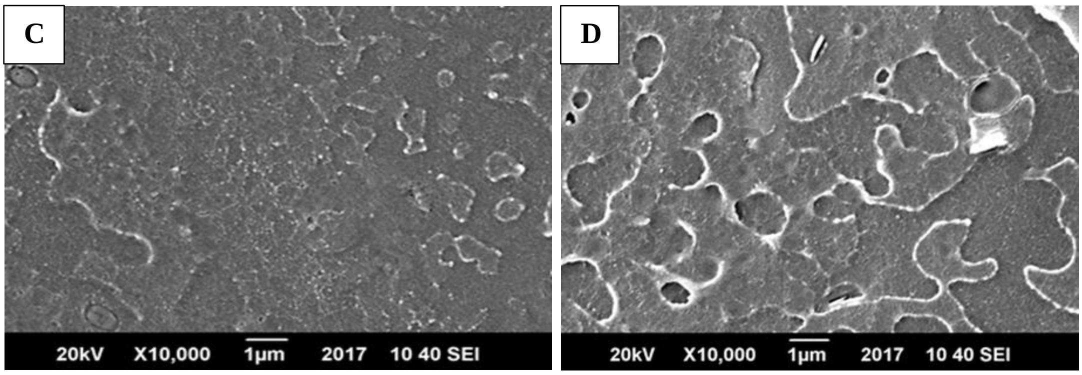


Fig. 31: SEM images of C; nanoclay composites in THF solvent, D; nanoclay composites in $CHCl_3$ solvent

SEM images confirmed the even and fine distribution of the nanoclay. Nanoclay formed a better adhesion with the phase of polymers to make compatible and miscible nanocomposites.

3.6 Conclusion

The polymer blends show better properties as compared to parent component as confirmed by different characterizing techniques as mentioned above. The stress of SIS polymer was increased by the addition of PSMMA polymer. They formed partially miscible blends with neglected phase boundaries. The little phase separation was controlled or eliminated by the addition of nanoclay. The resulting nanocomposites have even though better properties than the blends. So the properties of individual polymer can be enhanced or improved by the addition of the polymer (that should be compatible or miscible) and nanofiller.

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