

IMPACT OF ORGANO-CLAY (CLOSITE 20A AND MMT K-10 CLAY) ON MECHANICAL, MAGNETIC AND DIELECTRIC PROPERTIES OF PU/PS INTERPENETRATING POLYMER NETWORK

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ABSTRACT

In this paper, thin flexible sheets of polymer-Organo-Clay have been synthesized and studied for Mechanical, Magnetic and Dielectric Properties. For this, Cloisite 20A and MMT K-10 clay platelets & IPN (Interpenetrating Polymer Network) of Polyurethane (PU) and Polystyrene (PS) have been processed during In-situ polymerization has been reported. Broad hump at about 10°-20° in X-ray diffraction data confirms non crystalline nature of polymer- Cloisite 20A and MMT K-10 clay platelets in in matrix of thin flexible sheets of PU/PS which has also been confirmed from FTIR spectroscopy. Uniform distribution of Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) in matrix of PU/PS interpenetrating polymer has been analyzed from Microstructural analysis has carried out using scanning electron microscopy as well atomic force microscopy. The particle size of clay platelets of K-10 MMT Clay & Cloisite 20 A Clay has been calculated using transmission electron microscopy. The linear shaped Magnetization vs. Magnetic hysteresis confirms non-magnetic behavior of oil based polymer prepared using Castor oil (PU/PS) modified with Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet). Dielectric properties have been studied from ϵ' & ϵ'' vs. Frequency profile recorded using impedance analyzer of Cloisite 20A and MMT K-10 clay platelets filled PU/PS interpenetrating polymer network. The improvement in mechanical properties has been described from increase in elongation at break of PU/PS with Cloisite 20A and MMT clay platelets as organic filler. Presence of various bond due carbon and silicon which are essential components of organoclay and interpenetrating polymer network have been studied from FTIR spectroscopy.

KEYWORDS: Flexible Mats, Interpenetrating Polymer Network (IPN), FTIR, Thermal Stability, Castor Oil

INTRODUCTION:

Polymers commonly known as intricate molecular structures composed of repeating units called monomers, have become an integral part of our modern world, revolutionizing various industries and transforming the way we interact with our surroundings. These remarkable materials possess a wide range of applications, from the production of everyday household items to the development of advanced technological solutions. The versatility of polymers is exemplified by their ability to be synthesized from a diverse array of raw materials, including petroleum-based chemicals and renewable resources such as plant-derived biomass [1-2]. This diversity in source materials has enabled the creation of a vast array of polymer types, each with unique properties and functionalities that cater to the specific needs of various industries [3-4].

Although the reaction between isocyanate and hydroxyl compounds was originally identified in the 19th Century, the foundations of the polyurethanes industry were laid in the late 1930s with the discovery, by Otto Bayer, of the chemistry of the poly addition reaction between diisocyanate and diols to form polyurethane. The first commercial applications of polyurethane polymers, formillable elastomers, coatings and adhesives, were developed between 1945 and 1947, followed by flexible foams in 1953 and rigid foams in 1957. Since that time they have been finding use in an ever-increasing number of applications and polyurethanes are now all around us, playing a vital role in many industries– from furniture to footwear, construction to cars. Polyurethanes appear in an astonishing variety of forms, making them the most versatile of any family of plastic materials. Comfortable, durable mattresses and automotive and domestic seating are manufactured from flexible foam. Rigid polyurethane foam is one of the most effective practical thermal insulation materials, used in applications ranging from domestic refrigerators to large industrial buildings. Polyurethane adhesives are used to make a wide variety of composite wood products from load-bearing roof beams to decorative cladding panels. Items such as shoe soles, sports equipment, car bumpers and ‘soft front ends’ are produced from different forms of polyurethane elastomers. Many of us are clothed in fabrics containing polyurethane fibers or high-performance breathable polyurethane membranes. Highly demanding medical applications use biocompatible polyurethanes for artificial joints and implant coatings. Polyurethane coatings protect floors and bridges from damage/corrosion and adhesives are used in the construction of items as small as an electronic circuit board and as large as an aircraft. Advanced glass and carbon fiber reinforced composites are being evaluated in the automotive and aerospace industries are examples of typical applications. Although the reaction between isocyanate and hydroxyl compounds was originally identified in the 19th Century, the foundations of the polyurethanes industry were laid in the late 1930s with the discovery, by Otto Bayer, of the chemistry of the poly addition reaction between diisocyanate and diols to form polyurethane. The first commercial applications of polyurethane polymers,

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Many of us are clothed in fabrics containing polyurethane fibers or high-performance breathable polyurethane membranes. Highly demanding medical applications use biocompatible polyurethanes for artificial joints and implant coatings. Polyurethane coatings protect floors and bridges from damage/corrosion and adhesives are used in the construction of items as small as an electronic circuit board and as large as an aircraft. Advanced glass and carbon fiber reinforced composites are being evaluated in the automotive and aerospace industries are examples of typical applications.

Commercially, polyurethanes are produced by the exothermic reaction of molecules containing two or more isocyanate groups with polyol molecules containing two or more hydroxyl groups. Relatively few basic isocyanates and a far broader range of polyols of different molecular weights and functionalities used to produce the whole spectrum of polyurethane materials. Additionally, several other chemical reactions of isocyanates are used to modify or extend the range of isocyanate-based polymeric materials. The chemically efficient polymer reaction may be catalyzed, allowing extremely fast cycle times and making high volume production viable.

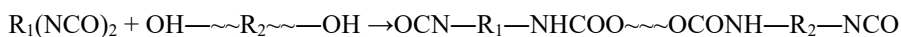
In recent years, the growing demand for sustainable and environmentally-friendly alternatives to traditional petroleum-based polymers has led to a surge in the development of biopolymers, which are derived from natural sources and possess inherent biodegradability and biocompatibility [9-10]. These biopolymers, such as polysaccharides and proteins, have found widespread applications in the biomedical field, where their ability to mimic natural tissues and deliver therapeutic agents has revolutionized the field of drug delivery and tissue engineering.

The medical industry, in particular, has significantly benefited from the advancements in polymer technology. Polymeric materials have been extensively utilized in the development of drug delivery systems, wound dressings, and orthopedic implants, among other applications. These polymeric materials not only provide the necessary structural support but also offer controlled release capabilities, enhancing the efficacy of medical treatments [11-12]. In conclusion, the versatility of polymers has transformed numerous industries, from biomedical to packaging, and continues to drive innovation and progress in our society. Moreover, the unique properties of polymers, such as their ability to be molded into complex shapes and their resistance to environmental factors, have made them indispensable in the packaging industry. The rise of Industry 4.0 has further amplified the importance of polymers in the development of sustainable and intelligent food packaging solutions, which are crucial for preserving the quality and safety of our food supplies.

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Polyurethanes, also known as polycarbonates, belong to a larger class of compounds called polymers. Polyurethane designates the polymer in which repeating unit is urethane linkage. The latter is obtained by reaction of a poly isocyanate with compounds containing two or more hydroxyl groups per molecule. There are many factors which made Polyurethanes as an important candidate among polymer in industrial usages such as food packaging, cutting or molding, steering wheels and dashboards in automotive, for thermal insulation like cork, glass fiber, mineral wool and another processing application due to its cost and processing.

Polyurethanes, also known as polycarbonates, belong to a larger class of compounds called polymers. Polyurethane designates the polymer in which repeating unit is urethane linkage. The latter is obtained by reaction of a poly isocyanate with compounds containing two or more hydroxyl groups per molecule. During the Second World War the same company in Germany applied the urethane reaction to drying oils. After the Second World War the early commercial applications of polyurethane chemistry was predominantly concerned with plastic foams and elastomers. Today the greatest consumption of urethane products is still the foam sector, but there is an increasing interest in the use of urethanes for surface coating application. Polyurethane resins are usually prepared by the reaction of a long chain diols with an excess of diisocyanate to obtain a “prepolymer” with terminal isocyanate group.



Where R_1 is an aromatic, aliphatic, or cycloaliphatic radical, and R_2 is usually an aliphatic group, derived from polyether or polyester. Polyurethanes (PUs) are one of the most important classes of polymers with wide applications and properties, which can vary from linear polymers to thermosetting plastics. The structural-property relationships in PU depends on many factors that include the volume fractions of the soft and hard segments, the chemical compositions of these segments and distribution of each segment, as well as the degree of cross-linking. These factors influence the physical, chemical, and thermal properties of PUs and could be manipulated by varying the stoichiometric balance of the components. The

reaction between diisocyanates and diols, proceeding in the presence of catalysts, is a basic reaction in synthesis of various polyurethanes [13-15].

There are a number of methods available for the preparation of polyurethanes, but the most widely used is reaction of di- or polyfunctional hydroxyl compounds, such as hydroxy-terminated polyethers or polyesters with di- or polyfunctional isocyanates. If the functionality of hydroxyl or isocyanate component is increased to three or more branched or cross-linked polymers are formed. The properties of the various types of urethane polymers are dependent mainly on molecular weight, degree of cross-linking, effective intermolecular forces, stiffness of chain segments, and crystallinity. Because of many structural variations that are possible in their formation the urethanes may be considered the most versatile polymers. They include fibers, soft and hard elastomers, coating and adhesives, flexible and rigid forms, and thermoplastic and thermosetting plastic. The base materials used to form polyurethane compounds are by-products of the oil refining process. The end product cast by the processor consists of two basic ingredients: a prepolymer and a curative. The "prepolymer" produced in the reaction can react separately with diols and diamines of low molecular weight to achieve further extension or polymerization (curing of the prepolymer). On the reaction with water, the prepolymer can also give foams. The properties of the polyurethane resin are controlled by the choice and ratio of the diisocyanate and polyol. The principle components of polyurethane are di- and poly-isocyanates and di- or polyhydroxy compounds. Active hydrogen compounds other than hydroxyl-compounds, such as compounds containing $-SH$, $-NH_2$ and other active hydrogen-functional groups, can also be used. Since aliphatic amino groups react too fast with isocyanates their use is mainly restricted chain extenders due to practical reasons. The major raw materials for these polymers are; isocyanate compounds, polyols and catalysts [16-18].

Vegetable oils, such as soybean oil, palm oil etc. are extracted primarily from the seeds of oilseed plants and have a wide variety of applications: as foods, fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers, and construction materials. They are also attractive monomers for polymer chemistry due to their natural abundance and reactive functionality. However, their use as monomers presents challenges due to their heterogeneous and variable structures. Indeed, it can be expensive to separate and extract the different triglycerides present because the oils are typically expressed in low concentrations and the composition of particular oil can vary seasonally. Recent advances in genetic engineering have heralded break-through: for example, the oleic acid component of variant sunflower oil can be increased to over 92%. The key chemical building blocks of vegetable oils are triglycerides: triesters of glycerin and fatty acids. Of the five commonly occurring fatty acids, two are saturated (palmitic and stearic) and three are unsaturated (oleic, linoleic, and linolenic). Triglycerides monomers are of interest due to their olefinic functionalities which could yield a cross-linked polymer directly. Vegetable oils are one of the most abundant biological sources and important raw materials for the production of bio-based polyurethanes because of their numerous advantages: low toxicity, inherent biodegradability, and high purity. As a result of the hydrophobic nature of triglycerides, vegetable oils produce polyurethanes that have excellent chemical and physical properties such as enhanced hydrolytic tendencies, high tensile strength and elongation, high tear strength, and thermal stability. Vegetable oils are triglycerides of fatty acids and except castor oil they do not contain appreciable quantity of free hydroxyl groups which are necessary for it being capable of participating in the urethane formation reactions. Castor oil is a naturally occurring monomer, which is triglyceride of ricinoleic acid containing three hydroxyl groups and three double bonds. Commercially castor oil consists of triglycerides that contain 90% ricinoleic acid residue and 10% non-functional acid residues, so that castor oil has effective hydroxyl functionality of 2.7 [19-21].

Castor oil: castor oil has been extensively used for polyurethane synthesis because of free hydroxyl present in it. Castor oil is obtained from the extracting from the seed of a plant which has botanical name is *Ricinus Communis* of the family of Euphorbiaceae. The extraction of castor oil from seed of castor is by one or a combination of mechanical pressing and solvent extraction.

In mechanical pressing, the seeds are crushed and then adjusted to low moisture content by warming in a steam jacketed vessel. There after the crushed seeds are loaded into hydraulic presses and then pressed by mechanical means to extract oil. The oil from mechanical pressing has light color and low fatty acid. The mechanical pressing only removes about 45% of the oil present and the remaining oil in the cake can be removed only by solvent extraction. It is an inexpensive and environment friendly. Castor oil is inexpensive source of secondary hydroxyl groups and it has been used as a polyol to synthesize cost effective polyurethane elastomer. Castor oil is a triglyceride acid with ricinoleic acid with ricinoleic acid being as a major constituent. Castor oil is a viscous pale yellow non-volatile and nondrying with a bland taste and is sometime used as purgative. It has a slightly characteristic odor while the crude oil taste slightly acrid with a nauseating after-taste relative to other vegetable oils. It has good self-life and does not turn rancid unless subjected to excessive heat. Since castor oil is triglyceride of fatty acid and its tri-hydroxyl structure help in producing highly cross linking urethane system. The pendent chain of fatty acid of acid impart flexibility and hydrolysis resistance to network and the double bond present in castor oil may serve as grafting center. The reason that why castor oil most widely used in synthesis of polyurethane due to its functionally which is about 2.7 and there for able to act as proton donor and because of its functionally it is unique dynamic between hard and soft segment of polyurethane which segregate into micro domain that constitute their excellent elastomeric properties. Castor oil is a triglyceride of ricinoleic acid in which about 90% fatty acid portion of the molecule consist of ricinoleic acid and 10% other acid in the form of non-hydroxyl acid. Castor oil is strongly dextrorotatory because of asymmetric c-atom at 12th position of ricinoleic acid and unlike other oil it is soluble in ethanol but insoluble in petroleum solvent. The major advantages of castor oil used for synthesis of polyurethane is its water resistant and flexible due to presence of long fatty acid chains lend themselves to thermosetting types structure due to tri functional nature. The long pendent chain of the fatty acid impart flexibility and hydrolysis resistance to the network and double bond present in castor oil serve as a grafting center and urethane polymer exhibit excellent abrasion resistance.

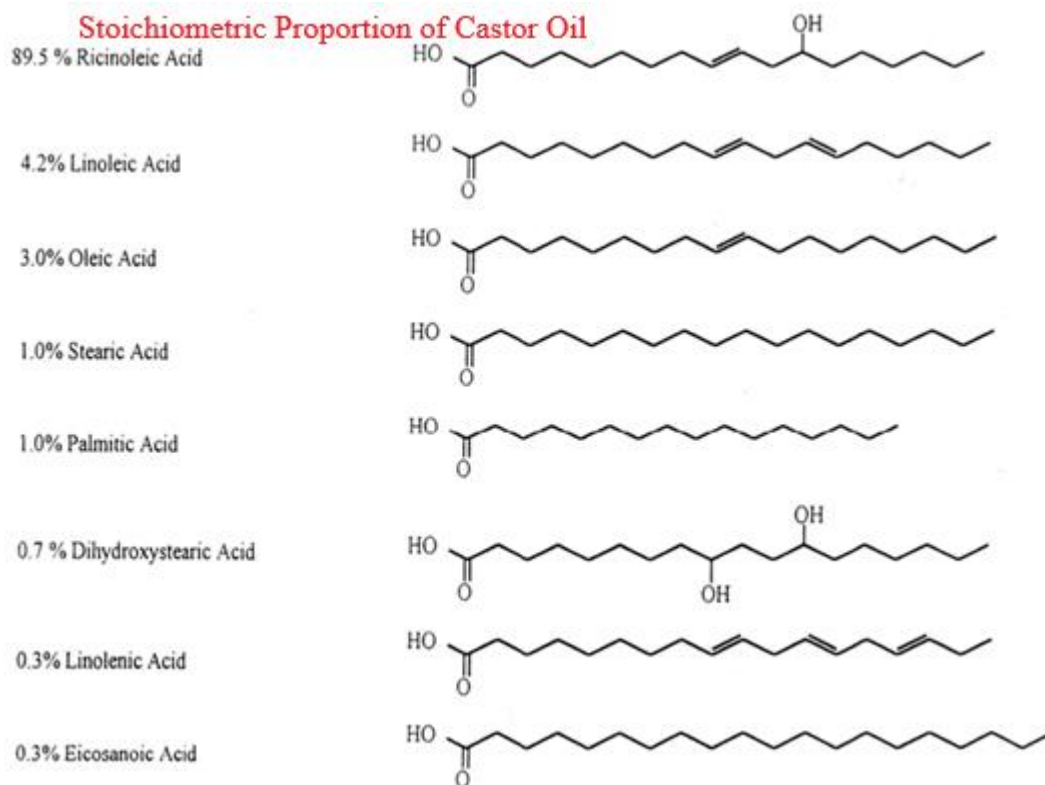


Figure 1: Stoichiometric Proportion of Various Acid in Castor Oil

Filler: Clay is a fine-grained natural soil material composed primarily of phyllosilicate minerals (sheet silicates), typically formed by the weathering of silicate-bearing rocks such as feldspar. It becomes plastic and moldable when wet, and hardens upon drying or firing. Clay is a commercially modified form of montmorillonite, a naturally occurring smectite clay mineral. It is produced by Southern Clay Products (now part of BYK Additives) and is commonly used as a Nano filler in polymer composites. It has been used in exfoliated form to modify mechanical and barrier properties of interpenetrating polymer network. Cloisite Montmorillonite has a layered structure with high aspect ratios and a large surface area, making it ideal for intercalation and exfoliation into polymer matrices. Cloisite clays are surface-modified with organic surfactants (typically quaternary ammonium salts) to improve their compatibility with hydrophobic or polar polymers, depending on the modifier used. In this paper, we used two clay (Montmorillonite and Cloisite Clay) uniformly dispersed in interpenetrating polymer network to improve its mechanical properties. Montmorillonite (MMT) is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming a clay. It has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometre. Members of this group include saponite. Montmorillonite is the main constituent of volcanic ash weathering product, bentonite. It has variable water contents and its volume increases due to absorption. Chemically it is hydrated sodium calcium aluminum magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Montmorillonite is used in the oil drilling industry as a component of drilling mud, making the mud slurry viscous which helps in keeping the drill bit cool and removing drilled solids. It is also used as a soil additive to hold soil water in drought-prone soils, to the construction of earthen dams and levees and to prevent the leakage of fluids. Cloisite are the popular nanoclays available in the market. Nanomer is a nanoclay product developed by Nanocor/AMCOL International Corporation, and Cloisite nanoclays are produced by Southern Clay Products, Inc., of Texas, USA. Cloisite additives have been used in injection-molded parts, films, bottles, trays, blister packs, and wire and cable coatings. Cloisite Na^+ is a natural montmorillonite well-known additive used to improve various plastic physical properties, such as reinforcement, heat deflection temperature (HDT), coefficient of linear thermal expansion (CLTE) and barrier properties. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species and therefore, naturally incompatible with a wide range of non-polar systems. Organophilic clay (also known as nanoclay) can be obtained by simply the ion exchange reaction of hydrophilic clay with an organic cation such as an alkyl ammonium or phosphonium ion. The inorganic ions, relatively small (sodium), are exchanged with more voluminous organic oniumcations. Cloisite 30B which is a natural montmorillonite is modified with quaternary ammonium salt containing organic modifier, methyl, tallow, bis-2-hydroxyethyl (MT2EtOH) to make it compatible with the polymer matrix to improve the properties and the modifier concentration in Cloisite 30B is 90 meq/100g clay. Cloisite 20A is a natural montmorillonite modified with quaternary ammonium salt containing organic modifier, dimethyl, dehydrogenated tallow (2M2HT) to make it compatible with polymer matrix to improve the properties and the modifier concentration in Cloisite 20A is 95 meq/100g clay. Cloisite additives have been used in injection-molded parts, films, bottles, trays, blister packs, and wire and cable coatings. Cloisite Na^+ is a natural montmorillonite well-known additive used to improve various plastic physical properties, such as reinforcement, heat deflection temperature (HDT), coefficient of linear thermal expansion (CLTE) and barrier properties [22-25]. In situ polymerization was used by Cao et al. [26] to create polyurethane (PU)/montmorillonite (MMT)

nanocomposites with organically modified layered silicates (organoclays), and a batch process was used to create the foams. Transmission electron microscopy and X-ray diffraction were used to study the clay dispersion of polyurethane nanocomposites. The synthesis process, molecular weight of polyols, and functional groups of the organic modifiers all have a significant impact on the form and characteristics of PU nanocomposites and foams. By including hydroxyl and organotin functional groups, silicate layers of organoclay can be exfoliated inside the PU matrix. When compared to pure PU foam, the presence of clay causes the cell density to increase and the cell size to decrease. PU nanocomposite foams with a substantially cross-linked structure showed opposite results. Using a high molecular weight hydroxyl-terminated polydimethylsiloxane (HTPDMS) graft of polyurethane (PU) and epoxy resin (EP), Chen et al. [27] produced a variety of interpenetrating polymer network (IPN) composites. Dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) were used to examine how the HTPDMS content affected the PU/EP IPN composites' phase structure, damping properties, and glass transition temperature (T_g). The thermal breakdown temperature of the composites increased in tandem with the amount of HTPDMS present, according to thermogravimetric analysis (TGA). Additionally, the tensile and impact strengths of the IPN composites were significantly improved. Through transesterification with pentaerythritol, Valero et al. [28] added reactive hydroxyl groups to castor oil. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry was used to identify the constituents of the castor oil pentaerythritol alcoholysis products. Pentaerythritol modified castor oil, diphenyl-methane 4-4diisocyanate polyurethane (PI-CO-PU), and polystyrene (PS) were all formed into simultaneous interpenetrating polymer networks using benzoyl peroxide as the initiator and divinyl benzene as the crosslinker. The effects of PU/PS composition on the morphology, miscibility, and physical properties of the resulting IPNs were investigated using scanning electron microscopy, dynamic mechanical thermal analysis, mechanical property measurements, and chemical reagent resistance. The effects of soft-segment on clay particle exfoliation and the ensuing mechanical and thermal properties of thermoplastic polyurethanes (TPU) and reactive layered silicate clay nanocomposites were examined by Pattanayak and Jana [29]. Butanediol, diphenyl methane diisocyanate, polyester and polyether polyol with molecular weight 2000, and up to 5 weight percent reactive layered silicate clay were used in a two-step bulk polymerization procedure to manufacture the composites. This nanocomposite was only produced in the case of polyester polyol due to its noticeably higher viscosity during clay-polymer mixing, even if the degree of clay-polymer tethering was the same for both polyester and polyether-polyol. The study also showed that hydrogen bonding has no effect on mechanical properties and that clay particles had no effect on hard segment hydrogen bonding. Polyurethane organoclay nanocomposites were synthesized by Rehab and Salahuddin [30] using the in situ polymerization process. The organoclay is made by intercalating diethanolamine or triethanolamine into montmorillonite clay (MMT) using an ion exchange method. First, the organoclay was swollen into different diols, and then diisocyanate was added to create polyurethane-organoclay hybrids. The nanocomposite used scanning electron microscopy and X-ray diffraction (XRD) to show the scattered structure of MMT. The results show that the peak characteristic has expanded with low intensity and shifted to d_{001} spacing to smaller 2θ , and that the MMT is equally distributed throughout the polymer matrix. The TGA showed that the breakdown temperature of the nanocomposites was higher than that of virgin polyurethane.

Experimental Methodology and Characterization

Castor oil was first dehydrated by boiling it continuously for 24 to 48 hours at 115 to 120 degrees Celsius. Because polyurethane reactions are extremely sensitive to moisture, even a small amount of moisture can produce foaming and the creation of urea, which is why castor oil needs to be dehydrated. When polyisocyanate is present, a polymeric substance that is insoluble and infusible is formed. To make castor oil appropriate for polyurethane reactions, it must be dehydrated to a moisture content of approximately 0.1-0.2%. Dehydration is carried out in a nitrogen-inert environment in a stainless steel container at a temperature of 115 to 120 °C. A stirrer that is connected to a motor will be installed in the middle of the neck. Using a Julabo high temperature circulating bath equipped with an electrostatic relay and a magnetic solenoid valve, the oil will be heated by passing it through the reactor's jacket. This bath has an accuracy of $\pm 0.1^\circ\text{C}$. After being dehydrated to a level of 0.1-0.2%, castor oil is utilized to create polyurethane. Castor oil was stored in hermetically sealed bottles with molecular sieves to eliminate any remaining water after dehydration. The dehydrated castor oil has been kept in closed necked bottle with insulating cock and molecular sieves to avoid further hydration or gaining moisture. In first step, uniform mixing of weighed castor oil, MDI, Benzoyl per oxide, organic clay (Cloisite 20A & MMT) and Montmorillonite clay in wt% (1, 2, 3, 4 & 5 by wt% of interpenetrating polymer network) dispersed in castor oil was done with the help of high shearing nonmagnetic electrical mixer and sonication. The mixture of clay & castor oil was kept at sonication for four to five hours and after that a high shearing mixing was done for two to three minutes and then again put the mixture in sonicator. In second step, Clay mixed castor oil and Diphenyldiisocyanate in 1:1 ratio by weight and Stirred at 45°C and then add styrene and 0.5% BPO and 1% N, N dimethyl aniline and stirred for 45 min and then put the whole in mold and kept mold at 60 °C for 24h and then at 120 °C for 4h and finally yellow color sheet was obtained. the yellow colored sheets further kept at temperature 120 °C for further 24 to 48 hours to remove moisture if any appears in sheets. The sheet then cut in different form for further characterization. The uniform distribution of clay in castor oil has been characterized using transmission electron microscope. For this, drops of clay mixed castor oil casted on grids and analyzed. For x-ray diffraction, piece of yellow sheet has been cut in 1 cm × 1 cm piece whereas for mechanical strength (Tensile Strength), dumb-bell shaped piece of yellow sheet has been used. The 3D morphology has been analyzed from atomic force microscope. The hardness testing has been tested by using Vickner hardness tester. Moisture absorption measurements were performed under water at 30°C. All specimens for moisture absorption experiments with dimensions of 30mm by 10mm were cut from composites sheets. Prior to the absorption experiments, all specimens vacuum dried at 40°C until a constant weight is attained. At predetermined intervals, specimens were taken out from the chamber and weighed a Sartorius model analytic balance (with a precision of 0.1 mg). Various bonds present have been studied using

FTIR spectroscopy whereas dielectric properties have been characterized using impedance analyzer. The magnetic property of non-magnetic polymer has been characterized from vibrational magneto-meter.

RESULTS AND DISCUSSION:

The uniform dispersion of filler MMT (Montmorillonite clay) & Cloisite 20 A in castor oil has been investigated using Transmission Electron Microscopy. The TEM micrographs of MMT (Montmorillonite clay) & Cloisite 20 A modified PU/PS interpenetrating polymer network for confirmation proper dispersion of clay platelets in the Nano composites have been shown in figure 1. The TEM micrographs shown are of 3 wt% of clays platelets dispersed in nanocomposites. It has been clearly seen in micrographs that whit colored thick rods like structures have been clearly visible. The white rods dispersed in random orientation reveals exfoliation like dispersion of clay platelets. Ultra-sonication facilitated the breaking of clay aggregates into fine clay particles and high Shear impact of homogenizer helped to disperse the clay platelets homogeneously throughout the composite matrix. The effect of the above treatments can be seen in the TEM images that have shown that the dispersion of the clay platelets into the nanocomposites is upto exfoliation level. The white lines in the TEM images are clay platelets and thickness of these clay platelets as depicted by TEM is ranging from 1-10 nm. The spaces between the platelets can be seen in the TEM images that represent the inter planner spaces between clay platelets. Tactoids consisting of the few platelets aggregates have also seen in the TEM images as black clouds. There are also some single as well as stacked clay platelets in the figure 1. The dispersion of the clay platelets in the Nano composites are the evidence that the clay is exfoliated in the composites. The figure 1 given below represents the random orientation of the clay platelets of MMT (K-10 Montmorillonite clay) & Cloisite 20 A clay platelets.

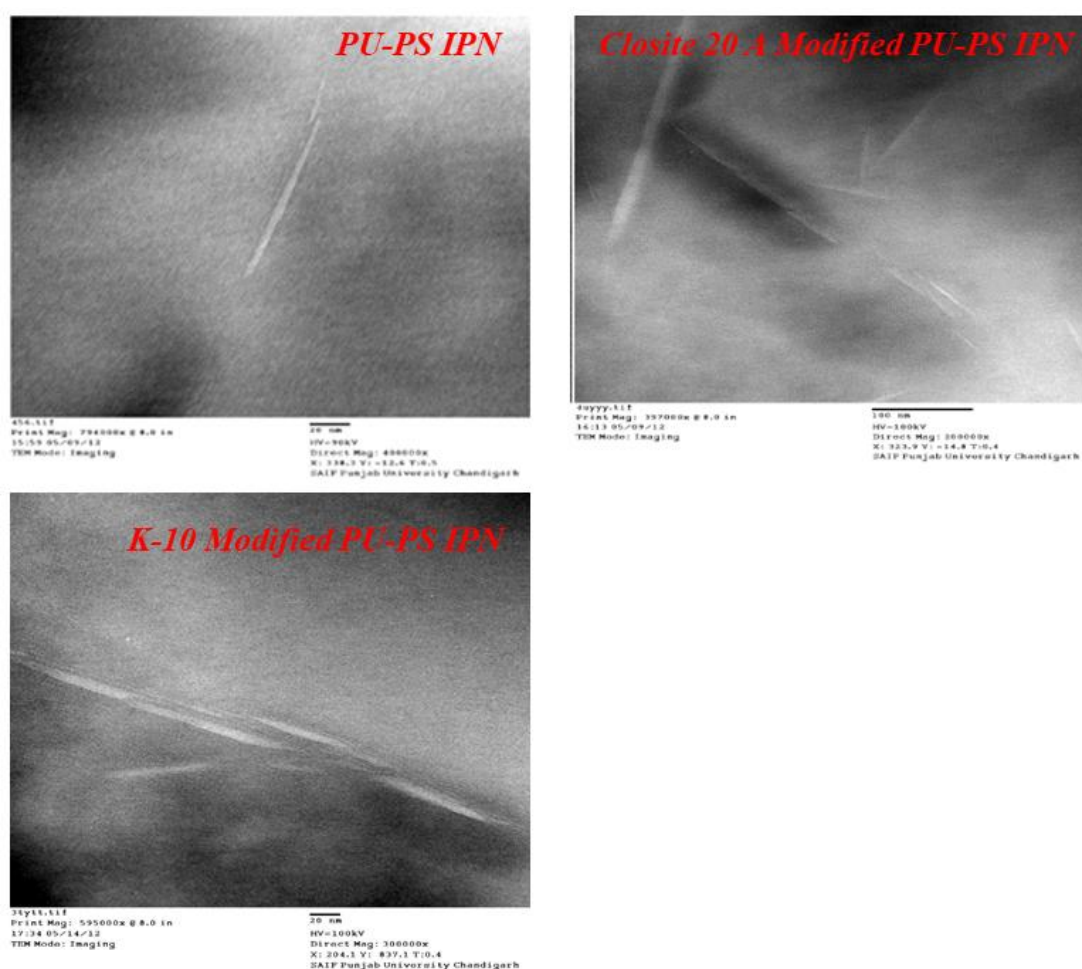


Figure 1: TEM Micrographs of MMT (K-10 Montmorillonite clay) & Cloisite 20 A modified PU-PS IPNs

As we know that polymer is amorphous in nature and clay platelets which enhances mechanical as well as barrier properties (Resistant against Moisture) also exhibits amorphous structure. So to verify it, X-ray diffraction of sheets of nanocomposites has been carried out. The X-ray diffraction pattern of MMT K-10 (Montmorillonite clay) & Cloisite 20 A modified PU/PS interpenetrating polymer network has been shown in figure 2. Instead of diffraction peaks corresponds to crystalline structure due to presence of multiple miller planes, broad hump reveals amorphous nature of prepared nanocomposites. Now sharp peak in diffraction data signature for absence of any crystalline plane and successful synthesis of polymer nanocomposites.

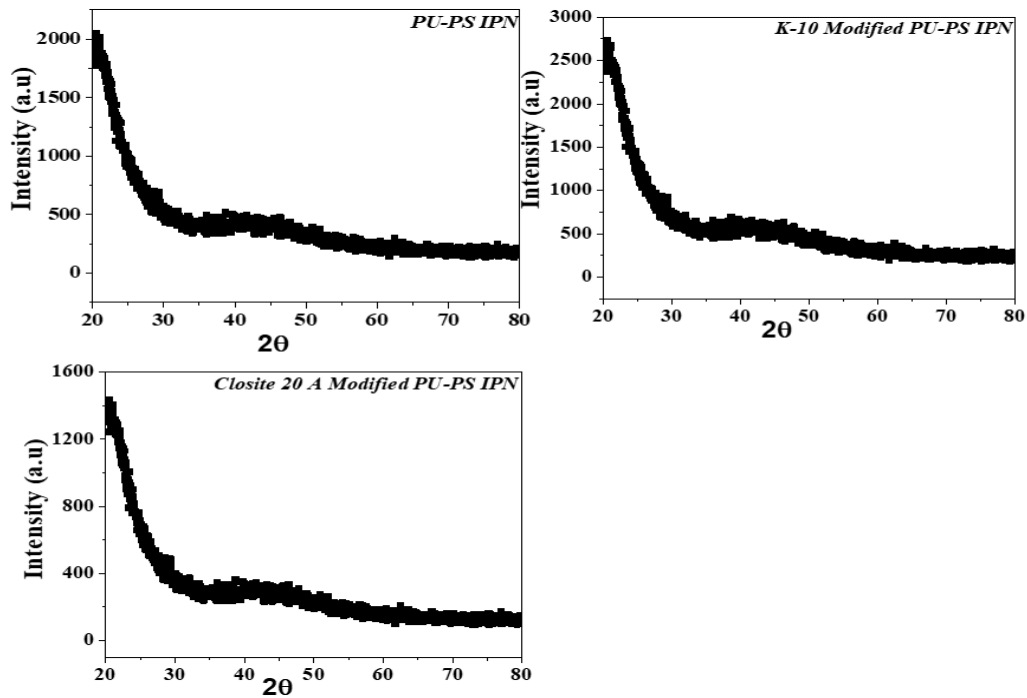


Figure 2: X-ray Diffraction Pattern of filler MMT (Montmorillonite clay) & Closite 20 A modified PU-PS IPNs

Distribution and morphology of filler MMT (K-10 Montmorillonite clay) & Closite 20 A modified PU-PS IPNs has been studied by scanning the surface of MMT (Montmorillonite clay) & Closite 20 A modified PU/PS interpenetrating polymer network. The micrographs shown in figure 3 reveals extent of distribution clay composites. It has been clearly reveals from micrographs that the phase of clay visually appears and uniformly distributed throughout. The formation of IPNs clay composites is clearly signature from appearing white colored finely mixed platelets in microstructure of Polyurethane and Poly Styrene. The uniformity of white colored fine rod likes shaped platelets direct evidence of Si, indicates that the mineral domain in submicron and homogenously dispersed in the polymer matrix. SEM micrographs also examine the fracture surface in compression-molded samples also not shows that the inorganic domains at maximum possible magnification. It has also been observed that no mineral domains appear. The uniformity of the white dots representative of Si, indicates that the mineral domain is submicron and are homogenously dispersed in the polymer matrix. The crystal structure of MMT & Closite clay consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Stacked layers of clay particles are held by weak dipolar or vander Waals forces.

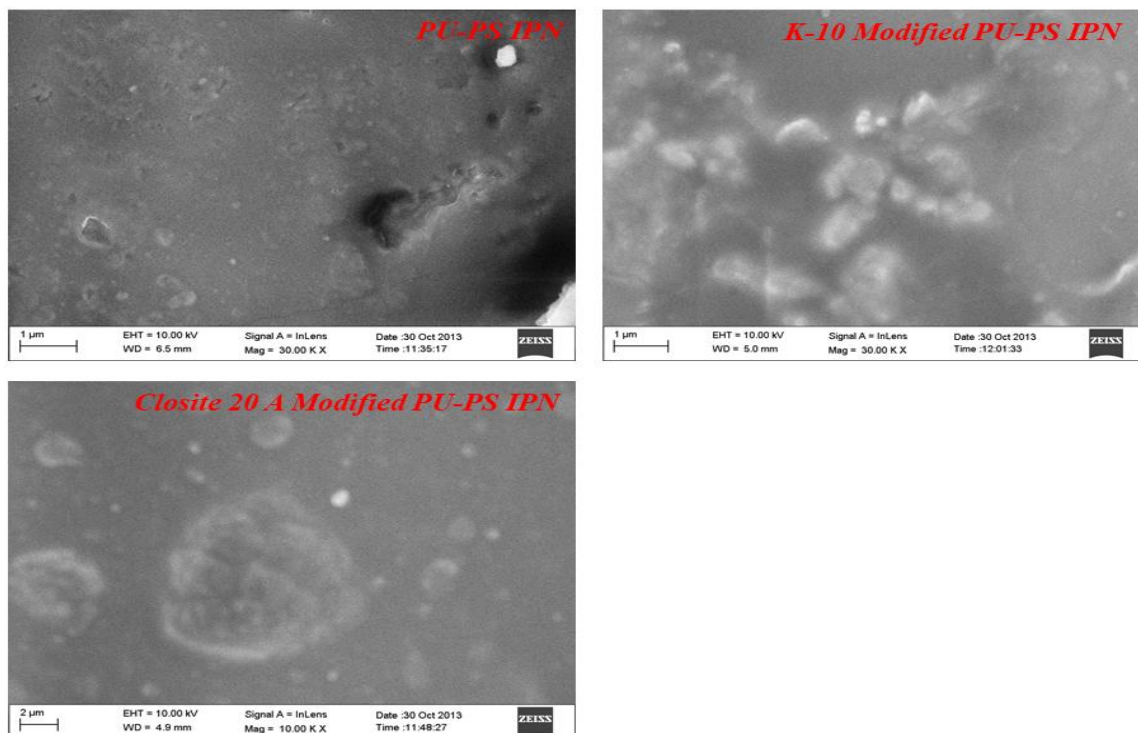


Figure 3: SEM Microstructure of filler MMT (K-10 Montmorillonite clay) & Closite 20 A modified PU-PS IPNs

Extent of dispersion of MMT (K-10 Montmorillonite clay) & Cloisite 20 A clay in matrix of PU/PS IPN nanocomposites has also been studied from 3D morphology recorded using Atomic Force microscope in non-contact mode operation whereas cantilever record surface roughness which also gives information of dispersion of filler MMT (Montmorillonite clay) & Cloisite 20 A clay Platelets in matrix of Polyurethane-Polystyrene matrix. AFM micrographs shows dispersion of MMT clay & Cloisite clay platelets in polyurethane matrix as cross-section samples of AFM were obtained shown in figure 4. It has been clearly reveals from AFM micrographs that in IPN nanocomposites with 3 wt% of filler MMT (Montmorillonite clay) & Cloisite 20 A, AFM images showed that K-10-MMTs clay and Cloisite 20 A Clay were able to uniformly disperse in polymer matrix without obvious clusters of clay particles observed. Comparisons with the composites at higher clay contents, the K-10-MMTs clay and Cloisite Clay in the polymer matrix for the nanocomposite with 3 wt% clay displayed a relatively uniform dispersion and relatively few clusters of clay particles were observed. With an increase of clay content, the K-10-MMTs clay and Cloisite 20 A Clay particles were more prone to aggregate and formed a bigger inorganic phase, meanwhile, the aggregation easily resulted in an inhomogeneous dispersion of K-10-MMTs clay and Cloisite 20 A Clay in the polymer at the lower K-10-MMTs clay and Cloisite 20 A Clay content, the sheets of the organically modified K-10-MMTs clay and Cloisite 20 A Clay were easily exfoliated and dispersed in the matrix due to the reaction of K-10-MMTs clay and Cloisite 20 A Clay with polyurethane pre-polymer. When the clay content reached a high concentration (>3 wt%), intercalated K-10-MMTs clay and Cloisite 20 A Clay easily aggregated together due to limited volume space in the matrix, thus resulting in an uneven.

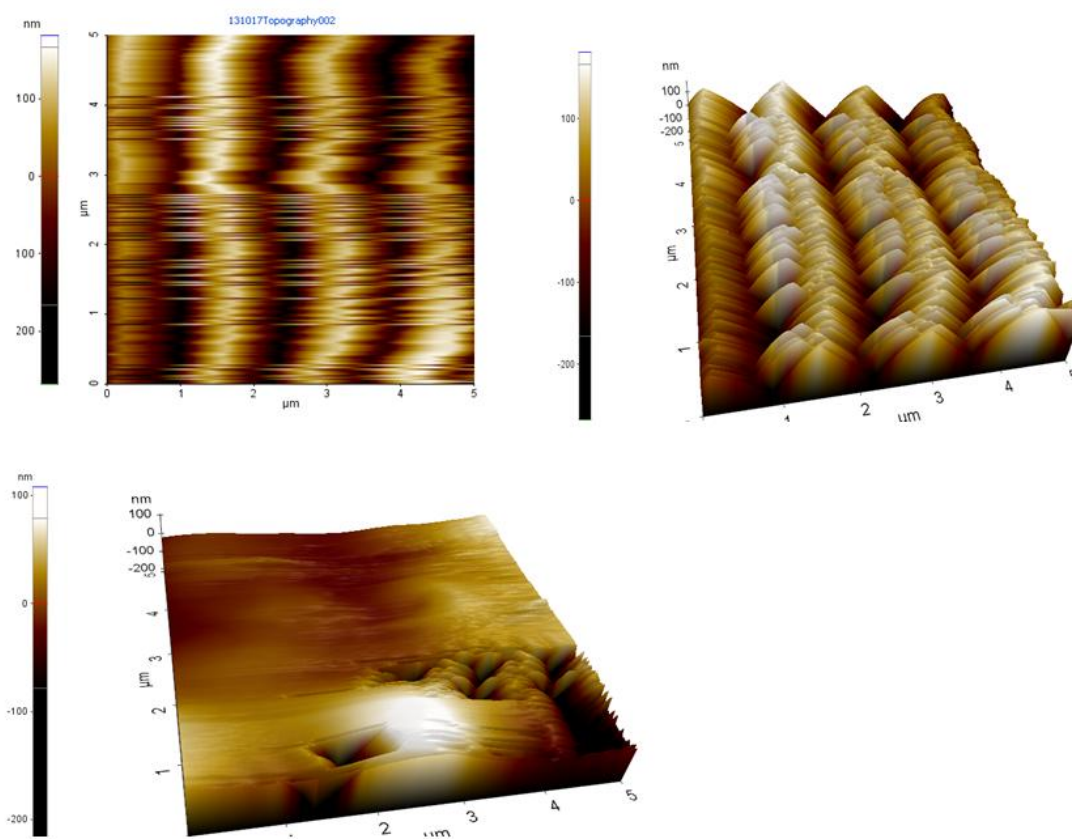


Figure 4: AFM Microstructure of filler MMT (Montmorillonite clay) & Cloisite 20 A modified PU-PS IPNs for 3D morphology

To explore or confirm the nonmagnetic nature of synthesized polymer, magnetization vs, Magnetic field profile has been carried out. Room temperature Magnetization vs. Magnetic Field hysteresis of prepared of MMT (Montmorillonite clay) & Cloisite 20 A clay modified PU/PS interpenetrating polymer network has been shown in figure 5. As it reported that magnetic properties of any materials has been due to unpaired partially filled d-orbitals or due to partially filled d-orbitals of transition metal ion especially Fe, Co, Mn or Ni [31]. In prepared organic clay modified PU/PS interpenetrating polymer network, no metal ion presents with unpaired electron in d-orbital strongly signature for paramagnetic nature of prepared interpenetrating polymer network. The Magnetization vs. Magnetic field plots shows that straight line in first and second quadrant shows paramagnetic nature of interpenetrating polymer network.

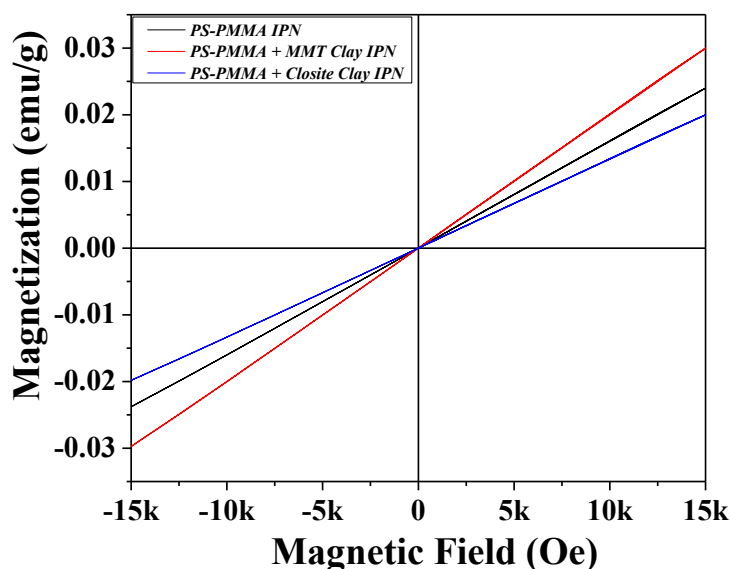


Figure 5: Magnetization vs. Applied Magnetic Field (T) Curve of filler MMT (Montmorillonite clay) & Cloisite 20 A modified PU-PS IPNs

Electrical properties of organic filler modified nanocomposites of MMT (Montmorillonite clay) & Cloisite 20 A modified PU/PS interpenetrating polymer network has been characterized from room temperature dielectric properties studied using impedance analyzer. ϵ' & ϵ'' vs. Frequency (Hz) at room temperature of (K-10 Montmorillonite clay) & Cloisite 20 A) modified PU/PS interpenetrating polymer network sheets of nanocomposites have been shown in figure 6. It has been clearly visualized from graphs that value of both real and imaginary part of dielectric constant is very low. The low value of real and imaginary part of dielectric constant reveals nonelectrical nature of MMT (K-10 Montmorillonite clay) & Cloisite 20 A modified PU/PS interpenetrating polymer network sheets. The value of both real and imaginary part of dielectric constant may resulted due to space charge which have been accumulated at interface of conducting electrode made from silver paint and surface of non-electrical clay modified PU/PS interpenetrating polymer network composites. As results, value of both ϵ' & ϵ'' starts decreases but after certain frequency range, orientation of dipoles with applied signal lags behinds. The value of both real and imaginary part of dielectric constant may be due to presence of carbon content because prepared polymer composites constitutes of carbon and silicon [32-34].

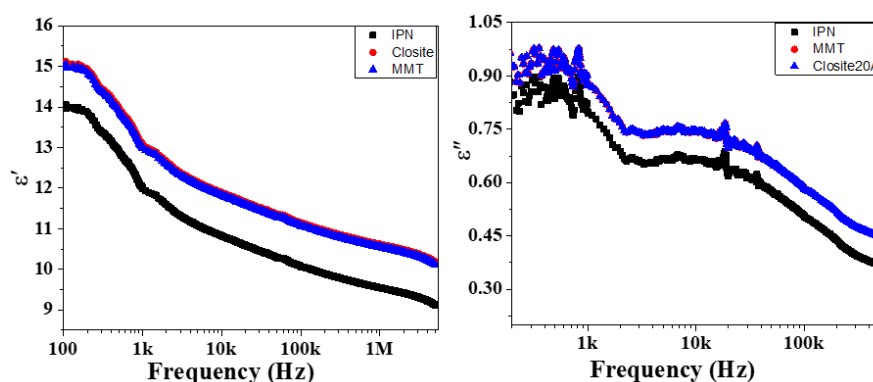


Figure 6: ϵ' & ϵ'' vs. Applied Electric Field profile of filler (MMT (Montmorillonite clay) & Cloisite 20A modified PU-PS IPNs

Since synthesized clay (MMT & Cloisite 20A & 30B) modified PU/PS interpenetrating polymer network nanocomposites constitute of carbon and silicon, so due to Si and Carbon, it has been expected that prepared nanocomposites shows conducting response. σ_{ac} vs. Frequency (Hz) profile of MMT (Montmorillonite clay) & Cloisite 20 A modified PU/PS interpenetrating polymer network sheets have been shown in figure 7. The σ_{ac} has been calculated from collected dielectric data using formula

$$\sigma_{ac} = 2\pi f \epsilon' \epsilon'' \tan \delta \quad [33-37],$$

Where f , $\tan \delta$, ϵ' & ϵ'' are frequency, dielectric loss, real and imaginary part of dielectric permittivity. It has been clearly visualized from conductivity graphs that graphs composed of two distinct regimes. The portion which behaves linearly as frequency increases and does not changes with frequency represents dc conductivity (σ_{dc}) whereas part which changes with increasing frequency and continuously increases with increase in frequency reveals ac conductivity (σ_{ac}). The conductivity profile has been generally analyzed by using Jonscher's power law [31];

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

Where σ_{ac} = ac conductivity, σ_{dc} = dc conductivity, A = dispersion parameter representing the strength of Polarizability & “n” is dimensionless parameter which gives information about interaction between mobile ions with the lattice in which they interact.

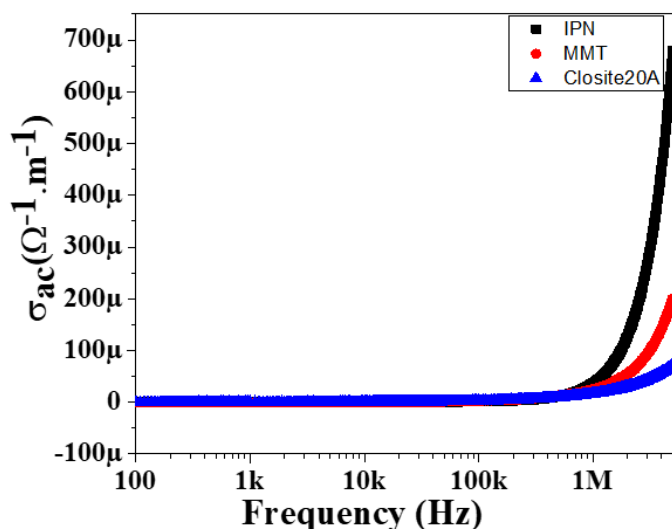


Figure 7: σ_{ac} ($\Omega^{-1} \cdot m^{-1}$) vs. Applied Electric Field profile of filler MMT (Montmorillonite clay) & Closite 20A modified PU-PS IPNs

It has been clearly seen in micrographs of TEM, SEM & AFM that filler (Platelets of MMT (K-10 Montmorillonite clay) & Closite 20A clay platelets) have been uniformly distributed in exfoliation form. Role of filler MMT (K-10 Montmorillonite clay) & Closite 20A clay platelets) in improvement in mechanical properties of modified nanocomposites has been studied from Tensile Strength and Elongation at break. The values of tensile strength, elongation at break and thickness of dumbbell shaped sheets of MMT (K-10 Montmorillonite clay) & Closite 20A modified PU/PS interpenetrating polymer network have been tabled in Table 1 & 2 given below. The variation of Tensile strength and elongation at break vs. Concentration of filler (wt%) has been shown in figure 8 given below. It has been clearly seen in table that Closite 20A modified PU/PS IPN nanocomposites shows elongation at break first increases from 61.8% to 98.8% from pure PU/PS IPN to 2%wt modified PU/PS with Closite 20A filler and then decreases whereas in case of K-10 MMT clay modified PU/PS IPN nanocomposites, it increases from 30.6% to 70.2% for 2%wt. whereas for K-10 MMT modified PU/PS IPN as well as Closite 20A modified PU/PS IPN nanocomposites the maximum value of elongation at break as well as tensile strength has been achieved up to $x = 3\%$ wt of K-10 MMT distributed in PU/PS IPN. The tensile strength increases from 61.8% to 72 % for Closite 20A modified PU/PS IPN nanocomposites whereas in case of K-10 MMT modified PU/PS IPN nanocomposites, tensile strength increases from 18% to 75% with 3wt% to 5wt% modified PU/PS IPN nanocomposites. It has been concluded that distribution of clay platelet in matrix of uniformly and exfoliation can be achieved up to 2%wt modification of Closite 20A whereas similar increased mechanical strength as well as elongation at break can be enhanced with 3%wt of K-10 MMT modified PU/PS IPN nanocomposites. The reason for increase in tensile strength and Elongation at break is due to the exfoliation of clay platelets in nanocomposites and chain interconnectivity generated by clay platelets and further decrease in tensile strength and Elongation at break of PU/P-closite 20A clay nanocomposite with further addition of clay is due to plastic deformation of the clay matrix or the uneven distribution and the clustering of the clay platelets at certain places due to increase in the viscosity in the polymer matrix. The non-homogeneous mixing due to increase of the viscosity of polymer matrix is also the one of the reason for decreases in the tensile strength and elongation at break for increase in clay percentage by weight. The similar trend is shown in Tensile Strength from 29 to 75 from nanocomposites without clay and nanocomposites with 3% clay by weight. The reason for increase in tensile strength and Elongation at break can be due to the exfoliation of clay platelets in nanocomposites and chain interconnectivity generated by clay platelets and further decrease in tensile strength and elongation at break with further increase in clay weight percentage indicates the plastic deformation of matrix and due to agglomeration of clay platelets.

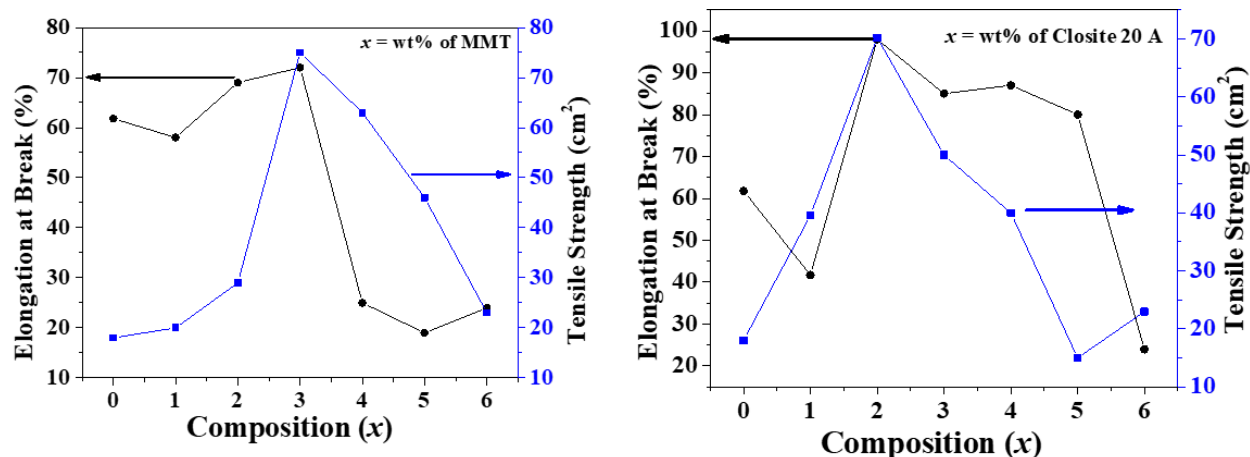


Figure 8: Tensile Strength and Elongation at Break vs. Composition (x) of Filler MMT (K-10 Montmorillonite clay) & Closite 20 a Clay Platelet modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

Table 1: Tensile Strength and Elongation at Break vs. Composition (x) of Filler (Closite 20 Clay Platelet) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

Clay wt% (x)	Thickness (mm)	Elongation at Break (%)	Tensile Strength (KG/CM ²)
0	2.3	61.8	30.6
1	2.6	41.7	39.6
2	2.35	98	70.2
3	1.45	85	50
4	2.2	87	40
5	3.0	80	15

Table 2: Tensile Strength and Elongation at Break vs. Composition (x) of Filler MMT (K-10 Montmorillonite clay Platelet) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

Clay wt% (x)	Thickness (mm)	Elongation at Break (%)	Tensile Strength (KG/CM ²)
0	2.8	61.8	18
1	3.5	58	20
2	4.2	69	29
3	3.8	72	75
4	4.0	25	63
5	2.75	19	46
6	4.0	24	23

Surface hardness is a measure of is a resistance of indentation. Surface hardness indicates the degree of compatibility and cross linking density. Surface hardness test was conducted for neat PU/PS and up to 5% by weight of clay filled with the help of shore A hardness. The table given above gives the value of shore A hardness no. of the neat PU/PS IPN and MMT (K-10 Montmorillonite clay) & Closite 20A Clay filled PU/PS nanocomposites from 1 percentage by weight to 5 percentages by weight of MMT (K-10 Montmorillonite clay) & Closite 20A Clay filled. The increase in the hardness by nano or micro fillers is due to random dispersion of filler in polymer matrix and interaction between the filler particles and polymer matrix results in complete dispersion up to exfoliation level of clay in polymer chain and the nano filler(clay) galleries influences the chemical structure of polymer chains. From table 3, it seems that there is increase in surface

hardness from 58-95 shore A after the dispersion of Closite 20A clay. The clay strictly restricts the indentation and increases the surfaces hardness of composites.

Whereas from table 4, it seems that there is increase in surface hardness from 48-90 shore A after the dispersion of K-10 MMT clay by weight percentage from 1%-5%. The clay strictly restricts the indentation and increases the surfaces hardness of composites.

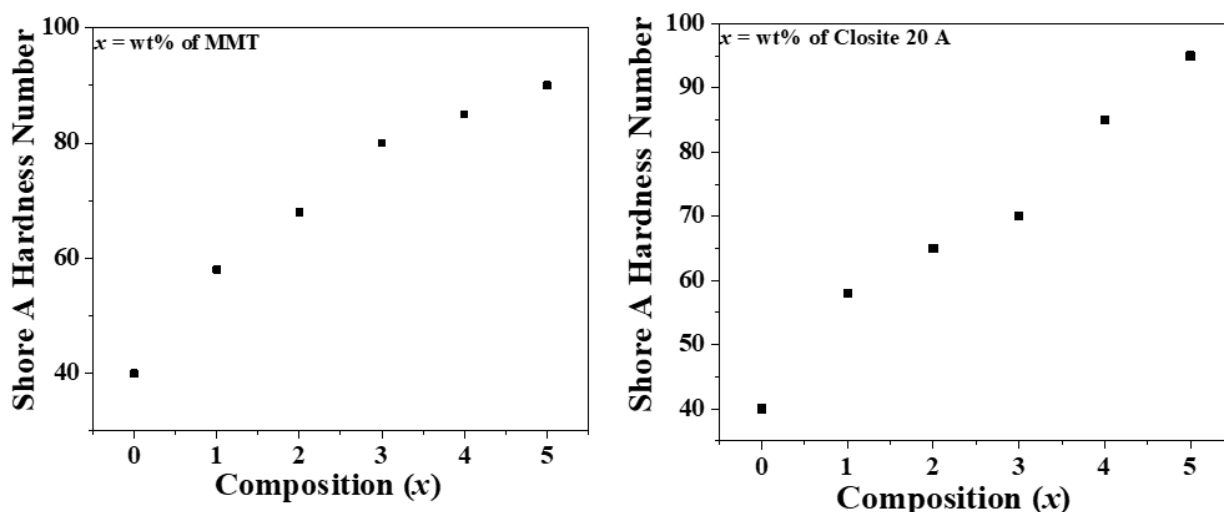


Figure 9: Shore A Hardness Number vs. Composition (x) of Filler (K-10 MMT Clay & Closite 20 A Clay Platelet) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

Table 3: Shore A Hardness Number vs. Composition (x) of Filler (Closite 20 A Clay Platelet) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

Clay%	Shore A hardness number
0	40
1	58
2	65
3	70
4	85
5	95

Table 4: Shore A Hardness Number vs. Composition (x) of Filler (K-10 MMT Clay) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

CLAY %	Shore A Hardness No
0	40
1	58
2	68
3	80
4	85
5	90

The confirmation of various types of bonds appears in filler (Platelets of K-10 MMT Clay and Closite 20A) modified PU/PS IPN nanocomposites have been investigated using FTIR spectroscopy and shown in figure given below. The Transmittance vs. Wave Number spectra of filler (Platelets of K-10 MMT Clay and Closite 20A) modified PU/PS IPN nanocomposites shown in figure. The peak at 3738.88 cm^{-1} corresponds the presence of -OH bonds of PU/PS IPN nanocomposites whereas 3333.22 cm^{-1} confirms Si-OH bond and stretching of -OH . The free urethane carbonyl stretching C=O appears as peaks in range of wavenumber $1740\text{-}1180\text{ cm}^{-1}$. The bands ranging from $1360\text{-}1180\text{ cm}^{-1}$ are due to the presence of C-N stretching. The band at $1047.2\text{-}1050.2\text{ cm}^{-1}$ corresponds to Si-O-Si stretching. The peaks ranging from $2963.62\text{-}2926.59\text{ cm}^{-1}$ is due to -NH stretching without H-bonding. The band at $2855.66\text{-}2854.59\text{ cm}^{-1}$ range due asymmetric and symmetric vibration of methylene group(CH_2) of the aliphatic carbon chains. The peaks in range 1740.76-

1728.02 cm^{-1} are due to free urethane carbonyl $\text{C}=\text{O}$ stretching. The bands ranging from 1360-1180 are due to the presence of C-N stretching. The band at 1047.2-1050.2 corresponds to Si-O-Si stretching whereas in case of K-10 MMT clay modified PU/PS IPN nanocomposites, band at 4000-3500 cm^{-1} range corresponds to -OH stretching vibration from either water or hydroxyl terminated compounds and silicates and -NH stretching vibration either from urea or amine group. The absorption peaks in FTIR spectra at band range from 3350.68- 3331.92 are due to the N-H stretching without H-bonding. The peaks at 3633.1-3394 are due to the Si-O and -OH stretching.

Table 5: Transmittance vs. Wave Number (Cm^{-1}) of Filler (K-10 MMT Clay & Cloisite 20 A) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

Wave Number (Cm^{-1})	Cloisite 20 A Modified PU/PS IPN	Wave Number (Cm^{-1})	K-10 MMT Modified PU/PS IPN
4000-3500	O-H Stretching vibration from either water or hydroxyl terminated compounds and silicates &N-H stretching vibrations from either urea or amine group.[40]	4000-3500	O-H Stretching vibration from either water or hydroxyl terminated compounds and silicates &N-H stretching vibrations from either urea or amine group.[27]
3328.88	Si-OH stretching[41]	3328.88	Si-OH stretching
3350.68-3331.92	Due to the N-H stretching without -H bonding.[41]	3350.68-3331.92	Due to the N-H stretching without -H bonding.[28]
2963.62-2926.59	Due to asymmetric and symmetric vibration of methylene group(CH_2) of aliphatic carbon chain[42]	2963.62-2926.59	Due to asymmetric and symmetric vibration of methylene group(CH_2) of aliphatic carbon chain[28]
2855.66-2854.59	Due to asymmetric and symmetric vibration of methylene group(CH_2) of aliphatic carbon chain[42]	2855.66-2854.59	Due to asymmetric and symmetric vibration of methylene group(CH_2) of aliphatic carbon chain[28]
1740.76-1728.02	Due to free urethane carbonyl $\text{C}=\text{O}$ stretching[41]	1740.76-1728.02	Due to free urethane carbonyl $\text{C}=\text{O}$ stretching[29]
1596.7-1579.4	$\text{C}=\text{O}$ stretching[42]	1596.7-1579.4	$\text{C}=\text{O}$ stretching
1460.1-1458	$-\text{CH}_2$ stretching	1460.1-1458	$-\text{CH}_2$ stretching
1360-1180	Due to the presence of carbon-nitrogen bond stretching[43]	1360-1180	Due to the presence of carbon-nitrogen bond stretching[30]
1050-1047.2	Si-O-Si stretching	1050-1047.2	Si-O-Si stretching
4000-3500	O-H Stretching vibration from either water or hydroxyl terminated compounds and silicates &N-H stretching vibrations from either urea or amine group.[40]	4000-3500	O-H Stretching vibration from either water or hydroxyl terminated compounds and silicates &N-H stretching vibrations from either urea or amine group.[27]

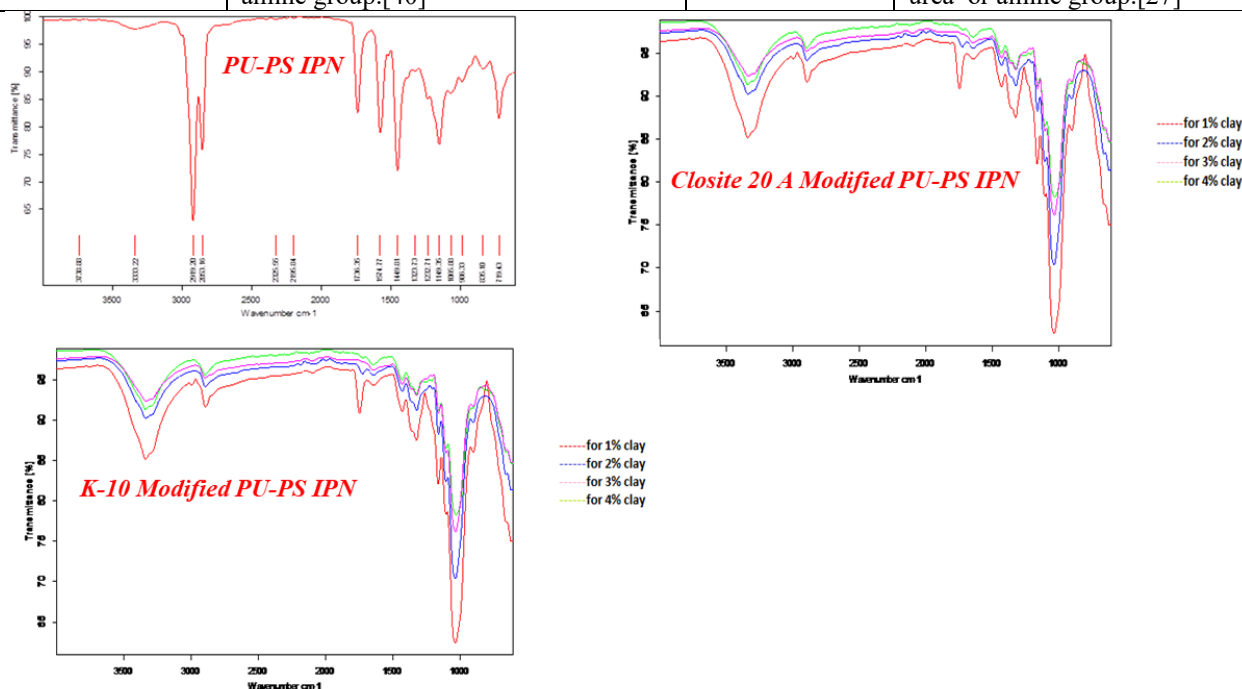


Figure 10: Shore A Hardness Number vs. Composition (x) of Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) modified PU/PS Interpenetrating Polymer Network Sheets of Nanocomposites

CONCLUSION:

Flexible Sheets of PU/PS IPN- Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) have been successfully prepared using In-situ polymerization PU/PS along with Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet). The X-ray diffraction data as well as FTIR spectra confirms presence of Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) in matrix of IPN. The magnetic hysteresis shows non-magnetic nature of Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) modified PU/PS also confirms presence Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) as organic filler in PU/PS matrix. The low value of dielectric properties also results due to presence of Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet) in matrix of PU/PS IPN. The increment in elongation at break directly reveals enhancement in mechanical properties with simultaneous magnetic behavior of PU/PS incorporated with Filler (K-10 MMT Clay & Cloisite 20 A Clay Platelet). The bonding analysis has been confirmed presence of bonds due to Carbon and Silicon which are essential parts of oil based polymer (PU/PS IPN) modified with organoclay.

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