Starch/MWCNT/Epoxy Composites for Biodegradable Batteries

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ABSTRACT

In this paper, the preparation of starch/multi-walled carbon nanotubes (MWCNTs)/epoxy composite and electrical properties of the composites were discussed. The introduction of MWCNTs restrained starch re-crystallization, improved the thermal stability of the starch/epoxy composites, improved modulus. From the thermal studies, the presence of starch promotes the degradability of the composites. However, the optimum loading of the starch in the composite has not been covered. The composites exhibited a low electrical percolation threshold of 0.05-0.10 wt% of MWCNTs which can be observed from the log P_v Vs MWCNT loadings curve and show improved conductivity of the composite with less than 0.1wt% of MWCNTs and 1wt% of starch content. There was amarginal increase in the capacitance of the composites upon the addition of MWCNT.

Keywords: MWCNT, starch, epoxy, composite, thermal stability,Thermomechanical modulus, SAXD, electrical properties, percolation threshold.

1 INTRODUCTION

The field of nanoscience and nanotechnology is extending the applications of physics, Chemistry, biology, engineering and technology into previously unapproached infinitesimal length scales. Since the polymer–nanocomposites have been the staple of modern polymer industry, their durability under various environmental conditions and degradability after their service life are also essential fields of research [1]. Polymer/MWCNT nanocomposites receive much attention due to their interesting mechanical, electrical and thermal properties [2]. Currently, the vast majority of plastics are made from petroleum-based synthetic polymers that do not degrade in a natural environment and their disposal poses a serious problem. An environmentally-conscious alternative is to design polymer nanocomposites that are biodegradable. The biodegradable nanocomposites based on MWCNT has been explored for application in batteries. Multi-walled carbon nanotubes (MWCNTs) are produced by chemical vapor decomposition (CVD) using acetylene gas or Methane gas in the presence of Ferrocene catalyst at 800 ^{0}C, and then oxidized with concentrated nitric acid at 150 ^{0}C [3]. Glycerol (about 2 ml) was added to 5-6 grams of starch, mixed thoroughly and added into the aqueous solution with MWCNTs of 0.2~1.0 wt%. The solutions were stirred and heated for upto 30 min using a water bath at 70^{0}C[4].

2 EXPERIMENTAL

2.1 Materials

MWCNTs used in this study were supplied by Nanocyl S.A. Belgium. NC7000 series, thin multi-wall carbon nanotubes with 90% carbon purity, were produced via the catalytic carbon vapor deposition (CCVD) process. It has an average diameter of 9.5 nm and length of 1.5μm which was used as the reinforcement in a matrix of epoxy resin (K-134) Araldite and hardener (K-134) supplied by Ciba-Geigy of Australia. Starch powder supplied by Penford Corporation Australia was used as a biodegradable particulate filler.

2.2 Sample Preparation

The formulations were prepared by using different composition of epoxy resin, hardener and fillers viz starch and MWCNT. The formulation is given in Table 1. The starch was treated with MWCNTs and dissolved in acetone for 5-10 min. The dispersion of MWCNTs and starch by ultrasonication instrument was achieved after which the mixtures were added to the monomer resin (epoxy) using propeller blade mechanical stirrer at 400-500 rpm for 20 min. The filler was further dispersed by ultrasonication for 10 min. The resin was degassed in vacuum until entrapped bubbles were removed completely. Then, the hardener was added and stirred using a magnetic stirrer. The weight ratio of the epoxy resin to the curing agent was 4:1 (stoichiometric amount). Appropriate amount of MWCNTs were weighed according to the required percentage and were added to the starch dispersed in 20ml of glycerol. MWCNT and starch particles were mixed thoroughly before adding the mixture to the epoxy resin system. The ratio of starch to epoxy resin was maintained at 1w% by weight. The Starch/MWCNT/epoxy emulsions were cast as thin sheet of ~1.5mm thickness onto a polyester sheet to facilitate removal of the samples for analysis. The Starch/MWCNT/epoxy composite sheets thus prepared were dried at room temperature for 24 hours.

Finally, the specimens were cured for 6 h at 70 ^{0}C to remove the excess glycerol. The neat epoxy samples were also prepared following the same procedure for comparison purposes. The produced nanocomposite of dimensions 10X10X1.5mm were polished for dynamic-mechanical analysis, thermal degradation studies and conductivity measurements.

Table 1: Sample formulation and identification of abbreviations for Starch/MWCNT/epoxy composites.

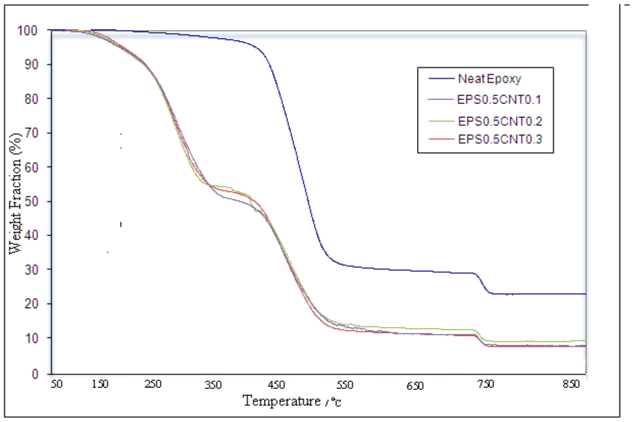
Samples ID	Epoxy Resin (wt%)	Hardener (wt%)	Starch (wt%)	MWCNT (wt%)
EP000	80	20	0	0
EPS00	80	20	1.0	0
EPS05	78.95	20	1.0	0.05
EPS10	78.90	20	1.0	0.10
EPS20	78.80	20	1.0	0.20

2.3 Characterization

The cured resin and composites were characterized by thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and small-angle X-ray diffraction (SAXD). Thermal stability and composition were assessed using thermogravimetry (Perkin-Elmer Pyris 1 TGA) Samples of about 3.0 mg were heated from 30-850 °C at 10 °C·min^{-1} under nitrogen with change to air at 700 °C. The purging gas (flow rate: 20 mL·min^{-1}) was nitrogen from 35-700 °C, then it was changed to air at 700 °C. Mechanical properties were determined using modulated-force thermomechanical analysis (Perkin-Elmer DMA 8000) from -50 to +150 °C at 2 °C·min^{-1}, 10 µm strain, with a synthetic multiplex frequency combining 1, 2, 4, 10 Hz into a complex frequency. The data for each frequency was resolved from the synthetic frequency by a Fourier transform method included in the instrument software to give storage modulus, loss modulus and tan (δ) at each of the frequencies. Composites were characterized using small angle x-ray diffraction (SAXD) 2θ ranging from 0^{0} to 13.5^{0}. Electrical properties were conducted using LCR Meter 4263B instrument, Hewelett Packad for surface and volume resistivity, surface and volume conductivity and capacitance of the composite. The tested frequency was at 1 kHz, at a voltage amplitude of 1 V. The resistance values were taken at low frequency of 1 kHz which is comparable to DC conductivity.

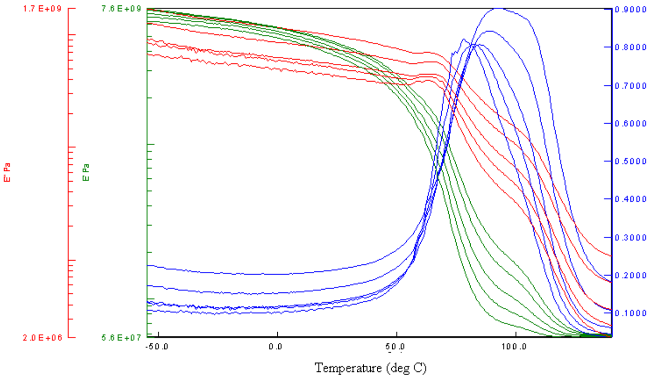
3 RESULTS AND DISCUSSION

Figure 1 depicts TGA curves of the composites containing MWCNTs and starch with different contents. We can see that by comparing with neat epoxy (EP000) which has only slightly affected the thermal decomposing temperature of epoxy resin, the MWCNTs have a great effect on the onset decomposing temperature. Introducing MWCNTs/starch mixture to epoxy resin decrease the initial decomposing temperature of neat resin more or less. Due to the strong interaction between the epoxy resin matrix and MWCNTs, the diffusion of small molecules can be retarded under high temperature. It is very interesting to note that adding of 0.20 wt% MWCNTs can greatly heighten the thermal decomposing temperature by about 40 ^{0}C. Comparing with each other MWCNTs, starch have the least effect on the enhancement ability on the epoxy resin, which may because of their weak structure. The curves for the pure epoxy shows 2 step mass loss degradation. The onset degradation point is at 360^{0}C. When combined with the starch the degradation occurred with two sharp mass losses. The first onset degradation at 180^{0}C and the second onset step at 370^{0}C. The combined starch/MWCNT/epoxy degradation exhibited some of the mass losses observed in the components with further degradation steps partially resolved. There was no observation of any increased stability of the composites, though moisture absorption was not observed due to the protection of starch against moisture by the glycerol. Increase in starch content in epoxy reduces the onset degradation temperature. However, presence of MWCNTs increases the degradation temperature which could be attributed to the high thermal stability of the MWCNTs and the interaction between the starch and epoxy matrix.



Figures 1. TGA curve of Epoxy/Starch/MWCNT composites.

Thermo mechanical properties are shown in Figure 2 for the pure epoxy at multi-frequency. The decrease in storage modulus over the glass transition region was dramatic, extending from 1.6 to 1.75 GPA to a few MPa. At sub-ambient temperatures the behaviour was mostly elastic. At the glass transition there was a crossover of the storage and loss modulus with tan (δ) becoming greater than 0.7 with maximum values of 0.78 to 0.9. In this transition region viscoelasticity predominates and excellent damping properties are expected. The peak maxima of the tan (δ) curves shift significantly with frequency, the highest temperature peak corresponds to the frequency of 20 Hz.



Figures 2. Storage modulus, Loss Modulus and Tan δ as a function of temperature of Starch/MWCNT/epoxy composites at various frequencies.

The crystallization behaviour of the Starch/MWCNT/epoxy composites were studied using small angle x-ray diffraction (SAXD) as shown in Figure 3 below. The molecular structures of MWCNT/epoxy and Starch/MWCNT/epoxy composites were investigated by small-angle X-ray diffraction (SAXD). Fig. 3 (a)-(d) shows that the MWCNT/epoxy exhibits an intense peak with a Bragg spacing of 58.9 Å. The weak multiple reflections correspond to Bragg spacings of 22.1, 14.7 and 11.05 Å. The starch/MWCNT/epoxy composite gives a similar pattern indicating that the structure of the composite is governed by MWCNT, and Starch induces only minor disturbances to this lamellar structure.

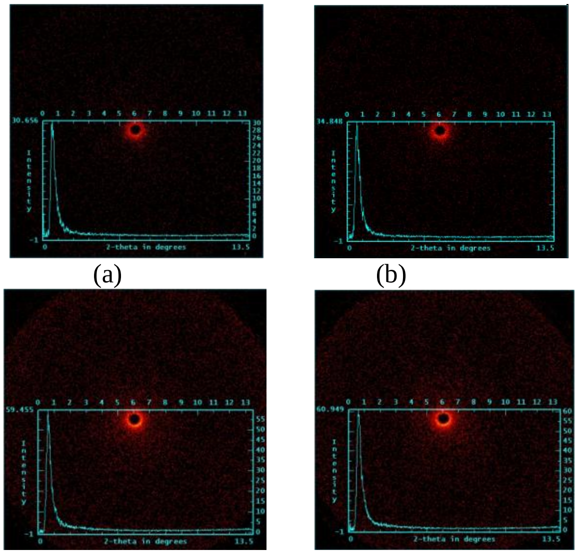

(a) (b)
(c) (d)

Figure 3. SAXD pattern of (a) EP000 (b) EP000 (c) EPS00 (d) EPS05

Figure 4 shows the effect of the MWCNT on the surface resistivity of the specimen. Electron transfer in MWCNTs' is through π bonds (C=C). Since MWCNTs has high aspect ratio, adding only a few MWCNTs significantly reduced the electrical resistivity. For instance, addition of 0.05wt% MWCNT has shown a decrease in the surface resistivity from 2.7X10^7 Ω/m to 2.56 X 10^7 Ω/m. Inclusion of starch in the composite increases the resistivity from 2.7 X10^7 Ω/m to 2.81X 10^7 Ω/m. From Figure 5, we can observe that the inclusion of starch has reduced the surface conductivity of the composite from 3.7X 10^{-8} S/m to 3.56X 10^{-8} S/m. Starch with MWCNT has increased the surface conductivity from 3.56 X 10^{-8} S/m to 3.78 X10^{-8} S/m. Figure 6 shows the Volume resistivity of the composite decreased from 48 X 10^5 Ω/m to 40 X 10^5 Ω/m as the MWCNT loading is increased from 0 to 0.05 wt% and it increases from 48 X 10^5 Ω/m to 53 X 10^5 Ω/m as the starch content increases from 0 to 1wt%. Figure 7 shows the volume conductivity of the composite increases from 20.8 X 10^{-8} S/m to 26.3 X 10^{-8} S/m as the MWCNT loading increase from 0 to 0.05wt% and it decreases from 20.8 X 10^{-8} S/m to 18.9 X 10^{-8} S/m as the starch content increases from 0 to 1 wt%. Figure 8 shows the scaling of log P_v versus the wt% MWCNT loadings. The curve shows the percolation threshold of the specimens 0.05wt% -0.10 wt% MWCNT loadings. Spitalsky *et al* (2009) have found the percolation of MWCNT/Epoxy at 0.05wt% in their research [5]. The high anisotropy of the MWCNTs with aspect ratio >1000 is an evident reason for such effect. The log of the volume resistivity whereby resistivity is inversely proportional to the conductivity was done, due to the clear region of the percolation threshold of the material at different wt% of MWCNT loadings. As the MWCNT loading increases in the bio-nanocomposite, the formation of the cluster increases and high probability of the formation of the conducting network. When the conductive filler content exceeds the critical concentration of the conductive filler, whereby, lowest percolation threshold around 0.05 wt%-0.10wt%. Relatively, MWCNT exhibits highest potential for an efficient enhancement of the electrical properties, due to the homogeneous dispersion of the MWCNT in the bio-nanocomposite and due to the high aspect ratio and low surface area. Figure 9 shows the effect of the MWCNT on the capacitance at 1kHz frequency. From the graph, it could be observed that the capacitance value decrease from 65nF to 55 nF as the starch content increase from 0wt% to 1wt%. On the contrary, the capacitance value of the composite increase from 55nF to 56nF as the MWCNT loading increases from 0wt% to 0.05wt%. As frequency increases from 1kHz to 10 kHz, the capacitance also increases since f is directly proportional to capacitance. Zhang et al (2009) have investigated and explained similar theoretical explanation for this capacitive behaviour as MWCNT loading increases [6].

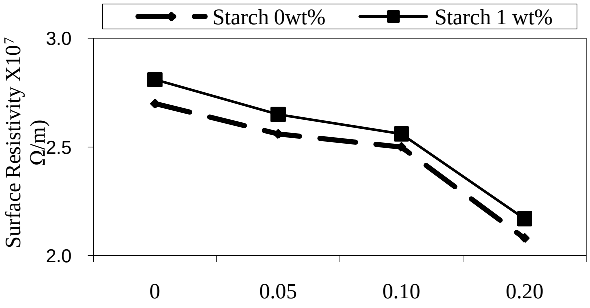


Figure 4. Effect of MWCNT on Surface Resistivity

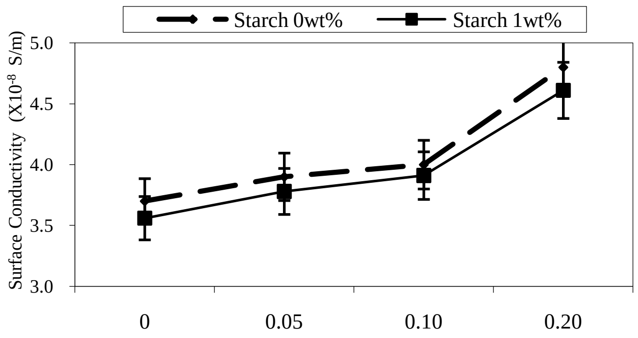


Figure 5. Effect of MWCNT loading (wt%) on Surface conductivity

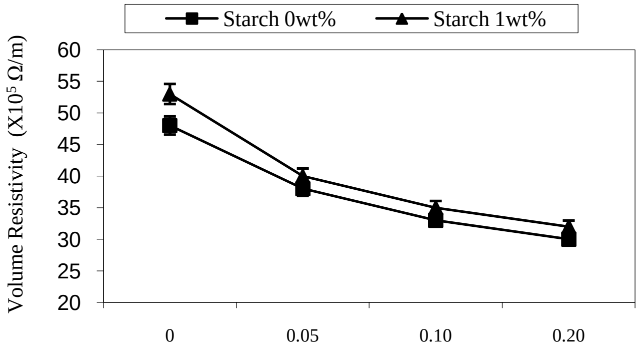


Figure 6. Effect of MWCNT loading on Volume Resistivity of composite

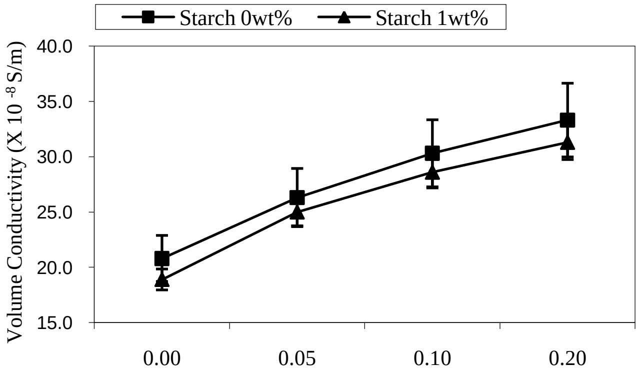


Figure 7. Effect of MWCNT loading on Volume Conductivity of composites

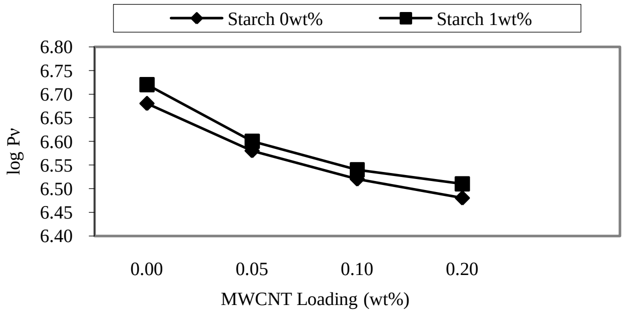


Figure 8. Scaling of log P_v versus the MWCNT loading (wt%)

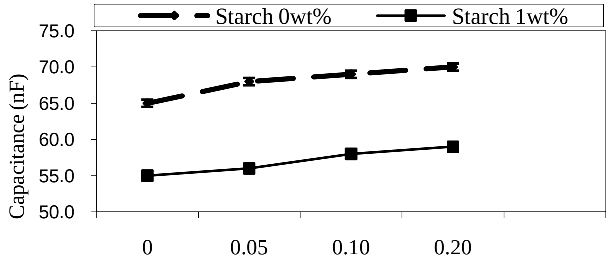


Figure 9. Effect of Starch/MWCNT on Capacitance of composite

4 CONCLUSIONS

Starch/MWCNT/epoxy composites were prepared by casting method. Starch/MWCNTs were well dispersed in epoxy matrix. The introduction of MWCNTs improved the electrical conductivity. As a natural biopolymer composite, starch/MWCNT/epoxy composite would be a promising alternative for the development of new electroactive polymers, which had a wide variety of potential applications such as antistatic plastics, biosensors, batteries, artificial muscles, corrosion protectives, electronic shieldings, environmentally sensitive membranes and solar cell materials.

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