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Polythiophene Coated Cellulose Fiber/High Density Polyethylene Composites for Capacitor Applications

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Conducting composites with enhanced flexibility and tunable electrical properties are highly desirable for applications in flexible electronics, wearable sensors, and actuators. In this study, polythiophene-coated banana stem fibers (PCFs) and high-density polyethylene (HDPE) were used to develop conducting composites. The PCFs, prepared via oxidative polymerization, exhibited a conductivity of 1.0 S/m. It was introduced into HDPE through a melt-mixing process, followed by compression molding. The composites were characterized for mechanical, morphological, thermal, electrical, and dielectric properties. Morphological analysis revealed poor interfacial adhesion between the polar PCFs and the nonpolar HDPE matrix, leading to decreased tensile strength and elongation at break with increasing fiber content. However, tensile modulus and thermal stability improved which was attributed to the formation of a network of PCFs and the protective effect of the polythiophene coating. Electrical conductivity increased significantly at fiber loadings above 20 phr, although moisture retained in the fibers and dopant migration partially limited conductivity. Dielectric properties improved with fiber content. The composites showed high dielectric constant and comparatively low dielectric loss. The study demonstrates the potential of polythiophene-coated natural fibers as flexible, conductive fillers in thermoplastic matrices, to develop efficient capacitors.

1. Introduction

Conducting composites that exhibit mechanical flexibility to any appreciable extent, have always been attractive in electronics industry due to the peculiar advantages they offer in the fields of flexible displays, wearable sensors, actuators, electromagnetic interference shields etc. A facile method to prepare these composites would be to incorporate conducting elements in a flexible polymer matrix. High density polyethylene (HDPE) is a thermoplastic polymer possessing sufficient flexibility to be qualified as a suitable matrix material for the above mentioned application fields. Conducting elements in fiber form is bound to be more effective in such composites in improving the conductivity at lower filler fractions. This can be attributed to the possibility of fibers forming a continuous network within the matrix, far more effectively, compared to particles at the same volume fraction. On account of this there have been attempts to use conducting fibers in polyethylene to impart desired conductivity to the resulting composites. Balta et al. used carbon fibers in PE matrix along with carbon black to make conducting composites [1]. Carbon nanofibers have been used as conducting elements in HDPE-Glass fiber composites [2]. An alternative option would be to effect a conductive coating on a non-conducting fiber and employ them to work as the conducting elements. The fiber material which is to be coated with the conducting polymer should not impair the flexibility of the resulting composites. Cellulosic fibers are expected to satisfy this primary requirement of the fiber component in the conducting composite. There are many reports on the use of cellulosic fibers from different sources in PE matrix and their effect on mechanical, thermal and morphological properties [3-8].[i],[iiiii],[iv],[v],[vi],Effect of surface modification and hybridization of the cellulosic fiber on the composite properties have also been major areas of interest [9-11].[vii],[viii],

Polythiophene (PTH) is a prominent conducting polymer widely recognized for its exceptional environmental and thermal stability, tunable electrical conductivity, and unique redox properties. By doping, its conductivity can be adjusted across a large spectrum, from insulating to metallic states, making it highly versatile for advanced applications. However, the practical utility of PTH is often hindered by its poor processability due to its inherent insolubility and infusibility. The same processing difficulties come in the way of preparing PTH in fiber form. To overcome this limitation, PTH can be coated onto cellulosic fibers to be used as conducting elements in fiber form. These coated fibers will combine the flexibility of cellulose with electrical and environmental benefits of PTH. Preparation and characterization of such short fibers from Banan stem, coated with PTH have been presented in our previous work.[ix] Such fibers, when integrated into matrices like high-density polyethylene (HDPE), offer an excellent balance of mechanical, and electrical properties, with processability. To the best of our knowledge there have been no previous reports on PTH coated cellulose fiber/HDPE system.

[x]In the present work cellulosic fibers from banana stem was selected as the reinforcing component and was given a thin coating of polythiophene on the surface. The modified fibers were incorporated into HDPE matrix via a facile melt mixing method to prepare conducting thermoplastic composites with considerable flexibility. Scanning electron microscopy was used to study the distribution of fibers and the fracture behaviour of composites. The static and dynamic mechanical properties as well as thermal and electrical properties of the composites were also analyzed systematically.

2. Experimental

2.1 Materials

High density polyethylene (HD50MA 180) was supplied by Reliance industries limited, Mumbai. Banana stem fibers were collected locally and were chopped to short fibers of 10 mm length. Thiophene, ferric chloride, dichloromethane and acetonitrile were supplied by E-Merck Mumbai., India.

2.2. Preparation of PTH coated fiber

Banana fibers were washed with distilled water and dried. 16 g of banana fibers were soaked in dichloromethane solution of thiophene (16 ml dissolved in 600 ml) for 30 min. 130 g of ferric chloride was dissolved in 300 ml acetonitrile and added drop wise to the banana fiber/thiophene mixture. The reaction mixture was stirred for 2 hours after which 10 ml of hydrogen peroxide (30%) was added slowly to convert ferrous ions formed 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 coated fibers were dried at 70 °C and incorporated into HDPE in the required amount.

2.2 Preparation of composites

Table 1 Formulation of HDPE/PTH coated fiber composites

Contents	phr				
HDPE	100	100	100	100	100
PTH coated fiber	0	10	20	30	40

Mixing was done in a Brabender plastograph at 145 °C. When the HDPE was softened due to temperature and shear, PTH coated fibers were added slowly to the HDPE matrix 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 chipped into small pieces and used for compression moulding. Moulding was done in a hydraulic press at a temperature of 150 °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 coated fiber (PCF) and PCF/HDPE 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 HDPE/PTH coated fiber composites

As the characterization of PTH coated banana fiber (PCF) that has been carried out in one of our previous studies, [12] and published earlier, it will be prudent to provide only a brief discussion on that. FTIR, SEM and thermogravimetric characterization of PCF had confirmed good adherence of PTH on fiber surface. Furthermore, thermogravimetry revealed delayed escape of moisture from the banana fiber due to the PTH coating on the surface. The conductivity of the coated fibers was found to be 1.0 S/m. This paper will focus on morphological, mechanical, electrical and thermal characterizations of the composites prepared by the incorporation of PCF in HDPE.

3.1 Mechanical properties

Variation of tensile strength of HDPE/PTH coated fiber composites with respect to the fiber content is shown in Fig. 1. Tensile strength decreases with the coated fiber content. The polar-non polar incompatibility between the matrix and the other components is responsible for the reduction in tensile strength. Low interfacial interaction between the matrix and the PTH coated fiber surface leads to poor stress transfer producing areas susceptible to stress concentration. This results in the formation of defects and voids at the interface which grow with the applied stress culminating in the premature failure of the matrix. The incorporation of PTH and the fiber may also disrupt the close packing of the molecular chains in the matrix, thus reducing the crystallinity and inherent strength of the matrix. Similar results have been reported earlier. [13,14]

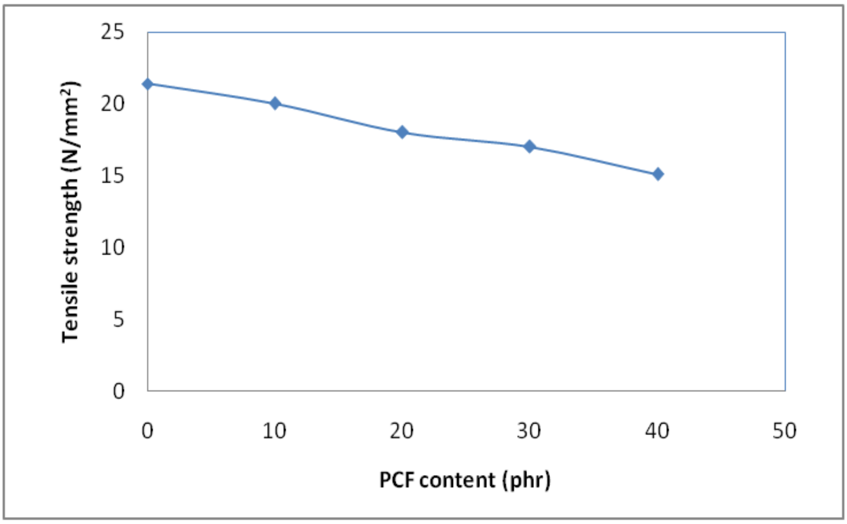

Fig. 1 Variation of tensile strength of PTH coated fiber/HDPE composites

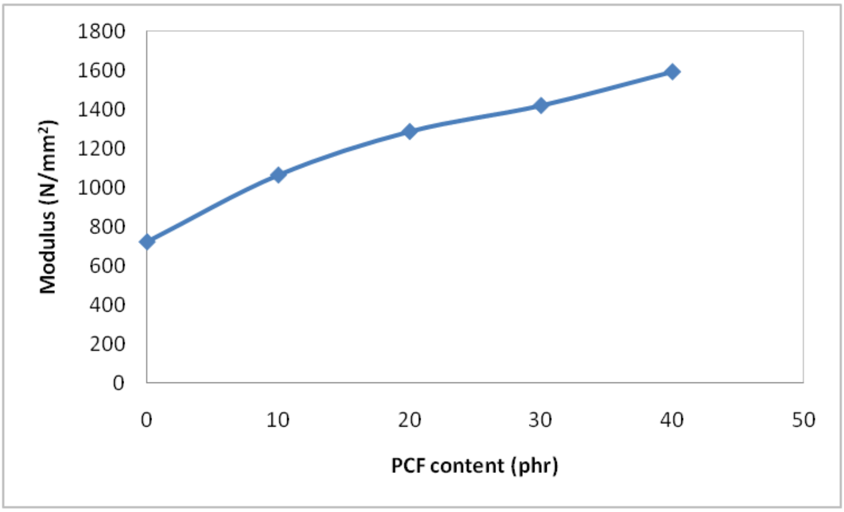

Fig. 2 Variation of tensile modulus of PTH coated fiber/HDPE composites

The effect of PTH coated fiber on the modulus of the composites is shown in Fig. 2. In contrast to the behaviour of tensile strength, tensile modulus increases with the increase in PTH coated fiber content. This is due to the formation of a network of PTH coated fibers within the matrix, which reduces the molecular mobility and improves the modulus. Modulus is measured at low strains at which defect and void formation is very low. So the detrimental effect of the same is not apparent in the modulus measurements.

The influence the coated fiber content exerts on the elongation at break of the composites, is depicted in Fig. 3. Elongation at break decreases with fiber content

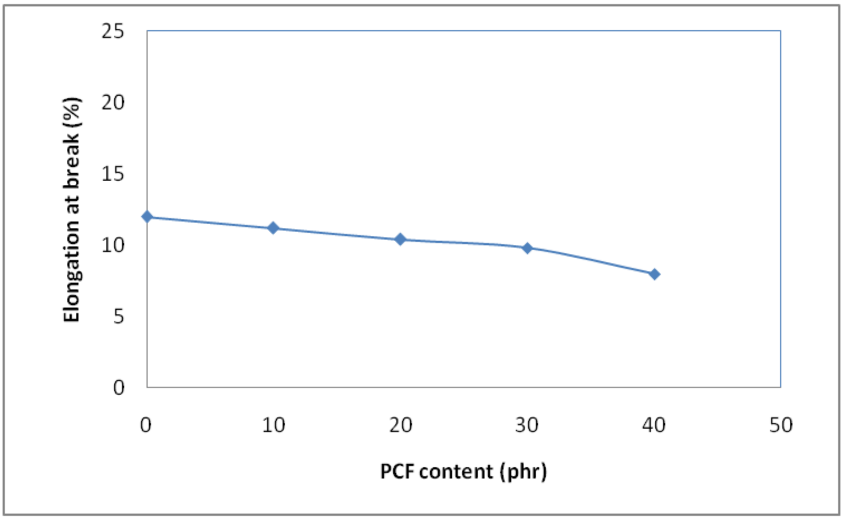

Fig. 3 Variation of elongation at break of PTH coated fiber/HDPE composites

which indicates the restriction to the molecular mobility imposed by the fibers. The lower interaction at the polar-nonpolar interface and the ensuing defects leading to generation of cracks are also responsible for the lowering of elongation by premature failure. With the increase in fiber content the chance for poor dispersion and agglomeration increases. These agglomerates act as points of stress concentration and thus points of weakness, resulting in the failure of the composites without attaining the full elongation.

3.1 Morphology studies

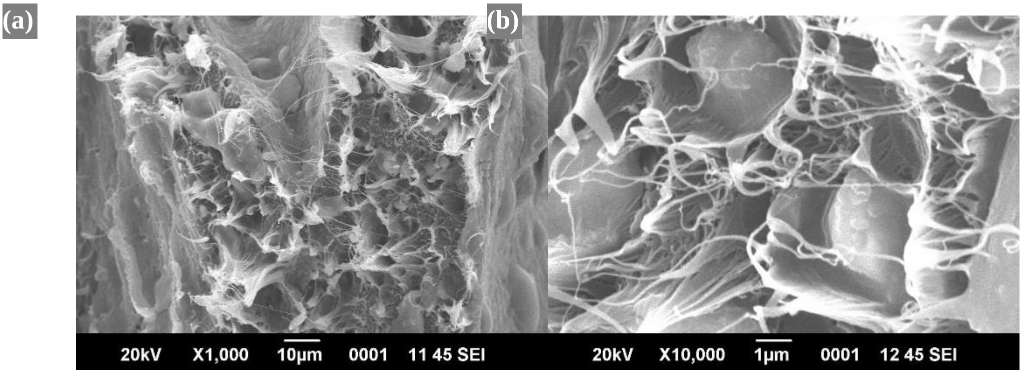

Fig. 4 (a&b) SEM image of fracture surface of PTH coated fiber/HDPE composites (40 phr) at different magnifications

SEM images of the fracture surface of PTH coated fiber/HDPE composites with 40 phr fiber loading are given in Figs. 4 (a & b) where a and b show different magnifications of the fracture surface. PTH coated fibers are seen to be protruding from the HDPE matrix indicating pull out of fibers from the matrix on application of tensile force. The instances of pull out, instead of breakage occur due to the incompatibility arising from low interaction between the nonpolar HDPE matrix and the polar PTH and cellulosic fiber. In the absence of efficient stress transfer between the matrix and the coated fiber stress concentration at interface and the resulting fracture through the interface is expressed as the pull out of fibers. It can be seen that the matrix part around the fibers gets elongated into fibrils in the typical fracture behaviour of polyethylene. However, the presence of incompatible components leads to premature failure and limits the elongation to a low value compared to that of the pure HDPE.

3.3 Thermal studies

Thermal degradation profile of HDPE and PTH coated fiber composites of HDPE is illustrated in Fig. 5 and Fig. 6. Thermogravimetric curves are given in Fig. 5 and derivative thermogravimetric curves in Fig. 6. Compared to pure HDPE, fiber composites show a notable weight loss before the main degradation which can be attributed to the water entrapped in the PTH coated fibers. The coating of PTH may prevent the removal of water during the drying of the coated fiber. In the composites the loss of water becomes even more difficult as the water molecules need to diffuse through the barrier of HDPE matrix. So the weight loss due to water removal gets delayed and occurs at a higher temperature. Compared to pure HDPE the main degradation peak of all the composites is at higher temperatures indicating improved thermal stability. Though degradation of pristine fibers occurs at a lower temperature compared to HDPE, the presence of PTH coating on the fiber imparts stability increasing the degradation temperature. The network of coated fibers existing within the HDPE matrix is responsible for the improved thermal stability of the composites. With increase in fiber content upto 30% the degradation peak shifts to higher temperatures. For 40% fiber content composite a decrease in thermal stability is observed. At higher fiber content agglomeration of fibers may leave parts of matrix exposed without the protection of the fiber network.

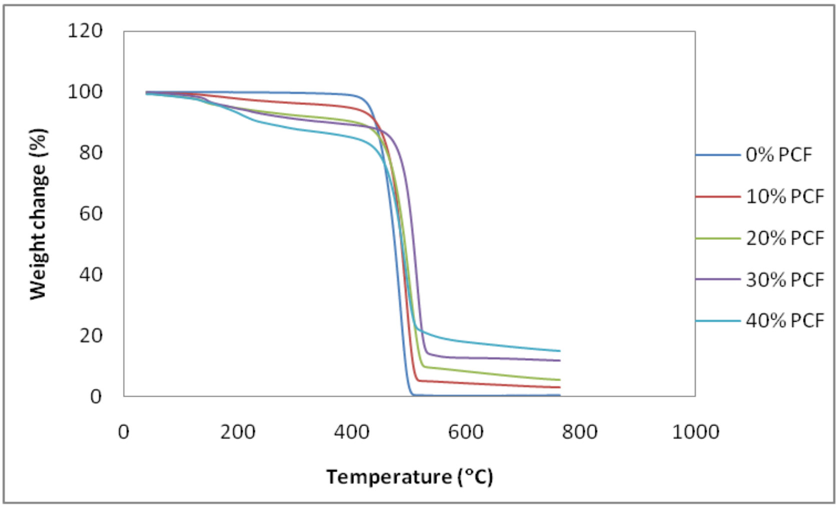

Fig. 5 Thermogravimetric curves of PTH coated fiber/HDPE composites

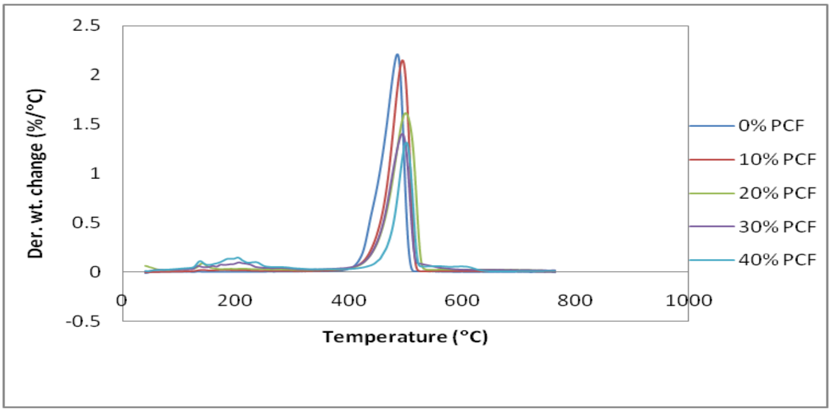

Fig. 6 Derivative thermogravimetric curves of PTH coated fiber/HDPE composites

This may result in a composite with lower thermal stability. It can be found from the derivative curves that with increase in fiber content, the rate of degradation reduces which may be explained by the increased difficulty with which the volatile products of degradation escape from the samples. The residue remaining in the case of fiber composites increases with the fiber content. The char formation by PTH and cellulose is responsible for this substantial amount of residue.

3.4 Conductivity studies

Effect of PTH coated fiber on the conductivity of PTH coated fiber/HDPE composites is shown in Fig. 7. It can be seen that conductivity of the composites increases with the PTH coated fiber content. There is a significant increase in conductivity of the composites beyond a fiber loading of 20 phr. At lower loadings of fibers the network formation within the HDPE matrix by the coated fibers may not be efficient enough to impart desirable conductivity. When the fiber loading is increased the network formed is endowed with higher number of interconnections, making the transfer of charge carriers more efficient and thus increasing the conductivity to a large extent. However the conductivity could not be increased by orders of magnitude as expected for a composite incorporated with conducting polymer coated fibers. The formation of crystallites in the HDPE matrix may have been affected by the incorporation of fibers. Then the amorphous phase in the composites would increase, necessitating the PTH coated cellulose fibers to be filled in a higher volume for the formation of a continuous conducting network. This, limits the conductivity of the fiber composites. The presence of moisture in the coated fiber may also play a major role in decreasing the conductivity of the composites. Water molecules can react with PTH causing incorporation of carbonyl groups in the PTH molecules. These carbonyl groups break the conjugation in PTH molecules rendering the polymer nonconductive [15]. Along with this, the possible migration of the dopant, $FeCl_3$, to the interior of the fibers by dissolving in the moisture and the resultant drop in the degree of doping may also play a detrimental role in the conductivity of the composites.

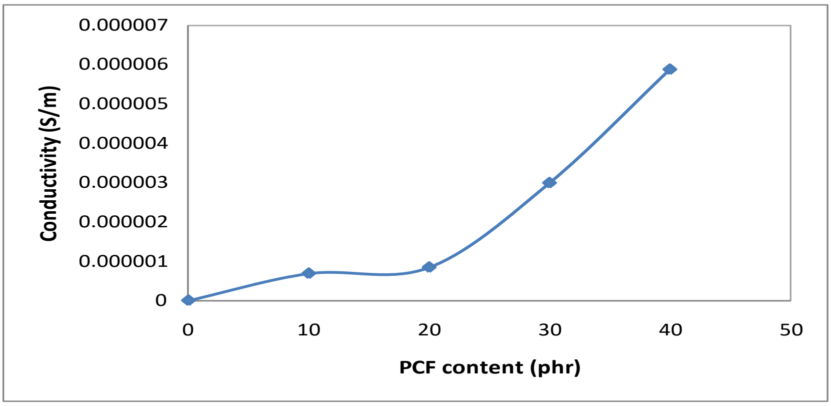

Fig. 7 Variation of DC conductivity of PTH coated fiber/HDPE composites

3.5 Dynamic mechanical properties

Variation of storage modulus with frequency in the dynamic mechanical analysis of HDPE and PTH coated fiber/HDPE composites is given in Fig. 8. In all cases storage modulus increases with frequency. The increase is more pronounced at lower frequencies. As the frequency increases the polymer chains get less time to respond by coiling and uncoiling. This results in a response similar to a situation where the temperature of the test is reduced. At lower temperatures mobility of polymer chains is reduced which appears as an increase in the rigidity and modulus of the sample. Correspondingly higher frequencies show increased modulus. Lowering of storage modulus in low frequencies can be considered as the transition from a glassy state to a flexible region. Here, pure HDPE and all of the composites show the transition region. The melting of the crystallites in HDPE as the temperature increases (or frequency decreases) may be responsible for the observed transition. Coated fibers when incorporated and distributed within the HDPE matrix form into a network increasing the rigidity of the samples, giving higher storage modulus. As the fiber loading increases storage modulus also increases. Similar storage modulus values of 10 and 20 phr composites at lower frequencies indicate that in the absence of crystallites at higher temperatures, the fiber network collapses in both these composites. At still higher fiber loadings the stronger fiber network formed is capable of sustaining itself even at higher temperatures. So, the higher loaded composites exhibit improved storage modulus even at higher temperatures or at lower frequencies.

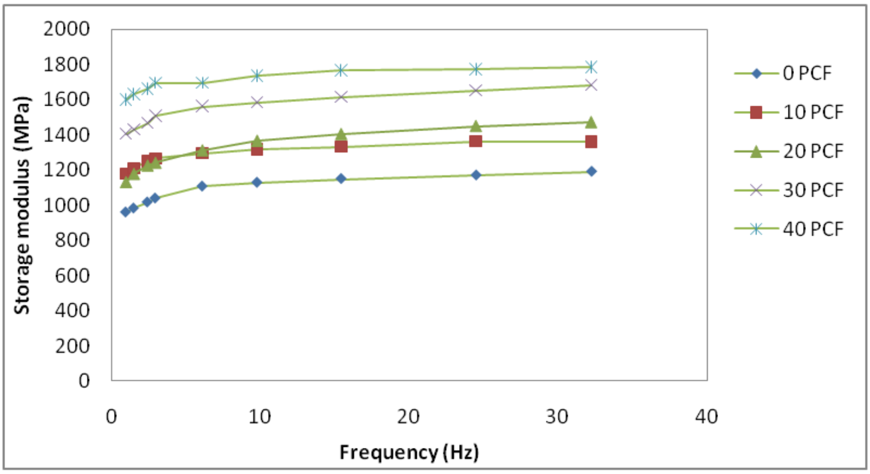

Fig. 8 Variation of storage modulus of PTH coated fiber/HDPE composites with frequency

Variation of storage modulus with respect to PCF content at a fixed frequency of 1 Hz is shown in Fig. 9. 20 phr composite shows a slightly decreased storage modulus compared to that of 10 phr composites, which may be due to improper distribution of PTH coated fibers in the matrix. Apart from this aberration a linear increase is in storage modulus is maintained with PCF loading.

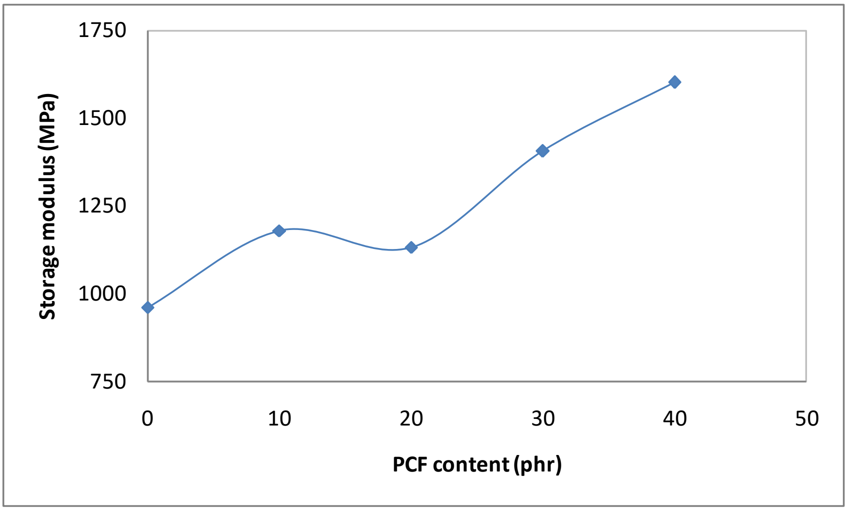

Fig. 9 Variation of storage modulus @ 1 Hz of PCF/HDPE composites

Behaviour of loss modulus with respect to frequency of HDPE and PTH coated HDPE composites is shown in Fig. 10. Loss modulus shows an inverse trend compared to storage modulus by showing a decrease with frequency. Loss modulus is a measure of energy dissipated during the dynamic application of force. As the frequency increases, which is equivalent to lowering of temperature, the molecular movements which are responsible for dissipation of energy are reduced giving lower loss modulus. On lowering the frequency, or increasing the temperature, the melting of crystallites enhances the viscous nature of the samples which results in higher energy loss and loss modulus. This becomes more apparent in pure HDPE and in 10 phr composite where the fiber network is not strong enough to curtail the detrimental effect of crystallite melting. With the increase in fiber content even though a stiffer network is formed, the loss modulus is also found to be increasing. Nonpolar HDPE matrix and the polar PTH and cellulosic fiber have an inherent incompatibility which is expressed as low interaction and consequent poor stress transfer at the interface. This will lead to energy dissipation at the interface. As the coated fiber content increases, fiber-matrix, fiber-PTH and PTH-matrix interfacial area increases resulting in higher energy dissipation and loss modulus.

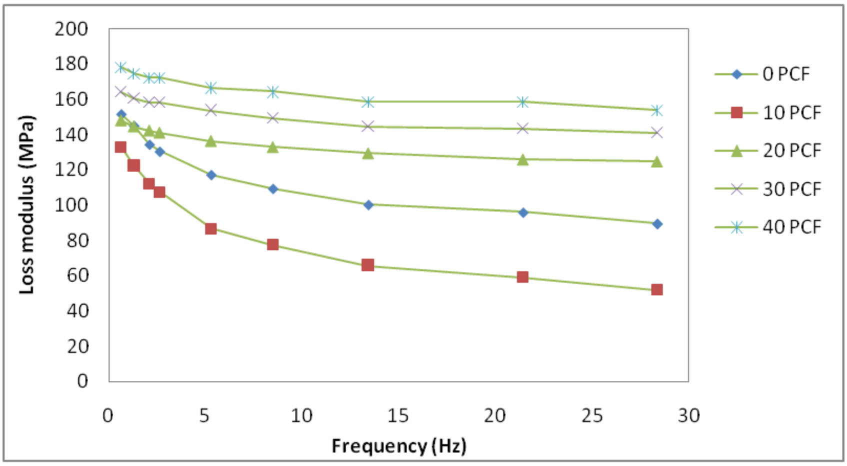

Fig. 10 Variation of loss modulus of PTH coated fiber/HDPE composites with frequency

3.6 Dielectric properties

Dielectric properties of the composites are examined with respect to frequency and PTH coated fiber content. Variation of dielectric constant in HDPE and fiber composites is given in Fig. 11 and that of dielectric loss in Fig. 12. Pure HDPE shows low dielectric constant and dielectric loss on account the absence of any dipoles or heterogeneity in the material. On incorporation of PTH coated fiber, dielectric constant of the samples increases especially at higher loadings. This can be credited to the introduction of dipoles through the presence of dopants in PTH and inherent dipoles in the cellulosic fibers. The resulting dipolar polarization enhances the dielectric constant of composites. Apart from this, difference in conductivity of the components in the composites brings about interfacial polarization by the accumulation of charges at the interface. In the composites, apart from PTH-HDPE interface there will be PTH-fiber interface and fiber-HDPE interface. Possibility of charge accumulation at all these interfaces induces increased interfacial polarization and higher dielectric constant. With increase in coated fiber content both dipolar and interfacial polarization increases thus improving the dielectric constant. Dielectric constant of the composites decreases with increasing frequency which is more pronounced at lower frequencies. The dipoles oriented in the electric field oscillates with the alternating field. At lower frequencies dipoles can keep up with the oscillation of the field. When the frequency increases there will be a lag in the dipole orientation and the resulting polarization, which is expressed as the lowering of dielectric constant.

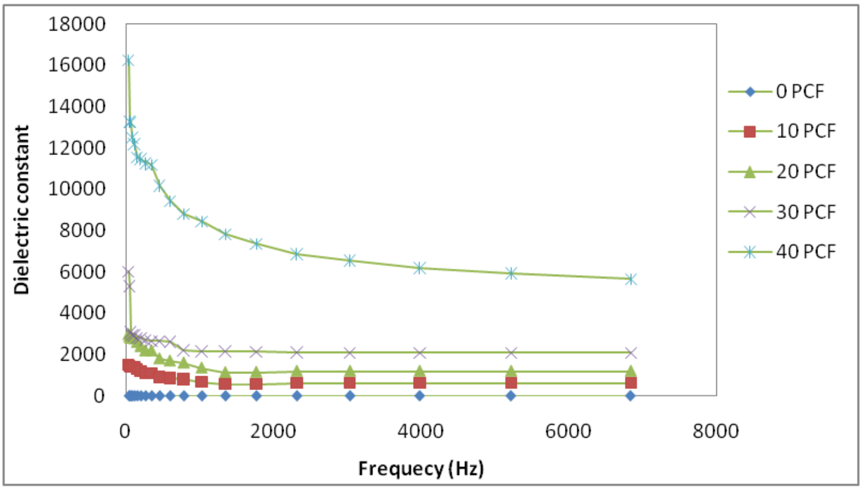

Fig. 11 Variation of dielectric constant of PTH coated fiber/HDPE composites with frequency

Dielectric loss also emulates dielectric constant with respect to the effect of both PTH coated fiber content and frequency. The dipoles present in the composites change orientation in every cycle with the alternating electric field. This produces friction between dipole and the surrounding molecules generating heat in the material. This loss of energy as heat is responsible for the dielectric loss of the composites. With increase in fiber content number of dipoles increases bringing about higher heat loss and subsequently higher dielectric loss. With increase in frequency the lagging behind of dipoles with respect to the alternating field reduces the heat dissipation due to friction which is manifested as lower dielectric loss. However increase in dielectric loss is comparatively lower compared to the increase in dielectric constant, making the composites suitable for capacitor applications.

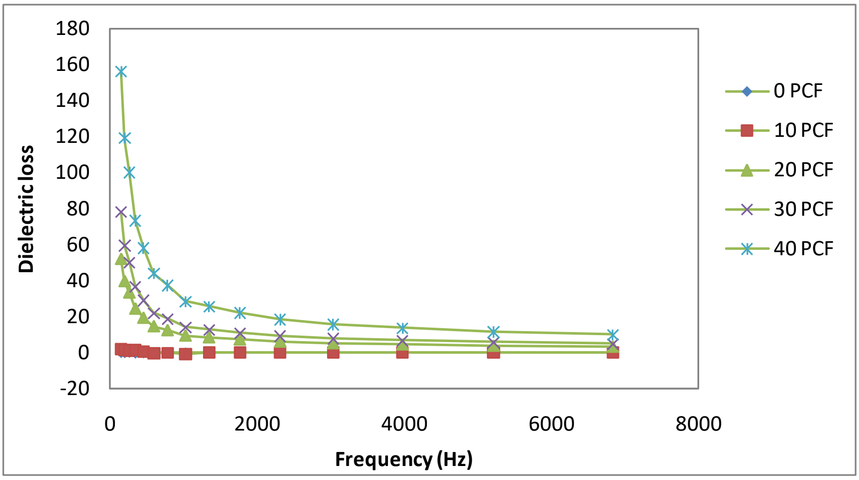

Fig. 12 Variation of dielectric loss of PTH coated fiber/HDPE composites with frequency

4. Conclusions

A commercial general purpose thermoplastic polymer, high density polyethylene, can be easily processed into a conducting composite by incorporation of polythiophene coated cellulosic fibers through a facile melt mixing process. The prepared composites exhibit marginal reduction in mechanical properties due to poor interfacial interaction. However, the cellulosic fibers is effective in retaining the flexibility of the composites even at high fiber content. Coated fibers are effective in delaying the thermal degradation of the matrix. Increase in conductivity on incorporation of PCF was limited due to moisture content in the cellulosic fibers. Development of a network of coated cellulosic fibers is revealed from dynamic mechanical analysis. High dielectric constant combined with low dielectric loss makes the composites suitable for capacitor applications. The study offers insights into optimizing composite performance through better fiber-matrix compatibility and moisture management.

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