SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE NANOPARTICLES AND THEIR NANOCOMPOSITES WITH POLYPROPYLENE

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SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE NANOPARTICLES AND THEIR NANOCOMPOSITES WITH POLYPROPYLENE

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE NANOPARTICLES AND THEIR NANOCOMPOSITES WITH POLYPROPYLENE

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Conducting polypyrrole (PPy) nanoparticles were synthesized via microemulsion polymerization system. The characterization of PPy nanoparticles was done by Fourier transform infrared spectrometer (FTIR) and scanning electron microscope (SEM). Nanocomposites were prepared by melt-mixing of polypyrrole with polypropylene (PP) and processed with injection molding. The amount of PPy in nanocomposites varied in the range of 1-20% by weight. The effect of PPy nanoparticles on mechanical, electrical properties and thermal stability of nanocomposites were investigated. Tensile test has revealed that increasing amount of PPy increased the strength and the stiffness of the nanocomposite while limiting the elongation of PP. Thermal gravimetric analysis has showed that incorporation of PPy nanoparticles has improved the thermal stability of the nanocomposites. Four probe conductivity measurement has exhibited that increasing amount of PPy nanoparticles increases the conductivity of nonconductive PP up to $2{,}4.10^{-4}$ Scm^{-1}. In order to improve the dispersion of PPy in PP, sodium dodecylsulphate was used as dispersant. The same techniques were used to characterize nanocomposites containing 2% by weight dispersant. Composites prepared with dispersant have exhibited improvement in some mechanical and thermal properties and involved smaller dimension PPy nanoparticles.

Keywords: Conducting polymers, polypyrrole, nanocomposite.

ÖZ

POLİPİROL NANOPARÇACIKLARININ VE POLİPROPİLENLE NANOKOMPOZİTLERİNİN SENTEZİ VE KARAKTERİZASYONU

Baytekin, Sevil
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İletken polipirol nanoparçacıkları mikroemülsiyon polimerizasyon sistemi ile sentezlenmiştir. Polipirol nanoparçacıklarının karakterizasyonu Fourier Transform kızılötesi spektroskopisi ve taramalı elektron mikroskobu ile yapılmıştır. Nanokompozitler polipirol ile polipropilenin eriterek karıştırma yöntemi ile hazırlanmış ve enjeksiyonlu kalıplama ile şekillendirilmiştir. Nanokompozitlerin içinde polipirol miktarı ağırlıkça 1-20% aralığında değiştirilmiştir. Polipirol nanoparçacıklarının nanokompozitlerin mekanik, elektriksel özelliklerine ve ısıl dayanıklılıklarına etkisi incelenmiştir. Çekme testi, artan polipirol nanoparçacık miktarının polipropilenin dayanımını ve sertliğini arttırırken yüzde uzamasını düşürdüğünü göstermiştir. Isıl gravimetrik analiz, eklenen polipirol nanoparçacıklarının nankompozitlerin ısıl dayanıklılığını arttırdığını ortaya çıkarmıştır. Dört nokta iletkenlik ölçümü, artan polipirol miktarının yalıtkan olan polipropilenin iletkenliğini $2,4.10^{-4}$ Scm^{-1}'e kadar arttırdığını göstermiştir. Polipirolün polipropilen içindeki dağılımını iyileştirmek için sodyum dodesilsülfat dağıtıcı olarak eklenmiştir. Ağırlıkça 2% dağıtıcı içeren nanokompozitleri karakterize etmek için aynı teknikler kullanılmıştır. Dağıtıcı ile hazırlanan kompozitler bazı mekanik ve ısıl özelliklerde iyileşme sergilemekte ve daha küçük boyutlu polipirol nanoparçacıklar içermektedir.

Anahtar kelimeler: İletken polimerler, polipirol, nanokompozit.

To My Family

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LIST OF ABBREVIATIONS

PP : Polypropylene
PPy : Polypyrrole
SDS : Sodium dodecylsulphate
FTIR : Fourier Transform Infrared Spectroscope
TGA : Thermal Gravimetric Analysis
SEM : Scanning Electron Microscope

CHAPTER 1

INTRODUCTION

1.1 History of Conducting Polymers

Historically, polymers have been considered as insulators and found application areas due to their insulating properties. Infact, so far, any electrical conduction in polymers which is generally due to loosely bound ions was mostly regarded as an undesirable fact [1]. However, emerging as one of the most important materials in the twentieth century, the use of polymers move from primarily passive materials such as coatings and containers to active materials with useful optical, electronic, energy storage and mechanical properties. Indeed, discovery and study of conducting polymers have already started this development [1,3]. Electrically conducting polymers are defined as materials with an extended system of conjugatedcarbon-carbon double bonds (Figure 1.1) [4]. They are synthesized either by reduction or oxidation reaction, which is called doping process, giving materials with electrical conductivities up to 10^5 S/cm. Conducting polymers are different from polymers filled with carbon black or metals, since the latter are only conductive if the individual conductive particles are mutually in contact and form a coherent phase [5].

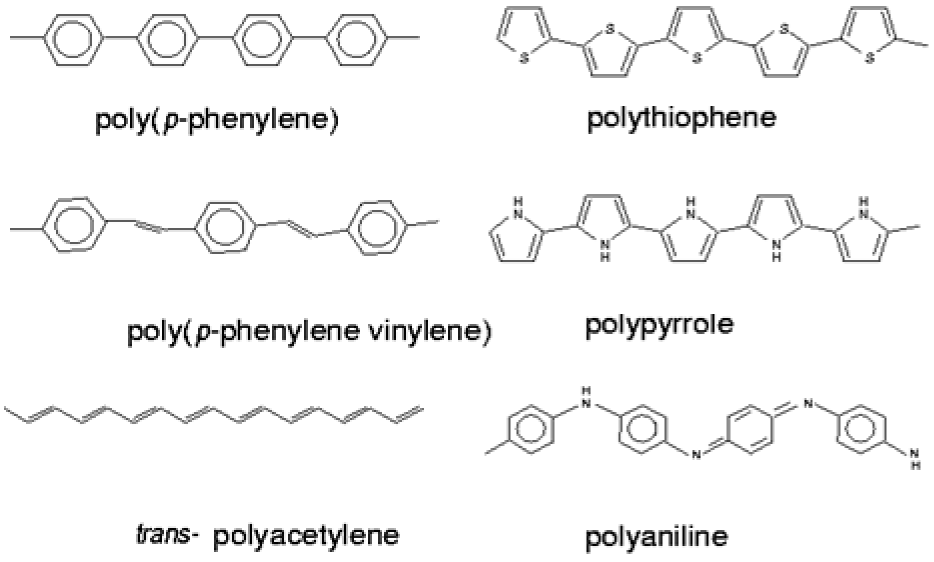


Figure 1.1 Some examples for conducting polymers

Although conducting polymers are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteeth century. In 1862, Henry Letheby prepared polyaniline by anodic oxidation of aniline, which was conductive and showed electrochromic behaviour. However, electronic properties of so called aniline black were not determined [1,3].

In 1958, Natta et al. synthesized polyacetylene as a black powder which was found to be a semiconductor with conductivity in the range of 10^{-11} to 10^{-3} S/cm, depending on the process conditions of the polymer [1]. In 1977, drawing attention on “conducting polymers”, the first intrinsic electrically conducting organic polymer, doped polyacetylene, was reported. Intrinsically conducting polymers are a different class of materials than conducting polymers, which are a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder [2].

The preparation of polyacetylene by Sirakawa and coworkers and the discovery of the large increase in its conductivity after “doping” by the group led by MacDiarmid and Heeger actually launched this new field of research [3].

Electronically conducting polymers possess a variety of properties related to their electrochemical behaviour and are therefore active materials whose properties can be altered as a function of their electrochemical potential. The importance and potential impact of this new class of material was recognized by the world scientific community when Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid were awarded the Nobel Prize in Chemistry in 2000 “for the discovery and development of electronically conductive polymers” [1,3].

1.2 Applications of Conducting Polymers

Electronic industry has been meeting its demand for electrically conducting polymers by using high loadings of conductive powders such as silver, gold and graphite sometimes as high as 80% by weight with the polymer matrix. However, there are numerous disadvantages of this such as high cost and deterioation in other properties of the polymer. Polyaniline, polypyrrole and polythiophene are examples of intrinsically conducting polymers that have been intensively studied during the last decade due to their high electrical conductivity and good environmental stability.

Polypyrole has drawn attention due to its high conductivity, simple preparation, stability and good mechanical properties. It has been found to have many potential applications in electronic and electrochromic devices, light-weight batteries, membrane separation, sensors, and chromatographic stationary phases [7]. There are other potential application areas of polypyrrole such as drug delivery, rechargable batteries, supercapacitors, anhydrous electrorheological fluids, microwave shielding and corrosion protection [26].

The improvement of mechanical properties of conducting polymers has increased their potential for commercial applications. One of the immediate applications of the conducting polymers is in electrostatic protection and electromagnetic interference (EMI) shielding. In the last few decades, due to their reasonably high environmental stability and electrical conductivity, the synthesis of polyheterocyclic polymers, such as polypyrrole (PPy) and polythiophene (PPt), has received a great deal of attention. However, these polymers tend to be insoluble and infusible. Inclusion of conducting polymer in the matrix of a mechanically strong insulating polymer has emerged as a useful approach to press these conducting polymers into useful and large articles. Although chemically prepared polyheterocyclic polymers are of poor quality and low electroconductivity compared with electrochemically prepared polyheterocyclic polymers, there are several advantages of the chemical oxidative polymerization such as simple preparation procedures, short reaction times, and mass production [2].

1.3 Principles of Electrical Conduction

1.3.1 Band Theory

The electronic properties of any material are established by its electronic structure. The most reasonable explanation of electronic structure of materials is achieved by the band theory. According to quantum mechanism the electrons of an atom can only have specific or quantized energy levels. However, in the lattice of a crystal, where the atoms are closely spaced, the energy levels form bands. The highest occupied electronic levels constitute the valence band and the lowest unoccupied levels constitute the conduction band. Depending on how the bands are filled, the electrical properties of conventional materials are determined. When bands are completely filled or empty no conduction is observed. If the band gap is narrow, at room temperature, thermal excitation of electrons from valence band to conduction band gives rise to conductivity which is the case of classical semiconductors. When the band gap is wide, thermal energy at room temperature is insufficient to excite electrons across the gap and the solid is an insulator. In conductors, there is no band gap since the valence band overlaps the conduction band and hence their high conductivity (Figure 1.2) [1].

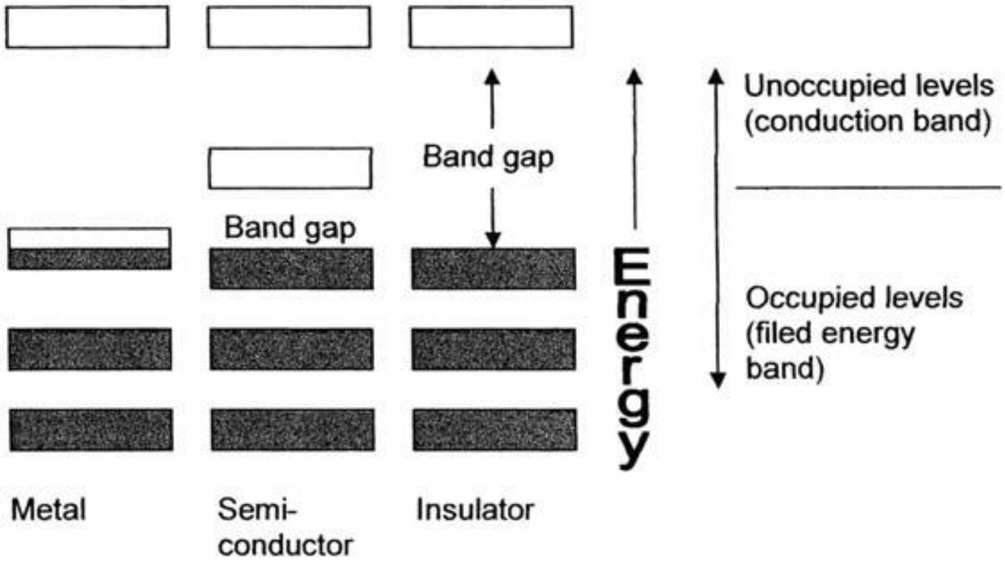


Figure 1.2 Band theory

1.3.2 Doping Process

Doping process is basically the process that transforms insulating polymers (e.g., polyacetylene, conductivity 0.1 S/cm) to excellent conductors (Figure 1.3) [8]. Doping is achieved by formation of charge-transfer complexes by electron donors such as sodium or potassium (n doping, reduction) or by electron acceptors such as I_2, AsF_5, or $FeCl_3$ (p doping, oxidation). As a result of the process the doped polymer backbone becomes negatively or positively charged with the dopant forming oppositely charged ions (Na^+, K^+, I^{3-} , I^{5-} , AsF^{6-}, $FeCl^{4-}$). Application of an electric potential results in motion of counterions in and out which enables to switch the polymer between the doped, conductive state and the undoped, insulating state (Figure 1.4) [5].

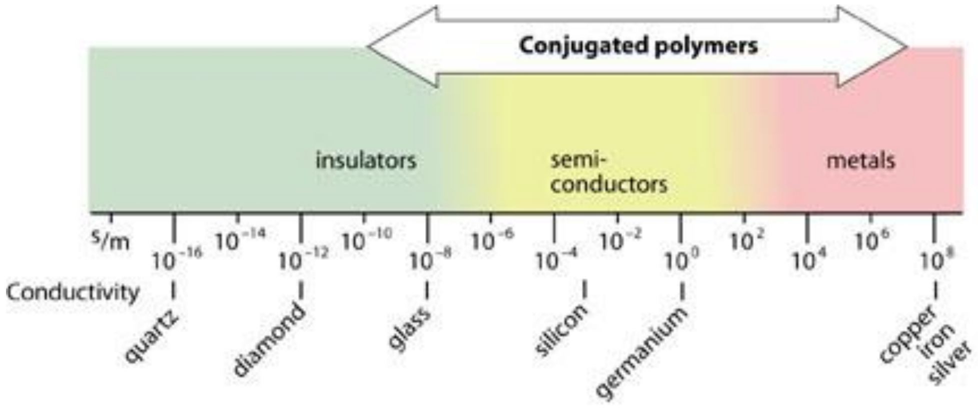


Figure 1.3 Conductivities of insulator, semi-conductors, metals and conjugated polymers

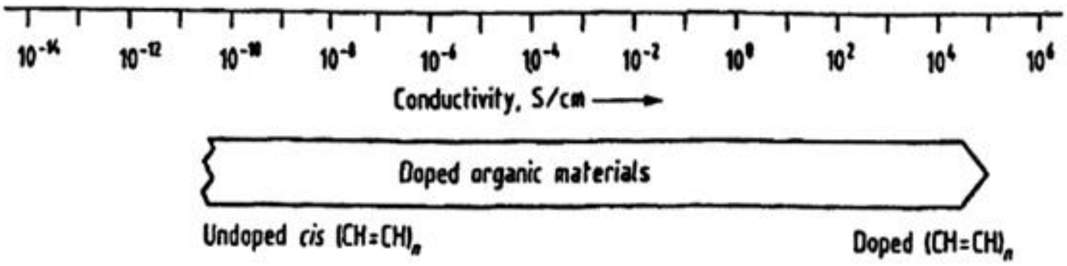


Figure 1.4 Conductivity of doped and undoped organic materials

1.3.3 Polaron and Bipolaron Model

The band theory is insufficient to explain the electrical conduction in electrically conducting organic materials such as polyphenylene, polyacetylene or polypyrrole where the charge-carrying species (electrons or holes) are spinless. Although the mechanism is not fully understood, conduction by polarons and bipolarons is now thought to be the dominant mechanism of charge transport in organic materials. This concept is also used for explanation of the drastic deepening of color changes produced by doping. A polaron which is a term used in solid-state physics is defined as a radical cation that is partially delocalized over several monomer units (e.g. in a polymer segment) where a bipolaron is a diradical dication. Doping level determines formation of polaron and bipolarons. Low doping levels gives rise to polarons, whereas higher doping levels produce bipolarons. Both polarons and bipolarons are mobile and can move along the polymer chain [5].

In order to explain the doping process, the oxidative doping of polypyrrole is described in Figure 1.5. The process begins when an electron is removed from the p-system of the backbone by the dopant producing free radical and a spinless positive charge. Due to local resonance of the charge and the radical, the radical and cation are coupled to each other. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates a new localized electronic states in the gap, with the lower energy states being occupied by a single unpaired electrons. The polaron state of polypyrrole are symmetrically located about 0.5 eV from the band edges. Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons. At higher doping levels it becomes possible that two polarons combine to form a bipolaron. Thus at higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV in the case of polypyrrole [9].

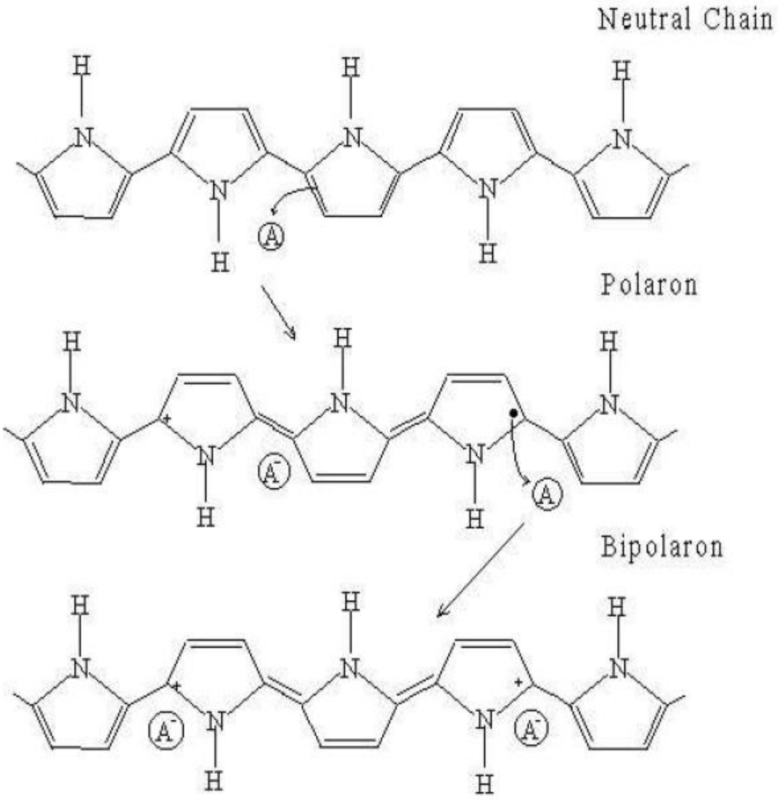


Figure 1.5 Oxidative doping of polypyrrole

Continuous doping eventually forms continuous bipolaron bands. Their band gap also increases as newly formed bipolarons are made at the expense of the band edges. For a very heavily doped polymer the upper and the lower bipolaron bands merge with the conduction and the valence bands respectively to produce partially filled bands and metallic like conductivity (Figure 1.6) [9].

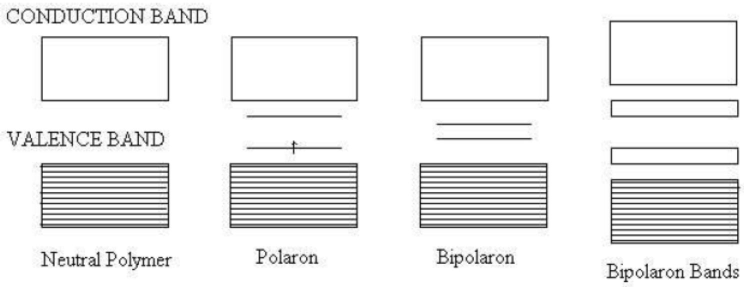


Figure 1.6 Band theory of conducting polymers

1.4 Composites

A composite is defined as a material created by combination of two or more components namely, a selected filler or reinforcing agent and a compatible matrix binder. The combination of these component results in formation of a new material with specific characteristics and properties. The synthetic assemblage of the components does not occur as a dissolvation but rather like merging into each other to act in concert. Although the components act together as a single material, both the components and the interface between them can usually be physically identified. Genarally, the behaviour and the properties of the composite is controlled by the interface of the components. Since the composite is a totally new material having new and specific characteristics, its properties cannot be achieved by any of its components acting alone.

The classification of composites can be done in different ways. The composites can be classified on the basis of the form of their structural components: (i) fibrous where the composite is composed of fibers in a matrix, (ii) laminar where the composite is composed of layers in a matrix, and (iii) particulate where the composite is composed of particles in a matrix [10].

Another type of classification can be done on the basis of filler or reinforcing agent used namely polymer matrix composites (PMCs), metal matrix composites (MMCs), ceramic matrix composites (CMCs), carbon-carbon matrix composites (CCCs), intermetallic composites (IMCs), or hybrid composites [11].

1.4.1 Polymer Matrix Composites

Composite materials have been utilized to solve technological problems for a long time. In 1960s with the introduction of polymeric-based composites, composites start capturing the attention of industries. Since then, composite materials have become common engineering materials. They are designed and manufactured for various applications including automotive components, sporting goods, aerospace parts, consumer goods, and in the marine and oil industries. Increasing awareness of product performance and competition in the global market for lightweight components also supported the growth in composite usage. Among all materials, composite materials have the potential to replace widely used steel and aluminum, and many times with better performance. Replacing steel components with composite components can save 60 to 80% in component weight, and 20 to 50% weight by replacing aluminum parts. Today, it appears that composites are the materials of choice for many engineering applications.

The matrix material used in polymer-based composites can either be thermoset (epoxies, phenolics) or thermoplastic resins (low density polyethylene, high density polyethylene, polypropylene, nylon, acrylics). The filler or reinforcing agent can be choosen according to the desired properties. The properties of polymer matrix composites are determined by properties, orientation and concentration of fibers and properties of matrix.

The matrix has various functions such as providing rigidity, shaping the structure by transfering the load to fiber, isolating the fiber to stop or slow the propagation of crack, providing protection to reinforcing fibers against chemical attack and mechanical damage (wear), and affecting the performance characteristics such as ductility, impact strength, etc. depending on its type. The failure mode is strongly affected by the type of matrix material used in the composite as well as its compatibility with the fiber. The important functions of fibers include carrying the load, providing stiffness, strength, thermal stability, and other structural properties in the composites and providing electrical conductivity or insulation, depending on the type of fiber used [12].

1.4.2 Composites of polypyrrole

Maria Omastova and Ivan Chodak prepared conductive polypropylene/polypyrrole composites using the method of chemically initiated oxidative modification of polypropylene particles in suspension by pyrrole. In order to prepare the composite, polypropylene particles were dispersed in water-methanol mixture and $FeCl_3$ was added to be used for chemical oxidation. Addition of pyrrole started formation of polypyrrole particles in polypropylene suspension. The electrical and rheological properties of the composite were compared with polypropylene/polypyrrole composite prepared by melt mixing of pure polypropylene with chemically synthesized polypyrrole and with polypropylene/carbon black composites also prepared by melt mixing. Elemental analysis verified presence of polypyrrole in polypropylene matrix. The conductivity studies show that even a very small PPy amount present in composites results in a significant increase in conductivity. Processing conditions are observed to have a great effect on electrical conductivites of composites. The composite prepared by sintering PP particles covered with PPy shows about 7 orders of magnitude higher conductivity than the composite prepared by melt mixing of pure polypropylene with chemically synthesized polypyrrole whereas the conductivity of sintered PP/PPy composites is comparable to that of PP/Carbon black composite. The PP/CB and injection molded PP/PPy composites exhibit similar flow properties. However, for compresion molded PP/PPy composites a considerable increase of complex viscosity was observed [13].

Jürgen Pionteck and Maria Omastova prepared an electrical-conducting polypropylene/polypyrrole (PP/PPy) composite by chemical oxidative modification reaction of pyrrole on the surface of PP particles in suspension. For comparison, another type of composite was prepared by mixing coated PP particles with noncoated PP particles. Both composites were processed with injection and compresion molding. Beter mechanical properties were achieved by injection molded composites compared to that of compression molded ones. However, compression molded composites exhibit beter antistatic behaviour and electrical conductivity. XPS studies proved that the PP in the PP/PPy powder is almost totally covered with PPy. Prevention of the outflow of PP melt by PPy layer as heating to 200˚C without shear was proved by hot-stage optical microscopy studies. The investigation of mechanical properties and melt viscosities of PP/PPy composites shows that PPy structure was almost completely destroyed by injection molding whereas compression molded composites exhibits presence of PPy networklike structure [14].

Miroslava Mravcakova and Maria Omastova prepared polypropylene/montmorillonite/polypyrrole (PP/MMT/PPY) composites by oxidative polymerization of pyrrole in the presence of dispersed polypropylene and montmorillonite particles in aqueous solution of an anionic surfctant, dodecylbenzenesulfonic acis (DBSA), or in water/methanol solution. The composites are compared with PP/PPy blends prepared by melt mixing. WAXS study showed the intercalation of PPy into galleries of MMT in PP/MMT/PPy composites. Rheology and conductivity studies showed that using DBSA as surfactant during PPy polymerization changed the gallery structure of MMT and stabilized the structure also during following processes. The conductivity of compression molded PP/MMT/PPy composites were found to be 10^{-5} Scm^{-1} already at 4,8% PPy content. However, due to destruction of the conductive shell of PPy particles during melt mixing, the PP/PPy blends exhibited lower conductivity [15].

Feifeng He and Mitsuru Omoto prepared conductive polypyrrole/polyurethane composite foam by vapor phase polymerization of pyrrole on polyurethne foam. $FeCl_2$ and $FeCl_3$ were used as oxidants. The study showed that increasing $FeCl_2/FeCl_3$ ratio results in increasing conductivity despite decreasing polypyrole content. The result was explained as indication of higher density or structurally different PPy formation from those obtained by $FeCl_3$ alone. Low contents of PPy in the composite is also pointed out as an advantage for the mechanical propeties of the composite foam. It is concluded that the mixtures of the two iron chlorides are preferable to $FeCl_3$ as oxidants for preparation of highly coductive composite foam. Also, it has been reported that lower reaction temperatures were preferable for higher conductivity. Regarding the mechanical properties, it is reported that the tensile strength and elongation of composite foam is comparable to those of pristine polurethane foam [16].

1.5 Nanocomposites

Nanomaterials and nanocomposites have always existed in nature and have been used for centuries. However, it is only recently that characterization and control of structure at nanoscale have drawn intense interest for research and these materials start to represent new and exciting fields in material science. A nanocomposite is defined as a composite material where at least one of the dimensions of one of its constituents is on the nanometer size scale [4]. In other words, nanocomposites can be considered as solid structures with nanometer-scale dimensional repeat distances between the different phases that constitute the structure. These materials typically consist of an inorganic (host) solid containing and an organic component or vice versa. They can consist of two or more inorganic/organic phases in some combinational form that at least one of the phases or features is in the nanosize.

In general, nanocomposite materials can exhibit different mechanical, electrical, optical, electrochemical, catalytic, and structural properties than those of each individual component. The multifunctional behavior for any specific property of the material is often more than the sum of the individual components [17].

1.5.1 Polymer-based and Polymer-filled Nanocomposites

In recent years, the limits of optimizing composite properties of traditional micrometer-scale composite fillers have been reached due to the compromises of the obtained properties. Stiffness is traded for toughness, or toughness is obtained at the cost of optical clarity. In addition, regions of high or low volume fraction of filler often results in macroscopic defects which lead to breakdown or failure of the material. Recently, a new resarch area has provided the opportunity to overcome the limitations of traditional micrometer-scale polymer composites. This new investigation area is the nanoscale filled polymer composites where the filler is <100 nm in at least one dimension.

Implementation of the novel properties of nanocomposites strongly depends on processing methods that lead to controlled particle size distribution, dispersion, and interfacial interactions. Processing technologies for nanocomposites are different from those for composites with micrometer-scale fillers, and new developments in nanocomposite processing are among the reasons for their recent success.

Nanoscale fillers can be in many shapes and sizes, namely tube, plate-like or 3D particles (Figure 1.7). Fiber or tube fillers have a diameter <100 nm and an aspect ratio of at least 100. The aspect ratios can be as high as 106 (carbon nanotubes). Plate-like nanofillers are layered materials typically with a thickness on the order of 1 nm, but with an aspect ratio in the other two dimensions of at least 25. Three dimensional (3D) nanofillers are relatively equi-axed particles <100 nm in their largest dimension. This is a convenient way to discuss polymer nanocomposites, because the processing methods used and the properties achieved depend strongly on the geometry of the fillers [17].

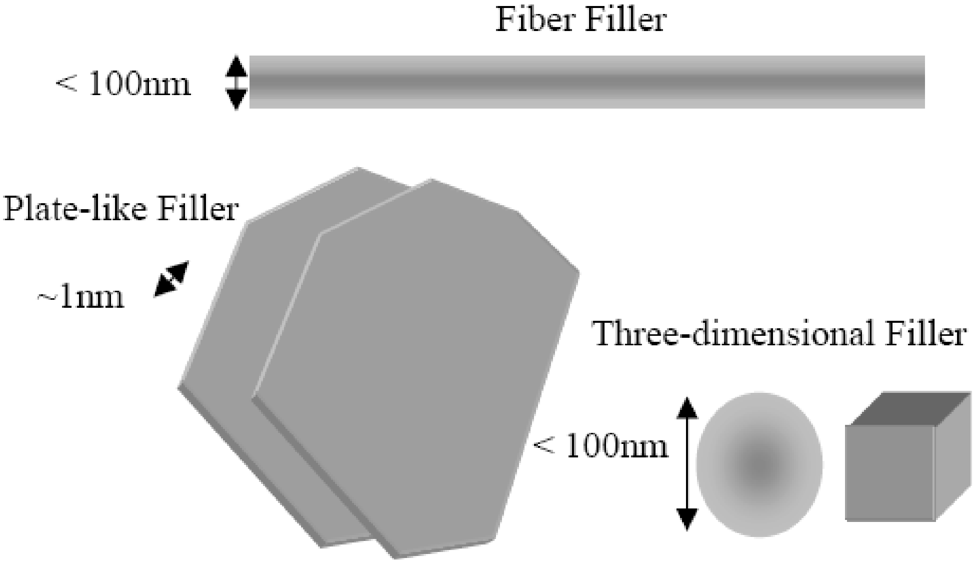


Figure 1.7 Various forms of nanoscale fillers

1.5.2 Nanocomposites of Polypyrrole

Eun Seong Lee and Jae Hyung Park prepared in situ formed procesable polypyrrole nanoparticle/amphiphilic elastomer composites which could have applications in biosenors, semiconductors, artificial muscles, polymeric batteries and electrostatic dissipation due to their processability and considerable conductivities. The polymerization process of pyrrole was achieved by chemical oxidation of the pyrrole monomer by $FeCl_36H_2O$ in the presence of multiblock copolymer dissolved in methanol/water mixture. The multiblock copolymer was used as a stabilizer during polypyrrole synthesis and when cast after removing the dissolved polymers, served as a flexible and elastomeric matrix. The polymerization time, concentration of multiblock copolymer and the oxidant, reaction medium composition were optimized in terms of conductivity measurements and the highest conductivity was reported as

3,0±0,2 Scm^{-1}. Mechanical properties such as tensile strength and elongation at break of the omposites were found to increase with increasing amount of multiblock copolymer [18].

Tzong-Ming Wu and Shiang-Jie Yen have reported synthesis, characterisation and properties of monodispersed magnetic coated multi-walled carbon nanotube/polypyrrole nanocomposites. Fe_3O_4 was used for coating multi-walled carbon nanotube (MWCNT). Fe_3O_4 coated c- MWCNT/PPy nanocomposites were synthesized via the in situ polymerization. The polymerization of pyrrole molecules was achieved on the surfaces of Fe_3O_4 coated c-MWCNT. The comparison of conducitivities have shown that Fe_3O_4 coaed c- MWCNT/PPy nanocomposites have about 4 times higher conductivity that that of pure PPy matrix. Fe_3O_4 coated c-MWCNT/PPy nanocomposites were observed to exhibit ferromagnetic behaviour [19].

Kada Boukerma and Jean-Yves Piquemal prepared montmorillonite/polypyrrole nanocomposites and investigated their interfacial properties. The synthesis of MMT/PPy nanocomposites was achieved by in situ polymerization of pyrrole in the presence of MMT. Scanning electron microscopy results have shown that the surface morpology of the nanocomposites were more like the surface of untreated MMT. X-ray photoelectron spectroscopy (XPS) exhibited that the nanocomposites have MMT-rich surfaces which inicates intercalation of polypyrrole in the host galleries. The increase in interlamellar spacing was measured by transmission electron microscope. Invers gas chromatography measurements showed high surface energy of the nanocomposites [20].

Miroslava Mravcakova and Kada Boukerma prepared montmorillonite/polypyrrole nanoomposites. The effect of organic modificaton of clay on the chemical and electrical properties were studied. The morphology investigations showed that the surface of MMT/PPy has a MMT-rich surface and relatively low conductivity

($3{,}1\times10^{-2}$ Scm^{-1}) indicating intercalation of PPy in the clay galleries. Whereas, the organically modified MMT/PPy nanocomposite has a PPy-rich surface and higher conductivity indicating PPy formation on the surface of MMT. The dispersive contribution of surface energy of o-MMT was measured to be significantly low compared to that of MMT due to the stearly chains from the ammonium chlorides used for organic modification [21].

A.U. Ranaweera and H.M.N Bandara prepared electronically conducting montmorillonite-Cu_2S and montmorillonite-Cu_2S-polypyrrole nanocomposites. MMT-Cu_2S nanocomposite was prepared by cation-exchange approach and its conductivity was measured as $3{,}03\times10^{-4}$ Sm^{-1}. The polymerization of pyrrole was achieved berween the layers of MMT-Cu_2S to obtain MMT-Cu_2S-PPy nanocomposite. The characterisation was performed by XRD, FT-IR anda c impedance measurements. The electronic conductivity was reported as 2,65 Sm^{-1} [22].

Panagiotis Dallas and Dimitrios Niarchos reported interfacial polymerization of pyrrole and in situ synthesis of polypyrrole/silver nanocomposites. The oxidizing agents used were Ag(I) or Fe (III). Depending on using different surfactants (SDS or DTAB) or not using any surfactant, the average diameter of polypyrrole structures was observed to be in the range of 200-300 nm. The electron microscopy images exhibited different morphologies of polypyrrole depending on using various surfactants or not using any as well as the size and shape of the silver nanocomposites. X-ray diffractometry showed amorphous structure of polymers. Further characterization was performed by thermogravinetric analysis and FT-IR spectroscopy [23].

1.6 Nanoparticle/Polymer Composite Processing

There are three general ways of dispersing nanofillers in polymers. The first is direct mixing of the polymer and the nanoparticles either as discrete phases or in solution. The second is in-situ polymerization in the presence of the nanoparticles, and the third is both in-situ formation of the nanoparticles and in-situ polymerization. Due to intimate mixing of the two phases, the latter can result in composites called hybrid nanocomposites [17].

1.6.1 Direct Mixing

Direct mixing is a well known and established polymer processing technique. When these traditional melt-mixing or elastomeric mixing methods are feasible, they are the fastest method for introducing new products to market. Although melt mixing has been successful in many cases, for some polymers, due to rapid viscosity increase with the addition of significant volume fractions of nanofiller, this processing method has limitations. There are many examples showing melt mixing method for composite production and exhibiting some limitations for the process. [17].

1.6.2 Solution Mixing

In solution mixing, in order to overcome the limitations of melt mixing method, both the polymer and the nanoparticles are dissolved or dispersed in solution. This method enables modification of the particle surface without drying, which reduces particle agglomeration. After dissolvation the nanoparticle/polymer solution can be cast into a solid, or solvent evaporation or precipitation methods can be used for isolation of nanoparticle/polymer composite. Conventional techniques can be used for further processing [17].

1.6.3 In-Situ Polymerization

In in-situ polymerization, nanoscale particles are dispersed in the monomer or monomer solution, and the resulting mixture is polymerized by standard polymerization methods. This method provides the opportunity to graft the polymer onto the particle surface. Many different types of nanocomposites have been processed by in-situ polymerization. Some examples for in-situ polymerization are polypyrrole nanoparticle/amphiphilic elastomer composites [18], magnetite coated multi-walled carbon nanotube/polypyrrole nanocomposites [19] and polypyrrole/ silver nanocomposites [23]. The key to in-situ polymerization is appropriate dispersion of the filler in the monomer. This often requires modification of the particle surface because, although dispersion is easier in a liquid than in a viscous melt, the settling process is also more rapid [17].

1.7 Polypyrrole

Among the conjugated polymers, polypyrrole (PPy) is the most representative one for its easy polymerization and wide application in gas sensors, electrochromic devices and batteries. Polypyrrole can be produced in the form of powders, coatings, or films. It is intrinsically conductive, stable and can be quite easily produced also continuously. The preparation of polypyrrole by oxidation of pyrrole dates back to 1888 and by electrochemical polymerization to 1957. However, this organic p-system attracted general interest and was found to be electrically conductive in 1963.

Polypyrrole has a high mechanical and chemical stability and can be produced continuously as flexible film (thickness 80 mm; trade name: Lutamer, BASF) by electrochemical techniques. Conductive polypyrrole films are obtained directly by anodic polymerization of pyrrole in aqueous or organic electrolytes.

Apart from electrochemical routes, polypyrrole can also be synthesized by simple chemical ways to obtain powders. Basically chemical oxidative polymerization methods can be used to sythesize bulk quantities of polypyrrole in a fast and easy way [5].

Like other conducting polymers polypyrrole exhibit more limited environmetal, thermal and chemical stability than conventional inert polymer due to the presence of dopant and its dynamic and electroactive nature [7].

1.7.1 Synthesis of Polypyrrole

Polypyrrole and many of its derivatives can be synthesized via simple chemical or electrochemical methods [14]. Photochemically initiated and enzyme-catalyzed polymerization routes have also been descibed but less developed. Different synthesis routes produce polypyrrole with different forms; chemical oxidations generally produce powders, while electrochemical synthesis leads to films deposited on the working electrode and enzymatic polymerization gives aqueous dispersions [40].

As mentioned above the electrochemical polymerization method is utilized extensively for production of electroactive/conductive films. The film properties can be easily controlled by simply varying the electrolysis conditions such as electrode potential, current density, solvent, and electrolyte. It also enables control of thickness of the polymers. Electrochemical synthesis of polymers is a complex process and various factors such as the nature and concentration of monomer/electrolyte, cell conditions, the solvent, electrode, applied potential and temperature, pH affects the yield and the quality of the film. Thus, optimization of all of the parameters in one experiment is difficult. In contrast, chemical polymerization does not require any special instruments, it is a rather simple and fast process. Chemical polymerization method involves oxidative polymerization of pyrrole monomer by chemical oxidants either in aqueous or non-aqueous solvents or oxidation by chemical vapour deposition in order to produce bulk polypyrrole as fine powders [7].

Iron (III) chloride and water are found to be the best oxidant and solvent for chemical polymerization of pyrrole respectively regarding desirable conductivity characteristics.

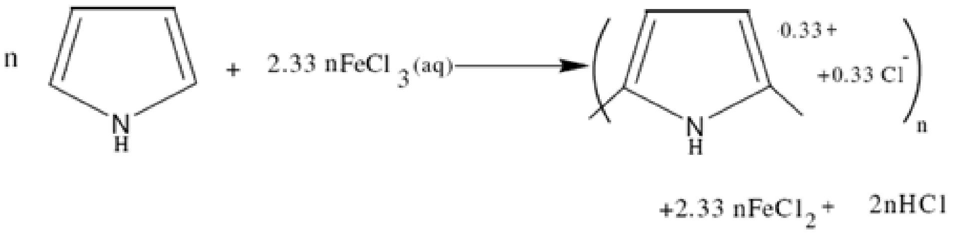


Figure 1.8 Chemical polymerization of polypyrrole

Previous studies have shown that the optimum initial mole ratio of Fe(III)/Pyrrole for polymerization by aqueous iron (III) chloride solution at 19˚C is 2,25 or 2,33. Also, several studies have revealed that factor such as solvent, reaction temperature, time, nature and concentration of oxidizing agent, affect the oxidation potential of the solution which affects the final conductivity of the product [7].

S.Goel and A. Gupta synthesized polypyrrole samples of different nanodimensions and morphologies by time dependent interfacial polymerization reaction. Pure chloroform was used as solvent for pyrrole and ammonium persulphate dissolved in HCl was used as the oxidizing solution. The polymerization occured in the interface of organic and aqueous phases and polypyrrole was formed as thin layer on the interface. Morphology study of polypyrrole nanoparticles was done by scanning electron microsopy and transmission electron microscopy [27].

Yang Liu and Ying Chu synthesized polypyrrole nanoparticles through microemulsion polymerization. Alcohol-assited microemulsion polymerization was performed in order to adjust the inner structure of polypyrrole nanoparticles for polymerization SDS was used as the surfactant, water was used as the solvent and aqueous solution of $NH_4S_2O_8$ was used as the oxidant. Characterisation of polpyrrole was done by FT-IR and morphology study was performed by SEM and TEM [26].

Hongxia Wang and Tong Lin synthesized polypyrrole nanoparticles by oxidation of pyrrole with ferric chloride solution during microemulsion polymerization process. Dodecyltrimethyl ammonium bromide (DTAB) was used as the surfactant. Particle characaterisation was performed by using FTIR, elemental analysis, UV-VIS spectra and SEM. Variation of particle size from about 50 to 100, 100 to 200 nm with the change in surfactant concentration was reported [29].

Xinyu Zhang and Sanjeev K. Manohar synthesized narrow pore-diameter polypyrrole nanotubes. The synthesis was performed by chemical oxidative polymerization of pyrrole using $FeCl_3$ oxidant and V_2O_5 nanofibers as the sacrificial template producing microns long electically conducting polypyrrole nanotubes having 6 nm average pore diameter [30].

M.R. Karim and C.J. Lee synthesized polypyrrole by radiolysis polymerization method. Conducting PPy was synthesized by the in situ gamma radiation-induced chemical oxidative polymerization method. This method was reported to provide a highly uniform polymer morphology [31].

Jyongsik Jang and Joon H. Oh. synthesized polypyrrole nanoparticles via microemulsion polymerization with using various surfactants. Iron (III) chloride was used as the oxidant. the selective fabrication of amorphous polypyrrole nanopartcles as small as 2 nm in diameter using microemulsion polymerization at low temperature was reported [32].

1.8 Microemulsion Polymerization

In general, polymerization in heterogeneous media results in formation of polymer colloids or latexes which are known as dispersions of polymer particles usually in water. The synthesized particles are almost always in the submicron range. The most widely used way for preparation of polymer colloids is certainly emulsion polymerization. The particle size of the latexes produced via emulsion polymerization usually ranges between 0,05 to 0,5 μm. Microemulsions has drawn attention since it enables production of thermodynamically stable latexes in the nanosize range which is not achievable with classical emulsion polymerization. Microlatexes having such characteristics are desirable in certain applications such as drug delivery or microencapsulation. Microemulsions have many interesting properties such as large internal interfacial area, optical transparency, thermodynamic stability, etc. The major difference between emulsion and microemulsions is the amount of surfactant required to stabilize the systems. Much more surfactant is needed for microemulsions since a large internal interfacial area is needed to be stabilized. However, using higher amount of surfactant limits the potential industrial uses of microemulsion polymerization due to cost [38].

Microemulsions can be used for polymerization of all types of structures. There are a number studies reporting synthesis of PPy in microemulsion system. Wang H. et al. have synthesized PPy nanoparticles having an average particle size of 67 nm with the distribution ranging from 7,5 nm to 127,5 nm using various surfactant concentrations and different temperatures. It has been reported that increasing surfactant concentration and decreasing temperature leads to smaller particle size. PPy nanoparticles are formed in micelles and high surfactant concentration leads to smaller micelle dimensions and hence smaller PPy particles. Furthermore, it has been reported that low reaction temperatures results in smaller micelles which limits the growth of large PPy particles and leading to smaller nanoparticles. [29].

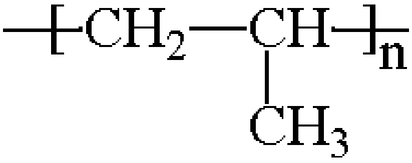
A previous study has shown the effect of using surfactant with different chain lengths using different polymerization temperatures. Surfactants with short carbon chains (hexyltrimethlammonium bromide) have found to be insufficient to form ordered structures due to weak hydrophobic interactions related to C-6 chains. On the other hand, surfactants with hydrocarbon chains longer than C-16 were found to be not suitable for low temperature microemulsion polymerization due to their liquid-crystalline state and high viscosity. The size of nanoparticle decrease with decreasing surfactant chain length. However, the enhanced flexibility of longer chain length leads to more free volume inside micelles and therefore larger particles. Moreover, increasing surfactant concentration has found to decrease the nanoparticle size whereas increasing polmerization temperature leads to increasing nanoparticle size due to enhanced mobility of surfactant chains. [32].

1.9 Polypropylene

Polypropylene (PP) is a thermoplastic material that is produced by polymerization of propylene molecules into very long polymer molecule or chains. There are number of different ways to link the monomers together, but its most widely used form is made with catalysts that produce crystallizable polymer chains. The resulting product is a semicrystalline solid with good physical, mechanical, and thermal properties. Another form of PP produced in much lower volumes as a by product of semicrystalline PP production and having very poor mechanical and thermal properties, is a soft, tacky material used in adhesives, sealants, and caulk products. The above two products are often referred to as “isotactic”(crystallizable) PP (i-PP) and “atactic” (noncrystallizable) PP (-PP), respectively.

The average length of the polymer chains and the breadth of distribution of the polymer chain lengths determines the main properties of PP. In the solid state, the main properties of the PP reflect the type and amount of crystalline and amorphous regions formed from the polymer chains.

Polypropylene has excellent and desirable physical, mechanical and thermal properties when used in room temperature applications. It is relatively stiff and has a high melting point, low density and relatively good resistance to impact [6,28].



$$-\!\!\left[CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} \right]_n$$

Figure 1.9 Structure of polypropylene

1.10 Sodium Dodecysulphate

Sodium dodecylsulphate is a member of sulphates group which is the largest and most important class of synthetic surfactants produced by reaction of an alcohol with sulphuric acid. It is the most common sulphate surfactant (abbreviated as SDS and sometimes referred to as sodium lauryl sulphate) and is extensively used both for fundamental studies as well as in many industrial applications.

Sodium dodecylsulphate is an anionic surfactant which is composed of a hydrophobic linear akyl group with a chain length of 12 carbon atoms as the tail and a hydrohilic sulphate group as the head of the molecule (Figure 1.10) [34]. The negatively charged molecule is neutralized by Na^+ which is called the counter ion.

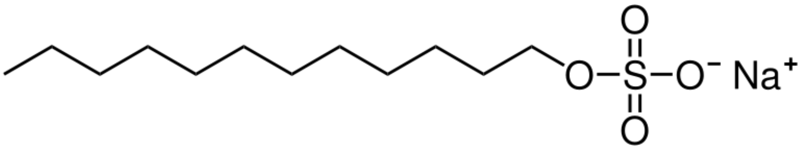


Figure 1.10 Sodium dodecylsulphate

In general the properties of sulphates depend on the nature of alkyl chain and the sulphate group. In the case of sodium dodecylsulphate which is an alkali metal salt, the molecule shows good solubility in water and it tends to be effected by the presence of electrolytes [39].

1.11Aim of This Study

Among conjugated polymers polypyrrole has attracted great interest due to its high conductivity, good thermal and environmental stability and ease of synthesis. However, it is an infusible, inprocessable polymer having relatively poor mechanical properties. On the other hand, polypropylene is a well known insulating thermoplastic with outstanding mechanical properties. In this study, the synergistic assemblage of polypyrrole with polypropylene is investigated. The aims of this study are synthesis of polypyrrole nanoparticles via microemulsion polymerization, preparation of PP/PPy nanocomposites in order to provide some level of processability to infusible and inprocessable PPy while inducing conductivity to insulating PP and preparation of PP/PPy nanocomposites with dispersant in order to improve the dispersion of PPy nanoparticles using identical procedures.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

The materials that have been used are: (i) Pyrrole used as the monomer, purchased from Sigma Aldrich Chemie GmbH. (Table 2.1), distilled under vacuum and stored at 3˚C in refrigerator before use. (ii) Iron(III) chloride hexahydrate, functioned as the oxidant and dopant, was obtained from Emir Kimyasalları (Table 2.2). (iii)Sodium dodecylsulphate, used as surfactant and dispersant, was purchased from Fluka BioChemika (Table 2.3). (iv)Methanol, used in washing process, produced by Fluka. (v) The polymer matrix used is Polypropylene which was obtained from Petkim (Table 2.4).

Table 2.1 Properties of Pyrrole

Molecular Formula	C_4H_5N
Molecular weight	67,09 g/mol
Melting point	-23˚C
Boiling Point	131˚C
Density	0,967 g/ml

Table 2.2 Properties of Ferric chloride hexahydrate

Molecular Formula	$FeCl_3\ 6H_2O$
Molecular weight	270,32 g/mol
Melting point	37˚C
Solubility	soluble in water

Table 2.3 Properties of Sodium dodecylsulphate

Molecular Formula	$C_{12}H_{25}NaO_4S$
Molecular weight	288,38 g/mol
Melting point	206˚C
Density	1,01 g/ml

Table 2.4 Properties of Polypropylene

Molecular Formula	$(C_3H_6)_n$
Molecular weight of repeat unit	42,08 g/mol
Melting point	173˚C
Crystalline density	0,95 g/cm^3
Amorphous density	0,85 g/cm^3

2.2 Synthesis of Polypyrrole

The surfactant (SDS, 0,86 g) was added to 30 ml distilled water and stirred moderately with a magnetic stirrer. The solution was stirred for 30 minutes at room temperature until the surfactant is completely dissolved. When a clear aqueous solution of surfactant was obtained, the monomer (pyrrole, 1 g) was added dropwise to the solution while stirring. After obtaining a mixture of aqueous surfactant solution and the monomer, an aqueous solution of the oxidant ($FeCl_3$ $6H_2O$, 9,25 g) in 5 ml distilled water was added dropwise to the mixture. Immediate formation of black PPy precipitate was clearly observed right after addition of the oxidant. The polymerization process was carried out for 3 hours at room temperature by moderate stirring. The black polypyrrole precipitate was filtered off and washed with water and methanol several times. The black polypyrrole powder was dried under vacuum at room temperature for 10 hours.

2.3 Preparation of PP/PPy nanocomposites

2.3.1 Preparation of mixed and moulded composites

PP/PPy nanocomposites were prepared by melt mixing of pure PP with PPy at 75 rpm for 10 minutes at 210˚C using Brabender Plasti-Corder. The composition of nanocomposites varied between 1-20% PPy by weight. In order to provide a regular shape, the nanocomposites were pressed in a mould for 5 minutes at 210˚C followed by fast cooling. The identical procedure is employed with addition of 2% by weight dispersant (SDS) during mixing process of pure PP with PPy.

2.3.2 Injection molding

The nanocomposites were processed by injection molding. A laboratory scale injection molding machine (Microinjector, Daca Instruments) was used. During molding, barrel and mold temperatures were set to 210˚C and room temperature respectively. The injection pressure (16 bars) and cycle time (3 min) were identical for the preparation of each sample.

2.4 Characterization

2.4.1 Fourier Transform Infrader Spectrometer (FTIR)

FTIR analysis was carried out on a Nicolet 510 FTIR Spectrophotometer. The FTIR spectrum of polypyrrole was obtained by preparing a thin KBr pellet containing the sample.

2.4.2 Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis of samples were done using DTG-60 H Shimadzu thermal gravimetric analyzer. The samples were investigated at a heating rate of 10˚C/min under N_2 atmosphere.

2.4.3 Tensile Tests

In order to discuss the changes in mechanical properties tensile tests were performed for each nanocomposite as well as pure PP. The test was performed according to ASTM D638 (Standard Test Method for Tensile Properties of Plastics), by using a Lloyd LR 30K Universal Testing machine at a test rate of 5 cm/min. The shape and dimensions of the specimens are exhibited in Figure 2.1 and Table 2.5. At least five samples were used for each nanocomposite.

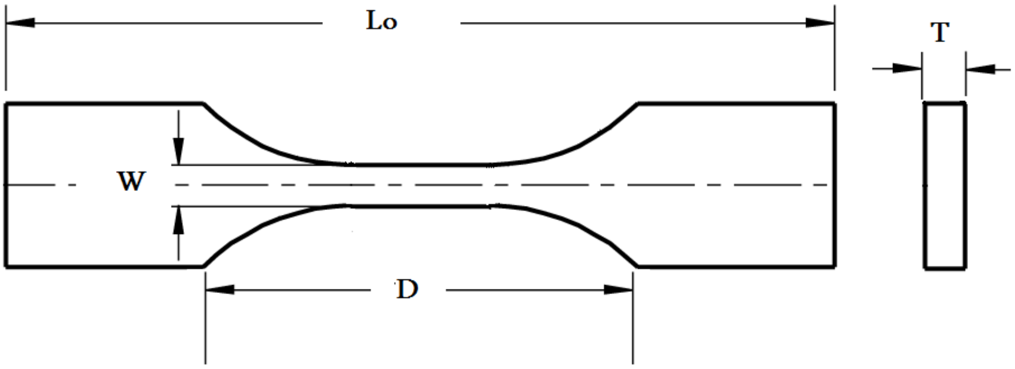


Figure 2.1 ASTM Tensile Test Specimen

Table 2.5 Dimensions of tensile test specimen

Symbol, Definition	Dimensions of Specimen (mm)
W, Width of narrow section	7.60
T, Thickness of the specimen	2.0
D, Distance between grips	50
L, Total length of specimen	110

Stress: Stress is defined as the force applied to produce deformation in a unit area of a test specimen. Stress is a ratio of applied load to the original cross-sectional area.

Strain: Strain is defined as the ratio of the elongation to the gauge length of the test specimen. In other words, it is the change in length per unit of the original length ($\Delta l/l$). It is expressed as a dimensionless ratio.

Young's modulus: Young's modulus is the ratio of stress to the corresponding strain below the proportional limit of a material. It is expressed in F/A. It is a measure of material's stiffness.

Tensile Strength= Force (load) / Cross-sectional area
Tensile Strength at Break= Load recorded at break / Cross-sectional area [35].

2.4.4 Conductivity Measurements

The conductivity measurements of the samples were done using four probe measuring system. In this system the instrument has four osmium tips that are equally placed. The outer probes source the current and the voltage drop across the inner probes is measured (Figure 2.2) [36].

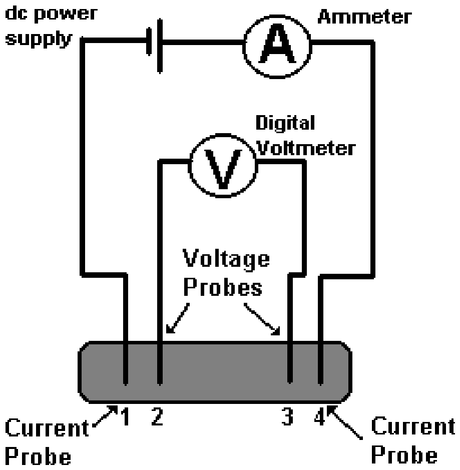


Figure 2.2 Four probe conductivity measurement system

Conductivity is given by $\sigma = \ln 2\ I / \Pi\ d\ V$ where,

σ: conductivity

I: current passing through outer probes

V:voltage drop across iner probes

d: sample thickness

In order to determine conductivities, the samples were placed under the probes of the instrument and the head of probes was lowered until it contacts the sample. The resistivity value of the sample was recorded and using this value conductivity was calculated. The conductivity measurement was done using FPP 0602 Electrometer.

2.4.5 Scanning Electron Microscopy (SEM)

The morphological studies of the samples were performed by FEI Quanta 400 F Scanning Electron Microscopy. All investigations are performed using secondary detector, 3.0 probe size and 20.00 kV acceleration voltage. The fracture surfaces of the samples were coated by a thin layer of gold before investigation. The aim of this study was to observe dispersion of PPy nanoparticles in PP matrix and to comment on dimensions of PPy particles.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis of polypyrrole nanoparticles

Synthesis of polypyrrole nanoparticles was achieved using microemulsion polymerization system by oxidation of pyrrole monomer with iron(III)chloride hexahydrate. As the oxidant was added, the color of the solution changed from colorless to deep greenish black which is an indication of oxidation of conducting polypyrrole. The reaction product polypyrrole was obtained in the form of black powder.

3.2 Characterization of polypyrrole

3.2.1 FTIR spectrum of polypyrrole

The FTIR transmission spectrum of polypyrrole nanoparticles exhibited characteristic vibration bands at 1531 cm^{-1}, 1480 cm^{-1}, 1469 cm^{-1} for pyrrole ring strecthing, 1458 cm^{-1} for conjugated C-N strecthing and 781 cm^{-1} for C-H wagging vibrations [29,32]. The vibration bands observed at 1300 cm^{-1}and 1036 cm^{-1}are due to C-H in-plane strecthing and C-H vibration of 2,5-substituted pyrrole [23]. The FTIR spectrum of PPy nanoparticles demostrating the representative vibrations bands is given in Figure 3.1.

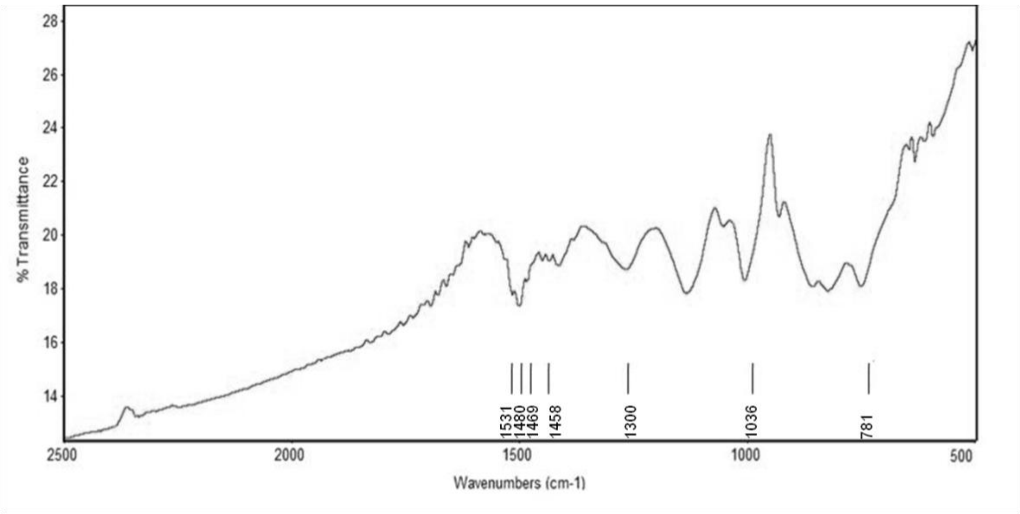
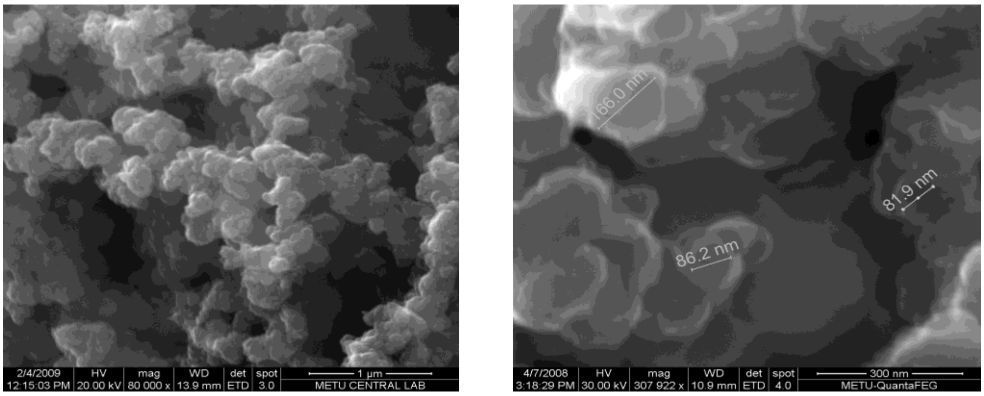


Figure 3.1 FTIR spectrum of polypyrrole

3.2.2 Scanning Electron Microscope Analysis of Polypyrrole Nanoparticles

Scanning electron microscopy was performed in order to investigate the dimensions and the morphology of polypyrrole nanoparticles. The scanning electron micrographs of polypyrrole nanoparticles are presented in Figure 3.2. The SEM micrographs of polypyrrole exhibited globular, nanometer-sized particles. The polypyrrole nanoparticles are observed to have a distribution of dimensions between 50–150 nm.



(a) (b)

Figure 3.2 SEM micrographs of PPy nanoparticles at magnifications of (a) 80000, (b) 300000.

The SEM results confirm that microemulsion polymerization system was succesful in the synthesis of nanodimensional polypyrrole particles. The SEM results proves that the microemulsion polymerization system provided similar dimensions of PPy nanoparticles with previous studies where 50-100 nm and 100-200 nm polypyrrole nanoparticles were reported [29,32].

3.3 Preparation of PP/PPy Nanocomposites

The polypyrrole nanoparticles prepared by microemulsion polymerization system were mixed with polypropylene in order to provide some level of processability to infusible and inprocessable polypyrrole while inducing conductivity to insulating polypropylene. In order to obtain PP/PPy nanocomposites, the polypyrrole nanoparticles were mixed with polypropylene by melt mixing technique followed by pressing to give a regular shape to nanocomposites. The nanocomposites were processed with injection molding and several black colored dog-bone shaped samples were obtained succesfully. The composition of nanocomposites varied in the range of 1-20% by weight polypyrrole nanoparticles in polypropylene.

3.4 Characterization of PP/PPy Nanocomposites

3.4.1 Tensile Tests

In this study, mechanical properties of PP/PPy nanocomposites were investigated by tensile tests. The effect of loading different amounts of polypyrrole nanoparticles into thermoplastic polypropylene matrix and the changes in mechanical properties produced by incorporation of polypyrrole nanoparticles were examined. In order to understand the effect of using sodium dodecylsulphate as dispersant in PP/PPy nanocomposites, identical tests were performed also for the nanocomposites prepared with dispersant.

A stress-strain curve is known to provide information about both linear elastic properties and mechanical properties related to plastic deformation of a material. In order to specify a material as ductile or brittle, the response of the material to applied stress is investigated. The area under stress-strain curve corresponds to the energy required to break the material. As it is clearly seen in Figure 3.3, pure PP is very ductile at a test rate of 5 cm/min and the area under the curve is very large indicating the great energy required to break the material. The Young’s modulus, tensile strength and percentage strain at break values of pure polypropylene are 430 MPa, 27,8 MPa and %424 respectively.

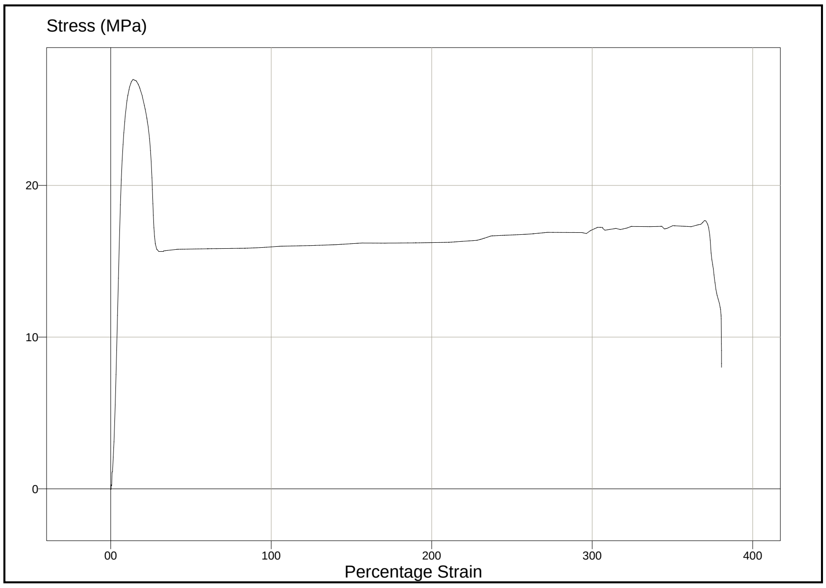


Figure 3.3 Stress vs strain curve of pure PP.

The changes in mechanical properties that are produced by loading different amounts of polypyrrole nanoparticles can be well understood from stress-strain curves of PP/PPy nanocomposites which are illustrated in Figure 3.4 through 3.8. As it is clearly observed in stress-strain curves of nanocomposites, addition of polypyrrole nanoparticles makes polypropylene matrix very brittle. In fact, addition of even the smallest amount of polypyrrole which is 1% causes a dramatic decrease in the energy required to break it.

The Young’s modulus, tensile strength and percentage strain at break values for PP/PPy nanocomposites are illustrated in Table 3.1. The change in percentage strain at break, tensile strength and Young’s modulus with increasing amount polypyrrole nanoparticles are shown in Figure 3.9 through Figure 3.11. As it is clearly seen in Figure 3.9, addition of 1% PPy to PP matrix causes a dramatic decrease in percentage strain at break value of pure PP. As the amount of PPy nanoparticles in

PP increases, the percentage strain of the nanocomposite decreases reaching its lowest value in PP/20%PPy nanocomposite (Figure 3.8). The reason for this is the fact that incorporation of PPy nanoparticles into pure PP causes disruption of polymer matrix. Due to the relatively weak interaction of PPy nanoparticles with PP, addition of even the smallest amount of PPy nanoparticles causes a great decrease in percentage strain at break value of pure PP. Since incorporation of PPy nanoparticles prevents elongation of ductile PP matrix, the decrease in percentage strain values is an expected result.

The increase in Young's modulus and tensile strength values show that addition of PPy nanoparticles in PP enhanced the strength and the stiffness of the nanocomposites. The greatest change for both properties was observed in PP/1%PPy nanocomposite. As it is seen in Figure 3.10 and Figure 3.11, incorporation of 1% PPy into PP matrix increased the tensile strength and Young's modulus of pure PP considerably. Increasing amount of PPy nanoparticles in PP matrix caused gradual increase in both tensile strength and Young's modulus of nanocomposites until addition of 10% PPy nanoparticles. Further addition of PPy nanoparticles slightly change the tensile strength and Young's modulus.

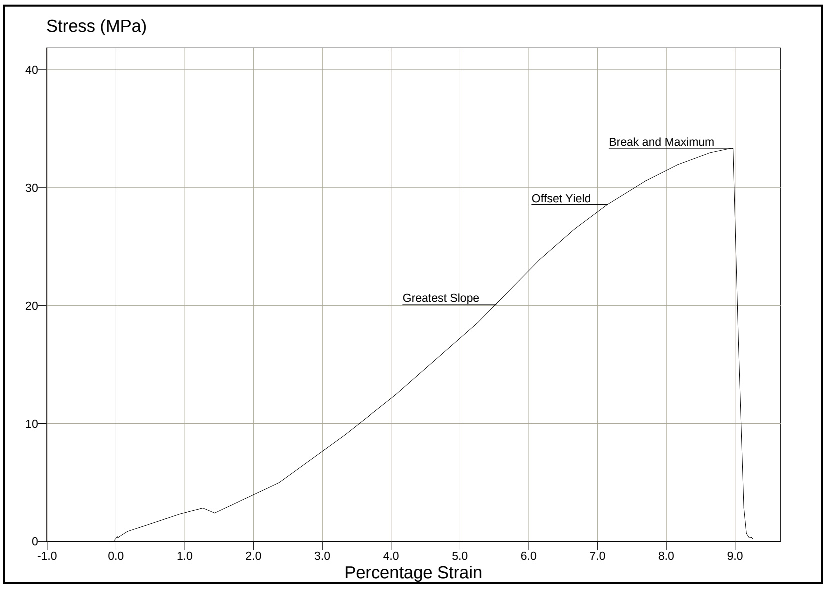


Figure 3.4 Stress vs strain curve for PP/1%PPy nanocomposite without dispersant**.**

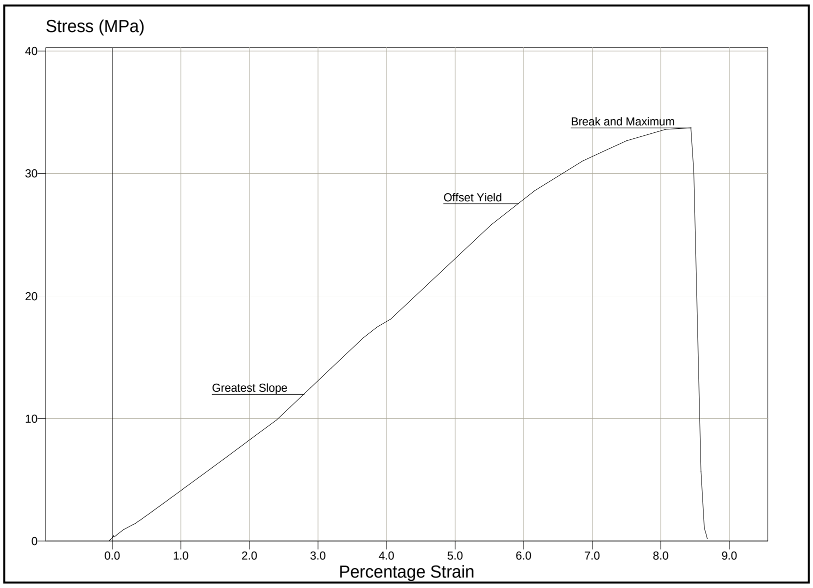


Figure 3.5 Stress vs strain curve for PP/5%PPy nanocomposite without dispersant.

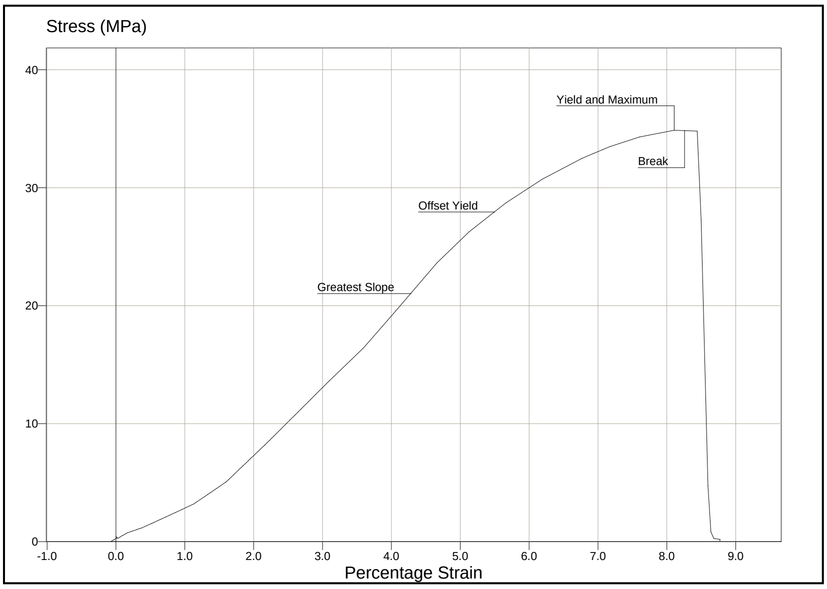


Figure 3.6 Stress vs strain curve for PP/10%PPy nanocomposite without dispersant.

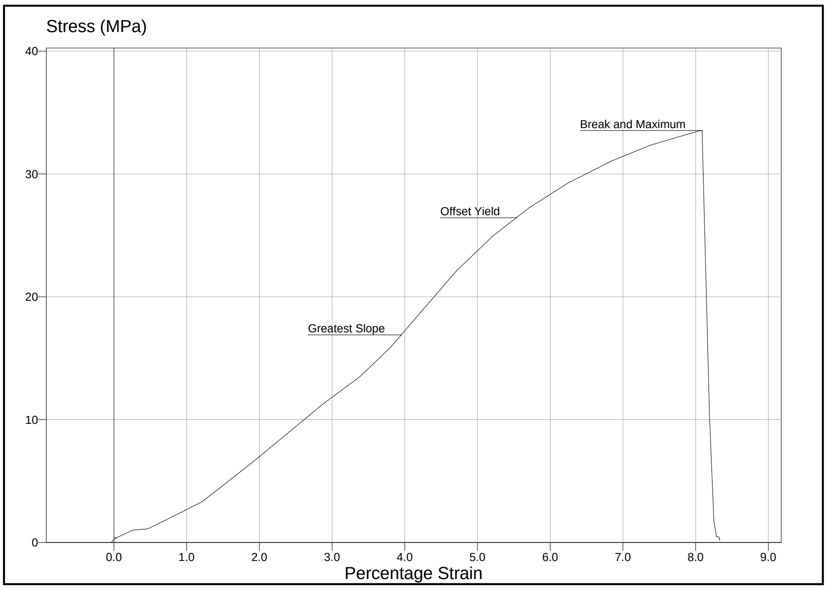


Figure 3.7 Stress vs strain curve for PP/20%PPy nanocomposite without dispersant.

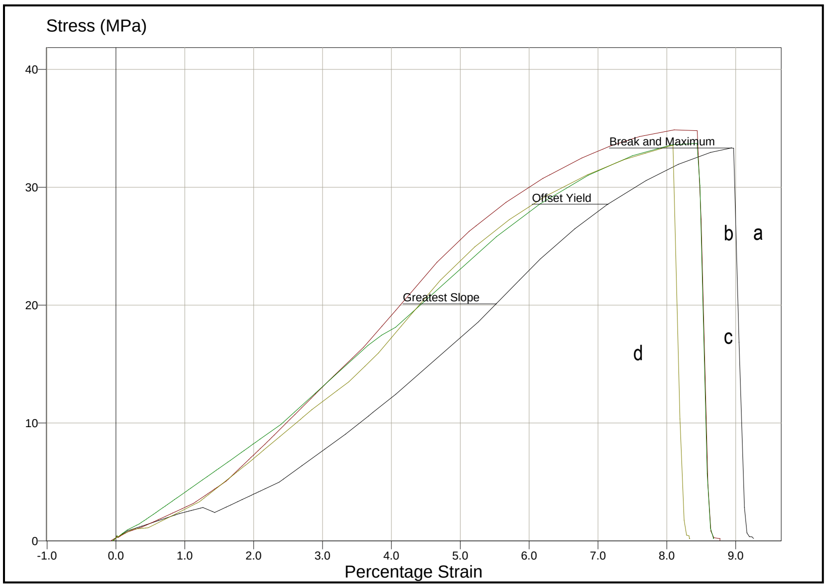


Figure 3.8 Stress vs strain curves for (a) PP/1%PPy, (b) PP/5%PPy, (c) PP/10%PPy, (d) PP/20%PPy nanocomposites without dispersant.

Table 3.1 Young’s modulus, tensile strength, percentage strain values for PP, PP/PPy nanocomposites without dispersant.

PPy content (w%)	Young's Modulus (MPa)	Tensile strength (MPa)	Percentage strain at break (%)
0	430±10	27,8±0,5	424±9
1	643±53	34,0±0,6	8,5±0,7
5	703±95	34,1±1,2	8,4±2,1
10	787±63	34,0±1,0	8,7±2,0
20	801±46	34,1±0,2	8,9±2,6

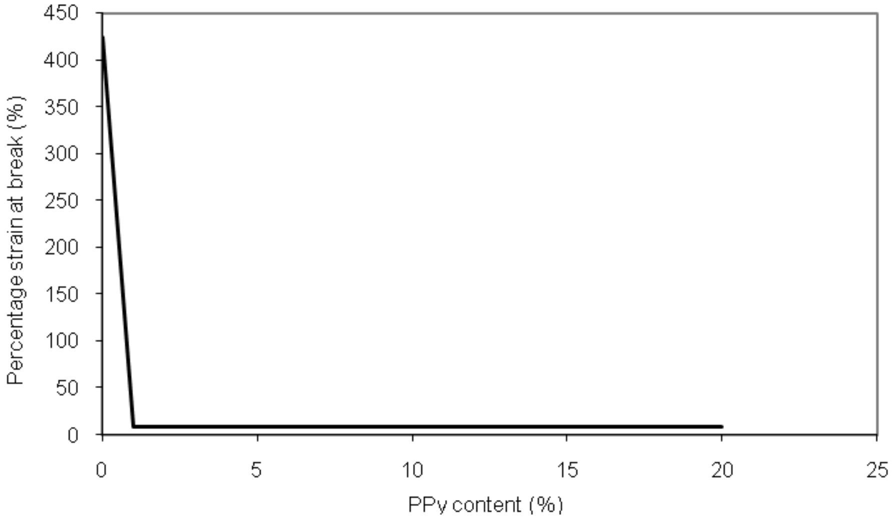


Figure 3.9 Percentage strain at break vs PPy content for PP/PPy nanocomposites without dispersant.

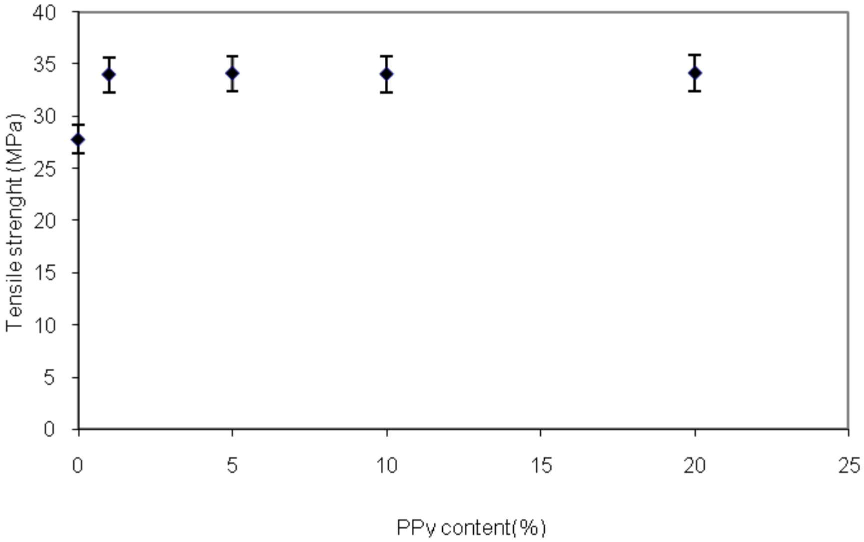


Figure 3.10 Tensile strength vs PPy content for PP/PPy nanocomposites without dispersant.

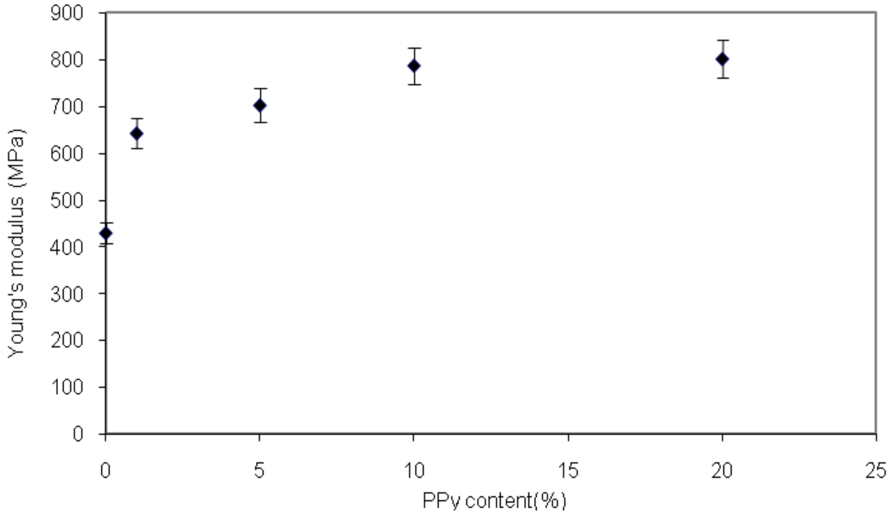


Figure 3.11 Young's modulus vs PPy content for PP/PPy nanocomposites without dispersant.

The tensile test results of PP/PPy nanocomposites show that incorporation of PPy nanoparticles in PP improves the strength and the stiffness while limiting the elongation of PP. In order to investigate the potential improvement in dispersion of PPy nanoparticles in PP, identical tensile tests were employed to nanocomposites prepared with dispersant. Due to the effect of dispersant, the interaction between PPy nanoparticles with PP matrix is expected to be improved. The Young's modulus, tensile strength and percentage strain at break values for nanocomposites prepared with dispersant are presented in Table 3.2. The change in percentage strain at break, Young's modulus and tensile strength with increasing polypyrrole content in nanocomposites prepared with dispersant are shown in Figure 3.17 through Figure 3.19. The gradual decrease in percentage strain at break values for increasing amounts of PPy is clearly seen in Figure 3.17. Addition of 1% PPy caused a significant decrease in percentage strain since it prevents extension of PP matrix.

However, the decrease in percentage strain is relatively smaller due to binding effect of dispersant used. Figure 3.18 and 3.19 exhibit the increase in tensile strength and Young's modulus of the nanocompoites with addition of PPy. The increase in both tensile strength and Young's modulus with increasing PPy content indicate the reinforcing action of PPy

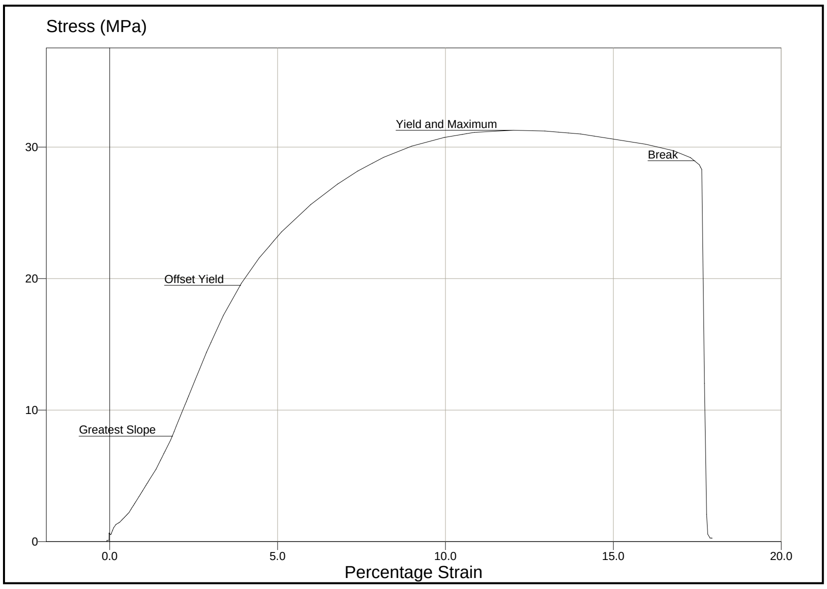


Figure 3.12 Stress vs strain curve for PP/1%PPy with dispersant.

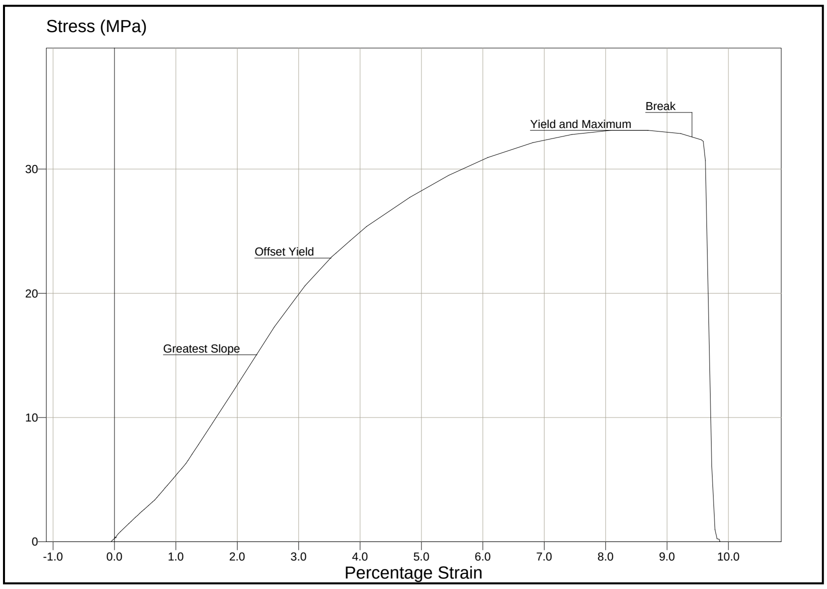


Figure 3.13 Stress vs strain curve for PP/5%PPy with dispersant.

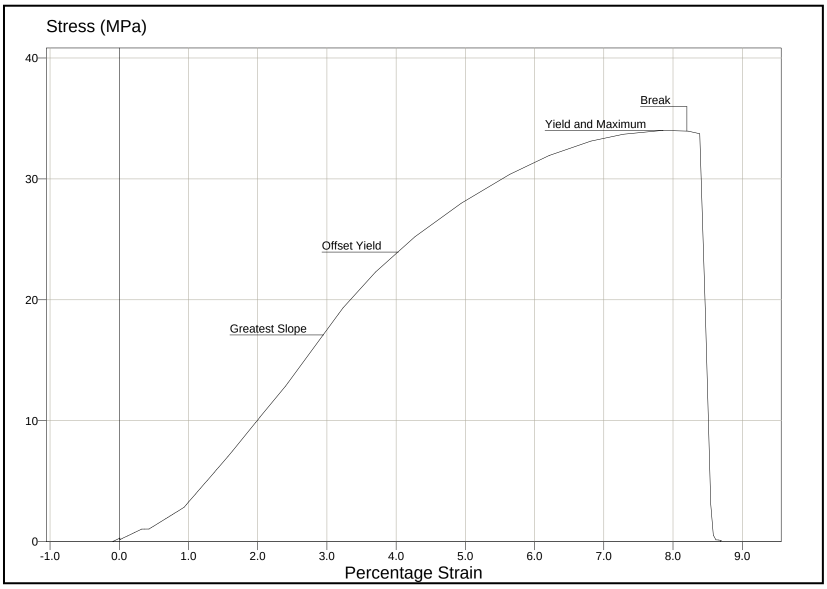


Figure 3. 14 Stress vs strain curve for PP/10%PPy with dispersant.

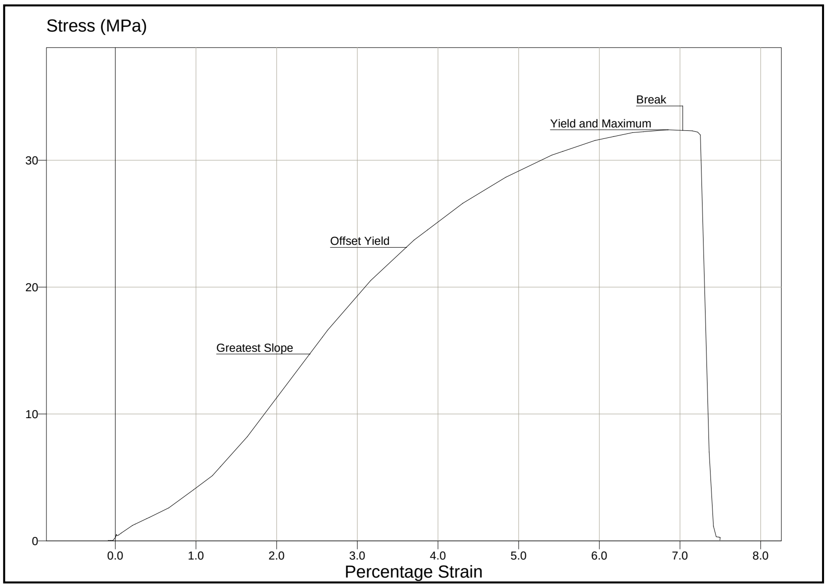


Figure 3.15 Stress vs strain curve for PP/20%PPy with dispersant.

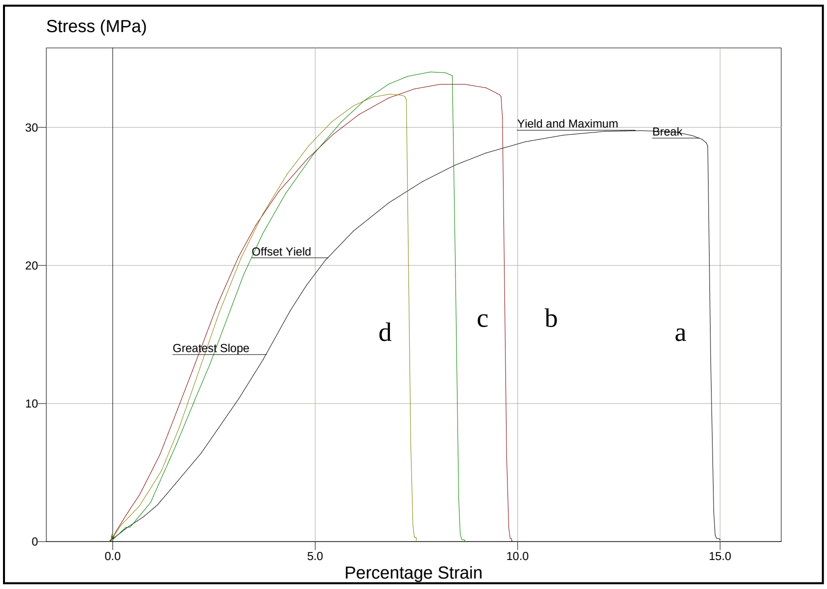


Figure 3.16 Stress vs strain curves for (a) PP/1%PPy, (b) PP/5%PPy, (c) PP/10%PPy, (d) PP/20%PPy nanocomposites with dispersant.

Table 3.2 Young’s modulus, tensile strength, percentage strain values for PP, PP/PPy nanocomposites with 2% dispersant by weight.

PPy content (w%)	Young's Modulus (MPa)	Tensile strength (MPa)	Percentage strain at break (%)
0	430±10	27,8±0,5	424±9
1	583±77	30,1±0,4	14,4±0,2
5	748±53	32,8±0,6	9,3±0,9
10	786±10	32,9±0,4	8,0±0,3
20	831±31	33,2±0,6	7,1±0,2

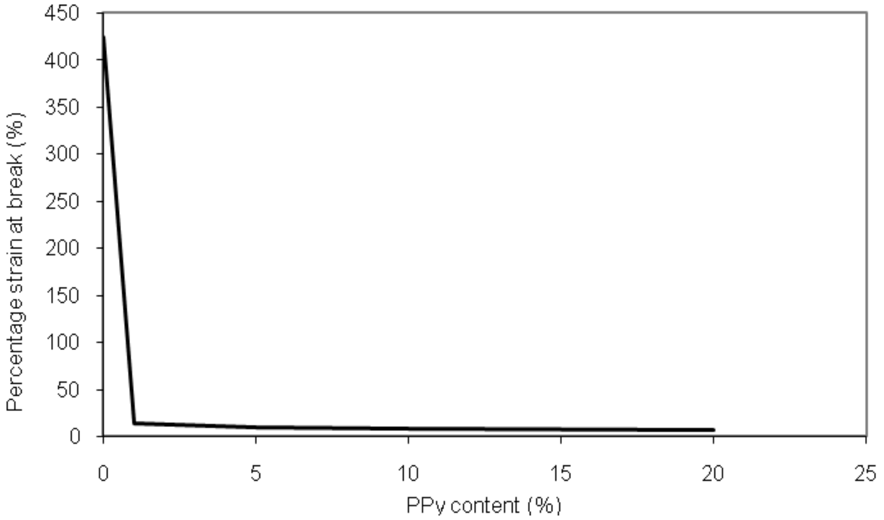


Figure 3.17 Percentage strain at break vs PPy content for PP/PPy nanocomposites with dispersant.

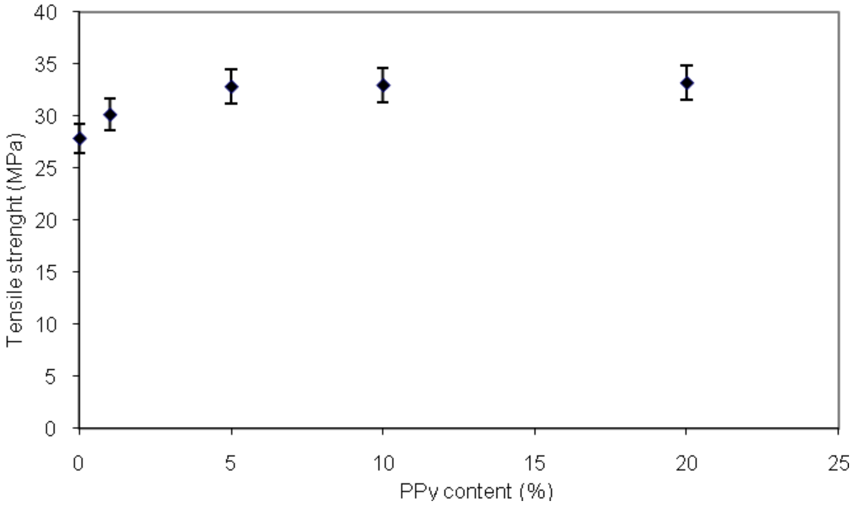


Figure 3.18 Tensile strength vs PPy content for PP/PPy nanocomposites with dispersant.

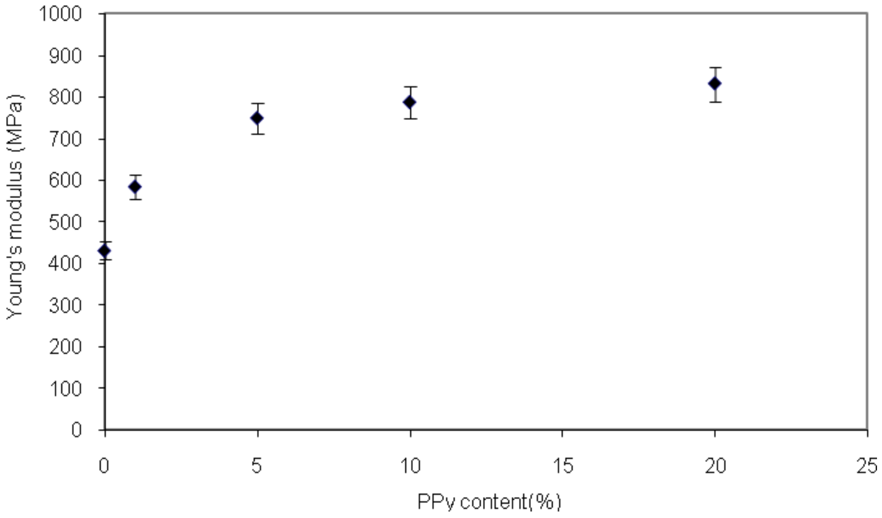


Figure 3.19 Young’s modulus vs PPy content for PP/PPy nanocomposites with dispersant.

In order to investigate the potential effect of dispersant in enhancement of dispersion of PPy nanoparticles, the change in tensile strength, precentage strain at break and Young's modulus for both nanocomposite sets prepared without and with dispersant are examined (Table 3.1, Table 3.2). The obtained results show that addition of PPy nanoparticles leads to a similar increase in tensile strength and Young's modulus of pure PP in both nanocomposite sets. Although the values are not identical, the values for nanocomposites involving dispersant did not exhibit significant difference compared to ones prepared without dispersant. However, the effect of dispersant is perceived in percentage strain at break values. The nanocomposites prepared using dispersant exhibited a regular decrease in percentage strain at break while a sudden decrease was observed for nanocomposites prepared without dispersant. The percentage strain at break values for PP/1%PPy nanocomposite prepared with and without dispersant are found to be 14,3 and 8,5 respectively. The higher decrease in nanocomposite prepared without dispersant can be explained by considering weaker interaction of polypyrrole with polypropylene. Same case is true for also nanocomposites with 5% polypyrrole content. Although, similar behaviour was observed for nanocomposites with 10% and 20% polypyrrole content, the difference in values are not as considerable as the ones for nanocomposites with 1% and 5% PPy content.

3.4.2 Electrical Conductivity Measurement

The change in electrical conductivity of PP matrix by incorporation of PPy nanoparticles was investigated. The amount of PPy nanoparticles in nanocomposites varied in the range of 1-20% by weight. In order to investigate the effect of dispersant, identical measurement was performed also with nanocomposites prepared with dispersant. The conductivity values of PP/PPy nanocomposites prepared without and with dispersant are shown in Table 3.3 respectively.

Table 3.3 Electrical conductivities of PP/PPy nanocomposites

	PP/PPy nanocomposites without dispersant	**PP/PPy nanocomposites with dispersant**
w% PPy	**Conductivity (Scm^{-1})**	**Conductivity (Scm^{-1})**
0	$1,0.10^{-16}$	$1,0.10^{-16}$
1	$5,60.10^{-5}$	$9,5.10^{-5}$
5	$1,24.10^{-4}$	$1,35.10^{-4}$
10	$1,32.10^{-4}$	$1,43.10^{-4}$
20	$2,25.10^{-4}$	$2,40.10^{-4}$
100	$5,2.10^{-2}$	$5,2.10^{-2}$

The electrical conductivity measurement of pure PP showed that conductivity of pure PP is about 10^{-16} S cm^{-1} while the conductivity of PPy nanoparticles is about $5,2.10^{-2}$ Scm^{-1}. The conductivity of PP/1%PPy nanocomposite was found to be about $5,60.10^{-5}$ Scm^{-1}. As it is clearly observed, addition of even the smallest amount of PPy results in a considerable increase in electrical conductivity of insulating PP matrix. Increasing amount PPy nanoparticles increases the conductivity of the nanocomposite up to $2,25.10^{-4}$ S cm^{-1}. Despite the significant increase in conductivity of pure PP with addition of 1% PPy nanoparticles, further addition of PPy did not considerably change the conductivity of the nanocomposites.

The conductivity of PP/1%PPy nanocomposite prepared with dispersant was found to be about $9,5.10^{-5}$ Scm^{-1} and addition of PPy nanoparticles increases the conductivity of insulating PP up to $2,40.10^{-4}$ S cm^{-1}. These results show that similar to nanocomposites prepared without dispersant, increasing amount of PPy nanoparticles increases the conductivity of pure PP considerably. However, increasing amount of PPy nanoparticles does not appreciably change the conductivity in nanocomposites prepared with dispersant.

As the amount of PPy nanoparticles increases, formation of a conducting network begins in PP matrix. Increasing amount of PPy supports formation of a stronger network while limiting the elongation of PP matrix. The change in conductivity and elongation with increasing amount of PPy in nanocomposites prepared without and with dispersant are shown in Figure 3.20 and Figure 3.21 respectively.

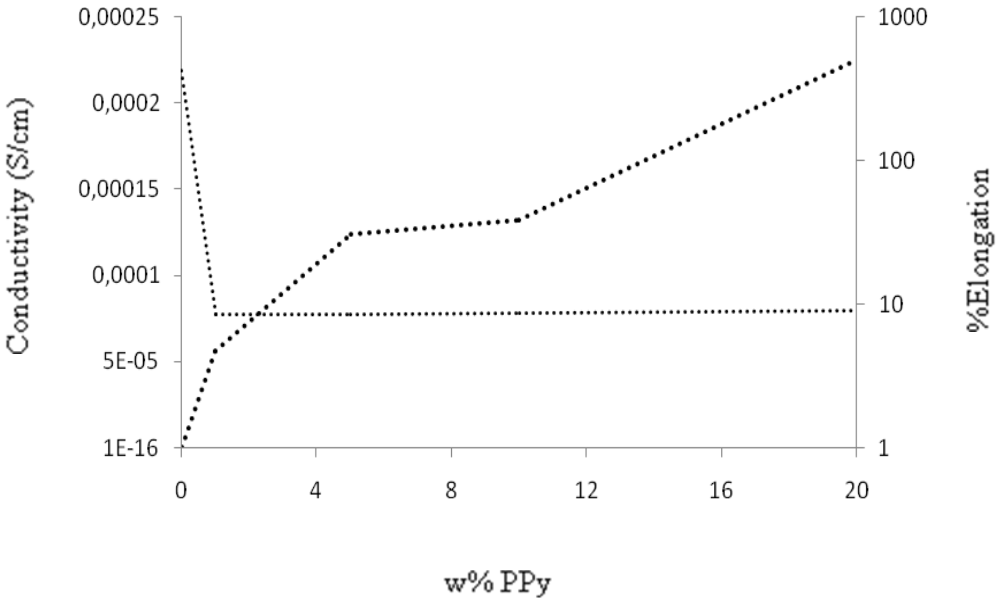


Figure 3.20 Conductivity-elongation graph of PP/PPy nanocomposites without dispersant.

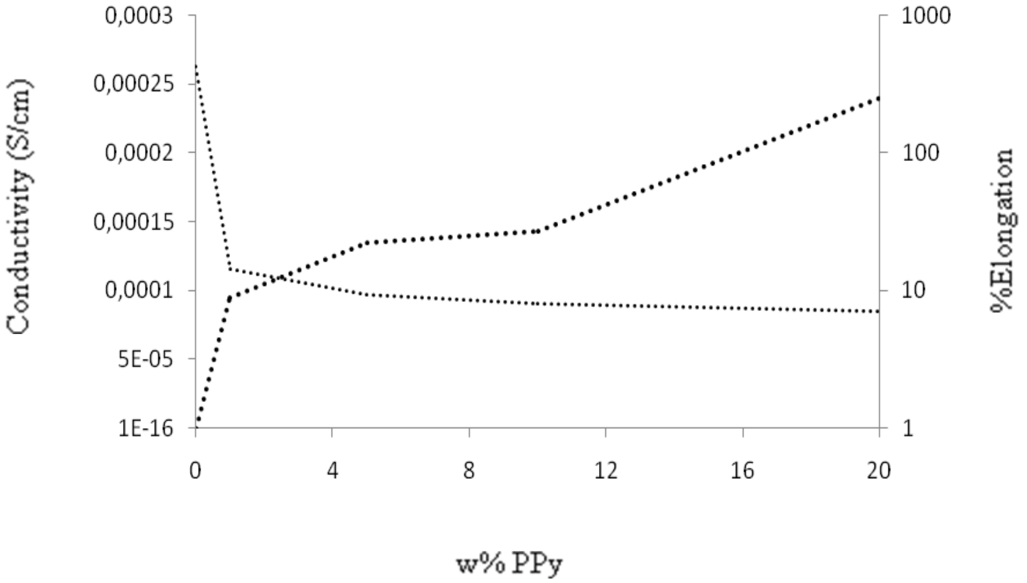


Figure 3.21 Conductivity-elongation graph of PP/PPy nanocomposites with dispersant.

As it is clearly observed in Figures 3.20 and 3.21, there is a range of filler concentration where the conductivity increases suddenly while the elongation decreases significantly. This phenomena occurs at a filler concentration range called percolation threshold. The percolation threshold for PP/PPy nanocomposites prepared without and with dispersant are found to be 2,0 and 2,4 respectively. These results confirms that addition of even 1% PPy into PP matrix results in a significant increase in electrical conductivity. These results are also in agreement with tensile tests results where the percentage strain values were found to decrease significantly with incorporation of 1% PPy into PP matrix.

The electrical conductivity results have exhibited that although the conductivity values of nanocomposite sets are not identical, the order of magnitude, the trend in conductivity and elongation with increasing PPy content are similar. This result show that dispersant does not have a significant effect on conductivity of the nanocomposites.

The electrical conductivity of a composite material depend on many factors such as preparation and processing conditions [14]. Similar to this, synthesis method of PPy is also crucial in electrical conductivity. Previous studies have shown that the conductivity of PPy synthesized by oxidative chemical polymerization vary in the range of 0,9-13 Scm^{-1} depending on the synthesis conditions [15,37]. Moreover, the conductivity of PPy nanoparticles synthesized via microemulsion polymerization system vary in the range of 0,06-9,6 Scm^{-1} depending synthesis conditions [26,29]. The conductivity of PPy nanoparticles synthesized in this study is found to be about 0,05 Scm^{-1} which is in agreement with the PPy nanoparticles synthesis studies using microemulsion polymerization system.

The composites prepared via melt mixing technique are known to have low conductivities on the order of 10^{-8} Scm^{-1} [13]. The reason for that is known to be due to aggregation and poor dispersion of PPy in PP. In order to overcome aggregation of PPy particles, researches have studied on potential routes for dispersion of PPy in PP matrix like surface coating, dispersion solution, in-situ polymerization some reaching conductivities of 10^{-2} Scm^{-1} for 8,9wt% PPy [15]. Since the conductivity of nanocomposites prepared in this study are in the order of 10^{-4} Scm^{-1}, the obtained results show that homogenization methods like coating or chemical modification yield composites with higher electrical conductivities.

3.4.3 Thermal Gravimetric Analysis

The thermal stability of nanocomposites was studied by Thermal Gravimetric Analysis. In order to investigate the effect of dispersant, identical test was employed also for nanocomposites prepared with dispersant. Figure 3.22 shows the thermal decomposition of pure PP, PPy PP/10%PPy and PP/20%PPy nanocomposites prepared without dispersant. From derivation of TGA curves, the maximum decomposition temperatures were estimated and summarized in Table 3.5.

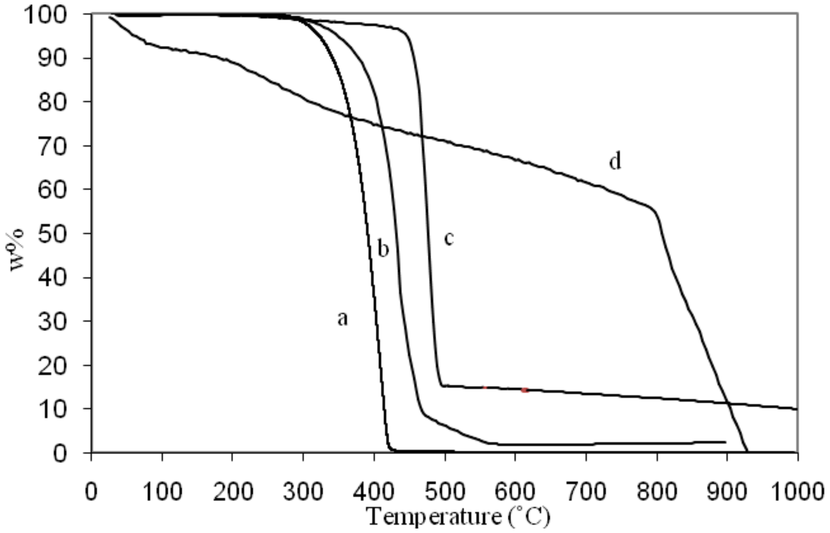


Figure 3.22 TGA plots of (a) pure PP, (b) PP/10%PPy, (c) PP/20%PPy nanocomposites prepared without dispersant, (d) PPy.

Table 3.4 Maximum decomposition temperatures of pure PP, PP/10%PPy and PP/20%PPy nanocomposites prepared without dispersant.

Sample	**Max decomposion temp. (˚C)**
Pure PP	412
PP/10%PPy	437
PP/20%PPy	477

Polypropylene which is a soft, ductile thermoplatic material decomposes readily depending on the analysis conditions such as heating rate, instrument, etc. The maximum decomposition temperature for polypropylene is about 412ºC. Both for PP/10%PPy and 20% nanocomposites prepared without dispersant, the maximum decomposition temperatures were shifted to higher values which indicates the improvement in thermal stability of polypropylene matrix by incorporation of polypyrrole nanoparticles. The maximum decomposition temperature for PP/20%PPy nanocomposite prepared without dispersant was found to be 477ºC which is 65ºC higher than that of pure polypropylene.

TGA results for PP/5%PPy and PP/10%PPy nanocomposites prepared with dispersant exhibited a significant difference in maximum decomposition temperature compared to PP/10%PPy nanocomposite prepared without dispersant. TGA results of pure PP, PPy, PP/5%PPy, PP/10%PPy and PP/20%PPy nanocomposites prepared with dispersant are presented in Figure 3.23. The maximum decomposition temperatures are summarized in Table 3.6.

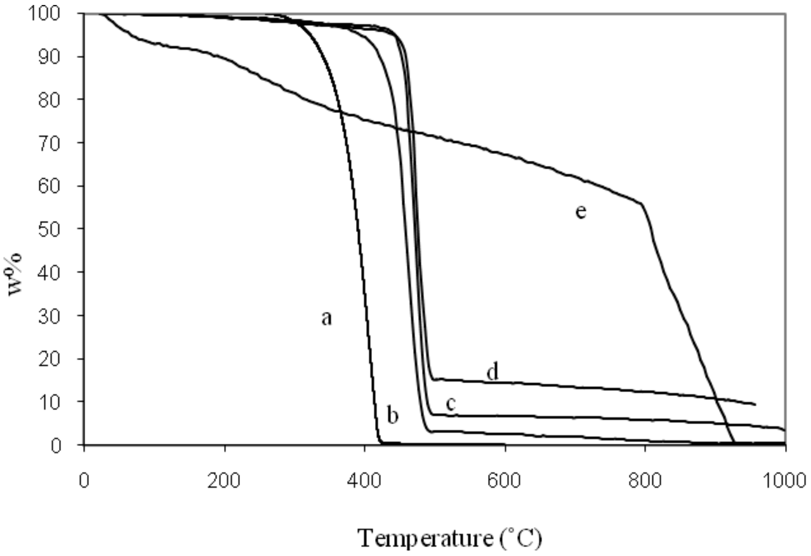


Figure 3.23 TGA plots of (a) pure PP, (b) PP/5%PPy, (c) PP/10%PPy (d) PP/20%PPy nanocomposites prepared with dispersant, (e) PPy.

Table 3.5 Maximum decomposition temperatures of pure PP, PP/10%PPy and PP/20%PPy nanocomposites prepared with dispersant.

Sample	**Max decomposition temp. (˚C)**
Pure PP	412
PP/5%PPy with dispersant	466
PP/10%PPy with dispersant	479
PP/20%PPy with dispersant	480

As it is clearly seen, despite lower polypyrrole content in PP/5%PPy nanocomposite prepared with dispersant, the maximum decomposition temperature of it is higher than that of PP/10%PPy nanocomposite prepared without dispersant. The maximum decomposition temperature difference between PP/10%PPy nanocomposite prepared without dispersant and PP/10%PPy nanocomposite prepared with dispersant is about 40ºC. The reason for that can be explained by the effect of dispersant used. Since dispersant provides better dispersion of polypyrrole nanoparticles in polypropylene matrix, the dispersion in the nanocomposite is improved. Thus, the interaction between polypropylene matrix and polypyrrole nanoparticles increases which results in improvement in thermal stability of the material.

However, TGA results of PP/20%PPy nanocomposite prepared without dispersant and PP/20%PPy nanocomposite prepared with dispersant show similar maximum decomposition temperatures which are 477ºC and 480ºC respectively. As the amount of polypyrrole increases, the dispersant becomes insufficient to provide homogenity in the nanocomposite.

The obtained results for both sets have shown that presence of PPy nanoparticles leads to enhancement in thermal stability of pure PP as expected from previous studies [37]. The greater shifts observed for maximum decomposition temperature of nanocomposites prepared with dispresant confirms greater enhancement in thermal stability of pure PP indicating the improvement in dispersion of PPy nanoparticles in PP matrix.

3.4.4 Scanning Electron Microscopy of PP/PPy Nanocomposites

The fracture surfaces of nanocomposites were examined by scanning electron microscope. The SEM micrographs of PP/PPy nanocomposites prepared without dispersant are shown in Figure 3.24 through Figure 3.27. Figure 3.24 shows the SEM micrographs of PP/1%PPy nanocomposite prepared without dispersant. In the micrograph at maginification of 30000, PPy is observed as particles incorporated into PP matrix. The micrographs exhibit presence of 150–300 nm clusters of polypyrrole nanoparticles embedded into polypropylene matrix.

Figure 3.25 shows SEM micrographs of PP/5%PPy nanocomposite at magnifications of 30000 and 80000. Both micrographs exhibit presence of globular polypyrrole nanoparticles with relatively large dimensions. The dimensions of polypyrrole clusters which are about 160–250 nm are clearly observed in the micrograph with 80000 magnification. The reason for formation of clusters can be explained by agglomeration of PPy nanoparticles due to poor dispersion in PP matrix.

The fracture surface of PP/10%PPy nanocomposite is shown in Figure 3.26. Unlike PP/1%PPy and 5% nanocomposites, the fracture surface of PP/10%PPy nanocomposite involves less nanoparticle images which indicates that large amount of PPy nanoparticles were embedded in PP matrix.

Figure 3.27 exhibits the fracture surface of PP/20%PPy nanocomposites at magnifications of 3000 and 30000 respectively. The micrograph at 30000

magnification clearly shows clusters of polypyrrole nanoparticles on the fracture surface of PP/20%PPy nanocomposite. This shows the fact that as the amount of PPy reaches 20%, by weight, PPy can not be found in the form of nanoparticles and formation of clusters can no longer be prevented.

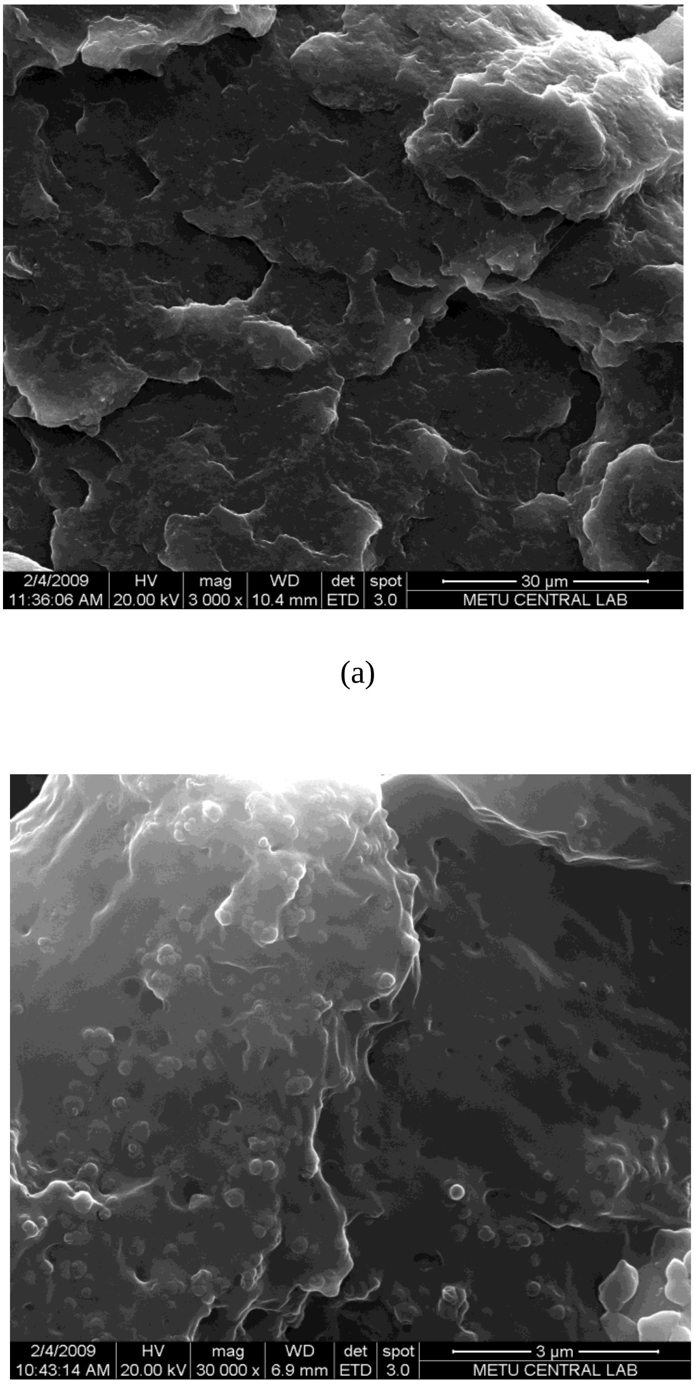
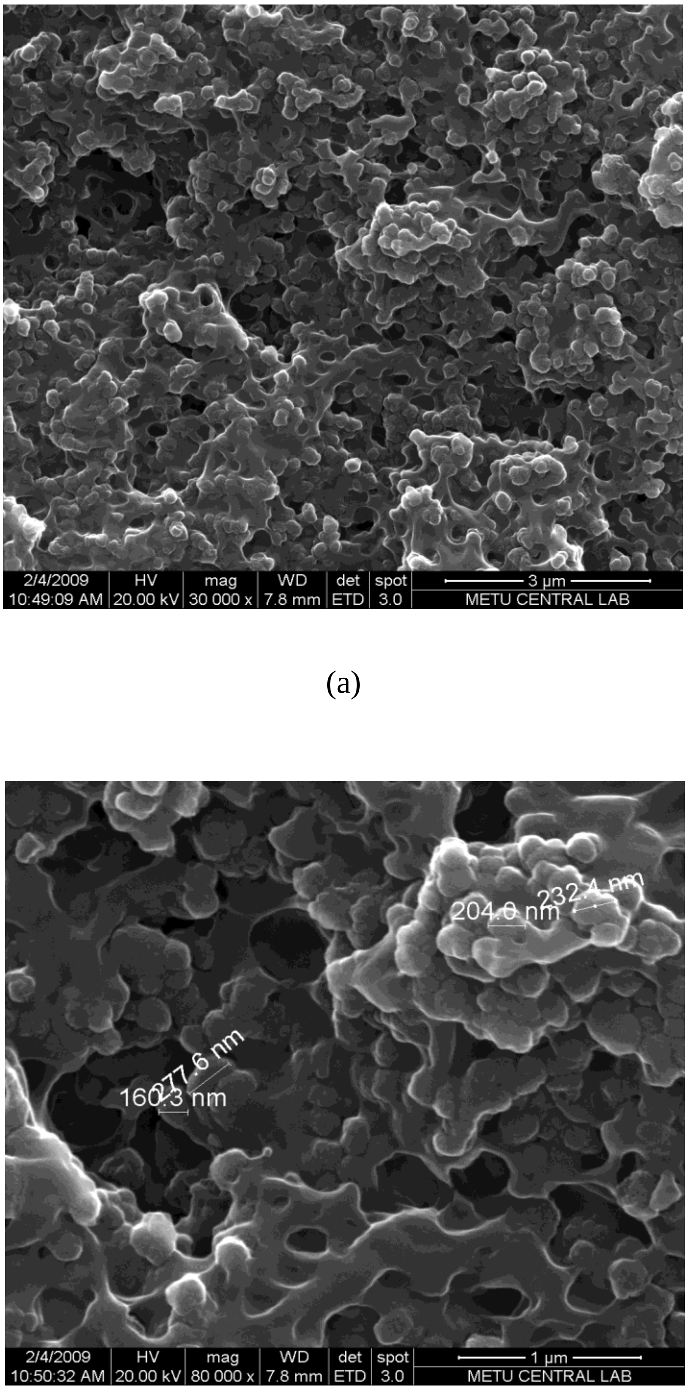


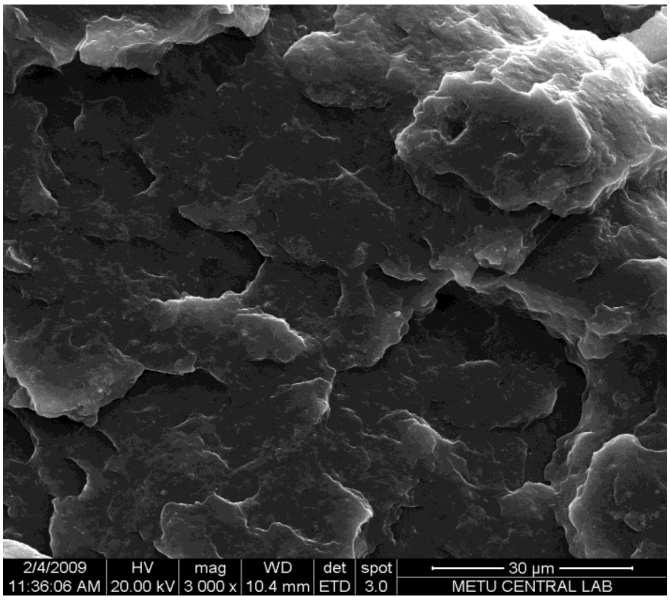
Figure 3.24 Fracture surface of PP/1%PPy nanocomposite without dispersant at magnification of (a) 3000, (b) 30000.



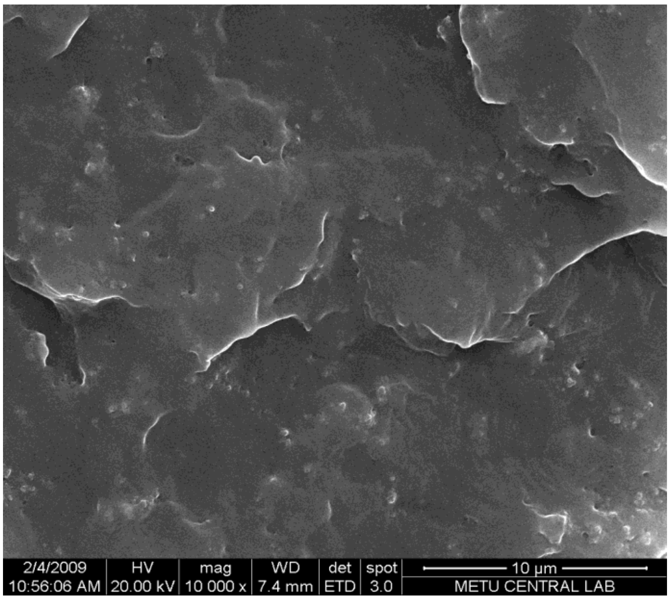
(a)

(b)

Figure 3.25 Fracture surface of PP/5%PPy without dispersant at magnification of (a) 30000, (b) 80000.

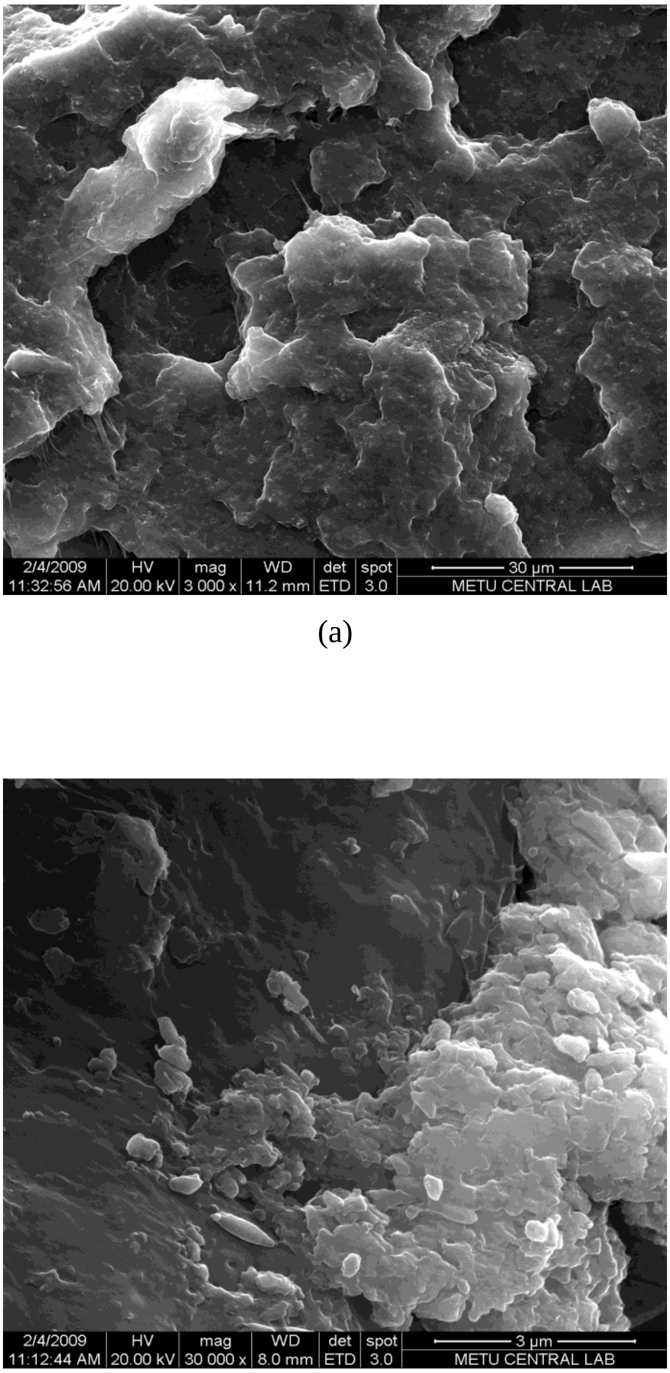


(a)



(b)

Figure 3.26 Fracture surface of PP/10%PPy without dispersant at magnification of (a) 3000, (b) 10000.



(a)

(b)

Figure 3.27 Fracture surface of PP/20%PPy without dispersant at magnification of (a) 3000, (b) 30000.

The fracture surfaces of PP/PPy prepared with dispersant are shown in Figure 3.28 through Figure 3.31. The SEM micrographs of PP/1%PPy nanocomposite prepared with dispersant which is exhibited in Figure 3.28 clearly shows the presence of regularly dispersed globular polypyrrole particles having nanodimensions. The enhancement in dispersion and decrease in nanoparticle dimension can be explained by the effect of dispersant used.

Figure 3.29 shows SEM micrographs of PP/5%PPy nanocomposite prepared with dispersant at magnifications of 30000 and 80000 respectively. Similar to PP/1%PPy nanocomposite prepared with dispersant, globular polypyrrole nanoparticles having dimensions about 60–100 nm is well observed in the micrograph with 80000 magnification.

The SEM micrographs of PP/10%PPy nanocomposite prepared with dispersant which are exhibited in Figure 3.30 show presence of polypyrrole both in nanoparticle and cluster fom embedded in PP matrix. This situation shows that as the amount of polypyrrole increases, the dispersant becomes insufficient to prevent formation of polypyrrole clusters.

Figure 3.31 exhibits the fracture surface of PP/20%PPy nanocomposite prepared with dispersant at magnifications of 3000 and 30000 respectively. Similar to previous case, the fracture surface of PP/20%PPy nanocomposite prepared with dispersant exhibits presence of polypyrrole both in nanoparticle and cluster form. Since 20% is the highest amount of polypyrrole used in nanocomposites, this situation is an expected result.

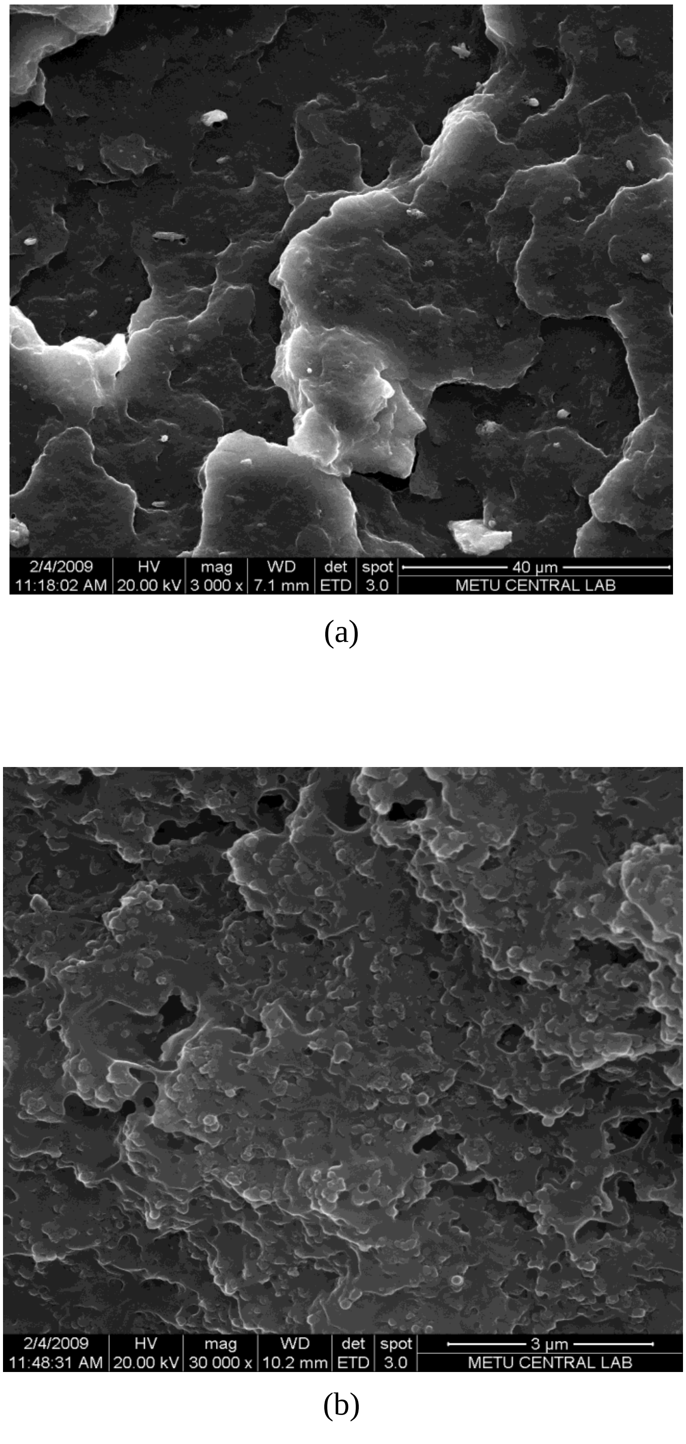
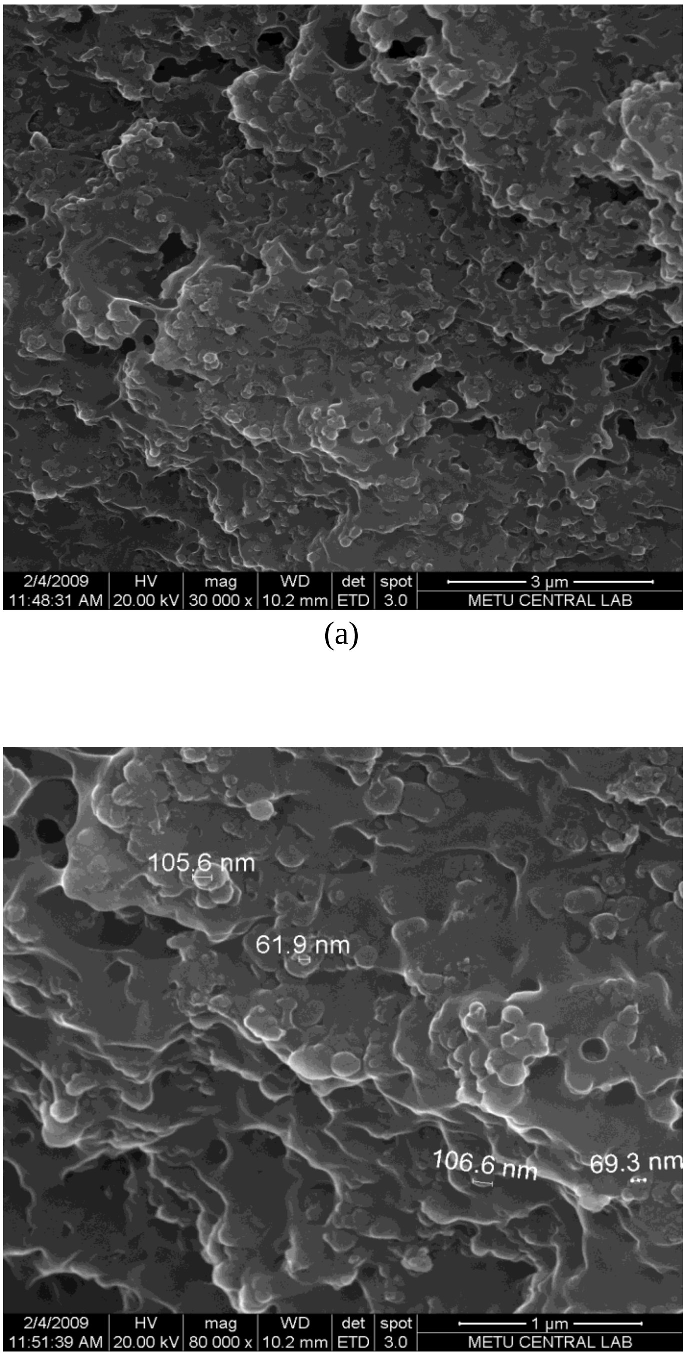


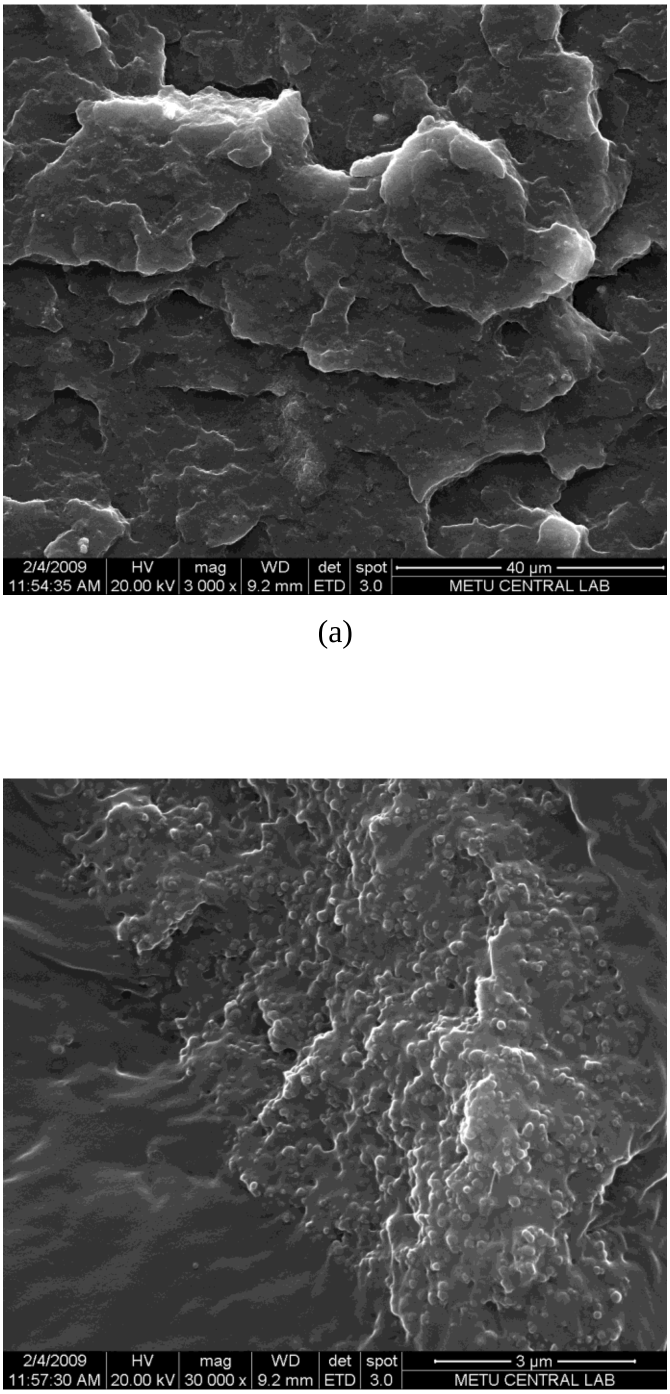
Figure 3.28 Fracture surface of PP/1%PPy with dispersant at magnification of (a) 3000, (b) 30000.



(a)

(b)

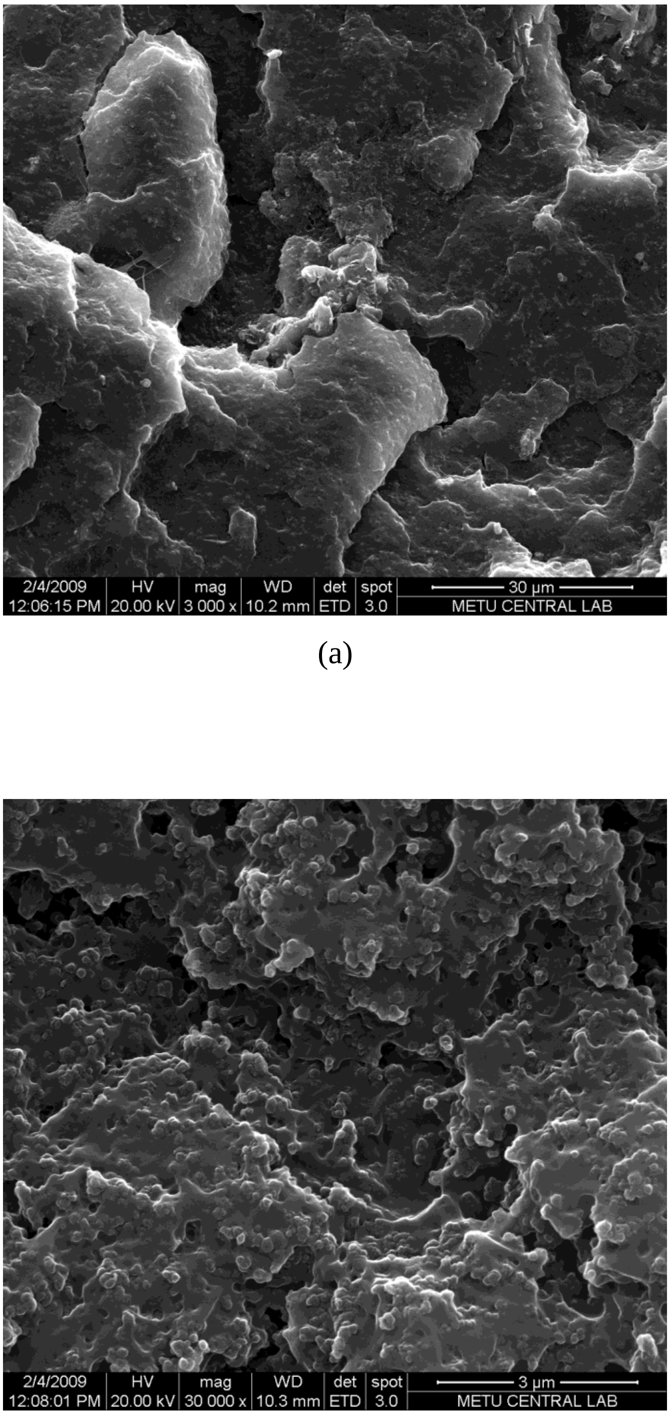
Figure 3.29 Fracture surface of PP/5%PPy with dispersant at magnification of (a) 30000, (b) 80000.



(a)

(b)

Figure 3.30 Fracture surface of PP/10%PPy with dispersant at magnification of (a) 3000, (b) 30000.



(a)

(b)

Figure 3.31 Fracture surface of PP/20%PPy with dispersant at magnification of (a) 3000, (b) 30000.

The SEM micrographs of PP/1%PPy and 5% nanocomposites prepared without dispersant were observed to involve larger polypyrrole nanoparticles compared to ones prepared with dispersant. Comparison of the micrographs of PP/5%PPy nanocomposites prepared without and with dispersant clearly shows the difference in dimensions and dispersion of polypyrrole nanoparticles (Figue 3.25-b, Figure 3.29-b). In PP/5%PPy nanocomposite prepared without dispersant, the dimension of polypyrrole nanoparticles were observed to be in the range between 160-200 nm whereas, PP/5%PPy nanocomposite prepared with dispersant was observed to involve polypyrrole nanoparticles with dimensions varying between 60-100 nm. PP/5%PPy nanocomposite prepared without dispersant exhibited relatively better dispersion and less cluster formation of polypyrrole nanoparticles through polypropylene matrix compared to the one prepared without dispersant.

PP/20%PPy nanocomposites prepared without dispersant was observed to contain clusters of polypyrrole embedded in PP matrix whereas, PP/20%PPy nanocomposite prepared with dispersant involved both polypyrrole nanoparticles and clusters with relatively better dispersion. These results show that the use of dispersant in nanocomposites leads to relatively better dispersion and decrease in dimensions of polypyrrole nanoparticles especially at low PPy nanoparticle contents.

CHAPTER 4

CONCLUSION

Polypyrrole nanoparticles were prepared by microemulsion polymerization system using iron chloride hexahydrate as the oxidant and sodium dodecylsulphate as the surfactant. The SEM micrographs of polypyrrole have exhibited presence of globular, nanometer-sized particles having dimensions between 50–150 nm. The electrical conductivity measurement has shown that electrical conductivity of polypyrrole is in the order of 10^{-2} Scm^{-1}.

The tensile test has shown that addition of PPy nanoparticles has increased the Young's modulus and tensile strength similarly in both sets indicating the enhancement in stiffness and strength of pure PP. However, the effect of dispersant was perceived in percentage strain at break values. The nanocomposites prepared with dispersant have exhibited a regular decrease in percentage strain at break while a sudden decrease was observed for nanocomposites prepared without dispersant. The higher decrease in nanocomposites prepared without dispersant can be explained by considering weaker interaction of polypyrrole with polypropylene matrix.

The electrical conductivity measurements have shown that increasing amount PPy nanoparticles increases the conductivity of the nanocomposites up to orders of 10^{-4} S cm^{-1} both sets. The electrical conductivity results have exhibited that the order of magnitude and the trend in conductivity-elongation with increasing PPy content were similar in both nanocomposites sets indicating that using dispersant does not have a significant effect on conductivity of the nanocomposites.

Thermal Gravimetric Analysis has shown that incorporation of PPy nanoparticles leads to enhancement in thermal stability of pure PP. The greater shifts observed for maximum decomposition temperature of nanocomposites prepared with dispersant confirms the greater enhancement in thermal stability of pure PP indicating the improvement in dispersion of PPy nanoparticles in PP matrix.

The SEM micrographs of PP/1%PPy and 5% prepared without dispersant have exhibited presence of globular PPy particles with dimensions in the range between 100 to 200 nm. However, PP/1%PPy and 5% nanocomposites prepared with dispersant have shown PPy nanoparticles having dimensions in the range of 60-100 nm. The SEM results have shown that low PPy content nanocomposites prepared with dispersant involve smaller dimension nanoparticles compared to ones prepared without dispersant. confirming the effect of dispersant in prevention of cluster formation.

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