Study of Structural and Mechanical Properties of Textile Material from Nano-Clay Reinforced Polymer

A THESIS SUBMITTED TO
THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
TEXTILE ENGINEERING

BY
AADHAR A. MANDOT

UNDER THE GUIDANCE OF
DR. S. S. BHATTACHARYA
PROFESSOR
DEPARTMENT OF TEXTILE ENGINEERING

Department of Textile Engineering
Faculty of Technology and Engineering
The Maharaja Sayajirao University of Baroda
Vadodara – 390 001

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DECLARATION

I hereby declare that the topic entitled ***"Study of Structural and Mechanical Properties of Textile Material from Nano-Clay Reinforced Polymer"*** which is submitted herewith to The Maharaja Sayajirao University of Baroda, Vadodara for the fulfillment of the award of the degree of **DOCTOR OF PHILOSOPHY IN TEXTILE ENGINEERING** is the result of the work carried out by me in Textile Engineering Department, Faculty of Technology & Engineering, The M. S. University of Baroda, under the guidance of Dr. S. S. Bhattacharya, Professor, Department of Textile Engineering, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara.

I further declare that the result of this work has not been previously submitted for any degree / fellowship.

Place: Vadodara (**Aadhar A. Mandot)**
Date:

FACULTY OF TECHNOLOGY AND ENGINEERING
THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
VADODARA

CERTIFICATE

This is to certify that the thesis entitled "***Study of Structural and Mechanical Properties of Textile Material from Nano-Clay Reinforced Polymer***" which is being submitted by **AADHAR A. MANDOT** In partial fulfillment for the award of **DOCTORATE DEGREE** in **TEXTILE ENGINEERING** to **THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA, VADODARA** has been carried under my supervision and guidance. This work presented in the form of thesis has not been submitted anywhere for the award of any other degree.

Guide

Dr. S. S. Bhattacharya
Professor
Textile Engineering Department
Faculty of Technology & Engineering.
The M. S. University of Baroda, Vadodara

Head

Dr. M. V. Koranne
Textile Engineering Department
Faculty of Technology & Engineering.
The M. S. University of Baroda,
Vadodara

Dean

Faculty of Technology & Engineering,
The M. S. University of Baroda,
Vadodara

DEDICATED

TO

MY PARENTS

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CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION TO NANOTECHNOLOGY

During the last few years terms like nanomaterials, nanocomposites and nanosystems have become fashionable. It seems that anything with ‘nano’ attached to it has nearly a magical effect – not so much on performance as on expectations. There is an extensive worldwide effort to introduce nanotechnology for the production of materials with specific functional characteristics, e.g., semiconducting, electromagnetic, optical, textiles, etc. The National Science Foundation (NSF) has solicited collaborative research proposals in the area of nanoscale science and engineering, including: nanoscale biosystems; nanoscale structures; novel phenomena and control; nanoscale devices and system architecture; nanosystems-specific software; nanoscale processes; multi-phenomena modelling and simulation at the nanoscale level; studies on societal implications of nanoscale science and engineering, etc. Nanostructures are of interest to many technologies. In short, there is a great potential for the wide use of nanotechnology for functional materials and devices. The central theme of this work is the use of nanotechnology for the development of new structural polymeric systems, the polymeric nanocomposites (PNCs), and particularly the clay-containing polymeric nanocomposites (CPNCs).

1.2 NANO COMPOSITES

Polymer nanocomposites are commonly defined as the combination of a polymer matrix and additives that have at least one dimension in the nanometer range. The additives can be one-dimensional (examples include nanotubes and fibres), two-dimensional (which include layered minerals like clay), or three-dimensional (including spherical particles). Over the past decade, polymer nanocomposites have attracted considerable interests in both academia and industry, owing to their outstanding mechanical properties like elastic stiffness and strength with only a small amount of the nanoadditives. This is caused by the large surface area to volume ratio of nanoadditives when compared to the micro- and macro-additives. Other superior properties of polymer nano-composites include barrier resistance, flame retardancy, scratch/wear resistance, as well as optical, magnetic and electrical properties. The most popular nanofiller in the CPNC industry is montmorillonite, over 40% of atoms rest on the surface – the clay lamellae should be treated either as giant inorganic molecules or at least as hybrids occupying the grey zone between molecules and particles. This is not mere semantics, but has profound consequences as far as the fundamentals of CPNC are concerned, *viz.*, miscibility or flow behaviour.

This work summarises the pertinent developments in the area of the science and technology of clay-reinforced polymeric nanocomposites. There are several reasons for using clays, *viz.*, availability, cost, and aspect ratio. The theory and experiments show that to maximise the benefits of nanotechnology the clay must be fully decomposed into individual crystalline lamellae (exfoliated) and these must be uniformly dispersed in a given matrix material.

The main difficulties for CPNC technology rest in the hygroscopic character of clay and strong solid-solid interactions. It is a relatively simple task to disperse clay platelets or lamellae (i.e., to exfoliate them) in water or in water-soluble, polar monomers or oligomers (e.g., amino acids or glycols). However, preparation of CPNC in a hydrophobic, non-polar high molecular weight polymer, e.g., a polyolefin or polystyrene, is difficult. The most sensible way to approach the problem is to consider the process of preparation of CPNCs as blending two highly immiscible ingredients, i.e., from the perspective of polymer blending and compatibilisation. As in polymer blends here also one is obliged to ensure good interaction between the two antagonistic components: hygroscopic clay and hydrophobic polymer.

This work covers both fundamental and applied research associated with polymer based nanocomposites, and presents possible directions for further development of high performance nanocomposites. Polypropylene polymer is selected for the preparation of PNC as it is commercially successful materials and used in the field of technical textiles. Two products i.e. yarn and nonwoven fabric has been prepared with addition of nanoclay in different proportion and evaluated. To provide condensed information, the work has been divided into five chapters which are entirely dedicated to those polymer Nanocomposites. Chapter 1, gives the brief introduction of the whole thesis and the type of work carried out. Chapter 2, shows the extensive survey of literature carried out and some of the work carried out by other researchers in this area. Chapter 3, deals with the selection of materials and methods used for the production and evaluation of prepared nanocomposites respectively by different techniques. Chapter 4, contains different observations of all the prepared samples obtained by the different evaluation techniques and the same are also discussed in this chapter. Chapter 5, gives the concluding remarks of the work. At the end, the thesis provides appendices for explanations of abbreviations, symbols, and references.

As two different products have been studied, to have comprehensive understanding of the work, chapter 3 and chapter 4 have been divided further into three sections:

***Section I* –** Presents a general method for the preparation of organoclay from bulk clay with the help of surfactant CTAB and making it miscible with polymeric substance.

***Section II* –** Discusses the preparation of polypropylene yarn with the incorporation of nanoclay at spinning stage. Nanoclay with varied percentage was mixed with PP and extruded through a lab model melt spinning machine. The prepared yarn was further analysed and evaluated for different properties.

Section III – Considering the upcoming field of technical textiles, these nonwoven fabrics are prepared with spun bond technique with the incorporation of nanoclay.

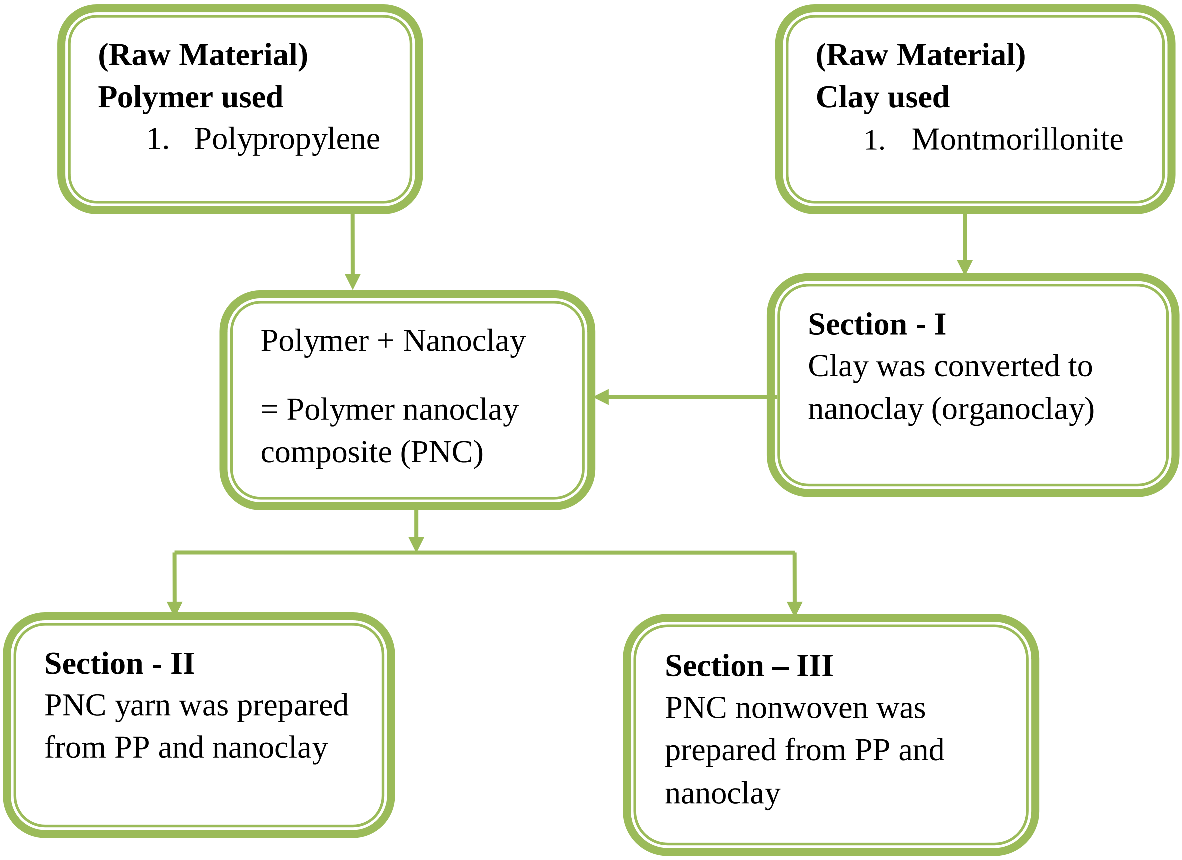
1.3 AIM OF THE STUDY

The main purpose of this work is to study the **structural** and **mechanical** changes occurred in **yarn** as well as **nonwoven fabric** prepared by the incorporation of nanoclay particles inside the polymer matrix. Montmorillionite clay was used for this purpose; it was converted to Organoclay to make it compatible with polymer. The prepared Organoclay was added in different proportion to polypropylene. The work is focused to develop high performance textiles, by the addition of nanoclay particles.

The composite material were analysed in terms of their structural and mechanical properties. The mechanical properties were evaluated by using standard techniques in terms of stress, strain, modulus, work of rupture, bending modulus; tear strength, bursting strength and air permeability compared to pristine polymer. The change in structure was observed and analysed using SEM, EDX and XRD techniques. The prepared PP/nanoclay composite material were further analysed for their thermal behaviour by DSC and TGA techniques. Also the changes in their moisture management behaviour as well as UV transmittance property were analysed using MMT and UV tester.

By incorporating the nanoclay particles in small proportion not only improves the existing property but also introduces the special property to the conventional material. Clay being cheap and abundantly available in nature the product cost does not increase much but functional properties enhances, which leads to preparation of better and cheaper products for their applications to various fields of technical textiles. Keeping this objective in mind, the thesis is organised in below given manner:

Organisation of Thesis



CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The new kinds of textiles possess characteristics that make them useful in numerous formerly unexpected applications. Although textiles are still the major component of the clothes for wearing and of many furnishings in homes and offices, they are also used widely in medicine, aeronautics, astronautics, pollution abatement, and numerous other fields. Some new textiles possess qualities that make them stain-resistant, flameproof, and even stiff. Some are "nonwoven" matrices of overlapping fibers. Innovation in textile technology continues and more unusual products will almost surely emerge.

Filament fiber extruders spin this fine yarn at a speed of 250 miles an hour. This ability to spin cobweb-size filaments at jet airplane speeds with sufficient precision to maintain constant elongation, molecular orientation, fiber diameter, and tenacity (fiber strength per unit weight) dramatically illustrates the sophistication of the new textile technology. Certain fibers and textile materials are especially suitable for use in building synthetic body parts and medical scientists are steadily expanding the types of body parts whose function can be mimicked.

The artificial kidney is made from 7,000 hollow fibers, each of which is about the size of a human hair. Without the especially prepared cuprammonium rayon hollow textile fibers, there would be no artificial kidneys and thousands of people would die each year. These rayon fibers have exactly the right pore size to allow poisons and waste products to pass through while retaining the blood for return to the body after cleaning. Artificial arteries made of knitted polyester textile tubes are used for many patients whose natural arteries leading to their legs are blocked. Sutures made from textile fibers of all types (silk, collagen, polyester, or nylon) for closing incisions after surgery are among the most expensive textiles, selling for more than $2,000 a pound. Bone replacements of carbon fiber composites are nonantigenic (not rejected by the body). By proper control of the composite porosity, it is becoming possible to have injured bone tissue accept and grow into the inserted replacement units. Disposable, sterile, nonwoven coverings for operating tables, surgeon's masks, and disposable gowns are other examples of textile technology at work in medicine.

In the fields of aerospace engineering, construction, water purification and pollution abatement, a similar proliferation of new applications is emerging from research laboratories.

2.2 SYNTHETIC FIBERS

Originally all textiles were made from natural fiber such as cotton, wool, mohair, linen, ramie, and vicuna. All of these were available only as staple fibers that had to be spun into yarns before they were converted to cloth. Silk was the first monofilament material, and for years scientists were obsessed with trying to make and 'artificial' silk. This was achieved in the mid-1800s when rayon was produced by dissolving cellulose and regenerating it into the shiny filaments resembling silk in appearance. This was rapidly followed by acetate, which was prepared by modifying cellulose with acetic anhydride and then "dry spinning" the syrupy solution to recover the organic acetone solvent.

These developments laid the foundation for the scientific principles that led Wallace Carothers at the Du Pont Company to invent nylon and polyester fibers and yarns. Nylon was and still is a tremendous commercial success. It offered greater strength, abrasion resistance, resilience, wrinkle recovery, and was easier to take care. The high strength of nylon led to its use in tires to replace most rayon cord.

Ziegler and Natta, invented stereo regular polypropylene, and Phillips Petroleum Company acquired the patent for controlled-regularity. The use of polypropylene is now common for indoor/outdoor carpets and for furniture from which spills and stains can be easily removed with soap and water. The textile industry has further learned that polypropylene nonwettable, waxy-based fibers can be spun into fine-diameter. Fibers are so constructed that they absorb as much moisture as highly absorbent natural fibers. Such fine fibers retain as much fluid by capillary action between fibers as natural fibers do by absorption within fibers. Thus today, cold-weather thermal underwear is worn next to the skin to keep the body dry, carrying perspiration away by capillary action to a more absorbent outer layer.

2.3 COMPOSITE MATERIAL

Composite materials are engineered materials made from two or more constituent material that remains separate and distinct on a macroscopic level while forming a single component. Composite materials are formed by combining two or more material that has quite different properties. Different materials work together giving unique property to composite, but within the composite one can easily apart the materials. They do not dissolve or blend into each other.[1]

Textile materials play critical role in the manufacture of advanced composite materials in the form of high performance fibres, hybrid yarns and preforms. The high performance fibres provide the basic reinforcement in the form of high strength and modulus to the materials. Hybrid yarns, an intermediate product in thermoplastic composite manufacturing, assist in combining the high performance fibres and the matrix in the form of fibres before preforming. All textile fabric manufacturing processes like weaving, knitting, braiding and non-woven techniques are suitably modified to provide 2D and 3D textile structures for reinforcement. Conventional textile structures and nonwoven webs can be combined with a wide range of elastomeric (rubber-like) and plastic materials to make composites.[2] In most composites, the textiles comprise less than 50 percent of the weight but account for more than 75 percent of the strength. This is particularly true when the matrix material has a high degree of elasticity or deformation as in tires, hoses, or conveyor belts. Similarly, the use of high-stiffness, high-performance fibers leads to exceptionally high-modulus composites when more rigid matrices are employed. Some examples of these are the new high-performance graphite fishing roads, golf clubs, and tennis racquets. By the proper combination of high-performance fiber and matrix it is possible to make products that will not burn when exposed to open blowtorches. Almost all products of high-performance composites are far stronger and far lighter than similar products made from metals. At present, the composite market in the United States totals about $ 1.1 billion and is growing at a rate of 30 percent a year.

Composites exist in nature. A piece of wood is a composite, with long fibres of cellulose (a very complex form of starch) held together by a much weaker substance called lignin[1]. Cellulose is also found in cotton and linen, but it is the binding power of the lignin that makes a piece of timber much stronger than a bundle of cotton fibres. Humans have been using composite materials for thousands of years. Take mud bricks for example. A cake of dried mud is easy to break by bending, which puts a tension force on one edge, but makes a good strong wall, where all the forces are compressive. A piece of straw, on the other hand, has a lot of strength when you try to stretch it but almost none when you crumple it up. But if you embed pieces of straw in a block of mud and let it dry hard, the resulting mud brick resists both squeezing and tearing and makes an excellent building material. Put more technically, it has both good compressive strength and good tensile strength. Another well-known composite is concrete. Here aggregate (small stones or gravel) is bound together by cement. Concrete has good strength under compression, and it can be made stronger under tension by adding metal rods, wires, mesh or cables to the composite (so creating reinforced concrete)[3].

So the most primitive composite material comprised straw and mud in the form of bricks for construction. The most advanced examples perform routinely on spacecraft in demanding environments. The most visible applications pave our roadways in the form of either steel or Portland cement concrete or asphalt concrete.

2.4 NANOTECHNOLOGY

A nanometer (nm) is one thousand millionth of a meter. A single human hair is about 80,000 nm wide; a red blood cell is approximately 7,000 nm wide, a DNA molecule 2 to 2.5 nm, and a water molecule almost 0.3 nm. The term *”nanotechnology”* was created by Norio Taniguchi of Tokyo University in 1974 to describe the precision manufacture of materials with nanometer tolerances[6], but its origins date back to Richard Feynman’s 1959 talk “There’s Plenty of Room at the Bottom”[7] in which he proposed the direct manipulation of individual atoms as a more powerful form of synthetic chemistry. Eric Drexler of MIT expanded Taniguchi’s definition and popularized nanotechnology in his 1986 book “Engines of Creation: The Coming Era of Nanotechnology”[8]. On a nanoscale, i.e. from around 100nm down to the size of atoms (approximately 0.2 nm) the properties of materials can be very different from those on a larger scale. Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, in order to understand and exploit properties that differ significantly from those on a larger scale.

Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size on a nanometer scale. Modern industrial nanotechnology had its origins in the 1930s, in processes used to create silver coatings for photographic film; and chemists have been making polymers, which are large molecules made up of nanoscale subunits, for many decades. However, the earliest known use of nanoparticles is in the ninth century during the Abbasid dynasty. Arab potters used nanoparticles in their glazes so that objects would change colour depending on the viewing angle (the so-called polychrome luster)[9]. Today's nanotechnology, i.e. the planned manipulation of materials and properties on a nanoscale, exploits the interaction of three technological streams[10]:

1. New and improved control of the size and manipulation of nanoscale building blocks
2. New and improved characterisation of materials on a nanoscale (e.g., spatial resolution, chemical sensitivity)
3. New and improved understanding of the relationships between nanostructure and properties and how these can be engineered.

Nanotechnology seeks to provide and apply knowledge of the behaviour of objects in the nanometer (nm) size range to the assembly of complex structures for use in a variety of practical applications. The tiniest substances promise to transform industry and create a huge market. In chemicals, cosmetics, pharmaceuticals, technology and textiles, businesses are researching and manufacturing products based on nanotechnology, which uses bits of matter measured in billionths of a meter. The technology, utilizing materials a thousand times smaller than the width of a human hair, is showing up in everything from auto parts to sunscreens and clothing[11, 12]. However, nanotechnology has been used to improve products that most of us use every day. These include laundry detergent, 6-pack rings, and surgical tools. One of the most widespread applications of nanotechnology is in clothing. Nanotechnology is also called a “bottom up” technology owing to using such small-scale building units, in contrast to bulky material engineering that is considered a “top down” approach[13]. Many textile industries and research organization has already developed fabrics with distinguish properties. Scratch-and-sniff clothing is one example. Pleasantly scented, tiny polymer beads were added to clothing, such as within a strawberry applied on a shirt. Then there were menthol pajamas, scented to open the nasal passages of people suffering from colds, ensuring a good night's sleep. Some other type of clothing niche being explored on many fronts, with perhaps more staying power than scratch-and-sniff shirts, involves the nanoscale improvement of fabrics and fibers. Nanotechnology is adding its labels to popular clothing brands with various products: Resists Spills, Resists Static, Coolest Comfort, and Repels and Releases Stains. Researchers all around the world looking at all sorts of metal additives and polymer additives, inorganic, organic materials to take them at nanoscale to impart lots of interesting properties to textiles. These research endeavours is mainly focused on using nano-size substances and generating nanostructures during manufacturing and finishing processes.

2.4.1 GENERAL APPROACHES FOR NANO MATERIAL PREPARATION

i) Top-down approach

The techniques generally used are grinding, cutting, spraying and etching. The top-down approach to nanotechnology has found a first application in research in the field of Micro-Electro-Mechanical System (MEMS). In MEMS, systems are building integrate electronic & mechanical component on a very small scale. Textile production can also benefit from development in the MEMS field.

Today we see textile processing methods in which clusters of objects are manipulated. E.g. in spinning or non-woven formation there is little or no control of individual fibers. Using MEMS, which can sense the position (sensors) and control the motion or position (actuators) of each in individual fibers, could lead to better. Stronger yam or non-woven structures with controlled properties. In weaving, warp tension of individual warp yams could be monitored and controlled by MEMS, leading first to warp yam break detection and to a decrease in warp brakes. Further MEMS could assist in or possibly repair the warp yam breaks, which would lead to a decrease in interventions and a higher production yield.

ii) Bottom-up approach

Bottom-up approaches have the potential to allow fundamentally new assembly and manufacturing processes at the atomic and molecular level. The opportunities for exploitation will expand, rather than narrow as the basic principles of the operation and tools are developed.

Bottom-up processes are less well developed in terms of their application, are less well developed, require more fundamental scientific study, and have far less certain outcomes in commercial terms. Some key processes under debate may never be realized. At best, their exploitation cycle will be relatively long.

2.4.2 MECHANICS OF NANO MATERIALS

Nano-chemistry makes its contribution as it is a science that investigates, designs, synthesizes, and fabricates matter that are in the nanometer-size regime through molecular control of systems.

Since the beginning, chemists (or alchemists) had been attempting to transform matter, but these attempts could not have progressed without a proper theory or model, at least in part, to help in the design of the method of transformation. The Greek Philosophers Leucippus and Democritus had proposed (450 B. C.) the idea that matter must be made of smaller building blocks, 'the atomos', a proposition which could have just been a rational extrapolation of the observation that the beach looks solid when viewed from afar, but is in fact granular on closer inspection. In 1985, Holton, et.al[15] explained different transformation of some of the known substances observed, based on the atomic theory developed by Dalton in his opus “A New System of Chemical Philosophy (1808)”.

Chemistry succeeded as a science because it was able to develop techniques for 'handling' atoms and molecules. The typical size of the atom & order of magnitude, it is about 1 Angstrom (Å) in diameter or 0.0000001 of a millimetre. Clearly, too small to touch or handle individually. The 'handling' is really a logical manipulation of the atomic model. By knowing the reactivity’s of the elements and compounds, chemists had a way of peering into the properties of the individual atoms or the molecules that they are made of.

Thus now, one can have a clearer understanding of the chemical reactivity’s of atoms or molecules, are able to predict the molecular shape and electronic properties, or predict how one will interact with light, electricity, magnetism or with other atoms, assess their stabilities and reactivity’s, and all of these with fairly good accuracy. These molecular properties are, in turn, related to the observed property of bulk matter. Bulk matter here is made of at least 10^{16} atoms or molecules (by Enriquez, E. P., presented at round table discussion on nanotechnology sponsored by the national academy of science & technology, and DOST-PCASTRD 16th Oct'2006, ATENED DE, Manila) in an assemblage that has a size that can be manipulated and handled in glass vessels or crucibles typically found in a chemical laboratory; a typical lab specimen size being of micro or milligrams, grams or even kilograms in quantity, which is readily weighed using a laboratory balance.

In explaining, an observed behaviour of bulk matter in terms of the properties of the molecules that it is made of. For instance: this author overheard an auto-mechanic trying to explain why battery acid spills on polyester pants do not readily burn into holes—so he explained: "it is because the acid did not easily absorb into the polyester fabric, unlike in cotton." A fine observation and a good explanation at that, but is still lacking of a molecular explanation. Chemists would prefer to explain the observation based on the molecular constitution of the fabric and what its properties are: "that polyester is made of molecules that are less polar than cotton, and are therefore less water-liking than cotton, among other things to be considered." In this perspective, a chemist could therefore 'design' a molecule whose property will be of a particular wettability, in contrast to forming a blend of cotton and polyester. The point is, chemical intuition is synonymous to molecular level understanding, and this is routinely used to rationalize observed bulk properties of matter and in the design of molecules for desired bulk properties.

In terms of forming new substances, synthetic chemists act like molecular engineer's designing and fabricating molecular structures of desired physico-chemical and electronic properties. They come up with steps to build a complex molecular structure in an atom-by-atom or molecular fragment-to-molecular fragment approach.

Whereas before, bulk behaviour was routinely measured, nowadays, the observation data on properties of matter are not only limited to bulk behaviour but also include those of matter made up of only a cluster of atoms in the hundreds, thousands, or just a few million atoms bonded together in assembled structures whose final dimensions are only in the tens or hundreds of Angstroms, in other words in the nanometre size regime. These structures which we may refer to as nanostructures are not like the molecules of old, but are materials yielding behaviour unlike their bulk counterparts. And as more of them are cropping up these days, new phenomena are being observed, and in turn, there is more impetus to create new ones and innovates methodologies for making them into various morphologies or modes of molecular organization. The motivation is both fundamental and practical.

- **Fundamental:** to discover and understand new phenomena exhibited by matter at these newly accessible dimensions, and
- **Practical:** to form them into useful something ; as novel electronic devices, as efficient drug delivery systems, as ultrasensitive sensors, as ultra-lightweight structural materials, as highly efficient alternative energy sources, as environmentally benign materials, or as new materials for an entirely new application.

2.4.3 TYPES OF NANOMATERIALS

2.4.3.1 Ultrathin Films (Two-Dimensional Nanostructures)

One can try to spread the atoms on a flat surface to form a single layer, and thus would have constructed an ultrathin film (or coating, if you will) which is only 1 Å thick and can cover roughly a square area of 1000 Å 2 or 1 μm^2 when compacted. The covered area is not nanometer-sized, but the film thickness is sub-nanometer, and thus, this film is within the realm of nanotechnology. This may be done in the lab by vaporizing the 10^6 atoms and allow them to adhere onto a solid substrate. In the lab, this technique is called atomic layer deposition as reported by George, et.al in 1996[16]. It is important to note, however, that to form a single layer of atoms on a flat substrate is not trivial, because it may not be stable. Atoms at a surface or interface experience an imbalance of forces. Below and beside them, they have other atoms that pull them inward due to bonding interactions, and above them it is just air or vacuum. Nature abhors this imbalance it is unstable, and thus, ordinarily, the surface atoms would seek ways to minimize this imbalance, to lower the surface energy. Clustering is one way to minimize surface energy. In fact, the growth of film formed by vapor deposition would most likely start with clustering of atoms (nucleation) and this growing cluster may begin to coalesce with the other clusters to eventually form a continuous film. In this case, the film may not be mono-atomic in thickness but would turn out to be several atomic layers thick. Nonetheless, it may still be nanometer-thin and so we have a nano structured system. The preparation of ultrathin films poses experimental and theoretical challenges, and thus many scientists are busying themselves with these concerns.

Another way would be for person to disperse the atoms into a solvent to form a solution, and from there, allow the atoms to spontaneously organize onto a solid substrate. Obviously, gravity would not do it because they are too small to be settling down; there are other forces in solution that will keep them dissolved. The formation of thin film will happen if there is a strong preferential attraction of atoms to the substrate. What one can hope to do here is to spontaneously crystallize our atoms onto a surface or interface: a self-assembling technique. Self-assembly is a generic term for forming nanostructures from a disordered state. This is a major technique, actually, that is widely used because it offers a generally straightforward manner of building nanostructures, and is amenable to mass production of the nano-material for commercial purposes. This is a bottom-up approach to nano-synthesis, because the structure is built in a manner that is one atom at a time. If self-assembly were not possible, a bottom-up approach is not going to be efficient, if one is to build atom-by-atom mechanically. This methodology is opposed to the top-down approach, wherein one first makes a bulk material, and then its size is decreased by mechanical or some other means until the material is divided or fabricated into the nanometer size range.

2.4.3.2 Nanoparticles (Zero-Dimensional Nanostructures)

If the 10^6 atoms are all in one solid mass, and are closed-packed in a particle, it will occupy a volume of about 6000 nm^3 with a width or diameter of only about 18 nm. A million atoms make a nano-particle! Many everyday-life particles that one encounters are already nanometer in dimensions, such as the micelles formed by soap molecules in water, smoke particulates, or clay particles. In fact, nanoparticles were used hundreds of years ago as colorants in Chinese vases or pigments in the stained glass windows of cathedrals in Europe. There is much renewed interests in nanoparticles because chemists and other researchers are able to characterize their behavior at higher precision using the advanced tools that are now available. There are also various ways to synthesize and stabilize them, and new possible applications are discovered.

2.4.3.3 *Nanowires (One-Dimensional Nanostructures)*

Going back to our starting 1 million atoms, to produce a one-dimensional structure, will need to align the atoms unidirectionally to make elongated structures. Based on the length of the nanostructure, it could be a nanowire or a nano rod. Bonding the atoms to make a linear polymer chain is not new, but this is possible only with elements that are amenable to extensive covalent linkages, otherwise, the structure will be unstable. For semiconductor or metallic elements, nanowires are made with nanometer-sized radii, such that the cross-section of the wire consists of hundreds or thousands of atoms. They may be formed by controlling the growth process, usually along preferred directions of crystallization or using a template to align the process.

2.4.3.4 *Supramolecular Assemblies*

As discussed so far, nanostructures that can be formed based on the dimensionality of the material produced. However, nanotechnology or nanochemistry is not limited to these types, and more often than not, the nanostructured system or material is a composite of various types. Ultimately, nanotechnology will approach molecular level control of the device or material architecture. What is uniquely nanotechnology today is that the design is molecular in approach to form materials that are supramolecular assemblies as quoted by Schneider, et.al[17] in 2000 is much of what is happening in biological cells, for example, is a molecular machinery of sorts that is responsible for the spontaneous copying, transcription, and reproduction of the DNA and proteins, for example. And some researchers have also begun to look at nature to come up with biologically-inspired nanomaterials. One such example stated by Podsiadlo, et.al, in 2005[18] is a nacre-like nanostructured composite formed by layer-by-layer assembly of polymers and clay materials that are nanometer-spaced — the resulting structure is brickwork in the nanometer scale. Apart from this Schevchengko, et.al[19] engaged in nanocrystal research in 2006 also discovered that nanoparticles can form superlattices, and a group of researchers has already begun forming various types based on binary nano-particle superlattices. In similar lines Krishnamoorthy, et.al in 2006[20] state that Polymers also form nanostructure assemblies such as those used in nano-patterning using block copolymers (or polymers with two parts of the chain that are different in chemical composition) in a self-assembly approach.

2.4.4 Advantages of Nano-sized Additions

The Nanocomposites 2000 conference (In November 2000, was held in Brussels. Organised by Emap’s ‘European Plastics) has revealed clearly the property advantages that nanomaterial additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include:

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

2.5 FIELDS OF NANOTECHNOLOGY

Describing about the application areas of nanotechnology, Nass et.al.[14] in 2004 stated that Nanotechnology, Nano science can be applied to absolutely any field. It brings about hybridization in all fields of science, to get the best out of it. Today nanotechnology consists of the following major fields:

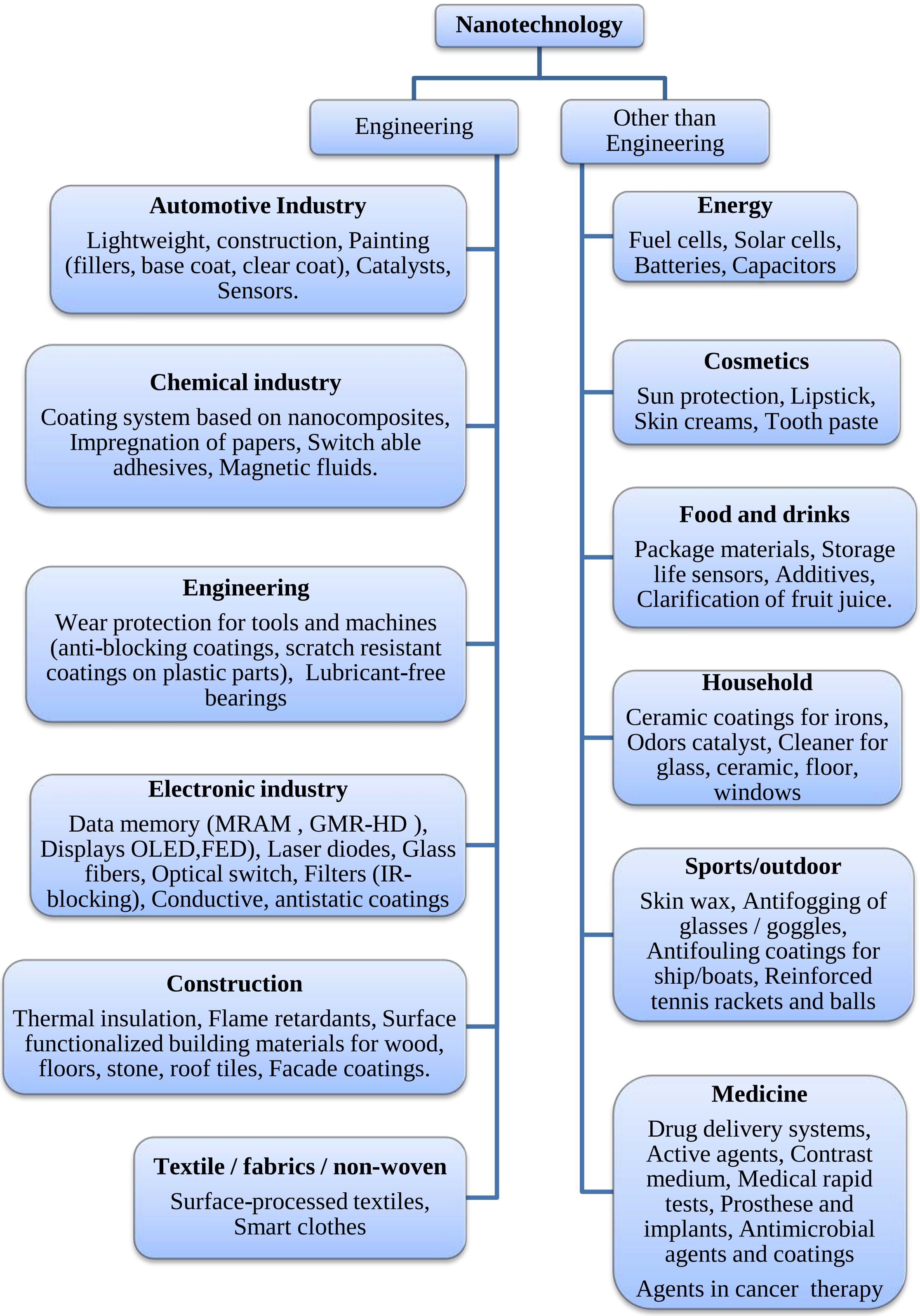


Table 2.1 Overview on applications of nanomaterial based products in different areas

2.6 NANOTECHNOLOGY IN TEXTILE

The textile industry has been already impacted by nanotechnology. Research involving nanotechnologies to improve performances or to create unprecedented functions of textile materials are flourishing. These research endeavours is mainly focused on using nanosize substances and generating nanostructures during manufacturing and finishing processes.

Nano-structured composite fibers are the area where we see the early blooming of nanotechnology: Those composite fibers employ nano-size fillers as nanoparticles (such as clay, metal oxides, carbon black, etc.), graphite nanofibers (GNF) and carbon nanotubes (CNT). Besides, nanostructured composite fibers can be generated through foam-forming processes.

The main function of nanosize fillers is to change the mechanical properties and improve the physical properties such as conductivity and antistatic behaviours. Due to their large surface area, these nanofillers have a better interaction with polymer matrices. Being in the nanometre range, the fillers might interfere with polymer chain movement and thus reduce the chain mobility. Being evenly distributed in polymer matrices, nanoparticles can carry load and increase the toughness and abrasion resistance; nanofibers transfer stress from polymer matrix and enhance tensile strength of composite fibers.

Additional physical and chemical performances imparted to composite fibers vary with specific properties of the nano fillers used. Distribution of nano fillers in polymer matrices through mechanical and chemical approaches is one of the important aspects leading to high quality of nanostructured composite fibers. Although some of the filler particles such as clay, metal oxides, carbon black have previously been used as microfillers in composite materials for decades, reduction of their size into nanometre range have resulted in higher performances and generated new market interest.

Clay is a type of filler which is used since ancient ages. Clay being effective, cheap and easily available in nature is used in all types of industry as well as textiles as filler. Nanoclay is one of the most affordable materials that have shown promising results in polymers, Nanoclays are known to enhance properties of many polymers such as nylon 6, EVA, epoxy, PET, PP, etc.

The impact of nanotechnology in textile finishing area has brought up innovative finishes as well as new application technique. Particular attention has been paid in making chemical finishing more controllable. Ideally, discrete molecules or nanoparticles of finishes can be brought individually to designated sites on textile materials in a specific orientation and trajectory through thermodynamic, electrostatic or other technical approaches.

2.7 CLAY

Clay is a naturally occurring material composed primarily of fine grained minerals, which shows plasticity through a variable range of water content and which can be hardened when dried or fired. Clay deposits are mostly composed of clay minerals (phyllosilicate minerals) and variable amount of water trapped in the mineral. Clay materials have been investigated because of their importance in agriculture, in ceramics, in construction and other uses. It was early recognized that soil containing clay could have the same colour, texture and general appearance yet differ widely in other characteristics. With the development of standard chemical analyses it was determined that the finest clay fractions are composed of silica and one or more of the following: alumina (most common), iron oxide, magnesia, potash and various other oxides. It was also found that two clay materials with the same chemical constituents often had very different physical properties and on the other hand, that clays with the same physical properties might have dissimilar chemical compositions. It then became apparent that clays varied not only in their chemical content but also in the manner in which they are combined.

Before understanding the structure and basic of clay, let us understand some basics terms related to clay.

Ion : Charged particle
Cation : Positively charged particle
Anion : Negatively charged particle
Hydroxyl : OH
Isomorphous substitution: substituting an ion of similar size and generally of lesser charge.

Generally clay is negatively charged and attract positively ions i.e. cations. On the basis of cation exchange capacity it absorbs or lose water at the surface or into interlayer spaces i.e shrinks or swells.

2.7.1 GENERAL STRUCTURE OF CLAY

Clay structure in general can be characterized by two dimensional sheet structure, of which silica tetrahedrons (SiO_4) and Alumina octahedrons (AlO_6) are the main components. As seen from Figure 2.1 (a) & (b) in case of silica tetrahedron, one silica is surrounded by four oxygen whereas in case of alumina octahedron, one alumina is surrounded by six oxygen.

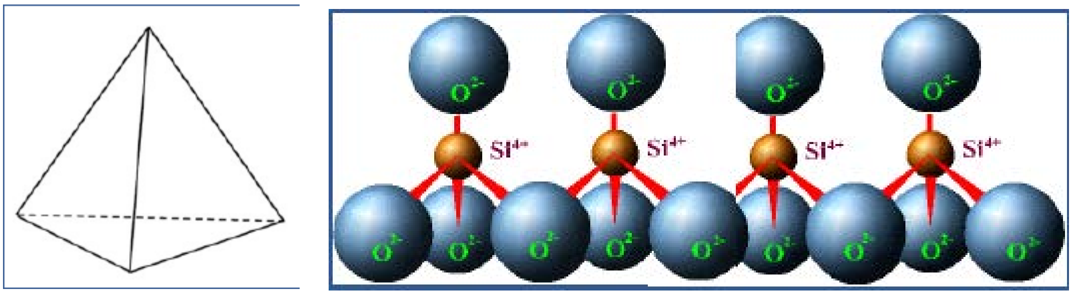


Figure 2.1 (a) Silica tetrahedron

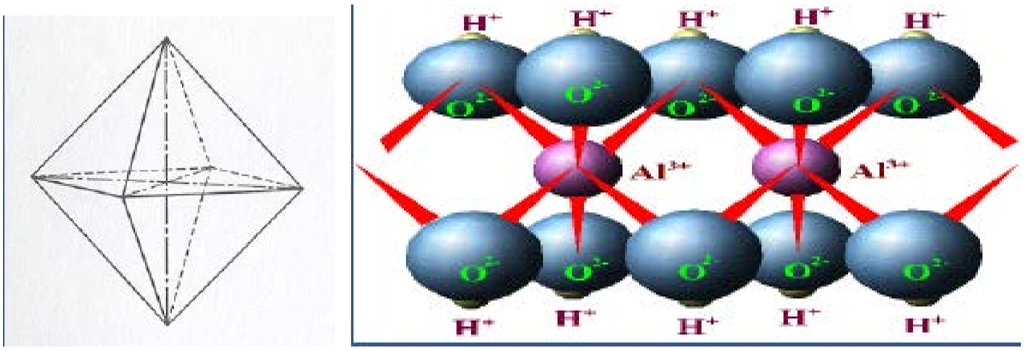


Figure 2.1 (b) Alumina octahedral

These ions, they combine and form a molecule and all these molecules combine and form a sheet. When these sheets are stacked together i.e. sheet upon sheet, it forms a layer. Combining these layers in way of sheet it finally forms a crystal.

So, clay minerals are characterized by two dimensional sheets of corner sharing SiO_4 and AlO_4 tetrahedron as shown in Figure 2.2. These tetrahedral sheets have the chemical compositions $(Al_2Si_3)O_4$ and each tetrahedron shares three of its vertex oxygen atoms with other tetrahedral, forming a hexagonal array in two dimensions.

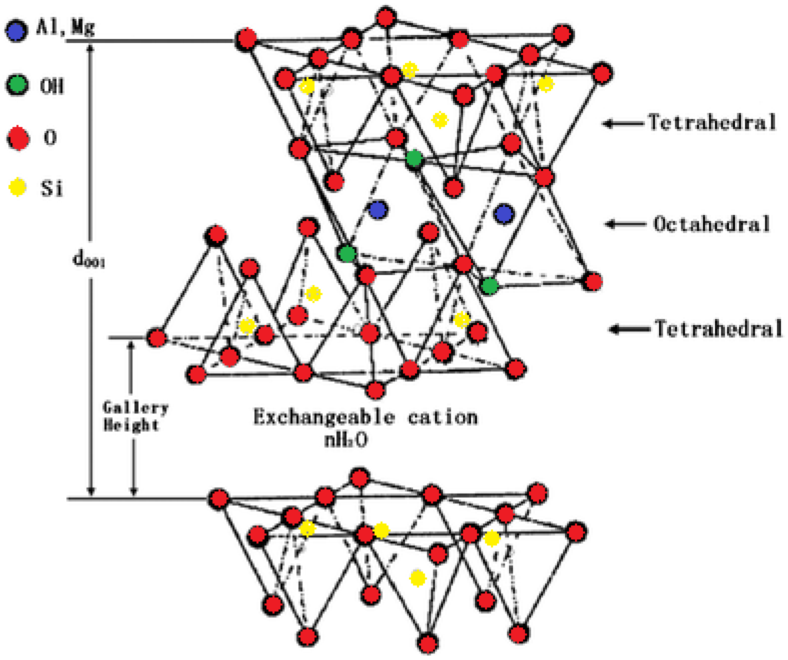


Figure 2.2 General structure of clay mineral

The forth vertex is not shared with another tetrahedron and all of the tetrahedral point in the same direction (i.e all of the unshared oxygen are on the same side of the sheet.) in clays, the tetrahedral sheets are always bound to octahedral sheets (formed from small cations like Al and Mg, coordinated by 6 oxygen atoms). The unshared vertex from the tetrahedral sheet also forms part of one side of the octahedral sheet, but an additional oxygen atom is bound to a hydrogen atom forming an OH group in the clay structure.

2.7.2 CLASSIFICATION OF CLAY

Clay can be categorized depending on the way that the tetrahedral and octahedral sheets are packed into layers. If there is only one tetrahedral and one octahedral group in each layer, the clay is known as 1:1 clay, and if there are two tetrahedral and one octahedral group in each layer, the clay is known as 2:1 clay. As seen from the Figure 2.3 (a) & (b), this schematically represents 1:1 and 2:1 structure. The shared oxygen binds these sheets into layers, where as hydrogen bonding holds these layers tightly together. Based on this the clay minerals used for polymer nanocomposites can be classified into three groups, they are 2:1 type, 1:1 type and layered silicic acid.

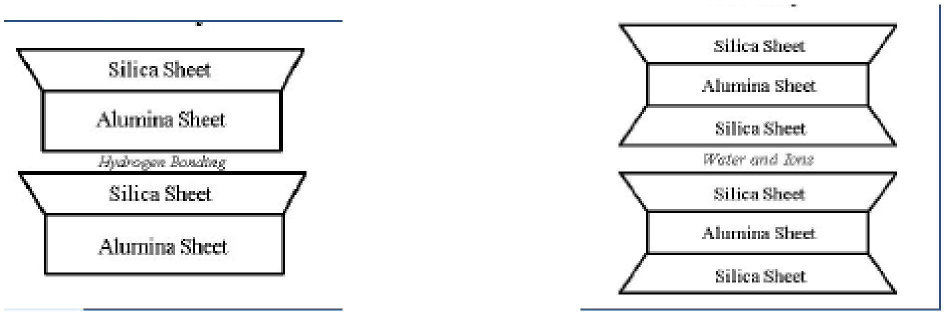


Figure 2.3 (a) 1:1 clay structure *(b) 2:1 clay structure*

2.7.2.1 2:1 Type

The clay belongs to the smectite family with the crystal structure consisting of nanometer thick layers (platelets) of aluminium octahedron sheet sandwiched in between two silicon tetrahedron sheets. Stacking of the layers leads to a van der waals gap between the layers. Isomorphic substitution of Al with Mg, Fe, Li in the octahedron sheets and /or Si with Al in tetrahedron sheets gives each three sheet layer an overall negative charge, which is counterbalanced by exchangeable metal cations residing in the interlayer space, such as Na, Ca, Mg, Fe, and Li.

2.7.2.2 1:1 Type

The clay consists of layers made up of one aluminium octahedron sheet and one silicon tetrahedron sheet. Each layer bears no charge due to the absence of isomorphic substitution in either octahedron or tetrahedron sheet. Thus, except for water molecules neither cations nor anions occupy the space between the layers, and the layers are held together by hydrogen bonding between hydroxyl group in the octahedral sheets and oxygen in the tetrahedral sheets of the adjacent layers.

2.7.2.3 Layered silicic acid

The clay consists mainly of silicon tetrahedron sheets with different layer thickness. Their basic structures are composed of layered silicate networks and interlayer hydrated alkali metal cations. The silanol groups in the inter layer regions favor the organic modification by grafting organic functional groups in the interlayer regions. They are natural clay minerals except octosilicates, but can be synthesized as well. Layered silicic acid is potential candidates for the preparation of polymer nanocomposites because they exhibit similar intercalation chemistry as smectite clays.

Besides they possess high purity and structural properties that are complementary to smectite clays.

The summary of the type of clay, its origin and other details, based on above classification is shown in table below:

Table 2.2 Types of clay, their origin and formula

Type of clay	**Formula**	**Origin**	**Substitution**	**Layer charge**
2:1 type				
MMT	$M_x\ (Al_{2-x}\ Mg_x)\ Si_4O_{10}(OH)_2.\ nH_2O$	N	Octahedral	Negative
Hectorite	$M_x\ (Al_{3-x}\ Li_x)\ Si_4O_{10}(OH)_2.\ nH_2O$	N	Octahedral	Negative
Saponite	$M_x\ Mg_3\ (Si_{4-x}\ Al_x)\ O_{10}(OH)_2.\ nH_2O$	N	Tetrahedral	Negative
Fluorohectorite	$M_x\ (Mg_{3-x}\ Li_x)\ Si_4O_{10}F_2.\ nH_2O$	S	Octahedral	Negative
Laponite	$M_x\ (Mg_{3-x}\ Li_x)\ Si_4O_{10}(OH)_2.\ nH_2O$	S	Octahedral	Negative
Fluoromica (Somasif)	$Na\ Mg_{2.5}\ Si_4O_{10}F_2$	S	Octahedral	Negative
1:1 type				
Kaolinite	$Al_2\ Si_2\ O_5\ (OH)_4$	N	---	Neutral
Halloysite	$Al_2\ Si_2\ O_5\ (OH)_4 \cdot 2H_2O$	N	---	Neutral
Layered silicic acid				
Kanemite	$Na_2\ Si_4\ O_9 \cdot 5H_2O$	N/S	Tetrahedral	Negative
Makatite	$NaH\ Si_2\ O_5 \cdot 7H_2O$	N/S	Tetrahedral	Negative
Octasilicate	$Na_2\ Si_8\ O_{17} \cdot 9H_2O$	S	Tetrahedral	Negative
Magadite	$Na_2\ Si_{14}\ O_{29} \cdot 10H_2O$	N/S	Tetrahedral	Negative
Kenyaite	$Na_2\ Si_{20}\ O_4 \cdot 10H_2O$	S	Tetrahedral	Negative

N = nature, S = synthetic, M indicates exchangeable ions represented by monovalent ions.

2.8 GROUPS OF CLAYS

There are four main groups of clays : kaolinite, montmottilonite-smectitie, illite and chlorite. Chlorites are not always considered as clay, sometimes being classified as a separate group within the phyllosilicates.

2.8.1 KAOLIN

Two layer type (sheet structure composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons). Kaolin was defined by as the "rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in colour. The kaolin minerals are not all of one mineral species but are collectively called the kaolinite group. This group includes the following four clay minerals: Kaolinite, dickite, halloysite and nacrite.

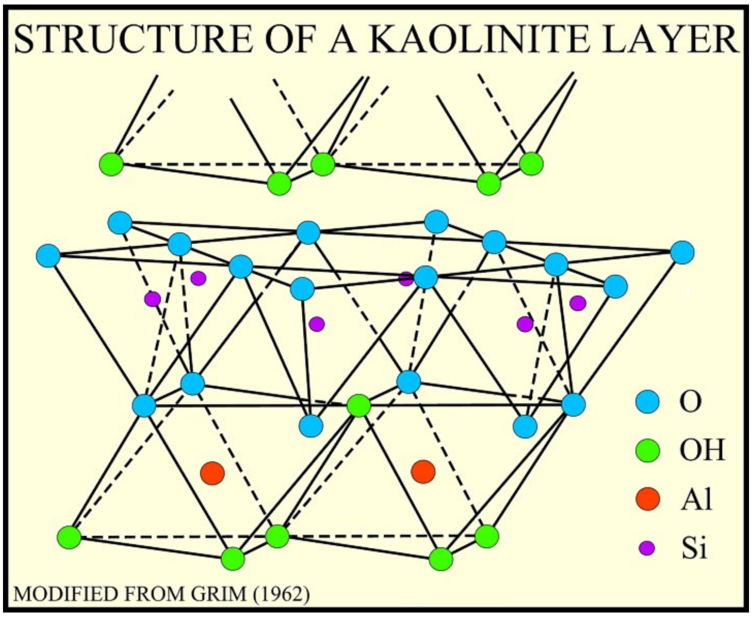


Figure 2.4 ***Structure & Charge distribution of Kaolinite layer***

Kaolinite is the most important member of the group. It occurs in residually weathered material and is a common constituent of soil. The basic kaolin mineral structure comprising the minerals kaolinite, dickite, nacrite and halloysite is a layer of a single tetrahedral sheet and single octahedral sheet. These two sheets are combined to form a unit in which the tips of the silica tetrahedrons are joined with octahedral sheet. All of the apical oxygen of the silica tetrahedrons point in the same direction so that these oxygens and/or hydroxyls which may be present to balance the charges are shared by the silicons in the tetrahedral sheet and the aluminum in the octahedral sheet. The structural formula for kaolinite is $Al_4Si_4O_{10}(OH)_8$ and the theoretical chemical composition is SiO_2 – 45.54%, Al_2O_3 – 39.50% and H_2O – 13.96%. Only two third of the octahedral positions are filled by an aluminium atom. The aluminum atoms are surrounded by four oxygen and eight hydroxyls as seen in Figure 2.4.

2.8.2 MONTMORILLONITE – SMECTITE

The major smectite minerals are sodium montmorillonite, calcium montmorillonite, saponite (magnesium montmorillonite), nontronite (iron montmorillonite), hectorite (lithium montmorrillonite) and beidellite (aluminum montmorillonite). Smectite minerals are composed of two silica tetrahedral sheets sandwiching a central octahedral sheet and are designated as a 2:1 layer mineral, shown in Figure 2.5. Water molecules and cation occupy the space between the 2:1 layers. Montmorillonite is very soft phyllosilicate mineral that typically forms in microscopiccrystals forming clay. The particles are plate shaped with an average diameter of approximately 1 micrometer. It is the main constituent of the volcanic ash weathering product, bentonite.

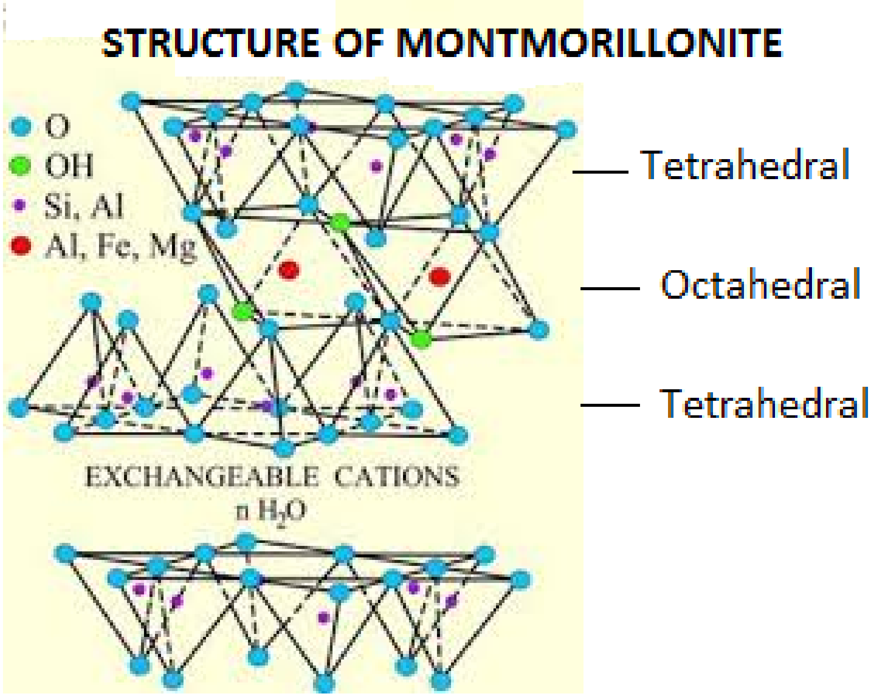


Figure 2.5 Structure & Charge distribution of montmorillonite

Many clays are aluminosilicates, which have a sheet like layered structure and consist of silica SiO_4 tetrahedral bonded to alumina AlO_6 octahedra in a variety of ways. A 2:1 ratio of the tetrahedra to the octahedral results in smectite clays, the most common of which is montmorillonite. The essential nanoclay raw material is montmorrllonite, a 2 to 1 layered smectite clay mineral with a platey structure. Individual platelet thickness are just one nanometer (one billionth of a meter) but surface dimensions are generally 300 to more than 600 nanometer resulting in an unusually high aspect ratio. Naturally occurring montmorillonite is hydrophilic.

2.8.3 ILLITE

Ilite is a potassium smectite clay mineral. The structure is a 2:1 layer in which the interlayer cation is potassium (Figure 2.6) the size, charge and coordination number if potassium is such that it fits snugly in the hexagonal ring of oxygen of the adjacent silica tetrahedral sheets. This gives the structure a strong interlocking ionic bond which holds the individual layers together and prevents water molecules from occupying the interlayer position as it does in the smectites.

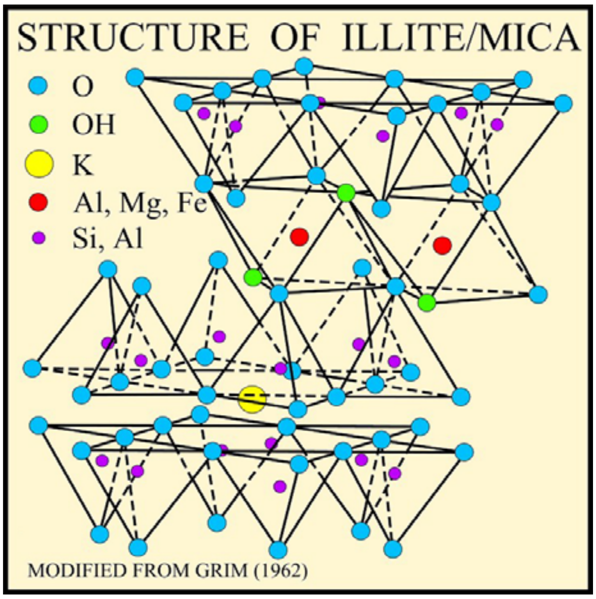


Figure 2.6 Structure of illite/mica

2.8.4 CHLORITE

Chlorite is commonly present in shales and also in underclays associated with coal seams. Clay mineral chlorites differ from well crystallized chlorites in that there is random stacking of the layers and also some hydration. Chlorite is a 2:1 layer mineral with an interlayer brucite sheet $Mg(OH)_2$ as shown in figure 1f. There is a quite a range of cation substitutions in chlorites, most commonly Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}. The composition of chlorite is generally shown as $(OH)_4\ (Si,Al)_8\ (Mg\text{-}Fe)_6\ O_{20}$. The brucite like sheet in the interlayer position has the general composition $(MgAl)_6\ (OH)_{12}$. There is considerable substitution of Al^{3+} by Fe^{3+}, Mg^{2+} by Fe^{2+} and of Si^{4+} by Al^{3+}. Chlorite is generally intimately intermixed with other clay minerals.

Montmorillonite is the most common type of clay used for nanocomposite formation, however other types of clay can also be used depending on the precise properties required from the product. These clays include hectorites (magnesiosilicates) which contain very small platelets and synthetic clays (e.g. hydrotalcite) which can be produced in a very pure form and can carry a positive charge on the platelets, in contrast to the negative charge found in montmorillonites.

2.9 GENERAL CHARACTERISTICS OF CLAYS

The important characteristics pertinent to application of clay minerals in polymer nanocomposites are their richest intercalation chemistry, high strength and stiffness and high aspect ratio of individual platelets, abundance in nature and low cost. First, their unique layered structure and high intercalation capabilities allow them to be chemically modified to be compatible with polymers, which make them particularly attractive in the development of clay based polymer nanocomposites. In addition their relatively low layer charge ($x = 0.2 – 0.6$) means a relatively weak force between adjacent layers, making the interlayer cations and molecules into the interlayer space are facile, which is an important aspect of their uses in polymer nanocomposite manufacturing. Among the smectite clays, MMT and hectorite are the most commonly used ones while other are sometimes useful depending on the targeted application. Moreover, although smectite clays are naturally not nanoparticles, they can be exfoliated or delaminated into nanometer platelets with a thickness of about 1nm and an aspect ratio of 100-1500 and surface areas of 700-800 m^2/g. Each platelet has very high strength and stiffness and can be regarded as a rigid inorganic polymer whose molecular weight (ca.1.3 x 10^8) is much greater than that of typical polymer. Therefore, very low loading of clay is required to achieve properties compared to the conventional composites. Finally, and importantly they are ubiquitous in nature and therefore inexpensive.

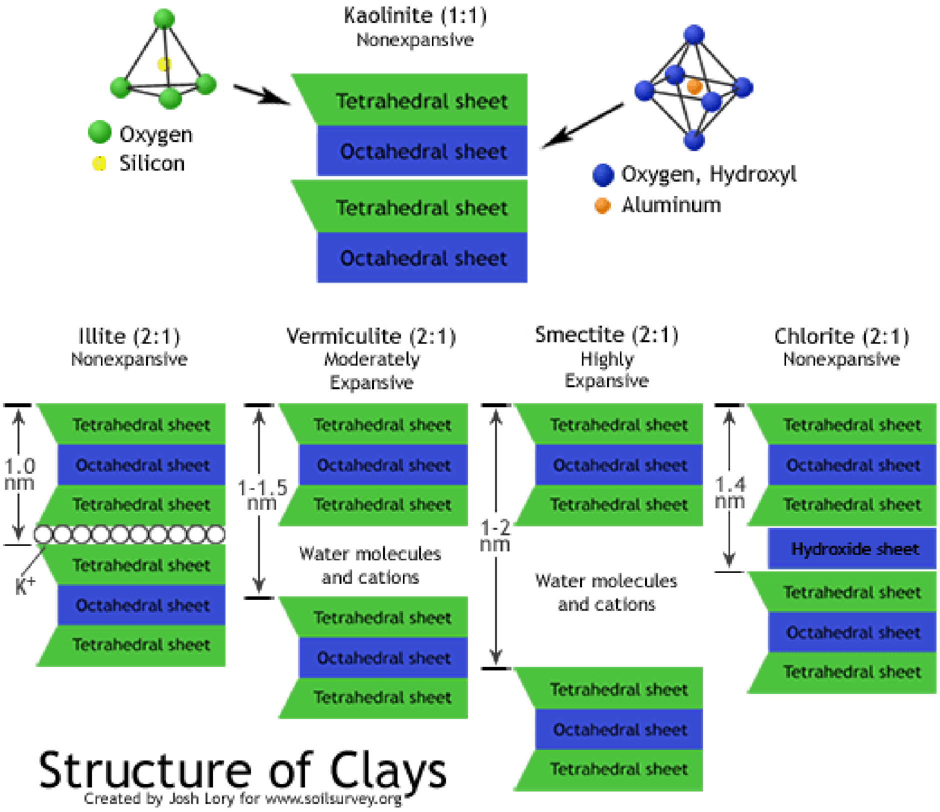


Figure 2.7 Structure of clays

2.10 CLAY MODIFICATION

2.10.1 ORGANOCLAY

Common clay is naturally occurring minerals and is thus subject to natural variability in their constitution. The purity of the clay can affect final nanocomposite properties[21]. The clays are also characterized by their ion (e.g. cation) exchange capacities, which can vary widely. One important consequence of the charged nature of the clay is that they are generally highly hydrophilic species and therefore naturally incompatible with a wide range of polymer types. Unmodified nanoclay disperses in polymer with great difficulty. Through clay surface modification, clay can be made organophilic and therefore compatible with conventional organic polymer.

A necessary prerequisite for successful formation of polymer clay nanocomposite is therefore alteration of the clay polarity to make the clay 'organophilic'[22]. Organophilic clay can be produced normally from hydrophilic clay by ion exchange with an organic cation such as an alkylammonium ion. The clay chemical complex, which exhibits definite gallery spacing between the platelets, is called a Nano Organoclay, Figure 2.5.

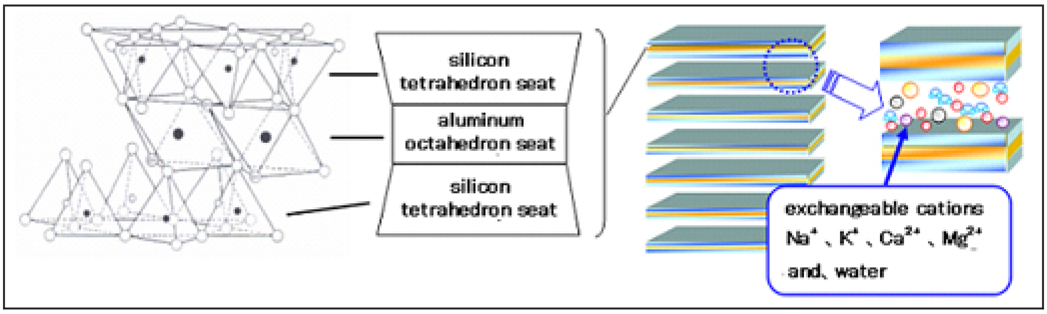


Figure 2.8 ***Schematic of ion-exchange reaction in layered silicates***

2.10.2 CATION EXCHANGE CAPACITY

Clay and organic matter provide the characteristic property of soil called cation exchange capacity (CEC). It is the capacity of the soil to hold cations, generally Al^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Na^{+}, K^{+} and H^{+} [23]. It is described as the quantity of positively charged ions held by the negatively charged surface of clay mineral. It can be expressed as centimol positive charge per Kg of soil or milliequivalent (meq) of positive charge per 100 g of soil. However in general most of the clay minerals tend to have a negative charge resulting from the substitution of silica cation (Si^{4+}), by aluminum cation (Al^{3+}) in the clay sheet structure. This phenomenon, referred to as isomorphous substitution produces the capacity in clay sheets to hold positive charges.

2.10.3 APPLICATION OF ORGANOCLAY

Some of the novel applications of Organoclay are mentioned below[22, 24 - 28]:

1. Organoclay is used in the ink formulation. It helps to adjust the consistency of printing inks to the desired value, avoiding pigment sedimentation, providing good colour distribution, obtaining desired film thickness, etc. by incorporation of small amount of organically modified layered silicate.

2. Thickening lubricating oils with Organoclays can produce especially high temperature resistant lubricating greases.
3. Organoclay also gives good working stability and water resistance to the greases. Such greases are typically used for lubrication in foundries, mills and on high speed conveyors, agriculture, automotive and mining.
4. The performance of cosmetics is enhanced by the use of Organoclays and they allow good colour retention and coverage for nail lacquers, lipsticks and eye shadows. They have been tested to be nonirritant for both skin and eye contact.
5. The applicability of Organoclays as rheological modifiers in paints, inks, greases and cosmetics.
6. Nanoclay as drug vehicle: The continuous development of new controlled drug delivery systems is driven by the need to maximize therapeutic activity while minimizing negative side effects. One class of drug delivery vehicle that has received more attention in recent years is layered minerals which can accommodate polar organic compounds between their layers and form a variety of intercalated compounds.
7. Waste water treatment: The use of Organoclays in waste water treatment has become common in industry today. Organoclay exhibits a synergistic effect with many commonly utilized water treatment unit processes including granular activated charcoal, reverse osmosis and air strippers.
8. Organoclay is one of the ideal materials for treating industrial waste water. In the process of manufacturing heater coils, as part of their quality control (QC), the company leak tests each unit. The leak testing is conducted by pressurizing the coils while they are submersed in large tanks of water. Since the leaks are spotted visually, the water in the tanks must be as clear as possible.

2.11 SELECTION OF MONTMORILLONITE

Clay can be categorized depending on the way that the tetrahedral and octahedral sheets are packed into layers. If there is only one tetrahedral and one octahedral group in each layer, the clay is known as 1:1 clay e.g. Kaolinite and 2:1 clay has two tetrahedral sheets with the unshared vertex of each other and forming each side of the octahedral sheet as known as layer silicates. The 2:1 layer silicates include mica, smectite, vermiculite and chlorite. Smectite group is further divided into montmorillonite (MMT), nontronite, saponite and hectorite species[29 - 31]. Among these layered silicactes, MMT is widely used as reinforcement for the polymer-clay nanocomposites because it is environmental friendly, readily available in large quantities at relatively low cost and its intercalation chemistry is good and well understood[32]. Montmorillonite is extremely fine grained, do not form macroscopic crystals and swell on addition of water or organic liquids[33, 34].

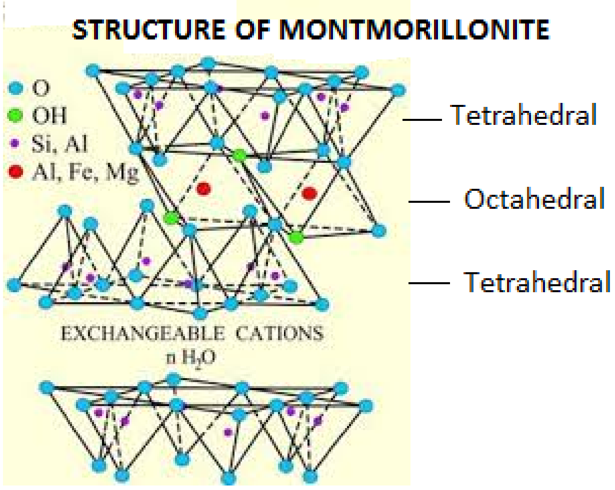


Figure 2.9 Structure of Montmorillonite Clay

Montmorillonite is a 2:1 type consisting of two silicon oxygen sheets held together by intervening cations with water molecules in the interlayer spaces. Schematic of sodium MMT is shown in Figure 2.9[35]. Two outer tetrahedral layers containing Si and O atoms are fused to an inner octahedral layer containing Al and Mg atoms that are bonded to oxygen or hydroxyl group. Individual clay particle has "platey" structure with lateral dimension of 200 to 600 nanometers and thickness of only 0.96 nm[36, 37]. These layers organize themselves to form stalks by vanderwalls force of attraction between them. Force of attraction occurs due to sharing of different forms of charge between them. Small amount of cation on surface is balanced by majority of these cations located inside galleries. So in pristine form, clay is hydrophilic (platelets contain Na^+ or k^+ ions)[38] . The attraction force between layers is relatively weak so polymer molecules can be intercalated between them[32, 39, 40]. Charge on the surface is expressed as cation exchange capacity (CEC) meq/100g[41].

In natural form clay can disperse only in hydrophilic polymers like Poly (ethylene oxide) and poly (vinyl alcohol) [42, 43]. In order to render the surface more organophilic, hydrated cations of clay surface are replaced by cationic surfactants (alkylammonuim or alkyphosphonium / onium) to lower the surface energy. Sodium ions in natural clay are exchanged with an amino acid such as 12-aminododecanoic. Schematic of reaction is shown in equation 1[44].

$$\mathrm{Na^{+}\text{- clay} + HO_2\,C - R - NH_3 + Cl \longrightarrow HO_2\,C - R - NH_3 + clay + NaCl}$$

– Equation 1.

The cations receding between the layers cause the organic molecules to radiate away and increase the interlayer spacing between platelets. So modified clay is more compatible and facilitates the intercalation of polymer chain between the clay galleries. At a given temperature, layer spacing depends on the organic chain length and CEC of layered silicate.

2.12 POLYMER NANOCOMPOSITES

In the past decade, polymer nanocomposites have emerged as a new class of materials and attracted considerable interest and investment in research and development worldwide. This is largely due to their new and often much improved mechanical, thermal, electrical and optical properties as compared to their macro and micro-counterparts. In general, polymer nanocomposites are made by inorganic and organic nanofillers into either a thermoplastic or thermoset polymer. Nanofillers can be three dimensional spherical and polyhedral nanoparticles (e.g. colloidal silica), two dimensional nanofibers (e.g. nanotube, whiskers) or one dimensional disc like nanoparticles (e.g. clay platelet). Such nanoparticles offer enormous advantages over traditional macro or micro particles (e.g. talc, glass, carbon fibers) due to their higher surface area and aspect ratio improved adhesion between nanoparticle and polymer and lower amount of loading to achieve equivalent properties. Organic – inorganic hybrid nanocomposites based on polymer and nanoclay are an important group of nanocomposite with unique set of mechanical and thermomechanical properties synergistically derived from both the constituents. One general approach to prepare these nanocomposites is to employ intercalation chemistry of layered inorganic solids in which polymer is inserted into the interlayer gallery space of layered silicates. Such layered solids include graphite, clay, minerals, transition metal dischalcogenides, metal phosphates, phosphonates and layered double hydroxides, etc. among them clay mineral have been widely used and proved to be very effective due to their unique structure and properties. Besides they are readily available and cost effective, making them ideal for industrial applications. Such minerals include both natural clays (e.g. montmorillonite, hectorite and saponite) and synthesized clays (e.g. fluorohectorite, laponite and megadilite) as shown in Table 2.2, among them, montmorillonite and hectorite are to date the most widely used one. There are many review of polymer nanocomposites in the literature on organoclays, clay polymer interaction or the processing aspects of clay polymer nanocomposites[45 - 49]. To sum up the ideal nanocomposite is a material which completely integrates and distributes the reinforcinf filler into the polymer at the nanoscale, effectively producing homogenous nanostructured material instead of a mixture of materials as with traditional filled systems.

2.12.1 POLYMER NANOCOMPOSITE PREPARATION METHOD

There are three types of preparation method of polymer/nanoclay composite according to the starting material and processing technique:

2.12.1.1 Solution Method

This method is based on a solvent system in which the polymer or pre polymer is soluble and the silicate layers are swellable. Initially the silicate layers are swollen in a solvent such as water, chloroform or toluene. When the polymer and layered silicates are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. The intercalated structure is obtained when the solvent is removed from the system. Solution method of preparing nanocomposites has been widely used with polymers based on poly(vinyl alcohol), poly(ethylene oxide), poly(vinylpyrrolidone), poly(acrylic acid), poly(ethylene glycol), poly (propylene), poly(ε-caprolactam) or poly(l-lactide). However, this process hinders the industrial application because of usage of large quantities of solvent and poor clay dispersion.

2.12.1.2 In-Situ Polymerization

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution. During polymerization, polymer formation can occur between the silicate layers. Polymerization can be initiated either by heat or radiation. The work initiated by Toyota research group on in-situ polymerization of nylon-6 based nanocomposite initiated the development of polymer layered silicate nanocomposites. They studied the ability of α,ω-amino acids ($^{+3}HN{-}(CH_2)n{-}1{-}COOH$, with n = 2, 3, 4, 5, 6, 8, 11, 12, 18 modified Na^+-MMT to be swollen by the ε- caprolactam monomer at 100°C and subsequently initiate its ring opening polymerization to obtain N6/MMT nanocomposites. It results in a significant improvement in thermal and mechanical properties.

The other types of nanocomposites produced by this method are based on poly (ε-caprolactone), poly (styrene), poly (propylene), poly (ethylene) and polyethylene terephthalate.

2.12.1.3 Melt Blending

Melt blending is believed to be the most convenient preparation process and traditional polymer process equipment can be easily used. The melt blending method involves annealing, statically or under shear, a mixture of the polymer and nanoclay above the softening point of the polymer. Melt intercalation method of preparation of nanocomposites has been widely used with polymers based on poly (ethylene oxide), nylon 6 and polypropylene.

The advantage of this method is that it is more flexible and environmentally benign due to the absence of chemical reactions and organic solvents. This method found to have great potential for industrial applications. Apart from this advantage, a few studies show that shear encountered in polymer melt processing techniques helps in homogenization of the polymer claynanocomposite. Due to these factors, melt intercalation method was chosen to prepare the PP/nanoclay composites. The different processing factors which affect the nanocomposite morphology will be discussed later.

2.13 POLYMER NANOCOMPOSITE STRUCTURE

When layered clays are filled into a polymer matrix, three levels of nanofiller organization can result; either conventional composite or nanocomposite can be formed depending n the nature of the components and processing conditions. These three systems as shown in figure are phase separated, intercalated and exfoliated. The distance between a plane in the unit layer and the corresponding plane in the next unit layer is the basal plane spacing d_{001}, as defined in figure type A is a phase separated system (conventional composite) obtained if the polymer cannot intercalate into the galleries between the silicate layers. The properties of such composite are similar to that of polymer composites reinforced by microparticles e.g. talc or mica filled polypropylene. These filled systems tend to display significant reduction in elongation and toughness compared to that of that host matrix polymer. Type B, is an intercalated nanocomposite, in which monolayer of extended polymer chains is inserted into the gallery of clay minerals resulting in a well ordered multilayer morphology stacking alternately polymer layers and clay platelets and a repeating distance of a few nanometers. This configuration in general will show an increase in material properties, but as the increased contact surface area between the polymer and the filler is still quite limited, the increase will be moderate. Type C, shows exfoliated or delaminated nanocomposite, in which the clay platelet are completely dispersed in the system at the nanoscale level with no ordering in the structure. This allows for maximum surface area exposure and as a result maximum improvements in the properties of the system. In reality, it should be noted that polymer nanocomposite incorporate more than one of these nanofiller organization states within the whole polymer matrix. In most cases the cluster (so-called partly exfoliated) nanocomposite is common. The basal planar spacing d_{001}, is a witness to the degree of interalation and exfoliation, but it does not directly disclose the proportion of clay that is exfoliated.

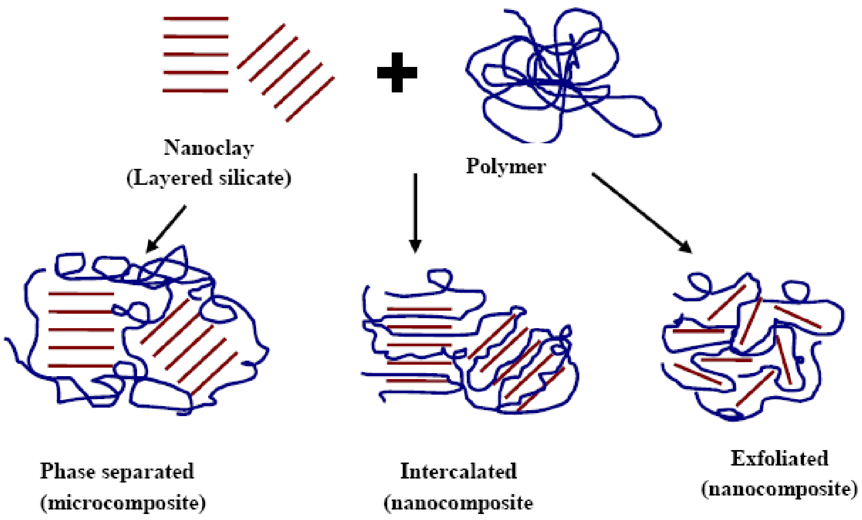


Figure 2.10 Phase separated, Intercalated and Exfoliated composite systems

2.14 TESTING AND ANALYSIS OF POLYMER NANOCOMPOSITE

The structure of polymer nanocomposites is generally characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). XRD in particular wide angle XRD is the most commonly used technique for examining the structure and occasionally for studying the process kinetics of polymer nanocomposites. Either intercalated or exfoliated nanostructure can be studied by monitoring the position, shape and intensity of the basal reflections of XRD patterns of the materials. For instance, the extensive layer separation in an exfoliated nanocomposite is reflected in the disappearance of any coherent XRD whereas the finite layer expansion in an intercalated nanocomposite is associated with the appearance of a new basal reflection corresponding to the larger gallery height. XRD offers a convenient method to determine the interlayer spacing of original layered clays and intercalated nanocomposites. Unfortunately, such technique cannot provide information about the spatial distribution of the clay layers or structural non homogeneities in nanocomposites. It is also difficult to study systematically systems having a broadening peak and weakening intensity. From this point of view information from XRD patterns is not sufficient to reveal the formation mechanism and ultimate structure of nanocomposites.

In contrast TEM can provide direct qualitative information of structure, morphology and spatial distribution of the various components as well as the defect structure.

However, one should be cautious about data from XRD when the layer spacing in intercalated nanocomposites exceeds 6-7 nm or when the layers become relatively disordered in exfoliated nanocomposites. In this case, the simultaneous use of small angle X-ray scattering (SAXS) with wide angle XRD can yield quantitative characterization of the structure in polymer nanocomposites. Besides nuclear magnetic resonance (NMR) is another important tool for probing surface chemistry and coordination in exfoliated polymer nanocomposites, which may help quantify the level of clay exfoliation. Fourier transformation infrared (FTIR) and Raman spectroscopy can be used to understand the structural formation of polymer nanocomposites. As per the work, the analysis techniques carried out related to structure and mechanical properties are discussed here:

a) Analysis of structural properties
b) Analysis of thermal behaviour
c) Testing of mechanical properties

2.14.1 ANALYSIS OF STRUCTURAL PROPERTIES

2.14.1.1 Surface analysis by Scanning Electron Microscopy (SEM)

The surface structure of polymer nanocomposites, fracture surfaces, nanofibres, nano-particles and nanocoating can be imaged through SEM with great clarity. As very high resolution images of the dimension 1 - 5 nm can be obtained, SEM is the most suitable process to study the nanofibres and nanocoatings on polymeric/textile substrate. The scanning electron microscope is an electron microscope that images the sample surface by scanning it with a high energy beam of electrons. The SEM shows very detailed three dimensional images at much high magnifications (up to x300000) as compared to light microscope (up to x 10000) but, as the images are created without light waves, they are black and white.

When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc.

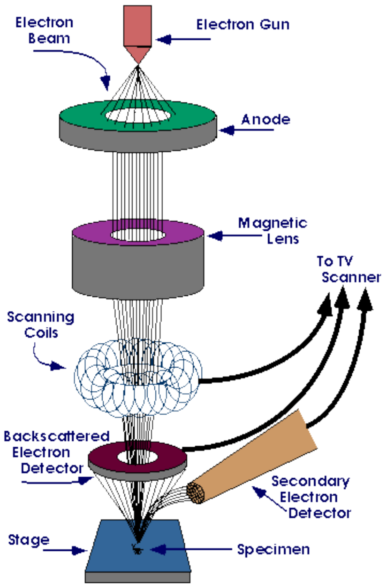


Figure 2.11 Scanning electron microscope and Schematic diagram of SEM

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a faster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the faster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

2.14.1.2 Elemental analysis by Oxford-Inca software on SEM

Energy dispersive X-ray analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample. The composition or the amount of nanoparticles near and at the surface can be estimated using the EDX, provided they contain some heavy metal ions. For example, the presence of Au, Pd and Ag nanoparticles on surface can easily be identified using EDX technique.

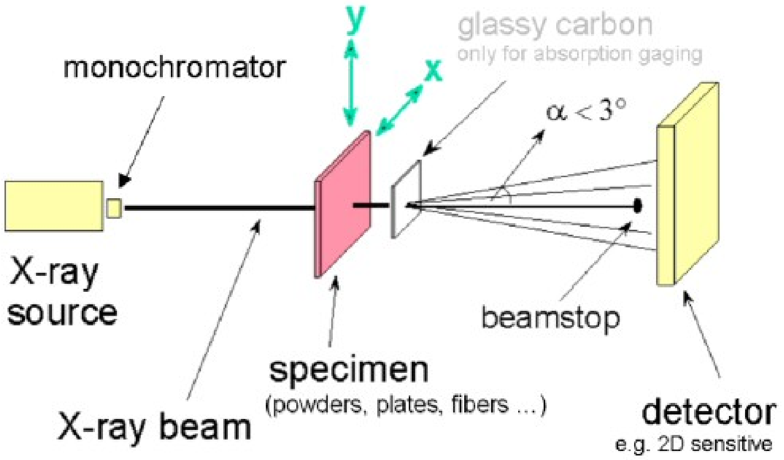


Figure 2.12 Elemental analyses of nanoparticles by EDX.

This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination.

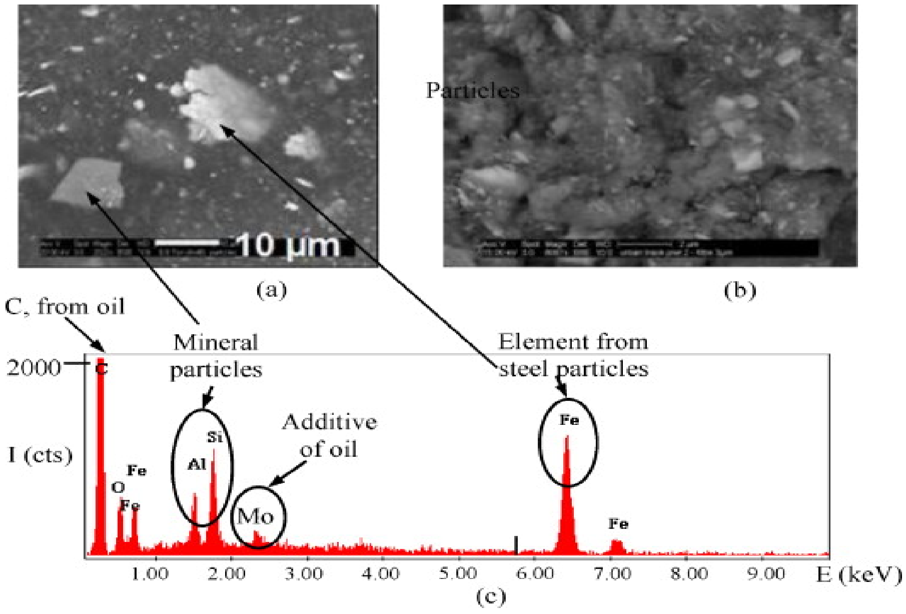


Figure 2.13 Elemental analyses of nanoparticles by EDX.

2.14.1.3 Wide Angle X-Ray Diffraction

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength (few Angstrom). They are produced when electrically charged particles of sufficient energy are decelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.

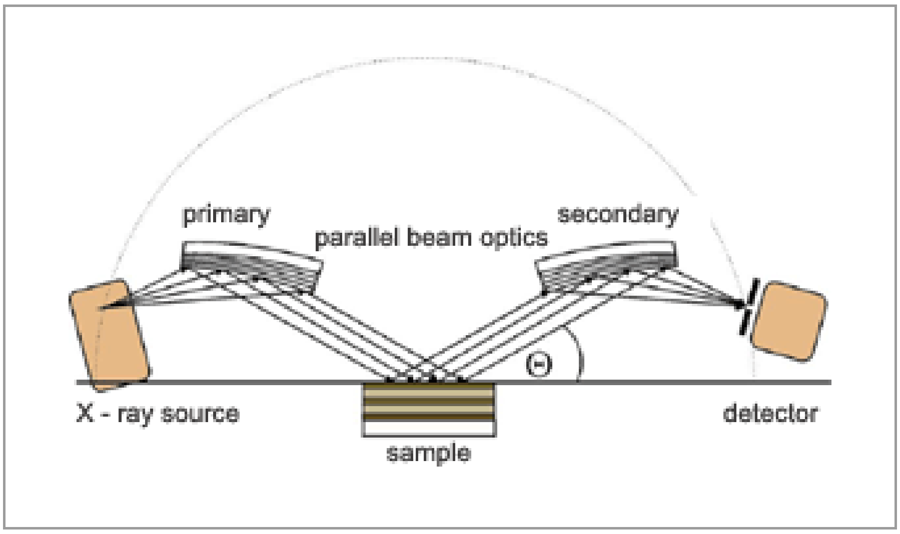


Figure 2.14 Diffractometer D8 advance with CuK α radiation

X-ray diffraction data from polymers generally provide information about crystallinity, crystallite size, orientation of the crystallites and phase composition in semi crystalline polymers. With appropriate accessories, X-ray diffraction instrumentation can be used to study the phase change as a function of stress or temperature, to determine lattice strain, to measure the crystalline modulus, and with the aid of molecular modeling to determine the structure of polymer.

Besides the above mentioned characterization for true nanocomposites, the clay nanolayers must be uniformly dispersed and exfoliated in the polymermatrix. The structure of polymer/layered silicates composites has typically been established using wide angle X-ray diffraction (WAXD) analysis. By monitoring the position, shape and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers.

Principally, an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg's law. As each crystalline material including the semi crystalline polymers as well as metal and metal oxide nanoparticles and layered silicate nanoclays have a characteristic atomic structure, it will diffract X-rays in a unique characteristic diffraction order or pattern.

2.14.1.4 Analysis of Chemical Compound by FT-IR Spectroscopy

The technique is based on the fact that a chemical substance shows marked selective absorption in the infrared (IR) region. After absorption of IR radiation, the molecules of a chemical substance vibrate at many rates of vibration giving rise to close packed absorption bands called IR absorption spectrum which will correspond to the characteristic functional group and bands present in a chemical substance. Thus an IR spectrum of a chemical substance is a finger print for its identification. FT-IR was carried out on Shimadzu FT-IR 8400S specto photometer using the Kbr pellet method.

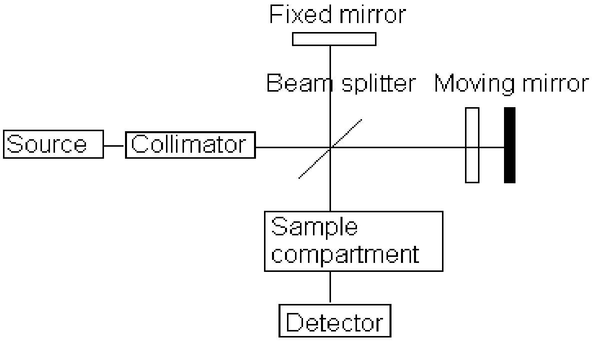


Figure 2.15 FT-IR Shimadzu 8400S Spectrometer instrument with its working principle.

2.14.2 DETERMINATION OF THERMAL BEHAVIOUR

*2.14.2.1 Analysis of Thermal Behaviour by Differential Scanning Calorimet*er

The thermal characterizations of material is analyzed using DSC (differential scanning calorimeter)

DSC measures:

- Glass transition temperature

- Melting and crystallization temperatures
- Heat of melting
- Various parameters related to the crystalline structure
- Temperatures of decomposition reactions.

The sample preparation was done by cutting the sample into small piece and weighing them accurately. The weighed sample is placed in aluminium pan and sealed. In DSC the given sample and the reference material (which does not undergo any transition in the temperature range of interest, here empty pan were taken as reference material) are kept in separate crucibles in the same furnace which is heated at programmed heating rate. There is an extra heater provided just below the crucible carrying the sample, which operates on the instructions received from the device measuring the temperature difference (ΔT) between the sample and the reference, to maintain the ΔT as zero. Thus the DSC records the extra heat (ΔH) supplied per unit time to the sample crucible as a function of the overall temperature of the furnace.

The DSC of the samples was carried out under the heat – cool – heat mode.Nitrogen gas was used as per the requirement of experiment. The thermograph obtained after the test was analyzed and the results were interpreted. The crystallinity percent (X) of studied samples was also calculated using the following equation.

$$X = \left(\frac{\Delta H}{(1-w_f)\Delta H^*}\right) \times 100 \quad \text{.................................Equation 2.1}$$

Where,

X = Crystallinity %

wf = weight fraction of nanocomposite filler,

ΔH = measured melting enthalpy,

ΔH* = extrapolated value of enthalpy corresponding to 100% crystalline polypropylene, that equals to 209 J/g [58].

2.14.2.2 Thermogravimetric analysis (TGA)

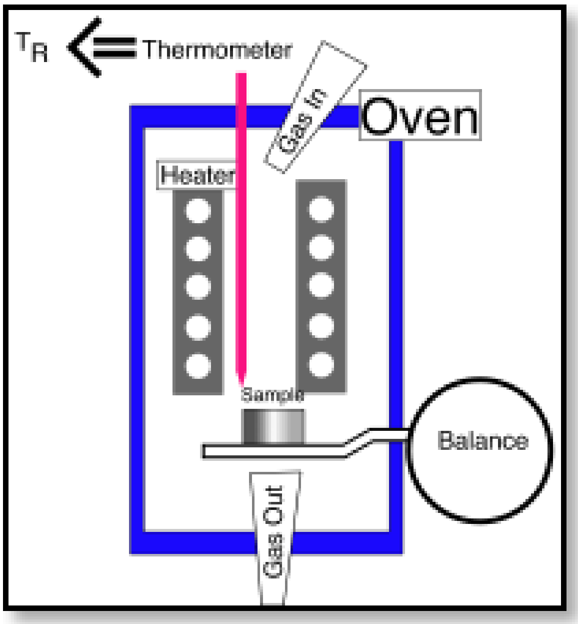


Figure 2.16 Shimadzu TGA-50 thermal analyzer

Thermogravimetry (TGA) was carried out for Na-MMT and Organoclay samples by using a Shimadzu TGA-50 thermal analyzer shown in Figure 2.16. The samples were heated from ambient temperature to 700^oC with 10^oC/min temperature in normal atmosphere. The thermograms associated with TG for control and treated sample were obtained from the instrument output. Detailed information with respect to mass loss degradation onset temperature were obtained from there thermograms for both the samples.

2.14.3 DETERMINATION OF MECHANICAL PROPERTIES

Incorporation of nanoparticles may change or/and improve the mechanical properties of textile fibers according to the corresponding application. Such properties include increased tensile strength, elasticity or fiber stiffness. These properties can lead to the production of stronger or more elastic textiles or increase the tear and wear resistance of a fabric.

- Tensile strength
- Tear strength
- Stiffness (Bending Length)

2.14.3.1 Tensile Strength Measurement

Tensile strength refers to the force acting upon a sample at the time of failure, this is usually the maximum force applied. Tensile strength is defined as the force or load per unit area required, to rupture a material. There are many different units used throughout the world in the textile industry to express strength. Basically in English speaking areas, the units most commonly used for fibers are pounds per square inch.

Tensile strength is the capability of a material to resist the stress put on it by tensile loading. Under tensile loading a structural element is subjected to a pulling action. Unit stress is the magnitude of the force 7 in the pounds that acts on the elements, divided by the cross sectional area A in the square inches, at the point of stress. Thus, S - 7/A. The internal strength of materials varies a good deal. In using structural material the designer must be careful that the tensile stress that the material will have to bear does not exceed its ultimate tensile strength.

Tensile strength is the ability to resists breakage as a result of stress or pull. Generally it is expressed in terms of the force per unit of cross sectional area, i.e. Kg/ m^2. The most common term of fiber and yarn strength is tenacity, which is the force per unit linear density, e.g., where the yam number is expressed as a inter unit length such as gm per denier tensile strength, and tenacity are not the same. Wet strength is often an important characteristic, particularly in the vegetable fibers, which have a higher wet strength than their dry breaks, and in the protein fibers and rayon, which characteristically have lower tenacities when wet than dry.

It should be noted that each of these physical properties contributes in some measure to property number are having to do with the spinnability of a fibrous material. It is not essential that all potential fibers possess all of these features, however, special techniques in spinning can compensate for some of the factories that may be missing in any particular fiber. There are other physical characteristics that contribute to yarn formation and about specification and use, applications of the fabric or apparel.

*2.14.3.2 Tear Strength Measu*rement

The major factors in tensile and tear strengths are the strength of the yarn and the fabric structure. The fiber tenacity is relatively less important because strong yarn or fabric structure can compensate for low individual fiber tenacities.

Tear strength is more clearly related to the serviceability of woven fabrics than is tensile strength. In testing tensile strength all the yarns share equally in the stress applied. But in tear strength, testing a few yarns, at most are subject to stress fabric construction in which groups of yarns are woven together will have the greatest tear strength since more yarns will group together to share the stress. Tenacity is the breaking strength of a sample, expressed in units of force, per unit of cross sectional area of the sample. In the case of yarn it is the breaking strength in grams per denier.

Resistance to rupture the greatest longitudinal stress, a substance can bear without breaking as under. It is usually expressed with reference to a unit area of cross section as the number of pounds per square inch or kilograms per square centimeter necessary to produce rupture. The strength of textile fibers is referred to as their tenacity according lo the American Society for Testing and Materials. Tenacity is determined by measuring the force required lo rupture or Break the fiber. Tenacity of fibers is measured either in gram per tex or gm per denier.

2.14.3.3 Stiffness (Bending Length) Measurement

A rectangular strip of fabric, 6 in. x 1 in., is mounted on a horizontal platform in such a way that it over change, like a cantilever, and bends downwards as shown in figure 2.17.

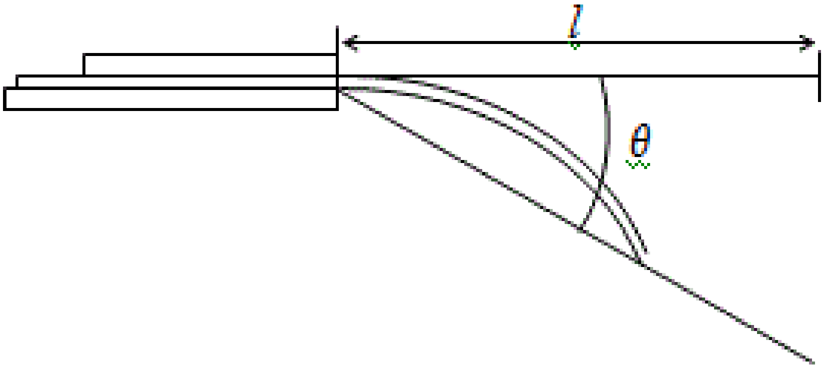


Figure 2.17 Fiber stiffness, cantilever principle

From length 1 and the angle θ a number of values are determined. Here the length of the fabric that will bend under its own weight to a definite extent is called bending length. It is a measure of stiffness that determines draping quality. The calculation is as follows:

$$c = lf_1(\theta)$$

Where $$f_1(\theta) = \left(\frac{\cos\frac{1}{2}\theta}{8\tan\theta}\right)^{\frac{1}{3}}$$

Three specimens in warp way and three in weft are usually tested and since he relative humidity can affect the results the test should be made in a standard testing atmosphere. The horizontal platform of the instrument is supported by two side pieces made of plastic. Attached to the instrument is a mirror which enables the operator to view both index lines from a convenient position. The scale of the instrument is graduated in centimetres of bending length and it also serves as the template for cutting the specimens to size.

2.14.4 DETERMINATION OF MOISTURE MANAGEMENT OF FABRIC (MMT)

Moisture management tester (Figure 2.18) is an instrument which specifically designed to know the water management of performance fabrics. The existing methods like water drop test and vertical wicking test suffer from disadvantages like time consuming, static test and test generates 1 test result, give piece of fabric’s performance info. The MMT is a unique, patented testing technology and measures the whole liquid transfer process in the textile material dynamically in 3 Dimensions.

The unit is connected to a PC and was calibrated and ready for use within 5 to 10 minutes. The fabric specimen was prepared, conditioned and placed in the MMT.

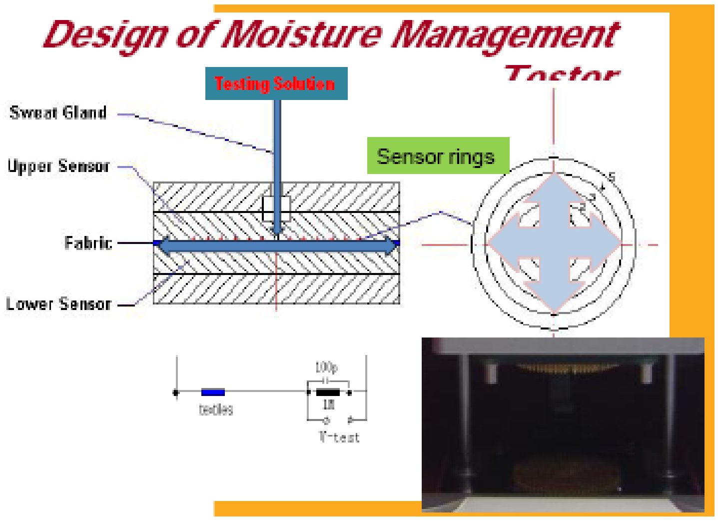


Figure 2.18 SDL ATLAS moisture management tester

Here, wetting time is correlated with absorbency, absorption rates with wicking and absorbency, wetting radius with absorbency and water resistance, spreading speed is correlated with absorbency, water resistance and wicking and finally one way transport and OMMC correlates. From the data generated, over all category of the fabric is decided. MMT categorizes seven different types of fabric based on the data obtained:

1) Water proof fabric
2) Water repellent fabric
3) Slow absorbing and slow drying fabric
4) Fast absorbing and slow drying fabric
5) Fast absorbing and quick drying fabric
6) Water penetration fabric
7) Moisture management fabric

2.14.5 EVALUATION OF ULTRAVIOLET PROTECTION FACTOR (UPF)

Ultraviolet Transmittance Analyzer (SDL ATLAS, USA; Figure 2.19) was used to measure ultraviolet transmittance of treated and untreated fabrics. The term transmittance refers to the percentage of radiant flux transmitted through the sample, relative to the incident energy. The term spectral transmittance refers to the transmission of light at a single wavelength. The UV-2000F instrument measures spectral transmittance across the 250 - 450 nm wavelength spectrum using an integrating sphere and two spectrometer instruments. The sample beam is generated inside the integrating sphere by a high energy ultraviolet pulsed flash lamp. The UPF of a textile material is determined from the total spectral transmittance and higher the value of UPF better is the UV protection.

Figure 2.19 UV-2000F Ultraviolet Transmittance Analyzer

The UV-2000F Ultraviolet Transmittance Analyzer is the most recent and highly application specific ultraviolet spectroscopy product offered by Labsphere. The function of the UV- 2000F is to measure the transmittance of ultraviolet (UV) radiation through sunscreen products and compute new internationally recognized effectiveness characteristics of the product.

2.15 BASIC PROPERTIES OF NANOCOMPOSITES

Polymer nanocomposites exhibit enormously enhanced properties and higher performance as compared to both their conventional polymer composites and pure polymers. In addition such improvement is obtained without the increase of polymer density and the loss of its optical properties and recycling. For example, polymer nanocomposites containing 2-8 % of clay demonstrate great increase in mechanical (tensile, stress, strain) properties together with the thermal (dimensional) stability. They also reduce the gas and liquid permeability. Moreover, they improve the flame retardancy while retaining optical clarity of pure polymer. Finally they can display interesting conductivity properties and improved biodegradability when conductive polymers and biodegradable polymer are involved respectively.

2.15.1 IMPROVING FUNCTIONAL PROPERTIES OF POLYMER NANOCOMPOSITES

Making good samples of polymer nanocomposites is a challenge and a range of processing techniques are being actively developed at present including melt mixing, in situ polymerization and other approaches. A single processing approach is unlikely to deliver viable composites in every system and the different processing techniques often do not give the same results. One of the main issues in preparing good polymer matrix nanocomposites is the good dispersion of the nanoparticles in the polymer matrix which is a strong function of the preparation technique. This is a particular problem as the volume fraction of the particles increases.

An important group of nanocomposites is those based on clay reinforcement where the processing critically depends on the final morphology required for the reinforcement within the composite, i.e. particulate, exfoliated or intercalated. In the intercalated form the matrix polymer molecules are introduced between ordered layers of clay resulting in an increase in the interlayer spacing. However, in the exfoliated form the clay layers are separated and distributed randomly within the matrix. It is possible that some portion of a particular composite will form the intercalation morphology whereas another part will form the exfoliated structure – this is determined by balancing the interaction between the polymer matrix and silicate platelets against interactions between the silicate platelets themselves and may depend on attractive and steric interactions. Exfoliation of layered materials is often hampered by the fact that the materials exhibit a strong tendency to agglomerate due to their large surface areas. However, in general, exfoliated materials show better properties than intercalated materials with the same nanoplatelet concentration and this has driven the development of exfoliated composite systems.

Intercalated nanocomposites are usually formed by mixing in the melt or in situ polymerization whereas exfoliation may require more complex processing depending on the properties of the clay. However, such layered silicate-based polymer nanocomposites have attracted considerable recent interest after the commercialization of polypropylene and nylon 6 based materials. The major barrier to commercialization has been developing techniques to ensure a reliable and reproducible product which has now been addressed for clay based composites some thirty or so years after they were first developed. The use of carbon nanotubes (CNT) in polymer composites has attracted considerable attention but considerable improvements in reliability and reproducibility will be required if CNT are to be used in composites in the same way that clay systems are used today.

To date much of the development of polymer nanocomposites has been for structural applications with current commercial applications such as the step assist for the Chevrolet Astro van introduced by General Motors in 2002. However, there are other composite functions, such as tribological resistance, low friction or fire retardancy which are important in other applications and with nanoscale reinforcements it is possible to mix several different types of reinforcement to generate improvements in a range of properties. The following sections discuss how such properties are improved in nanocomposites.

2.15.2 IMPROVING MECHANICAL PROPERTIES OF POLYMER NANOCOMPOSITES

Many workers have reported that the elastic modulus of nanocomposites increases as the size of the reinforcement is reduced, provided that there was a good interaction between the filler and the polymer matrix. For some nanocomposites with very small reinforcement particles, Young’s modulus is greater than might be expected from the volume law of mixtures of the constituents and this is attributed to the modification to the structure of the matrix surrounding the nanoparticles due to their high surface area.

For polymer systems where a high degree of crystallinity is possible, the increase in modulus with a reduction in particle size is found to be even greater unless there is poor interaction between filler and matrix. The modulus increases with the volume fraction of the reinforcement as expected until aggregation of the particles occurs when the modulus can be reduced in some systems. The yield strength of a polymer nanocomposite is critically dependent on the interaction between the reinforcement and the matrix. Where this interaction is strong the yield stress tends to increase with increasing volume fraction of reinforcement and decreasing particle size. This changes when there is poor interaction where an increase in volume fraction leads to a yield stress decrease from the value for the unreinforced matrix, regardless of the filler concentration or size. The ultimate tensile strength follows a similar pattern to the yield stress. Thus, to achieve nanocomposites with good mechanical properties it is critical that the matrix reinforcement interfacial chemistry is controlled to give strong adhesion.

As the stiffness of the nanocomposite increases, so, in general, does its strength and this is accompanied by a reduction in its strain to failure. The strain to failure for a nanocomposite material is often higher than when the reinforcement is micrometre-sized. However, there are exceptions to this and, as with strength, it critically depends on the bonding between the reinforcement and the matrix – if this is poor then both the strength and strain to failure are reduced. For clay reinforced nanocomposites, increases in modulus compared with the unfilled polymer matrix have been observed in many systems with the effect increasing with filler content as expected but the properties are highly sensitive to microstructure. In general, to maximize stiffness (and thermal properties) it is necessary to achieve full exfoliation and dispersion which is not readily achieved.

Filler particles are added to composite materials to improve their viscoelastic properties. The heat distortion temperature for nanocomposites tends to be higher than that of the unfilled matrix or microreinforced materials because of an increase in viscosity during composite manufacture and a reduction in viscous deformation afterwards.

The increase in tensile strength or Young’s modulus for nanocomposites compared with microcomposites can partly be explained by the details of the interaction between the filler and the matrix. Good adhesion between matrix and particle results in less de-bonding when a stress is applied and consequently the strength is improved. The polymer in the proximity of a particle to which there is good adhesion tends to have higher density which also results in an increase in stiffness. The polymer adjacent to this high density region will have a lower density as the chains are moved towards the particle to make the high density region. For large particles this lower density region will be relatively large and the contribution of the high modulus filler will be diminished compared with the case when the filler particle is small.

For nanocomposites, the number of particles for a given volume fraction is much larger and the particles will be much closer to each other. If the reinforcement particles are very densely packed then the high density boundary layer will make up a larger proportion of the matrix and the modulus will increase. Thus, the major improvements to the mechanical properties of nanocomposites arise from the small particle spacing, rather than directly from the size or volume fraction of the reinforcement particles used. The use of CNT in polymer composites has also received considerable attention. The combination of the high aspect ratio and extreme mechanical properties (strength and stiffness) of CNT provides the ultimate reinforcement for composite materials.

2.15.3 IMPROVING FIRE-RETARDANT PROPERTY OF POLYMER NANOCOMPOSITE

Polymer/clay nanocomposites have been shown to greatly improve the barrier properties and fire retardancy of polymers as might be expected from their highly distributed inorganic material content. This has been reviewed by several authors for both polymer/clay and polymer nanoparticle composites. Intercalated and exfoliated complexes show increased thermal stability compared with the unreinforced polymer. The fire properties of materials are evaluated in many different ways including by cone calorimetry, radiative gasification and limiting oxygen index measurement. Cone calorimetry is the most widely used laboratory method to assess Nanocomposites. This technique generates information on the heat which is released during combustion of the material and the reduction in peak heat release rate (PHRR) is often used to characterize potential fire retardant materials. For instance, in polystyrene/clay nanocomposites, reported that the peak heat release rate may be decreased by up to 58% depending on the composite structure and filler content.

Improvements in fire performance have been reported for polymer/clay nanocomposites with a range of polymer matricies including polyethylene, polypropylene, polyamide, epoxy, polystyrene, acrylonitrile butadiene styrene and ethylene vinyl acetate copolymer. In most cases the fire performance of a polymer/clay nanocomposite is dictated by its composition, rather than by the details of the microstructure, in contrast to the mechanical properties of the composite. The benefits increase as the clay content increases and further improvements can be achieved by the use of compatibilisers. It has also been shown that the use of synthetic clays to improve fire performance is more effective than the use of natural clays in the composite.

Improvements in fire performance have also been reported for nanocomposites reinforced with nanoparticles. For instance, PMMA silica nanocomposites show improved thermal stability compared with the unreinforced polymer and polyimide silica nanocomposites show improved fire retardancy. Oxide nanoparticles generate a decrease in PHRR with a range of fillers and the effect increases with filler content. Synergistic effects have also been reported with the combination of TiO_2 and organoclays.

2.16 INDUSTRIAL APPLICATIONS OF POLYMER NANOCOMPOSITES

The development of composite materials with nanostructured reinforcements is well documented; such composites may have metallic, ceramic or polymeric matrices and be developed in bulk or thin film form. Reinforcements are often chosen to improve the structural performance of the composite without compromising other properties though in some cases it is possible to enhance both structural and functional properties considerably. This has led to emerging applications in a number of industries, particularly the automotive and sports goods industries.

For textile applications polymer matrix composites are the most relevant. In polymer nanocomposites the reinforcements are typically selected to increase the strength of the material and many workers have demonstrated the benefits of adding exfoliated clays, nanoparticles and even carbon nanotubes. The major problems arise in ensuring reliability of processing and achieving a uniform dispersion and distribution of the reinforcement. However, the benefits in structural strength are not always much greater than can be achieved with traditional reinforcements, and to get the greatest benefits from such nanocomposites, additional functionality must be considered. Since a given improvement in mechanical properties can be achieved by a smaller volume fraction of nanoscale reinforcement, there is volume available for the addition of particles which can deliver other properties rather than structural strength and stiffness. Thus there is considerable potential for multifunctional nanocomposite materials, both as bulk composite materials and fibres.

2.17 NANOFILLED POLYPROPYLENE FIBRES

Polypropylene (PP) is, besides polyesters, one of the most widely used polymers for producing synthetic fibres, especially for technical applications. PP fibres are mostly used in different technical fields due to their excellent mechanical properties, high chemical stability and processability. However, because of low surface energy, lack of reactive sites and sensitivity to photo or thermal oxidation the polymer properties are insufficient for some applications. Therefore, several techniques for fibre modification have been reported, e.g. plasma treatment, chemical modification and nanomodification, i.e. production of nanocoated and nanofilled materials.

Polypropylene (PP) fibres have good mechanical properties and can withstand temperatures up to 140°C (softening point 140–160°C) before melting at about 170°C[50]. The low polymer density (0.90 g/cm3) offers several specific application possibilities[51]. Low costs, good chemical resistance to acid and alkaline environments have greatly influenced the high production quantity of this polymer type[50, 52]. Modifications are needed for some purposes due to PP’s high hydrophobicity (moisture regain < 0.1%) and chemical non reactivity and to obtain functional materials with superior physical and mechanical properties for different applications. There is a wide variety of both synthetic and natural crystalline fillers that are able, under specific conditions, to influence the properties of PP. In PP nanocomposites, particles are dispersed on the nanoscale[51, 53]. The incorporation of one, two and three dimensional nanoparticles, e.g. layered clays[54], nanotubes[55, 56], nanofibres[57, 58], metal containing nanoparticles[45], carbon black[46, 47] etc. is used to prepare nanocomposite fibres. However, the preparation of nanofilled fibres offers several possibilities, such as the creation of nanocomposite fibres by dispersing of nanoparticles into polymer solutions, the polymer melt blending of nanoparticles, *in situ* prepared nanoparticles within a polymeric substrate (e.g. PP/silica nanocomposites prepared *in situ* via sol–gel reaction)[59, 60], the intercalative polymerization of the monomer, and the introduction of nanoparticles from dispersion into a porous polymer.

Nanomodification creates improved fibre characteristics, e.g. mechanical strength, thermal stability, the enhancement of barrier properties, fire resistance, ion exchange capability, etc., for use in different application fields. In order to follow modification efficiency, various characterization techniques can be used, e.g. X-ray analysis to study composite structure, morphological observations by electron microscopy, mechanical tests, determination of electrokinetic properties, calorimetric measurements. The dispersion of particles within the hybrid system is of fundamental importance, and thus to observe particles a method based on selective etching of the polymer using a plasma or chemical etching can be used[61 - 63]. The dimensions of spherulites and nanoparticles can be determined by image analysis of the micrographs[63].

2.18 POLYMER LAYERED SILICATE NANOCOMPOSITES

Recently, in order to design materials with the desired properties, nanotechnologies have become of great importance since organic inorganic nanoscale composites frequently exhibit unexpected hybrid properties synergistically derived from the two components[64, 65]. The properties of the particles themselves (size, shape, distribution) can profoundly change the characteristics of a polymer system. Therefore understanding the structure / property relations in polymer/nanoparticles nanocomposites is of major significance[65, 66].

The idea of mixing polymers with appropriately modified clay minerals and synthetic clays is not new. Polymer layered silicate nanocomposites (PLNC) were reported by Carter and coworkers in patent literature, as early as 1950[67]. However, two major findings have led to its revival. Firstly, researchers from Toyota reported a polyamide 6/montmorillonite (MMT) composite with a remarkable enhancement of thermal and mechanical properties due to very moderate inorganic loading. In addition, it was discovered that it is possible to melt mix polymers with clays without the use of organic solvents[65, 68]. Since then, the technology for incorporating nanoparticles into a PP matrix has offered several challenges for research, and for industrial applications. Several different nanoparticles for nanofilled composites, e.g. layered silicates,[51, 65, 69 - 73] silica nanoparticles[46, 74, 75], carbon black[46, 47], carbon nanotubes[55, 56], metal containing nanoparticles[45], elastomeric nanoparticles[76] and TiO_2,[77] have been reported. The most common PP nanocomposites are composed of organically modified silicates, e.g. MMT and polymeric matrix.

Generally, polymer/clay nanocomposites use smectic-type clays as fillers, such as hectorite, MMT, kaolin or synthetic mica, all minerals with a layered structure[51, 69, 78,].

They are of great industrial value because of their high aspect ratio, plate morphology, intercalative capacity, natural abundance and low costs[69].

2.19 THE STRUCTURE AND PROPERTIES OF LAYERED SILICATE POLYPROPYLENE NANOCOMPOSITES

2.19.1 STRUCTURE OF LAYERED SILICATE POLYPROPYLENE NANOCOMPOSITE

Generally isotactic polypropylene (iPP) is used for nanofilled materials, although nanocomposites prepared from syndiotactic polypropylene (sPP) have also been reported[80, 81]. The degree of crystallinity in PP depends on the processing conditions, but is usually between 50 and 60%. The common crystalline PP form is α monoclinic, but other forms (β and γ) have been observed. Polymorphism is important for technological reasons, because each phase has different physical and mechanical characteristics. The crystals are chain folded lamellae and are aggregated into spherulites or row nucleated structures, depending on the processing conditions[50].

Some additives in polymers become nucleation centres, leading to an increase of crystal growth in the crystallization process of the polymer. A foreign surface reduces the nucleus size needed for crystal growth through the creation of the interface between polymer crystal and substrate. The important effect of such nucleation is a modification of polymer morphology, which can result in change of crystallographic form. The nucleating efficiency of various organic and inorganic fillers of iPP talc, chalk, wood flour, nanoclay particles, carbon black, chitosan was studied by Mucha and Królikowski[82]. The best nucleating agents in this research were talc and carbon black. The organic filler as a chitosan powder forms amorphous inclusions in the composites on which iPP molecules cannot be adsorbed. Their presence disturbs a macromolecular diffusion and delays the crystallization process of iPP[82].

The formation of an intercalated nanocomposite structure can be defined by analyzing the interlayer spacing (d_{001}) of clay, although the diffraction maximum originating from the (002) crystallographic plane can be observed on the scattering curves also[69]. Only when d_{001} in the composite is higher than in the pure clay then the polymer molecules were positioned between clay layers and, hence, an intercalated nanocomposite is produced. If the peak corresponding to d_{001} is not observed in a polymer/clay diffractogram, this implies that an exfoliated nanocomposite structure was most likely obtained[69].

2.19.2 PROPERTIES OF LAYERED SILICATE POLYPROPYLENE NANOCOMPOSITE

Nanoparticles are able to provide PP with stiffening, reinforcing and toughening effects at rather low filler concentration. The influence of processing conditions on the nanocomposite structure, i.e. intercalated or exfoliated, and on the enhancement of mechanical properties of PP nanocomposites was studied by different researchers[83]. Most polymer/clay nanocomposites studies report tensile properties as a function of MMT content[65]. The enhancements are strictly related to the processing conditions, the filler content and the presence of compatibilizer[83]. When comparing properties of neat PP and nanocomposites, there is a sharp increase of the Young's modulus for very small inorganic loadings followed by much slower increase beyond approximately 5 wt%. With increasing MMT content the yield stress does not change markedly compared to the neat polymer value.

Considering the same processing conditions, the elastic modulus is higher in the presence of compatibilizer for different filler contents due to the polymer inorganic adhesion improvement. This implies that the stress is much more efficiently transferred from the polymer matrix to the inorganic filler, resulting in a higher increase in the Young's modulus[65, 84]. Similar improvements in mechanical properties can also be achieved by other layered fillers; however, much higher filler loadings are required (e.g. by loading 30–60 wt% of talc or mica)[65]. Silicate clay can increase the modulus, decomposition temperature, yield strength and fatigue strength, and has no effect on glass transition temperature and melt temperature[85].

Polymer/silicate nanocomposites are characterized by very strong reduction of gas and liquid permeability and at the same time the solvent uptake decreases accordingly[65]. When single layers are dispersed in a polymer matrix the resulting nanocomposite is optically clear in the visible region, as clays are just 1 nm thick, whereas there is a loss of intensity in the UV region mostly due to scattering by the MMT particles[65].

Five principal types of generic flame-retardant systems for inclusion in PP fibres have been identified as phosphorus containing, halogen containing, silicon containing, metal hydrate and the more recently developed nanocomposite flame-retardant formulations[86, 87]. The most effective are halogen antimony and phosphorus bromine combinations; however their application is limited by ecological criteria[86]. Several kinds of nanocompounds can be used to enhance the flame retardancy of PP, such as modified MMT, TiO_2, Sb_2O_3 and boroxosiloxanes. Of these, the sodium cation exchanged MMT is the most common because of its low price[65, 86, 88]. The general view of the flame retardant mechanism is that a high performance carbonaceous silicate char builds up on the surface during combustion: this insulates the underlying material and slows the mass loss rate of decomposition products[65, 88]. All MMT-based composite systems nowadays reported show that MMT must be nano dispersed for it to affect the flammability[88]. Investigations have shown that the largest increase in mechanical properties is obtained in exfoliated nanocomposite forms while the intercalated materials show the best fire performance[86].

The results for thermal ageing showed that PP compounds based on organically modified bentonite had higher thermal stability than those with natural clay[69] because of the formation of a nanocomposite structure with reduced oxygen diffusion into the material. However, the thermal degradation of PP with the modified clay is higher than the pure polymer. The phenomenon is attributed to the acidic nature of the clay, the interaction between the clay and PP stabilizers and the decomposition of the organic salt during processing. When the degradation was done in the melt state the thermal stability of the composites may be higher than the pure polymer[69].

Nanostructured materials, i.e. PP filled with an extra pure synthetic fluorohectorite modified by means of interlayer exchange of sodium cations for protonated octadecylamine NH^{3+} (ODA) in a weight concentration of maximum 6%, may find new and upgraded application in the electrical and electronic industry, replacing conventional insulation[89].

2.20 EFFECT OF NANOCLAY ADDITION ON COMPOSITE PROPERTIES

2.20.1 EFFECT ON MECHANICAL PROPERTIES

Polymer layered silicate nanocomposites has found to improve many properties of the host polymer. One of the main properties under study by most of the researchers is mechanical property. Mechanical property of the nanocomposite is directly related to the amount of intercalation or exfoliation of the nanoclay particles. When the nanoclay particles are well dispersed and exfoliated in the polymer matrix, the load bearing capacity will increase and it results in good improvement in mechanical properties, state that stiffness of the silicate layers creates immobilized or partially immobilized polymer phases at the interphase regions is the one of the main factor for the improved mechanical property. Specific surface area of the clay particles is another reason for the improved mechanical properties. Specific surface area of the clay particles increases with decrease in particle size.

Decrease in particle size contributes to increase in volume of the interfacial regions and it contributes to better stress transfer. In the conventional microcomposites, the particles are in micrometer range and hence the thickness of the interfacial regions can be neglected as they are in nanometer range. But in nanocomposite, the effect of interfacial region is also significant as the particles are in nanoscale range. Many researchers developed a model to predict the tensile modulus of the nanocomposites by taking into account of interfacial region. The study shows that increase in interfacial region contributes to increase in tensile strength. Study shows increase in Young’s modulus up to 30% for PP based nanocomposites in presence of PP-g-MA as compatibilizer. Although there is greater increase in young’s modulus, there is no improvement in maximum tensile stress at break. This is due to the lack of interfacial adhesion between PP and nanoclay, presence of PP-g-MA helps in compensating the interfacial adhesion and maintains the maximum stress at break comparable to that of PP. Most of the studies on nanoclay based PP composite were done on polymer films, some workers studied the PP/nanoclay composite based on monofilament samples in presence of PP-g-MA as a compatibilizer. Improved tensile and modulus was obtained for filaments even at a clay loading at 0.25 to 0.5 wt%. The greater increase in strength is attributed to the improvement orientation of the molecular chains obtained during drawing.

2.20.2 EFFECT ON THERMAL PROPERTIES

Many studies on nanoclay composites show significant improvement of thermal stability. Nanoclay acts as a superior insulator and mass transport barrier to the volatile products generated during the decomposition process and improves the thermal stability. Improved thermal stability based on nanoclay composite was first reported by Blumstein [1965] on intercalated PMMA/clay composites. PMMA/clay composites found to have 40-50°C higher decomposition temperature. Improved thermal stability is attributed to the intercalation or exfoliation of the clay particles. Due to intercalation, the polymer chains between the clay layers have restricted thermal motion and thus there is improved thermal stability. Study by Giannelis and Burnside [1995] on cross-linked poly (dimehtylsiloxane) nanocomposite system shows up to 150°C increase in decomposition temperature at 50% degradation. The improvement in thermal stability is attributed to the restriction of the diffusion of the volatile decomposition products formed during degradation, as presence of nanoclay particles decreases the permeability. The mechanism of improved thermal stability based on nanoclay composites is due to the following factors:

1. As the clay particles are inorganic in nature, they act as a heat barrier and enhance the thermal stability of the nanoclay composite system.
2. In the initial stage, silicate layers absorbs the heat supplied and in the later stage this accumulated heat along with supplied heat is used to degrade the sample. Therefore there is a rapid degradation of the nanoclay composite obtained at the later stage.

2.20.3 EFFECT ON DYEABILITY

Polypropylene fibers are difficult to dye because of its nonpolar nature. PP can be chemically modified by graft copolymerization of fibers with monomers such as acrylic acid, vinylpyridine, acrylonitrile, styrene and vinyl acetate and dyeing can be achieved. These methods are commonly used in pilot production. For industrial applications, PP is physically modified by the addition of low molecular and polymer compounds containing functional groups which are able to bind the dyes. Commonly used techniques are as follow:

i) Addition of organometallic compounds such as Al, Cu, Zn, Ni in the form of salts of organic acids, alcoholates, phenolates, amines, triazols etc.

ii) Oligomer and polymer additives with primary, secondary amino groups or with tertiary nitrogen able which are able to bind water soluble dyes containing acid groups.

iii) Addition of oligomers such as ethylene and vinyl acetate copolymers, polyethyleneterephthalate and its copolymers, polyamides etc.

iv) Mass coloration by the pigmentation process. Widely used pigments for PP is carbon black and TiO_2.

Recent studies by Fan et al. [2003], shows that PP can be dyed by using nanoclay additives. It was reported that presence of nanoclay in the PP matrix creates a polar group and hence PP can be dyed with the use of suitable dyes like disperse acids or acid dyes. The main factors which decide the dyeing of PP are van der Waals forces and ionic interaction between nanoclay and dyes [Yang et al., 2005]. Based on the dyeing study on PP modified nanoclay Fan et al. [2003] developed a model which states that exfoliation of the clay particles greatly influences the dyeing behavior of PP. The disperse dyes penetrate into the clay layers and remain in the intergallery spacing of the clay. Therefore exfoliation results in high surface area and hence number of active spots for dye increases and hence dye absorption.

Mani et al., [2003] used disperse and acid dyes to dye the nanoclay modified PP film produced by solution method. They obtained uneven dyeing on the polypropylene film which is due to the improper dispersion of nanoclay particles in the PP matrix. The intensity of dyeing increases with nanoclay loading as the number of active sites increases with increase in nanoclay particles. Razafimahefa et al., [2008] carried out dyeing of PP/nanoclay produced using melt intercalation method in presence of PP-g-MA as compatibilizer. They found that compared to acid dyes disperse dyes was effective in dyeing PP fibers modified with nanoclay. They also found that type of cationic surfactant used to modify the nanoclay has a great influence on the nature of dyeing. Cationic surfactant with alkyl groups found out to have good interaction with disperse dyes than cationic surfactants with hydroxyl groups.

2.20.4 EFFECT ON REINFORCEMENT PROPERTY

Solid state mechanical properties of the composites such as modulus are one of indirect measure of the extent of dispersion of clay particles in the polymer matrix. Also, this study of viscoelastic properties of polymer nanocomposites is mainly important for load bearing applications where the stress is applied for longer period of time. Dynamic mechanical analysis (DMA) measures the response of the material to a cyclic deformation as a function of the temperature. Three main parameters are obtained from DMA:

a. The storage modulus (E') - represents the elastic response to deformation
b. The loss modulus (E") – represents the plastic response to deformation
c. Tan δ= E'/E" , for determining the occurrence of molecular mobility transitions such as the glass transition temperature

All 3 parameters are useful to analyze the nature of interaction between the polymer matrix and the clay particles. For polymer/nanoclay systems, a marked improvement in storage modulus represents good interaction between polymer chains and the nanoclay particles. When the clay particle intercalates or exfoliates in the polymer matrix, the polymer chains between the clay platelets will have restricted chain mobility and hence there will be increase in storage modulus.

Kawasumi et al., [1997] first studied the reinforcement effect of the nanoclay particles on PP matrix. PP nanoclay composites were prepared based on 2 different compatibilizers. Relative storage moduli was found to be 1.3 to 1.4 times that of PP below Tg and it increases up to 1.7 to 2.0 above Tg at a temperature range of 50-80˚C. The increase in storage moduli is due to the good dispersion of the nanoclay particles on the polymer matrix. PP nanoclay composites based on higher molecular weight compatibilizer found to have higher storage moduli compared to compatibilizer based on lower molecular weight. This is because of the good miscibility obtained with the presence of higher molecular weight compatibilizer. The results were supported by XRD and TEM results where shift in the basal spacing to higher inter gallery distance and proper dispersion of clay particles were noticed. Similar trend of increase in storage modulus below Tg and greater increase in storage modulus above Tg were observed for composite samples based on PLA, Nylon.

Study by Joshi et al., [2001] showed up to 2-order increase in storage modulus for PP based nanoclay added samples even for a lower clay loading of 0.5%. PP-g-MA was used as compatibilizer for the system with clay to compatibilizer ratio as 1:2. The increase in storage modulus denotes increase in the elastic component of the nanocomposite filaments. In general, both loss modulus and tan delta increases with decrease in storage modulus with increase in temperature till glass transition temperature. The rise in loss modulus is due to the increase in the structure mobility of the polymer, a relaxation process that permits motion along larger portions of the individual polymer chains than would be possible below the transition temperature. As the material becomes soften above Tg, the reinforcement effect by the silicate layers is prominent due to the restricted movement of polymer chains.

2.21 POLYMER/ CLAY NANOCOMPOSITE APPLICATIONS, MARKET AND FUTURE DIRECTIONS

Approximately 80% of the polymer/ clay nanocomposites is destined to the automotive, aeronautical and packaging industry. The car part industry pioneered in the use of polymer/ clay nanocomposites, since these nanocomposites present stiffness and thermal and mechanical resistances able to replacements, and its use in car reduces power consumption. Car parts, such as handles, rear view mirror, timing belt, components of the gas tank, engine cover, bumper, etc. also used nanocomposites, specially with nylon (polyamide), produced by the companies Bayer, Honeywell Polymer, RTP Company, Toyota Motors, UBE and Unitika. A nylon MDXD6/ clay nanocomposite used as a barrier in beer and carbonated drink bottles, in meat and cheese packaging and in internal coating of juice and milk by product packaging. In the biomedical industry, the flexibility of the nanocomposites is favorable, which allows their use in a wide range of biomedical applications as they fill several necessary premises for application in medical materials such as biocompatibility, biodegradability and mechanical properties. For this reason and for the fact of being finely modulated by adding different clay contents, they can be applied in tissue engineering – the hydrogel form, in bone replacement and repair, in dental applications and in medicine control release.

Table 2.3 Application areas and products in which polymer / clay nanocomposites are used

Automotive	**Packaging**	**Energy**	**Biomedical**	**Construction**	**Home furnishing**
Dash board	Beer and soft drink bottles	Fuel cells	Artificial tissues	Tubes	Furniture
Foot board	Meat and cheese packaging	Capacitors	Dental and bone prosthesis	Cords	Home appliances
Station wagon floor	Internal films of juice boxes	Nuclear reactors	Medicines		
Timing belts		Lithium batteries			

Handle	Solar panels
Gas tank component	
Engine covers	
Bumpers	

Due to the aforementioned reasons, a considerable increase in investigations and the commercialization of nanocomposites in the packaging area, selective catalyzers, conductive polymers and filtration of toxic materials are expected. A light growth in the applications related to an increase of catalysis efficient and of material conductivity, new types of energy, storage information and improved membranes are also expected. Although nanocomposites present a series of advanced properties, their production is still considered low in comparison with other materials due to the production costs. Once they become cheaper, polymer/ clay nanocomposites can be largely used in a series of applications[90, 91 - 93].

- ✓ Global consumption of nanocomposites was an estimated 118,768 metric tons with a value of over $800 million in 2010. In 2011, the market should reach 138,389 metric tons and $920 million. By 2016, the market should amount to 333,043 metric tons and $2.4 billion, a five year compound annual growth rate (CAGR) of 19.2% in unit terms and 20.9% in value terms.
- ✓ Clay nanocomposites accounted for more than 50% of total nanocomposite consumption by value in 2010. Its market share is expected to increase to approximately 58% in 2016.
- ✓ Carbon nanotube composites accounted for 21% of total nanocomposite consumption in 2010 and this market share is expected to decrease to 16% in 2016.

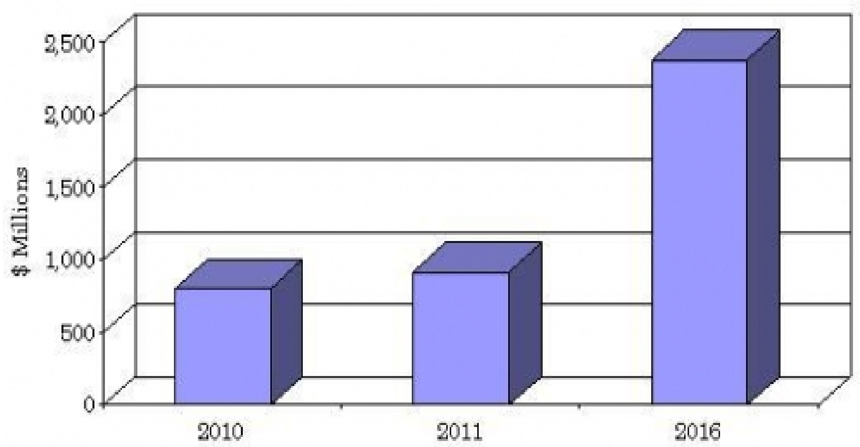


Figure 2.20 Global Consumption of Nanocomposites, 2010-2016 (in $ MILLIONS)[94]

2.22 SCOPE OF STUDY

“Nanoparticle”, the tiniest substances promise to transform industry and create a huge market. In chemicals, cosmetics, pharmaceuticals, technology and textiles, businesses are researching and manufacturing products based on nanotechnology, which uses bits of matter measured in billionths of a meter to improve or impart functional performance of the product. The morphological features of nano material and structures need to be determined at various stages of production in terms of size distribution, porosity, pore size distribution, surface structure and composition, which are critical to ensure the materials and structures are in nano scale to archive special properties[95-97].

As very less literature is available in this area, in the present investigation clay which is used as filler material in textiles has been modified to organoclay, also known as nanoclay. After preparation the clay particles have been observed by SEM technique, the elemental and chemical composition was recorded by EDX and FTIR, the structural properties were evaluated by TGA and XRD analysis.

Recently works reported[97-107] on the composite material which presents possible direction for further development of high performance textile material. In many literature[108-132] high performance polymer composite were prepared by incorporation of different nanomaterials to achieve special properties but very less literature is available on the technical analysis of polymer and its composite making in different forms and also in terms of structural, thermal and mechanical changes. So another purpose of this work is to develop polymer / nanoclay composite material with improved structural and mechanical properties. Looking to the huge potential of utilizing polymer/ clay nano materials in textiles the actual research done in this field is really seems to be in its embryo stage. Under this background the proposed research will concentrate on the following three areas:-

Section I Preparation of nanoclay by modifying it with CTAB as cationic surfactant and analysis of the prepared nanoclay for their elemental and structural composition.

Section II Preparation of polypropylene / nanoclay filament on melt spun filament machine and analysis of the prepared filament for their structural composition and mechanical properties compared to the filament prepared without the addition of nanoclay.

Section III Preparation of polypropylene / nanoclay nonwoven fabric using spun bond machine, testing and evaluation of their structural, thermal and mechanical properties.

CHAPTER 3
MATERIALS AND EXPERIMENTAL METHODS

3.1 INTRODUCTION

To meet the challenges in the recent era, new generation of materials are the present demand of the market. As traditional materials are unable to fulfil these requirements, new materials like nanocomposite, nanomaterials, etc. plays an important role. As these materials are becoming need of an hour, we have concentrated our research on polymer nanocomposite material.

Recently, much literature is available pertaining to the huge potential applicability of organoclay particles. So in the present experimental work, clay being cheap and easily available material in nature was selected as filler for producing different polymer nanocomposite textile products. Aiming to the area of technical textile, we have confined our study on polypropylene (PP) polymers which is widely used in the area of technical textile. In this work an attempt has been made to prepare composite material in two commercial product i.e., filament and nonwoven, mixing of nanonmaterial directly in polymer melt techniques of preparing composite has been adopted. All textile products were produced out of these polymers were checked for its effectiveness against different applications.

To get easy understanding, the whole experimental plan has been divided into different sections. They are:

Section I deals with conversion of clay to Organoclay with the help of surfactant called CTAB and evaluated for its properties.

Section II deals with preparation of filament with varying percentage of Organoclay added inside.

Section III deals with preparation of spun-bond nonwoven fabric with varying percentage of Organoclay added inside.

3.2 SECTION – I: PREPARATION OF NANOCLAY

Bulk clay which is naturally available in abundance is hydrophobic by nature which does not have affinity towards polymeric material. So, in this section, attempt has been made to convert bulk clay into Organoclay with the help of surfactant called CTAB and made it miscible with polymeric material. The analysis of Organoclay was done with the help of SEM, FTIR and XRD.

3.2.1 MATERIALS

Montmorillionite clay with cation exchange capacity of 60 meq/100 gm was taken as the starting material. All the chemicals mentioned in table 3.1 were used without any further purification.

Table 3.1 Chemical specifications

Sr no	**Name**	**Formula**	**Grade**	**Mol.wt. gm/mol**	**Supplier**
1	Cetyl trimethyl ammonium bromine (CTAB)		AR	364.45	Sd Fine chemicals.
2	Silver nitrate	Ag NO_3	AR	311.80	Sd Fine chemicals.
3	Montmorillonite (MMT)	M_x (Al_{2-x} Mg_x) $Si_4O_{10}(OH)_2$. nH_2O	-	-	Bhavnagar Clay Ltd, Bhavnagar

Figure 3.1 Bulk clay

3.2.2 EXPERIMENTAL METHODS

3.2.2.1 Preparation of Organoclay Nanoparticles

Sodium Montmorillonite (Na-MMT) clay (5 gms) was dispersed in 500 ml of distilled water. The suspension was vigorously stirred for 24 hrs at room temperature using magnetic stirrer. An aqueous solution of 0.03M (1.09 gm in 100 ml distilled water) CTAB (Cetyl Trimethyl Ammonium Bromide) was gradually added to the Na-MMT dispersion. The resulting Organoclay suspension was further stirred for 12 hours at room temperature. The suspended product was filtered under vacuum, using whatman paper no. 1. The resulting product was further dispersed into 50 ml fresh distilled water and stirred again for another 4 hours.

Resultant modified clay was washed thoroughly to remove chloride. The product was washed repeatedly till it become free from the chloride which was confirmed by checking against $AgNO_3$ solution. The final Organoclay which was free from chloride was dried at 60°C for 24 hours and finally ground using a Pestle Mortar in order to obtain fine powder. The experiments were carried out with different molarities of CTAB. The resultant product was characterized by FTIR, TGA and SEM.

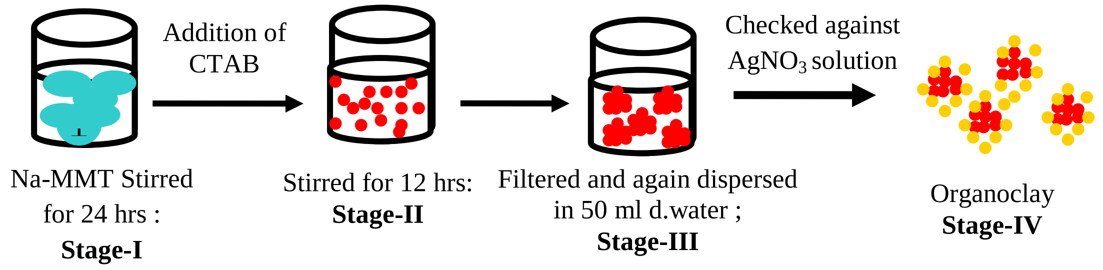


Figure 3.2 ***Schematic process diagram of Organoclay preparation***

3.2.3 TESTING AND ANALYSIS OF ORGANOCLAY NANO PARTICLES

3.2.3.1 Surface Analysis by Scanning Electron Microscopy (SEM)

Figure 3.3 ***Photograph of SEM, Model JSM-5610 LV, Version 1.0, Jeol Japan***

Scanning Electron Microscopy was used to observe the nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1,00,000 X with resolution up to 100A^{o}. Organoclay nanoparticles were deposited on carbon coated aluminum sheet, dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer. Working principle is described on page number 38.

3.2.3.2 Elemental Analysis by Oxford-Inca Software on SEM

The elemental analysis of the prepared modified clay nanoparticles was performed on scanning electron microscope (SEM) using Oxford Inca software. The Organoclay nanoparticles were deposited on carbon coated aluminum sheet. EDX analysis of these samples was carried out using Oxford Inca software on scanning electron microscope. The instrument reports the presence of elements in pure and oxide state qualitatively.

3.2.3.3 FT-IR Spectroscopy

The technique is based on the fact that a chemical substance shows marked selective absorption in the infrared (IR) region. After absorption of IR radiation, the molecules of a chemical substance vibrate at many rates of vibration giving rise to close packed absorption bands called IR absorption spectrum which will correspond to the characteristic functional group and bands present in a chemical substance. Thus an IR spectrum of a chemical substance is a finger print for its identification. FT-IR was carried out on Shimadzu FT-IR 8400S specto photometer using the Kbr pellet method. Working principle is described on page number 41.

Figure 3.4 Photograph of FT-IR Shimadzu 8400S spectrometer instrument.

3.2.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetry (TGA) was carried out for Na-MMT and Organoclay samples by using a Shimadzu TGA-50 thermal analyzer shown in Figure 3.5. The samples were heated from ambient temperature to 700^{o}C with 10^{o}C/min temperature in normal atmosphere. The thermograms associated with TG for control and treated sample were obtained from the instrument output. Detailed information with respect to mass loss degradation onset temperature were obtained from there thermograms for both the samples. Working principle is described on page number 43.

Figure 3.5 Photograph of Shimadzu TGA-50 thermal analyzer

3.2.3.5 X-Ray Diffraction (XRD)

Figure 3.6 Photograph of Diffractometer D8 advance with CuK α radiation

The initial basal spacing in the Organoclay is an important parameter for the determination of the potential for polymer intercalation. This is determined by X-ray diffractometer. X-ray diffraction was performed on dried powder sample. The Organoclay was grounded into a fine power prior to XRD measurements using a Pestle Mortar with sufficient pressure so as to make a fine powder. The scans were performed for each sample and the values are reported for the basal spacing. The X-ray diffraction patterns were obtained using diffractometer D8 advance with CuK α radiation (λ= 1.54 Å). Working principle is described on page number 39.

3.3 SECTION – II: PP / NANOCLAY COMPOSITE FILAMENT

The present section deals with the preparation of nanocomposite filament from polypropylene and nanooclay. Varied percentage of nanoclay was added to polypropylene chips and filaments were prepared on lab model melt spinning machine. These prepared filaments were further evaluated for change in its properties.

3.3.1 MATERIALS

Polypropylene polymer was used for the manufacturing of nanocomposite filaments. Polypropylene polymer fibre grade chips of 16 MFI were procured from Reliance Industries.

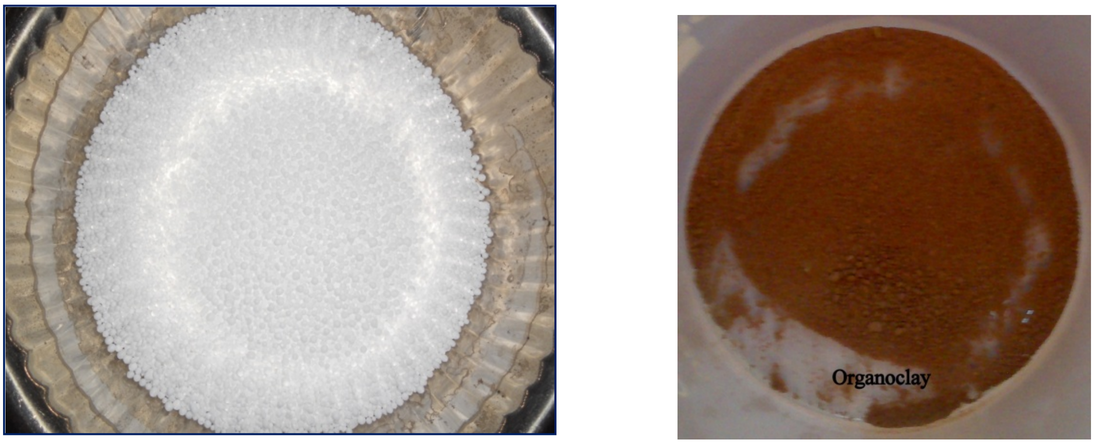


Figure 3.7 (a) polypropylene chips and (b) Organoclay

3.3.2 EXPERIMENTAL METHODS

3.3.2.1 Preparation of Polypropylene Nanoclay Composite Filament

To get better dispersion of nanoclay in PP matrix, manufacturing of PP / organoclay nanocomposite filament was done in two stages. First the extrusion was carried out with optimized parameters for all yarns and then after drawing, all monofilaments, except pure polypropylene, were chopped and re-extruded to obtain better dispersion and distribution of the nanoclays in polymer matrix. These chopped yarns were further fed into the hopper of laboratory model melt spinning machine, shown in Figure 3.8 (a). The organoclay particles were mixed with polypropylene chips in varied concentration on weight basis as shown in Table 3.2.

Table 3.2 Composition of pure and composite filament

Sr.	**Sample code**	**PP granules in gms**	**Weight of clay in gms**	**% Concentration**
1	S (Pure PP)	250	0	0
2	S1 (PP/MMT-1)	250	0.25	0.1
3	S2 (PP/MMT-2)	250	1.75	0.7
4	S3 (PP/MMT-3)	250	3.75	1.5
5	S4 (PP/MMT-4)	250	5	2

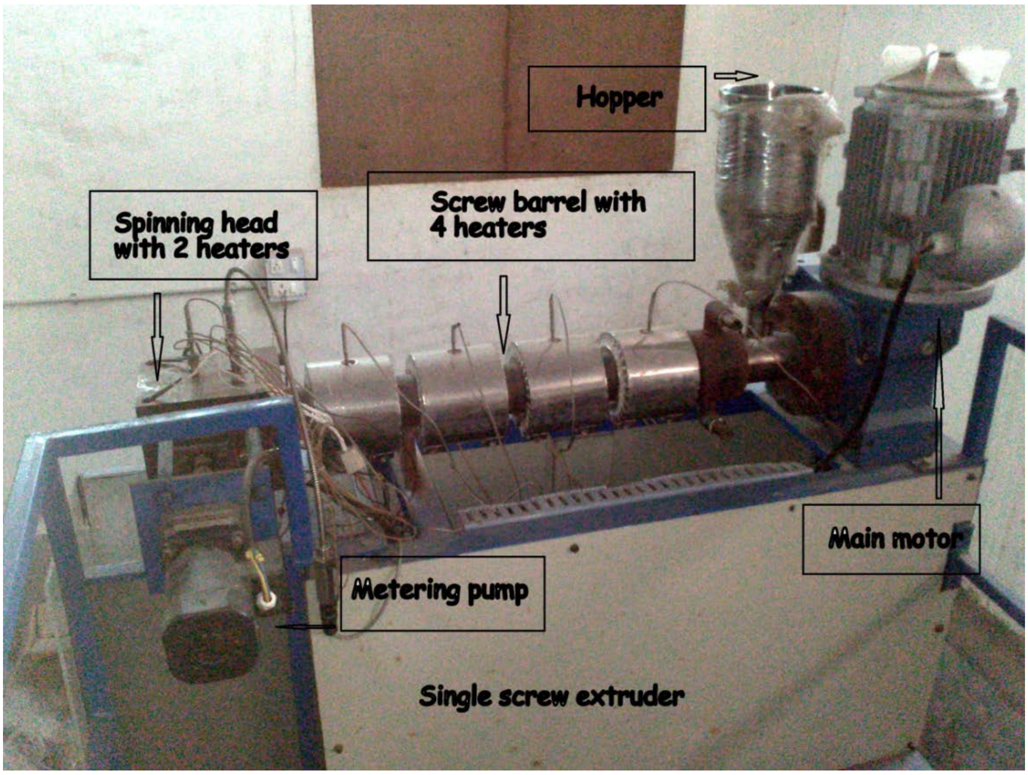


Figure 3.8 (a) Extruder unit of laboratory model melt spinning plant

The machine consists of extruder with four zone heating and a heated spinning head with metering pump. The measured quantity of material comes of the spinneret into the cooling zone. At the bottom of the cooling zone, filament wraps around godet 1 and passing over godet 2, 3 and 4 filament goes to winder for winding on package. The whole machine is computerised and value of individual parameters like speed and temperature can be altered. Before manufacturing filament from composite chips, the machine parameters were optimised by taking number of trials. Further all filaments with different proportion of organoclay were prepared on optimised parameters to retain consistency of the product.

A control sample with pure PP chips was also prepared for comparative study at same optimised parameters, as shown in table below.

Table 3.3 Melt spinning machine parameters

Sr.	**Machine parameters**		**Temp in ° C**	**Speed**
1	Extruder temperature	Heater 1	165	--
		Heater 2	200	--
		Heater 3	210	--
		Heater 4	215	--
2	Spinning head with metering pump	Heater 1	235	--
		Heater 2	230	--
3	Godet	Godet 1	RT	0
		Godet 2	RT	0
		Godet 3	RT	300 rpm
		Godet 4	RT	400 rpm
4	Extruder pressure	--	40 bar	--
5	Metering pump	--	--	5 rpm
6	Winding	Friction roller	--	400 mpm
		Grooved roller	--	250 mpm

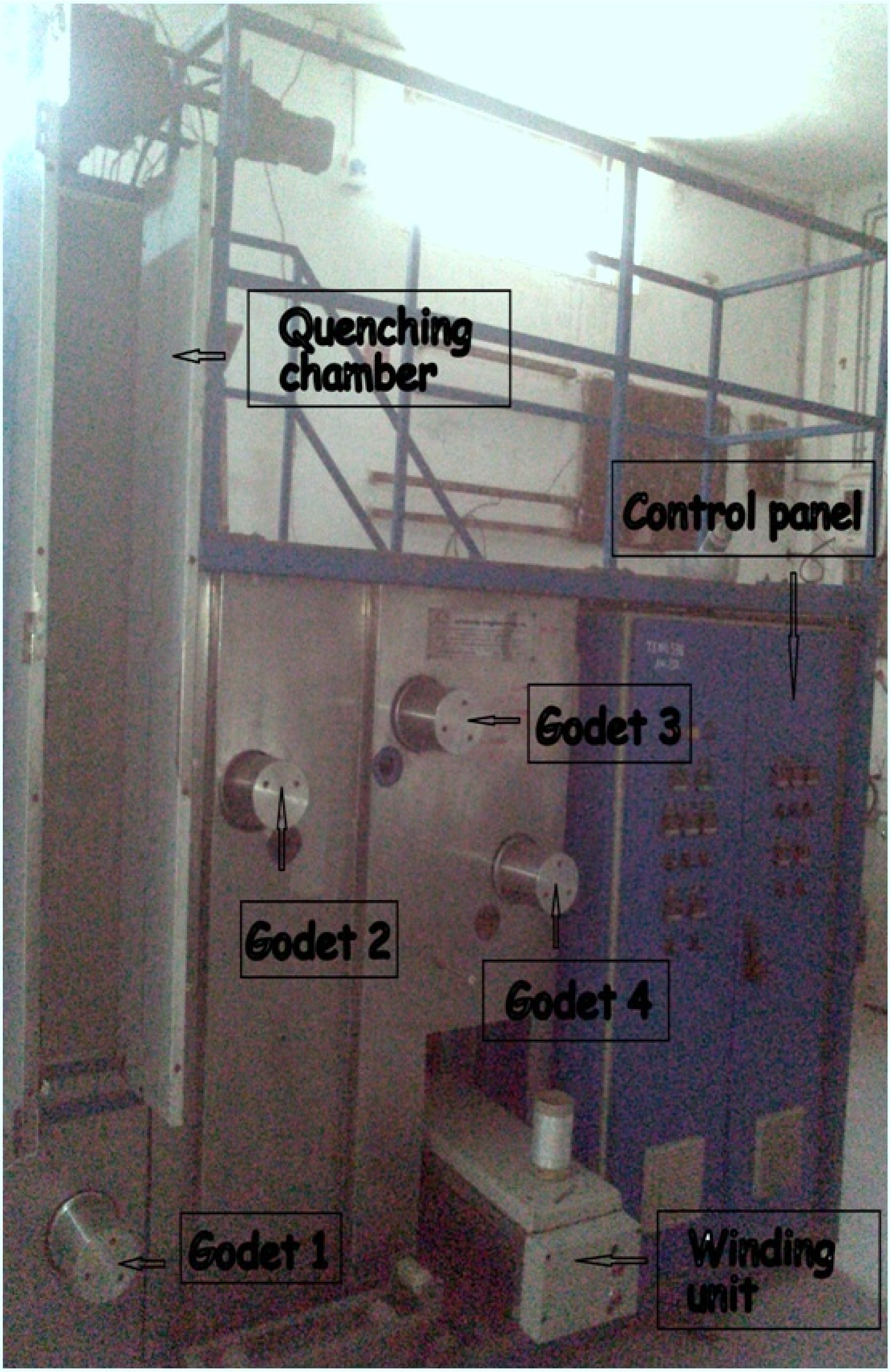


Figure 3.8 (b) Quenching and winding unit of laboratory model melt spinning plant

3.3.3 TESTING AND ANALYSIS OF COMPOSITE YARN

3.3.3.1 Surface Analysis of Filament by SEM

The dispersion of clay nanoparticles inside polypropylene filaments were observed through Scanning Electron Microscope Model JSM-5610 LV, Version 1.0, Jeol Japan. As given in section I.

3.3.3.2 Elemental Analysis by Oxford-Inca Software on SEM

The amount of MMT Clay as element in the polymer structure was detected and measured on SEM using oxford–Inca software (Oxford, U.K.). As described in section I.

3.3.3.3 Structural Evaluation by X-Ray Diffraction

WAXD scans of the prepared nanocomposite yarn were scanned on X-ray diffractometer (X'Pert-Pro®, PAN Analytical, Singapore). Cu Kα radiation at 45 Kv and 40 mA of 1.54 ˚A was utilized. Samples were scanned for 2θ between 5 ° and 80°.

3.3.3.4 Determination of Mechanical Properties

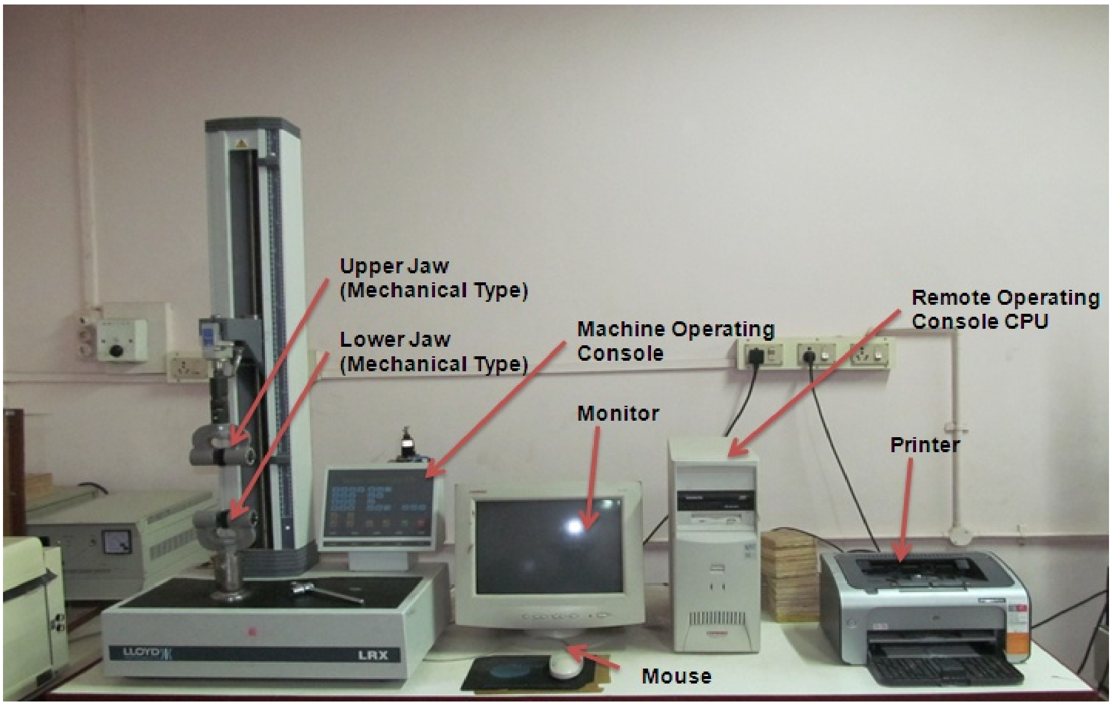


Figure 3.9 Lloyd tensile strength testers

The specimens were conditioned at 65 ± 2 % relative humidity and 27 ± 2°C before physical testing. The breaking strength of yarn with different concentration was measured with 100 mm G.L. and 100 mm/min crosshead speed as per ASTM D 2256-02, on tensile strength tester: (LRY Model, Lloyd, U.K) as specified.

3.3.3.5 Determination of Thermal Behaviour by DSC

The thermal characterizations of filament were analyzed using DSC model 6000 from PerkinElmer, Singapore temperature range from 50°C to 400°C. The thermal analysis of the prepared samples was performed using differential scanning calorimeter, DSC instrument shown in Figure 3.10.

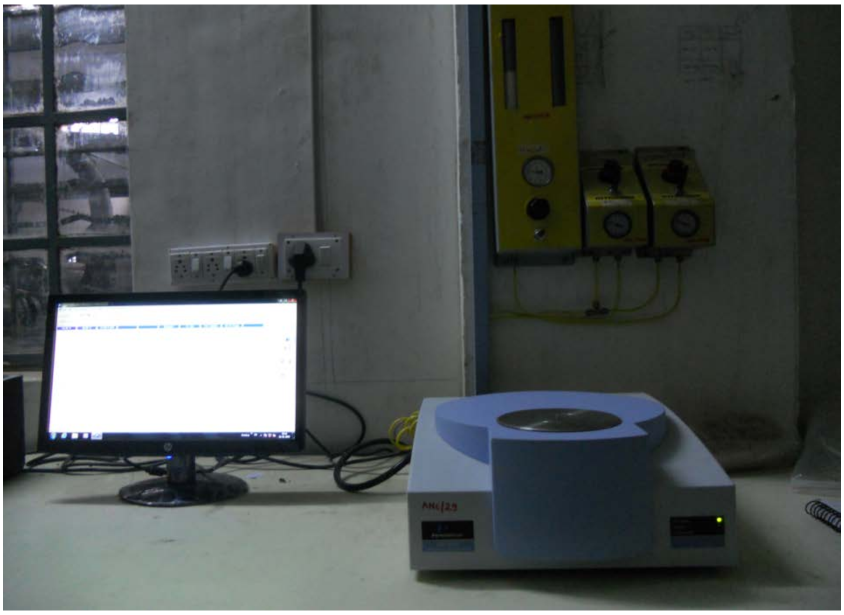


Figure 3.10 Differential scanning calorimeter

The DSC of the samples was carried out under the heat – cool – heat mode as given below:

- 1st Heating – Heating from 30˚C to 180˚C
- Rate of heating - 10˚C/ min
- Cooling - From 180 ˚C to 30˚C
- Rate of cooling - 10˚C/ min
- 2nd Heating – Heating from 30˚C to 300˚C
- Rate of heating - 10˚C/ min

Nitrogen gas was used as the purge gas for the above experiment. Pressure of about 3 bars was maintained for the gas flow of 20 ml/ min in the instrument. The thermograph obtained after the test was analyzed and the results were interpreted.

3.3.3.6 Thermogravimetric Analysis by TGA

Thermal analysis (TGA & DTA) of composite filament was recorded on EXSTAR TG/DTA 6300. The samples were heated from ambient temperature to 550^{o}C with 10^{o}C/min temperature in N_2. The thermograms associated with TG for control and treated sample were obtained and analyzed.

3.4 SECTION – III: PP/NANOCLAY COMPOSITE NONWOVEN FABRIC

In line with earlier study, we extended our work to check the effect of nanoclay particles for the upcoming technical products. In this section we have tried to produce nonwoven fabric by spun bond technology, with varied concentration of nanoclay particles to investigate the development of structure and properties during spun bonding with nanoclay. These prepared samples were evaluated for structural, mechanical and thermal properties with the help of standard techniques, to get its better consideration in the field of high performance technical textile.

3.4.1 MATERIALS

Polypropylene polymer was used for the manufacturing of nanocomposite nonwoven fabric. Polypropylene polymer fibre grade chips of 35 MFI were procured from Reliance Industries.

3.4.2 EXPERIMENTAL METHODS

3.4.2.1 Preparation of Polypropylene/Nanoclay Composite Nonwoven

The obtained polypropylene granules were thoroughly mixed with nanoclay particles with different concentration, as given in table. Precise weight of nanoclay was obtained using electronic balance having accuracy of 0.0001 gms. This mixture was further fed to the extruder to get different spun bond samples.

For proper evaluation of the parameters, through mixing of the clay particles in with PP granules is necessary. To achieve this, twin screw extruder was used. Material in different proportion was added to twin screw extruder and homogeneous mixed granules of PP contained nanoclay were obtained. These chips were further fed into the hopper of laboratory model melt spinning machine, shown in Figure 3.11. Spun bond fabrics with additives were produced using Lab model spun bonding machine. Processing conditions maintained for the production of different samples are included in Table 3.4. Extruder and spinning conditions were maintained same for all the samples with the target fabric weight of 160 grams per square meter (GSM).

The machine consists of extruder with four zone heating and a heated spinning head with metering pump. The measured quantity of material which comes of the spinneret suddenly enters into the stretching zone. The chamber consists of air suction and distributing unit, which stretches the filaments a high rate and then uniformly distributes on the conveyor below. This prepared layer is further passed through pair of heated rollers to make an uniform nonwoven fabric. A control sample with pure PP chips was also prepared for comparative study at same optimised parameters, as shown in table below. All the fiber and fabric samples produced in the experiments were conditioned for 24 hours under standard textile laboratory conditions before testing and evaluation.

Table 3.4 Sample code and their composition for nonwoven

Sr.	**Sample code**	**PP granules (Wt in gms)**	**Nanoclay (Wt in gms)**	**% Concentration**
1	NW-S	250	---	0
2	NW-S1	250	0.25	0.1
3	NW-S2	250	1	0.4
4	NW-S3	250	1.75	0.7
5	NW-S4	250	2.5	1
6	NW-S5	250	4	1.6

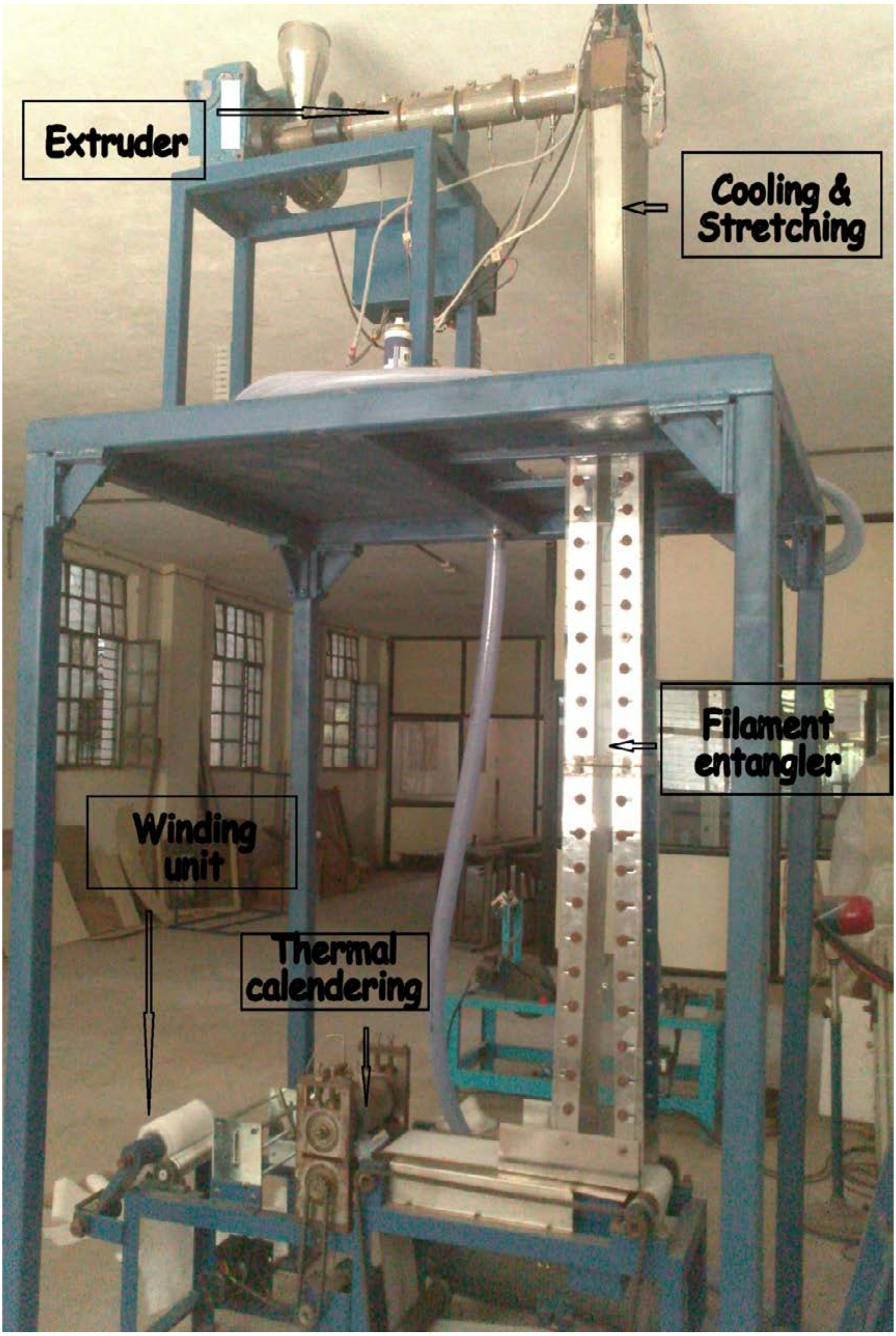


Figure 3.11 Laboratory model spun bond nonwoven machine

Table 3.5 Spun bond nonwoven machine parameters

Sr.	Machine parameters		Temperature in ° C
1	Extruder temperature	Zone 1	170
		Zone 2	200
		Zone 3	215
		Zone 4	230
2	Spinning head	Heater	235
	Metering pump	Heater	235
3	Calender roller	Bottom	140
		Top	145
4	Cooling blower		18
	Machine running parameters		
5	Metering pump pressure	Pressure	50 bar
		Speed	4 rpm
		Capacity	3 cc
6	Winding speed	Mts/min	10
7	Air suction (Blower speed)	Rpm	1440
8	Cooling blower	Cfm	60
9	Number of holes		120
10	Through put		0.09 gms/hole/min

3.4.3 TESTING AND ANALYSIS OF NONWOVEN FABRIC

3.4.3.1 Surface Analysis of Nonwoven by SEM

The dispersion of clay nanoparticles on polypropylene nonwoven fabric were observed through Scanning Electron Microscope Model JSM-5610 LV, Version 1.0, Jeol Japan. As given in section I.

3.4.3.2 Determination of Clay Content in Nonwoven Fabric by EDX

The amount of MMT Clay as element in the polymer structure was detected and measured on SEM using oxford Inca software (Oxford, U.K.). As given in section I.

3.4.3.3 Structural Evaluation by X-Ray Diffraction

The prepared nanocomposite nonwoven fabric was scanned on an X-ray diffractometer (X’Pert-Pro®, PAN Analytical, Singapore). Cu Kα radiation at 45 Kv and 40 mA was utilized and scanned for 2θ between 5 ° and 80°.

3.4.3.4 Determination of Mechanical Properties

The specimens were conditioned at 65 ± 2 % relative humidity and 27 ± 2°C before physical testing. The breaking strength of yarn with different concentration was measured with 100 mm G.L. x 5 cm width fabric strip and 100 mm/min crosshead speed as per ASTM D 5736 - 95, on tensile strength tester: (LRY Model, Lloyd, U.K) as specified in section-II.

3.4.3.5 Determination of Tear Strength

The tear strength of the fabric was estimated on Elmendrof tearing tester as per ASTM D1424-09. The pendulum of this instrument is sector shaped as shown in Figure 3.12. Sample is mounted between two clamps on fixed and other movable. When the pendulum is released, movable clamp moves away from fixed clamp and the fabric teas across the width. A pointer indicates the tearing force in gms.

Figure 3.12 Elmendrof tear strength tester

3.4.3.6 Determination of Bursting Strength

Figure 3.13 Bursting strength tester

The bursting strength of the samples was performed as per ASTM 3786/3787. As seen in Figure 3.13, specimen is clamped by a ring over a thin flexible rubber diaphragm. The liquid used is glycerine and hydraulic pressure is increased. At some point the fabric bursts and pressure is indicated on dial in kg/cm^2.

3.4.3.7 Determination of Flexural Rigidity

Figure 3.14 Shirley stiffness tester

The flexural rigidity of the samples was analysed on “Shirley stiffness tester” as per ASTM D1388-08. A fabric strip with 6” x 1” was mounted on horizontal platform in such a way that it overhangs like a cantilever and bends downwards as shown in Figure 3.14. From the length ‘l’ and angle ‘θ’, flexural rigidity was calculated.

3.4.3.8 Determination of Air Permeability

The air permeability of polypropylene pure and composite nonwoven fabrics were measured on Metefem air permeability tester, show in Figure 3.15. The testing was carried out as per ASTM D 737 test method. The result of the test measured in m^3/h/m^2 to three significant digits.

Figure 3.15 Metefem Air Permeability Tester

3.4.3.9 Thermal Behaviour of Nonwoven Fabric by DSC

The thermal characterizations of polypropylene nonwoven fabric were analyzed using DSC model 6000 from PerkinElmer, Singapore temperature range from 50°C to 300°C. The thermal analysis of the prepared samples was performed using differential scanning calorimeter, DSC instrument as per given in section II.

3.4.3.10 Analysis of Moisture Management

Moisture management tester is an instrument which specifically designed to know the water management of performance fabrics. It works on AATCC TM195-2009 standards for Liquid Moisture Management Properties of Textile Fabrics. It measures the whole liquid transfer process in the textile material, dynamically, in 3 Dimensions.

Figure 3.16 Moisture management tester

Test procedure

The unit is connected to a PC and is calibrated and ready for use within 5 to 10 minutes. The fabric specimen is prepared, conditioned and placed in the MMT. The door is closed and the windows based program run. The test requires 3 to 5 specimens, each specimen taking 2 minutes to complete with instant results. It generates 10 data in a 2 minute test for: Wetting Time – top/bottom surface, Absorption Rate – top/bottom surface, Maximum Wetting Radius – top/bottom surface, Spreading Speed – top/bottom surface, Accumulative One Way Transport Capability and overall Moisture Management Capability (OMMC). MMT Categorizes seven different types of fabric based on the data obtained as per stated in page # 47.

3.4.3.11 Determination of UV Transmission

The UV transmittance of nonwoven fabric was measured by using The Labsphere UV-2000F ultraviolet transmittance analyzer The UV-2000F satisfies all the requirements of following standards viz., AS/NZ 4399:19961, EN 13758-1:2001, AATCC TM 183-2000 and GB/T18830. The detail procedure is mentioned in earlier section.

Figure 3.17 UV-2000F ultraviolet transmittance analyzer

The UV-2000F instrument measures spectral transmittance across the 250 - 450 nm wavelength spectrum using an integrating sphere and two spectrometer instruments. The UPF of a textile material is determined from the total spectral transmittance and higher the value of UPF better is the UV protection.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter reports the outcome of the experiments conducted to fulfil the objectives of the work. In line with experimental methods this chapter has three subsections, further the results are discussed technically and logically.

SECTION – I

4.1 PREPARATION OF ORGANOCLAY PARTICLES

Na-MMT clay was converted to Organoclay by using CTAB as surfactant. The morphological, structural and thermal characteristics were recorded. These have been discussed related to the objective of the study, in this section.

4.1.1 PROCESS OBSERVATION

The Na-MMT clay has been converted into Organoclay nanoparticle by a simple swelling technique using de-ionized water. The prepared Organoclay was tested against $AgNO_3$ solution to ensure removal of chloride content. SEM micrographs technique has been used to observe morphology of prepared material and FT-IR spectra of the Organoclay was recorded for the confirmation of chemical compounds.

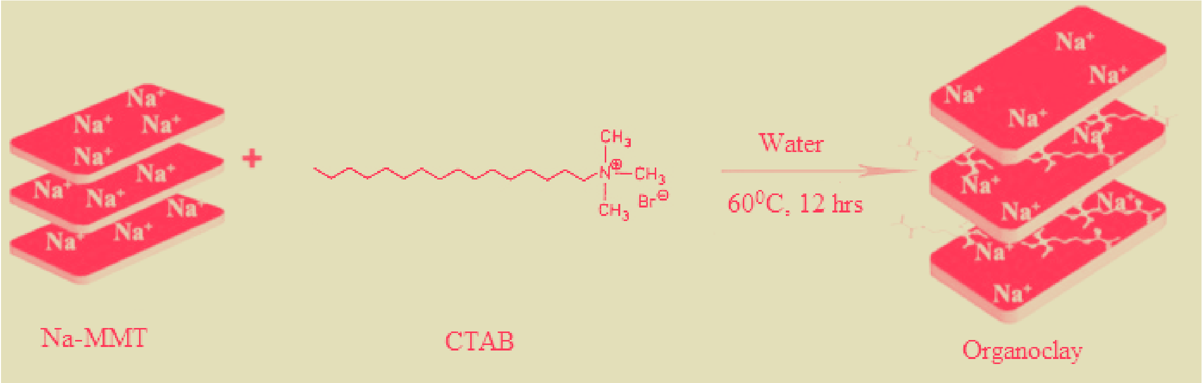


Figure 4.1 Conversion of organoclay nano particles from Na-MMT clay

It has been seen from the experimental work (schematically presented in Figure 4.1) as well as from the literature that the clay exhibits expansion in water due to ingress of free water and also due to the presence of minerals with predominantly expands the lattice.

Figure 4.2 Photograph of Organoclay nano particles prepared from Na-MMT clay using CTAB

4.1.2 ANALYSIS OF CLAY FORMATION

Montmorillonite is among the most widely known clay minerals, and is extensively tried by various researchers across the world in adsorption applications because of its large surface area and relatively wide interlayer space being expandable in aqueous media. In this study, montmorillonite were converted to Organoclay had a dominant opaque brownish black appearance. The morphology of powder was studied by SEM, the chemical composition and structure was confirmed by FT-IR spectroscopy & XRD pattern respectively. Finally the thermal behavior was studied by Thermogravimetric analysis (TGA). Discussions upon formation and properties of MMT Organoclay are provided in the following subsections:

4.1.2.1 SEM Analysis

Figure 4.3 shows the scanning electron microphotographs of prepared MMT Organoclay nanoparticles deposited on carbon coated aluminium sheet. The average size as seen from the scale of the photograph is ranging between 50 – 90 nm. Figure 4.3(a) shows aggregates of Na-MMT clay where as 4.3(b) shows uniform dispersion of the Organoclay nanoparticles.

Surface morphology of Na-MMT clay Figure 4.3(a) clearly indicates that the particles in Na-MMT clay before the treatment was in closely attached or in aggregates form due to the intermolecular forces. The surface morphology can be supported by various reports available in literature that alumina silicates type clay consists of silica SiO_4 tetrahedral bonded to alumina AlO_6 octahedral in a variety of ways, which have a sheet like (layered) structure[98]. A 2:1 ratio of the tetrahedral to the octahedral results in smectite clays, montmorillonite; which is used for the further investigation throughout this study. It has been observed from Figure 4.3(b) represent surface morphology of modified or swollen Na-MMT Organoclay particles with cationic surfactant CTAB.

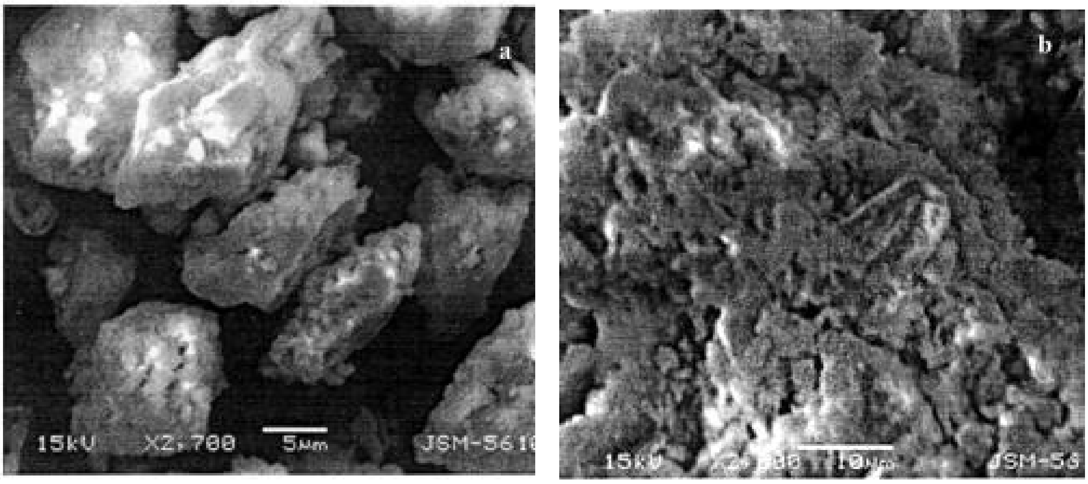


Figure 4.3 Scanning electron microphotographs of (a) Na-MMT clay particles and (b) Organoclay nanoparticles deposited on carbon coated aluminium sheet

Uniformly dispersed small particles of Organoclay were observed compared to Na-MMT particles. It has been also seen from the Figure 4.3(b) that the modified clay particles clearly fall in nano scale. This may be due to the sodium ions in the clay can be exchanged for an amino acid such as CTAB[99]:

$$Na^+\text{- Clay} + HOOC\text{-}R\text{-}NH_3 + Cl^- \longrightarrow HOOC\text{-}R\text{-}NH_3\text{ +- Clay} + NaCl$$

4.1.2.2 FT-IR spectral Analysis

The technique is based on the fact that a chemical substance shows marked selective absorption in the infrared (IR) region. After absorption of IR radiation, the molecules of a chemical substance vibrate at many rates of vibration giving rise to close packed absorption bands called IR absorption spectrum which will correspond to the characteristic functional group and bands present in a chemical substance. Thus an IR spectrum of a chemical substance is a finger print for its identification. FT-IR spectra of Na-MMT clay recorded on Shimadzu FT-IR 8400S spectrophotometer using the Kbr pellet method is shown in Figure 4.4

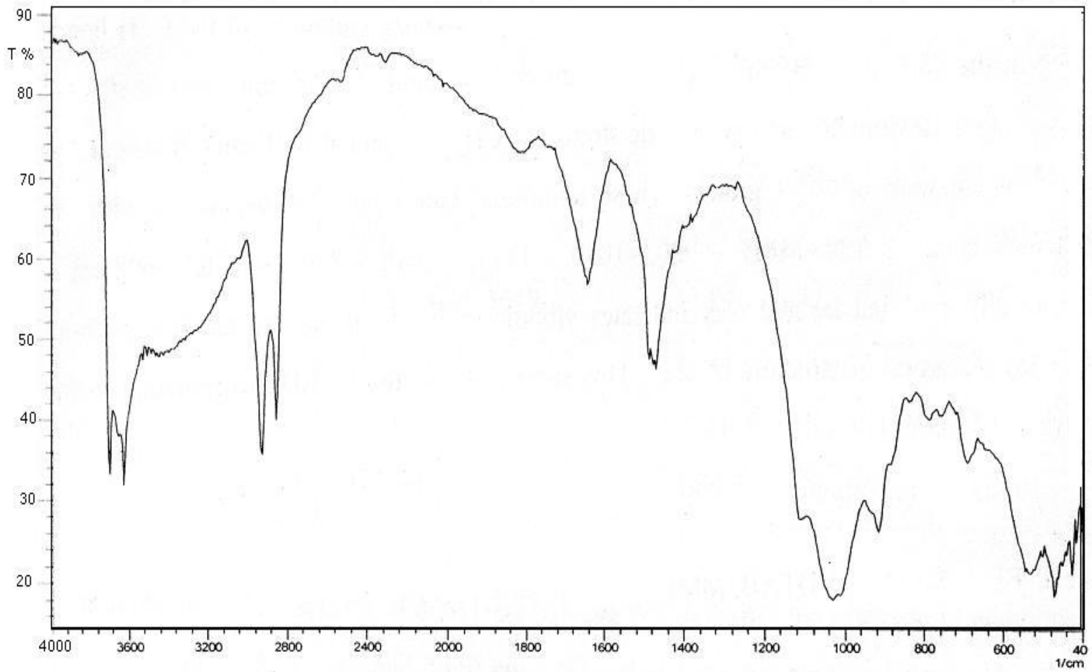


Figure 4.4 FT-IR spectra of Na-MMT clay particles

Table 4.1 Infrared characteristic absorption peaks of Na-MMT clay particles

Absorption Peak (cm^{-1})	**Reported values, Wave Number (cm^{-1})**	**Characteristic vibration of Na-MMT**
~920	~ 918, 915	Bending vibration of Al-Al-OH
~1030	~ 1049, 1035	Si-O stretching vibration for layered structure
~1110	~ 1120, 1114	Si-O stretching out of plane for Na-MMT
~1640	~ 1636, 1637	-OH bending mode in water
~3400	~ 3427	Broad band due to the –OH bending for Inter layered water
~3620, 3690	~ 3630, 3626	-OH bond stretching for Al-OH and Si-OH

From Figure 4.4 and corresponding Table 4.1 IR spectra peaks for Na-MMT clay of montmorillonites located near 1030 cm^{-1} belongs to the Si-O stretching vibrations. OH bending modes of structural hydroxyl groups and water molecules lie in the spectral region of 3400 cm^{-1}. The position of the hydroxyl stretching band of Al-OH and Si-OH lies at 3620 cm^{-1} and 3690 cm^{-1} respectively in IR spectrum of Na-MMT.

A weak absorption at 920 cm^{-1} confirms of Al-Al-OH bending vibrations. A peak at 1640 cm^{-1} is observed which shows the bending mode in water.

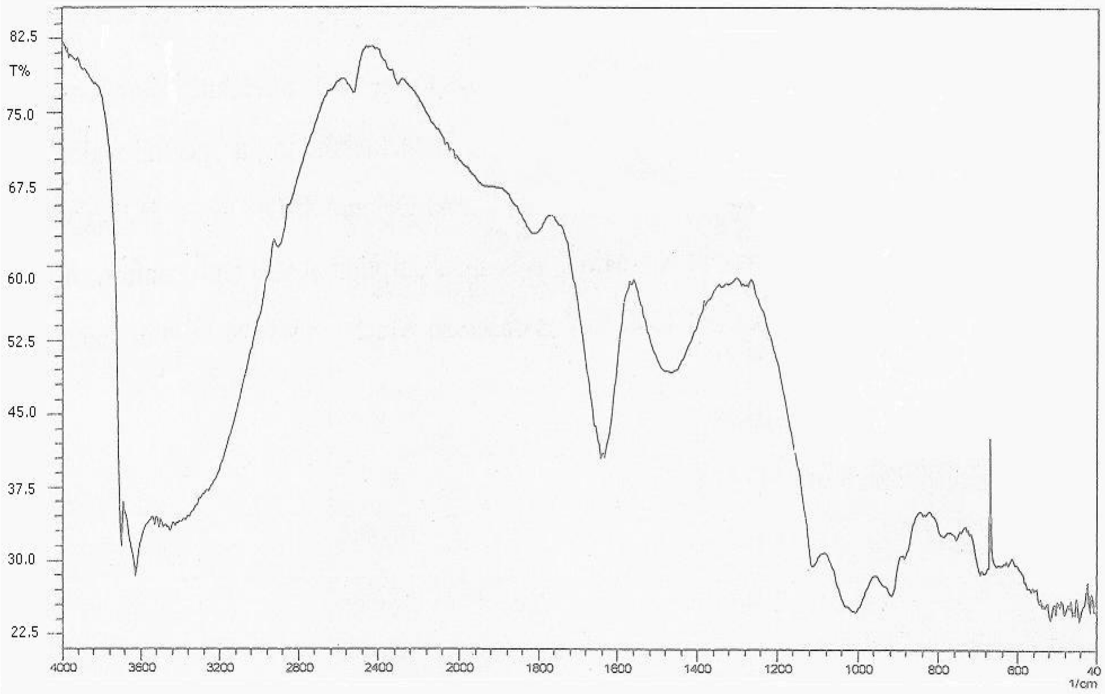


Figure 4.5 FT-IR spectra of CTAB MMT clay particles (Organoclay)

Table 4.2 Infrared characteristic absorption peaks of Na-MMT clay particles

Absorption Peak (cm^{-1})	**Reported values. Wave Number (cm^{-1})**	**Characteristic vibration of CTAB MMT**
~ 2900	~ 2925	CH_2 - Asymmetric Stretching
~ 2830	~ 2850	CH_2 - Symmetric Stretching
~ 1610	~ 1642	H_2O Deformation vibration
~ 3680	~ 3630	-O-H Stretching vibration
~ 3600	~ 3628, 3624, 3619	O-H Stretching
~ 1030	~ 1049, 1035	Si-O stretching vibrations
~ 1450	~ 1487	-NH Bending vibration
~ 920	~ 918, 915	Bending vibration of Al-Al-OH

Figure 4.5 and corresponding Table 4.2 shows the FR-IR spectra of MMT-CTAB 0.03M which shows the presence of additional bands at 2900 cm^{-1} and 2830 cm^{-1}. The stretching vibrations of the C-H bonds occurring in the 2800 – 2900 cm^{-1} region, peaks for the same also observed at absorption band 2900 cm^{-1} and 2830 cm^{-1} and 1450 cm^{-1}. The stretching vibrations of the C-H bonds occurred in the 2800 – 2900

cm^{-1} region. The absorption band at 2900 cm^{-1} and 2830 cm^{-1} corresponding to asymmetric and symmetric stretching -CH_2. A band at 1450 cm^{-1} is assigned to the bending vibration of N-H groups. These additional bands are observed along with the characteristic bands at Na-MMT, ~920, ~1030, ~1115, ~1640, ~3400, ~3620, ~3698 cm^{-1} [100.101]. Organically modified layered clay indicated vibration bands or organic modifier without causing any distortion of structure of clay. This spectrum shows the CTAB incorporation in the inter layers of Na-MMT clay[102].

4.1.3 THERMO GRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis is done to elucidate decomposition behaviour thermally. The weight loss arising from the degradation was studied by thermogravimetry analysis. Data are recorded as thermogram of weight versus temperature weight loss with time at constant temperature called isotherm TGA. A modern TGA instrument allows thermogram to be recorded on microgram quantities of material. Samples of 12 mg were heated till 700˚C. The TGA trace was used to determine the % weight loss at 700˚C which is sufficient temperature to degrade the organic content present in modified Na-MMT clay.

TGA gives the information about the thermal stability of the Organoclay. The TA curves for unmodified Na-MMT clay and organically modified clay are shown in Figure 4.6(a) and Figure 4.6(b). It was noted that the TGA of the Na-MMT occurred in three mass loss steps: Between ambient and 100˚C, at 480˚ – 500˚C and stable till 700˚C. These mass loss steps were attributed to desorption of water from the clay, dehydration of the hydrated cation in the interlayer and the dehydroxylation of the montmorillonite respectively.

From the Figure 4.6 (a) and 4.6 (b) it has been observed that the mass loss observed in four steps of steps for the Organoclay. In case of MMT-$CTAB_{0.03M}$, the first step was from the ambient to 80˚C – 120˚C and was attributed to desorption of water. The second step occurs from 220˚C to 330˚C and was assigned due to decomposition due to organic matter (of surfactant)[103].

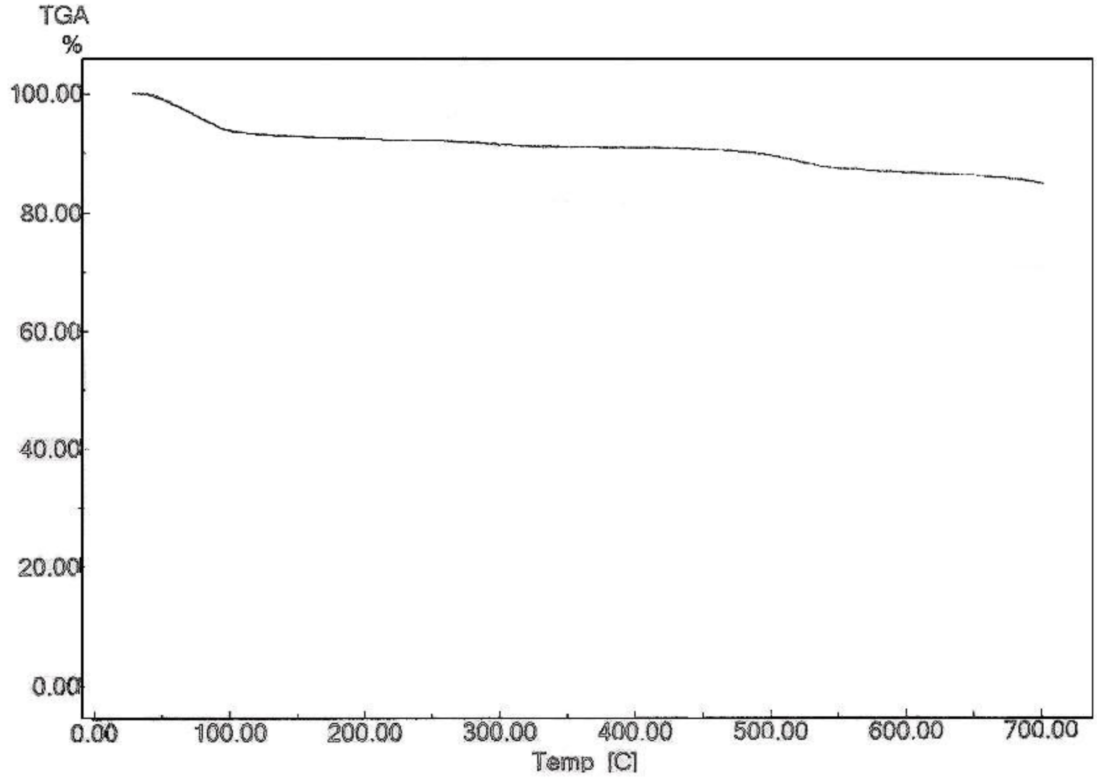


Figure 4.6 (a) Thermographimetric curve for Na-MMT clay

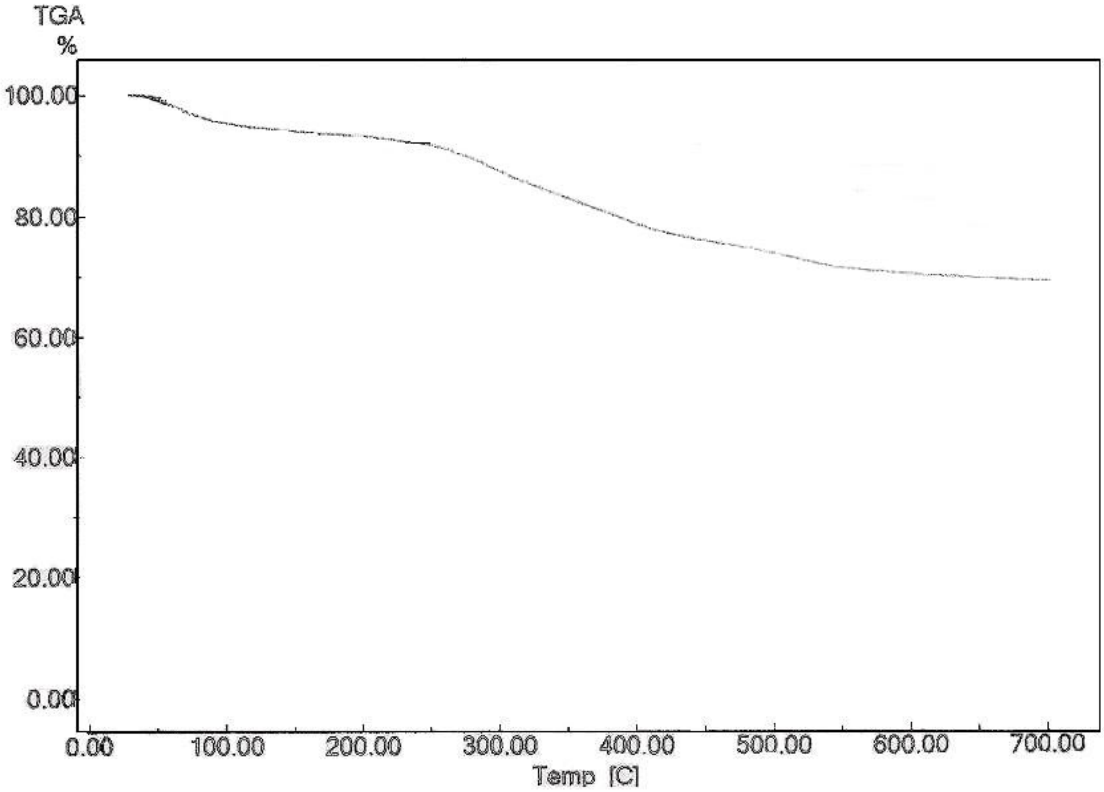


Figure 4.6 (b) Thermogravimetric curve for CTAB MMT clay

The third mass loss step till 700˚C was attributed due to the loss of structural hydroxyl group from within the clay. That was an indication of the thermal stability of modified clay. Further, the TGA curve of MMT- $CTAB_{0.03M\ and}$ clay shows first degradation step from ambient to 70˚C temperature range. The second step occurs from 200˚C to 260˚C and third step occurs at 300˚C.

4.1.4 XRD PATTERN ANALYSIS

Organophilic clay can be produced usually from hydrophilic clay by ion exchange with an organic cation such as an alkylammonium ion. The clay chemical complex, which exhibits definite gallery spacing between the platelets, is called a nano Organoclay

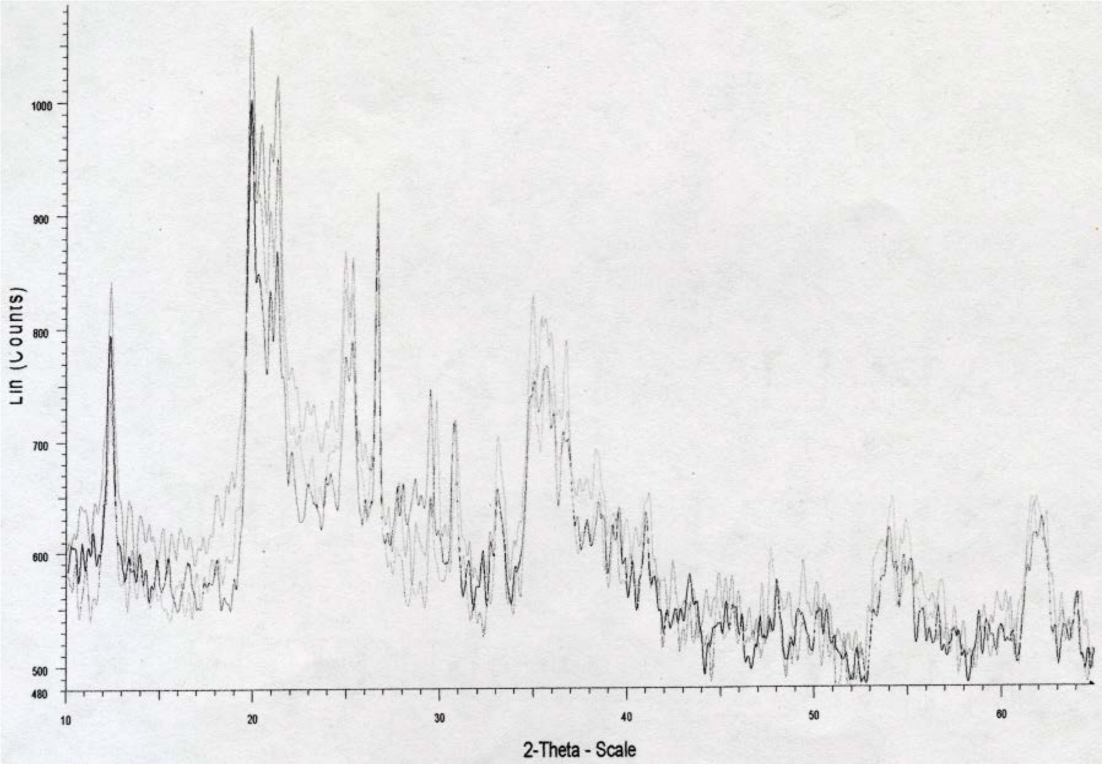


Figure 4.7 X-ray differection pattern of Na-MMT nad CTAB- MMT clay

Fine powder of Organoclay was scanned on diffractometer for the measurement of basal spacing. The recorded values for Na-MMT clay and CTAB- MMT (Organoclay) are reported in Table 4.3.

Table 4.3 Final basal spacing recorded for Na-MMT and organoclay

Sr. No.	**Sample**	**Final Basal Spacing**	
		Nm	**2θ**
1	Na-MMT	44.689	19.851
2	MMT-CTAB	44.711	19.841

The basal spacing of Na-MMT and MMT-CTAB$_{0.03M}$ are shown in Table 4.3 X-diffractograms of Na-MMT and MMT-CTAB$_{0.03M}$ exhibits an increase in d-spacing compared to the original unmodified clay i.e. Na-MMT, indicating the formation of intercalated structures[104]. The high intensity reflection for MMT-CTAB$_{0.03M}$ confirms a high degree of order for a lamellar stacking of layers of these organically modified clays[105]. The increase in the value of basal spacing depends upon two factors. One is the presence of large hydrophobic groups on surfactants and second is the decrease in surface energy of Na-MMT. As the size of hydrophobic groups are increases the basal spacing increases to a large extent as seen from the Table 4.3 and corresponding X-ray diffractograms.

SECTION II

In this section an inorganic polymer composite filament was formed through nanosize clay filler particles that were incorporated inside a polypropylene matrix. The montmorillonite clay was modified and converted to Organoclay at laboratory in optimized condition. The PP/Clay nanocomposite filament was prepared on lab model melt spinning machine. Morphology of composite filament was examined with SEM. The filament was also analyzed by FT-IR spectra and further analyzed by EDX. This composite filament was evaluated for the change in their mechanical and thermal properties compared to the pure polypropylene filament.

4.2 PREPARATION OF PP / NANOCLAY COMPOSITE FILAMENT

The aim of the present investigation was to prepare establish simple technique to prepare polypropylene / nanoclay composite filament with improved mechanical and thermal properties compared to the pure polypropylene filament.

There are different techniques to disperse the nanofillers at nanoscales in polymer matrix; in situ polymerization, solution blending, and melt intercalation[106-110]. Melt intercalation is the most widely used method for monofilament processing, and it is environmental friendly due to lack of solvent during mixing or processing. The features of the extruder and screw configuration are important to obtain good Organoclay dispersion. Better dispersion can be achieved with longer residence times in the extruder. In some cases, having a higher melt viscosity is useful in obtaining dispersion, because of the higher stresses that can be enforced on the clay particles[111]. Other parameters such as barrel and die temperature, draw down ratio, and heater temperature can be adjusted for better exfoliation. Correct settings of these parameters can change the reinforcing effect, agglomeration of clay, and synergistic effect of nanoparticles.

4.2.1 PROCESSING OBSERVATIONS

The dispersion of nanoclay in PP matrix for preparation of PP/Clay nanocomposite monofilaments was done by melt mixing. The mixing and extrusion of filaments was carried out in a laboratory model single screw extruder. The melt spinning parameters i.e. screw speed, temperature of different zones, take-up speed were optimized and set as per discussed in chapter 3, to get a uniform filament. The spun PP filament was quenched in a water bath maintained at around 15˚C before drawing section. After the drawing, all monofilaments, except pure polypropylene, were chopped and re-extruded to obtain better dispersion and distribution of the nanoclays in polymer matrix. Thus, PP / Clay nanocomposite monofilaments with 0.1, 0.7, 1.5 and 2 wt. % were prepared.

Figure 4.8 Photographs of pure polypropylene and polypropylene / nanoclay composite filament

It was observed that process ability was not very good for 1.5 wt. % and more addition of nanoclay particles. With higher level of nanoclay addition, there was increase in back pressure and polymer flow problem in the die. Drip formation and frequent breakages were also observed during higher loading but somehow, managed to spin lesser quantity if filaments as the run was only carried out for short duration. The photographs of the composite yarn prepared are also shown in Figure 4.8.

4.2.2 EFFECT ON STRUCTURAL PROPERTIES OF PP/ NANOCLAY COMPOSITE FILAMENT

4.2.2.1 Surface Analysis of Filament by SEM

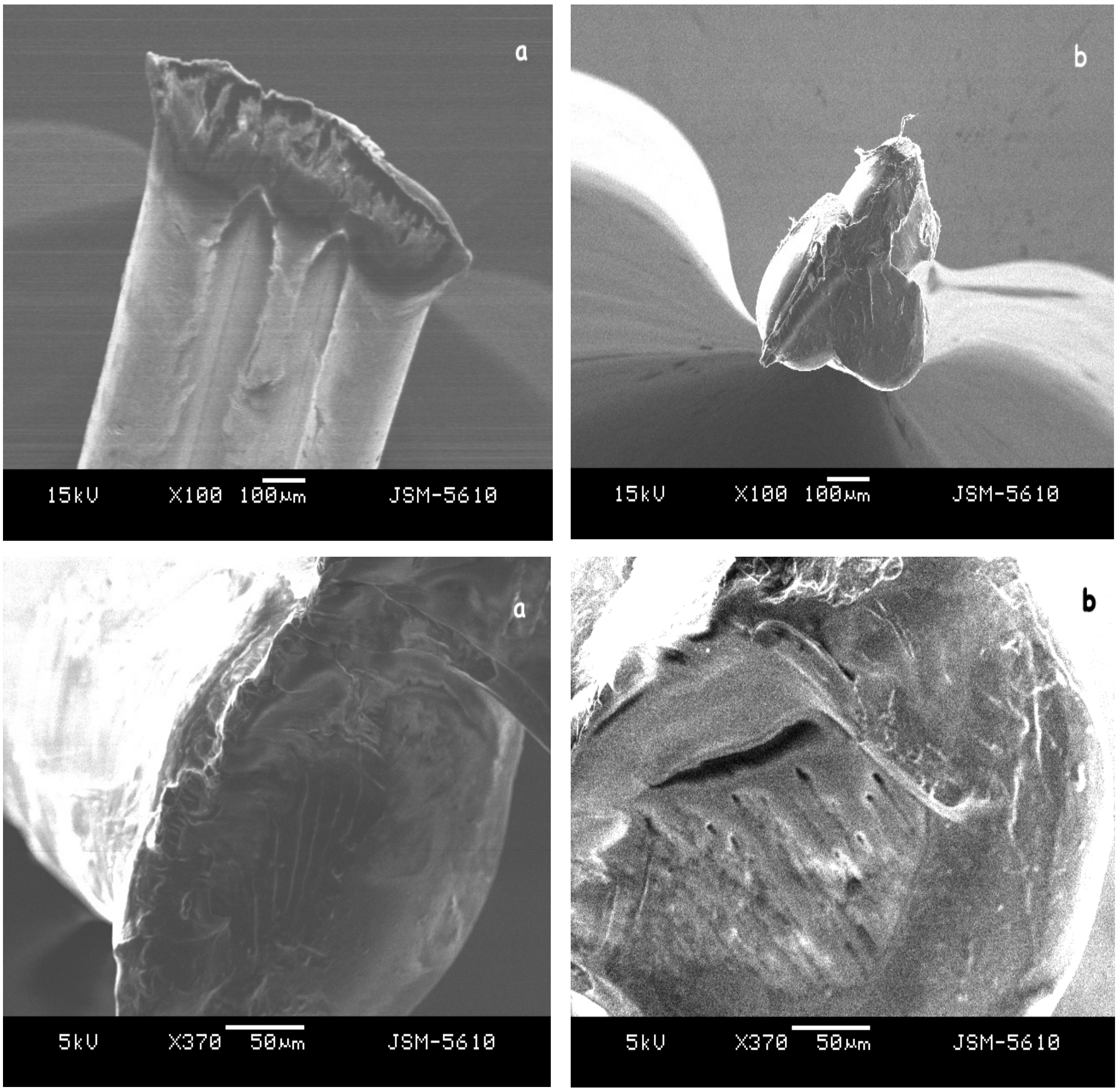


Figure 4.9 ***SEM images of (a) pure polypropylene and (b) polypropylene / nanoclay composite filament***

Figure 4.9(b) shows microphotograph of polypropylene polymer matrix revels that the nanoclay particles not only uniformly dispersed on the outer surface of the polymer but also incorporated inside the polymer matrix, whereas Figure 4.9(a) represents microphotograph of pure polypropylene polymer where no particles on or into the polymer were seen. To ensure the uniform distribution of nanoclay or to observe lumps formation on the filament the prepared nanoclay polymer composite filaments were further observed at 200X, 550X 1000X and 2000X magnification.

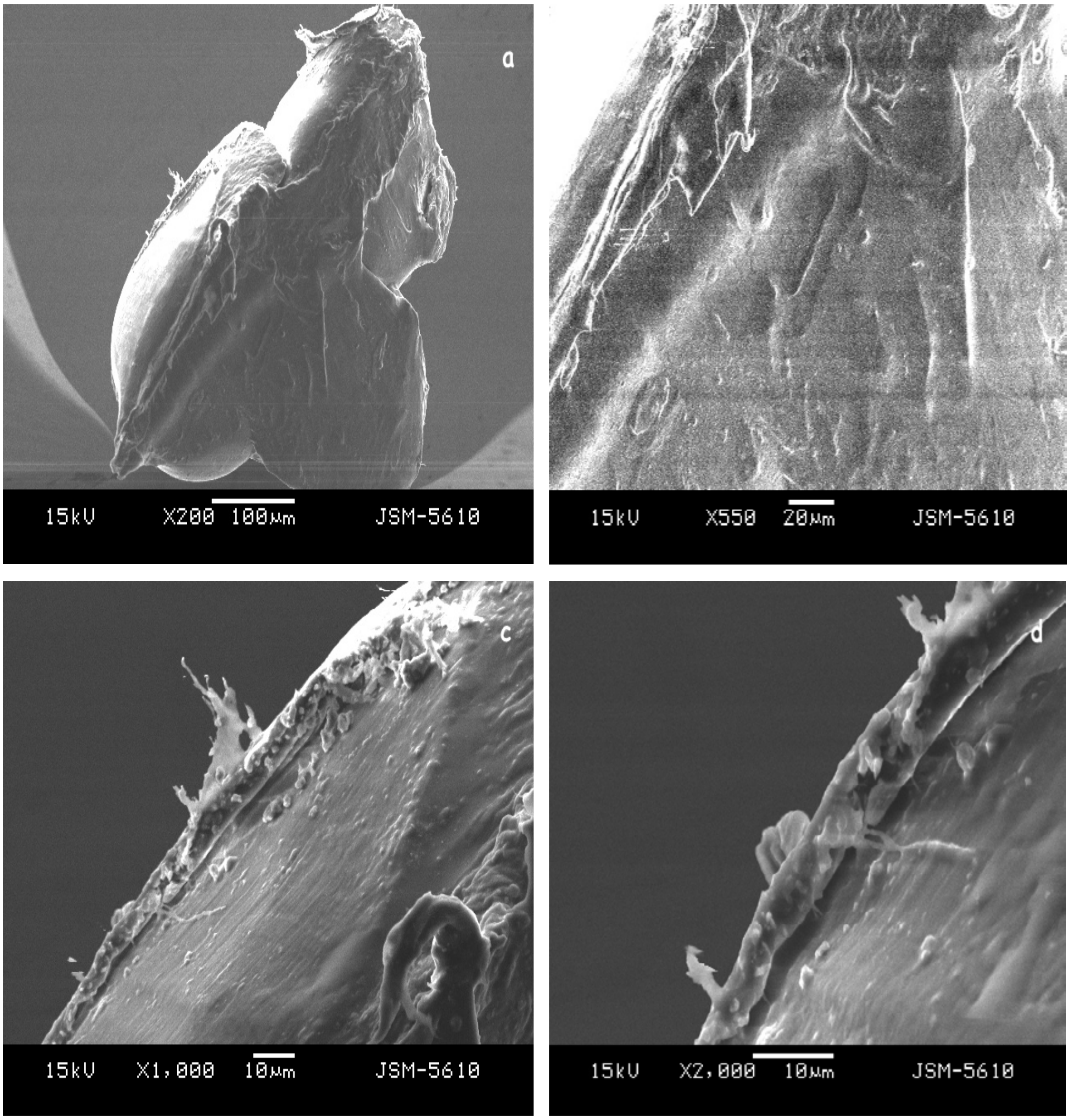


Figure 4.10 ***SEM images of polypropylene / nanoclay composite filament at different magnifications (a, b, c, d at 200X, 550X, 1000X and 2000X respectively)***

The surface morphology of composite filaments at different magnification is shown in Figure 4.10 - a, b, c, d at 200X, 550X, 1000X and 2000X respectively. The polypropylene / nanoclay composite filament contains the smallest MMT nanoparticles with negligible aggregation were observed by SEM. SEM micrographs taken from different sample localities revealed an even distribution of the MMT nanoparticles throughout the filament. The SEM micrographs indicated that the MMT particles were non-aggregated and well dispersed on the nanoclay polypropylene composite filament.

4.2.2.2 Elemental analysis by Oxford-Inca software on SEM

Figure 4.11 and Table 4.4 shows presence of elements in the prepared polypropylene filaments detected by using Oxford Inca software on SEM.

Table 4.4 Elements detected on pure polypropylene structure

Sample Code	Structure	Amount of element in weight percentage			
		C K	O K	Fe K	Ca K
S1	Pure polypropylene	86.75	13.11	0.00	0.13

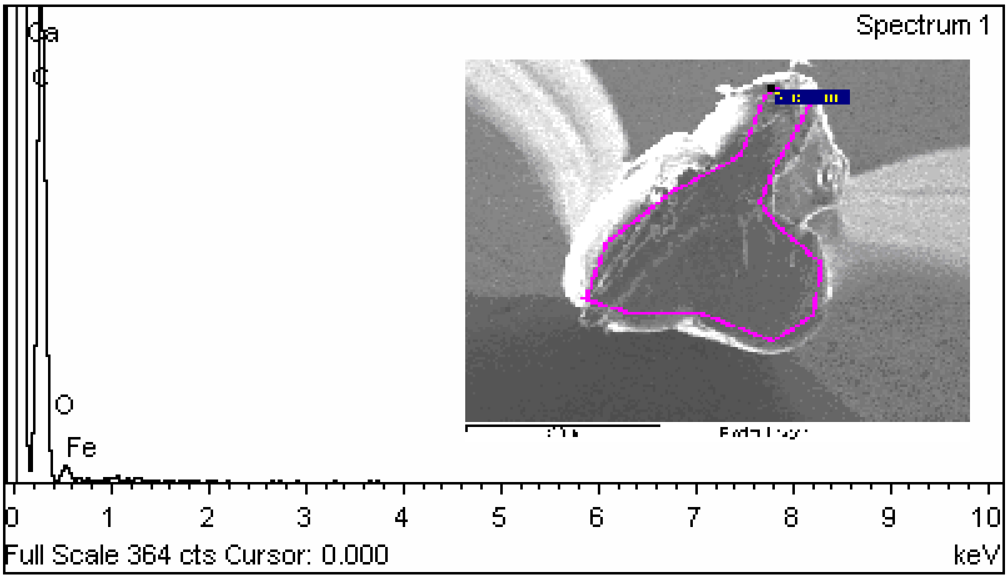


Figure 4.11 Elemental analysis results of pure polypropylene filament

Whereas Figure 4.12 and Table 4.5 shows the elemental analysis of MMT incorporated yarn. The elemental analysis results presented in the Table 4.5 confirms the presence of MMT particles. It is observed that sample S1 being pure polypropylene yarn has elements like C, Mg, and Al but they are present in their oxide form i.e. $CaCO_3$, MgO and Al_2O_3 where as sample S2 being composite polypropylene filament i.e. filament with nanoclay, shows peaks for C, Mg, Fe, Na, Ca, and Si being part of Organoclay.

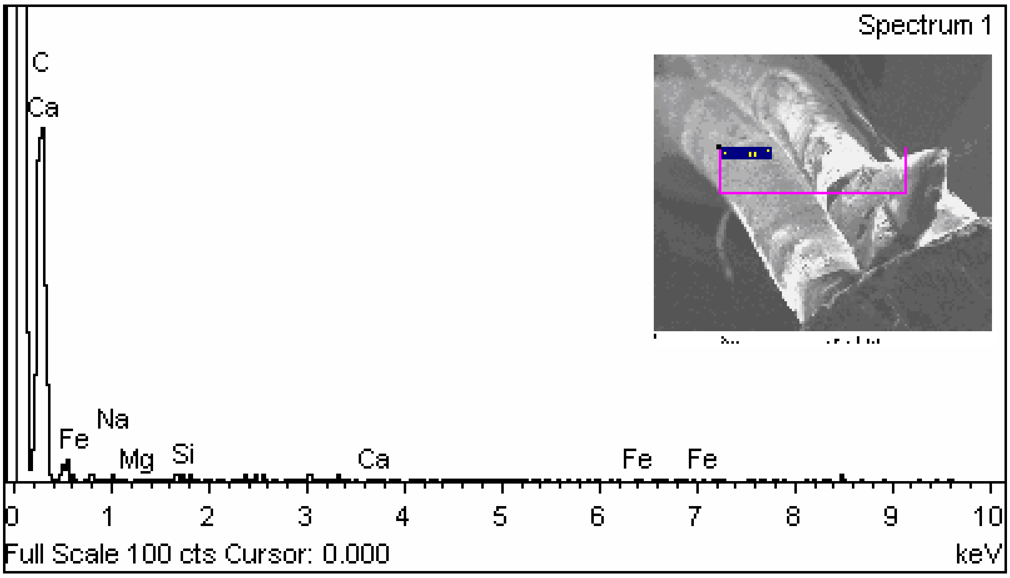


Figure 4.12 ***Elemental analysis results of polypropylene/ nanoclay composite filament***

Table 4.5 Elemental detected on polypropylene / nanoclay composite filament using EDX

Sample Code	Structure	Amount of element in weight percentage						
		C K	Mg K	Al K	Fe K	Na K	Ca K	Si K
S2	Polypropylene / nanoclay composite	97.23	0.23	--	0.87	0.45	0.94	0.27

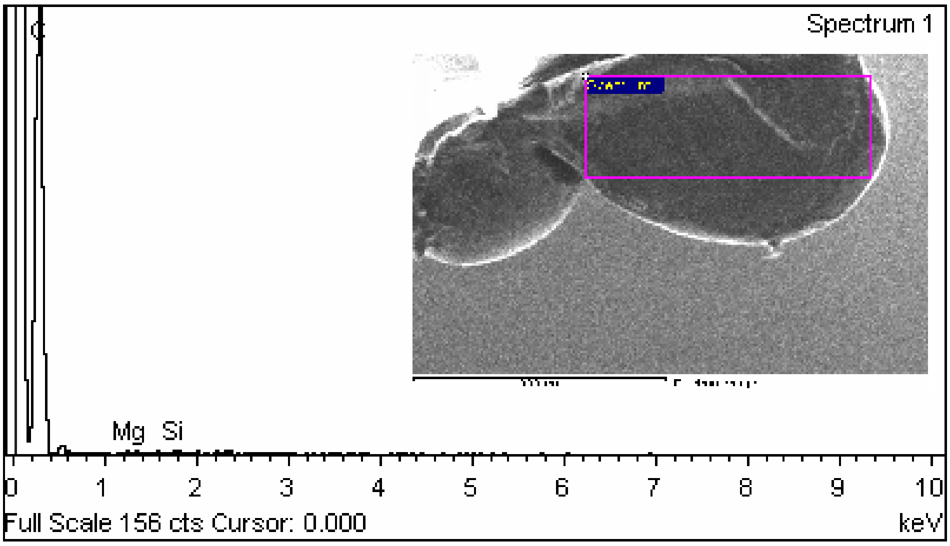


Figure 4.13 ***Elemental analysis results of polypropylene / nanoclay composite filament at selected area***

From the selected area of Figure 4.11, 4.12 and 4.13 it has also been observed that the nanoclay particles are uniformly distributed inside the polymer matrix apart from its surface. This may confirm the exfoliated structure being obtained.

4.2.2.3 Structural Analysis by X-Ray Diffraction

WAXD scans of the pure PP and nanocomposite PP filament are included in Figure 4.14 and 4.15. In both the figure no peaks for nanoclay have been appeared. This may be due to the exfoliated structure and good dispersion of nanoclay in polymer matrix or PP molecules have intercalated in the clay layers, thereby gallery spacing between the clay platelets might have expanded or loss of structural registry to an extent beyond the detection limit of X-ray in polymer matrix. This good dispersion may be attributed to the specific interaction originated from hydrogen bonding between the materials[113-115].

Table 4.6 Final d-spacing recorded for PP and PP / nanoclay composite filament

Sr.	**Pristine PP**		**PP / nanoclay composite**	
	Position 2θ	d-spaing A	Position 2 θ	d-spaing A
1	24.657	3.607	25.781	3.452
2	25.681	3.466	25.951	3.430

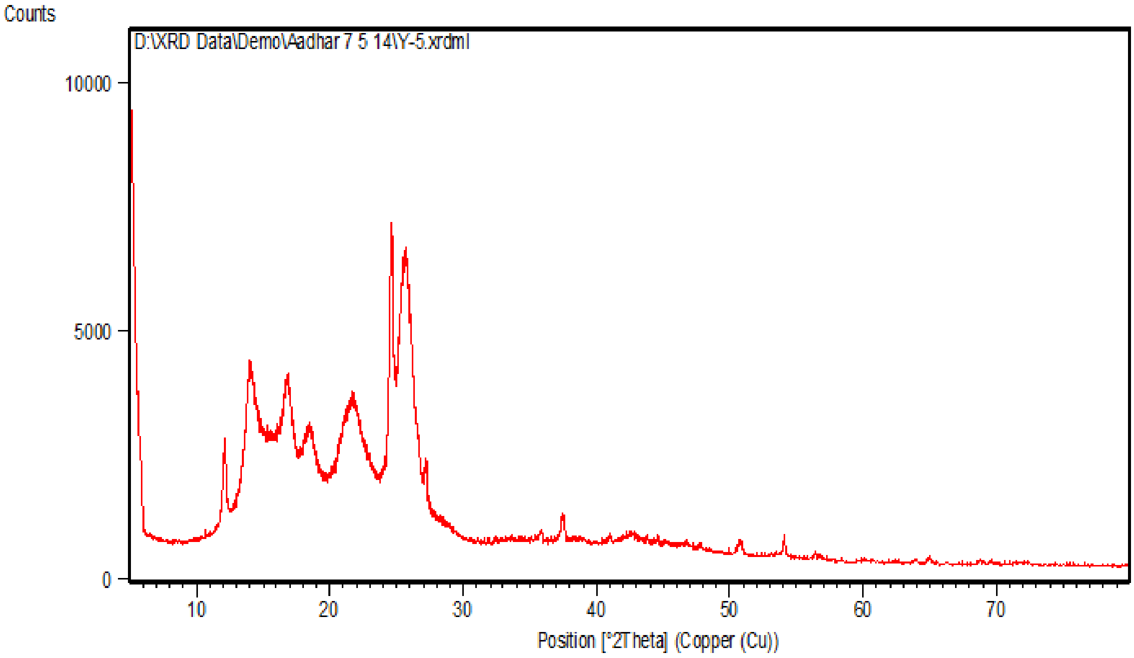


Figure 4.14 XRD pattern for pure polypropylene filament

An X-ray pattern of pure PP filament is shown in Figure 4.14. At spinning speed (250 m/min), the broad peak of monoclinic crystalline (α form), which is indicative of poor crystallinity, is observed. This form is characteristic for a low orientation of polypropylene. An addition of nanoclay in leads to an appearance of β form crystallinity which is seen from the Figure 4.15. In case of nanoclay infused PP filament, β- form crystallinity appears in the X-ray pattern of filament drawn without addition, indicating that infused nano clay is capable of acting as β form nucleating agent for isotactic PP[116]. Similar observations were made by Jan Broda, Andrzej Gawlowski et. al for PP filament yarn due to presence of nanoclay in PP structure, decrease in 2θ value is seen at 16.0 and 21.1 degrees which results in β- form crystallinity.

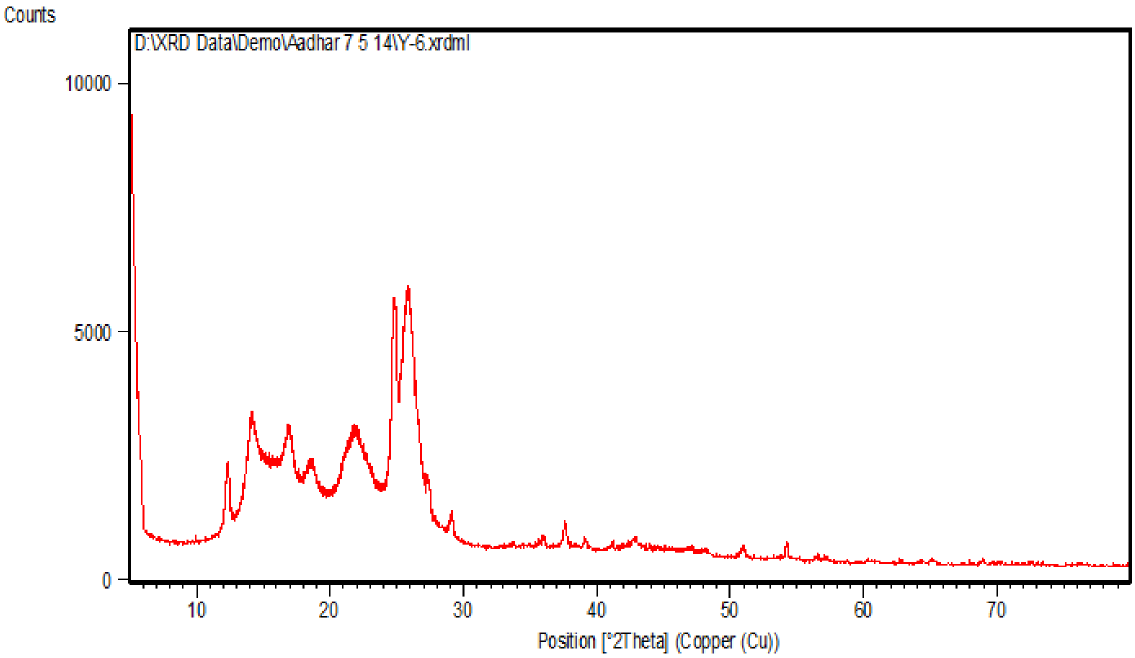


Figure 4.15 XRD pattern for PP/ nanoclay composite filament

4.2.3 EFFECT ON MECHANICAL PROPERTIES OF PP/ NANOCLAY COMPOSITE FILAMENT

Polypropylene is a semicrystalline polymer, and most of the properties depend on crystallinity, spherulites size, and the size of lamellar crystals. On the other hand nanoclays are known as nucleating agents and accelerate the crystallization process[112].

4.2.3.1 Effect on Tensile Strength

Polymer layered silicate nanocomposites has found to improve many properties of the host polymer. One of the main properties under study by most of the researchers is mechanical property. Mechanical property of the nanocomposite is directly related to the amount of intercalation or exfoliation of the nanoclay particles. When the nanoclay particles are well dispersed and exfoliated in the polymer matrix, the load bearing capacity will increase and it results in good improvement in mechanical properties. Tsagaropoulos et al. [1995] state that stiffness of the silicate layers creates immobilized or partially immobilized polymer phases at the interphase regions is the one of the main factor for the improved mechanical property. Specific surface area of the clay particles is another reason for the improved mechanical properties. Specific surface area of the clay particles increases with decrease in particle size. Decrease in particle size contributes to increase in volume of the interfacial regions and it contributes to better stress transfer.

Table 4.7 Mechanical property of pure polypropylene and polypropylene / nanoclay composite filament

Sample code	**Composition**	**Specific strength in gms / denier**	**% Strain**	**Modulus in gms / denier**	**Work done in Kg.mm**
S1	Pure PP filament	0.49	173.22	0.01	24.36
S2	PP + 0.1 Nano clay	0.74	433.90	0.11	44.16
S3	PP+ 0.7 Nano clay	0.85	305.92	0.05	56.63
S4	PP + 1.5 Nano clay	0.89	320.96	0.07	35.62
S5	PP + 2.0 Nano clay	0.45	532.03	0.08	160.06

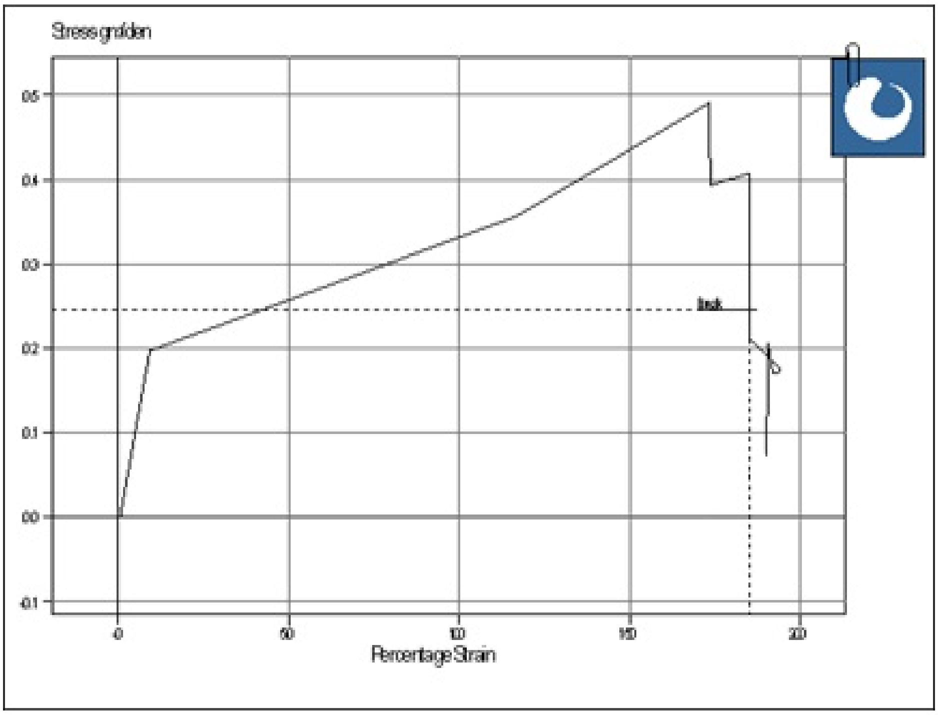


Figure 4.16 Stress strain curve of pure PP monofilament (S1)

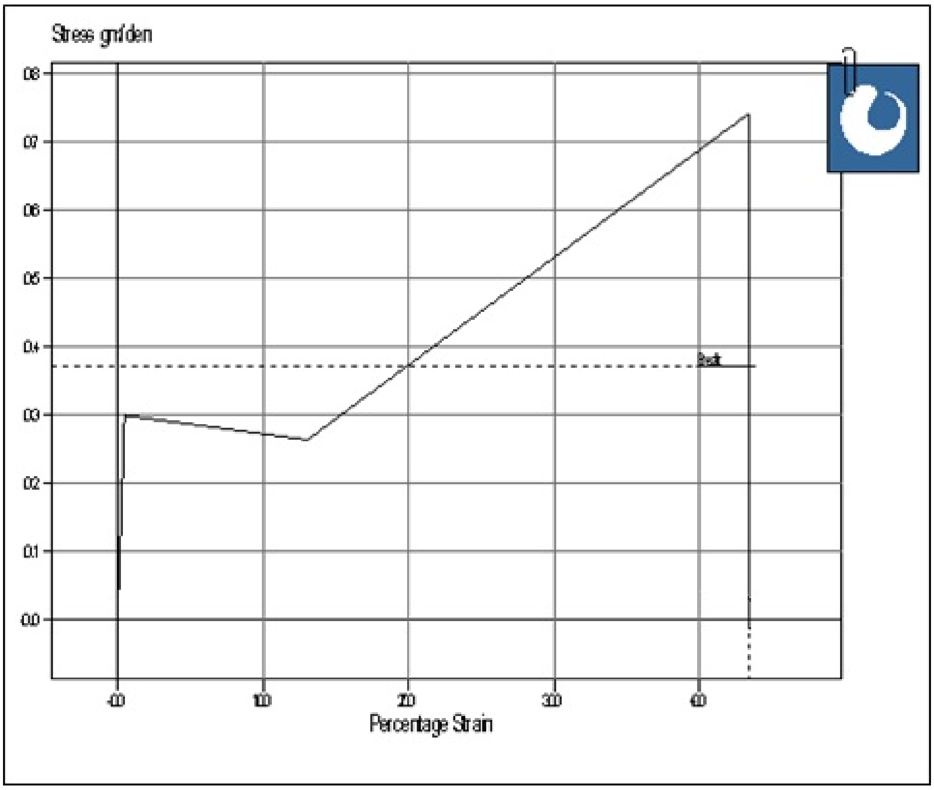


Figure 4.17 Stress strain curve of 0.1 wt % nanocomposite monofilament (S2)

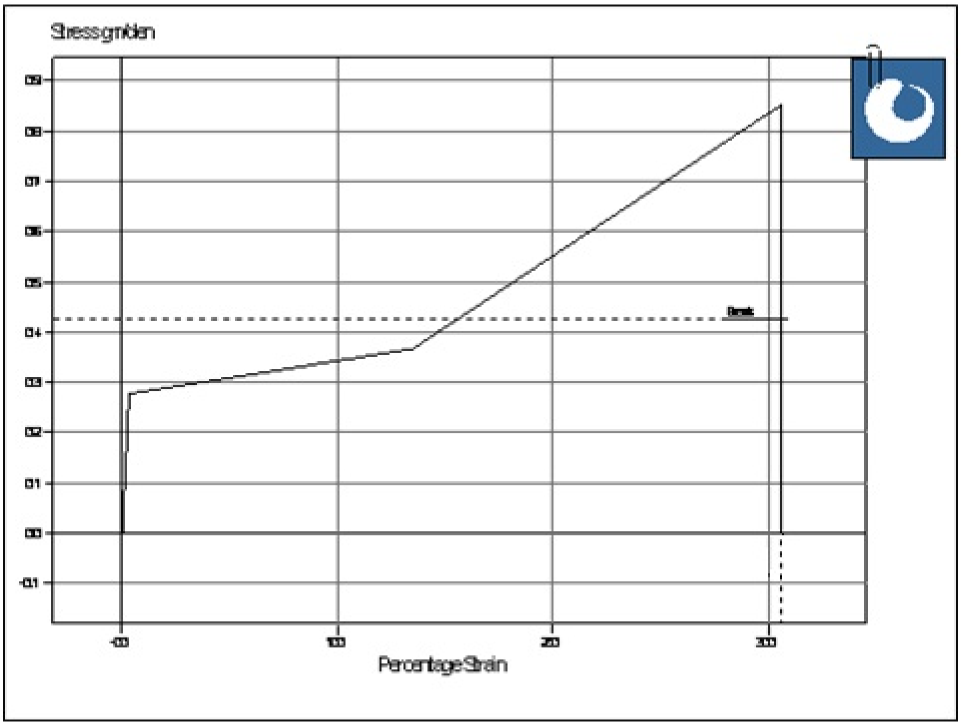


Figure 4.18 Stress strain curve of 0.7 wt % nanocomposite monofilament (S3)

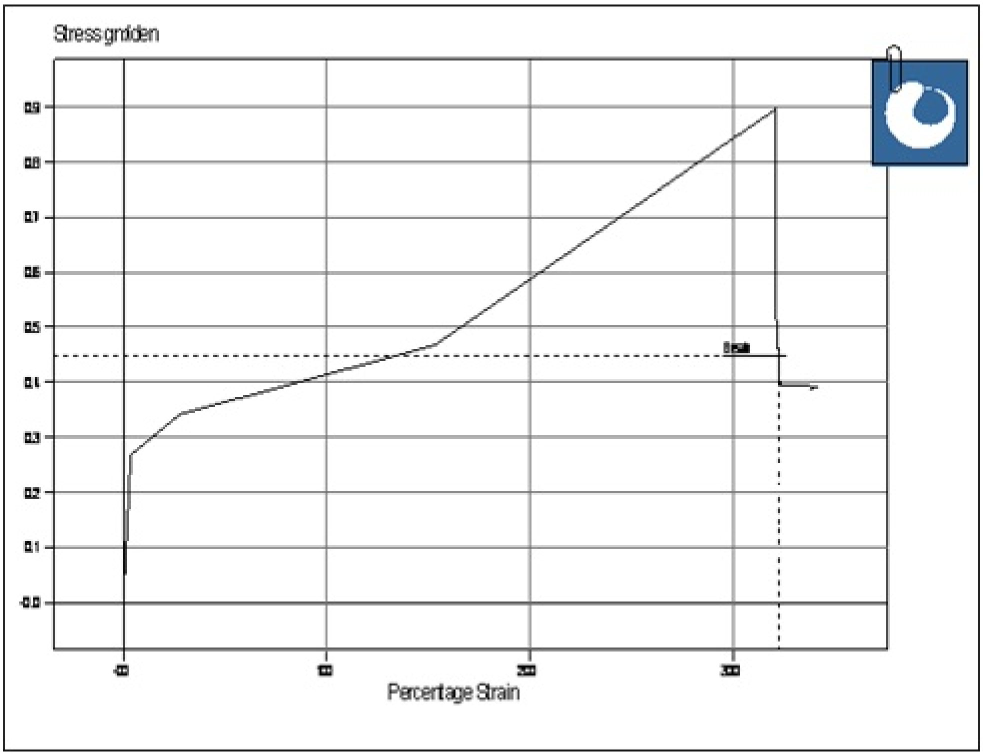


Figure 4.19 Stress strain curve of 1.5 wt % nanocomposite monofilament (S4)

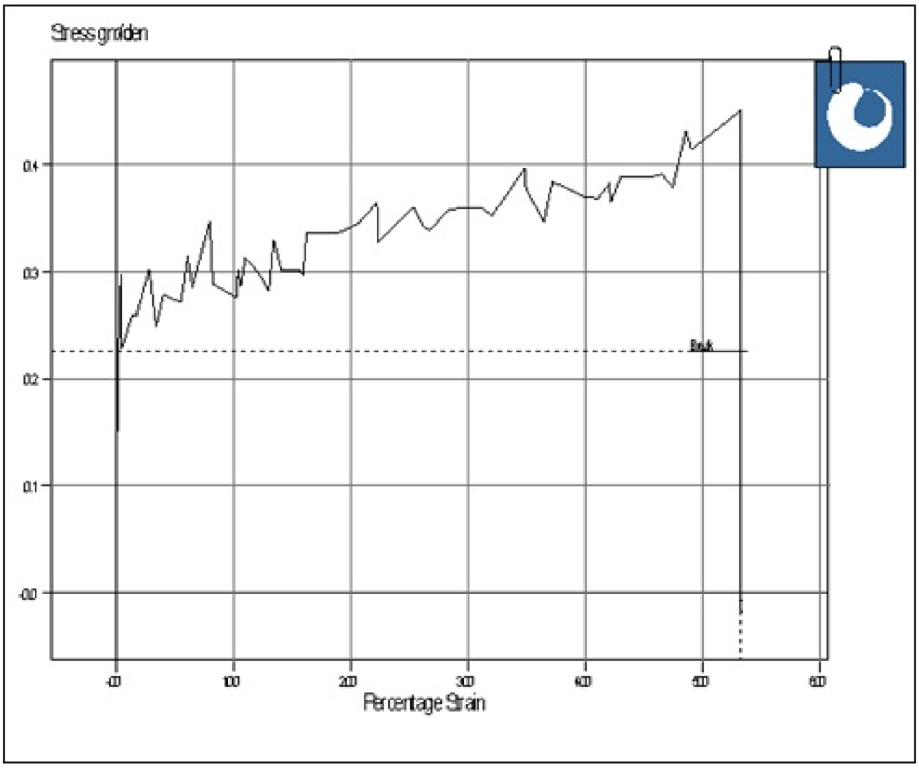


Figure 4.20 Stress strain curve of 2 wt % nanocomposite monofilament (S5)

The effects of clay loading on the tensile properties like stress, strain, modulus and work done are summarized in Table 4.7. It was apparent that the addition of nanoclay altered the shape of the stress and strain curve; Figure 4.16 to 4.20 indicates the stress stain curve obtained from the tensile tester, where change in the curve was observed and analyzed.

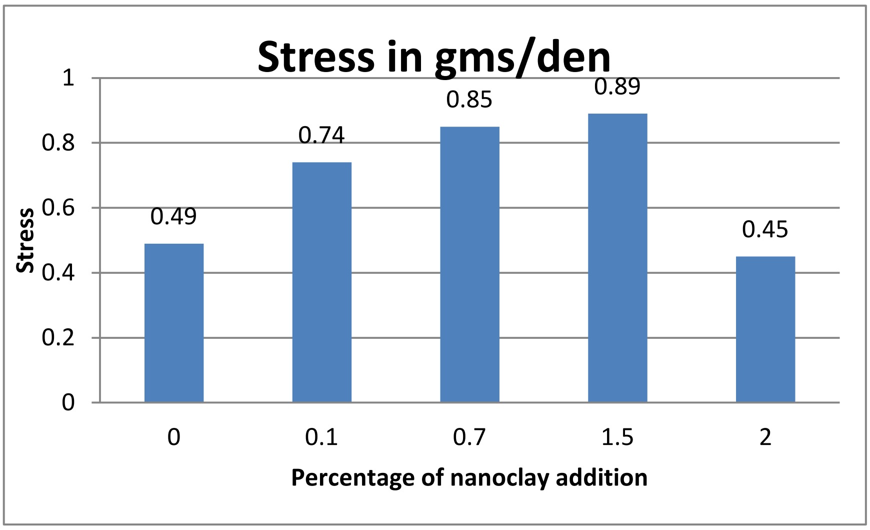


Figure 4.21 Change in stress value of composite with 0.1, 0.7, 1.5 and 2 wt % Organoclay content, compared to pure polypropylene.

The load elongation values obtained were converted to stress strain values to avoid any mistake due to denier variation. The tenacity of the prepared nanocomposite monofilament increases with the addition of nanoclay particles but as seen from Figure 4.21 this trend was seen up to 1.5 wt. % of clay loading, with further increase in clay content apparent decrease in the tenacity value was observed.

In contrast with the stress value, as seen from Figure 4.22 for the same samples the strain percentage goes on increasing. It has been observed that the elongation of the composite monofilament is more than the pristine PP yarn, which is a unique feature. Though the stress value increase the stain % does not decrease. The reduction of orientation could have also been one reason for the higher strain at break in the nanoclay–PP composite fibers. However, this could be the case as we have produced POY, which may have resulted in increased % strain behaviour of composite yarn.

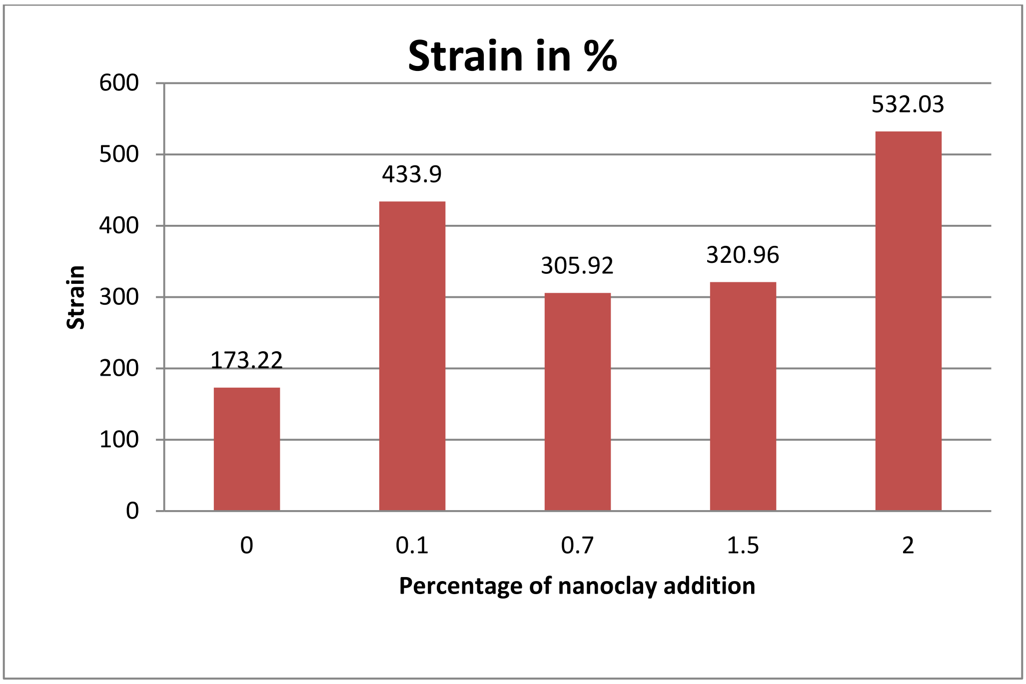


Figure 4.22 Change in strain % of composite with 0.1, 0.7, 1.5 and 2 wt % Organoclay content, compared to pure polypropylene.

4.2.3.2 Effect on Modulus of Composite Filament

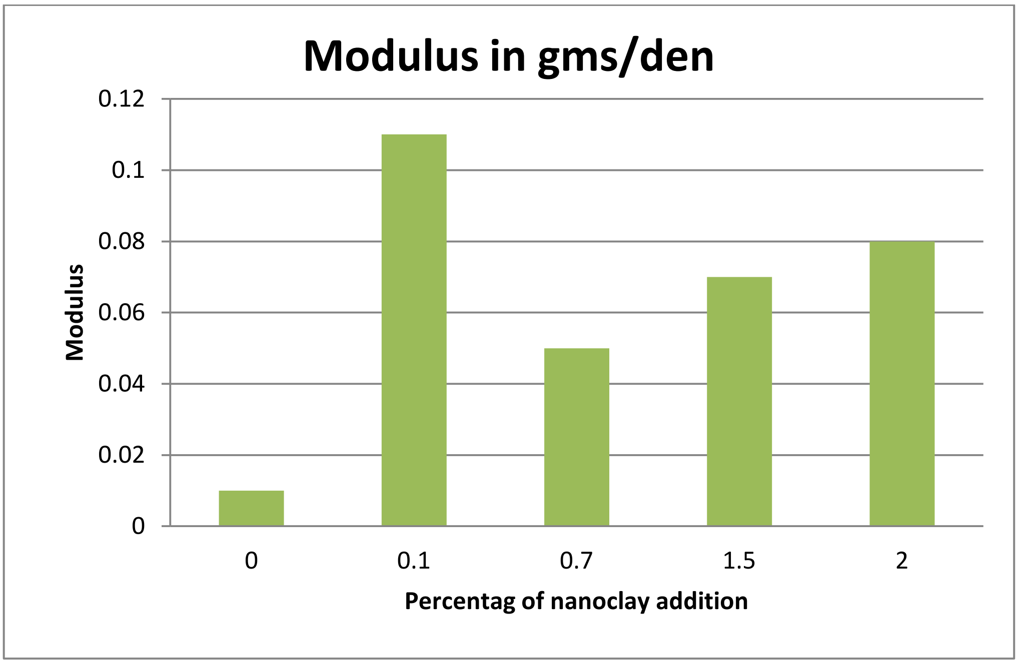


***Figure 4.23** Change in modulus of composite with 0.1, 0.7, 1.5 and 2 wt % Organoclay content, compared to pure polypropylene.*

The fiber modulus also exhibited increasing trends with clay addition irrespective of percentage clay loading (Figure 4.23). In contrast, the strain at break was dramatically enhanced when nanoclay was added.

4.2.3.3 Effect on Work

From Figure 4.24, it can be seen that the overall work done by the prepared composite yarn increased. Work done is the area under stress strain curve and as with increase in stress value, strains also increases, which results in better work obtained from the nanocomposite filament compared to pristine.

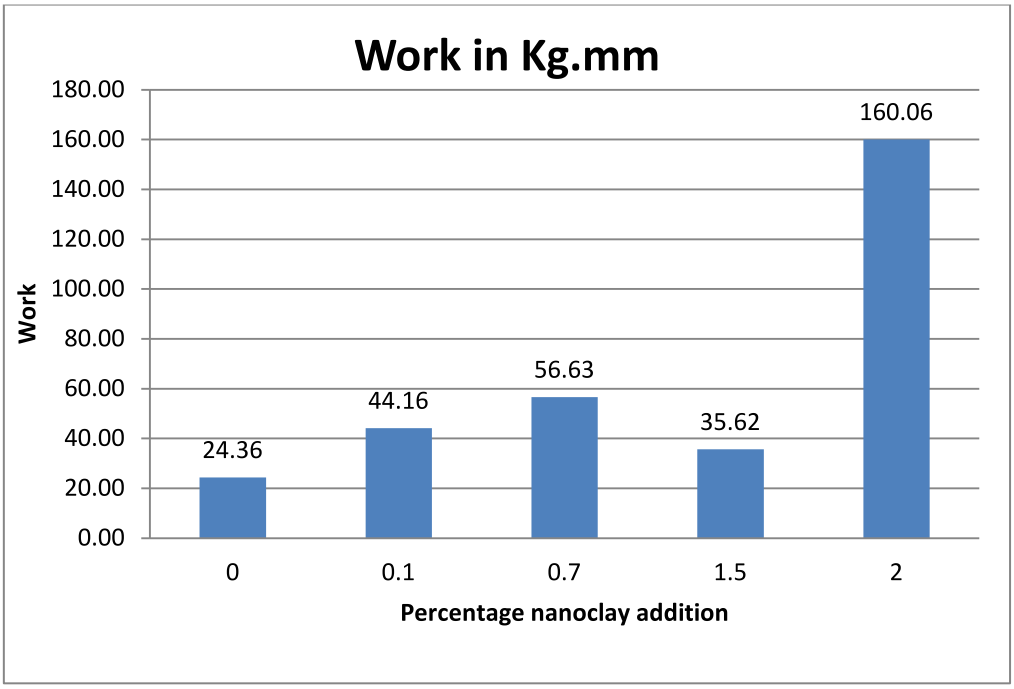


Figure 4.24 Change in work done of composite with 0.1, 0.7, 1.5 and 2 wt % Organoclay content, compared to pure polypropylene.

In general, the tensile behavior of polymeric fibers is the result of the inherent polymeric chain properties (chain rigidity, secondary bond strength between polymeric chains, and molecular weight of the polymers used) and the microstructures of the fibers formed by polymer chain alignment. Higher clay loading caused premature tensile failure compared to the sample with a low clay loading. This may be due to structural defects in the fibers when a high concentration of nanoclay was added. Thought work of nanocomposite filament with higher percentage shows better results, it could be noted that the stress strain behaviour of that particular composite i.e. S5 is showing irregular pattern.

4.2.4 EFFECT ON THERMAL PROPERTY

4.2.4.1 Analysis by DSC

Effect of nanoclay incorporation on the thermal stability of PP composite filaments was evaluated in terms of onset temperature, T° peak temperature and delta H value, compared to the pure PP filaments by DSC.

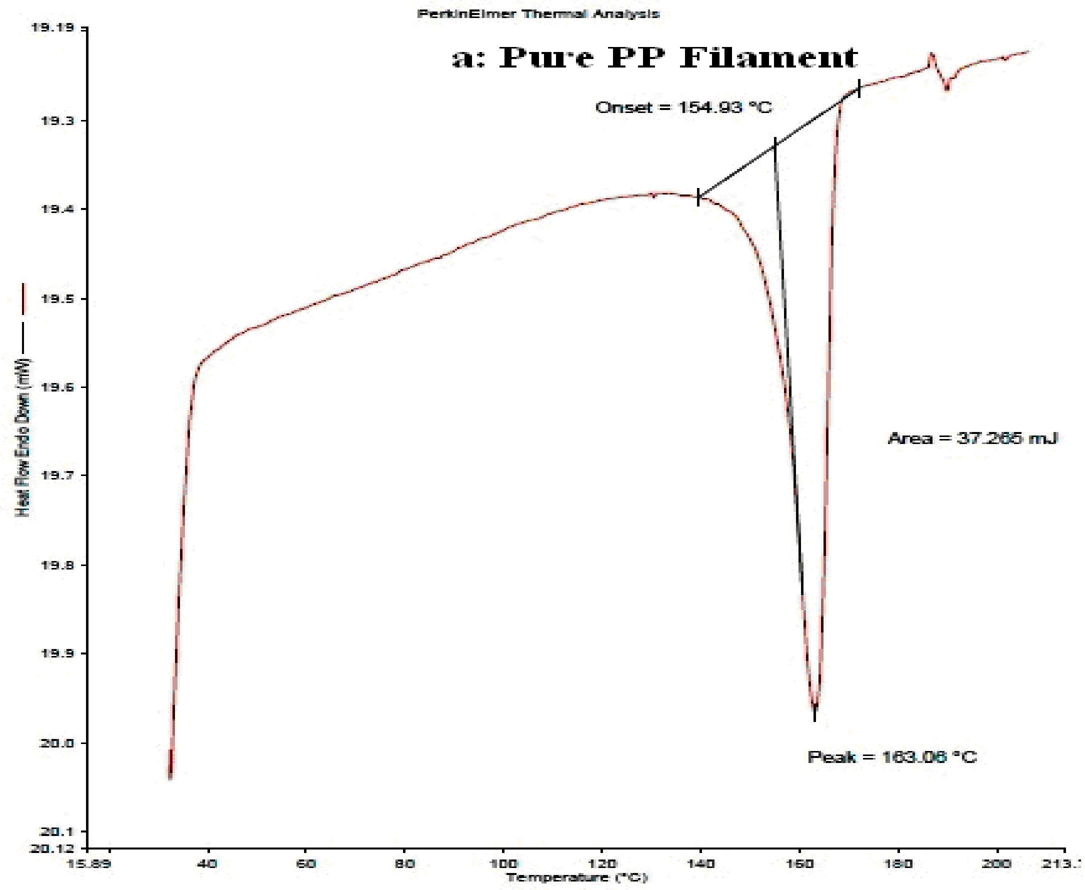


Figure 4.25 (a) DSC curve of pure polypropylene filament (S1)

From Figure 4.25 (a) and corresponding Table 4.8, the thermal degradation behaviour of pure PP filament was followed with DSC. The onset degradation temperature of pure PP filament was found to be 154.93 °C and at 163.06 °C the maximum of endothermic peak (T^o peak) was observed.

Table 4.8 Thermal analysis (DSC) of pure and composite filament

Sample code	**Composition**	**On Set Temperature Range °C**	**T^o peak °C**	**ΔH^o (Enthalpy) MJ**
S1	Pure PP filament	154.93	163.06	37.265
S3	PP+ 0.7 Nano clay	155.26	163.12	51.237
S4	PP + 1.5 Nano clay	157.54	163.64	116.84

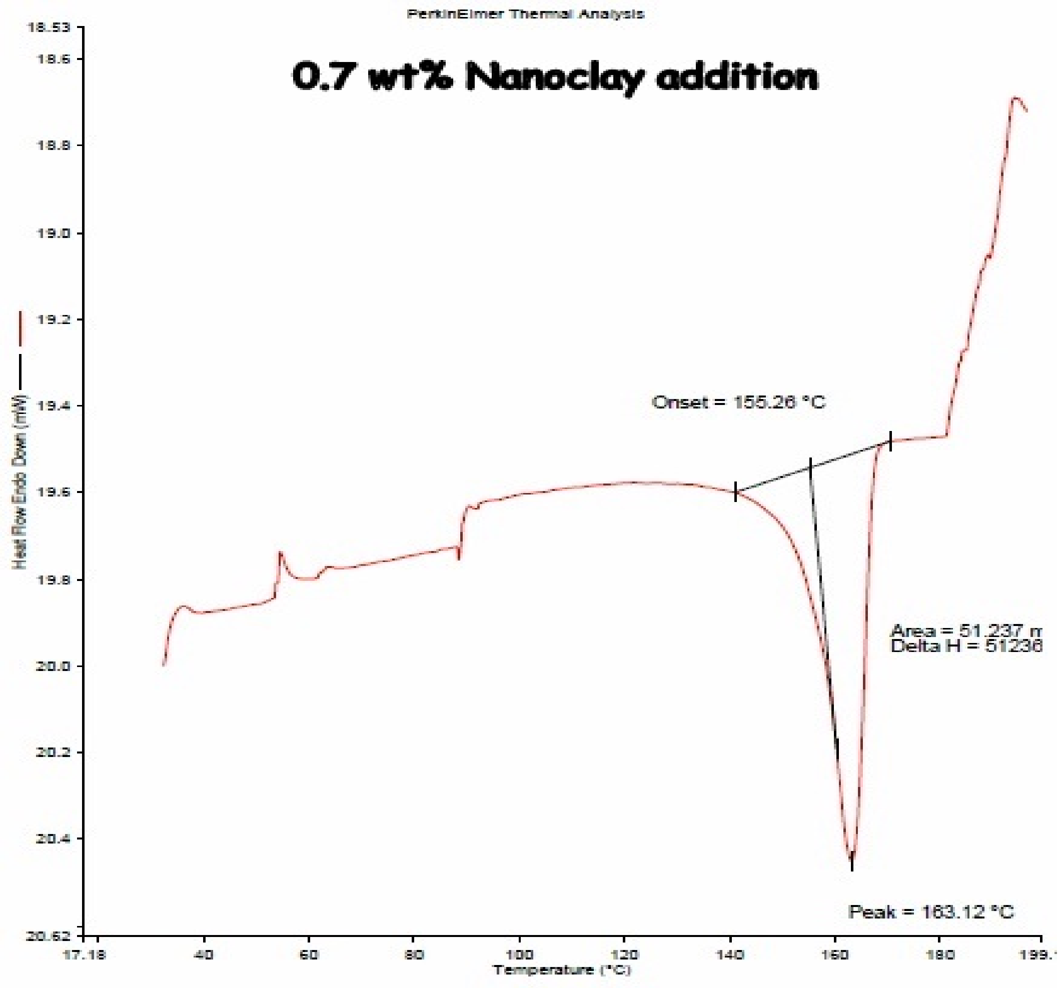


Figure 4.25 (b) DSC curves of polypropylene/ nanoclay 0.7 wt. % composite filament

On inclusion of 0.7 wt. % of MMT to PP filament (Figure 4.25 b), the onset temperature was found increased by ~ 1°C, and minor increase in the maximum peak temperature was also recorded. The peak shown in Figure 4.25(b) around 100°C, can be attributed to the formation of some crystals due to incorporation of clay where as minor fluctuations could be seen due to machine noise.

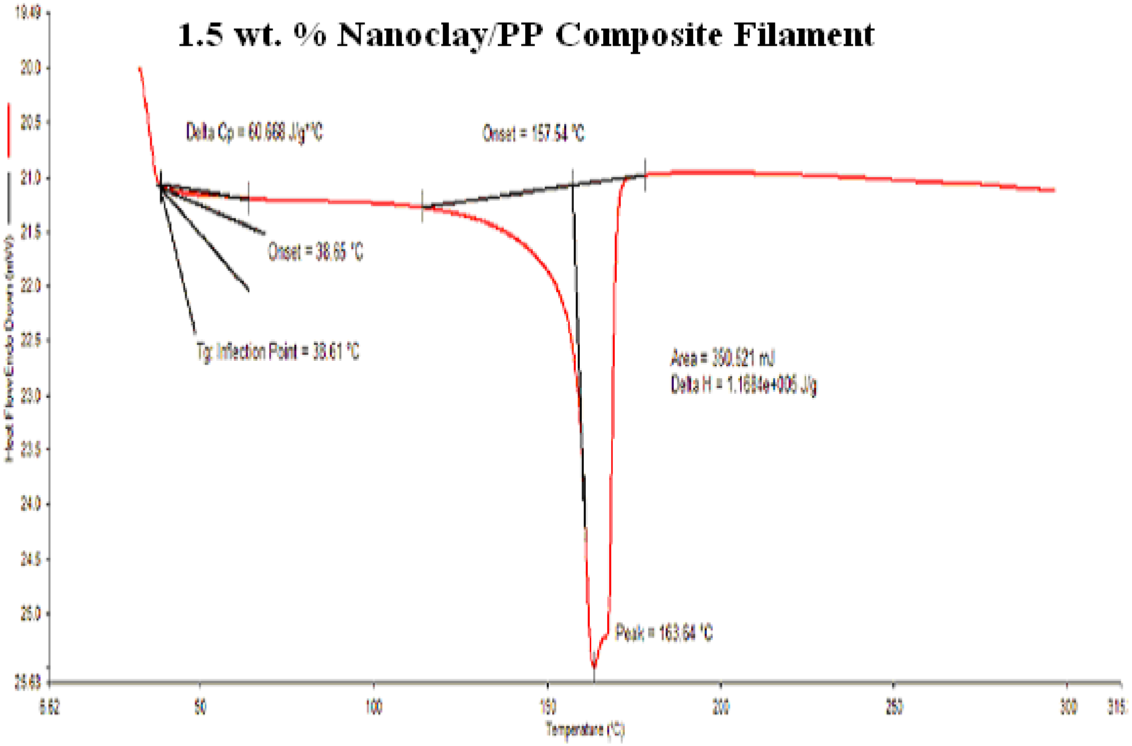


Figure 4.25 (C) DSC curve of polypropylene/ nanoclay 1.5 wt. % composite filament

Figure 4.25(C), shows thermal behaviour of composite filament with 1.5 wt. % addition of nanoclay, indicates the presence of MMT nano in PP polymer matrix, data in Table 4.8 also shows the onset temperature was increased by ~ 3°C, and minor increase in the maximum peak temperature, this may provide higher thermal stability to the composite filament, compare to the PP filament without nanoclay. Improvement in thermal stability was also supported by higher delta H value of the composite film. This may be due to the catalysis effect of clay towards the degradation of the polymer.

4.2.4.2 Thermogravimetric Analysis (TGA)

An EXSTAR TG/DTA 6300 thermal gravimetric analyzer (TG/DTA) was used to determine the thermal behaviour of prepared composite samples. Each sample was analyzed from 50 to 540°C at a rate of 10°C/ min in a nitrogen environment and data of all the compounds are given in Table 4.9 and Figure 4.26 (a, b & c). Using DTA (Differential Thermal Analysis) and TGA (Thermogrametric Analysis), under particular operative conditions, it is possible to obtain a deposit containing clay nanoparticles. Figure 4.26 (a, b & c) shows a typical DTA–TGA profile, the line marked ‘Temp’ indicates the temperature profile. The ‘TG’ line in indicates the mass (m) loss percentage ($\partial m/\partial t$). This curve indicates that, during the process, the materials are oxidized. The ‘DTA’ curve represents the DTA analysis, which indicates the mass reduction with respect to an inert mass.

Table 4.9 Thermo gravimetric analysis of pure and composite filament

Sample	**TG %**	**DTA °C**	**DTG °C**
Pure PP filament	99.49	156.92	403.87
PP+ 0.7 Nano clay	98.57	158.46	434.01
PP + 1.5 Nano clay	103.01	155.83	438.68

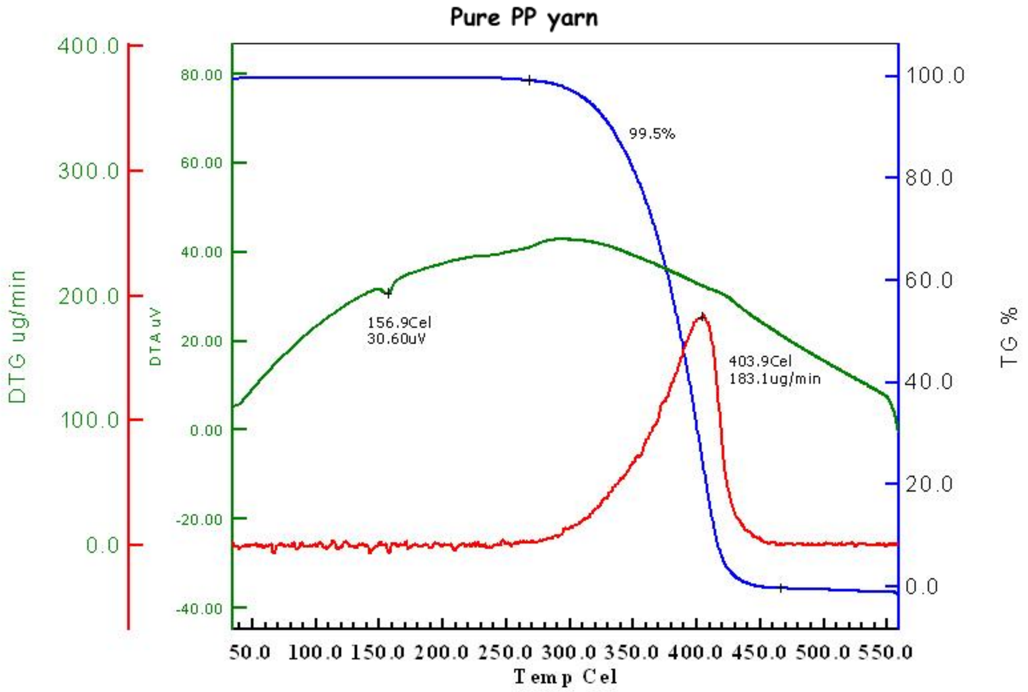


Figure 4.26 (a) Thermogravimetric curve for pure polypropylene filament

The multi stage mass loss for polymer is observed with DTG peak and corresponding DTA peaks. The DTA curve (in green) exhibits endothermic peak, from which generally occurs without corresponding DTG peak is due to the phase change and is assigned to solid to rubbery state phase transition of polymer. From the Figure 4.26 (a) it can be seen that pure PP yarn is thermally stable up to 270°C after that it shows the mass loss which could be due to either thermal degradation or evaporation. It shows 99.5% mass loss at 465°C which can be attributed to either complete thermal degradation or evaporation of compound at higher temperature. The DTA curve (in red) shows that at 403.9°C energy is required for this degradation.

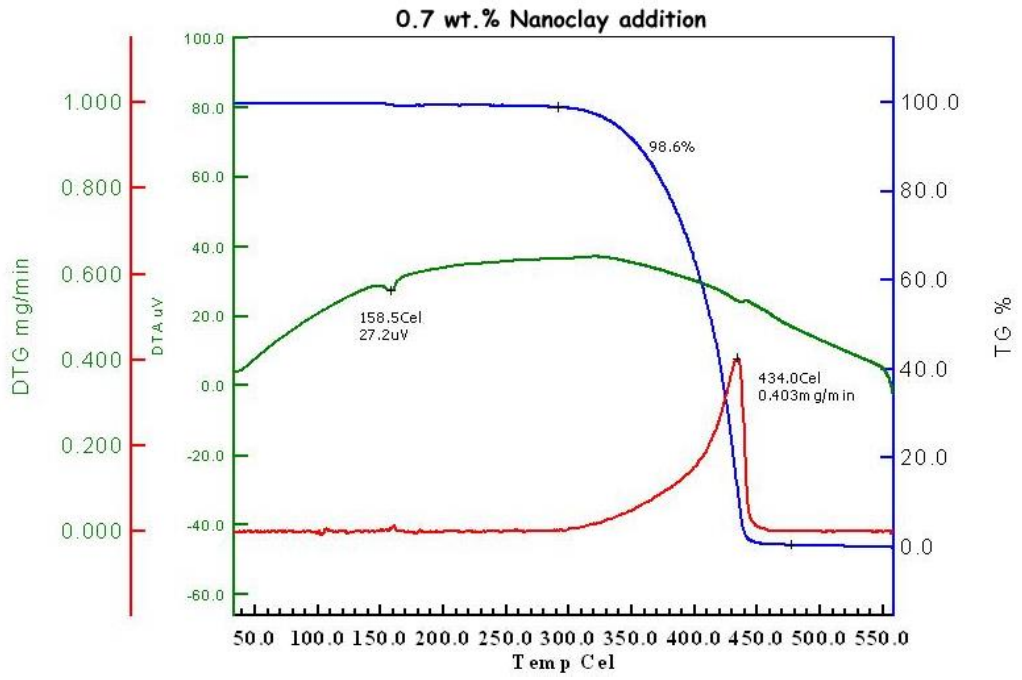


Figure 4.26 (b) Thermogravimetric curve for polypropylene / nanoclay 0.7 wt% composite filament

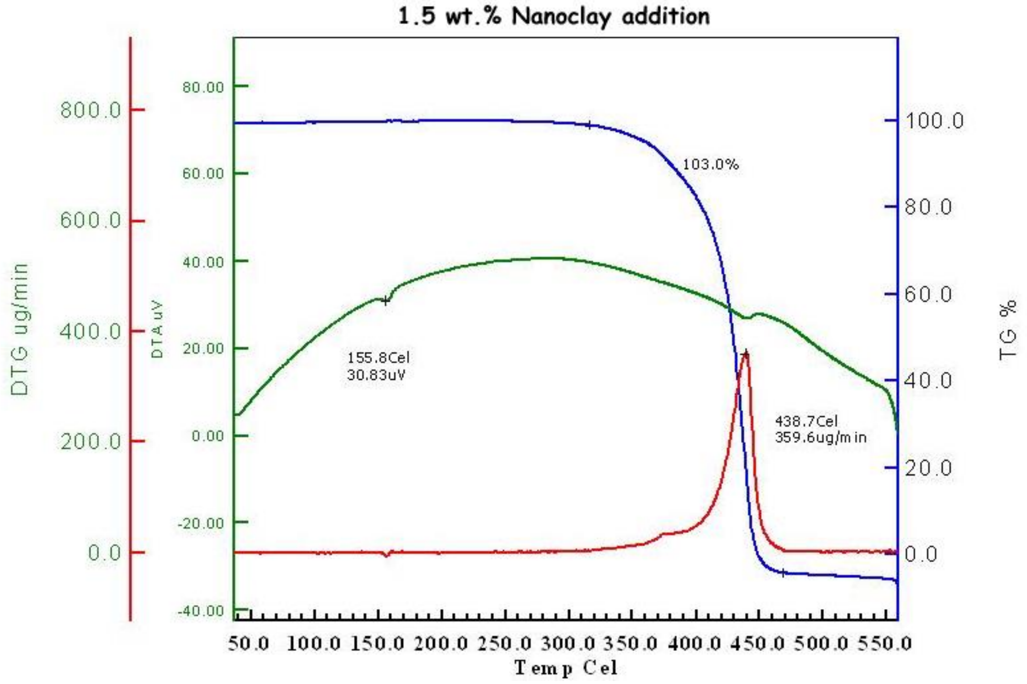


Figure 4.26 (c) Thermogravimetric curve for polypropylene / nanoclay 1.5 wt% composite filament

With the addition of the inorganic material i.e. nanoclay into the polymer matrix, it is observed from the Figure 4.26 (b) & (c) that the composite yarn with addition of 0.7 and 1.5 wt. % nanoclay becomes more thermally stable up to 300°C and 320°C respectively. It also shows that mass loss also reduced to 98.6% with 0.7 wt % nanoclay addition whereas it becomes 103% as more quantity of nano material is added to polymer matrix i.e. 1.5 wt. %. The DTA curve also shows high energy 434°C and 438.7°C used for degradation of nanocomposite yarn with 0.7 and 1.5 wt% nanoclay additions. This attributes to making of more thermal stable and heat resistance material with minor quantity of nanoclay addition in comparison to pure PP.

SECTION - III

In order to develop high performance inorganic-polymer composite nonwoven textile material for industrial application, nanoclay particles were incorporated as filler inside a polypropylene matrix. Structure of prepared nonwoven composite was observed under SEM, elementally analyzed by EDX and further analyzed by FT-IR spectra for their chemical compound. This composite nonwoven fabric was also evaluated for the change in their mechanical, water barrier, air permeability and thermal properties compared to the nonwoven fabric prepared without addition of nanoclay.

4.3 FORMATION OF POLYPROPYLENE / NANOCLAY COMPOSITE NON WOVEN FABRIC

Polypropylene / clay nanocomposite nonwoven fabric was prepared with addition of nanoclay particles in different proportions viz., 0.1, 0.4, 0.7, 1 & 1.6 into polymer matrix. The PP/clay nanocomposite material was prepared on lab model spun-bond nonwoven machine as discussed. The difficulties came across during the preparation are discussed here:

4.3.1 PROCESSING OBSERVATIONS

As evident from studies that viscosity of samples with the nano additives is higher than that of the control[117]. The main effect of these viscosity differences was on the processability, where the pressure in the spin pack increased with increase in viscosity. This may require the use of higher melt temperature for proper processing.

However, in this study, the melt temperatures were kept same. Processing was almost without any major problem up to 1% addition of nanoclay particles. Also, it was observed that processability of the melt was not very good for more than 1% addition of nanoclay particles.

With higher level (1.6% in this case) of clay, there was increase in back pressure and polymer flow problem in the die. To avoid any further problem, at this stage the metering pump rpm was increased to 5, which increased the through put value from 0.09 gms / hole / min to 0.11 gms / hole / min. For maintaining the GSM, minor increase in take-up speed was done. Since the run was only carried out for short duration, we did not observe any possible buildup on spinneret face. However there was drip formation after a while and good quality fabrics could not be collected especially with higher % of nanoclay samples.

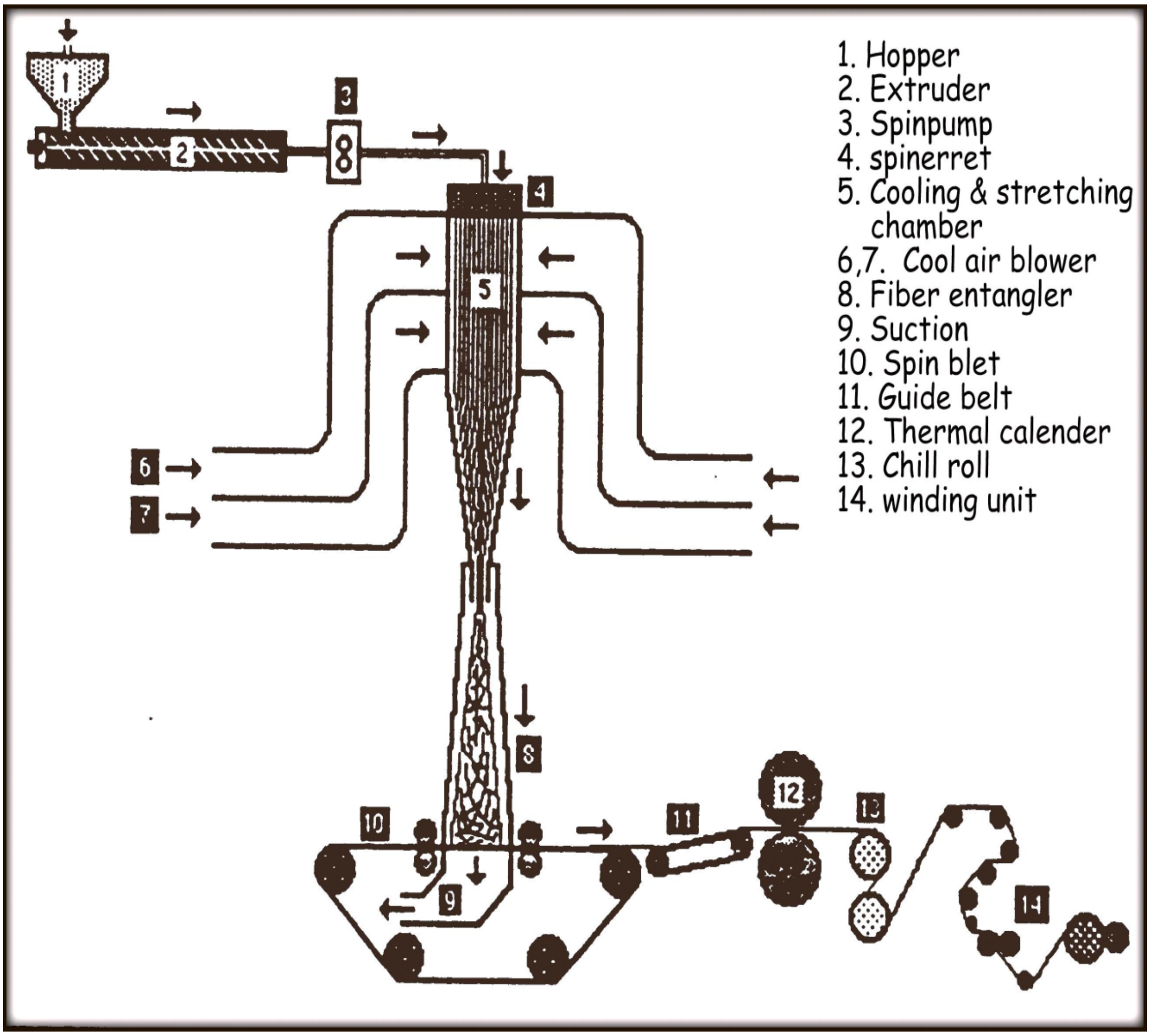


Figure 4.27 ***Schematic flow diagram of web formation spun bond nonwoven machine***

As seen from Figure 4.27, nonwoven composite fabric of average 160 gms exhibits good dispersion of nanoclay particles. It is observed that, for any further improvement in properties of material the distribution of the inorganic filler particles in the polymer matrix has to be as homogeneous as possible. For this the nanoclay particles in different proportions were thoroughly mixed with PP granules, these granules then where fed into the hopper of lab model spun bond nonwoven machine. Finally, with controlled process parameters, different samples were produced and tested.

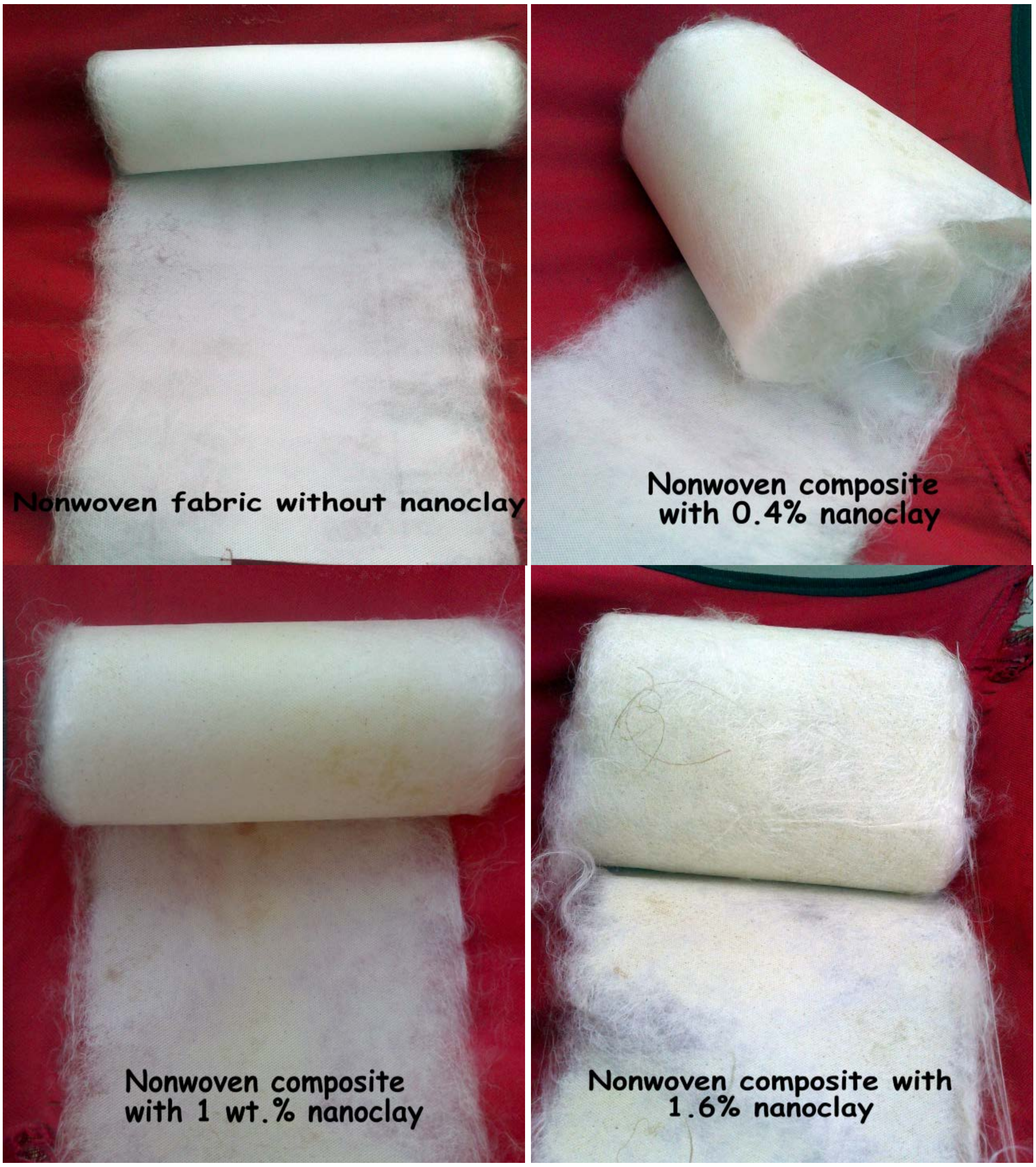


Figure 4.28 ***Photographs of pure polypropylene and polypropylene / nanoclay composite nonwoven fabric***

4.3.2 ANALYSIS OF POLYPROPYLENE / NANOCLAY COMPOSITE NONWOVEN FABRIC

The prepared samples were analyzed for its surface characteristics, mechanical properties, thermal and functional properties

4.3.2.1 Surface Analysis by SEM

The thermal bonding conditions were kept same for all spun bond nonwoven fabrics. From the SEM micrographs as in Figure 4.29 good bonding was observed for samples with and without nanoclay addition. From the comparison of SEM micrographs of bond points with additive and without additive, it is clearly evident that, presence of nanoclay up to 1% leads to stronger and uniform fabrics by improving the properties of fibers and the quality of bonding. However, careful examination of several bond points revealed difference in bond point and surface microstructure.

SEM micrographs indicate that the fibers with additive maintain better integrity during calendering. Increased clay loading had adverse effect on the surface topology. Going to higher levels of nanoclay does not show further improvement, may be due to difficulties in getting better dispersions and exfoliation of clay in the polymer. SEM micrograph of fiber surface with 1.6 wt % clay is shown in Figure 4.30. This is due to non-uniform dispersion, agglomeration of clay platelets, and protrusion of tactoids from surface. As mentioned before, there were processing difficulties as well, suggesting that in such processing schemes, nanoclay additives should be kept at a level of less than two percent. Increased percentage of clay loading also affects the bonding structure of the fabrics.

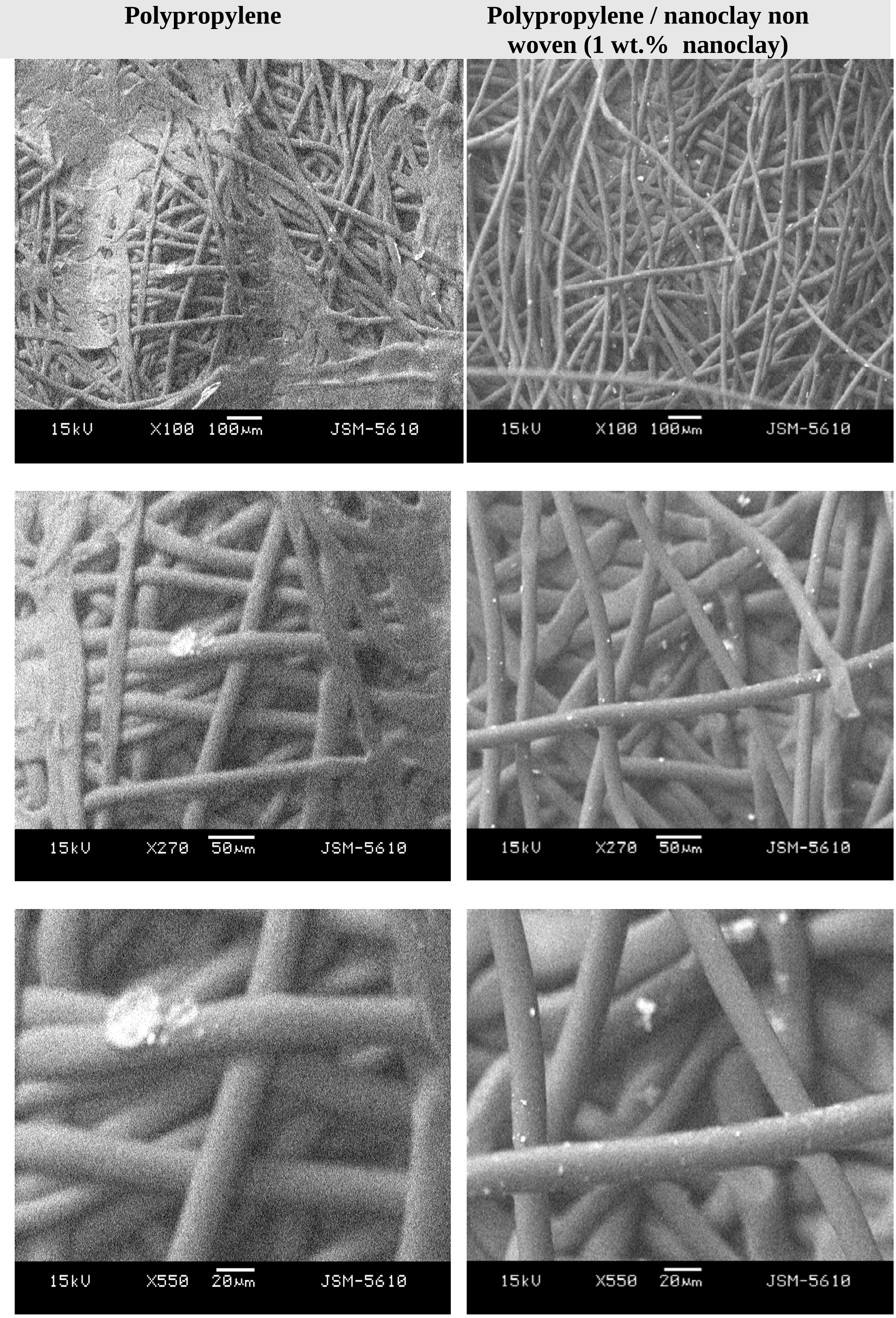
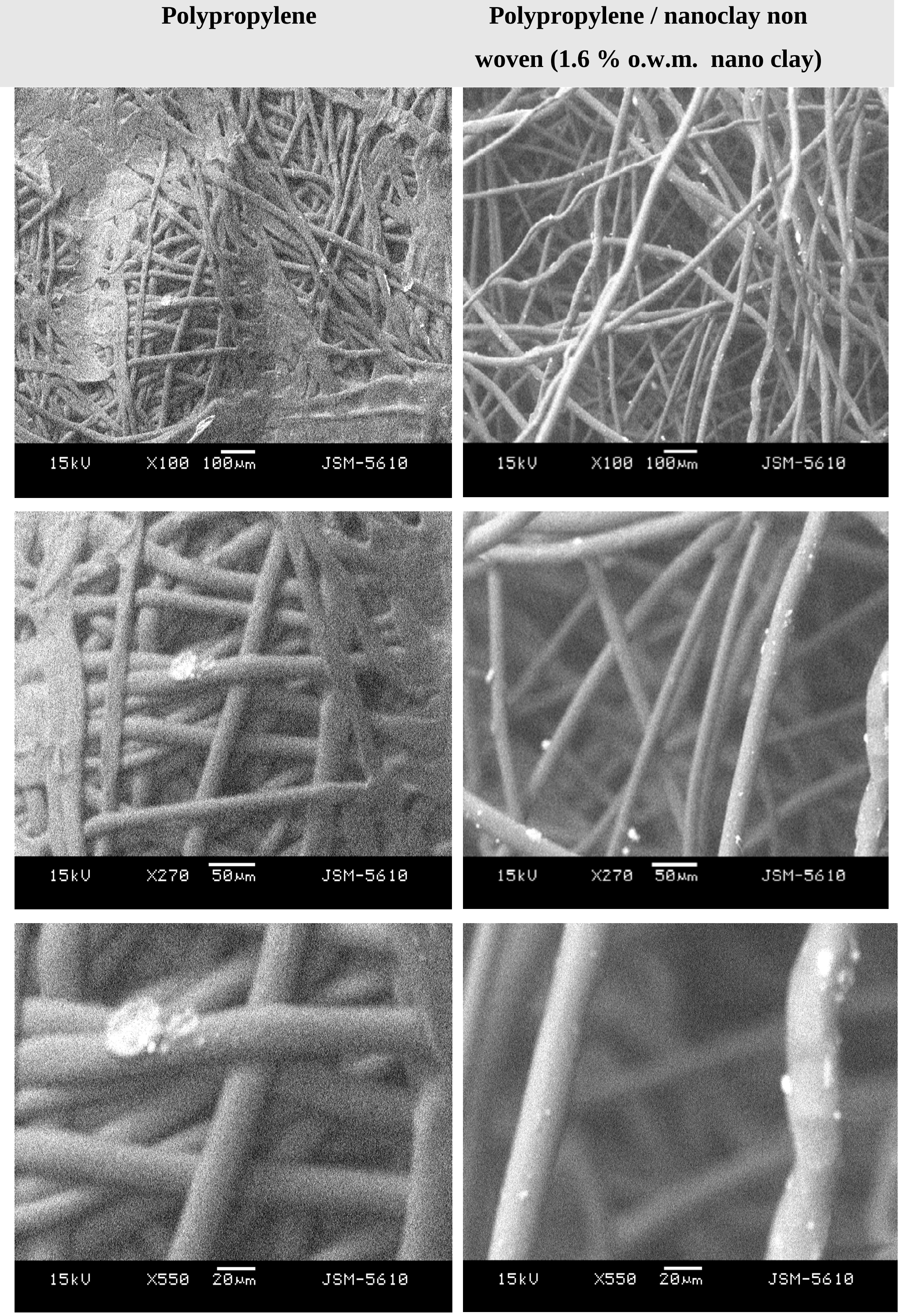


Figure 4.29 SEM images of pure polypropylene and composite non woven fabric with 1wt.% nanoclay particle



Polypropylene

Polypropylene / nanoclay non woven (1.6 % o.w.m. nano clay)

Figure 4.30 *SEM images of pure polypropylene and composite non woven fabric with 1.6 wt. % nanoclay particle*

4.3.2.2 Elemental analysis by EDX

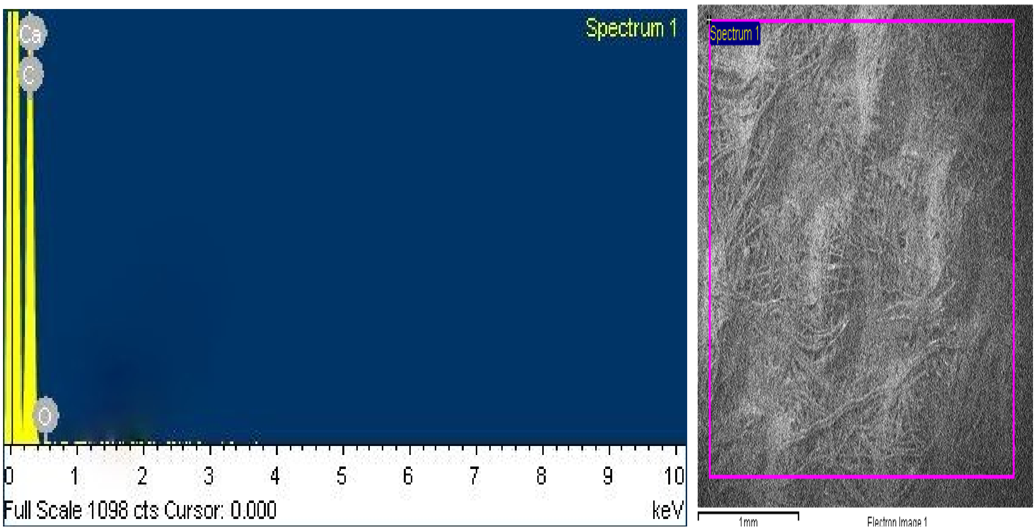


Figure 4.31(a) Elemental analysis of nonwoven fabric without nanoclay addition

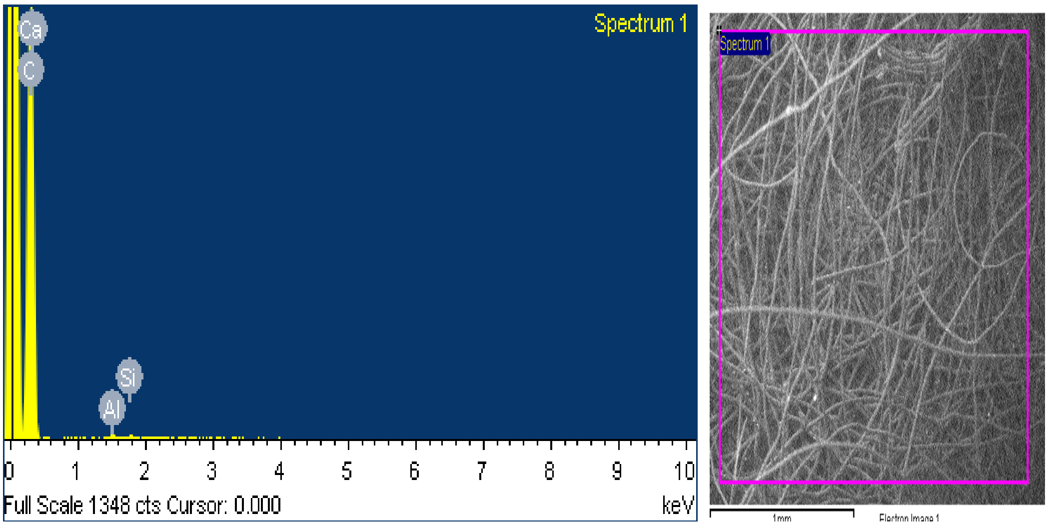


Figure 4.31(b) Elemental analysis of nonwoven fabric with 1% nanoclay addition

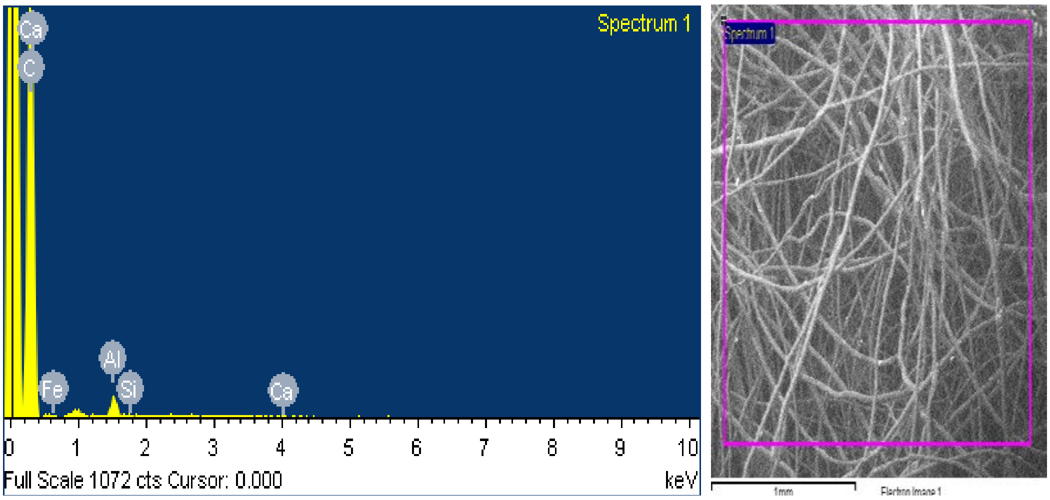


Figure 4.31(c) Elemental analysis of nonwoven fabric with 1.6 % nanoclay addition

To investigate the composition of interspherulite region, combination of EDX and SEM was used. EDX scan of sample without nanoclay and with 1wt. % and 1.6 wt. % nanoclay are shown in Figure 4.31 (a, b & c). EDX scans revealed that nanoclay particles are present in the produced composite fabric.

4.3.2.3 Analysis by XRD

As XRD is used to identify crystalline phases and orientation, it can be exploited to determine atomic arrangement and structural properties. As polypropylene, have generally polymorphic forms, for which α, β, γ and mesomorphic forms can be stated. Since phase transformations among them can be existed with increasing temperature or changing other parameters, these transformations can be determined using XRD[118-120].

WAXD scans of the pristine PP and nanocomposite PP spun bond nonwoven samples are included in Figure 4.32 WAXD scans do not show any peak corresponding to natural nanoclay (around 2θ of 6.07°;[121]), which is due to high level of extrusion involved during spun bond process and delamination of the clay platelet beyond 100 A°[122].

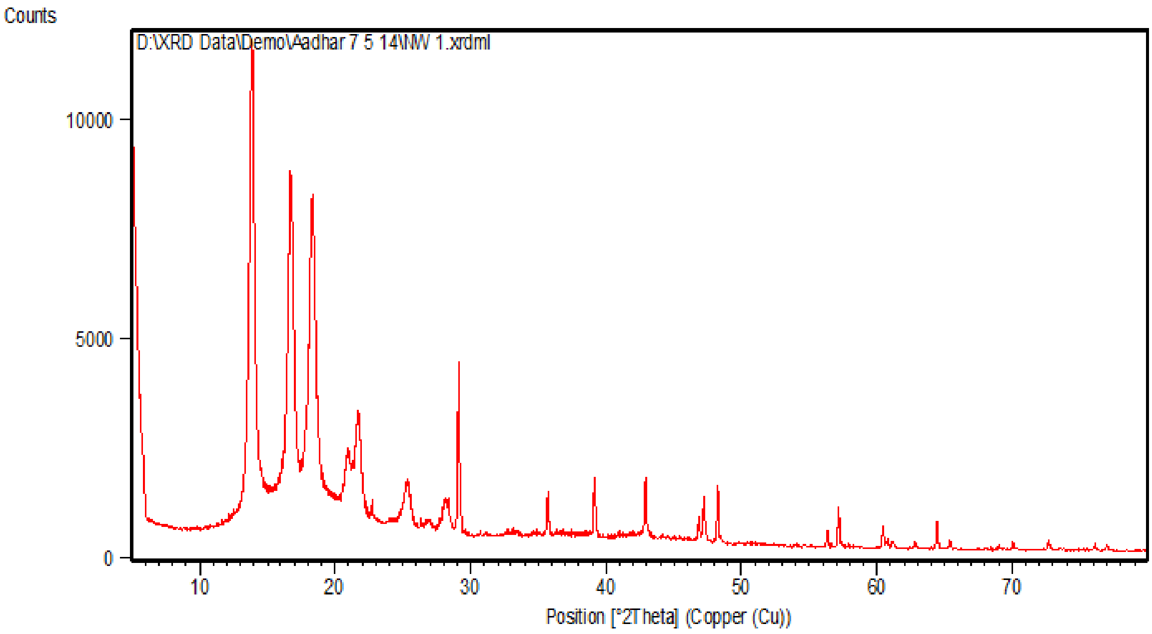


Figure 4.32 (a) XRD pattern for pristine PP nonwoven fabric

Figure 4.32(a) shows XRD pattern of pristine PP nonwoven fabric and Figure 4.32(b) represent XRD pattern of PP/ nanoclay composite nonwoven fabric indicate no specific peak for nanoclay. The absence of clay peaks suggest that silicate layers are completely exfoliated and well dispersed in polymer matrix or PP molecules have intercalated in the clay layers, thereby gallery spacing between the clay platelets might have expanded or loss of structural registry to an extent beyond the detection limit of X-ray in polymer matrix. This good dispersion may be attributed to the specific interaction originated from hydrogen bonding between the materials. Similar observations were also reported by Bradley F et al, 2005 and Cheol Ho Dan a et al, 2006[114,115].

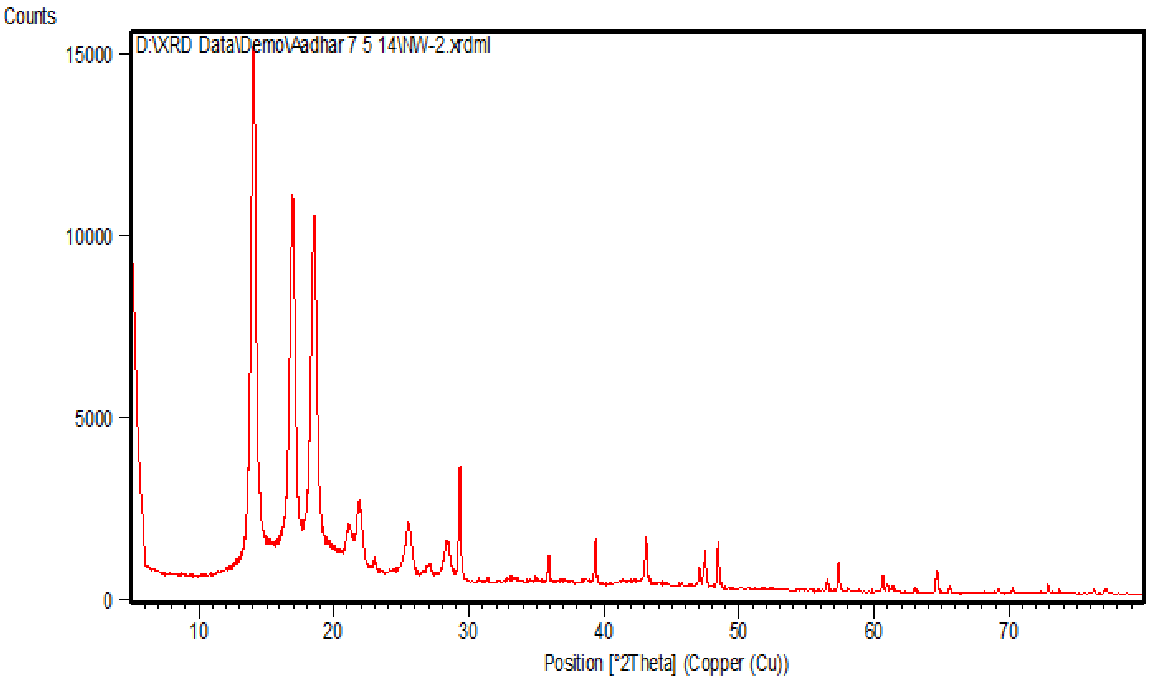


Figure 4.32 (b) XRD pattern for PP/ nanoclay composite nonwoven fabric

Table 4.10 Final d-spacing recorded for PP and PP / nanoclay nonwoven composite

Sr.	**Pristine PP**		**PP / nanoclay composite**	
	Position 2θ	d-spacing A	Position 2θ	d-spacing A
1	13.911	6.360	14.115	6.269
2	16.659	5.317	16.913	5.232
3	18.308	4.842	18.460	4.802

It has also been from the Table 4.10 that the corresponding unit cells for observed lines and typical XRD pattern of polypropylene, including α and β phases. Similar type of findings is also reported by other workers[121, 123-128].

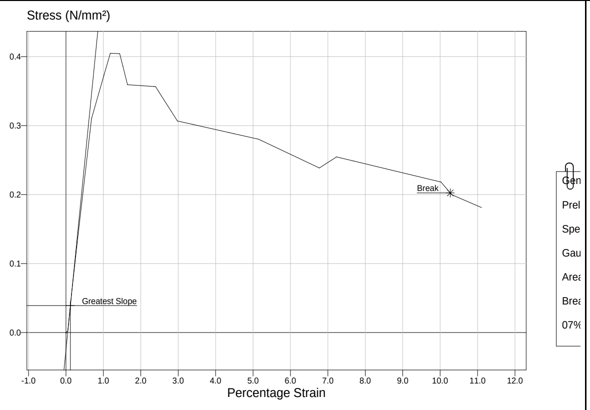
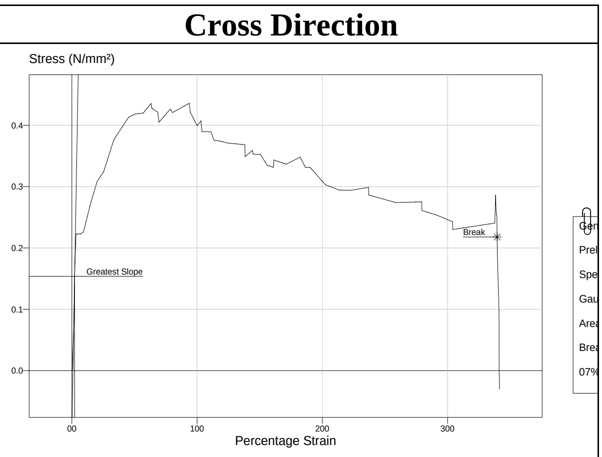
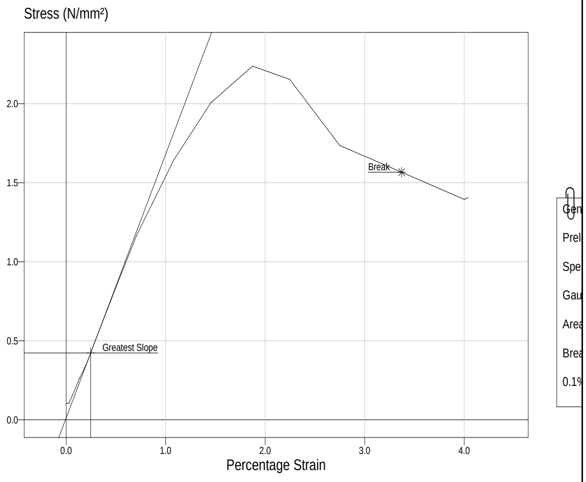
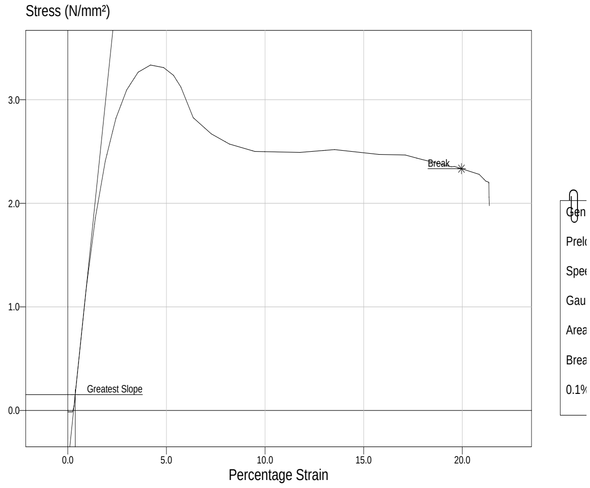
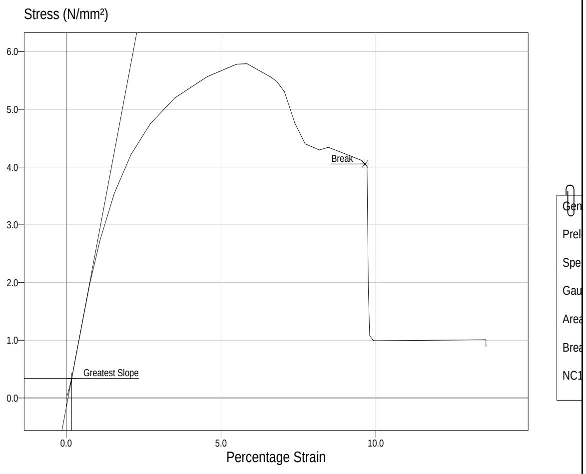
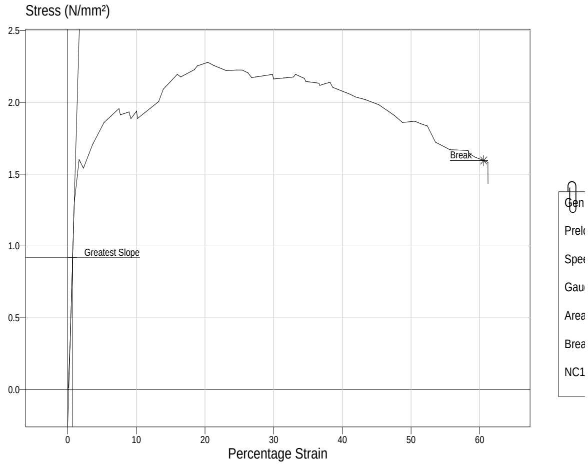
4.3.3 MECHANICAL ANALYSIS OF POLYPROPYLENE / NANOCLAY COMPOSITE NONWOVEN FABRIC

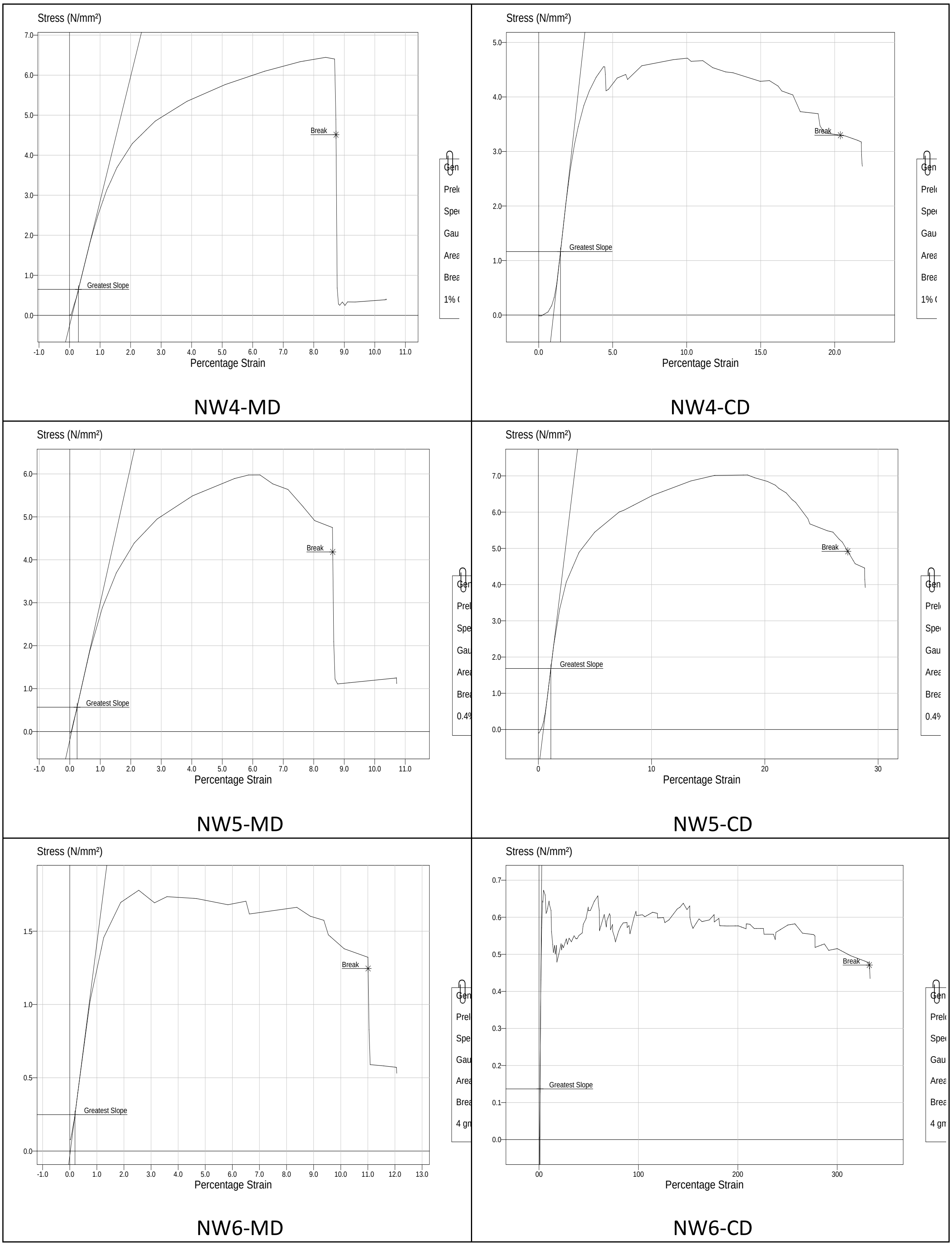
To get further information, the prepared samples were evaluated for their mechanical testing i.e. tensile strength, tearing strength, elongation, modulus, stiffness and bursting strength. All the tests were performed using standard test methods and under standard lab condition.

Table 4.11 Mechanical property of pure polypropylene and polypropylene / nanoclay composite nonwoven fabric (Machine Direction)

Sample code	**Sample composition**	**Specific strength (N/mm^2)**	**Percentage Strain (%)**	**Modulus (N/mm^2)**	**Work done (kgf.mm)**
NW1	Pure PP nonwoven	0.47	1.68	0.4	0.81
NW2	PP + 0.1 Nanoclay	2.44	2.25	0.9	15.62
NW3	PP + 0.4 Nanoclay	5.62	6.55	0.43	60.49
NW4	PP + 0.7 Nanoclay	5.73	6.27	0.68	112.00
NW5	PP + 1.0 Nanoclay	6.08	9.19	0.57	217.55
NW6	PP + 1.6 Nanoclay	1.49	2.82	0.24	8.93

An extremely important curve is produced when load on the specimen is plotted against the elongation. This curve describes the behaviour of the specimen from zero load and elongation up to breaking point. For detailed study, load elongation curve has to be converted to stress-strain curve which enables direct comparison to be made between different materials and structure[129]. Below given are the stress strain curves of the prepared and analyzed nonwoven samples for its machine and cross directions.

Machine Direction	Cross Direction
 NW1-MD	 NW1-CD
 NW2-MD	 NW2-CD
 NW3-MD	 NW3-CD



NW4-MD NW4-CD

NW5-MD NW5-CD

NW6-MD NW6-CD

Figure 4.33 ***Stress strain curve of nanoclay composite nonwoven fabric for machine and cross direction***

Table 4.12 Mechanical property of pure polypropylene and polypropylene / nanoclay composite non woven fabric (Cross Direction)

Sample code	**Sample**	**Specific strength (N/mm^2)**	**Percentage Strain (%)**	**Young modulus (N/mm^2)**	**Work done (Kgf.mm)**
NW1	Pure PP nonwoven	0.46	65.24	0.05	99.09
NW2	PP + 0.1 Nanoclay	3.05	11.07	1.32	23.44
NW3	PP + 0.4 Nanoclay	2.31	22.89	0.54	94.63
NW4	PP + 0.7 Nanoclay	4.10	7.99	0.36	98.22
NW5	PP + 1.0 Nanoclay	4.50	16.81	1.59	221.96
NW6	PP + 1.6 Nanoclay	0.72	24.78	0.31	5.33

4.3.3.1 Effect on Tensile Strength

The samples prepared were evaluated for its tensile strength in both machine and cross directions. The stress strain curves for the same are shown in Figure 4.34, which shows the breaking behavior and pattern of the samples. From the data given in Table 4.11 and Figure 4.34 for tensile strength in machine direction (M.D.), It can be seen that the tensile strength of the fabric increased with nanoclay addition up to 1wt.% but the strength drop drastically at 1.6 wt.% loading of nanoclay. As it is evident from XRD and EDX the nanoclay particles are embedded inside the structure of the polymer, thus the increase in the crystallinity value results in increase in the stress. With further increase in percentage of inorganic filler (nanoclay), the material become more brittle and the stress value reduced, apart from that it was observed that processing with higher percentage of nanoclay addition was easy, it generated back pressure and dropping were also observed, this may also have led to further decrease in the stress value of the nonwoven.

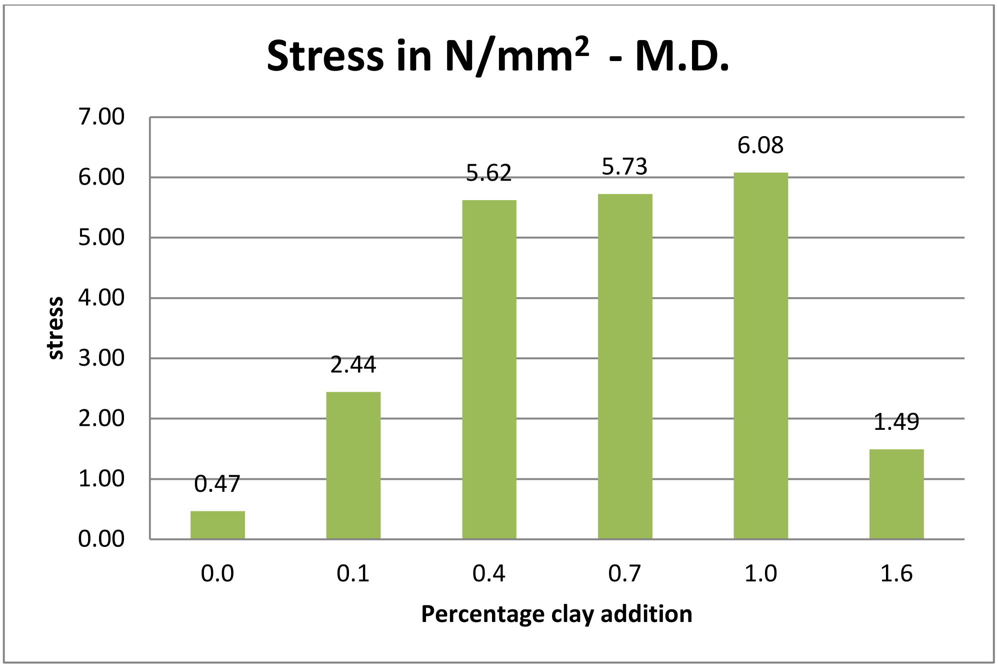


Figure 4.34 *Stress value of nanoclay composite nonwoven fabric for machine direction*

Similarly in case of tensile strength in cross direction, the bar chart for stress is shown in Figure 4.35. From the date given in Table 4.12 and Figure 4.35, almost similar trend in the stress value was found. However slight decrease in the stress value with 0.4% nanoclay addition is observed and further the trend remains the same. As this decrease is not significant, it may have happen due to improper handling of the material which could be neglected.

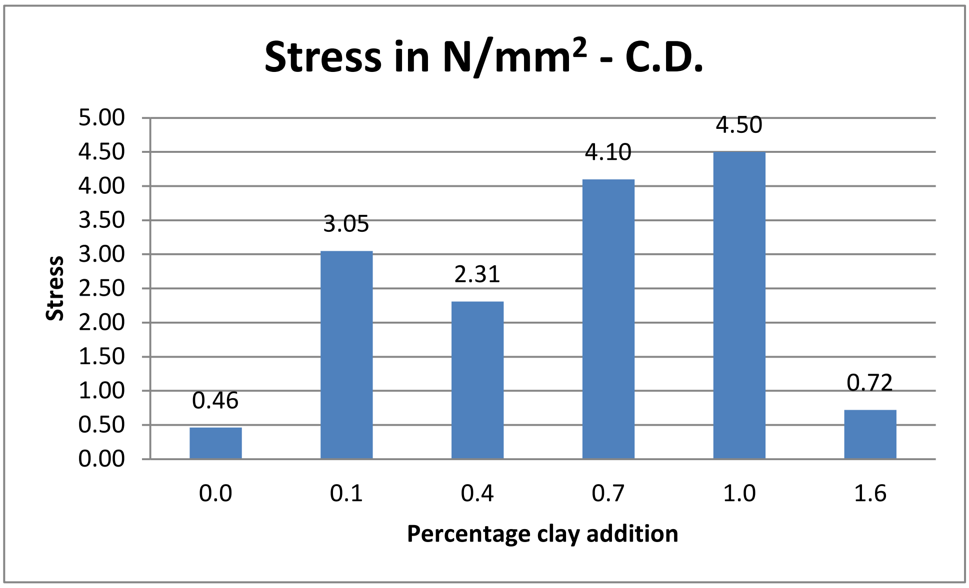


Figure 4.35 *Stress value of nanoclay composite nonwoven fabric for cross direction*

4.3.3.2 Effect on Elongation

Results obtained for elongation of nonwoven fabric as shown in Table 4.11 and 4.12, they are converted in % strain to have proper comparison. Normally, elongation is mainly concerned with the deformation of the amorphous regions in which the primary and secondary bonds are stretched and sheared[129]. From the results obtained and Figure 4.36 for machine direction, it is observed that with the incorporation of the nanoparticles, along with the stress value the percentage elongation also increases, which is an unique feature. Normally, the elongation of the material decreases with increase in stress value, but due to structural difference of material i.e. nonwoven it can be due to reduced bonding points. From SEM micrographs, it has also been observed that the overall structure of the spun bond nonwoven fabric becomes open with increase in nanoclay loading. This may have resulted in generation of uneven bond points which lead to the unpredictable behaviour of strain %. Though the incorporation of nanoclay material inside the structure of polymer has increased the stress value but reduced bond points has reduced inter friction, which results in slippage and increased strain percentage.

The results obtained for percentage strain in case of cross direction indicates no significant trend. It has been clearly seen from the Figures 4.37 that addition of 0.1 wt % nano clay increased the strain but addition of 0.4, 0.7, 1.0 and 1.6 wt % nanoclay resulted in mixed variation in strain values. These observations are not showing any trend or particular behaviour, as per theory[129] the strain % should reduce with the addition of filler material but we are not getting such results, may be due to the method of spun bond production.

4.3.3.3 Effect on Modulus

An important part of the stress-strain curve is the initial portion starting at zero stress and strain. Figure 4.38 presents the plot of tensile modulus against clay loading in intercalated PP nanocomposite for machine direction. The rate of improvement in the modulus is only up to 0.1 % clay loading, which is significant also as it is more than 100% but beyond that the modulus goes on decreasing. It may also be noted that though the modulus value reduces but it is still more than pure pp nonwoven fabric up to 1% clay loading. The value related to 0.4% clay loading may be neglected.

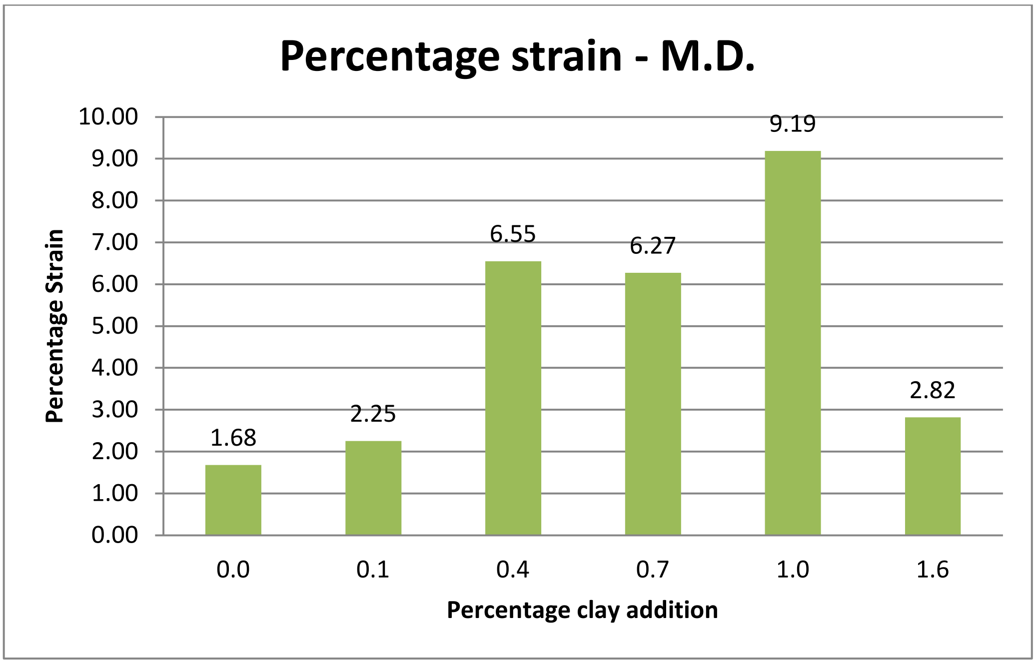


Figure 4.36 Effect of nanoclay loading on elongation of nonwoven fabric for machine direction

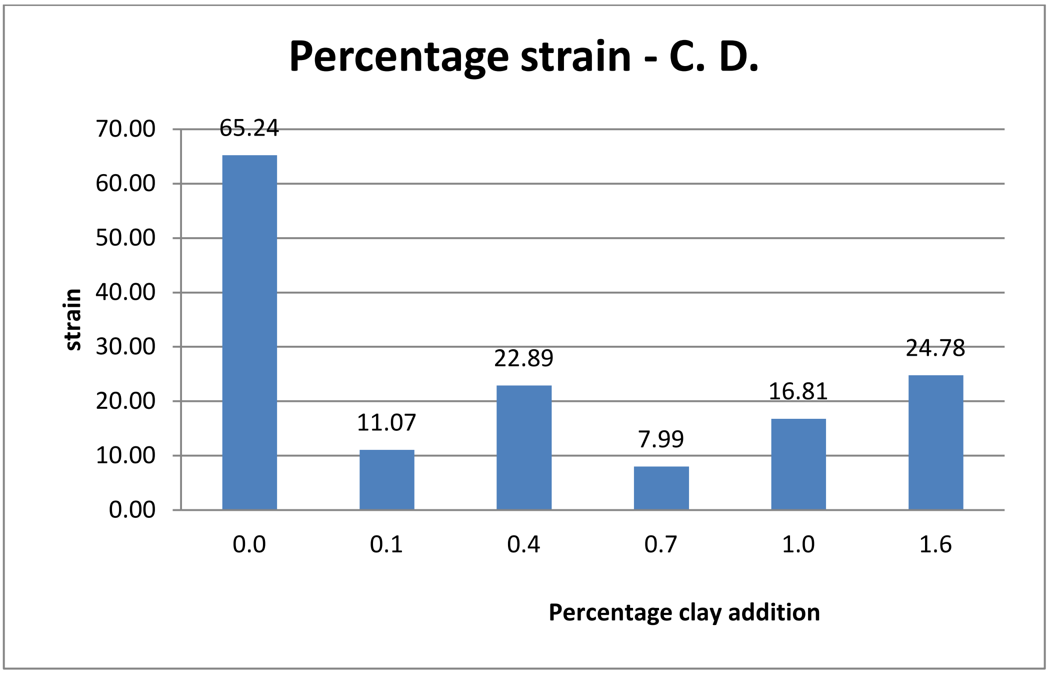


Figure 4.37 Effect of nanoclay loading on elongation of nonwoven fabric for cross direction

In the case of modulus obtained for cross direction, it is observed from the Figure 4.39 that, a mixed pattern of modulus is observed, which could not be concluded but neglecting the value obtained by 1% clay loading, we can say that the same trend is obtained as in case of machine direction, i.e. very high modulus for 0.1% clay loading and further goes on decreasing with increase in percentage of clay loading.

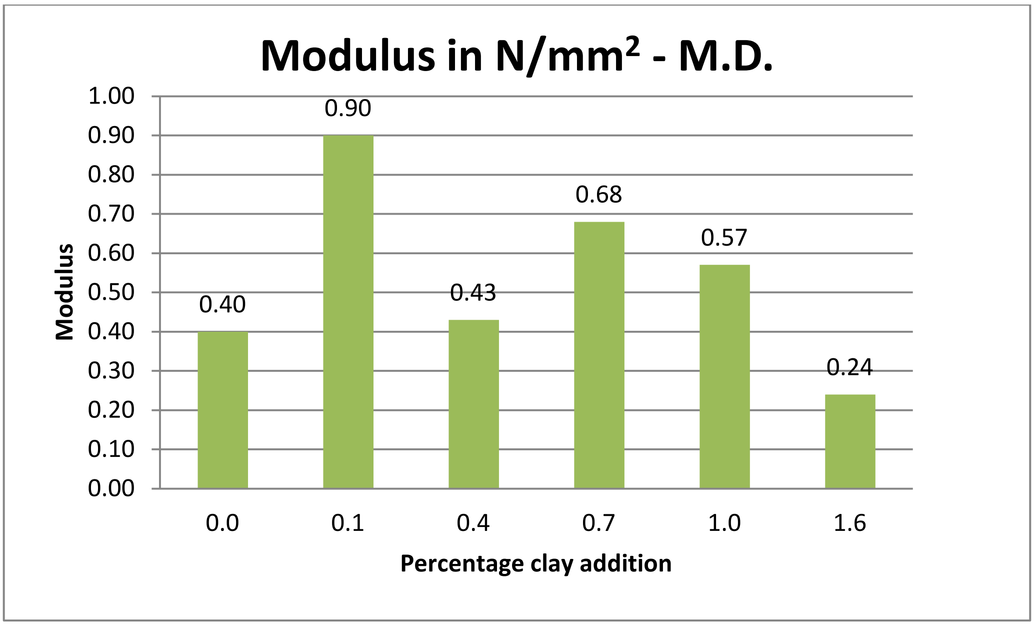


Figure 4.38 Effect of nanoclay loading on modulus of nonwoven fabric for machine direction

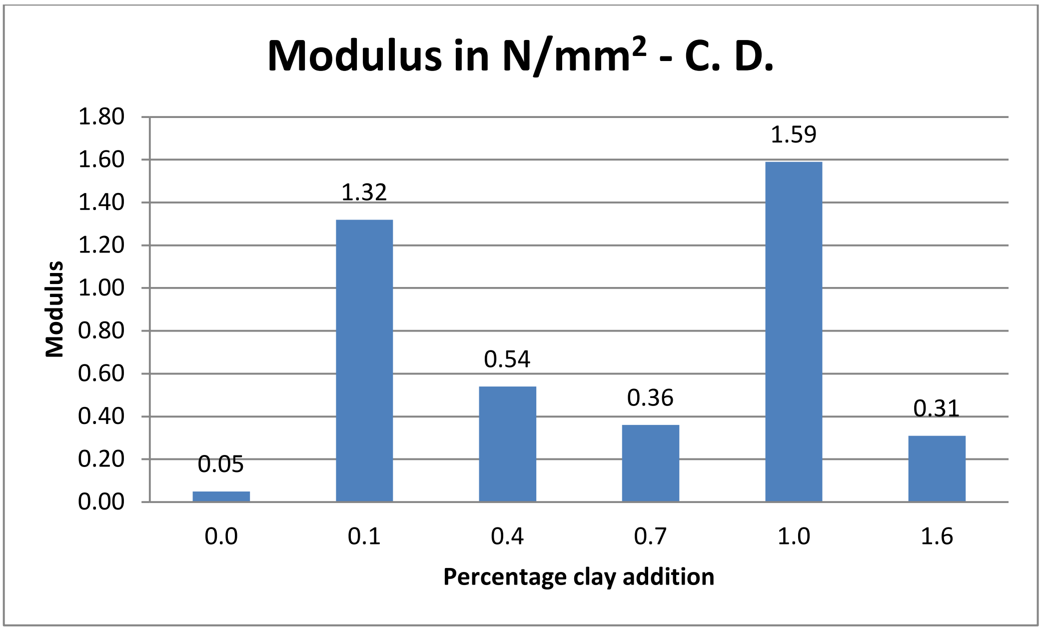


Figure 4.39 Effect of nanoclay loading on modulus of nonwoven fabric for cross direction

4.3.3.4 Effect on Work of Rupture

This is a measure of the ‘toughness’ of the material. It is energy or work required to break the specimen. The area under the stress strain curve represents the work done in stretching the specimen to breaking point. As seen in the Figure 4.40, the work done by the product goes on increasing up to 1% of clay loading and after that it reduced. It states that, as the nanoparticles have been incorporated inside the polymer matrix, which not only increases the stress value but also increases the toughness and life of the product.

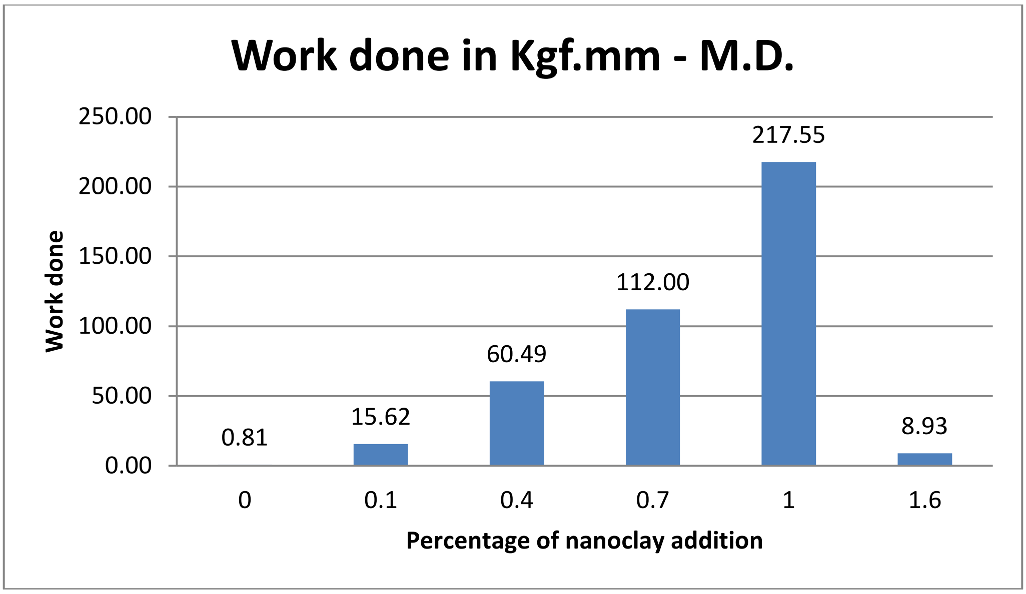


Figure 4.40 Effect of nanoclay loading on work done of nonwoven fabric for machine direction

Figure 4.41, which represent the work of the material when analyzed in cross direction, also exhibit the same trend as seen for machine direction, neglecting the value obtained by 0.1% clay loading.

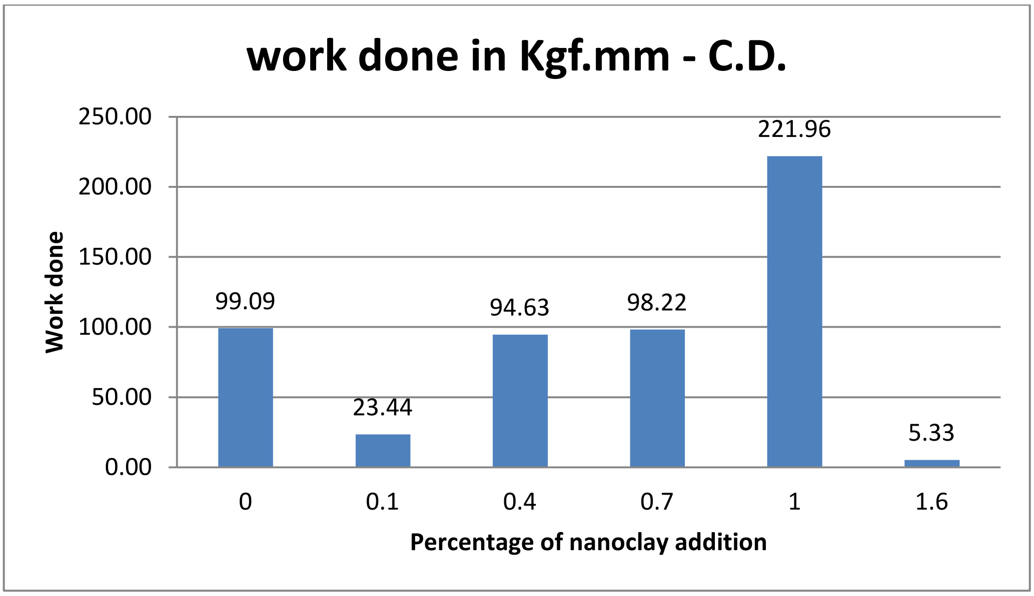


Figure 4.41 Effect of nanoclay loading on work done of nonwoven fabric for cross direction

4.3.3.5 *Effect on Tearing Strength*

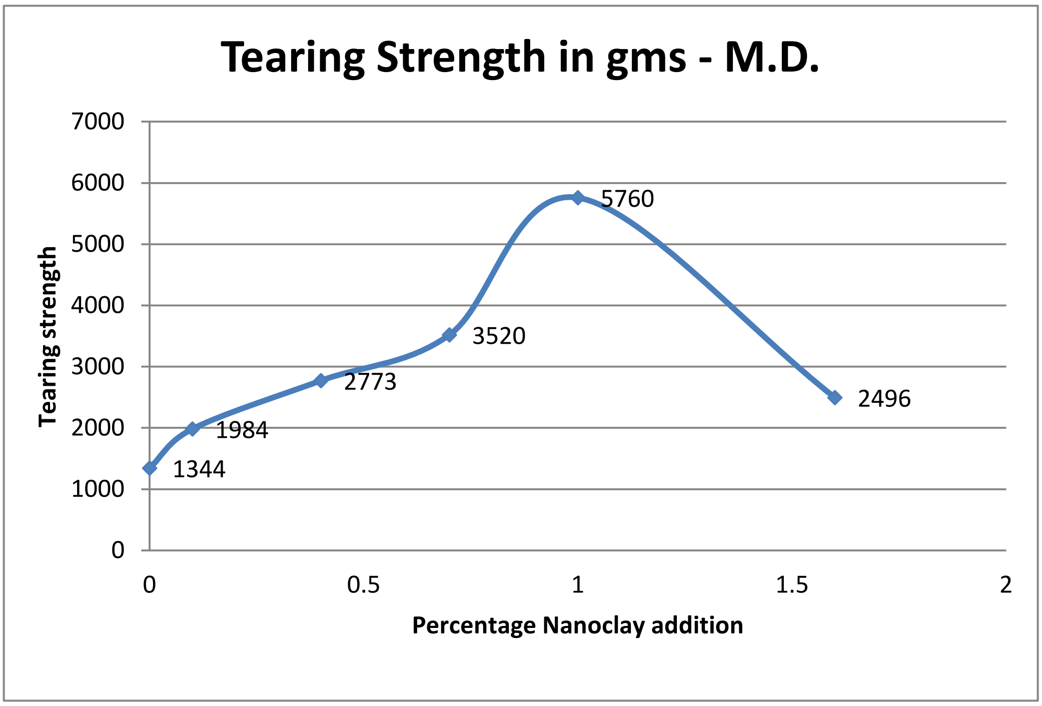


Figure 4.42 *Effect of nanoclay loading on tearing strength of nonwoven fabric for machine direction*

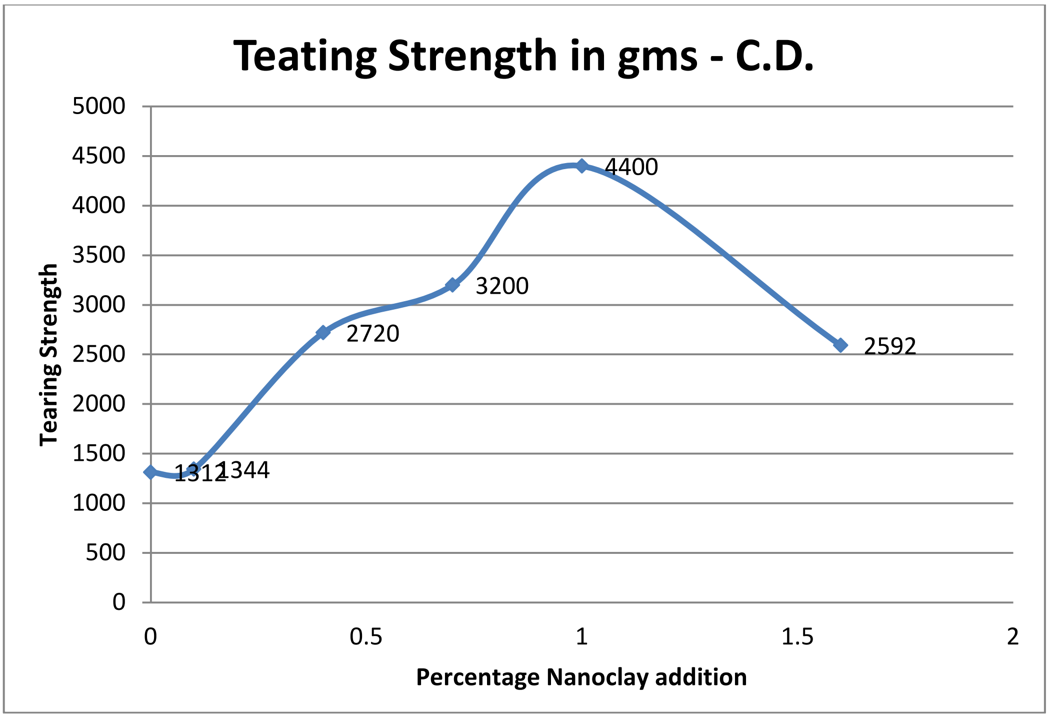


Figure 4.43 *Effect of nanoclay loading on tearing strength of nonwoven fabric for cross direction*

Table 4.13 Tearing strength of pure polypropylene and polypropylene / nanoclay composite non woven fabric in machine and cross direction

Sample code	**Composition**	**Tearing strength in gms – M.D.**	**Tearing strength in gms – C.D.**
NW1	Pure PP nonwoven	1344	1312
NW2	PP + 0.1 Nanoclay	1984	1344
NW3	PP + 0.4 Nanoclay	2773	2720
NW4	PP + 0.7 Nanoclay	3520	3200
NW5	PP + 1.0 Nanoclay	5760	4400
NW6	PP + 1.6 Nanoclay	2496	2592

Results for tearing strength of the fabric are shown in Table 4.13 for MD and CD. About 35 to 45 % increase in both directions (MD & CD) tear strength was observed for 1 wt % clay loading. Figure 4.13 indicate that beyond 1 wt % clay loading, tear strength shows decreasing trend.

In this process, the filaments / fibers are not positively stretched from spinneret. The fibers are arranged in a particular manner by means of air. The fibres are slightly oriented in cooling and stretching chamber and entangled and spread on conveyor belt. It may be possible that, due to less orientation of fibers and that to along with addition of nanoclay as filler particles.

4.3.3.6 Effect on Stiffness

According to Pierce, fabric stiffness is the key factor in the study of handle and drape. In our study “Shirley stiffness tester” has been used to find the stiffness of the nanocomposite nonwoven fabric in comparison with control fabric. As shown in Table 4.14, the values have been divided into Bending length, Flexural rigidity and Bending modulus for better analysis. Table 4.14 presents the data for machine direction whereas Table 4.15 for cross direction.

Table 4.14 Effect on bending length, flexural rigidity and bending modulus of pure polypropylene and polypropylene / nanoclay composite nonwoven fabric in machine direction

Sample code	**Sample – M.D.**	**Bending Length in cms**	**Flexural Rigidity in gms.cm**	**Bending Modulus in gms/cm^2**
NW1	Pure PP nonwoven fabric	13.05	4422.89	0.30
NW2	PP + 0.1 Nanoclay	13.75	5196.64	0.36
NW3	PP + 0.4 Nanoclay	14.15	5665.34	0.39
NW4	PP + 0.7 Nanoclay	12.5	3822.18	0.26
NW5	PP + 1.0 Nanoclay	11.5	2828.69	0.19
NW6	PP + 1.6 Nanoclay	9.25	1567.32	0.11

Table 4.15 Effect on bending length, flexural rigidity and bending modulus of pure polypropylene and polypropylene / nanoclay composite nonwoven fabric in cross direction

Sample code	**Sample – C. D.**	**Bending Length in cms**	**Flexural Rigidity in gms.cm**	**Bending Modulus in gms/cm^2**
NW1	Pure PP nonwoven fabric	13.6	5029.28	0.34
NW2	PP + 0.1 Nanoclay	12.75	4123.85	0.28
NW3	PP + 0.4 Nanoclay	12.25	3674.23	0.25
NW4	PP + 0.7 Nanoclay	15	6738.75	0.46
NW5	PP + 1.0 Nanoclay	14.25	5784.61	0.40
NW6	PP + 1.6 Nanoclay	11.15	2728.27	0.19

Bending length is the length of the fabric that will bend under its own weight to a definite extent. Bending length and Flexural rigidity are the measure of stiffness that determines draping quality. From the Figure 4.44 it is seen that bending length and flexural rigidity almost remains unchanged with the addition of nanoclay, slight increase in the bending length and flexural rigidity is observed up to 0.4 wt. % of nanoclay addition which is not significant but with further addition of clay the material becomes limpy. This can be due to less bonding points as seen from SEM at higher percentage of clay addition. In the case of Figure 4.45 which represents data for cross direction, the change in the bending length and flexural rigidity is not significant.

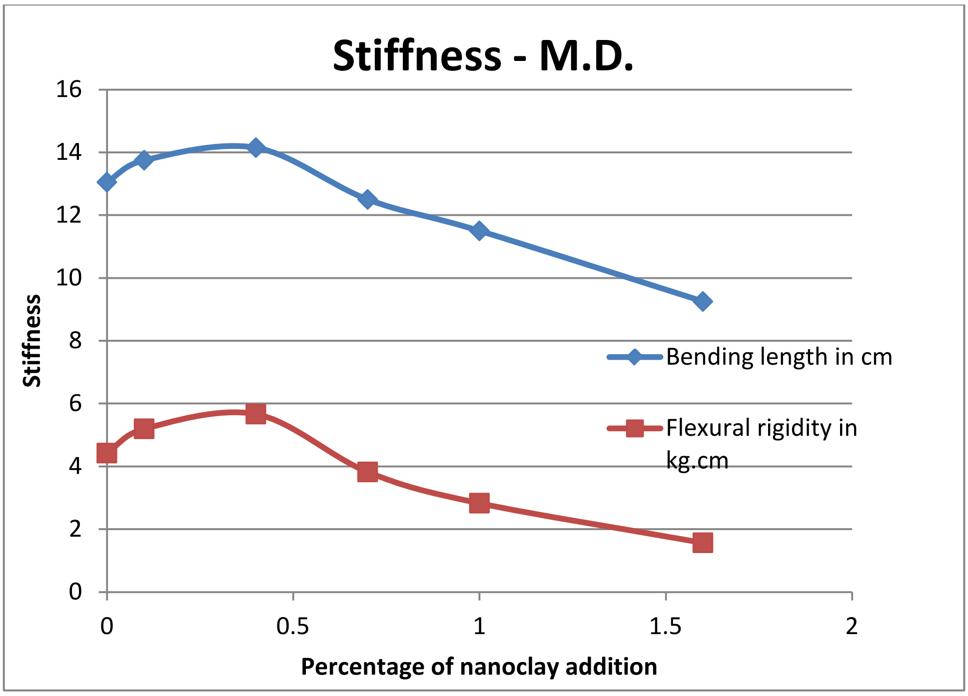


Figure 4.44 *Effect of nanoclay loading on stiffness of nonwoven fabric for machine direction*

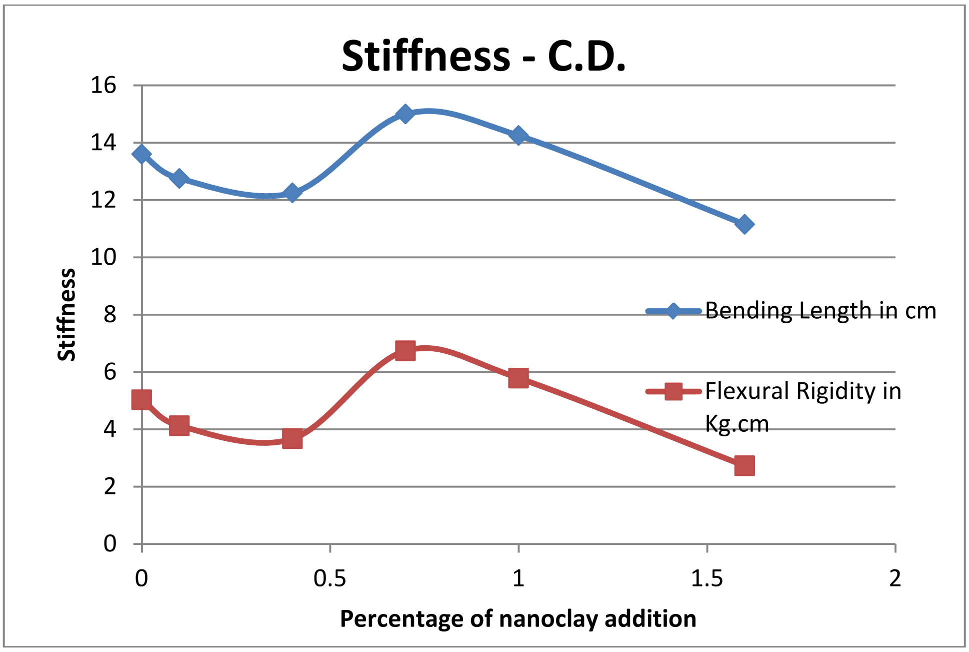


Figure 4.45 *Effect of nanoclay loading on elongation of nonwoven fabric for machine and cross direction*

Bending modulus is a value independent of dimension of strip tested and is regarded as 'intrinsic stiffness'. It can be seen from the Figure 4.46, which represents the data of bending modulus for machine direction, it is observed that bending modulus increases with the nanoclay addition in the polymer matrix. This trend is up to 0.4 wt% nanoclay addition but at the same time the change is not significant. However there is minor decrease in the bending modulus beyond 0.4 wt% nanoclay addition. This may be due to the small size of the nano particles which do not interfere in the polymer matrix or web[118]. At the same time, the inorganic matter inside and outside the polymer matrix, did not allow to increase the bonding points.

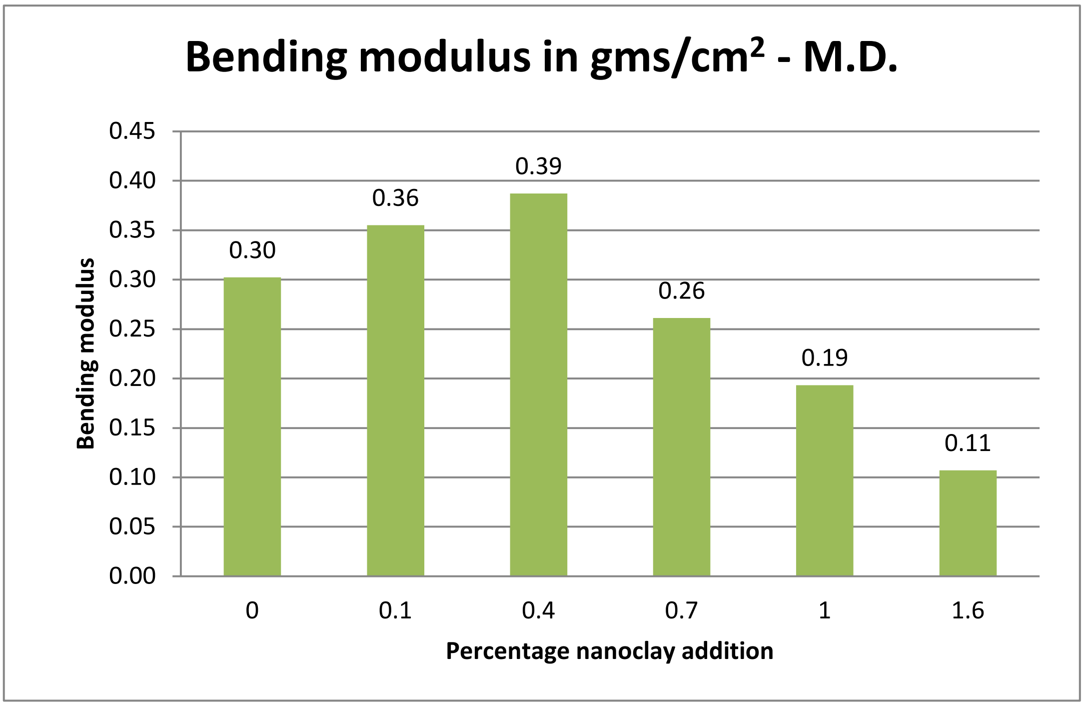


Figure 4.46 ***Effect of nanoclay loading on bending modulus of nonwoven fabric for machine direction***

Figure 4.47 presents bending modulus for cross direction of the prepared nonwoven fabric, which gives no significant trend of the modulus / stiffness of the material. However it can be seen that the bending modulus of the material decreases.

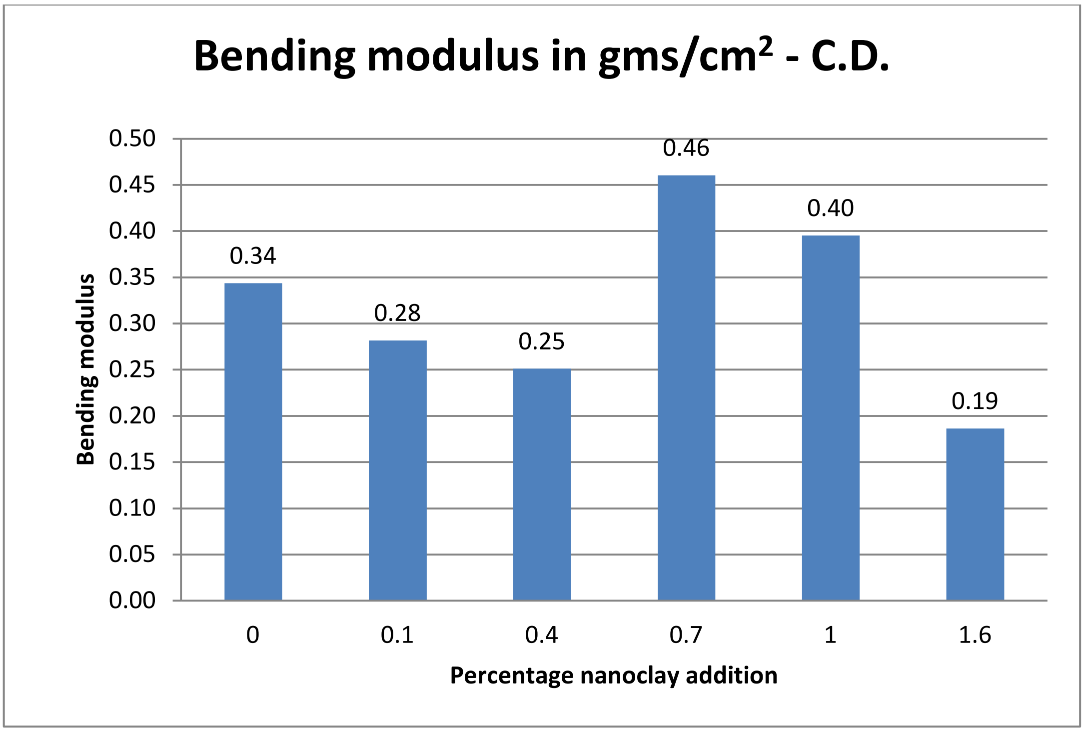


Figure 4.47 Effect of nanoclay loading on bending modulus of nonwoven fabric for cross direction

4.3.3.7 Effect on Air permeability

It has been observed from the SEM analysis that with the addition of nanoclay particles, the structure becomes more open. The addition of inorganic compound as filler does not allow to bond.

Table 4.16 Air permeability of pure polypropylene and polypropylene / nanoclay composite nonwoven fabric

Sample code	**Sample**	**Air permeability ($m^3/m^2/min$) at 100 Pa**
NW1	Pure PP nonwoven fabric	280
NW2	PP + 0.1 wt.% Nanoclay	306.67
NW3	PP + 0.4 wt.% Nanoclay	313.33
NW4	PP + 0.7 wt.% Nanoclay	348.13
NW5	PP + 1.0 wt.% Nanoclay	393.33
NW6	PP + 1.6 wt.% Nanoclay	393.33

The bonding is done at around 145°C with the help of calendar rollers, nanoclay particles present in the material does not allow the material to bond properly which results in an open structure of nonwoven fabric. This is evident from the results obtained for air permeability and bursting strength.

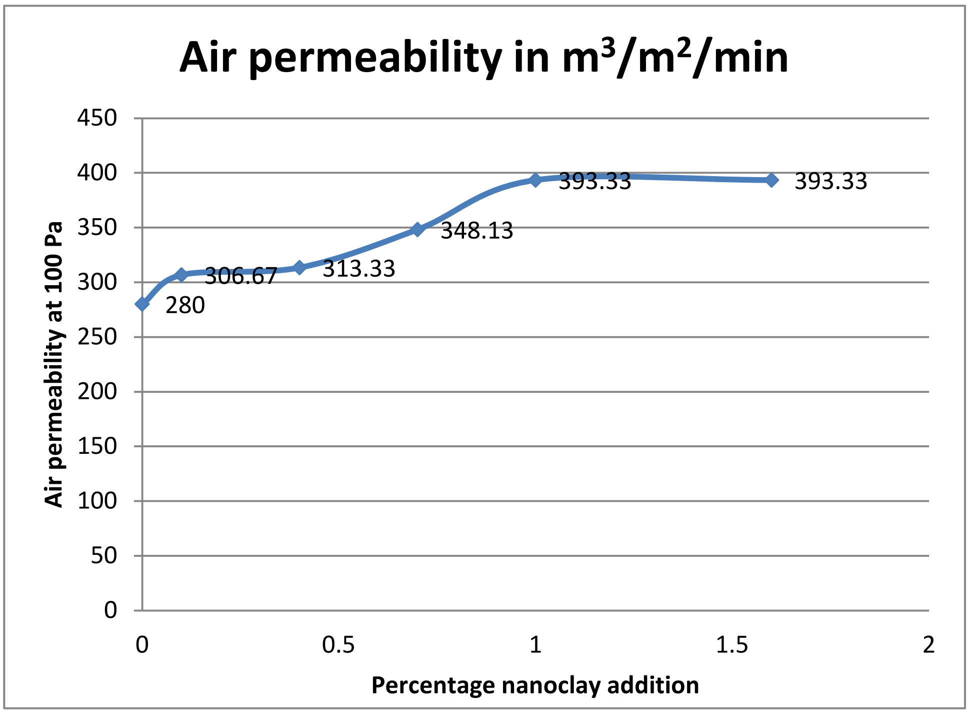


Figure 4.48 ***Effect of nanoclay loading on air permeability of nonwoven fabric***

From the Table 4.16 it can be seen that air permeability of the fabric increases with increase in the addition of nanoclay particles. As the quantity of filler material the structure becomes more and more open, which results in increase of air permeability. It was also observed from Figure 4.48 that the percentage increase in air permeability is only up to certain level i.e.1 wt. % nanoclay incorporation, further addition of nanoclay particles, does not change the air permeability value.

4.3.3.8 Effect on Bursting Strength

The bursting strength of the composite material also shows the same trend. As shown in Table 4.17, it was observed that the bursting strength decreases with increase in nanoclay particles. This can be attributed to the open structure of the material. As seen from the Figure 4.49 that, the decrease in bursting strength is not following any trend, this decrease in strength pattern is very irregular but overall there is decrease in the bursting strength value with increase in nanoclay particles addition.

Table 4.17 Bursting strength of pure polypropylene and polypropylene / nanoclay composite nonwoven fabric

Sample code	Sample	Bursting strength (Kg/cm^2)
NW1	Pure PP non woven fabric	7.56
NW2	PP + 0.1 wt.% Nanoclay	6.35
NW3	PP + 0.4 wt.% Nanoclay	5.55
NW4	PP + 0.7 wt.% Nanoclay	4.19
NW5	PP + 1.0 wt.% Nanoclay	5.81
NW6	PP + 1.6 wt.% Nanoclay	3.75

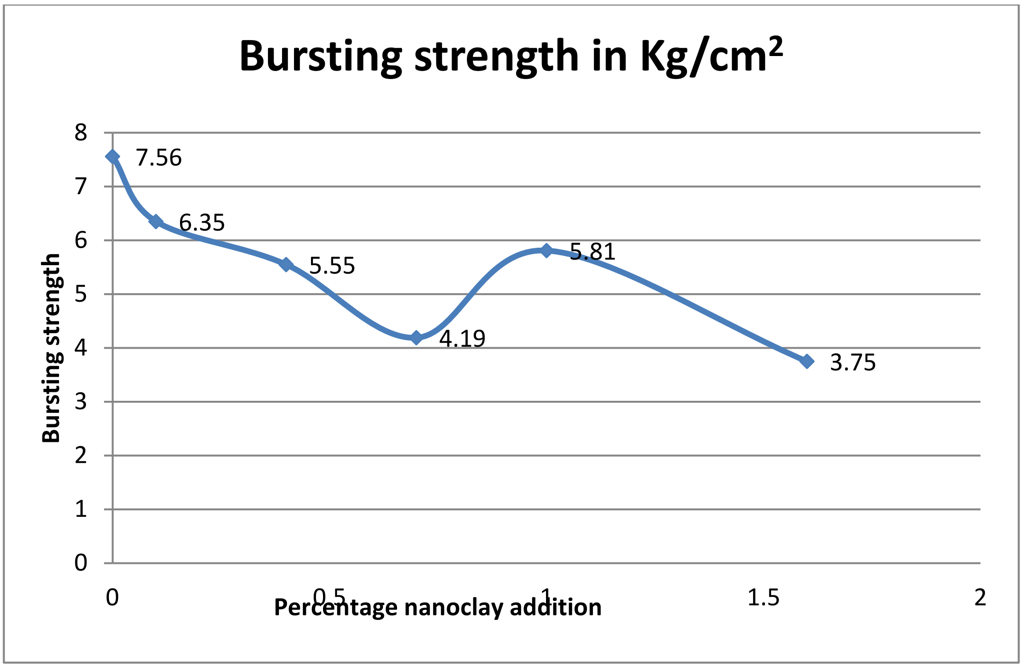


Figure 4.49 Effect of nanoclay loading on bursting strength of nonwoven fabric

4.3.4 THERMAL ANALYSIS OF POLYPROPYLENE / NANOCLAY COMPOSITE NONWOVEN FABRIC

Results of nonwoven thermal behaviour of pure PP and PP nonwoven with addition of nanoclay are shown in Table 4.18 and Figure 4.50. Figure 4.50(a) shows the differential scanning calorimetry (DSC) curve of pure polypropylene nonwoven fabric. Here the pure polypropylene nonwoven sample was heated at 10°C/min rate up to 300°C, in which it shows the T° peak temperature of the polypropylene nonwoven fabric as 163.64°C and the total heat required to melt i.e. enthalpy (ΔH) is 350.52 mJ.

Table 4.18 Thermal analysis (DSC) of pure and composite nonwoven fabric

Sample code	Sample	On Set Temperature °C	T° Peak °C	ΔH^0 mJ (Enthalpy)	Tg : Inflection point in °C
NW1	Pure PP nonwoven fabric	157.64	163.64	350.521	38.61
NW5	PP + 1 wt. % Nanoclay	158.52	162.81	287.651	34.92
NW6	PP + 1.6 wt. % Nanoclay	156.50	163.67	390.274	34.94

Figure 4.50 (b & c) shows the DSC curves of nanocomposite nonwoven fabric of polypropylene and clay nanoparticles at 1.0% and 1.6%. The T° peak temperature and enthalpy of both the composite fabric are given in Table 4.18. The T° peak temperature of nanoclay polypropylene composite non woven is 162.81°C and 163.67 respectively for 1.0% and 1.6% nanoclay loaded PP composite nonwoven fabric. Data shows there is no significant effect on melting temperature of all the nanocomposite fabric due to addition of clay nanoparticles.

From the results the ΔH value initially decrease with 1 wt. % addition of nanoclay but it is further increased with the increase in 1.6 wt. % of nanoclay loading. There is no significant change in T° peak value as well as onset temperature of the samples; however the Tg inflection point was found decreased with the addition of nanoclay compared to the web produced without the addition of nano filler. This may be due to the segregation of clay platelets at the spherulite boundary, similar results was also reported by Maiti et al. in case of their studies on polypropylene/clay hybrids[130].

The Tg inflection point as well as the ΔH value was found lower for nonwoven with nanoclay addition, this may be due the hindrance of nanoclay particles to the intermolecular structure of PP because of uniform dispersion.

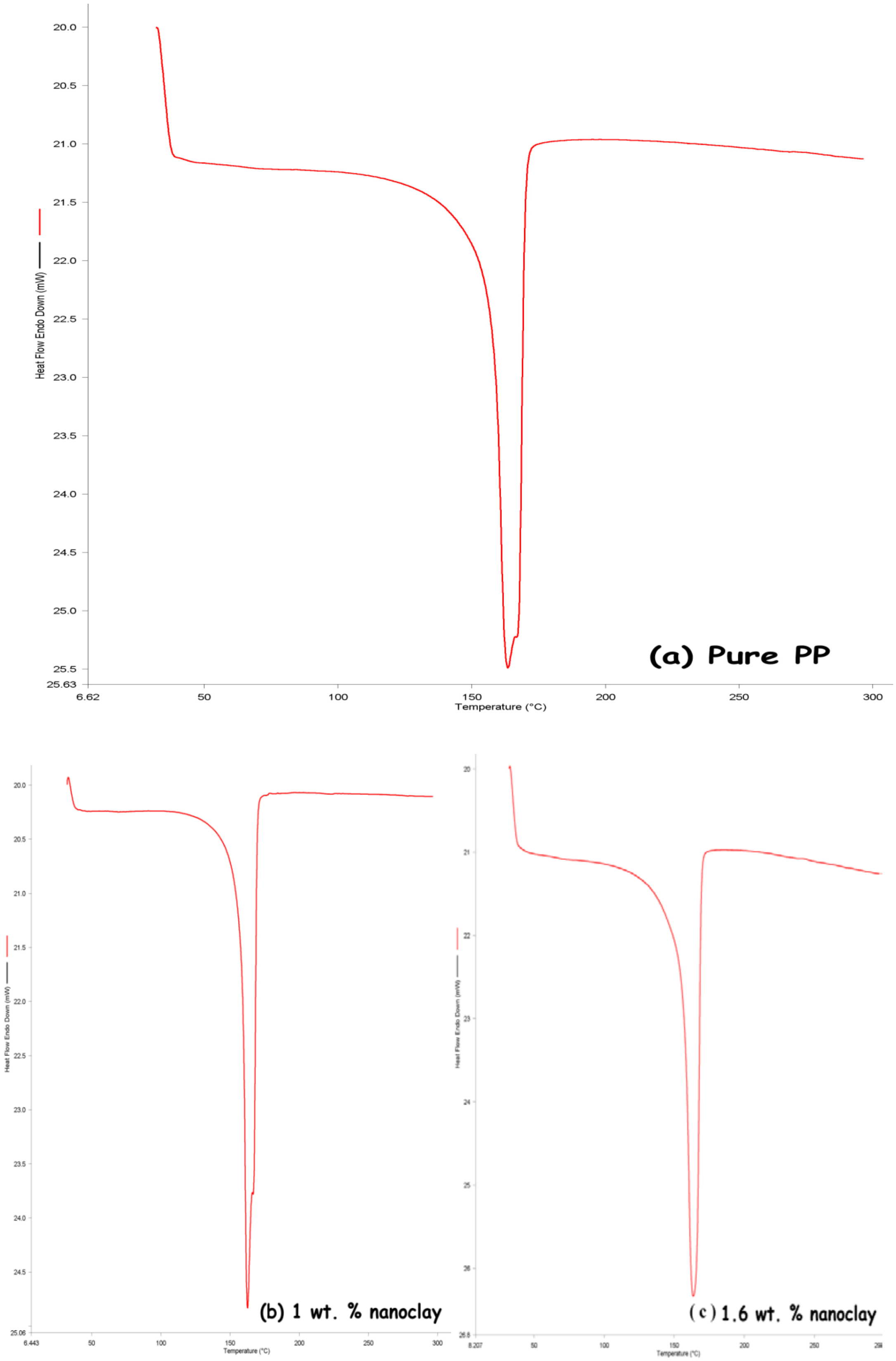


Figure 4.50 ***DSC curve of (a) pure polypropylene, (b) Nonwoven composite fabric with 1 wt% and (c) Nonwoven composite fabric with 1.6 wt. % nanoclay***

4.3.5 EFFECT ON MOISTURE BEHAVIOUR

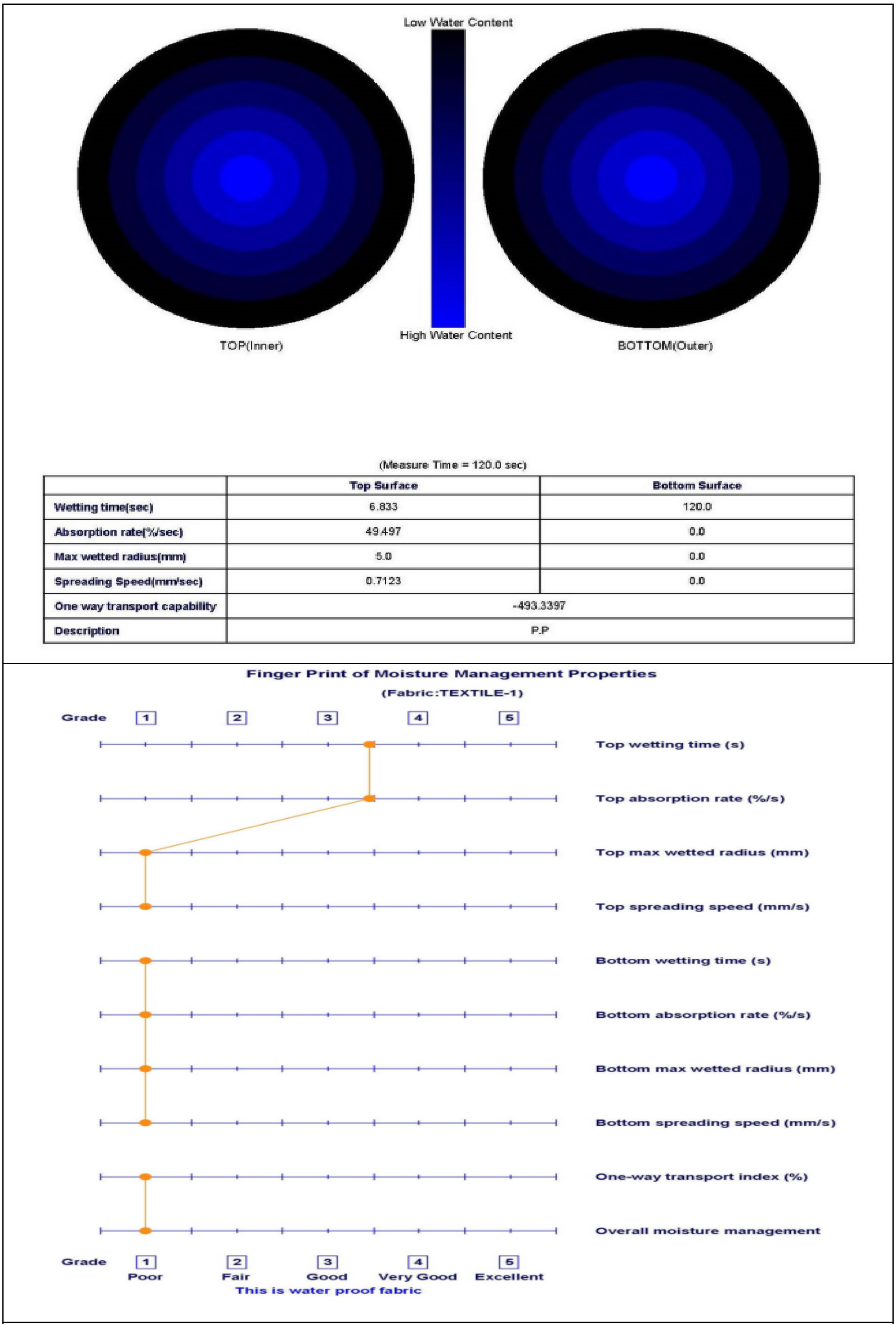
Table 4.19 Moisture behaviour analysis of pure and composite nonwoven fabric

Sample code	**Wetting time (sec)**	**Absorption rate (% / sec)**	**Spreading speed (mm/sec)**	**One way transport capability**	**Overall rating**
NW1	6.83	49.49	0.71	-493.33	WF
NW2	9.92	329.03	0.49	316.60	WP
NW3	10.10	416.28	0.48	443.68	WP
NW4	13.10	417.24	0.37	471.06	WP
NW5	11.04	410.49	0.44	480.91	WP
NW6	11.04	425.69	0.44	479.05	WP

Note : WF = Water proof fabric; WP = Water penetrating fabric

The prepared nonwoven nanoclay composite fabric was tested for its moisture behaviour on moisture management tester from SDL. It is evident from the results as shown in Table 4.19 and Figure 4.51 that one way moisture transport capability of the control fabric (NW1) i.e. without addition of nanoclay particles is negative (-493.33) and percentage absorption rate is also 49.49% per sec, which means that the fabric is not supporting the flow of water and it comes under the category of water proof fabric.

Addition of nanoclay particles even in small proportion makes drastic changes in the moisture behaviour of the fabric. Nanoclay in different proportions was added viz., 0.1%, 0.4%, 0.7%, 1% and 1.6% on the weight of PP granules. It has been observed that moisture behaviour of the fabric becomes better and one way moisture transport capability of the fabric improves, the values become positive viz; 316.60, 443.68, 471.06, 480.91 and 479.05 respectively. Along with it the absorption rate and wetting time is also increased as we increase the percentage nanoclay addition. The composite fabric thus produced supports the flow of water and it comes under water penetrating fabric category. This can be attributed to, as the nanoclay particles are incorporated inside the polymer structure; it makes the polypropylene more absorbent. This may also increase the dyeing capability of the polypropylene.

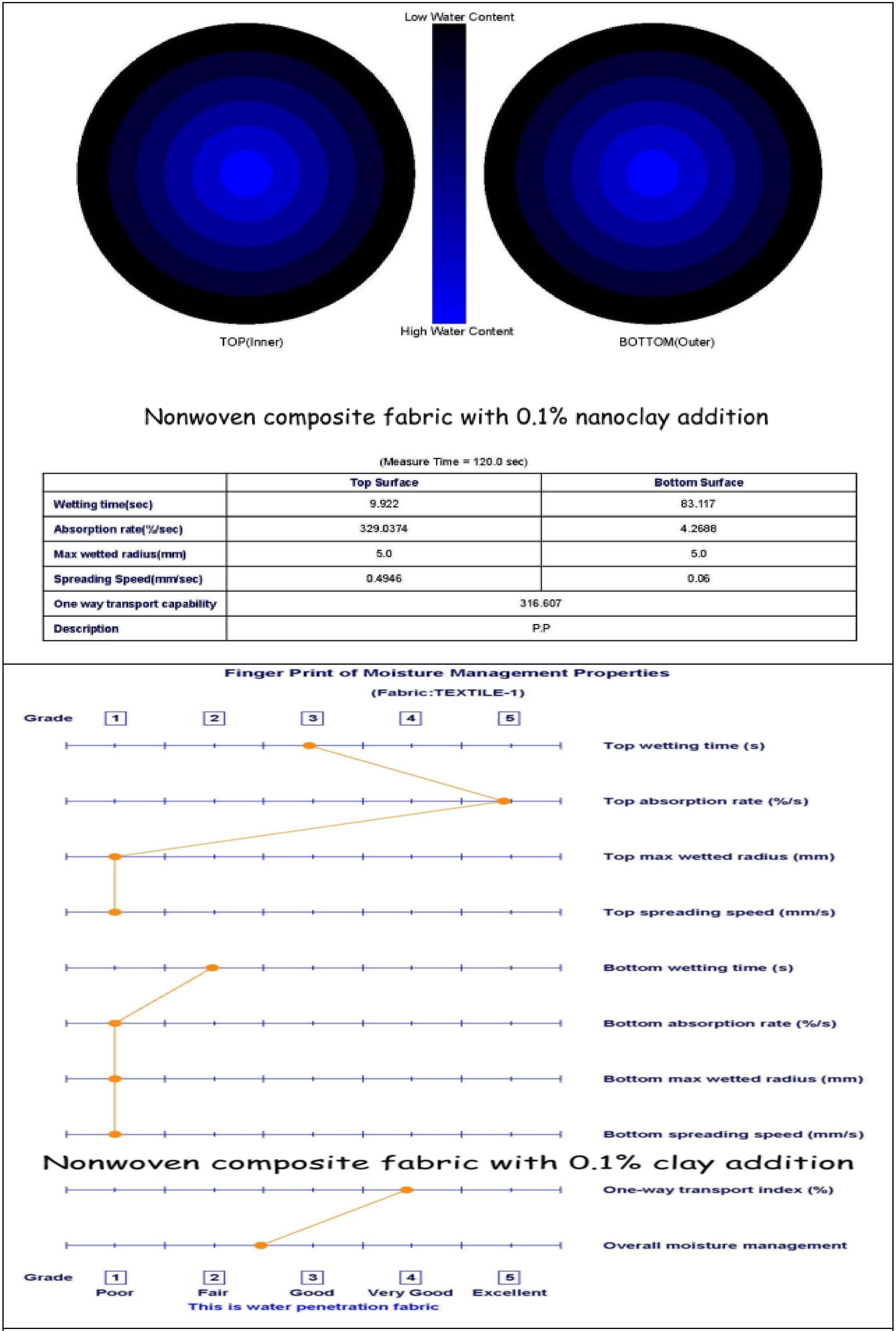


(Measure Time = 120.0 sec)

	Top Surface	Bottom Surface
Wetting time(sec)	6.833	120.0
Absorption rate(%/sec)	49.497	0.0
Max wetted radius(mm)	5.0	0.0
Spreading Speed(mm/sec)	0.7123	0.0
One way transport capability	-493.3397	
Description	P.P	

Control sample : PP nonwoven fabric without nanoclay addition

Figure 4.51(a) Moisture management graphs of Sample NW1



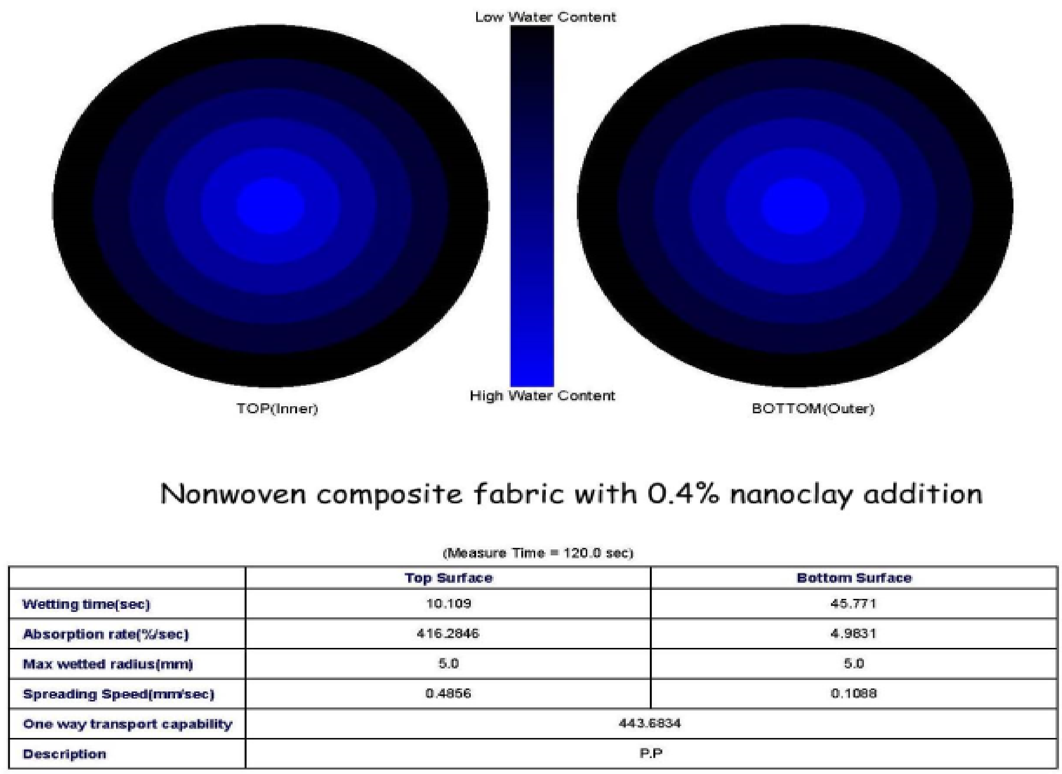
Nonwoven composite fabric with 0.1% nanoclay addition

(Measure Time = 120.0 sec)

	Top Surface	Bottom Surface
Wetting time(sec)	9.922	83.117
Absorption rate(%/sec)	329.0374	4.2688
Max wetted radius(mm)	5.0	5.0
Spreading Speed(mm/sec)	0.4946	0.06
One way transport capability	316.607	
Description	P.P	

PP nonwoven composite fabric with 0.1 wt. % nanoclay addition

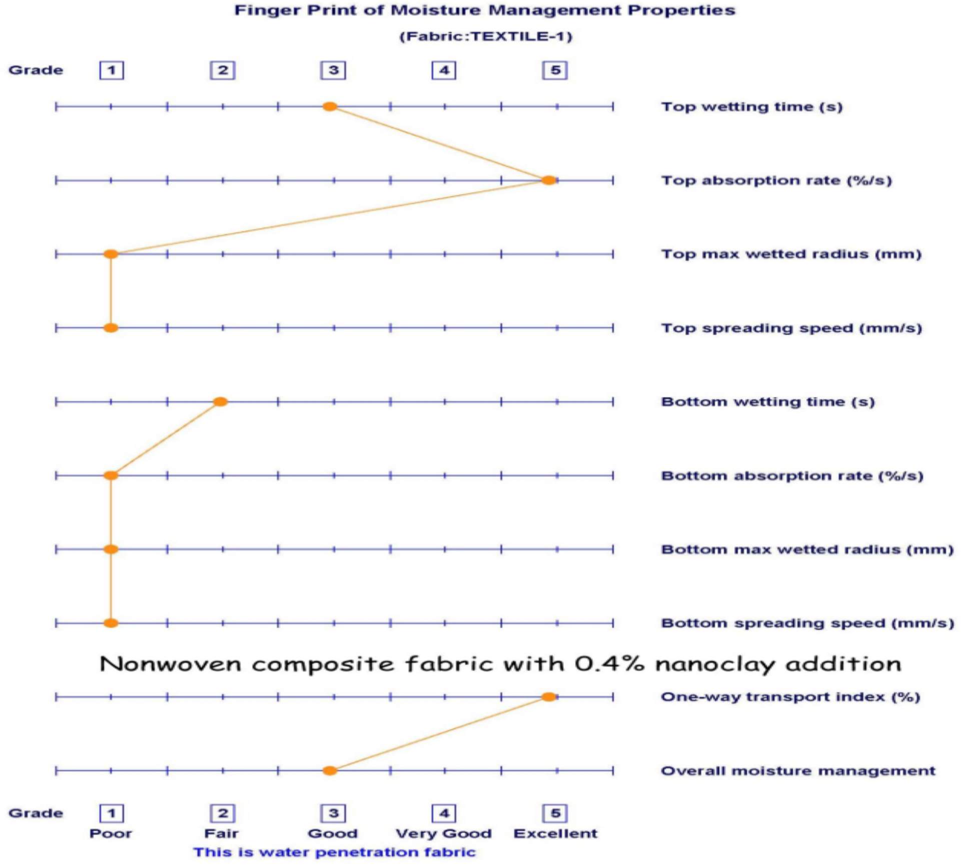
Figure 4.51(b) Moisture management graphs of Sample NW2



Nonwoven composite fabric with 0.4% nanoclay addition

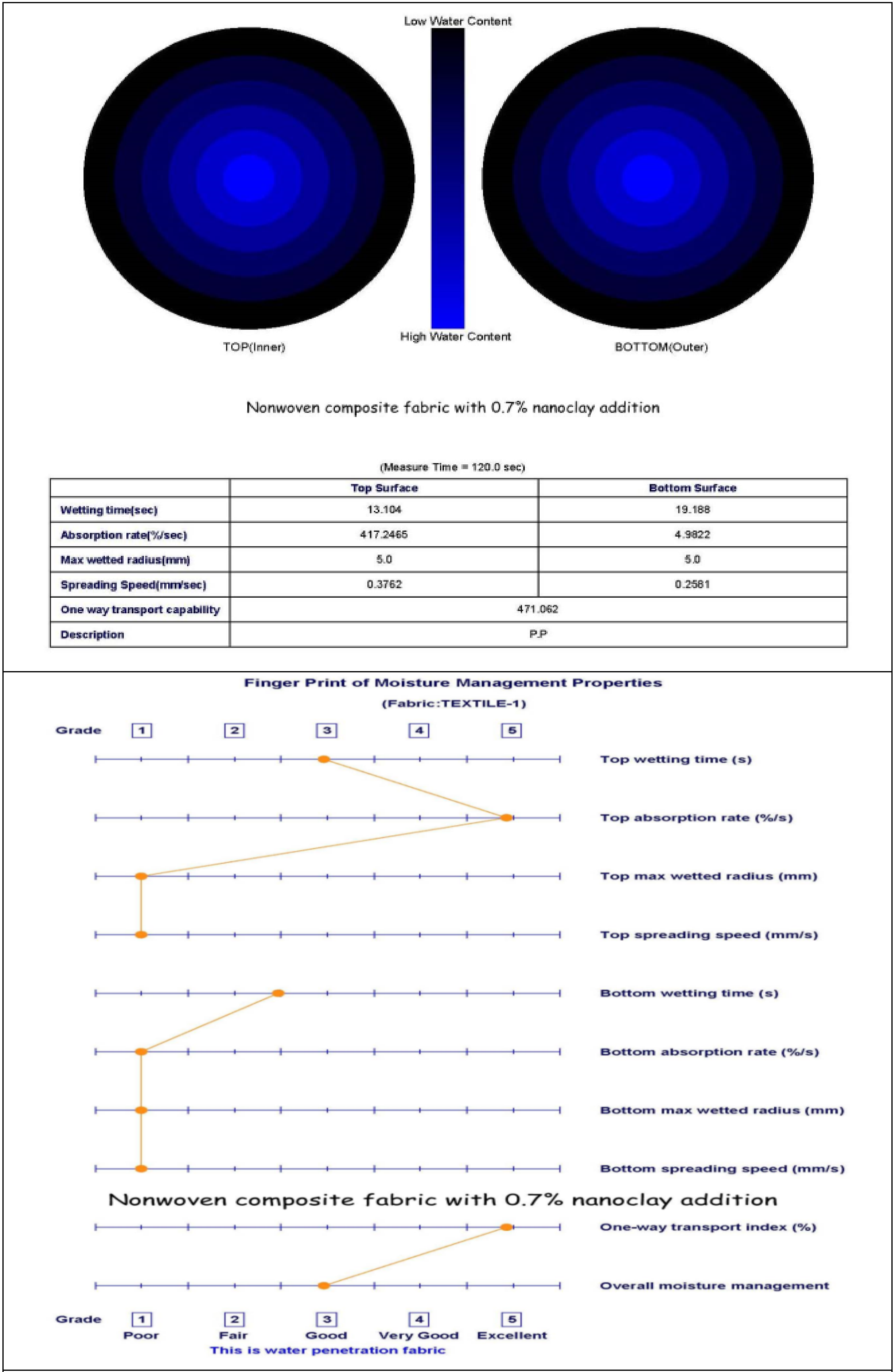
(Measure Time = 120.0 sec)

	Top Surface	Bottom Surface
Wetting time(sec)	10.109	45.771
Absorption rate(%/sec)	416.2846	4.9831
Max wetted radius(mm)	5.0	5.0
Spreading Speed(mm/sec)	0.4856	0.1088
One way transport capability	443.6834	
Description	P.P	



PP nonwoven composite fabric with 0.4 wt. % nanoclay addition

Figure 4.51(c) ***Moisture management graphs of Sample NW3***

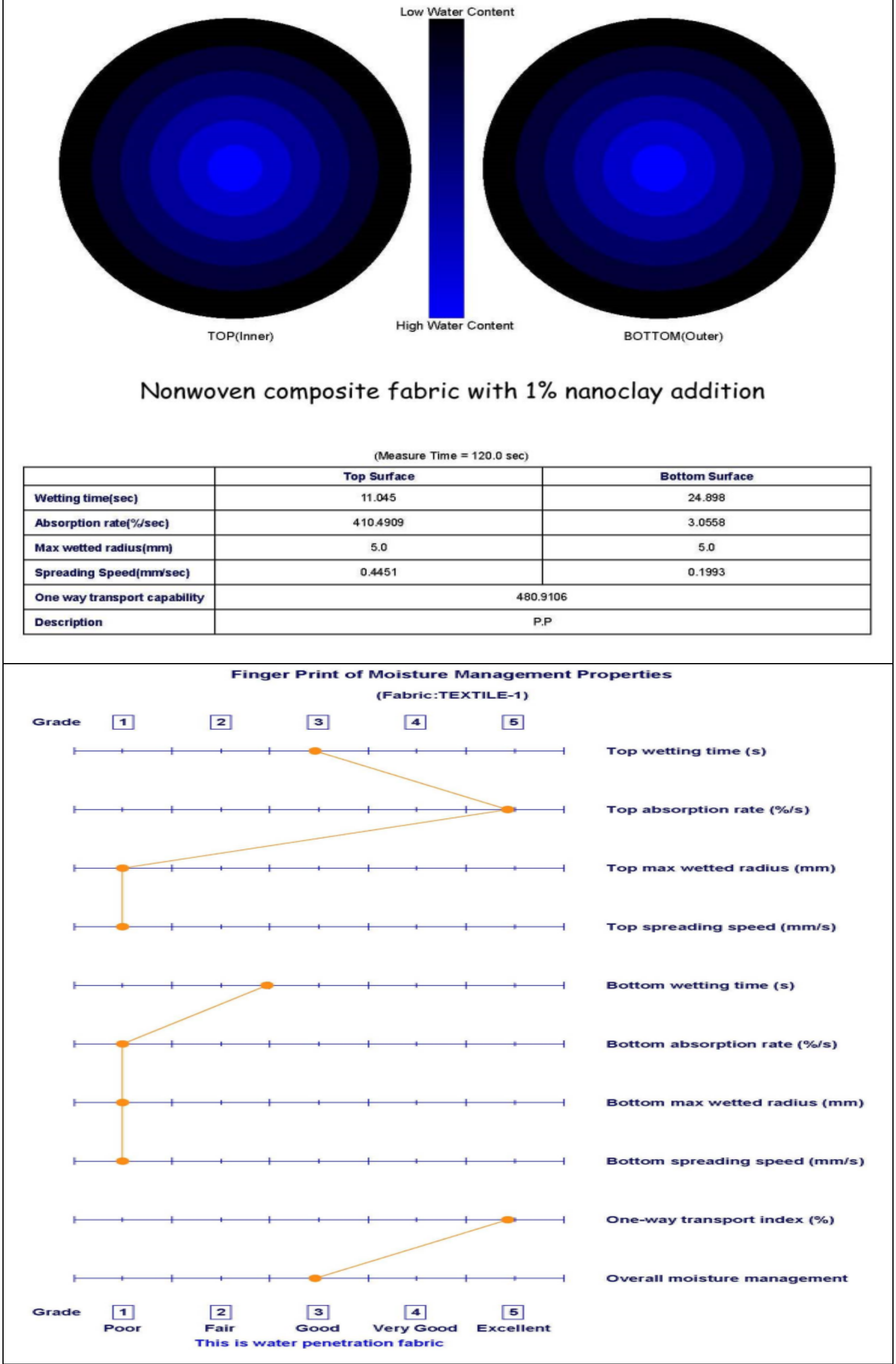


(Measure Time = 120.0 sec)

	Top Surface	Bottom Surface
Wetting time(sec)	13.104	19.188
Absorption rate(%/sec)	417.2465	4.9822
Max wetted radius(mm)	5.0	5.0
Spreading Speed(mm/sec)	0.3762	0.2561
One way transport capability	471.062	
Description	P.P	

PP nonwoven composite fabric with 0.7 wt. % nanoclay addition

Figure 4.51(d) ***Moisture management graphs of Sample NW4***

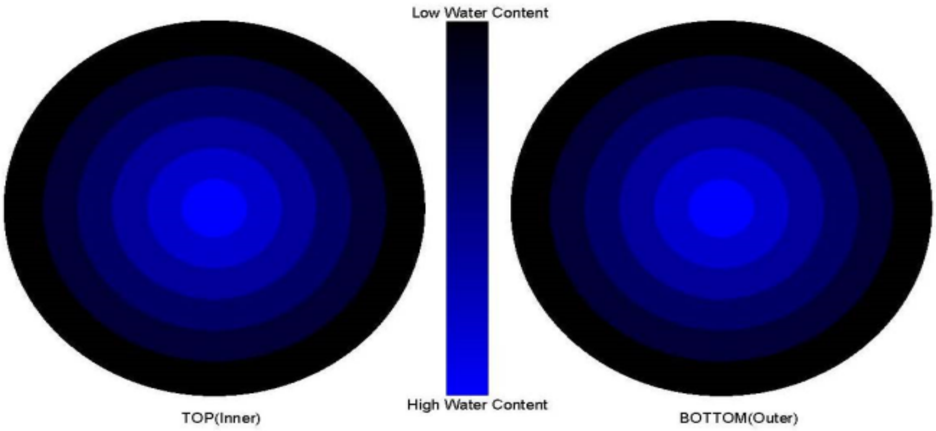


(Measure Time = 120.0 sec)

	Top Surface	Bottom Surface
Wetting time(sec)	11.045	24.898
Absorption rate(%/sec)	410.4909	3.0558
Max wetted radius(mm)	5.0	5.0
Spreading Speed(mm/sec)	0.4451	0.1993
One way transport capability	480.9106	
Description	P.P	

PP nonwoven composite fabric with 1 wt. % nanoclay addition

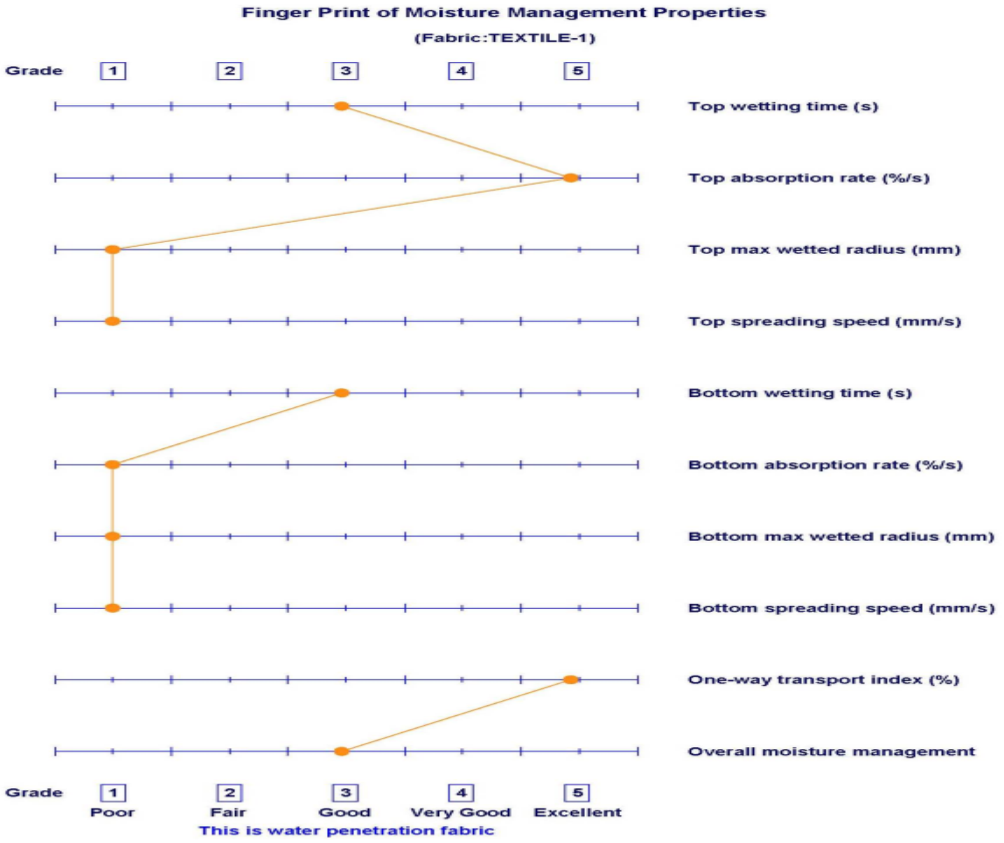
Figure 4.51(e) Moisture management graphs of Sample NW5



Nonwoven composite fabric with 1.6% nanoclay addition

(Measure Time = 120.0 sec)

	Top Surface	Bottom Surface
Wetting time(sec)	11.045	11.7
Absorption rate(%/sec)	425.6912	3.5919
Max wetted radius(mm)	5.0	5.0
Spreading Speed(mm/sec)	0.4452	0.4206
One way transport capability	479.0509	
Description	P.P	



PP nonwoven composite fabric with 1.6 wt. % nanoclay addition

Figure 4.51(f) ***Moisture management graphs of Sample NW6***

It was also observed that the difference in one way transport capacity and wetting tine in the case of 1% and 1.6% nanoclay addition is negligible or it's almost constant. Thus one can say that by little addition of nanoclay the polymer structure has become more porous and further increase in nanoclay addition does not support the at the same time seen from figure, the value of one way water transport becomes almost constant from 1% addition and thereafter. Thus, with the addition of negligible percentage of nanoclay particle, the most hydrophobic material PP can be converted to hygroscopic material.

4.3.6 EFFECT ON ULTRAVIOLET RAYS

Table 4.20 UPF ratings of pure and composite nonwoven fabric

Sample code	UPF rating	T(UVA) in %	T(UVB) in %
NW1	05	17.69	15.12
NW2	06	13.14	7.10
NW3	09	14.6	6.77
NW4	10	10.77	4.46
NW5	10	13.35	6.26
NW6	17	9.41	3.74

It is known that sunlight of invisible ultraviolet (UV) radiation; exposure to UV rays can lead to sunburn, accelerated to skin ageing and skin cancer. From three types of UV rays, UVA (range 320 – 400 nm) and UVB (range 290 – 320 nm) are most harmful.

The UV-2000F measures the spectral transmittance of ultraviolet light through a sunscreen material and calculates certain characteristic parameters of the sunscreen sample using AATCC TM 183-2000 methods. The Ultraviolet Protection Factor (UPF) rating system measures the UV protection provided by textiles. It is very similar to the SPF (Sun Protection Factor) rating system used for sunscreens. A textile with a UPF of 50 only allows 1/50th of the UV radiation falling on the surface of the garment to pass through it. In other words, it blocks 49/50ths or 98% of the UV radiation[131]. Along with this interpretation table given below is also adopted by the manufacturers.

Table 4.21 UPF ratings of pure and composite nonwoven fabric

UPF Rating	**Protection category**	**Effective UV-R Transmission (%)**	**UPF Rating**
15 – 24	Good	6.7 – 4.2	15, 20
25 – 39	Very good	4.1 – 2.6	25, 30, 35
40 – 50, 50 +	Excellent	Less than 2.5	40, 45, 50, 50+

As seen from the Table 4.20, the UPF rating of the samples increases with the increase in addition of nanoclay particles. As the UV rays transmits through the space between yarns and also through the fibers. The UPF is affected mainly by the thickness and density of textiles, as well as by dyes, pigments and other compounds in fibers and textiles, such as pectin, wax, water, etc.[132]. For the samples prepared, it is evident that UPF rating of the pure PP nonwoven is 5, which is very low whereas increment in the percentage nanoclay addition increases the UPF factor to 6, 9, 10, 10 and 17. It has been observed that 1.6% nanoclay addition gives best results and comes under "Good" protection category. This may have happened as nanoclay particles embedded inside the polymer matrix would have scattered / absorbed the radiations and reduced the transmittance. This has designated this material as high UV blocking material which can be used as an industrial product.

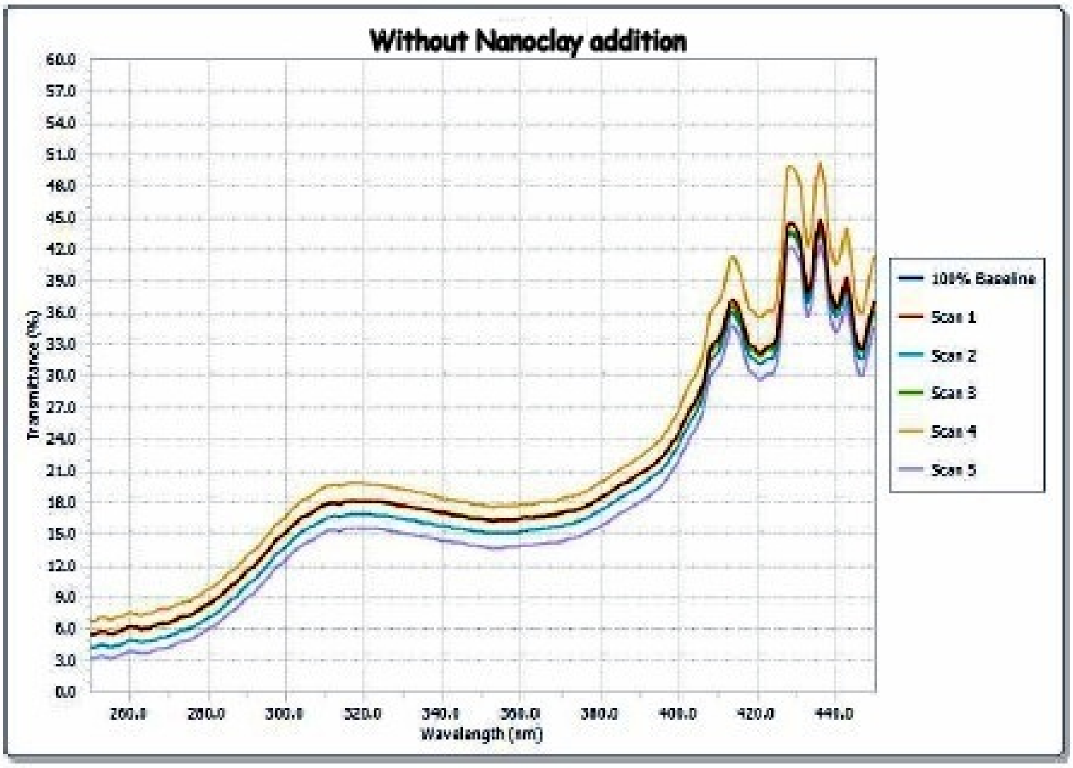


Figure 4.52(a) UV rays transmittance of Sample NW1

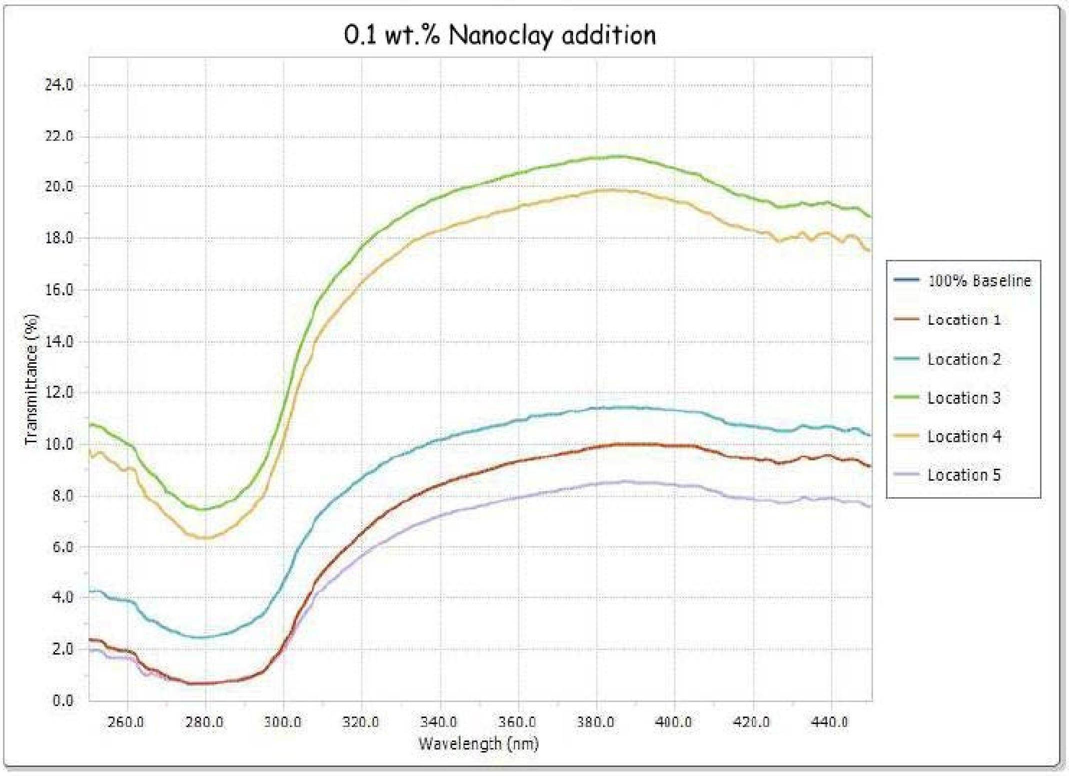


Figure 4.52(b) UV rays transmittance of Sample NW2

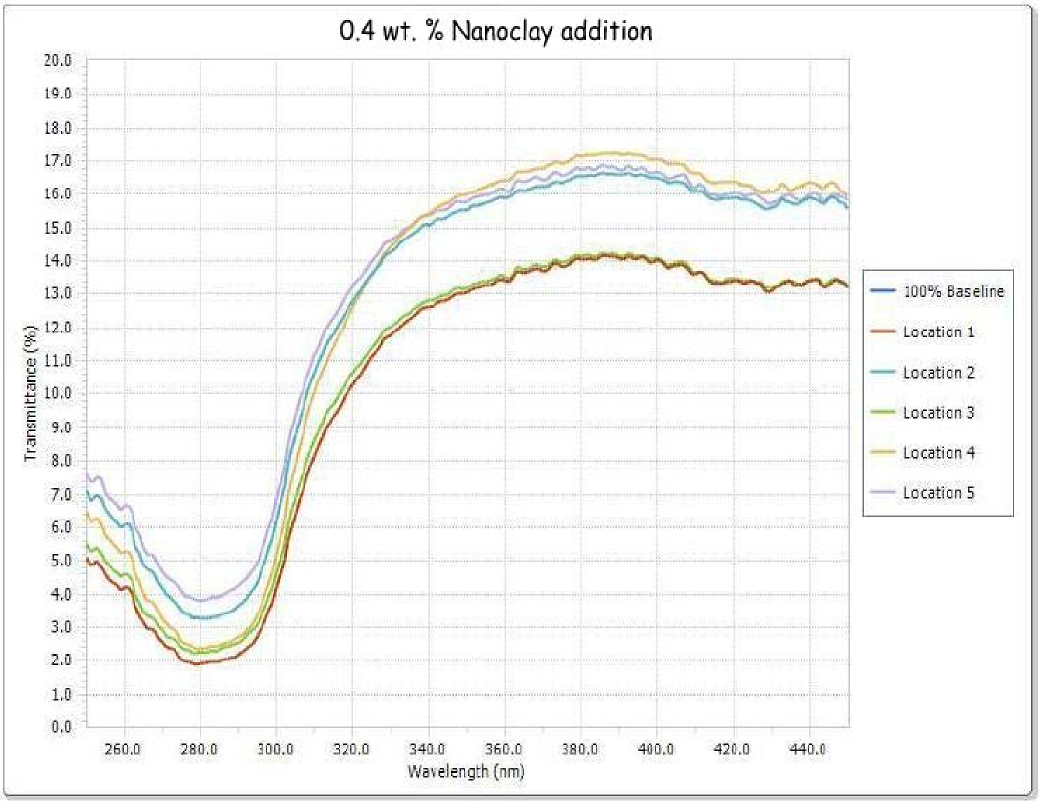


Figure 4.52(c) UV rays transmittance of Sample NW3

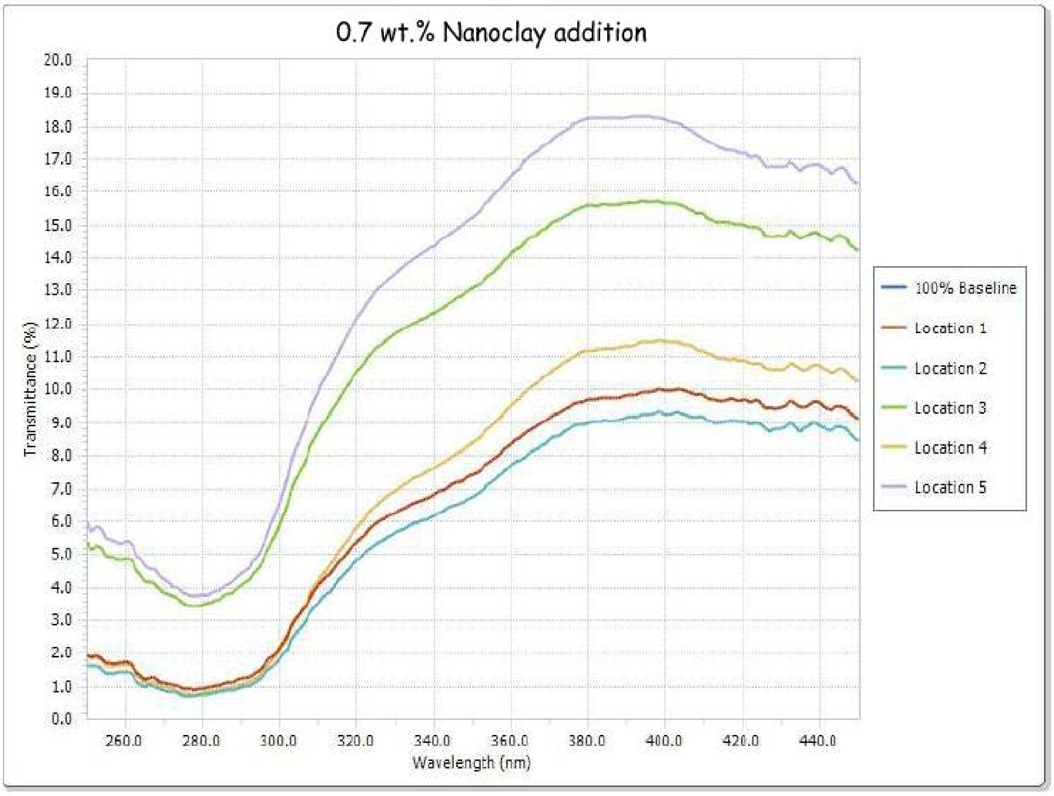


Figure 4.52(d) UV rays transmittance of Sample NW4

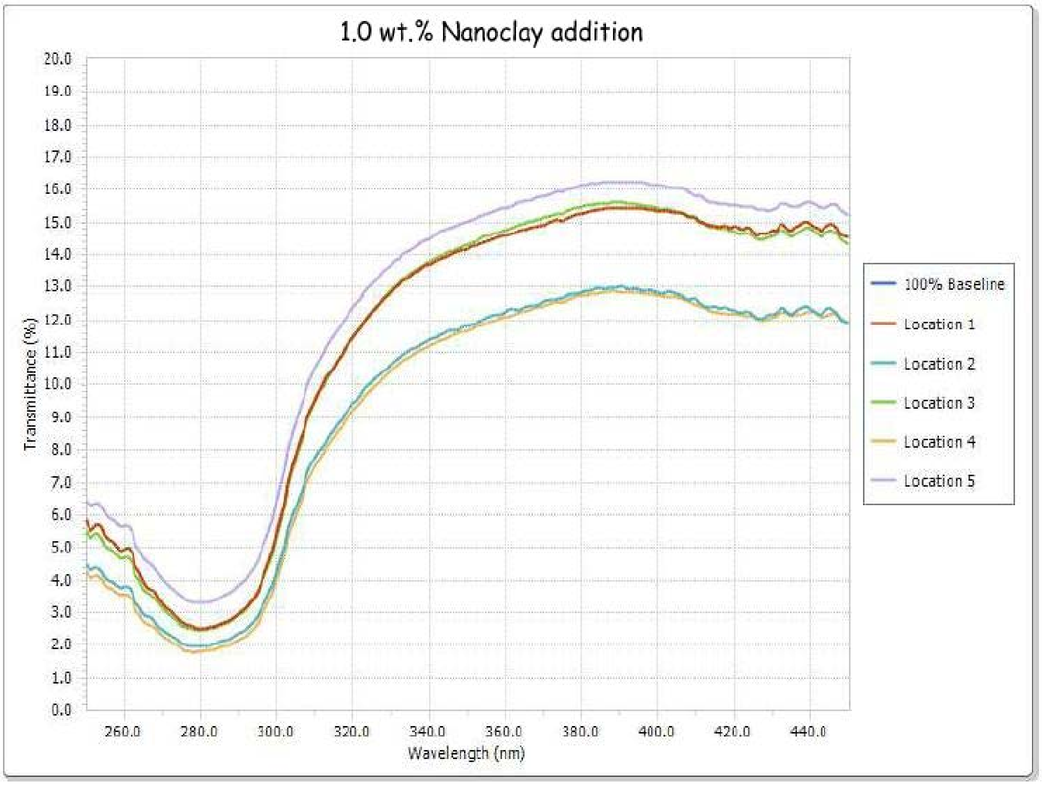


Figure 4.52(e) *UV rays transmittance of Sample NW5*

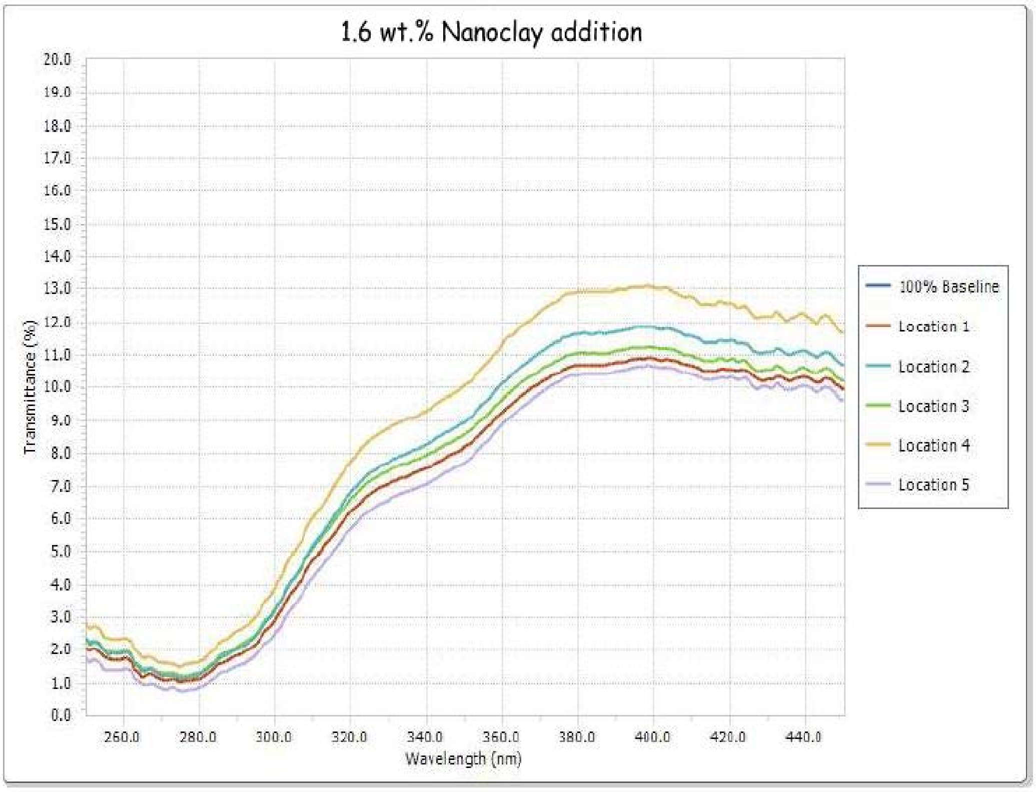


Figure 4.52(f) *UV rays transmittance of Sample NW6*

CHAPTER 5

CONCLUSIONS

PP/nanaoclay composite filament as well as nonwoven fabrics was successfully prepared. Influence of different percentage of nanoclay on the structure, morphology and mechanical properties of polypropylene nanocomposites products was investigated.

1. In first phase of the research montmorillonite which is a 2:1 smectite; whose individual nanolayers are 1 nm thick and their lateral dimensions are about 100 nm was successfully modified to Organoclay using CTAB as surfactant. The hydrophilic face of the clay platelets is modified by CTAB as surfactants, in order to enhance the interaction between the mineral and the organic polymer. The surface morphology of the prepared Organoclay was observed by SEM micrographs and its chemical composition was confirmed by FT-IR spectroscopy. The SEM images as well as increase in basal spacing of MMT-CTAB$_{0.03M}$ from X-Ray diffractograms indicate the intercalation of organic moiety between the layers of montmorillonite. The thermal stability study of Organoclay by TGA shows that the incorporation of organic cation (CTAB; surfactant) alters the thermal stability of the Na-MMT.

2. Polypropylene nanoclay composite yarns were successfully spun by melt intercalation method. Spinning variables like extruder temperature, extruder pressure, godet speed, temperature, and winding speed were optimized. It was found that with this process condition up to 1.5 wt. % addition of nanoclay, there was no difficulty in spinning but at 2 wt.% addition of nanoclay spinning of filament was difficult and dripping was observed. Composite with 1.5 wt. % addition of nanoclay, good dispersion was observed by SEM. The presence of nanoclay on/in the polymer matrix was confirmed by EDX. The mechanical property of yarn were found improved with addition of nanoclay up to 1.5 wt. %.

Change in structure of the PP composite filament was further confirmed by XRD pattern, indicates formation of exfoliated structure and increase in crystallanity of composite filament.

Thermo gravimetric analysis of the composite yarn shows increased heat bearing capacity of the PP, it is due to incorporation of nanoclay particles inside the polymer matrix.

3. PP / nanoclay nonwoven nanocomposites nonwoven fabric was successfully prepared by spun bond technique using existing lab model equipment. The machine parameters like extruder temperature, metering pump temperature & rpm, air pressure, calendar roller rpm & temperature were optimized. Higher wt% nanoclay addition leads to processing difficulties. SEM and EDX confirm the presence of nanoclay within the prepared material and also showed uniform distribution of nanoclay whereas XRD revels exfoliated structure obtained. The DSC data indicated that the Tg inflection point as well as the ∆H value was found lower for nonwoven with nanoclay addition.

   In case of mechanical properties, for machine direction there is an increase in tensile strength and strain as a function of filler wt % added [0.1 to 1.0 wt %]. Abrupt decrease in mechanical property was observed at 1.6 wt % addition of nanoclay in PP nonwoven fabric. In correlation with the stress value the strain value also exhibits the same feature which is quite unique. For cross direction the trend of stress remains same apart for only one value of 0.4 wt % clay addition. The strain percentage in cross direction reduces with the addition of nanoclay but the variation is high and difficult to predict.

   The modulus of the prepared composite samples increases for both M.D. and C.D. where as the work of rupture also increases with the addition of nanoclay as filler. Increment in both the values was observed for loading up to 1%. The overall results predict better fabric in terms of tensile strength with nanoclay addition than pristine fabric. Results were further confirmed with the help of tearing strength, which also follows the same trend.

In the case of stiffness of the material, the bending modulus increases up to 0.4 wt% clay loading and then it decreases for machine direction, where for cross direction no particular trend is seen.

As the structure of the prepared nonwoven fabric becomes open, as seen from SEM, and number of bond points decreases, air permeability of the fabric increases with addition of nanoclay up to 1 wt% loading and becomes stead thereafter. Due to the same, the bursting strength of the fabric decreased, the slight increase at about 1% loading can be due to increase in stain value.

Incorporation of nanoclay particles inside the structure of the polymer, has also changed the moisture properties of PP which is remarkable. By addition of nanoclay, the fabric becomes “water penetrating fabric” from “water proof fabric”. This can lead to major breakthrough in industry. This also lead to increase in UPF rating of the fabric, which increases the durability of the fabric in sun, as PP is most used in agrotextile for green house effect.

Polypropylene is a commodity polymer used in a wide range of products ranging from automotive applications, agro textile application to packaging applications. Conventional fillers such as talc and mica are used at a rather high loading of 20 to 40 wt. % to improve mechanical properties and dimensional stability while also increasing part weight. Organoclay have much larger aspect ratios and can enhance stiffness and scratch resistance significantly at a much lower loading.

The application of such nonwoven composite fabric can be at various fields like food packaging, medical and biological applications. This also can be very useful product for automobile industry.

By combining the attractive functionalities of nanoclay and different polymeric components, resultant nanocomposites material could potentially be applied in various areas such as automotive, aerospace, opto-electronics, medicinal etc. owing to their engineered structural and mechanical properties.

SCOPE FOR FURTHER STUDY

- These results encourage further investigation to be conducted for weaving this yarn in to fabric and analyze.
- As we have used POY, yarn can also be fully drawn and analyzed, as well as other properties related to thermal studies i.e. flammability can be carried out.
- The barrier properties can also be further studied.
- Can be utilized to develop multifunctional textiles to meet the challenges faced by textile industries.

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ABBREVIATIONS

PPCN-Polypropylene/montmorillonite nano-composites

MMT-Montmorillonite

OMMT-Organo-montmorillonite

PP/MMT-Polypropylene/montmorillonite

PET- Poly (ethylene terephthalate)

PP- Polypropylene

i-PP- isotactic Polypropylene

N6-Nylon 6

ΔH–Entropy

AFM-Atomic force microscopy

DSC-Differential scanning calorimetry

TGA-Thermo gravimetric analysis

TMA-Thermo mechanical analysis

EDS- Energy dispersive spectrometers

MB-Melt blowing

SB- Spunbonding

PP-Polypropylene

GSM-Grams per square meter

MFR- Melt flow rate

TEM -Transmission Electron Microscope

WXRD -Wide angle X-ray Diffraction

PNCs – Polymeric nanocomposites

CPNCs – clay containing Polymeric nanocomposites

GL - Gauge length