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Polythiophene/Thermoplastic Polyurethane Flexible Composites for Electronic Applications

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Designing conducting composites which possess high flexibility and good mouldability is highly challenging. This study explores the potential of polythiophene (PTH) as a conducting filler in a flexible matrix, thermoplastic polyurethane (TPU), for developing composites with good electrical, mechanical, and dielectric properties. The composites were prepared by a facile melt mixing route. The addition of PTH significantly reduced electrical resistivity, with a linear increase in DC conductivity directly related to PTH content. Dielectric studies showed that the PTH/TPU composites had high dielectric constant and low dielectric loss, making them ideal for capacitor applications. Mechanical characterization revealed an increase in modulus with increasing PTH content. The ultimate elongation, though lower for the composite, was still good enough for applications requiring flexibility and toughness. Thermal analysis indicated marginal reduction in thermal stability of the TPU matrix in the presence of the conducting filler. With their characteristic properties PTH/TPU composites can be a valuable choice in the field of flexible electronics.

Keywords: polythiophene (PTH), thermoplastic polyurethane (TPU), electrical conductivity, mechanical properties, dielectric constant.

1. Introduction

Conducting polymer composites consisting of a conducting polymeric filler and a nonconducting polymer have many advantages such as light weight, resistance to corrosion, ease of fabrication, and low cost compared to the conventional conductors [1–6]. Thermoplastic elastomers is a class of polymers with thermoplastic-like processing characteristics and rubber-like physical properties. A combination of a thermoplastic elastomer with a conducting filler would offer desired electrical conductivity coupled with rubber like flexibility, which is highly desirable for flexible electronics applications. Thermoplastic polyurethane (TPU) is a well-known thermoplastic elastomer with high gum strength and elongation. Hard and soft segments in the polymer bestow it with the desirable properties of plastics as well as elastomers. Hard segments which melt on application of heat to facilitate melt processing and associate themselves on cooling to act as physical crosslinks. Soft segments constitute the flexibile component of the polymer. Combination of these desirable properties can be utilised to prepare highly flexible conducting composites by incorporating a conducting material into the TPU matrix through melt processing. [6–9]

Carbon black/carbon nanofiber hybrid system was incorporated into TPU matrix by melt processing to reduce electrical resistivity.[10, 11] Effect of melt processing conditions on the electrical percolation threshold of expanded graphite/TPU composites has been reported by Zhang et al.[12] Carbon nanofiber was used as the conducting element to fabricate a porous nanocomposite with piezoresistive behaviour.[13] Carbon nanotubes have been used in TPU matrix to achieve very low percolation threshold.[14] Effect of processing methods on percolation threshold of carbon nanotube/TPU composites has been studied.[15] Carbon nanotube/TPU flexible foam which can be used as pressure sensor has been developed by Huang et al.[16] Effect of filler dimensionality on percolation threshold was demonstrated by comparing carbon black and carbon nanotube composites of TPU.[17] Graphene, noted for its high conductivity and strength to weight ratio, has also been used to prepare TPU based composites.[18, 19]

Another important technique to impart conductivity to the TPU matrix is the incorporation of conducting polymers. Wen et al. [20] studied the effect of polypyrrole on morphology and conductivity of TPU. Ramoa et al. [21] used montmorillonite-polypyrrole nanocomposites prepared by insitu polymerization to make TPU conductive. Nanomembranes of solution blended TPU and poly(3-thiophene methyl acetate) prepared by spin coating has been reported by Pérez-Madrigal et al.[22].

Polythiophene (PTH) as a conducting polymer, has received great attention because its electrical conductivity, can be tuned by doping from insulator to semiconductor to metal range, enabling its application in various fields[23–27]. It has been widely used in devices which need to be environmentally and thermally stable, such as electrostatic coatings, chemical and optical sensors, light-emitting diodes, photovoltaic devices, batteries, smart windows, DNA detectors, polymer transistors, electromagnetic shields, super capacitors and catalyst support materials. [27–35]

By incorporating PTH in a TPU matrix a conducting composite with high flexibility, which is highly desirable in electronic applications can be fabricated. In this study the PTH/TPU composite was prepared through melt mixing in an internal mixer and compression moulding in a hydraulic press. The flexible and easily processable composites were evaluated for mechanical, thermal and electrical properties.

2 Materials and methods

2.1 Materials

Thermoplastic polyurethane elastomer (Elastollan C 80 A) is polyester based. It was supplied by BASF-India. Thiophene, ferric chloride, dichloromethane and acetonitrile were supplied by E- Merck Mumbai., India.

2.2 Preparation of Polythiophene

The preparation and characterization of PTH was reported in our earlier work [36]. 16 ml of thiophene was dissolved 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 1:4 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.

2.3 Preparation of composites

Table 6.A.1. Formulation of PTH/TPU composites

Contents	phr				
TPU	100	100	100	100	100
PTH	0	10	20	30	40

Mixing was done in a Brabender Plastograph at a temperature of 190 °C. When TPU was softened by temperature and shear, PTH powder was added slowly to TPU 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 to small pieces and used for compression moulding in a hydraulic press at a temperature of 195 °C under 200 MPa pressure.

2.4 Characterization methods

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 at 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 Mechanical properties

Mechanical properties of the composites were studied with respect to varying PTH concentration. It was expected that TPU, with the polar ester linkages, will interact with the TH particles and strengthen the matrix. However, Fig. 1 shows that the tensile strength decreases with the increase in PTH content. This may be due to the fact that the polarity on PTH, induced by the presence of the dopant, may not be sufficient for significant interactions. On application of a tensile force the interfacial interaction fails, causing crack initiation and propagation through the interface. Additionally, the PTH agglomerates formed due to improper wetting act as points of weakness. Combination of these factors lower the tensile strength.

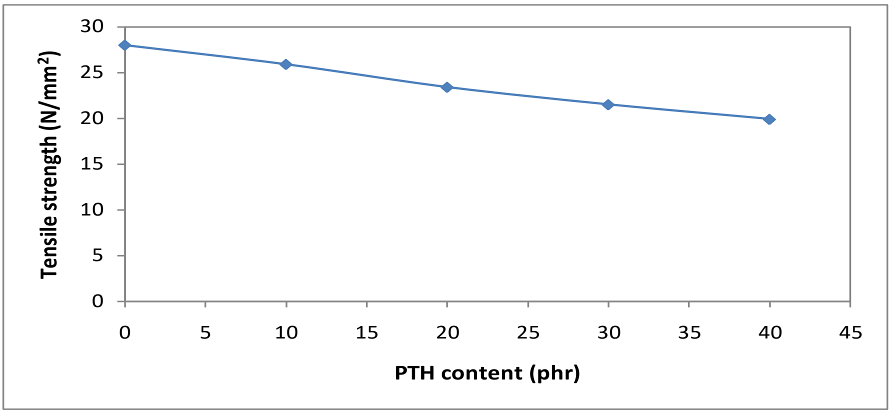

Fig. 1 Variation of tensile strength with PTH content

Effect of PTH particles on modulus of the composites is shown in Fig. 2. Modulus increases with increase in PTH content. Even though agglomerations are present the PTH particles distributed throughout the matrix offer an interconnected network through interaction between themselves. The interfacial interaction between the matrix and the network of PTH particles, even though not significant enough to improve tensile strength, impart additional rigidity to the composite. At the strains where modulus is measured, the interfacial interaction is not completely destroyed and hence the composite is more rigid.

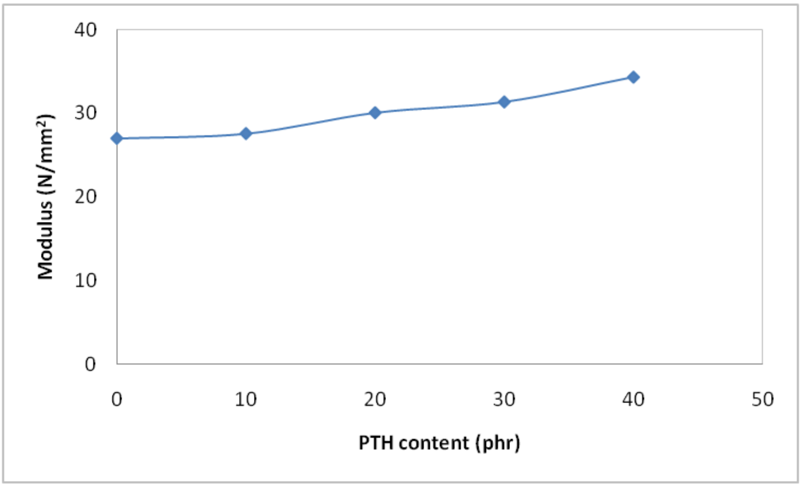

Fig. 2 Variation of modulus with PTH content

Variation of elongation at break of the composites with increasing addition of PTH is given in

Fig. 3. A large reduction in elongation at break is observed on addition of PTH. The reduction is significant at even at 10 phr loading. Compared to PP and PE in pure form, TPU exhibits very high elongation. At these high elongations maintaining an interface without defect initiation requires very good interfacial adhesion. The lower than sufficient polarity of PTH particles is not capable of providing the required interfacial interaction at these strains. As a result, defects are initiated at the interface. Further application of stress induces stress concentration at these defects and the samples fail at low elongations. At higher loadings of PTH, chances of agglomeration increases, reducing the elongation at break further.

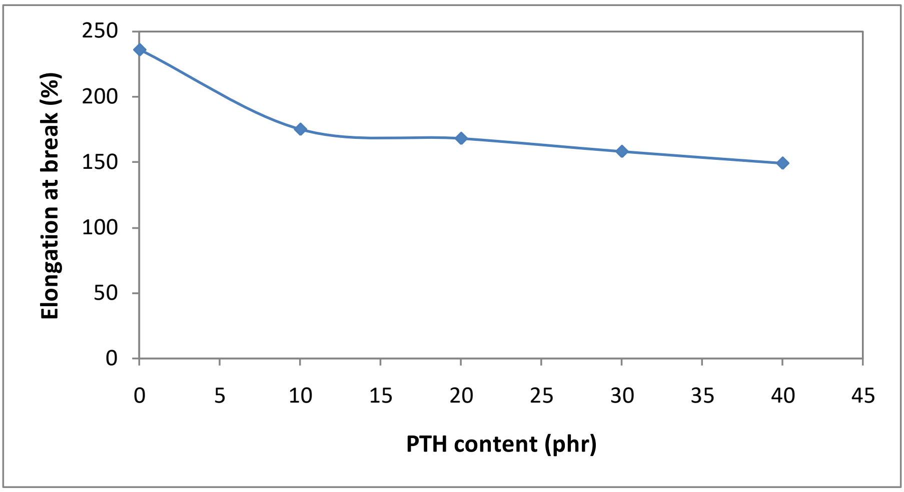

Fig. 3 Variation of elongation at break with PTH content.

3.2 Morphology studies

Morphology of tensile fracture surface of PTH/TPU composites was analyzed from scanning electron microscopy images. Figs. 4(a) and 4(b) show images of different magnifications. Fracture surface is rough and irregular on which PTH particles are seen distributed throughout, mostly in the form of agglomerates. Tensile forces applied on the samples enlarge the defects present in the sample, and develop them into tear lines propagating through the interface. These tear lines are frequently interrupted and are forced to take alternate paths by the PTH particles which are bonded to the matrix by polar-polar interaction. This, coupled with intermittent pull out of agglomerates, lead to a highly irregular texture of the fracture surface. The agglomerates seen on the fracture surface suggest improper wetting of polar PTH particles by the polar matrix. The polarity of PTH particles, produced by the presence of dopant $FeCl_3$ molecules, may not be sufficient for proper wetting by the matrix. The polarity mismatch disrupts uniform dispersion of individual particles in the matrix leading to agglomeration. However, these agglomerates are smaller in size and distributed uniformly in the matrix, giving a uniform stress response on the application of a tensile force.

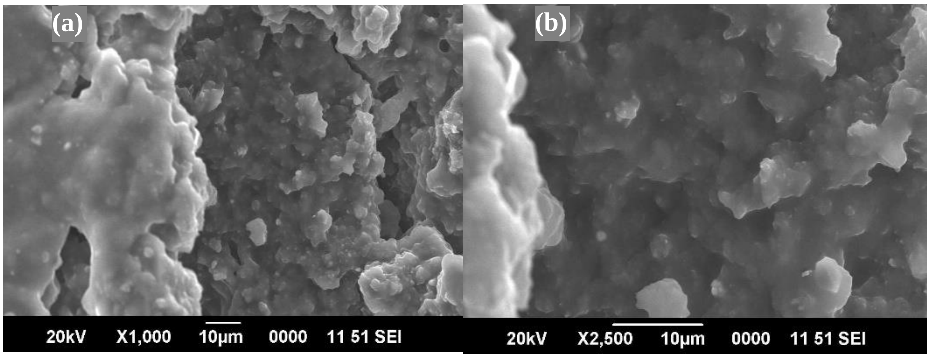

Fig. 4 (a & b) SEM image of fracture surface of PTH/TPU composites (40 phr) at different magnifications

3.3 Thermal studies

Thermal analysis of PTH, TPU and PTH/TPU composites was carried out. Fig. 5 shows thermogravimetric curves of PTH and Fig. 6 gives thermogravimetric curves of TPU with different concentrations of PTH. 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. The next step in the degradation in the temperature range 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. About 40% of residue remaining shows the char forming characteristics of PTH on thermal degradation.

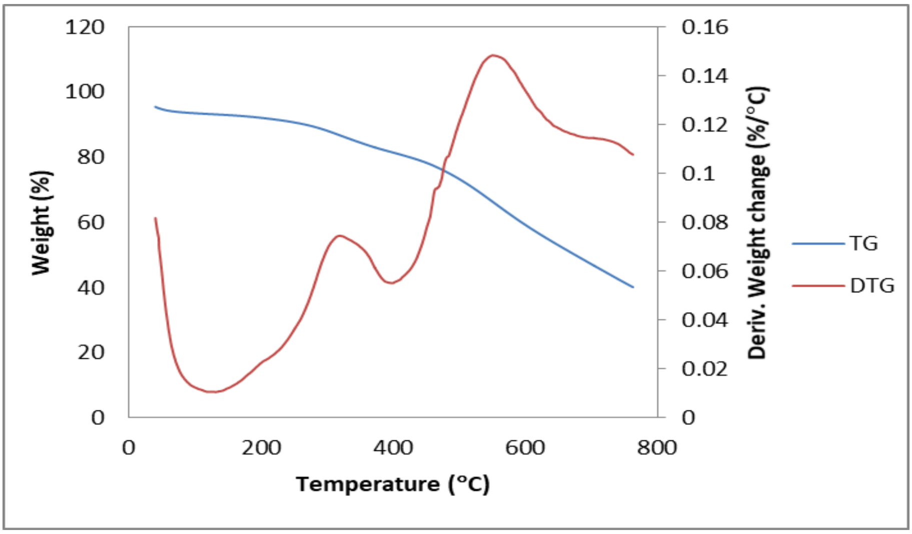

Fig. 1 Thermogravimetric curves of polythiophene

Derivative thermogravimetric curves of TPU and PTH/TPU composites are given in Fig. 6.

Weight loss curves are given as inset. From the derivative thermogravimetric curves it is evident that TPU degrade by a two-step mechanism producing two peaks in the thermograms. First peak at around 340 °C corresponds to the degradation of hard segments containing urethane linkages as urethanes are comparatively thermally unstable materials. Second peak at around 390 °C corresponds to the degradation of the soft segments containing ester linkages which shows relatively higher thermal stability.[37–39] TPU composites exhibit a lowering of thermal stability on addition of PTH as evident from the shifting of peaks to lower temperatures in the DTG curve. Urethane and ester groups in TPU are easily hydrolysable in an acidic environment. $FeCl_3$ retained in the TPU matrix as the dopant, in combination with the moisture that ingress into the material, produce HCl, which induce hydrolysis of urethane and ester linkages thus causing depolymerization. The resultant low molecular weight products is responsible for the low thermal stability of the composites. With increase in PTH content the amount of $FeCl_3$ will also increase resulting in higher extent of molecular degradation and lower thermal stability. Larger than expected amount of residue in the case of composites, indicates that the char first formed from the PTH network protects the remaining matrix material from further degradation.

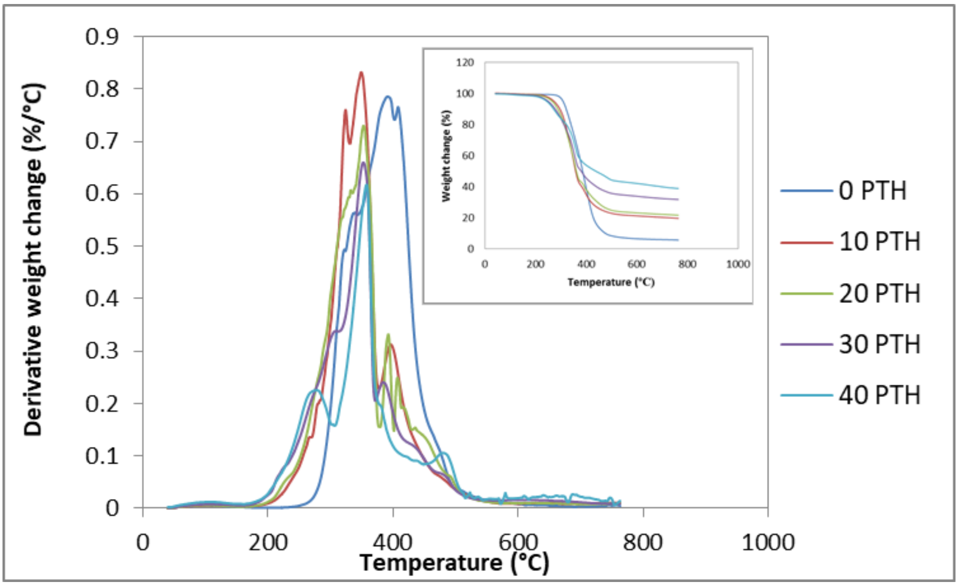

Fig. 6 Thermogravimetric curves of TPU and PTH/TPU composites

3.4 Conductivity studies

Effect of PTH content on DC conductivity of PTH/TPU composites is depicted in Fig. 7. PTH/TPU composites exhibit a linear increase in conductivity with PTH content which may be due to the uniform distribution of PTH particles in the TPU matrix. TPU matrix is capable of

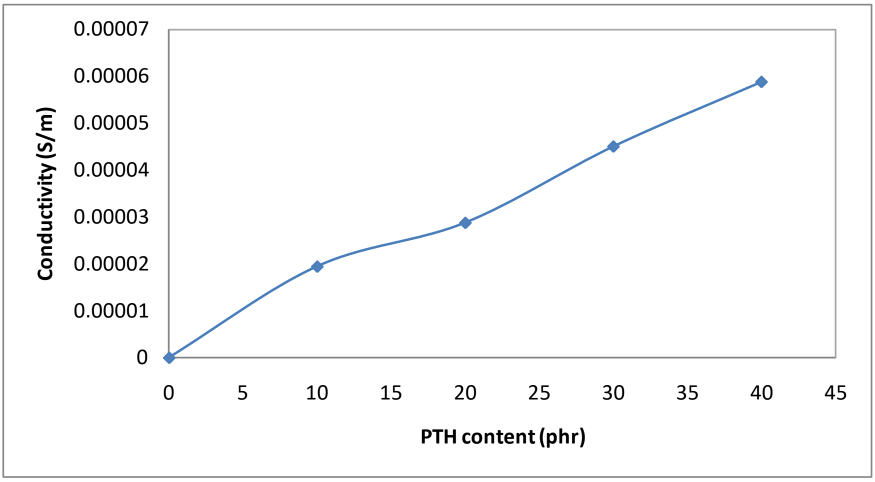

Fig. 2 Variation of conductivity with PTH content of PTH/TPU composites

wetting PTH particles on account of polar-polar interaction. Uniformity in distribution establishes an effective conducting network of PTH particles at even low loadings. However there is no exponential increase in conductivity as shown by PTH/ PP composites in our earlier work.[36] This may be attributed to the amorphous nature of TPU matrix. In the absence of crystallites in the matrix preferential distribution of PTH particles is not possible which necessitates higher number of PTH particles to establish a continuous conducting network and lower conductivity.

3.5 Dynamic mechanical properties

Variation of storage modulus with frequency of TPU and PTH/TPU composites in dynamic mechanical analysis is given in Fig. 8. For the composites storage modulus increases with frequency, the increase being more visible at lower frequencies. Pure TPU does not show any appreciable change with frequency. In dynamic mechanical analysis, behaviour at lower frequency corresponds to that at higher temperature. So decrease in frequency can be considered as increase in temperature, which can simulate a transition from a glassy state to a rubbery state. The dispersion of PTH particles within the TPU matrix results in the development of a network which impart rigidity to the composite and improve storage modulus. During the transition from glassy to rubbery state, matrix softens and would not be able to support the PTH network under dynamic application of force. This results in the collapse of the network leading to a decrease in modulus. With increase in PTH content the network of PTH particles within the matrix becomes more extensive and stronger, increasing the modulus of the composites. Stronger the network, higher will be the change in modulus on its collapse.

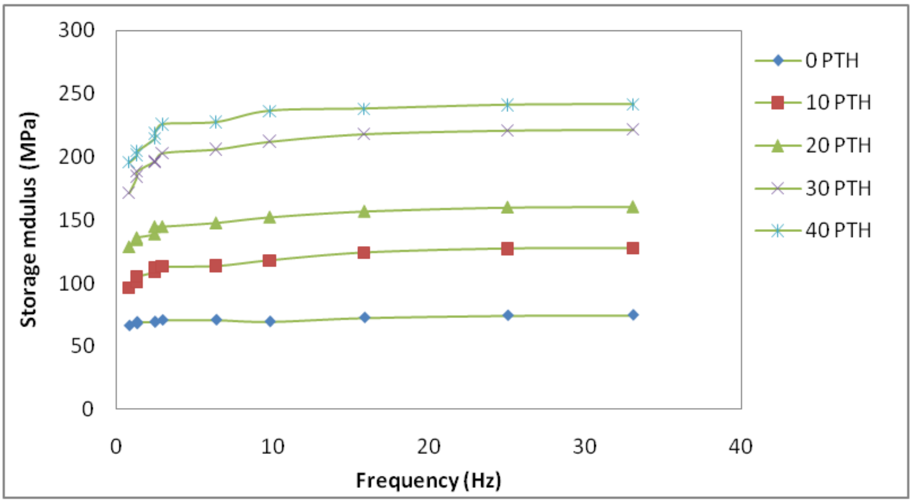

Fig. 3 Variation of storage modulus of PTH/TPU composites with frequency

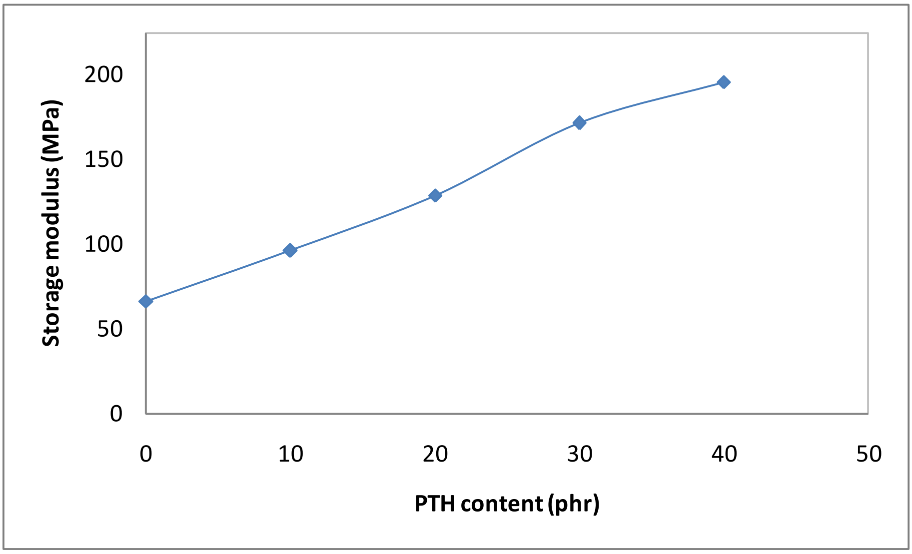

Fig. 9 Variation of storage modulus @ 1 Hz of PTH/TPU composites with PTH content

Storage modulus at a frequency of 1 Hz is plotted against PTH content in Fig. 9. A linear increase in storage modulus indicates the PTH network becoming extensive and good interaction between matrix and PTH.

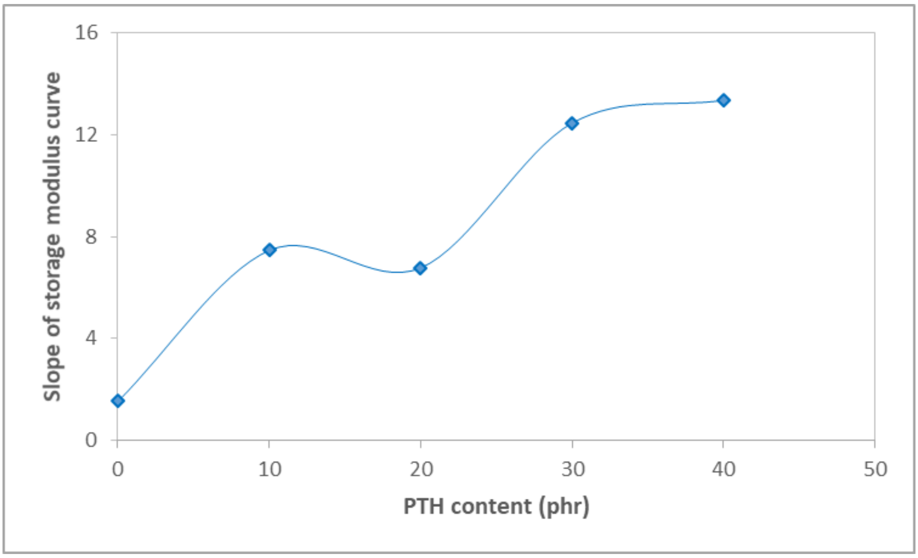

Fig. 10 Variation of slope of the initial portion of storage modulus curve of PTH/TPU composites with PTH content

Slope of the initial portion of the storage modulus curve is analysed against PTH content of the composites (Fig. 10). Generally the slope increases with PTH content indicating a sharper response to increase in frequency or decrease in temperature. When translated to the effect of increase in temperature, this can be interpreted as the large loss in stiffness which arises from the breakage of the PTH network.

Variation of loss modulus with frequency and PTH content is shown in Fig. 11. With frequency, loss modulus shows an inverse trend compared to that of storage modulus. At lower frequencies, which correspond to higher temperature, matrix becomes flexible and is no longer able to hold together the network of PTH particles. The collapse of the PTH network within the matrix results in a further increase of flexibility. This results in higher loss of energy during dynamic application of force which is expressed as high loss modulus at lower frequencies. Further, at lower test frequencies the elastomer molecules in the sample respond by uncoiling and coiling during stretching and contraction which brings about friction between molecules and results in loss of energy. As the frequency of test increases this uncoiling and coiling may lag behind the frequency, decreasing the loss of energy and hence loss modulus. Energy is also lost at the matrix-particle interface. This too contributes to the loss modulus. With increase in PTH content interfacial area also increases which enhances the energy loss and consequently the loss modulus.

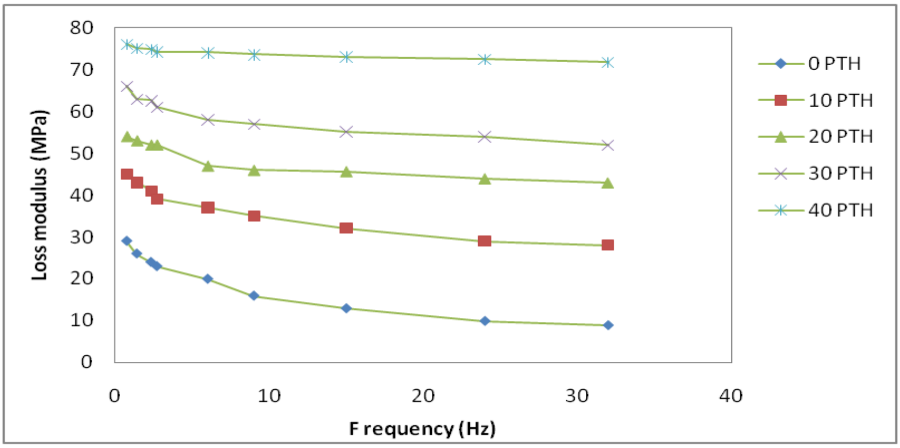

Fig. 11 Variation of loss modulus of PTH/TPU composites with frequency

3.6 Dielectric properties

Dielectric properties of pure TPU and PTH/TPU composites were examined with respect to frequency and PTH content. Variation of dielectric constant and dielectric loss is illustrated in Fig. 12 and Fig. 14, respectively. Dielectric constant of the composites at 118 Hz with PTH content is depicted in Fig. 13. Dielectric constant of pure TPU has contribution from the dipoles originating from the polar groups in the material. With the addition of PTH, dielectric constant increases in multiple orders of magnitude. With the increase in PTH content the number of dipoles increases which results in increased dipolar polarization. Apart from this, the difference in conductivity of PTH and the matrix results in charge accumulation at the interface leading to interfacial polarization. With increase in PTH content interfacial area and hence interfacial polarization increases. Both dipolar and interfacial polarization contribute to dielectric constant raising it to high levels.

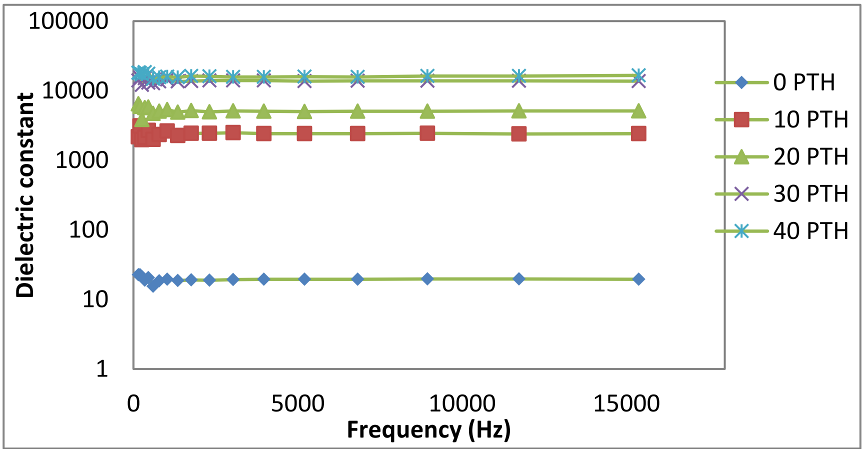

Fig. 12 Variation of dielectric constant of PTH/TPU composites with frequency

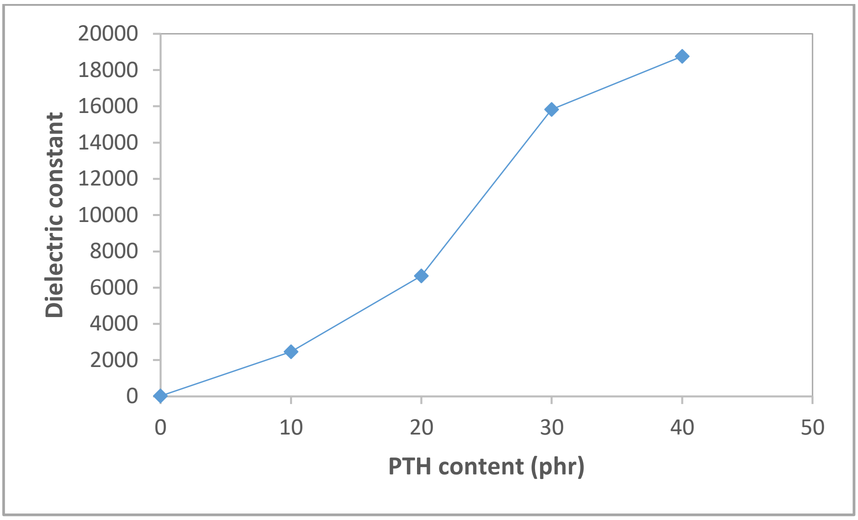

Fig. 13 Variation of dielectric constant at 118 Hz with PTH content

Dielectric constant and dielectric loss of the composites decreases with frequency. As the frequency increases the orientation of dipoles and the charge accumulated at the conducting-nonconducting interface lag behind the alternating electric field leading to lower polarization and resultant lower dielectric constant. The lag in orientation has its effect on the heat generated due to friction of the dipoles with the surrounding molecules, which is reflected as a lowering of the dielectric loss.

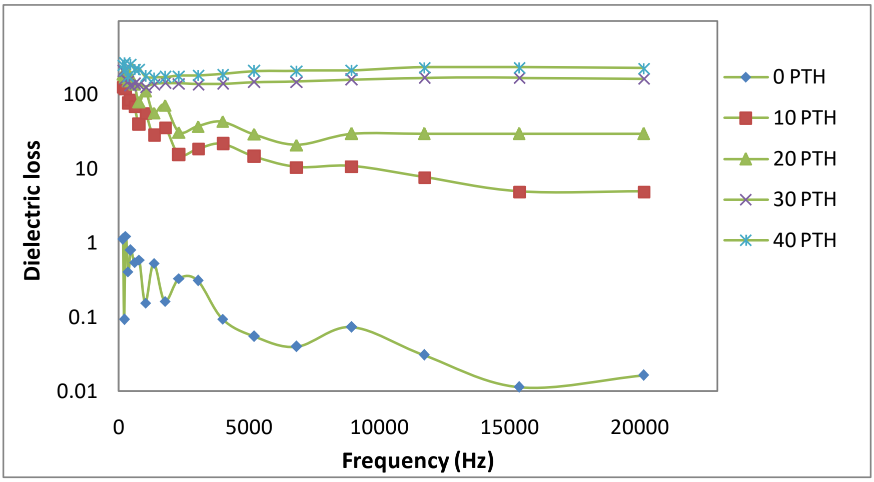

Fig. 14 Variation of dielectric loss of PTH/TPU composites with frequency

4 Conclusions

Conducting composites with high flexibility can be prepared by incorporating polythiophene (PTH) in a commercial thermoplastic elastomer, TPU, by melt mixing in an internal mixer. Morphology of the fracture surface indicates polar-polar interaction between PTH particles and the matrix. However, it is not good enough to impart reinforcement in the composites. Thermal stability of the composites is reduced due to hydrolytic degradation of TPU molecules. Good wetting of PTH particles and the resulting uniform distribution within the matrix results in a linear increase in conductivity of PTH/TPU composites with filler content. The prepared composites offer very high dielectric constant and comparatively low dielectric loss making them promising materials for capacitor fabrication.

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