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Synthesis of gas barrier starch by dispersion of functionalized multiwalled carbon nanotubes

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ABSTRACT

Nanocomposite films were prepared successfully by simple solution casting method from plasticized starch/functionalized multiwalled carbon nanotubes (PS/f-MWCNTs). The interaction of starch with functionalized multiwalled carbon nanotube (f-MWCNT) was evidenced by ultraviolet–visible (UV–vis) spectroscopy and Fourier transforms infrared (FTIR) spectroscopy. The morphological and thermal properties of the composite films were investigated using scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), X-ray diffraction (XRD) and thermo gravimetric analysis (TGA). The electrical conductivity of the composites was increased significantly by sixteen times, from 0.1×10^{-9} to 1.6×10^{-9} S/cm. This reveals better dispersion of f-MWCNT with low concentration of f-MWCNT. The oxygen permeability of the composites was reduced by half as compared to virgin PS. This indicates better dispersion of f-MWCNT in PS matrix due to formation of strong hydrogen bonding with PS matrix.

1. Introduction

Polymer nanocomposites offer a wide range of promising applications due to their much enhanced properties arising from the reinforcement of nanoparticles. In comparison to the conventional composites, polymer nanocomposites maximize the polymer nanoparticles interaction due to the dispersion of filler on a nanoscale dimension. These results in lighter materials with high performance are giving them the desirable utility for many applications (Zeng, Yu, & Lu, 2008). Petrochemical based polymers have brought many advantages to the mankind. However, it is observed that the ecosystem is considerably disturbed and damaged as a result of nondegradable plastic products for disposable items. As a consequence, the disposal of these products possesses a serious environmental threat. Therefore it is an urgent need to design and synthesize polymers that are renewable source based on environmentally benign materials, which are novel materials of the present century and would be which of great importance to the material field.

Considering the biodegradable polymers, starch is one of the most promising and abundant and naturally occurring polymer in nature for biodegradable plastics because of universality and low cost (Choi, Kim, & Park, 1999; Mohanty, Misra, & Hinrichsen, 2000). The important sources of starch are wheat, potato, rice and corn. The starch granules consist mainly of highly branched amylopectin and linear amylose molecules. Plasticizers like water, glycerol, sorbitol, sugars and other organic compounds were mixed with starch in order to prepare thermo plastic starch (TPS) or plasticized starch (PS) adopting solution casting or melt extrusion processing method (Averous, 2004; Carvalho, Job, Alves, Curvelo, & Gandini, 2003; Rodriguez-Gonzalez, Ramsay, & Favis, 2004; Talja, Helen, Roos, & Jouppil, 2007; Yang, Yu, Feng, & Ma, 2007). The considerable attention of PS during the past decade is due to its interesting alternative for synthetic polymers where desirable rapid degradation is required and long term durability not needed (Vansoest, Benes, De Wit, & Vliegenthart, 1996; Dintcheva & La Mantia, 2007). Carbon nanotubes (CNTs) have attracted considerable attention in research since its discovery by Iijima (1991), and industrial communities due to their unique mechanical and electrical properties (Potschke, Fornes, & Paul, 2002). CNT polymer nanocomposites at very low concentration of CNT filler possess high stiffness, high strength, and good electrical conductivity (Haggenmuller, Gamma's, Rinzler, Fischer, & Winey, 2000; Jin, Pramoda, Xu, & Goh, 2001; Lozano & Barrera, 2001; Schadler, Giannaris, & Ajayan, 1998). CNTs are found mainly in two types: singlewalled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). The strong Vanderwalls interaction among the CNTs molecules result their aggregation and bundling. This shows poor solubility in aqueous media as well as

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in organic solvents. Therefore, the dispersion of CNTs should be very fine in polymer matrix, that means the interfacial interaction between CNTs and the matrix should be optimized. This problem has been solved by both covalent and noncovalent functional modifications of CNTs through different polymer matrix (Chen et al., 2002; Coleman, Khan, Blau, & Gunko, 2006; Peng & Wong, 2009). MWCNTs are stiff macromolecular structures having outer diameter of about 30 nm and length of 1–100 μm (Ajayan, 1999). The high modulus (1 TPa) along their length direction and high bending modulus (0.9–1.24 TPa) (Qi et al., 2003) of MWCNTs can be considered as an ideal reinforcing fillers for polymer matrices to achieve high performance and extensive applications. MWCNTs have also been proved to be very effective filler at very low loadings due to high aspect ratio (as high as 1000), and shows excellent mechanical properties (as high as 1 TPa tensile modulus), thermal and electrical properties.

The very common method for making polymer composites with inorganic fillers are melt blending and solution casting, which are also adopted for making MWCNTs enhanced polymer composites (Pirlot, Willems, Fonseca, Nagi, & Dalhalle, 2002; Shaffer & Windle, 1999). Therefore the dispersibility of MWCNTs has been explored by the use of surfactant (Hughes, Chen, Shaffer, Fray, & Windle, 2002), oxidation or chemical functionalization of the MWCNTs surface through introduction of carboxyl, carbonyl or hydroxyl groups on MWCNTs surface by refluxing in acid medium (Thostenson & Chou, 2002). Recently electroactive polymer based on thermo plastic starch (TPS) has a great deal of interest. Wang, Zhang, Liu, and Wang (2009) used both ionic liquid and N,N-dimethyl acetamide combined with lithium chloride (Wang, Zhang, Liu, et al., 2009; Wang, Zhang, & Wang, 2009) as novel plasticizers to enhance the ionic conductivity of TPS. The amylose chain that has been found can wrap around the SWCNTs, the inner core of the helix being filled by SWCNT (Kim et al., 2003). This method can be used for the homogeneous dispersion of SWCNTs in water. It (Stobmski et al., 2003) was suggested that small SWCNTs can be enveloped by amylose to form nanoshok absorber. This explained that the interaction of SWCNTs with waxy corn amylopectin is stronger than its interaction with potato amylopectin (Lii, Stobinski, Tomasik, & Liao, 2003). This success in dispersion of CNTs in solution will be of great help to prepare different polymer/CNT nanocomposite by solution casting method. Sodium dodecyl sulphate (SDS) has also been used as surfactant for MWCNTs and also for the preparation of glycerol plasticized starch/MWCNT composites (Ma, Yu, & Wang, 2008). Starch/MWCNT nanocomposites were also prepared by addition of small quantity of MWCNT (Fama, Pettarin, Goyanes, & Bernal, 2011). This not only enhances the mechanical property of the composite but also its electrical conductivity. The chemo-resistive properties of starch and amylose functionalized CNT transducers are used as sensor for polar and nonpolar solution (Kumar, Castro, & Feller, 2012).

The hydrophilicity and biocompatibility of CNTs can be improved by modifying with biopolymers. The natural biopolymer like guar gum (GG) can covalently graft on the surface of MWCNT to form GG-MWCNT nanocomposites (Yan, Chang, Zheng, & Ma, 2012). For high performance of TPS/MWCNTs a flexible way is to introduce hydrophilic groups on the surface of MWCNTs. This can be done by covalent functionalization of CNT to introduce carboxylic acid groups on surface of CNTs by refluxing in a mixture of concentrated H_2SO_4 and HNO_3 (Kuznetsova et al., 2000). Similarly TPS/carboxylate multiwalled carbon nanotubes (CMWCNTs) nanocomposites were also synthesized by facile solution dispersion method (Liu, Zhao, Chen, & Yu, 2011). This improves the dispersion and hydrophilicity of CMWCNTs. The enhanced compatibility and homogeneity of TPS/CMWCNTs nanocomposites show better electric conductivity and mechanical property.

A number of papers have been reported regarding the preparation of polymer composites using f-MWCNT as filler. Research work, however investigating both conductive and gas barrier properties of starch are limited. In the present study the interaction of starch with f-MWCNT was established in order to investigate the gas barrier properties of starch nanocomposites. The structural properties of starch/f-MWCNT nanocomposites were studied by XRD, SEM, and HRTEM. Further, the substantial enhancement in thermal conductivity in starch was noticed by incorporation of small amount of f-MWCNT.

2. Experimental

2.1. Materials

MWCNTs with average diameter of 10–15 nm and length of 0.1–10 μm was received from Sigma–Aldrich, USA, and used after functionalization. Starch (rice) was extra pure and a product of Fisher scientific, Mumbai, India and used as such. Glycerol of analytical grade was purchased from Merck, India and used as received. The other reagents H_2SO_4, HNO_3 and H_2O_2 were of analytical grade chemicals and used as such.

2.2. Synthesis of plasticized starch/MWCNT nanocomposites

The functionalization of MWCNT was done as per our earlier publication (Pradhan & Swain, 2012a,b). The MWCNTs were treated with concentrated H_2SO_4 and HNO_3 in the volume ratio of 3:1 and sonicated by using ultrasonic cleaner (120 W/60 kHz) at 40 °C for 24 h in a flask. The solution was diluted by distilled water and filtered. The remaining residue was washed by distilled water. Then the open ended tubes were polished with hydrogen peroxide and H_2SO_4 in volume ratio of 1:4 with stirring at 70 °C for 30 min. The resulting solution was diluted by distilled water and centrifuged to get f-MWCNT. Starch/f-MWCNT nanocomposites film was prepared by convenient solution casting and evaporation method. The f-MWCNTs were dispersed in double distilled water with stirring for 10 min taking in a flask. Calculated amount of glycerol was added and homogenized in an ultrasonic bath for 30 min. The required quantity of starch was added into the flask and the solution was charged by constant stirring with heating at 95 °C for 30 min to form the plasticized starch. The prepared solution was cast onto a polystyrene (PS) petridish and placed in an air circulating oven at 60 °C until it become dry (about 6/8 h). The obtained films of thickness 0.5 mm were placed in a conditioning desiccators of 50% relative humidity(RH) for at least 48 h at room temperature prior to all testing.

2.3. Characterization

The UV–vis spectra of Starch/f-MWCNT nanocomposites were obtained with the help of UV–vis spectrophotometer (model UV-2450, Shimadzu Corporation, Japan). The chemical interaction of starch with f-MWCNT was confirmed by Fourier transform infrared (FTIR) spectrometer (model Perkin-Elmer Paragon 500). The IR spectra of starch and starch/f-MWCNT composites in the form of KBr pellet were recorded. The synthesized starch/f-MWCNT composites were grinded to powder form with pestle applying uniform pressure. The powder materials were placed in a sample holder for X-ray diffraction (XRD) study. X-ray diffraction pattern were recorded in a reflection mode in an angular 2θ value of range up to 40° at ambient temperature by a Rigaku X-ray machine (model no P-DD 966 diffractometer) operated at Cu kα wavelength 1.54 Å. The radiation from anode operated at 40 kV and 150 mA. The diffractometer was equipped with 1° divergence slit, a 16 mm beam

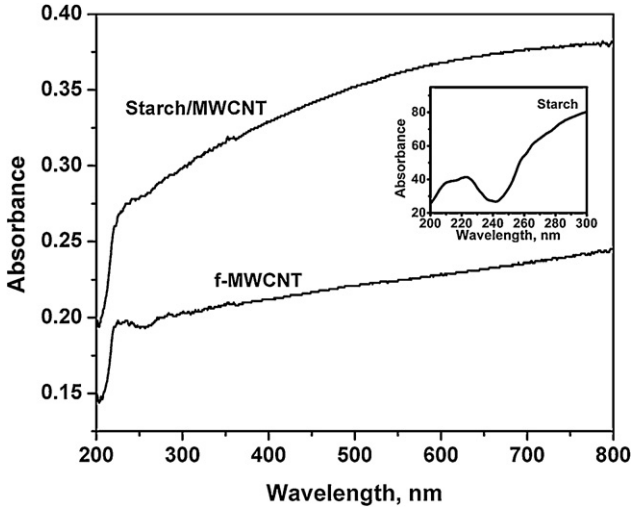

Fig. 1. UV–vis spectra of starch/f-MWCNT, f-MWCNT and raw starch (inset).

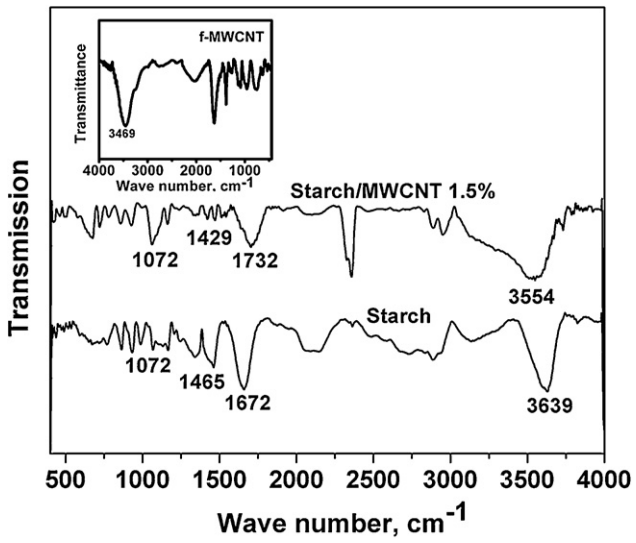

Fig. 2. FTIR of Starch, starch/f-MWCNT nanocomposites, f-MWCNT (inset).

basks, a 0.2 mm receiving slit and a scatter slit of 1°. The morphology and dispersion of MWCNTs in starch matrix were investigated using a combination of field emission scanning electron microscopy (FESEM) utilizing JEOL-JSM-5800, model and high resolution transmission electron microscopy (HRTEM) of model Tec-nai 12, Philips. Thermal properties of the powdered composites were measured with thermo gravimetric analyzer (TGA) apparatus (model DTG-60, Shimadzu Corporation, Japan) under nitrogen purge at a heating rate of 10 °C/min. The conductance of the 0.5 mm thickness composite films was measured with 3532-50 with LCR-Hi-Tester (HOIKI) Japan using a double probe method. Oxygen permeability of the above nanocomposite film were measured with ASTM F 316-86 by using oxygen permeation analyzer (PMI instrument, model GP-201-A, NY, USA).

3. Results and discussion

3.1. Structural characterization of starch composites

The UV–vis spectrum was provided to support the evidence of the chemical interaction between starch and f-MWCNT. In Fig. 1 the major absorption peak of starch at 224 nm originate from π–π^* transition of starch. The absorption peak of f-MWCNT at 245 nm originated from the surface of f-MWCNT and ascribed to a plasmon band (Strano et al., 2003). The UV–vis absorption peak of starch/f-MWCNT composites showing the interaction between the carboxyl group of f-MWCNT and hydroxyl group of starch was observed at 262 nm. This result furnished the evidence that starch macromolecules were grafted to the surface of f-MWCNT. The FTIR spectra of starch/f-MWCNT nanocomposites were studied to identify the functional groups present for interaction of starch with f-MWCNT as shown in Fig. 2. The FTIR spectrum of starch/f-MWCNT composites had absorption peak at 1732 cm^{-1} corresponding to carbonyl group which was also present in the same position in the FTIR of f-MWCNT (in set figure). From the spectra of starch, the strong and broad peak at 3639 cm^{-1} was assigned to the characteristic absorption peak due to stretching vibration of —OH group. The strong and wide absorption band at 3554 cm^{-1} of starch/f-MWCNT composite indicated the presence of H-bonded —OH group on the surface of the starch/f-MWCNT composites. This shifting of —OH stretching from 3639 to 3554 cm^{-1} may be due to the hydrogen bonding between —OH group of starch and carboxyl group of f-MWCNT.

The structural properties of starch, f-MWCNT and Starch/f-MWCNT nanocomposites were studied by XRD in Fig. 3. Starch gave three diffraction peaks at 2θ values of 17°, 19° and 21° which are as shown in Fig. 3a. These may explain the crystalline peak of starch which is similar to the earlier report (Ma & Yu, 2004a,b; Chen & Evans, 2005). The f-MWCNT gave one diffraction peak at 2θ value of 25° in Fig. 3b. But in the starch/f-MWCNT nanocomposites the diffraction peak of 2θ values 17°, 19° and 21° of starch decreases significantly. This peaks disappeared with increase in concentrations of f-MWCNT. These result indicated that with increase in concentrations of f-MWCNT, the crystalline structure of starch was destroyed, which may be due to the intra and intermolecular hydrogen bonds of crystalline structure of starch and f-MWCNT (Ma & Yu, 2004a,b). Hence it was concluded that the f-MWCNT was completely dispersed and chemically interacted with the starch matrix.

3.2. Morphological study of starch composites

Dispersion of f-MWCNT in starch matrix was one of the key elements to study the electrical conductivity and mechanical properties of starch/f-MWCNT nanocomposites. The SEM micrograph of starch/f-MWCNT nanocomposites was evidenced in Fig. 4. It was found that the cutting f-MWCNTs were well dispersed in the

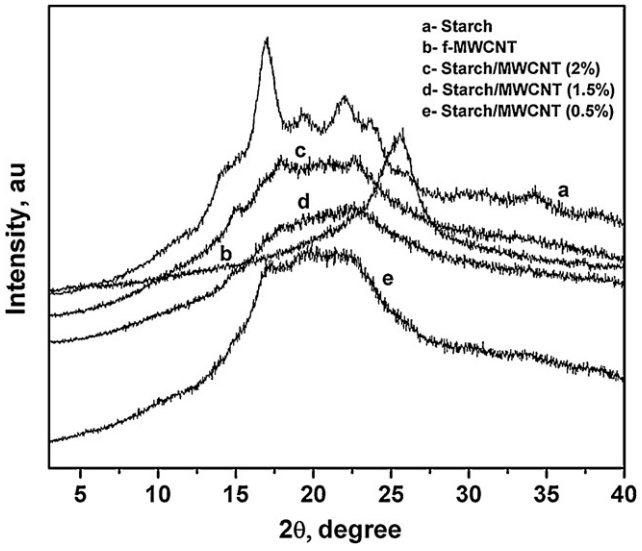

Fig. 3. XRD of starch, f-MWCNT and starch/f-MWCNT nanocomposites.

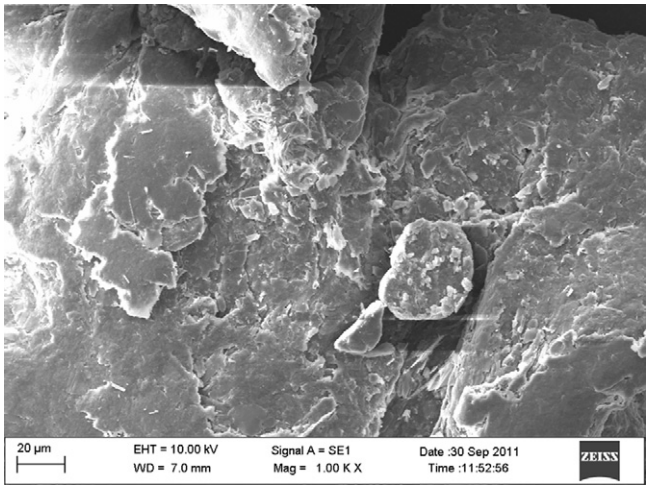

Fig. 4. SEM micrograph of starch/f-MWCNT nanocomposites at 2 wt% of f-MWCNT.

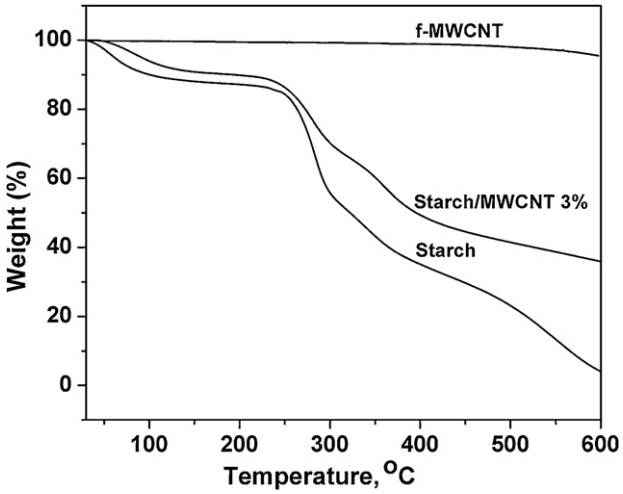

Fig. 6. TGA of f-MWCNT, starch/f-MWCNT and starch at 2 wt% of f-MWCNT.

starch matrix and formed a homogeneous dispersion of f-MWCNT in its starch/f-MWCNT nanocomposites. Fig. 5 showing the HRTEM image of starch/f-MWCNT nanocomposites gives the visual representation of the dispersion of f-MWCNT within the polymer matrix. The starch was distributed on the f-MWCNT surface forming a nanotube network. The morphology of f-MWCNT in starch matrix also explained the good dispersion of f-MWCNT forming a well connectivity to explain the good conductivity of the nanocomposites.

3.3. Study of thermal properties

The thermal stability of f-MWCNT, starch and starch/f-MWCNT nanocomposites was performed by thermo gravimetric analysis (TGA) in Fig. 6, in the temperature range from 30 to 600 °C. The thermal decomposition of starch occurred at 248 °C in a three step reactions with maximum decomposition to water loss, the second step to starch and third step to the oxidation of partial decomposition of starch. The first degradation temperature of starch is lower than starch/f-MWCNT nanocomposites. The degradation of starch and starch/f-MWCNT were started from 248 °C and 255 °C. From TGA analysis, it was observed that starch decomposed completely where as residue of 40% was remained in case of starch/f-MWCNT nanocomposites. Hence thermal stability of starch/f-MWCNT nanocomposites was better than that of virgin starch due to well dispersion of f-MWCNT in starch matrix.

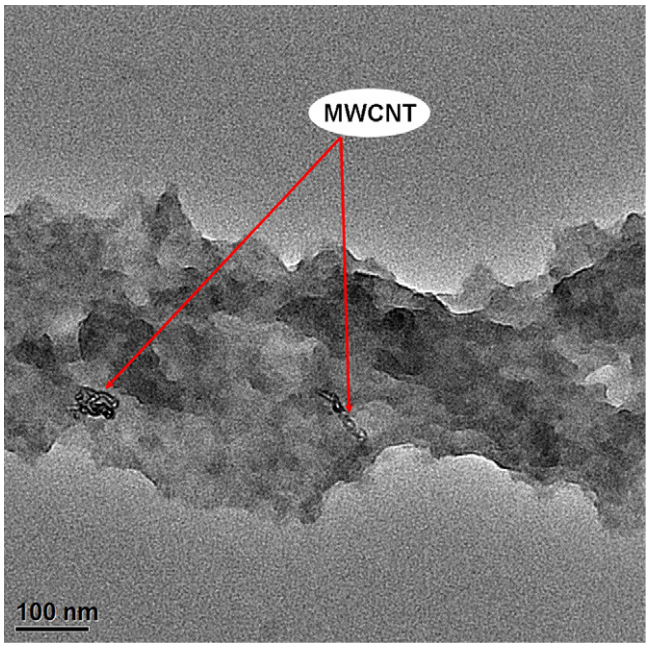

Fig. 5. HRTEM image of starch/f-MWCNT nanocomposites at 2 wt% of f-MWCNT.

3.4. Study of electrical properties

The electrical conductivity of starch/f-MWCNT nano composites were studied at a frequency of 500 kHz at room temperature to investigate the effect of f-MWCNT content on electrical conductivity as shown in Fig. 7. It is evidenced that the addition of a conductive particle to an insulating polymer can form electrically conductive nanocomposites if the particle concentration exceeds the percolation threshold. The value of percolation threshold is very sensitive to the polymer type as already shown for carbon particles (Miyasaka et al., 1982) but also for fibers and f-MWCNT (Pradhan & Swain, 2012a,b; Dufresne et al., 2002). This is also dependent on the aspect ratio and the random distribution inside matrix. So at critical concentration of fillers beyond which the polymer composite become conductive is referred to as the percolation threshold. Since CNTs are very effective fillers with a 1000 times higher current

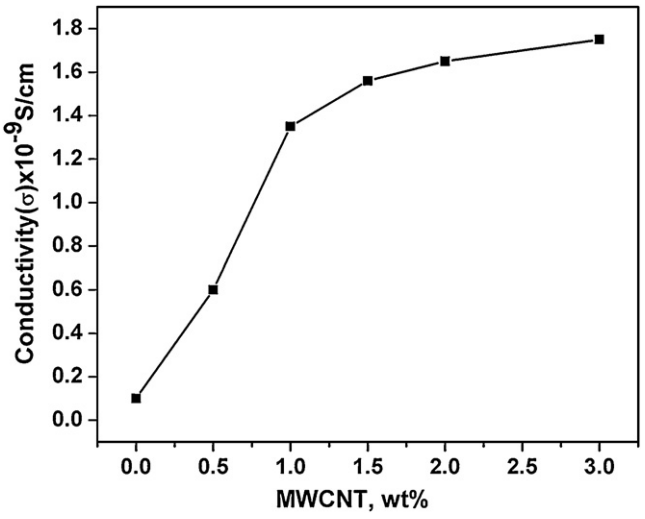

Fig. 7. Electrical conductivity of starch/f-MWCNT nanocomposites at 3 wt% of f-MWCNT.

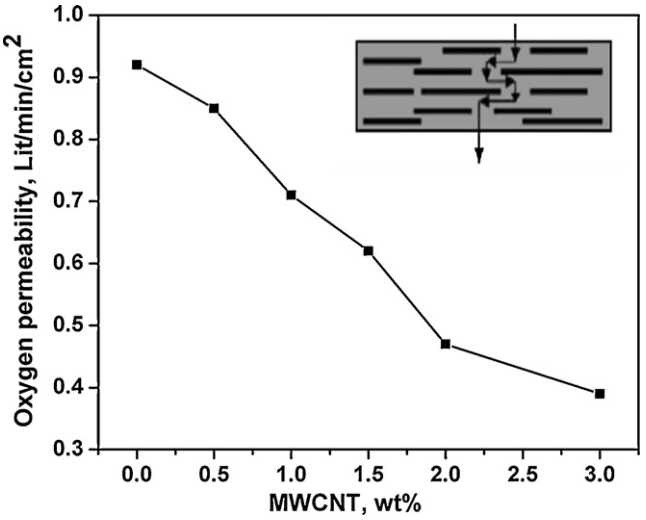

Fig. 8. Oxygen permeability of starch/f-MWCNT nanocomposites as a function of f-MWCNT at constant pressure of 3.4×10^3 Pa (inset: schematic model for oxygen barrier properties of starch/f-MWCNT nanocomposites).

carrying capacity than copper wire (Collins, 2000), this permits the movement of charge carried by the fillers through the matrix and the composite achieve a certain degree of electrical conductivity. The percolation threshold is characterized by a sharp jump in the conductivity by many orders of magnitude which were attributed to the formation of a conductive network within the matrix. Thus, the polymer/CNT composites show very low percolation threshold for electrical conductivity because of the large aspect ratio and nanoscale dimension of nanotubes. The percolation threshold for electrical conductivity in polymer/CNT composites is also influenced by different nanotube characteristics like aspect ratio, dispersion and alignment.

In the present experiment, the electrical conductivity of starch/f-MWCNT nanocomposites has been measured and it was found that the electrical conductivity increased with increase in the concentrations of f-MWCNT in the starch matrix. The conductivity of the composite increased with addition of very low concentrations (0.5–3 wt%) of f-MWCNT. The electrical conductivity increased gradually from 0.6×10^{-9} to 1.6×10^{-9} S/cm due to addition of filler. The sharp jump in conductivity from 0.5 to 1.0 wt% of f-MWCNT shows that the percolation threshold exceeds its critical value and enhances the electrical conductivity. This is also supported by the better dispersion of f-MWCNT in the starch matrix as shown in SEM image which enables to form a conductive network for better electrical conductivity.

3.5. Study of oxygen permeability

Polymer based nanocomposites, because of their oxygen barrier property, have proven to be extremely useful in packaging industries. The dispersion of f-MWCNT in starch matrix may provide the huddles for oxygen permeation through its composites. Oxygen permeability of starch/f-MWCNT nanocomposites was measured to study the effect of f-MWCNT concentrations on the starch matrix as shown in Fig. 8. The oxygen flow rate through all nanocomposites was found to be less in comparison to the virgin starch at constant pressure of 3.4×10^3 Pa. It was found that the flow rate decreased with increase in percentage of f-MWCNT loading. Further it was observed that the oxygen permeability of starch/f-MWCNT nanocomposites with 3 wt% loading was reduced by five times as compared to that of the virgin starch. The gas permeability data in

Table 1
Comparison of experimental and calculated values of oxygen permeability of starch/f-MWCNT nanocomposites.

f-MWCNT (wt%)	Oxygen permeability values (L/min/cm^2)	
	Experimental	Calculated
0	0.93	0.93
0.5	0.85	0.84
1.0	0.70	0.72
1.5	0.61	0.59
2.0	0.46	0.47
3.0	0.38	0.38

Fig. 8 can be modeled by using third order polynomial regression equation as follows.

$$y = (0.0328x^3) - (0.1174x^2) - (0.1266x) + 0.931$$

And $R^2 = 0.9954$, where, R^2 is the square correlation coefficient.

In order to establish the accuracy, the calculated values of oxygen permeability using this equation are compared with experimental values as Table 1. Further, the gas barrier properties of starch/f-MWCNT nanocomposites can be schematically modeled as 'inset' of Fig. 8. Starch/f-MWCNT nanocomposites have highly ordered nanostructure which create tortuous path for oxygen penetration whereas conventional composite have a less restrictive path for oxygen penetration in their microstructure. Hence the remarkable reduction in oxygen permeability may be due to nanostructural dispersion of f-MWCNT within starch matrix.

4. Conclusions

The starch/f-MWCNT nanocomposites film was prepared by solution casting method. The chemical interaction of f-MWCNT in starch matrix was investigated by UV–vis and FTIR study. The dispersion of f-MWCNTs in the starch/f-MWCNT nanocomposites was achieved by SEM and HRTEM. The thermal conductivity of starch/f-MWCNT nanocomposites was enhanced by incorporation of small amount of f-MWCNT. The electrical conductivity of starch/f-MWCNT was increased due to well connectivity of carbon nanotubes. The substantial decrease in oxygen permeability was noticed due to nanostructural dispersion of f-MWCNT. The reduction in gas barrier property of starch/f-MWCNT nanocomposites in addition to enhancement of electrical and thermal properties may enable the material for electronic, electrostatically dissipative material, aerospace or sporting goods and supercapacitors applications.

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