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Research Article

# DEVELOPMENT OF POLYPROPYLENE COMPOSITES WITH GOOD ELECTRICAL CONDUCTIVITY AND HIGH DIELECTRIC CONSTANT

**Jabin Thekkedath[1], Bipinbal PK[1], Teena Thomas[2], Sunil K. Narayanankutty*[1]**

[1]*Department of Polymer Science & Rubber Technology, Cochin University of Science & Technology, Kochi, Kerala, India*
[2]*Department of Chemistry, St. Peter's College, Kolenchery, Ernakulam, Kerala, India*
**Corresponding author: sncusat@gmail.com*

## ABSTRACT

Polythiophene (PTH) with high electrical conductivity was prepared by oxidative polymerization using $FeCl_3$ and characterized by FTIR, XRD, thermal analysis and conductivity measurement. The synthesized PTH was used to prepare conducting composites based on polypropylene (PP). Electrical, thermal, mechanical and dynamic mechanical properties were studied. An exponential increase of conductivity with respect to PTH content was observed in the composites, indicating the formation of a continuous conducting network. PTH improved the modulus of the composites while decreasing the tensile strength. The composite containing PTH showed higher thermal stability and exceptional dielectric constant. The study was successful in converting a commercial general purpose thermoplastic polymer into a composite suitable for capacitor applications.

**Keywords:** Polythiophene, polypropylene, conducting composites, thermal stability, high dielectric constant

## 1. INTRODUCTION

Polythiophene (PTH) is a thermally stable conjugated polymer that can be used as electrical conductor, antistatic coating, sensors, electromagnetic shielding material, microwave absorbing material and in optical devices. PTH has been the subject of considerable interest because of its good environmental stability, unique redox electrical behavior, stability in doped or neutral states, ease of synthesis, and possibility of wide range of applications in diverse fields. Creative new designs and development strategies of new polythiophenes have led to interesting new materials and enhanced performance in devices.

The drawbacks of conducting polymers, which impair processability, are their infusibility and insolubility in common solvents. To improve the processibility and making them suitable for different specialised applications, conducting polymers have been incorporated into insulating matrices to prepare composites which combine conductivity with mechanical strength and other desirable characteristics of the insulating polymers [1-4]. Polythiophene has been made into composites in different matrices to exploit its electrical properties [5-8]. Polypropylene, a general purpose commercial thermoplastic, has been tried as base matrix with polyaniline [9,10] and polypyrrole [11, 12].

In the current study polythiophene is incorporated into a general purpose plastic, polypropylene, through melt mixing in an internal mixer. If a commercial plastic can be endowed with conductivity, it will be a huge advantage. Morphology of the prepared PTH/PP composites was analysed by scanning electron microscopy. Effect of PTH on DC conductivity, dielectric properties and static and dynamic mechanical properties of the composites was examined at varying PTH concentrations. Thermal stability of the composite was also evaluated.

## 2. MATERIAL AND METHODS

Polypropylene was purchased from Alpha Chemicals, India. Thiophene, ferric chloride, dichloromethane and acetonitrile were supplied by E- Merck Mumbai., India.

### 2.1. Preparation of Polythiophene

Sixteen (16) ml of thiophene was dissolved in 600 ml dichloromethane. 130 g of ferric chloride was dissolved in 300 ml acetonitrile and added drop wise to the thiophene solution so that a monomer/catalyst molar ratio of 1:3 could be maintained. The reaction mixture was stirred for 2 hours after which 10 ml of hydrogen peroxide (30%) was added slowly to convert ferrous ions to ferric ions. The stirring was continued for 2 more hours. The resultant mixture was washed with acetonitrile and ether until the washings were colourless. Washed polythiophene was dried at 70°C under vacuum and powdered.

### 2.2. Preparation of composites

Mixing was done in a Brabender Plastograph at 145°C. When the PP was softened by the temperature and shear, PTH powder was added slowly and the mixing was continued for another 5 min. The mix was taken out from the mixing chamber and pressed between aluminium platens. The pressed sheets were cut into small pieces and used for compression moulding in a hydraulic press at a temperature of 150°C under 200 MPa pressure.

**Table 1: Formulation of PTH/PP composites**

| Contents | phr | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| PP | 100 | 100 | 100 | 100 | 100 |
| PTH | 0 | 10 | 20 | 30 | 40 |

### 2.3. Characterization methods

Infrared spectrum was recorded on a Bruker FTIR spectrophotometer model Tensor 27 (spectral range of 4000 $cm^{-1}$ to 600 $cm^{-1}$ with standard KBr beam splitter) in attenuated total reflectance (ATR) mode. X-ray diffraction of PTH was recorded using a Bruker AXS D8 Advance Diffractometer using CuK radiation ($\lambda$= 1.54 Å) at 35 kV and 25 mA. Scanning electron microscope studies were carried out using SEM model 6390LA JEOL instrument. Samples were sputter coated with gold for 25 s. Mechanical properties were measured using Shimadzu Universal Testing Machine Model AG-I 10 kN according to ASTM D638. Thermogravimetric analysis was carried out on TA Instruments TGA Q50 with a heating rate of 20°C/min under nitrogen atmosphere. DC electrical conductivity of PTH and PTH/PP composites were measured by a two-probe method using a Keithley 2400 source-measure unit. Dielectric measurements were carried out at frequencies ranging from 40 Hz to 80 MHz using an Impedance analyzer, Agilent E 4980 A Precision LCR Meter.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of polythiophene

#### *3.1.1. Morphology*

Scanning electron microscopy images of prepared polythiophene particles are shown in Fig. 1. The particles are found to possess a spherical morphology and appear to be aggregated to some extent. These aggregations need to be broken when the conducting polymer is dispersed in the non-conducting matrix to obtain optimum performance from the composite material.

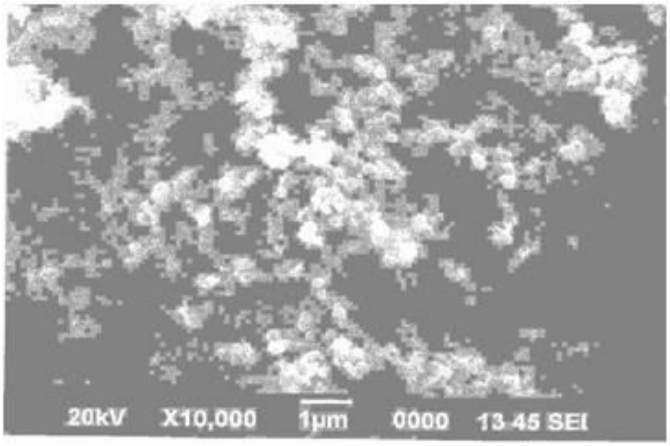

**Fig. 1: SEM image of PTH**

#### *3.1.2.* Fourier Transform Infrared Spectroscopy

FTIR spectrum of prepared PTH is shown in Fig. 2. The bands at 1633 $cm^{-1}$ and 1342 $cm^{-1}$ correspond to C=C asymmetric and symmetric stretching vibrations of thiophene ring, respectively. C-S-C ring deformation stretching in thiophene ring is seen at 643 $cm^{-1}$. Vibration bands observed at 1155 $cm^{-1}$ and 1033 $cm^{-1}$ are due to C-H bending and C-H in plane deformation. The characteristic band of PTH indicating 2,5-disubstitution is seen at 787 $cm^{-1}$ is confirming successful polymerization of thiophene.

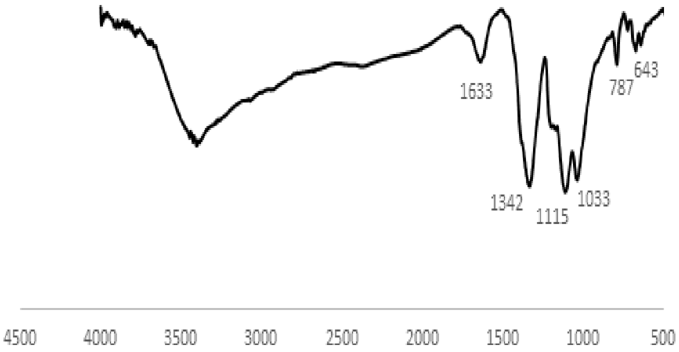

**Fig. 2: FTIR spectrum of prepared polythiophene**

#### *3.1.3. X-ray Diffraction*

X-ray diffraction was used to analyse crystalline nature of polythiophene. XRD spectrum of the prepared polythiophene is shown in fig. 3. Doped polythiophene shows sharp peaks at 2$\theta$ about 26, 28, 33 and 36

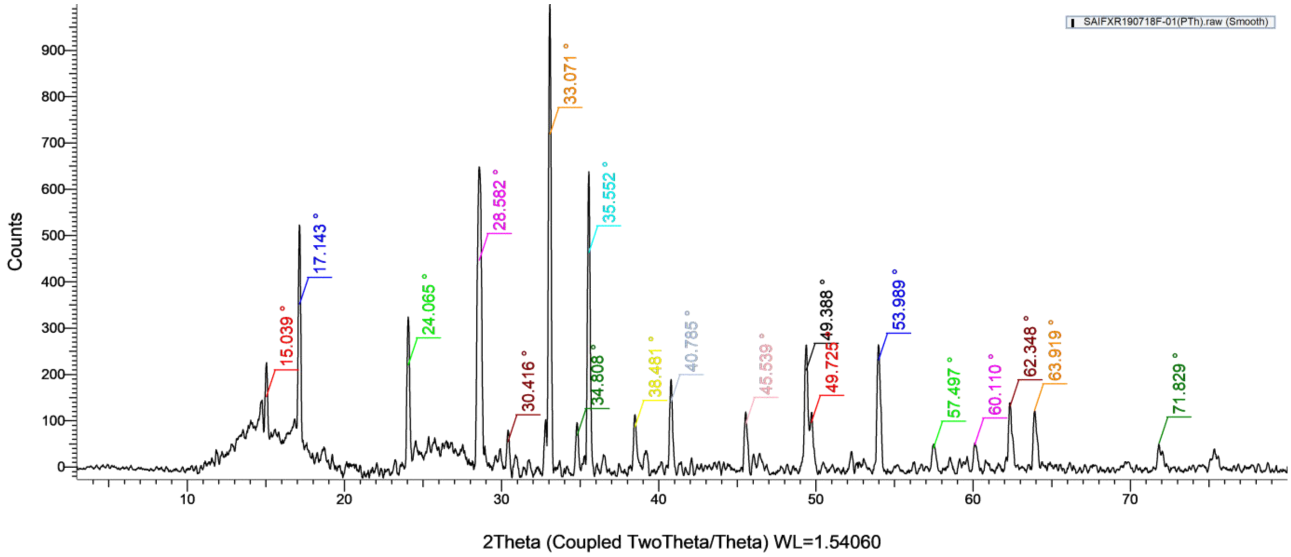

**Fig. 3: XRD spectrum of prepared polythiophene**

indicating semicrystalline nature. The peak at 2θ of 26 is due to the scattering from polythiophene chains at the interplanar spacing. The peaks at about 17 and 26 are due to π-π stacking of polymer chains. This shows that during synthesis polythiophene molecules are stacked into crystallites giving semicrystalline nature to the polymer. Crystallinity induces improved conductivity in conducting polymers.

### *3.1.4. Thermogravimetric analysis of PTH*

Thermogravimetric and derivative thermogarvimetric curves of the synthesized PTH is shown in Fig. 4. Distinct weight loss regions are observed in the thermal analysis curves of PTH. The first weight loss below 120°C corresponds to the loss of moisture absorbed in the polymer together with the elimination of solvents, monomer and oligomers.

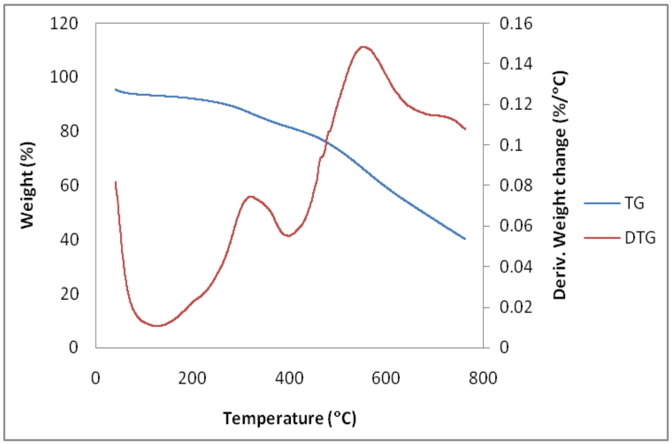

**Fig. 4: Thermogravimetric and derivative thermogravimetric curves of PTH**

The next step in the degradation in a temperature range of 170°C to 400°C may be corresponding to the loss of dopant molecules from the conducting polymer. A sharp increase in dopant loss is observed only after 210°C, indicating sufficient thermal stability of PTH even at temperatures intended for melt processing of the composite. The third degradation step starting at around 400°C and extending beyond 700°C can be attributed to the degradation of polymer main chain.

### *3.1.5. Conductivity*

The prepared polythiophene was pelletized using a hydraulic press and DC electrical conductivity was determined by 2 probe method. The conductivity was found to be 1.6 $Sm^{-1}$ which is considerably higher compared to previously reported data [13]. This can be attributed to the semicrystalline nature of the synthesized polythiophene as evident from XRD spectrum.

## 3.2. Characterisation of PTH/PP composites

### *3.2.1. Morphology studies*

Scanning electron microscopy images of the tensile fracture surface of 40 phr PTH filled polypropylene composite is shown in Fig. 5. The two images are of different magnifications. PTH particles are seen uniformly distributed throughout the fracture surface. The strong network of PTH particles acts like a skeleton improving the rigidity of the composite which will be reflected in the modulus values of the composites. The rough texture of the fracture surface with ridges and valleys indicates the influence of the conducting network on the fracture. The incompatibility of the nonpolar PP matrix with the polar PTH particles weakens the interface between the polar-nonpolar phases.

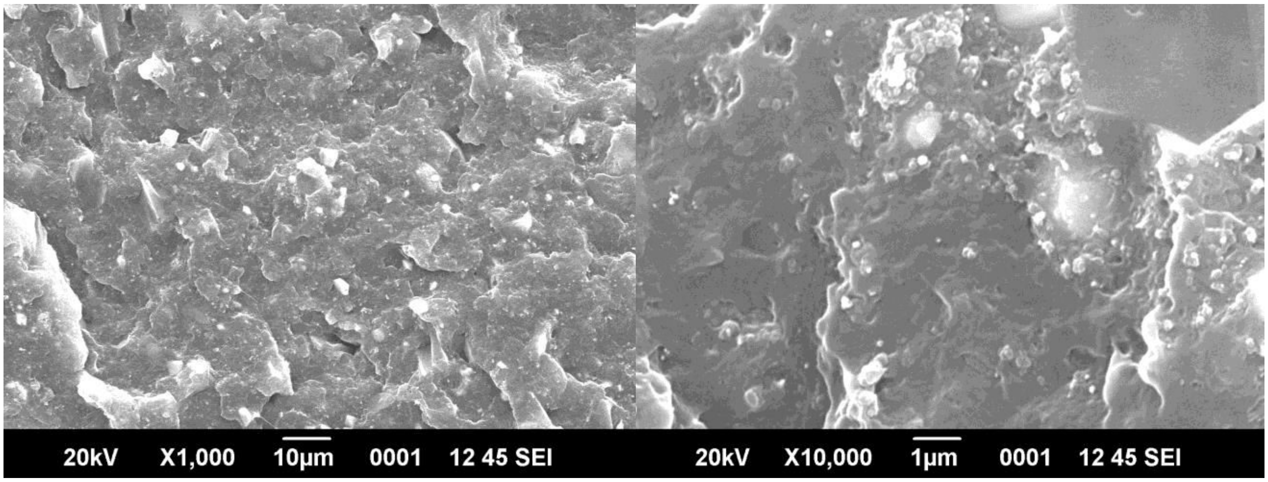

**Fig. 5: SEM image of PTH/PP composite**

Fracture front can easily propagate through these weak interfaces. The fracture propagation through these phase boundaries is responsible for the irregular nature of the surface in the SEM images. The incompatible phases results in a brittle mode of failure.

### *3.2.2. Mechanical properties*

Variation of tensile strength of PTH/PP composites with PTH content is depicted in Fig. 6. Tensile strength decreases in a linear fashion with increase in PTH content. The inherent incompatibility of nonpolar polypropylene and polar polythiophene results in weak interfacial interaction between them. When a tensile force is applied this weak interface develops cracks easily, resulting in lower tensile strength. Increase in PTH content is associated with increase in the weak interfaces and reduction in the stress required for the propagation of cracks leading to further lowering of tensile strength.

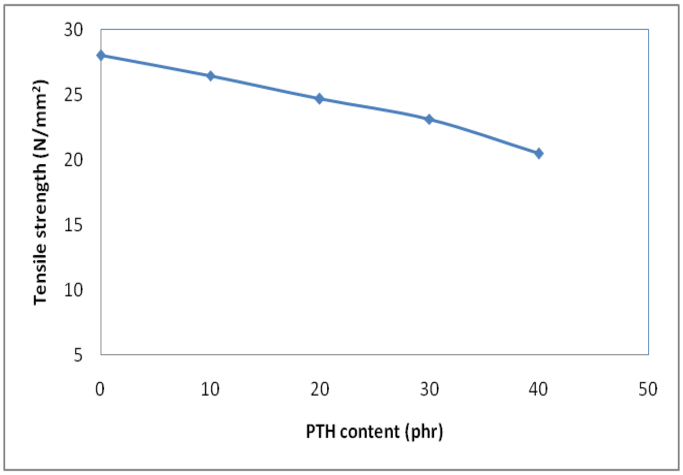

**Fig. 6: Variation of tensile strength with PTH content in PTH/PP composites**

The modulus of the PTH/PP composites (Fig. 7) shows an inverse trend compared to that of tensile strength. Increase in PTH content results in an increase in modulus. The incorporation and optimal distribution of PTH particle in the PP matrix results in the formation of a network of conducting particles in the matrix which improves the rigidity and modulus of the composites. With increase in the PTH content, the network becomes more continuous. The strong association of the polar PTH particles between themselves makes the network more rigid which contributes to better modulus.

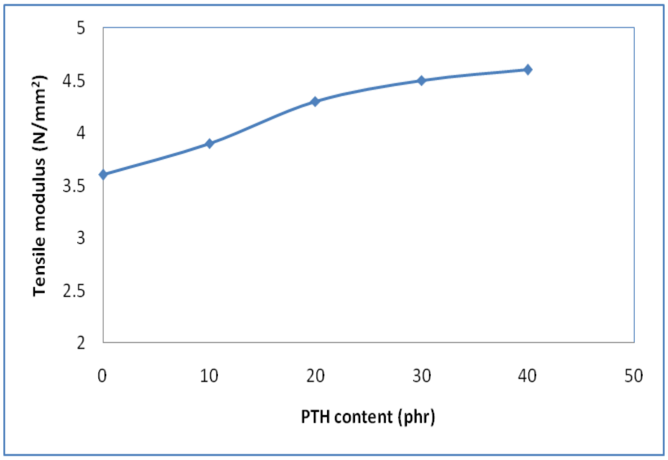

**Fig. 7: Variation of modulus with PTH content in PTH/PP composites**

Variation of the elongation at break of the PTH/PP composites with PTH content is shown in Fig. 8. Similar to tensile strength, elongation at break decreases almost in a linear fashion with PTH content. The weak interfacial interaction at the nonpolar-polar interphase leads to initiation of cracks at the interface. The cracks act as stress concentration points resulting in premature failure of the composites before attaining the maximum potential elongation of the pure matrix. With increase in PTH content the chances of crack initiation and propagation through the interface increases culminating in further decrease in the elongation at break. 40 phr PTH filled composite shows upto 55% reduction in elongation.

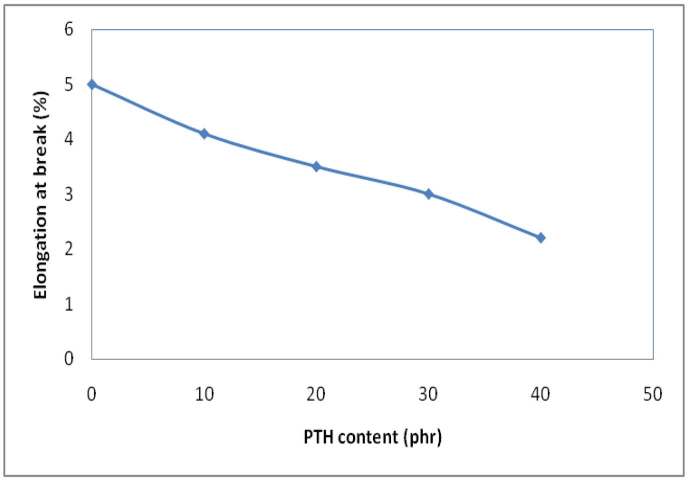

**Fig. 8: Variation of elongation at break with PTH content in PTH/PP composites**

### *3.2.3. Thermal studies*

Thermogravimetric curves of PP and PTH/PP composites are depicted in Fig. 9. For more accurate description of the degradation behavior of the samples, derivative thermogravimetric curves were also plotted which are given in Fig. 10.

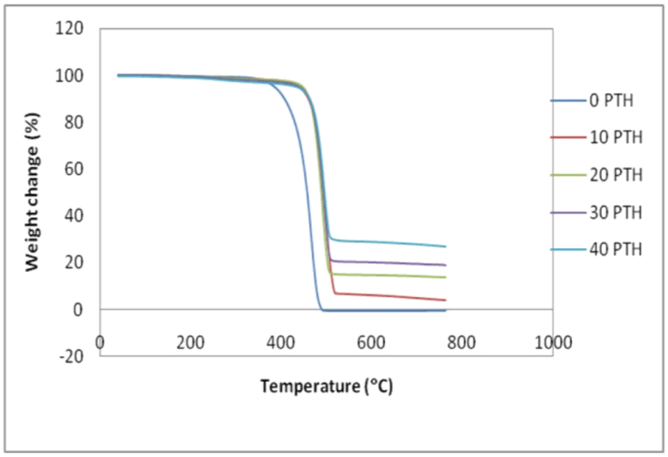

**Fig. 9: Thermogravimetric curves of PP and PTH/PP composites**

It can be seen that there is a considerable improvement in thermal stability of the composites. An increase of around 25°C in the peak degradation temperature is observed for the composites compared to neat PP samples. The main chain degradation of PTH occurs at a temperature beyond 400°C and peaks at around 550°C. Even though the degradation temperature of PP starts at around 350°C, the presence of a continuous network of thermally more resistant PTH particles delays the overall degradation of the composites, thus increasing the thermal stability. Pure PP degrades almost completely without residue, while its composites with PTH give residue corresponding to the weight percentage of PTH content. This confirms the formation of a char by the degradation of PTH which acts as a protective heat barrier layer and delays the degradation of PP matrix.

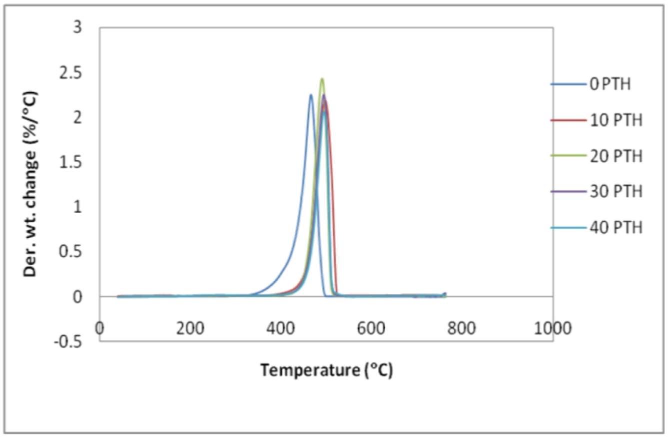

**Fig. 10: Derivative thermogravimetric curves of PP and PTH/PP composites**

### *3.2.4. Conductivity studies*

Variation of conductivity of PTH/PP composites with PTH content is shown in Fig. 11. Conductivity increases with the loading of PTH in the composites. An exponential increase of conductivity with respect to PTH content is seen in the figure.

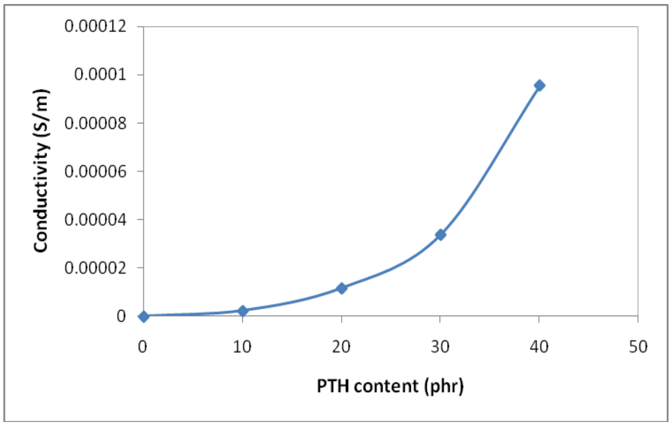

**Fig. 11: Variation of conductivity with PTH content of PTH/PP composites**

PTH particles in the matrix are the conducting elements in the composites. Conductivity is proportional to the effectiveness of the network, the PTH particles form in the matrix. Due to the nonpolar nature of the matrix and polar nature of PTH, the filler has a tendency to aggregate together through polar-polar association, instead of getting distributed evenly throughout the matrix. This behavior obstructs the formation of an effective conducting network at lower concentrations of PTH. But, beyond a critical concentration called percolation threshold, the volume of the conducting particles is sufficient so that the aggregates can establish connectivity with each other thus forming a continuous conducting network. In the case of PTH/PP composites the percolation threshold can be considered to be attained at a loading of 30 phr PTH, beyond which a remarkable increase in conductivity can be observed.

### *3.2.5. Dynamic mechanical properties*

Variation of storage modulus with frequency of PP and PTH/PP composites is illustrated in Fig. 12. With increase in frequency, storage modulus of the samples shows an increase which becomes more pronounced in the samples with higher PTH content. The increase in storage modulus with frequency is more discernible at lower frequencies. In dynamic mechanical analysis lower frequencies corresponds to higher temperature, which explains the lower storage modulus at lower frequencies. These lower frequencies can be considered as equivalent to the state when the material is heated through its transition region in a temperature sweep experiment. At higher PTH content, the filler network formed in the matrix improves the elastic nature of the composite and thereby increases the storage modulus.

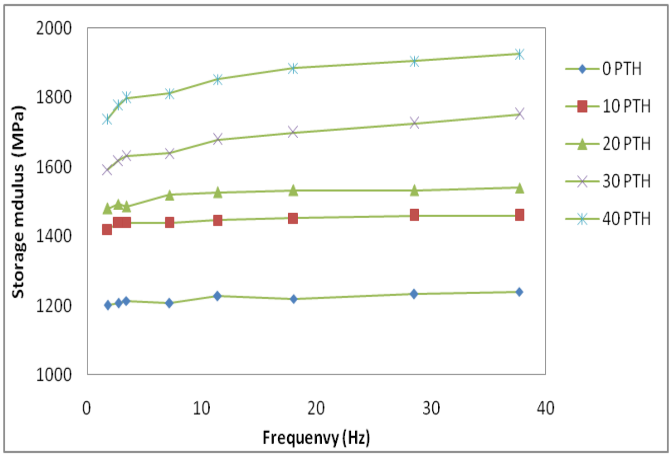

**Fig. 12: Variation of storage modulus of PTH/PP composites with frequency**

At higher temperatures the increased matrix flexibility separates the matrix from the rigid PTH network thus leaving the PTH network to be free standing, without the support of the matrix. This results in the easier breakage of the PTH network under dynamic stress. Since low frequency tests emulate the high temperature behavior of the samples, a change in storage modulus corresponding to the network breakage is visible. At higher loadings the effect of PTH network breakage is higher, producing a correspondingly higher change in the storage modulus at low frequencies. There is no significant change in storage modulus with frequency in the case of pure PP.

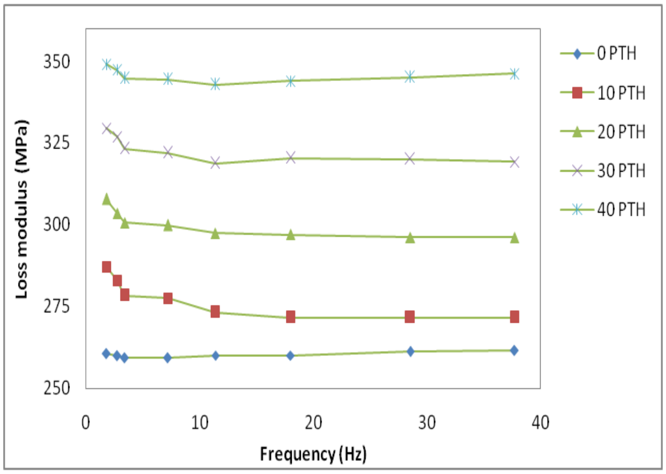

**Fig. 13: Variation of loss modulus of PTH/PP composites with frequency**

The variation of loss modulus with increasing frequency in dynamic mechanical analysis of PP and PTH/PP composites is given in Fig. 13. With increase in PTH content, loss modulus increases. The interface between the matrix and the PTH filler is a cause for dissipation of energy, especially when there is low interaction between the phases. The polar-nonpolar interface in the composites is ideal for energy loss due to its incompatibility. At higher filler content interfacial area is also higher resulting in increased possibility of energy dissipation which is reflected in the increased loss modulus. On considering the frequency dependent behaviour, the loss modulus is found to follow an inverse trend as that of storage modulus at lower frequencies, as expected. As low frequencies correspond to higher temperatures where the matrix exhibits a more viscous nature, loss modulus shows higher values. As frequency of the test increases matrix polymer cahins show a more rigid response equivalent to a decrease in temperature. The consequent increase in elastic nature of the matrix leads to lower loss modulus values. Whereas difference in storage modulus at initial and final frequencies of the composites increases with PTH content, difference in loss modulus at the same frequencies is found to decrease.

Variation of tan δ with frequency of PP and PTH/PP composites is depicted in Fig. 14. Tan δ follows a similar trend as that of loss modulus. Tan δ shows a decrease with frequency, especially at lower frequencies. Since the storage modulus is increasing and loss modulus is decreasing with frequency, the tan δ which is the ratio of loss modulus to storage modulus shows a profound decrease. This is more evident at lower PTH content since the effect of collapse of the PTH network is lower at lower loadings.

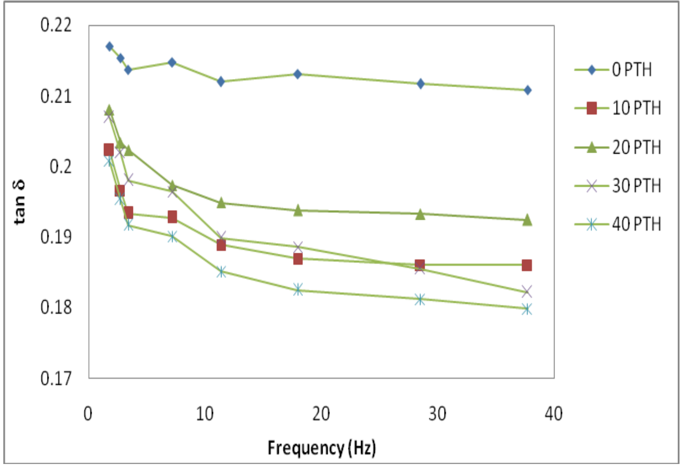

**Fig. 14: Variation of tan δ of PTH/PP composites with frequency**

### 3.2.6. Dielectric properties

Dielectric properties of the composites were explored with respect to frequency and PTH loading. Dielectric constant (Fig. 15) and dielectric loss (Fig. 16) were the properties evaluated. Pure PP samples show low dielectric constant and dielectric loss, as expected, since there are no dipoles or heterogenity in the material that can cause considerable extent of polarization. Dielectric constant of the composites is found to increase with PTH content. Multiple orders of increase in dielectric constant is observed at 30 and 40 phr loadings of PTH in the PP matrix. Increase in dielectric constant is due to increase in polarization, especially dipolar and interfacial polarization in the composites. Increase in the amount of doped PTH which possesses substantial amount of dipoles due to the presence of $Fe^{3+}$ ions and $Cl^{-}$ ions are bound to increase the dipolar polarization in the composites. Interfacial polarization developed on account of charge accumulation on the boundaries of conducting PTH and non conducting PP phases increases with PTH content. Increased dipolar and interfacial polarization, results in very large dielectric constants.

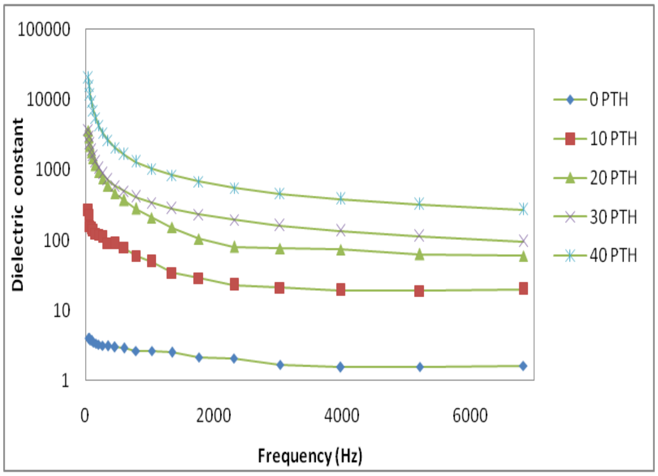

**Fig. 15: Variation of dielectric constant of PTH/PP composites with frequency**

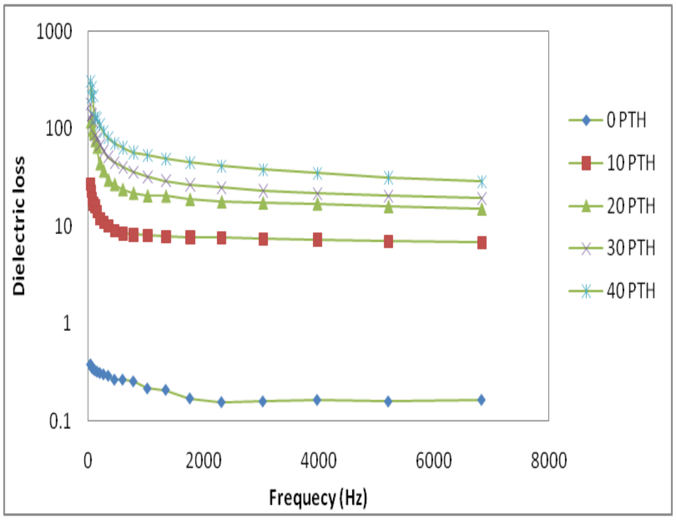

**Fig. 16: Variation of dielectric loss of PTH/PP composites with frequency**

For the composites, dielectric constant decreases with frequency. The dipoles in the composites change orientation with the alternating electric field. At low frequencies change in orientation follows the change in polarity of the electric field. All the dipoles orient in same direction with every change in electric field creating a large polarization in the material. With increase in frequency the dipoles will find it difficult to orient along the direction of electric field overcoming the friction from the surrounding molecules. So there will be a lag in the polarization compared to the electric field direction.

This becomes more evident at high frequencies which is reflected as the decrease in dielectric constant.

Dielectric loss also follows a similar trend as that of dielectric constant, with respect to both PTH content and frequency. Pure PP shows low dielectric loss due to the lack of dipoles in the material. The dipoles in the composites changes orientation in every cycle following the alternating electric field. This causes friction between the dipoles and the surrounding materials which appears as heat. The dissipation of energy as heat is reflected as the dielectric loss. With increase in PTH content, number of dipoles also increases which in turn increases the dielectric loss.

With increase in frequency, the dipoles will not be able to follow the alternating electric field and lags behind. So the dissipation of energy as heat due to friction from the surrounding bulk also decreases, which is reflected as lowering of dielectric loss in the material.

## 4. CONCLUSIONS

Polythiophene was prepared through oxidative polymerization of thiophene using $FeCl_3$. FTIR, XRD and thermal characterization and conductivity measurement of the synthesized material confirms successful polymerization of thiophene monomers. Conducting composites can be prepared by incorporating the prepared polythiophene into polypropylene matrix through melt mixing in an internal mixer. A continuous network of conducting particles is formed within the PP matrix which exhibits low interaction with the matrix on account of polar-nonpolar incompatibility. Tensile modulus is improved by the incorporation of PTH while tensile strength and elongation at break are reduced. PTH addition is effective in improving the thermal stability of the composites. Incorporation of appropriate amount of PTH in PP results in a composite with exceptionally high dielectric constant making them promising candidates for capacitor applications.

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