

Mechanical and electrical properties of multiwall carbon nanotube/polycarbonate composites for electrostatic discharge and electromagnetic interference shielding applications†

Cite this: *RSC Adv.*, 2014, 4, 13839

Shailaja Pande,* Anisha Chaudhary, Deepak Patel, Bhanu P. Singh and Rakesh B. Mathur

Home-made multiwall carbon nanotubes (MWCNTs) were used as a reinforcing conducting filler for a thermoplastic polymer, polycarbonate (PC) and the mechanical and electrical properties of the composites were investigated for electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding applications. A uniformly dispersed MWCNT/PC composite system was fabricated using solvent casting and a combination of solvent casting and compression molding techniques. The effect of MWCNTs on the failure mechanism of the polymer under tensile loading showed a ductile to brittle transition with increasing amount of carbon nanotubes. ESD studies showed that the composite films of 2 and 5 wt% functionalized-MWCNT/PC with respective charge decay times of 1 and 0.6 s show promise as electrostatic dissipative materials. EMI shielding effectiveness of a five-layered system (~2 mm thickness) of as-synthesized-MWCNT/PC composite films at 20 wt% loading reached 43 dB in the X-band (8.2–12.4 GHz). The primary mechanism of shielding was absorption, suggesting possible use as an EMI absorbing material. By using low pressure (contact pressure) compression molding the EMI shielding properties of bulk composites (~2 mm thickness) improved by about 14 dB at 10 wt% MWCNT loading.

Received 6th December 2013
Accepted 28th February 2014

DOI: 10.1039/c3ra47387b

www.rsc.org/advances

1 Introduction

The growing demand for electrostatic discharge (ESD) protection and electromagnetic interference (EMI) shielding in the plastics industry for the electronics sector has increased the research on developing electrically conductive polymer composite materials particularly using carbon-based conducting fillers. Compared to conventional metal-based EMI shielding materials carbon-based conductive polymer composites are attractive due to their light weight, resistance to corrosion, flexibility and processing advantages.^{1,2} Additionally, a major advantage of using carbon nanotubes (CNTs) is that conductive composite can be formed at low loading of CNTs due to low percolation thresholds and with higher mechanical strength.³

Several studies have previously discussed the EMI shielding properties of CNT/polymer composites.^{2,4–9} EMI shielding in the range of 8.2 to 12.4 GHz (the so-called X-band) is more important for military and commercial applications. Doppler, weather radar, TV picture transmission, and telephone microwave relay systems lie in X-band.^{4,9} Huang *et al.*⁴ fabricated single wall

carbon nanotube (SWCNT)/epoxy composites using long, short, and annealed SWCNTs, with different aspect ratios and wall integrities. Very low percolation volumes and 20–30 dB EMI shielding effectiveness (SE) values were obtained in the X-band for 15 wt% SWCNT loading. Liu *et al.*² obtained an EMI SE up to 17 dB in X-band for SWCNT/polyurethane (PU) composites with 20 wt% SWCNT loading. Kim *et al.*⁵ studied the EMI shielding properties of multiwall carbon nanotubes (MWCNT)/polymethylmethacrylate (PMMA) films in the range 50 MHz to 13.5 GHz and reported up to 27 dB SE of MWCNT/PMMA composite films for high CNT loadings of about 40 wt%. Yang *et al.*⁶ found that with the addition of 1 wt% CNTs into a 10 wt% carbon nanofiber/polystyrene (PS) composite, SE value of 20.3 dB was obtained for a 1 mm thick sample. Arjmand *et al.*⁷ studied the EMI shielding properties of MWCNT/polycarbonate (PC) composites and obtained EMI SE values of about 25 dB for 5 wt% MWCNT/PC composites. However, most of these studies do not discuss the mechanical properties of composites tested for EMI shielding properties except our own studies on EMI shielding properties of MWCNT/PMMA and MWCNT/PS composites.^{8,9} It is desirable that the conducting plastic should have a proper balance of electrical and mechanical properties. In this paper, the importance of mechanical properties has been highlighted because typically, the behavior of composites changes upon addition of CNTs. For a thermoplastic, such as

Physics and Engineering of Carbon, Division of Materials Physics and Engineering, CSIR-National Physical Laboratory, New Delhi – 110012, India. E-mail: shailajapande@yahoo.com; Fax: +91-11-45609310; Tel: +91-11-45608460

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra47387b

PC, which has been used in the present studies, there is a change from ductile to brittle failure mechanism during tensile loading as the CNT content increases. This behavior is important to consider if CNT/PC composites are to be used for EMI shielding and ESD applications. There are no studies on actual electrostatic dissipative character of CNT/PC composites.

Studies on mechanical properties of CNT/PC composites show that while modulus mostly increases with CNT loading the level of reinforcement with respect to tensile/flexural strength depends upon several factors such as the type (as-received/surface-modified; randomly oriented/aligned) and amount of CNT, the state of nanotube dispersion and polymer/nanotube interfacial bonding.^{10–14} In their studies on MWCNT/PC composites using as-received or surface-modified MWCNTs Eitan *et al.*¹¹ found that elastic modulus and yield strength increased with increasing MWCNT content at 2 and 5 wt% CNT loading levels and the dispersion and load transfer efficiency improved by using surface-modified CNTs. Studies have revealed that extrusion during melt-processing may result in a considerable reduction or shortening of CNTs and supposedly weaken the effect of CNTs as a reinforcing agent or as conductive filler.¹² Those studies revealed that tensile strength decreased from 60.64 MPa in neat PC to 25.55 MPa in 8 wt% MWCNT/PC though the elastic modulus increased by 78% from 2350 MPa to 4183 MPa. In those studies the tensile strength of PC composite with 1 wt% MWCNT was 4.5% higher than that of pure PC but when the content of MWCNT exceeded 3 wt% the tensile strengths of PC decreased further.¹² Studies on aligned CNT/PC composites showed that both modulus and yield strength of nanocomposite fibers increased and ductility decreased as MWCNT content increased.¹³ Kim and Jo¹⁵ used a compatibilizer to improve dispersion of MWCNT in PC and obtained superior mechanical properties of MWCNT/PC composites. More studies may therefore help to add new insights to develop nanotube/polymer composite systems with effective mechanical properties and realize use of such types of composites for structural/electrical applications.

The focus of this paper is effect of MWCNTs on the mechanical and electrical properties of MWCNT/PC composites for ESD and EMI shielding applications. Among the thermoplastic group of polymers, polycarbonates have attracted a great deal of attention due to their combination of properties such as high impact resistance, excellent toughness, very good dimensional stability, transparency and thermal stability.^{15,16} Unlike PMMA and PS, which are commodity plastics, PC is an engineering thermoplastic widely used in commercial and military/defence sectors as shatter-proof or bullet-resistant windows, lightweight eyeglass lenses, motorcycle windshields, windows and vision blocks for armored vehicles and boats, transparent armor for military, face shields, protective helmets, safety goggles, aircraft windows, fighter jets canopies, laptop casings and screens, CDs and DVDs, glazing *etc.* The scope of applications of PC can be further increased by incorporating CNTs into PC to not only enhance mechanical properties but also develop conductivity in an otherwise non-conducting matrix for newer applications such as ESD and EMI shielding materials. A modification in their properties to suit specific requirements is

an interesting proposition. A uniform dispersion of CNTs in the polymer matrix is of primary importance to translate the properties of CNTs into the polymer matrix. Different processing methods have been studied to improve nanotube dispersion in polymer matrix and enhance interfacial bonding between nanotubes and polymer.^{17–23} We used a combination of ultrasonication and magnetic stirring to disperse MWCNTs in PC and fabricate a uniformly dispersed MWCNT/PC composite system using solvent casting and a combination of solvent casting and compression molding techniques. The change in material properties of composite in terms of electrical and mechanical reinforcement or sacrifice upon CNT addition was analyzed in order to have a composite for EMI shielding and ESD applications with known and suitable material properties. In a first study of its kind, the electrostatic dissipative properties of MWCNT/PC composites were investigated. Composite films of 2 and 5 wt% functionalized-MWCNT/PC (f-MWCNT/PC) showed potential for ESD applications. Also, for the first time, low pressure (contact pressure) compression molding technique as against full pressure molding was used as a method to obtain composites with improved EMI shielding properties. The EMI SE of low pressure compression-molded samples was measured and compared with the EMI SE of full pressure compression molded samples and the corresponding shielding mechanisms were analyzed. It has been previously reported that EMI shielding properties of composites decrease after compression molding.^{9,24} No studies have been reported on the use of contact pressure molding as a method to improve EMI shielding properties of composites though Molenberg *et al.*²⁵ have reported foamed nanotube/polymer composites for improved EMI shielding properties.

2 Experimental

2.1 Synthesis and functionalization of MWCNTs

MWCNTs were synthesized by chemical vapour deposition (CVD) using toluene as a carbon source and ferrocene as iron catalyst precursor at about 750 °C and atmospheric pressure.⁸ As-synthesized-MWCNT (a-MWCNT) had a uniform diameter in the range of 60–70 nm, lengths in the range of 50–100 μm and purity about 90%.⁸ a-MWCNT were refluxed with 60% (v/v) nitric acid (HNO₃) for 35 h to obtain acid-functionalized MWCNTs (f-MWCNT).^{16,26} The treated material was washed several times with distilled water till washings were neutral to pH paper and dried in an oven at 100 °C for 12 h before use.

2.2 Fabrication of MWCNT/PC composites

MWCNT/PC composite films were prepared by solvent casting technique.¹⁶ MWCNT were first ultrasonically dispersed in tetrahydrofuran (THF) for 2 h to obtain a stable suspension of CNTs in THF. The suspensions were then mixed with solutions of PC in THF to obtain a series of mixtures of MWCNT/PC containing different weight percent (wt%) of MWCNT varying from about 0.1 to 23 wt% of a-MWCNT and about 0.1 to 5 wt% of f-MWCNT in PC. Under similar processing conditions dispersion of >5 wt% of f-MWCNT in PC was difficult due to

high viscosities of the mixtures resulting from increased surface area of f-MWCNTs. The mixtures were magnetically stirred for 24 h to obtain a uniform dispersion of CNTs in PC. Thin polymer composite films were cast from this solution by pouring the solutions into a Teflon spray coated Petri dish (diameter 4") and allowing the solvent to evaporate over 3–5 days followed by drying in oven. Blank PC was also cast by the same technique. The composite films (thickness about 0.25–0.3 mm) of MWCNT/PC were removed from the Petri dish and the samples were cut to desired size for various measurements. To prepare molded bulk composites the solvent casted films were broken down into pieces and stacked in a specially fabricated die mold (60 mm × 20 mm × 2 mm) and compression molded at 170 °C at contact pressure (~10 kg cm⁻²) or full pressure of 50 kg cm⁻². The resulting composites of MWCNT/PC had a thickness of about 1.8–2.0 mm.

2.3 Characterization

The morphologies of MWCNT/PC composite films were investigated by SEM (Leo 440S, UK). TGA studies of polymer composites were performed on Mettler Toledo TGA/SDTA 851E thermal analysis system in air from room temperature to 900 °C at a heating rate of 10 °C min⁻¹. Electrical conductivity of the composite films was measured by 4-point contact method.⁸ The polymer composite film was cut into rectangular strips of size 70 mm in length and 10 mm in width. Current was supplied using Keithley 224 programmable current source and the voltage drop was measured using Keithley 197 A auto ranging micro volt DMM. EMI SE measurements of the MWCNT/PC composites were carried out on an Agilent E8362B Vector Network Analyzer in the frequency range of 8.2 to 12.4 GHz (X-band).⁹ SE of two layers of bulk composite and various layers of composite film was measured using sample specimen size of 21.32 mm × 10.66 mm to fit the wave guide sample holder. John Chubb Instrument (JCI 155 v5) charge decay test unit was used for ESD studies for the measurement of static decay time of f-MWCNT/PC samples at room temperature.²⁷ The static decay time was measured by applying a positive as well as negative high corona voltage of 5000 V on the surface of material to be tested and recording the decay time at 10% cut-off. A fast response electrostatic field meter observes the voltage received on the surface of sample and measurements were to observe how quickly the voltage falls as the charge is dissipated from the film. The basic arrangement for measuring the corona charge transferred to the test sample during corona charge decay measurements is given in ESI section SP1 (Fig. S1†). Mechanical properties of MWCNT/PC composites were determined using Instron machine model 4411. For the measurement of Young's modulus and tensile strength the composite film samples were cut into dog bone shape using a specially fabricated die-punch. The gauge length and width of the test sample (ASTM D638) were 30 and 6 mm respectively. The cross-head speed was maintained at 0.5 mm min⁻¹. Four to five samples were tested for each composite type. For the measurement of flexural modulus and flexural strength (ASTM D790) of the composite bars the span to depth ratio was about 25 and cross-head speed was maintained at 0.5 mm min⁻¹.

3 Results and discussion

3.1 Electrical conductivity of MWCNT/PC composite films

The electrical conductivity of MWCNT/PC composites prepared by solvent casting is shown in Fig. 1. Conductivity increases in a classical percolating way with increasing concentration of MWCNT. Conductivity increased by almost 12 orders of magnitude with increase in MWCNT loading from 0.1 to 23 wt%. The percolation at 2–3 wt% suggests the formation of a conductive pathway of CNTs at this loading that transforms the insulating PC matrix to a conductive plastic. Conductivities as high as 3 S cm⁻¹ were achieved with 10 wt% loading of MWCNT in PC. Other studies have also reported similar increase in conductivity with percolation threshold varying between 1 and 5 wt%.^{12,14,28,29}

3.2 Tensile properties of a-MWCNT/PC and f-MWCNT/PC composite films

The stress–strain curves of a-MWCNT/PC and f-MWCNT/PC composites are shown in Fig. 2(a) and (b) respectively. As seen from Fig. 2(a), as a-MWCNT content increases the elongation at break decreases and there is a transition from the characteristic ductile fracture behavior of pure PC matrix to a brittle failure mechanism. The change from ductile to brittle behavioral mode is also evident from figures of actual failed composite samples of a-MWCNT/PC after tensile tests with increasing CNT loading as shown in Fig. 2(a) from left to right. This type of a qualitative change in the stress–strain behavior with the composite becoming less ductile as CNT concentration increases has also been reported by other workers.^{12,14,30} The reduced ductility of CNT/PC composites by addition of CNTs has also been reported for oriented melt-spun fibers of CNT/PC composites^{10,13} and for CNT/PC composites studied at cryogenic temperatures.^{31,32}

Interestingly the 2 wt% (Fig. 2(a)) and 3 wt% samples did not show a pure ductile or a pure brittle behavior rather a behavior indicative of strain hardening, which suggests that 2 to 3 wt% loading level is probably the transition zone between the two types of behaviors *i.e.* ductile behavior below 2 wt% and brittle behavior above 3 wt%. The stress–strain curves of f-MWCNT/PC

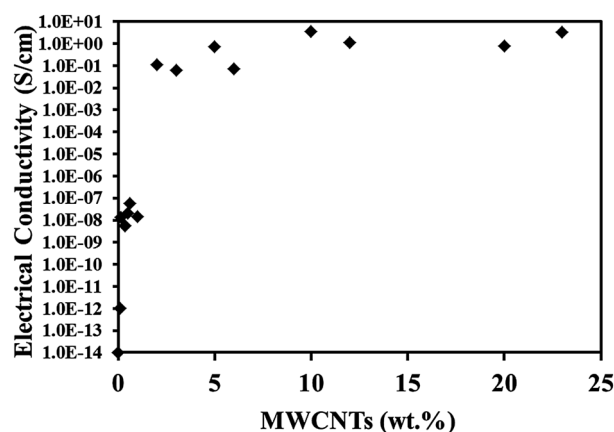


Fig. 1 Electrical conductivity of a-MWCNT/PC composites as a function of CNT loading.

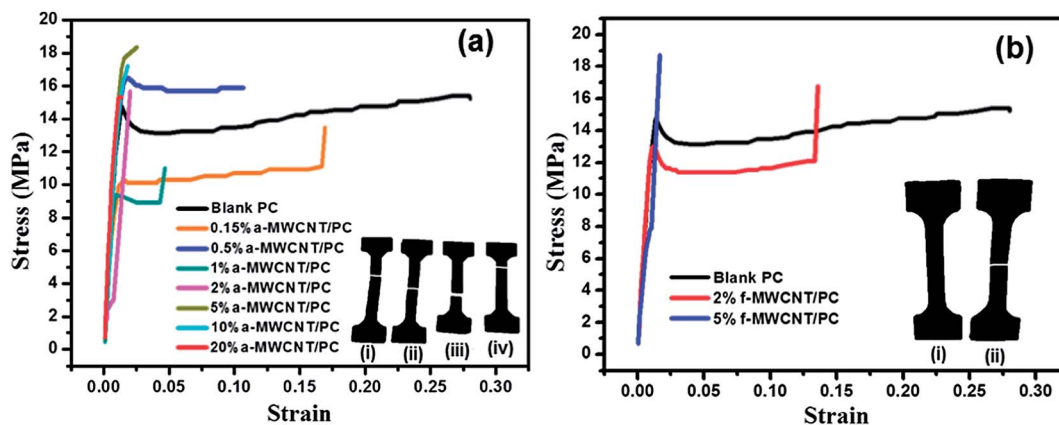


Fig. 2 Tensile stress–strain curves of (a) a-MWCNT/PC composites and failed composite samples of (i) and (ii) 0.5 wt% MWCNT/PC, (iii) 5 wt% MWCNT/PC, (iv) 20 wt% MWCNT/PC; (b) f-MWCNT/PC composites and composite sample of 5 wt% f-MWCNT/PC (i) before and (ii) after failure.

(Fig. 2(b)) showed ductile behavior up to 2 wt% and strain hardening at 5 wt% loading level. Fig. 2(b) also shows 5 wt% f-MWCNT/PC composite before and after tensile test.

Fig. 3(a) shows the general scatter of data for tensile strength (ultimate tensile strength (UTS)) and elastic modulus of pure PC and the composite samples of a-MWCNT/PC. The trend in elastic modulus with CNT loading is consistent with other studies.^{11,12,14} The reinforcement effect of CNTs on elastic modulus was evident up to 20 wt% loading level. The average elastic modulus increased by 43% (1650 MPa) at 20 wt% and by 29% (1480 MPa) at 10 wt% loading over the neat polymer (1150 MPa). Increase in elastic modulus with increase in CNT loading suggests that CNTs are uniformly dispersed and influence or restrict the polymer mobility by imparting stiffness to the polymer matrix.

The tensile strengths do not vary much with CNT loading. Rather the average tensile strengths lie in a plateau. King *et al.* also found no effect of CNT loading on tensile strength of composites.¹⁴ Pure PC samples and composite samples with <5 wt% a-MWCNT generally showed a larger variation in strain to failure in stress–strain curves compared to CNT-reinforced PC samples at and above 5 wt% loading, and this reflected in their UTS values. The UTS values of all samples tested for 5 and 10 wt% a-MWCNT/PC composites were more consistent at

about 17 to 18 MPa suggesting that the samples are dominated by CNT reinforcement. The UTS decreased to 15 MPa at 20 wt%. Pure PC has extensive variation in strain to failure in general.³¹ When CNT content is low there are not enough CNTs to dominate the composite properties. As there is a gradual transition between two behavioral modes from ductile to brittle with increasing CNT concentration there are sufficient CNTs to affect and dominate the composite properties which is reflected as a consistency in the data scatter at MWCNT loadings ≥ 5 wt%.

The UTS values did not give much information about the role of CNTs in the composites. Since the fracture behavior changed from a ductile fracture to a brittle fracture with increasing CNT content the role of CNTs at higher concentrations ≥ 5 wt% could be understood better by comparing stress values at a given strain for pure PC and the MWCNT/PC composites (Fig. 2(a)). At low strains before the yield point of PC, composites exhibited higher stress values (14 to 15 MPa for 5, 10 and 20 wt% a-MWCNT/PC composites) compared to pure PC (11 to 12 MPa). At strain levels of about 1.3% to 1.8% (after the yield point of PC) a comparison of tensile stresses showed that the composites exhibited higher tensile stresses (16 to 18 MPa for 5 and 10 wt% a-MWCNT/PC composites) compared to pure PC (about 14 to 15 MPa). Importantly, the 20 wt% composite sample also exhibited stress values of about 15 MPa comparable to that of

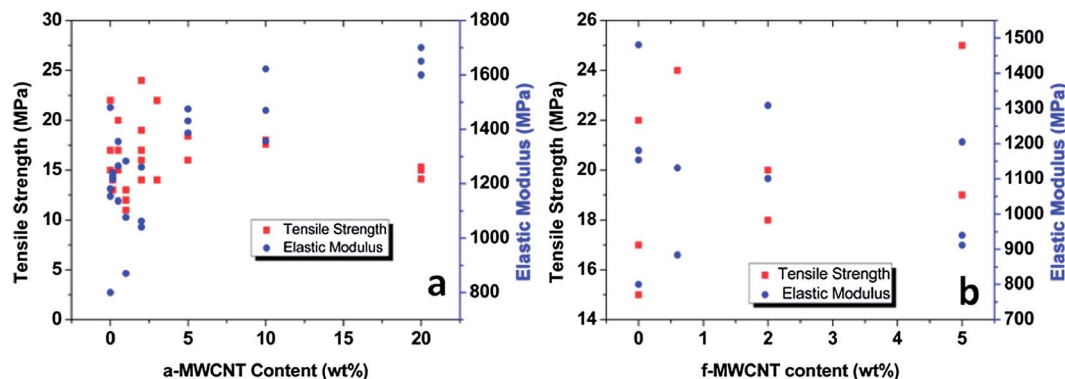


Fig. 3 Tensile strength and elastic modulus of (a) a-MWCNT/PC composites; (b) f-MWCNT/PC composites.

pure PC at similar strain levels. This comparison may be important for applications demanding a composite part to be stiff and not undergo yielding or strain beyond a certain level and yet maintaining high-strength properties. A good level of stiffness is often desired but it comes at the expense of ductility which was shown in case of 10 and 20 wt% a-MWCNT/PC composites. Due to the CNT-reinforced material properties of PC in 10 and 20 wt% a-MWCNT/PC composites in terms of modulus and electrical conductivity and maintaining strength comparable to the polymer these composite systems were further studied for EMI shielding applications which have been discussed later.

Fig. 3(b) shows the effect of f-MWCNT reinforcement on the elastic modulus and tensile strength of the f-MWCNT/PC composites. The data scatter for tensile strength of f-MWCNT/PC composites was less and the dominating effect of f-MWCNT was evident from 0.6 wt% loading level. The average elastic modulus increased by only 5% at 2 wt% loading and was found to decrease at 0.6 and 5 wt% loading level. The average tensile strength increased by about 35% at 0.6 and 5 wt% loading level and by about 12% at 2 wt% loading level over the neat polymer. The increase in tensile strength of composites suggests that the load transfer from the matrix to the nanotubes is improved by using surface-modified CNTs. The main load transfer mechanism in a-MWCNT/PC composites is van der Waals forces between MWCNT and PC.³¹ Acid-treatment of CNTs results in introduction of -COOH groups on the surface of CNTs.^{16,20,26} In f-MWCNT/PC composites the filler matrix interface is strengthened due to additional hydrogen-bonding interactions between acid-functionalized CNTs and the PC matrix.

The lower values of elastic modulus of f-MWCNT/PC composites suggest that the shortened f-MWCNTs are less effective than longer a-MWCNTs in restricting mobility of polymer chains. To maximize composite strength and stiffness, long tubes are required.¹⁸ Since long tubes are difficult to disperse and moreover the requirements of load transfer efficiency demand that nanotube surfaces be compatible with the host matrix, chemical modification of CNTs through surface functionalization is desirable.^{18,20,33} However, acid-functionalization results in shortening the length of CNTs.^{20,16}

The results of tensile strength and elastic modulus show that the role of both CNT-matrix adhesion and CNT lengths is maximum at 0.6 wt% and 5 wt% f-MWCNT loading level and minimum at 2 wt% f-MWCNT loading. It may be stressed that these conclusions are based on the average results obtained from testing the limited number of samples shown for f-MWCNT/PC composites for each sample type. At 2 wt% f-MWCNT content there are sufficient CNTs to reduce the ductility but not enough to increase the strength (Fig. 2(b)). Despite having similar values of tensile strength and elastic modulus a study of the stress-strain curves of 0.6 and 5 wt% f-MWCNT/PC composites showed their different mechanical characteristics. The stress-strain curve of 5 wt% f-MWCNT/PC (Fig. 2(b)) composite showed that after initial slight yielding the presence of CNTs restricted further movement of the plastic phase (strain hardening) and had a strengthening effect by better sustaining the applied load and resulting in a brittle

failure. The stress-strain curve of 0.6 wt% f-MWCNT/PC (Fig. S2 in ESI† section SP2) showed yielding and plastic deformation resulting in a ductile failure (with necking and cold drawing) and rapid increase in stress at which failure occurred. In a study by Kim and Jo¹⁵ the use of a small amount of compatibilizer P3HT-g-PCL improved tensile strength, Young's modulus and elongation at break with an optimum at 0.5 wt% loading level. In the absence of the compatibilizer the mechanical properties of the composites containing 0.1 to 1 wt% MWCNT decreased compared to PC. Man *et al.*³⁰ studied tensile mechanical properties of acid-treated MWCNT-filled PC composites and found that coincidentally a tough-to-brittle transition took place when the interface achieved the state of percolation at 2 wt% loading. Elastic modulus increased constantly with MWCNT loading up to 10 wt%. However they compared the yield stresses only up to 2 wt% loading level due to the tough to brittle transition occurring at 2 wt% MWCNT loading. They found that the yield stress increased by 18.2% in 2 wt% MWCNT/PC composites.

3.3 Dispersion and CNT/polymer matrix characteristics

Fig. 4(a–c) show SEM images of cross-section of the fracture surfaces of 10 wt% a-MWCNT/PC molded composite (Fig. 4(a) and (b)) and 20 wt% a-MWCNT/PC composite film (Fig. 4(c)) and. As seen from the figures CNTs are uniformly dispersed. The good dispersion ensures maximum surface area for CNT/polymer interaction. A coating of PC visible on individual tubes suggests good wetting of CNTs by PC and is also a good indicator of strong interaction between CNTs and the polymer. The network of CNTs as visible in the images ensures good connectivity throughout the polymer matrix. These samples generally showed a rough but uniformly dispersed surface which may also be indicative of the brittle fracture behavior.

The f-MWCNT/PC composite film samples had a good surface finish compared to a-MWCNT/PC composites at the same loading level suggesting excellent dispersion characteristics. Fig. 4(d) shows the SEM image of 2 wt% f-MWCNT/PC

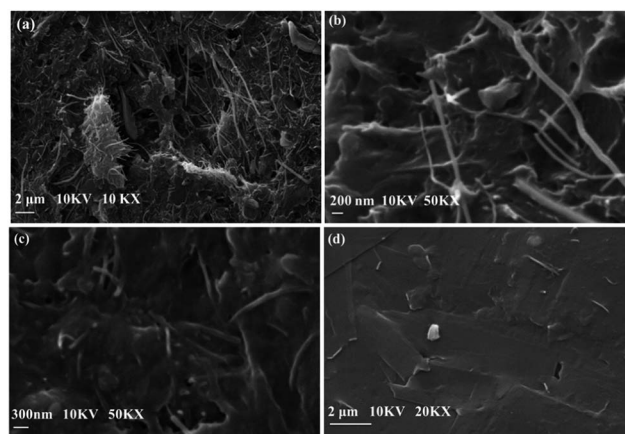


Fig. 4 SEM image of (a and b) cross-section of fracture surface of 10 wt% a-MWCNT/PC molded composite at low and high magnification respectively; (c) 20 wt% a-MWCNT/PC composite film; (d) 2 wt% f-MWCNT/PC composite film.

composite film sample. The CNTs are partially visible and mostly covered or embedded in the polymer matrix. These samples showed a smoother more uniformly dispersed surface which probably resulted in ductile failure.

TGA of pure PC and MWCNT/PC composites was carried out to study the effect of MWCNT addition on the thermal decomposition behaviour of PC. While mechanical properties such as strength and stiffness are enhanced by the reinforcing filler the effect of filler on the thermal decomposition properties of the composite is also important since the service temperature of the composite is defined by the thermal stability of the matrix. TGA studies showed that in the presence of CNTs the PC matrix starts decomposing at a slightly lower temperature and CNTs slow down the thermal degradation of PC. Fig. 5(a) and (b) show the TGA curves of pure PC and its composites with 10% a-MWCNT. The use of CNTs with PC slowed the first step of two-step thermal decomposition of composite as compared to pure PC. In the first step at a temperature of about 410–420 °C where about 70% weight loss took place in case of pure PC, loading of CNTs resulted in only about 39% weight loss when that temperature was reached suggesting that presence of CNTs slows down the decomposition of PC.

3.4 ESD and EMI shielding studies of MWCNT/PC composites

In order to study the potential of MWCNT/PC composites for electronics applications, their ESD and EMI shielding properties were investigated. Generally, conductivities less than 0.01 S cm^{-1} suffice for dissipating electrostatic charge.¹⁹

For ESD studies only f-MWCNT/PC composites were selected since they had a better surface finish and were essentially free of any impurities thus eliminating the role of impurities.

For EMI studies only a-MWCNT/PC composites were preferred. It is known that EMI shielding of as-synthesized CNTs containing iron catalyst is more than purified CNTs.⁵ However, the role of iron, which affects or enhances EMI shielding in lower frequency ranges has not been studied here.

3.4.1 ESD studies. Static decay rate is often used as a criterion for ESD protection *i.e.* the time required for a surface charge to be dissipated. A time of 2 s, maximum, is the standard

for the dissipation of a 5 kV potential applied to a surface, if the material is to be considered electrostatic dissipative.²⁷ Fig. 6(a) and (b) show the charge decay curves of 2 and 5 wt% f-MWCNT/PC composites.

A conducting network to dissipate static charge is formed at 2 wt% CNTs. The 0.1 wt% f-MWCNT/PC composite showed a decay time of >100 s probably due to the absence of a conducting network to conduct charge away from the surface. At and above 2 wt% loading level, the films have a good rate of discharge *i.e.* 1 and 0.6 s respectively for 2 and 5 wt% f-MWCNT/PC composites. These conductive plastics show promise for applications demanding fast and controlled static discharge.

The enhanced mechanical strength and good ESD properties of 2 and 5 wt% f-MWCNT/PC composites suggest use of these composites for ESD applications in automobile and electronic sector. Without losing the strength of the polymer the composite film is conductive and suitable for ESD applications.

3.4.2 EMI shielding studies. There are several studies on EMI shielding properties of CNT/polymer composites^{2,4–6,8,9,24,34–40} and a few studies on EMI shielding properties of CNT/PC composites.^{7,41} The studies show EMI SE of composite increases with increase in CNT loading or electrical conductivity. Moreover in most of these studies EMI shielding is dominated by absorption.^{2,5,8,9,38} However, in a study on CNT-PS foam composites Yang *et al.*³⁴ found the composites more reflective than absorptive to electromagnetic radiation. The EMI SE values of SWCNT/or MWCNT/polymer composites in the X-band mostly vary between 20 and 30 dB. Arjmand *et al.*⁷ studied the EMI shielding properties of MWCNT/PC composites in the X-band region and obtained EMI SE values of about 25 dB for compression molded 1.85 mm thick 5 wt% MWCNT/PC composites. They did not study the mechanical properties of the composites. In order to enhance EMI SE of stainless steel (SS) and Nickel-Coated Carbon Fiber (NCCF), which are traditionally used as fibrous additives for EMI plastics such as PC, Bryant⁴¹ used MWCNT with SS or NCCF at different loading levels and studied the SE of PC-based SS and NCCF shielding compounds in 100 to 1500 MHz range for sample specimen size of 0.12" thick. The studies showed that addition of CNT resulted in a significant increase in the SE of the composites. However with CNTs alone the SE did not exceed 25 dB at the highest loading

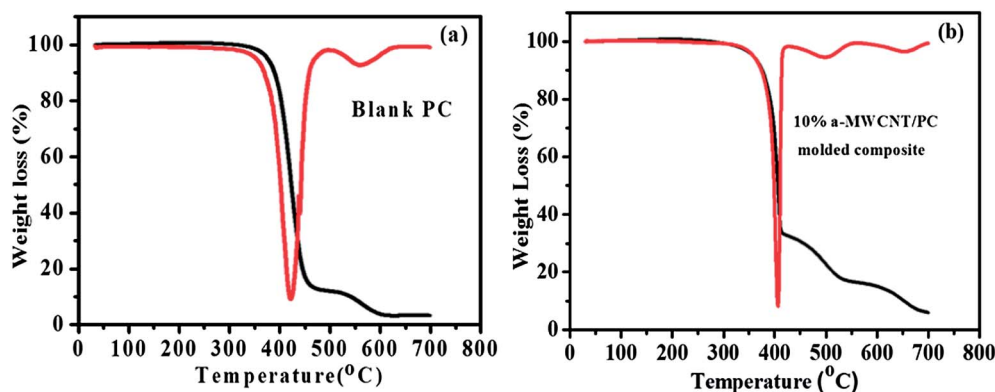


Fig. 5 TGA curve of (a) pure PC; (b) 10% a-MWCNT/PC molded composite.

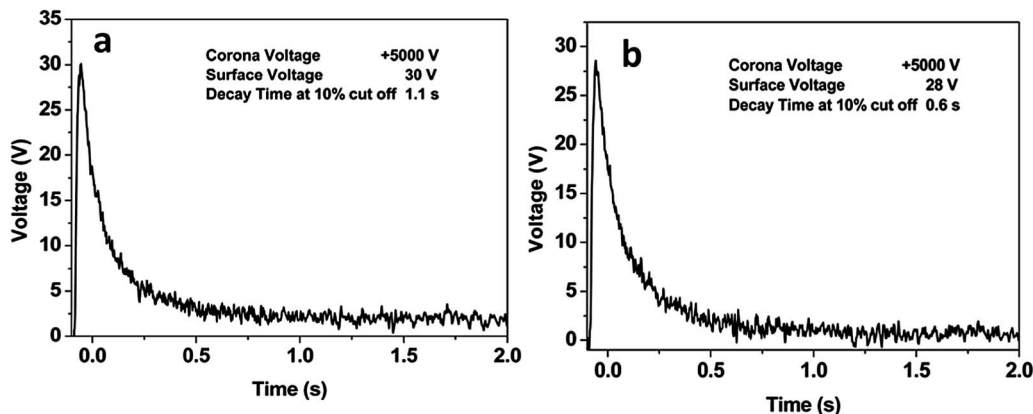


Fig. 6 Decay curve of (a) 2 wt% f-MWCNT/PC; (b) 5 wt% f-MWCNT/PC composites.

level. EMI SE values of MWCNT/PMMA composites were found to increase by using layered composites.^{9,24} The stacking process where composite films were put in layers was found to be better than using a thick piece of compression molded composite of similar thickness.^{9,24}

In this study we measured EMI shielding properties of mechanically tested MWCNT/PC composites at CNT loadings of 10 and 20 wt% using composite stacking process by applying two methods. In the first method the solvent casted composite films were stacked one over the other and EMI SE was measured with increasing number of layers. In the second method a single piece or two pieces of a compression molded composite was used. However, unlike our previous studies,⁹ we modified the compression molding step by performing compression molding at low pressure and then compared the EMI SE values obtained by the two methods. The idea behind using low pressure compression molding was to maintain a loosely held CNT network structure instead of compact structure and thus increase the internal interface area and porosity. The presence of non-homogeneity and porosity may increase EMI shielding as has been shown in foamed composites.²⁵ In their studies on MWCNT/PC composites prepared by melt-mixing Pegel *et al.*⁴² found that melt-processing conditions such as pressing speed and melt temperature influence the electrical conductivity and in order to obtain a composite with high electrical conductivity it is favorable to form loosely packed conductive secondary agglomerates.

No studies have previously been reported on use of low pressure compression molding as a method to improve EMI shielding properties.

Fig. 7(a) shows the EMI shielding properties of 10 wt% a-MWCNT/PC composite fabricated by compression molding at high pressure or full pressure (FP) and Fig. 7(b) shows the EMI shielding properties of 10 wt% a-MWCNT/PC composite fabricated by compression molding at low pressure or contact pressure (CP). The details of measurement procedure for EMI shielding including the EMI SE equations are given in the ESI† section SP3.

As seen from the figures SE_{Total} increased from 21 to 35 dB by reducing the molding pressure. The primary mechanism of shielding was absorption in both the cases since SE_A was greater

than SE_R in both the samples. However, by using the CP molding method the SE_A increased more compared to SE_R leading to higher SE_{Total} . The SE_A increased from 16 to 27 dB while SE_R increased from 5 to 8 dB (Fig. 7(a) and (b)) by reducing the molding pressure. The increase in SE_A by reducing the molding pressure is primarily due to increase in porosity and surface area of the composites resulting in greater contribution of skin effect. Due to skin effect the electromagnetic radiation at high frequencies penetrates only the near surface region of an electrical conductor and the strength of the electric field drops to $1/e$ of the incident value with each skin depth.^{7,25,43} This loss or drop appears as the SE due to absorption loss. In polymer composites the dispersed conducting fillers contribute to shielding and availability of more surface area for interaction with the electromagnetic radiation results in greater shielding due to absorption. The composite structure fabricated by low pressure molding method with increased interfaces and surface area in an already heterogeneous system has greater chances of multiple absorptions and reflections resulting in greater absorption of power inside the material which results in enhanced EMI shielding properties.

The effect of molding pressure on the flexural strength of MWCNT/PC composites was investigated (Fig. 8(a) and (b)). For a fairer comparison blank PC samples were also prepared by the two methods *i.e.* CP method or reduced compaction method and FP method or compaction method. For yielding thermoplastics such as PC the yield strength is considered an important parameter in flexural tests. However, as seen from Fig. 8(a) and (b) the addition of MWCNT to PC resulted in a brittle failure of the composite unlike blank PC which showed yielding. It was also seen that for both the methods the strength of the composite was higher than blank PC in the initial and middle portions of the curve though obviously the reduced compaction method decreased the strength of the samples.

The load–displacement curves of Fig. 8(a) and (b) gave ultimate strengths as 49 MPa for composite processed by FP method and 45 MPa for composite processed by CP method. The increased porosity, characterized by lower density (Table 1) due to reduced pressure decreased the strength of the composite however the resulting composite structure increased the EMI shielding

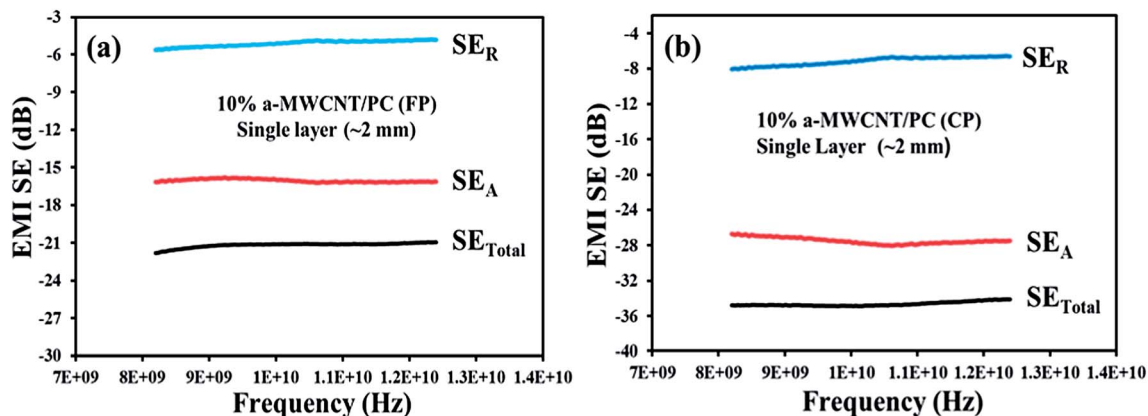


Fig. 7 EMI SE of 10 wt% a-MWCNT/PC processed by (a) FP compression molding method; (b) CP compression molding method.

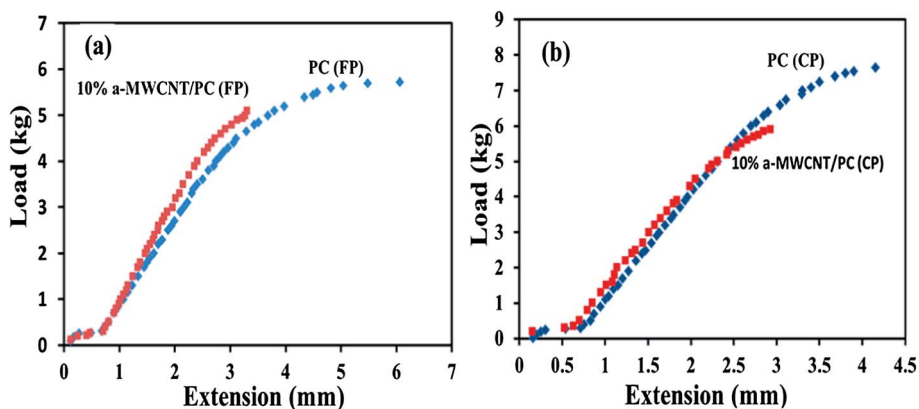


Fig. 8 Flexural load-displacement curves of blank PC and 10 wt% a-MWCNT/PC composite processed by (a) FP compression molding method; (b) CP compression molding method.

properties of the composite. Thus in order to use MWCNT/PC composites as EMI shielding materials strength may have to be sacrificed at the cost of SE if a higher shielding is required. In other words this is not a load bearing structural application.

As shown the CNTs primarily shield by absorption and a further increase in CNT content may further increase the absorption component of shielding. It was shown in our earlier studies on MWCNT/PMMA composites that reflection component increases slower than the absorption component as CNT amount is increased at concentrations ranging from 0 to 10 vol % CNTs.⁹ Kim *et al.*⁵ studied the EMI shielding properties of MWCNT/PMMA films in the range 50 MHz to 13.5 GHz and reported up to 27 dB SE of MWCNT/PMMA composite films for high CNT loadings of about 40 wt%. In this work MWCNT/PC composites with a high CNT loading of 20 wt% were used and the effect of thickness, stacked layers and composite processing method on the EMI shielding properties of the composites was investigated. The EMI shielding properties of MWCNT/PC composites in the X-band were measured using a single layer or a stacked composite system of solvent casted films of different thickness or MWCNT/PC molded composites fabricated by CP method. Table 1 shows the results.

As shown in Table 1, SE_{Total} increases with increase in thickness of the composite films and with increase in number of composite layers. The increase in SE with increase in thickness of the films is due to the greater amount of free electrons available due to greater amount of CNTs present to interact with EM radiation. Additionally, the increase in SE with number of stacked layers is due to absorption of most part of the power over the depth of the structure by multiple absorptions and reflection phenomena at the interface of each layer.⁹

Fig. 9(a) and (b) show the EMI shielding properties of four and five layers of 20 wt% 0.43 mm thick MWCNT/PC composite films. As the number of layers is increased from four to five a dip appears at about 11 GHz which results in a sharp increase in SE_{Total} from 32 to 43 dB corresponding to SE_A increase from 27 to 37 dB. Thus by using layered method the potential of applications increases since it gives the flexibility to use desired number of layers of composite films for the required EMI shielding applications.

The EMI SE of molded composite prepared by CP molding reached 39 dB. Fig. 9(c) shows the EMI shielding properties of the composite with contributions of SE_A and SE_R to total SE. The SE_A of 20 wt% MWCNT/PC was higher than that of 10 wt%

Table 1 EMI SE of film and molded a-MWCNT/PC composites in the X-band using a single layer or stacked composite layers

a-MWCNTs (wt%)	Density (g cm ⁻³)	Number of layers	Thickness (mm)	SE _{Total} (dB)
10	1.17 (FP)	One	1.785	21
10	1.1 (CP)	One	1.97	35
20	—	One	0.15	12
		Two	0.30	15
		Three	0.45	17
		Four	0.60	19
		Five	0.75	21
20	—	One	0.43	19
		Two	0.86	21
		Three	1.29	25
		Four	1.72	32
		Five	2.15	43
20	1.13 (CP)	One	1.08	23
		Two	2.16	39

MWCNT/PC. The higher SE_A of 20 wt% MWCNT/PC is due to higher CNT content and a combination of layered system with low pressure molding. Higher SE_A compared to SE_R obtained by using a combination of layered system and low pressure compression molding suggests that reflection significantly reduces at the interface of the layer and power entering the composite is maximized *i.e.* most of the power is absorbed by

the conducting network structure of CNTs and dissipated. A significantly higher SE_A compared to SE_R suggests that these materials can be used primarily as EMI absorbing materials. The stress-strain curve of 20 wt% MWCNT/PC composite is given in ESI section SP4 (Fig. S3†). The average flexural modulus of the composite was 1837 MPa and flexural strength was 45 MPa, suggesting a composite with good material properties.

Thus CP molding method and layered method are promising approaches towards obtaining composites with good EMI shielding properties. Conducting filler amount and conductivity (or connectivity) are important factors when considering a shielding material but thickness and skin effect are also important especially in polymer composites. The skin effect becomes more important in microwave absorbers such as MWCNT/PC composites. Greater surface/interface area results in higher shielding and greater thickness of the shield results in more contribution of absorption to the SE. For commercial applications SE of 30 dB is generally sufficient. Ramasubramaniam *et al.*⁴⁴ studied the electrical properties of f-SWCNT/PS or/PC composites and based on the electrical conductivity data obtained they suggested the use of these composites for ESD and EMI applications. In this study we have determined the ESD and EMI properties of MWCNT/PC composites and also reported their mechanical properties.

Table 2 summarizes the important mechanical results and EMI shielding/ESD performances of desirable compositions of

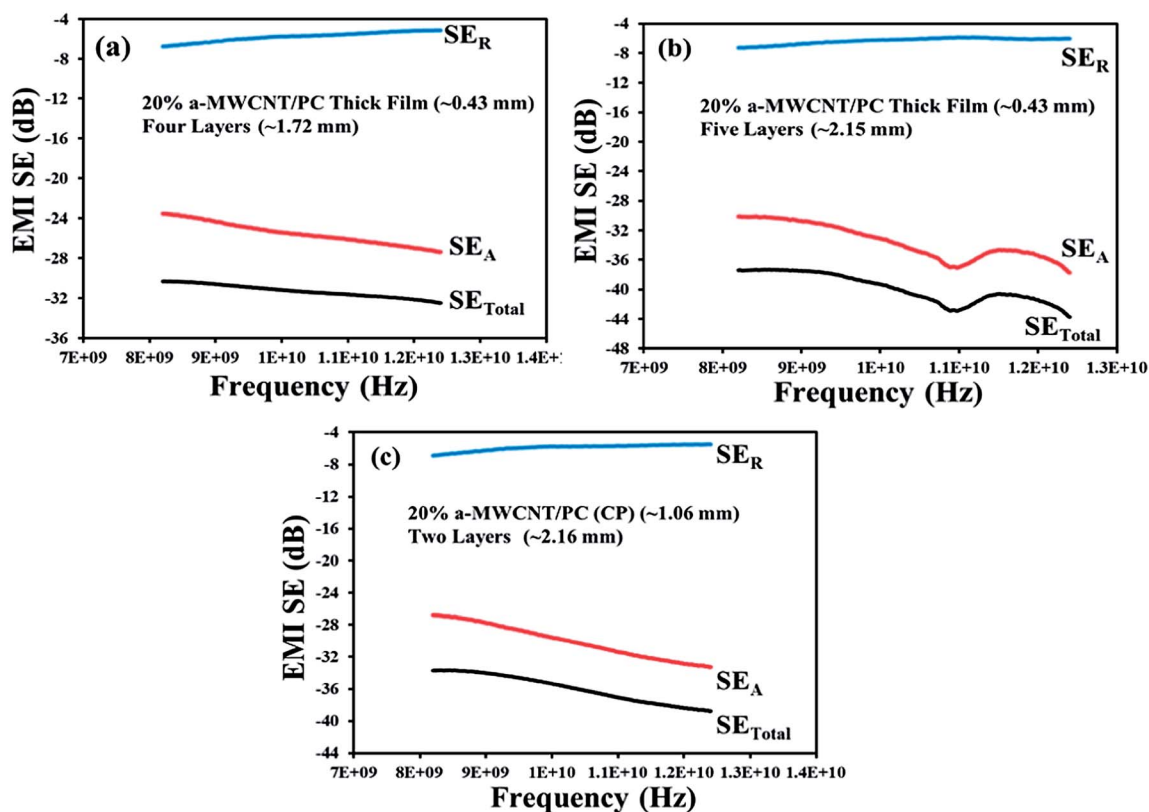


Fig. 9 EMI SE of (a) four layers of stacked 20 wt% a-MWCNT/PC films processed by solvent casting method; (b) five layers of stacked 20 wt% a-MWCNT/PC films processed by solvent casting method; (c) two layers of stacked 20 wt% a-MWCNT/PC composite processed by CP compression molding method.

Table 2 Characteristic properties of MWCNT/PC composites^a

Sample	EM (MPa)	UTS (MPa)	FS (MPa)	Failure mode	Decay time (s)	SE _{Total} (dB)
PC (film)	1150	17	—	Ductile	—	—
PC (FP)	—	—	45 (YS)	Ductile	—	—
PC (CP)	—	—	46 (YS)	Ductile	—	—
10 wt% a-MWCNT/PC(FP)	—	—	49	Brittle	—	21
10 wt% a-MWCNT/PC (CP)	—	—	45	Ductile/brittle	—	35
20 wt% a-MWCNT/PC (film)	1650	15	—	Brittle	—	43
20 wt% a-MWCNT/PC (CP)	—	—	45	Brittle	—	39
2 wt% f-MWCNT/PC (film)	1205	19	—	Ductile/brittle	1.1	—
5 wt% f-MWCNT/PC (film)	1019	23	—	Brittle	0.6	—

^a EM – elastic modulus; UTS – ultimate tensile strength; FS – flexural strength; YS – yield strength; film – solvent casted film; FP – full pressure compression molding; CP – contact pressure compression molding.

a-MWCNT/PC and f-MWCNT/PC composites discussed above for different composite preparation types which are best suited for EMI shielding/ESD applications.

4 Conclusion

MWCNT/PC composites were fabricated by solvent casting/compression molding method and the potential of these composites for electronic applications was analyzed by measuring their ESD and EMI shielding properties. Shown in Table 2 are the significant results of this work highlighting the type of MWCNT, the composite processing conditions and the amount of CNTs best suited for an application.

It was found that the composite films of 2 and 5 wt% f-MWCNT/PC with respective charge decay times of 1 and 0.6 s show promise as electrostatic dissipative materials.

EMI shielding effectiveness of a five-layered system (~2 mm thickness) of a-MWCNT/PC composite films at 20 wt% loading reached 43 dB in the X-band (8.2–12.4 GHz). The primary mechanism of shielding was absorption, suggesting possible use as an EMI absorbing material. Layered method is a tailor-made method to increase the potential of applications since it gives the flexibility to use desired number of layers of composite films for the required EMI shielding applications. Significantly, at loadings as high as 20 wt% also the mechanical properties such as strength was comparable to the matrix while modulus and electrical conductivity improved. Conventional fillers such as carbon black are known to degrade the mechanical properties of the polymer, when used in large amounts.

By using low pressure (contact pressure) compression molding the EMI shielding properties of bulk composites (~2 mm thickness) improved by about 14 dB at 10 wt% MWCNT loading. This work demonstrates the ability of CNTs as a reinforcing agent and conducting filler.

Acknowledgements

The authors are grateful to Prof. R. C. Budhani, Director National Physical laboratory (NPL), for his permission to publish the research work. The authors would like to thank Dr Parveen Saini and Mr Avneesh of Polymeric & Soft Materials

Section, Materials Physics and Engineering, NPL for help in ESD and EMI shielding measurements and Mr K. N. Sood, NPL for carrying out SEM. One of us (Shailaja Pande) is grateful to the Department of Science and Technology (DST) for providing research grant to carry out the studies under the “Women Scientists Scheme” (WOS-A) (Grant no. SR/WOS-A/CS-35/2008).

References

- 1 D. D. L. Chung, *Carbon*, 2001, **39**, 279–285.
- 2 Z. Liu, G. Bai, Y. Huang, Y. Ma, F. Du, F. Li, *et al.*, *Carbon*, 2007, **45**, 821–827.
- 3 D. T. Colbert, *Plast. Addit. Compd.*, 2003, **5**, 18–25.
- 4 Y. Huang, N. Li, Y. Ma, F. Du, F. Li, X. He, X. Lin, H. Gao and Y. Chen, *Carbon*, 2007, **45**, 1614–1621.
- 5 H. M. Kim, K. Kim, C. Y. Lee, J. Joo, S. J. Cho, H. S. Yoon, *et al.*, *Appl. Phys. Lett.*, 2004, **84**, 589–591.
- 6 Y. Yang, M. C. Gupta and K. L. Dudley, *Nanotechnology*, 2007, **18**, 345701.
- 7 M. Arjmand, M. Mahmoodi, G. A. Gelves, S. Park and U. Sundararaj, *Carbon*, 2011, **49**, 3430–3440.
- 8 R. B. Mathur, S. Pande, B. P. Singh and T. L. Dhama, *Polym. Compos.*, 2008, **29**, 717–727.
- 9 S. Pande, B. P. Singh, R. B. Mathur, T. L. Dhama, P. Saini and S. K. Dhawan, *Nanoscale Res. Lett.*, 2009, **4**, 327–334.
- 10 P. Pötschke, H. Brünig, A. Janke, D. Fischer and D. Jehnichen, *Polymer*, 2005, **46**, 10355–10363.
- 11 A. Eitan, F. T. Fisher, R. Andrews, L. C. Brinson and L. S. Schadler, *Compos. Sci. Technol.*, 2006, **66**, 1162–1173.
- 12 L. Chen, X.-J. Pang and Z.-L. Yu, *Mater. Sci. Eng., A*, 2007, **457**, 287–291.
- 13 T. D. Fornes, J. W. Baur, Y. Sabba and E. L. Thomas, *Polymer*, 2006, **47**, 1704–1714.
- 14 J. A. King, M. D. Via, J. A. Caspary, M. M. Jubinski, I. Miskioglu, O. P. Mills, *et al.*, *J. Appl. Polym. Sci.*, 2010, **118**, 2512–2520.
- 15 K. H. Kim and W. H. Jo, *Carbon*, 2009, **47**, 1126–1134.
- 16 P. Jindal, S. Pande, P. Sharma, V. Mangla, A. Chaudhury, D. Patel, *et al.*, *Composites, Part B*, 2013, **45**, 417–422.
- 17 O. Breuer and U. Sundararaj, *Polym. Compos.*, 2004, **25**, 630–645.

- 18 J. N. Coleman, U. Khan, W. J. Blau and Y. K. Gun'ko, *Carbon*, 2006, **44**, 1624–1652.
- 19 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792.
- 20 X.-L. Xie, Y.-W. Mai and X.-P. Zhou, *Mater. Sci. Eng., R*, 2005, **49**, 89–112.
- 21 J.-H. Du, J. Bai and H.-M. Cheng, *EXPRESS Polym. Lett.*, 2007, **1**, 253–273.
- 22 E. T. Thostenson, Z. Ren and T.-W. Chou, *Compos. Sci. Technol.*, 2001, **61**, 1899–1912.
- 23 E. T. Thostenson, C. Li and T.-W. Chou, *Compos. Sci. Technol.*, 2005, **65**, 491–516.
- 24 S.-M. Yuen, C.-C. M. Ma, C.-Y. Chuang, K.-C. Yu, S.-Y. Wu, C.-C. Yang, *et al.*, *Compos. Sci. Technol.*, 2008, **68**, 963–968.
- 25 I. Molenberg, I. Huynen, A.-C. Baudouin, C. Bailly, J.-M. Thomassin and C. Detrembleur, *Advanced Microwave and Millimeter Wave Technologies: Semiconductor Devices Circuits and Systems*, InTech, Croatia, 2010, pp. 453–470.
- 26 S. Pande, R. B. Mathur, B. P. Singh and T. L. Dhami, *Polym. Compos.*, 2009, **30**, 1312–1317.
- 27 H. Bhandari, S. A. Kumar and S. K. Dhawan, *Conducting Polymer Nanocomposites for Anticorrosive and Antistatic Applications, Nanocomposites – New Trends and Developments*, ed. Farzad Ebrahimix, InTech, 2012, DOI: 10.5772/50470, ISBN: 978-953-51-0762-0.
- 28 P. Potschke, T. D. Fornes and D. R. Paul, *Polymer*, 2002, **43**, 3247–3255.
- 29 P. Potschke, A. R. Bhattacharyya and A. Janke, *Eur. Polym. J.*, 2004, **40**, 137–148.
- 30 Y. H. Man, Z. C. Li and Z. J. Zhang, *Mater. Trans.*, 2009, **50**, 1355–1359.
- 31 A. Oliver, J. Bult, Q. V. Le, A. L. Mbaruku and J. Schwartz, *Nanotechnology*, 2008, **19**, 505702.
- 32 T. Takeda, Y. Shindo, F. Narita and Y. Mito, *Mater. Trans.*, 2009, **50**, 436–445.
- 33 S. Banerjee, T. H. Benny and S. S. Wong, *Adv. Mater.*, 2005, **17**, 17–29.
- 34 Y. Yang, M. C. Gupta, K. L. Dudley and R. W. Lawrence, *Nano Lett.*, 2005, **5**, 2131–2134.
- 35 M. H. Al-Saleh and U. Sundararaj, *Carbon*, 2009, **47**, 2–22.
- 36 N. Li, Y. Huang, F. Du, X. He, X. Lin, H. Gao, *et al.*, *Nano Lett.*, 2006, **6**, 1141–1145.
- 37 Y. Yang, M. C. Gupta, K. L. Dudley and R. W. Lawrence, *J. Nanosci. Nanotechnol.*, 2005, **5**, 927–931.
- 38 B. P. Singh, Prabha, P. Saini, T. Gupta, P. Garg, G. Kumar, *et al.*, *J. Nanopart. Res.*, 2011, **13**, 7065–7074.
- 39 M. H. Al-Saleh and U. Sundararaj, *Carbon*, 2009, **47**, 1738–1746.
- 40 T. K. Gupta, B. P. Singh, S. R. Dhakate, V. N. Singh and R. B. Mathur, *J. Mater. Chem. A*, 2013, **1**, 9138–9149.
- 41 N. Bryant, *Electromagnetic Compatibility (EMC), 2010 IEEE International Symposium on*, Fort Lauderdale, FL, ©2010 IEEE, 2010, pp. 194–197.
- 42 S. Pegel, P. Pötschke, G. Petzold, I. Alig, S. M. Dudkin and D. Lellinger, *Polymer*, 2008, **49**, 974–984.
- 43 D. D. L. Chung, *J. Mater. Eng. Perform.*, 2000, **9**, 350–354.
- 44 R. Ramasubramaniam, J. Chen and H. Liu, *Appl. Phys. Lett.*, 2003, **83**, 2928–2930.