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# A novel polymer nanotube composite for photovoltaic packaging applications

J Ravichandran<sup>1</sup>, A G Manoj<sup>2</sup>, J Liu<sup>2</sup>, I Manna<sup>1</sup> and D L Carroll<sup>2</sup>

<sup>1</sup> Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur, WB 721302, India

<sup>2</sup> Center for Nanotechnology and Molecular Materials, Department of Physics, Wake Forest University, Winston Salem, NC 27105, USA

E-mail: [carroldl@wfu.edu](mailto:carroldl@wfu.edu)

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## Abstract

Packaging of organic photovoltaic (OPV) devices is an important issue which has been rarely addressed in the past. With the recent reports of high efficiency organic photovoltaics (6%), the need to produce materials which can effectively protect the device from degradation due to exposure to oxygen, moisture and radiation is pressing. We report a novel Saran (a co-polymer of vinylidene chloride and acrylonitrile) based polymer nanotube composite, which shows high transparency in the visible region, good barrier properties and thermal stability, for use as an encapsulant for OPV devices. Different loadings of Saran and boron nitride nanotubes were taken and the composites were prepared to optimize the composition of the composite. UV-visible spectroscopy, infra-red spectroscopy and thermal analysis were used to characterize the composite. The barrier properties of the composite were tested on poly(3-hexylthiophene), which is used in high efficiency OPV devices.

## 1. Introduction

### 1.1. Photovoltaic packaging technology

Photovoltaic devices offer an efficient method for converting solar energy to electrical energy and hence provide an alternative and non-conventional source of energy [1]. For a long time, silicon based photovoltaic technology has been studied and efficiency in excess of 30% has been achieved [2]. In spite of the high efficiency, there are a host of problems like high cost of fabrication, rigidity of substrate etc. At the same time, organic photovoltaics provide a low cost solution to domestic electricity needs and have attracted a lot of research interest over the past few decades. They provide a lot of added advantages over conventional silicon photovoltaics like low cost and capital requirement, high optical absorption coefficient, compatibility with plastic and flexible substrates etc. Continued research on this topic has led to a high efficiency above 6% [3]. The major hurdles for organic photovoltaics to overcome to reach the stage of commercial exploitation are raising the efficiency close to that of silicon based photovoltaic devices and solving problems related to the life of the devices, etc. The degradation of the polymer due to the oxidation, moisture and photochemical reactions

greatly decreases the working life of these devices. The most obvious solution seems to be the packaging or encapsulation of the photovoltaic cells in polymer matrix composites. Some efforts have been made in this direction, using polyisobutene (PIB) [4] and ethylene vinyl acetate (EVA) [5]. In the present study, we investigate the possibility of producing encapsulant for the OPV devices using polymer nanotube composites with improved thermal stability, insulation and transparency.

### 1.2. Packaging materials and requirements

Some of the key requirements for an encapsulant for OPV devices are transparency in the visible range, barrier to oxygen and moisture ingress, and mechanical and thermal stability. Hence, the choice of the materials is very crucial. The properties required for food packaging materials have close similarity to those for encapsulants for OPV devices. Hence, Saran, a commercial food packaging polymer, was chosen as the matrix for the composite encapsulant. Recent advances in the synthesis and understanding of the properties of one-dimensional nanostructures like nanotubes have led to a broad range of possibilities for the fillers in composites. Boron nitride nanotubes possess attractive thermal properties like very high



**Figure 1.** Bright field TEM image of the boron nitride nanotube sample.

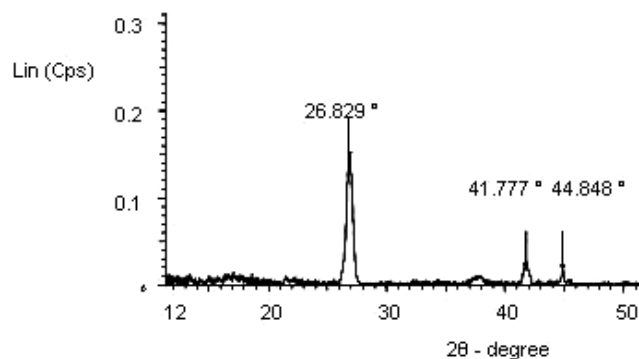
thermal conductivity and high thermal stability besides a wide band gap of 5.5 eV [6]. These are the ideal properties for a filler material to be used in the composite encapsulant.

## 2. Experimental details

The synthesis of boron nitride nanotubes (BN-NT) was carried out by a method similar to the one reported by Zhi *et al* [7]. A homogeneous mixture of boron, iron oxide and magnesium oxide was taken in a quartz crucible placed in a horizontal alumina tube furnace. The furnace was heated to 1200 °C with a constant flow of 100 sccm (standard cubic centimeters per minute) of NH<sub>3</sub> and maintained at this temperature for 30 min. On cooling down, a gray colored powder was found in the crucible. The powder contained multiwalled boron nitride nanotubes with some catalyst particles. These impurities were removed by acid washing with concentrated nitric acid. Characterization of the resultant sample was carried out using x-ray diffraction (XRD) and transmission electron microscopy (TEM).

The polymer employed for making the composite was commercial F-310 grade Saran, obtained from Dow Chemicals. Saran F-310 resin is a co-polymer of vinylidene chloride and acrylonitrile. The solvent employed for the preparation of the composite was 2-butanone (Sigma Aldrich), as recommended in the product sheet (methyl ethyl ketone—MEK). Another polymer used in the experiment is commercially available poly(3-hexylthiophene) (P3HT; Sigma Aldrich). Saran and MEK were taken in the weight ratios of 1:10 and 1:5 and the corresponding solutions were named A and B. Solutions A and B were magnetically stirred for 2 h to get a homogeneous viscous solution. Then, 0.5, 1.0 and 1.5 wt% of boron nitride nanotubes (with respect to Saran) were added to these solutions and these solutions were named A1, A2, A3 and B1, B2, B3 corresponding to the base solutions A and B, respectively. These six solutions were again magnetically stirred for a further 6 h to get a homogeneous solution.

The composites were characterized by UV-visible spectroscopy, infra-red spectroscopy and differential thermal analysis. The UV-visible, infra-red and differential thermal



**Figure 2.** XRD pattern of the boron nitride nanotube sample.

measurements of the composites were carried out using an Ocean optics absorption measurement setup, 4020 Galaxy series FTIR setup and Perkin Elmer Instruments device respectively. The films for spectroscopic measurements were made by either spin coating or drop casting the composites onto glass or silicon substrates. All the composite samples were spin coated onto glass or silicon substrates at 1500 rpm for 30 s to get thin films.

## 3. Results and discussion

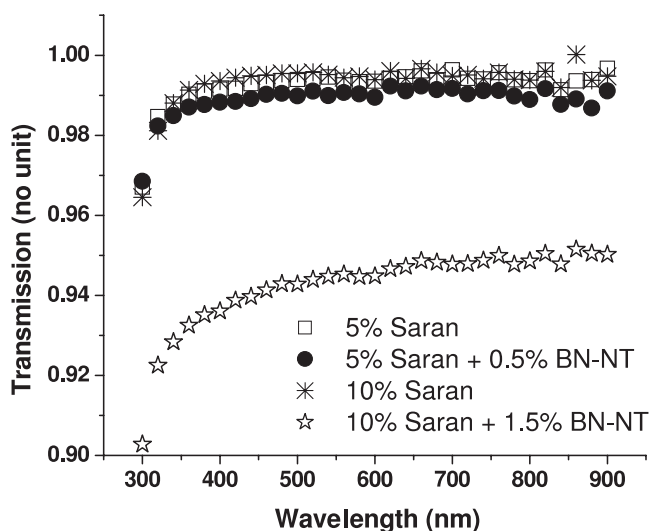
A TEM image of the purified boron nitride nanotubes is shown in figure 1. The diameter of the tubular structures ranged from 10 to 100 nm. After acid washing the sample was quite clean as is evident from the TEM image. The XRD plot is shown in figure 2; it shows that the product is single-phase hexagonal boron nitride. The plot showed all the characteristic peaks of the hexagonal boron nitride without any stray peaks indicating the absence of any impurity phases.

It is known that the minimum transparency required for the encapsulating material of photovoltaic devices is about 90% [8] and hence the optical absorption spectra of these composites were taken to arrive at suitable compositions for the composites. To quantify the effect of the nanotube addition on the transparency of the polymer, the transmission spectrum of the composites over the visible range was obtained and compared for four different concentrations, namely A (5% Saran), A1 (5% Saran + 0.5% BN-NT), B (10% Saran) and B3 (10% Saran + 1.5% BN-NT). The transmission spectra of the composites are given in figure 3. The transmission spectrum of samples showed a very high transmittance with the solution B3 (the densest composite) showing a healthy 93 + % transmission over the entire visible range. The composite A1 appears to be the best choice among the present lot, as it shows almost same transmission as the pure polymer. However, the thermal stability of the composite needs to be evaluated before the decision on the optimum composite composition can be arrived at.

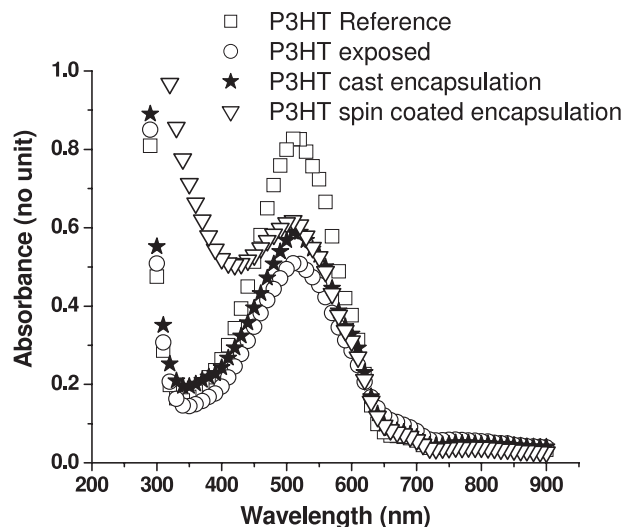
The most crucial property of the encapsulant is the barrier property. One way of evaluating this property is by analyzing the degradation of the polymers used in photovoltaic devices with or without the packaging, which is carried out by analyzing the spectral signatures obtained from

**Table 1.** Peak values and the corresponding transmittances for the IR spectra of reference, encapsulated and exposed P3HT films and the encapsulant film.

Reference P3HT		Encapsulated P3HT		Exposed P3HT		Encapsulant	
Peak (cm <sup>-1</sup> )	Transmittance (%)	Peak (cm <sup>-1</sup> )	Transmittance (%)	Peak (cm <sup>-1</sup> )	Transmittance (%)	Peak (cm <sup>-1</sup> )	Transmittance (%)
3055.24	78.81	3056.69	71.73			2983.04	108.6
2954.87	0.52	2955.06	10.9	2953.94	56.67	2935.74	109.68
2854.73	3.21	2855.6	17	2855.51	59.67	2266.58	126.81
1509.66	41.7	1509.59	40.23	1508.76	90.17	1709.08	104.33
1453.58	16.8	1445.88	21.28	1457.43	82.64	1433.23	107.84
1377.31	73.59	1364.49	42.14	1376.83	92.08	1363.47	112.47
820.59	28.79	820.33	42.58	820.34	78.96	1074.28	79.84
725.5	91.15	723.9	60.26			657.21	104.8
660.45	100.3	657.56	48	670.86	89.77		
		2245.17	62.55				
		1709.52	28.5				
		1076.52	21.16				

**Figure 3.** Transmission spectra of Saran and Saran–nanotube composites.

these polymers. Here, poly(3-hexylthiophene) (P3HT) was employed as the reference polymer for evaluating the barrier properties. P3HT has proved to be a prototypical organic electronic material with various groups having produced high efficiency devices using this polymer [9]. The thin films of P3HT were made on a glass substrate by spin coating a solution of P3HT in chlorobenzene at 1500 rpm for 30 s. The reference P3HT film (F1) was not exposed to the atmosphere to avoid degradation of the polymer. The remaining films were exposed to atmosphere for 24 h to experience degradation. Film F2 was not encapsulated whereas the remaining two films (F3 and F4) were encapsulated with spin coated composite film and drop cast composite film respectively. The UV–visible spectra of these films are shown in figure 4. The plot clearly shows a better characteristic absorbance peak of P3HT (~500 nm [9]) for the encapsulated samples compared to the exposed sample. The intensities of the absorbances for encapsulated samples are not very high compared to those for the exposed samples. The absorbance cannot be directly compared as the thickness of

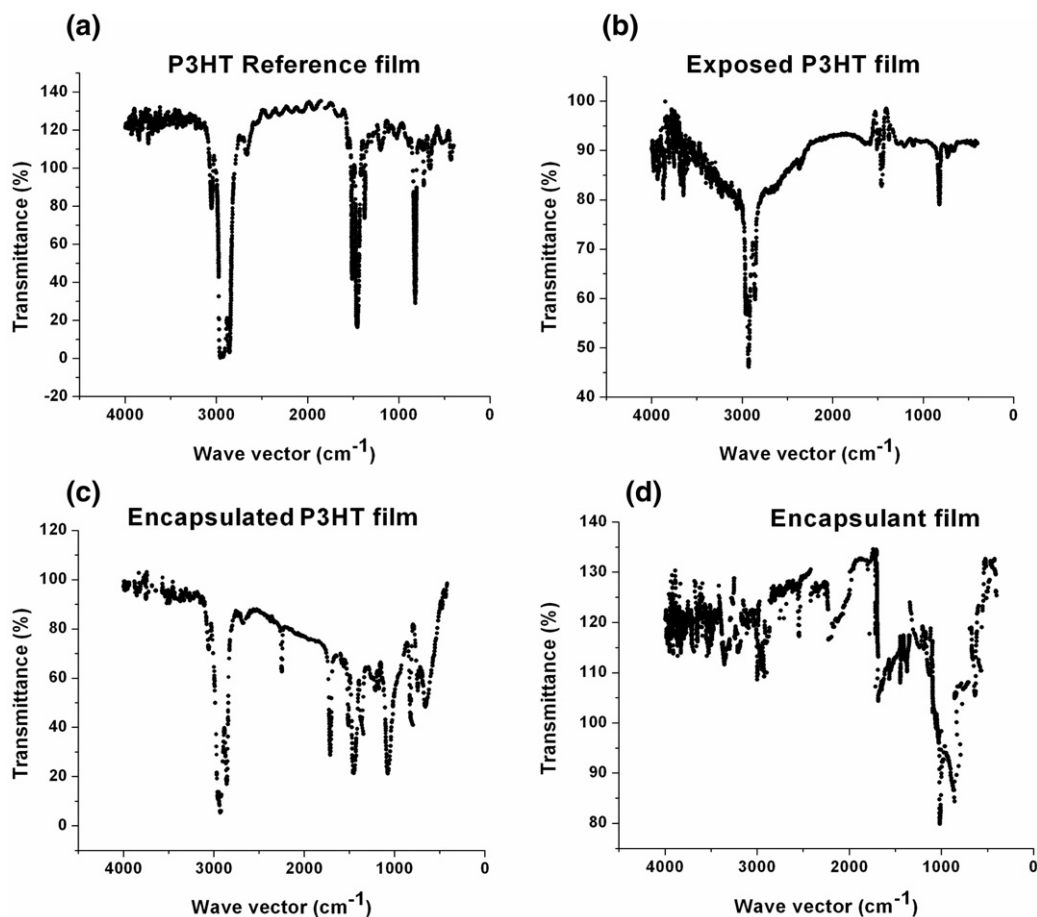
**Figure 4.** UV–visible spectra of reference, exposed and encapsulated P3HT films on glass substrates.

the samples concerned is different. According to the Beer–Lambert law, the absorbance is an exponential function of thickness as shown below.

$$\frac{I}{I_0} = \exp(-\epsilon lc) \quad (1)$$

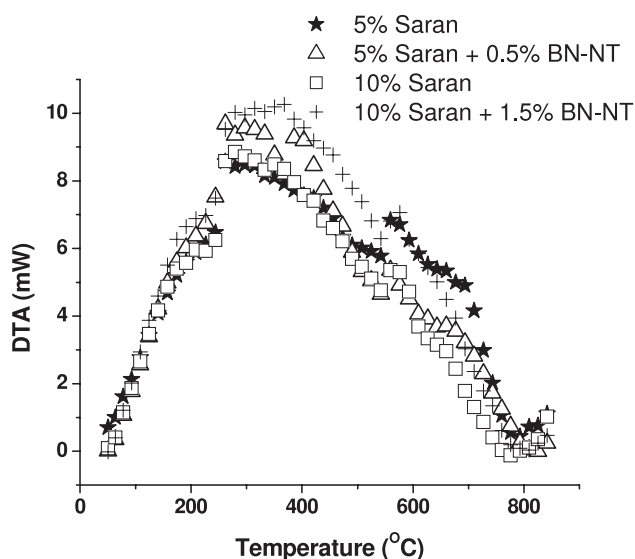
where  $\epsilon$  = molar absorptivity of the absorber,  $l$  = transmission length,  $c$  = concentration of absorbing species.

Due to higher thickness of the encapsulated films, we see a lower absorbance than what was actually expected. To quantify the comparison, the thickness of the polymer film was ~100 nm, the spin coated composite film ~200 nm and the cast film a few microns. The absorbance for a multilayered film is given by  $\epsilon cl = \epsilon_1 c_1 l_1 + \epsilon_2 c_2 l_2$  where subscripts 1 and 2 refer to the first and the second layers of the film and their corresponding extinction coefficients, thicknesses and concentrations. However, the decrease in the absorbance of a similar polymer film which was exposed to air clearly shows that the polymer gets degraded to the oxidation and



**Figure 5.** Infra-red spectra for (a) reference, (b) exposed and (c) encapsulated P3HT films and (d) encapsulant composite film on silicon substrates.

other photochemical processes and, hence, we can see that the composite encapsulation can actually be effective in protecting the polymer from degradation by acting as a protective layer. It is imperative to justify this statement with conclusive evidence and, hence, infra-red (IR) spectroscopy was carried out on similar samples. Glass is not transparent to the entire IR range and, hence, silicon substrates were used. The comparison was carried out with just drop cast films as the spin coated films showed very high transmission in the IR range such that the characteristic signatures were not clearly distinguishable. The IR spectra of the reference exposed and encapsulated P3HT and the encapsulating composite films are given in figure 5. The spectra of the reference P3HT is in accordance with reported literature. The characteristic peaks are found in 700–900 and 2800–3200  $\text{cm}^{-1}$  regions, where the former corresponds to the modes of the thiophene ring and the later the alkyl part of the polymer [10]. Table 1 shows the peak values and the corresponding transmittances for all four samples. It is evident that all the characteristic signatures show a small increase in transmittance in the case of the encapsulated film as compared to the reference film. On the other hand, the exposed film shows very high transmittance for all the characteristic signatures, which represents the degradation of the polymer on exposure to air. Additional peaks found for the encapsulated film correspond to the encapsulation materials, listed at the



**Figure 6.** Differential thermal plots for Saran and Saran composites with different loadings of nanotube fillers.

end separately. Thus, we can conclusively state that the encapsulant film has been successful in creating a protective barrier between P3HT and air.

**Table 2.** Areas under the differential thermal curves for Saran and Saran composite samples.

Sample	Area under the curve (mW K)
Saran 5%	3793.0
Saran 5%–0.5% BN-NT	3807.3
Saran 10%	3966.9
Saran 10%–1.5% BN-NT	6271.4

The other important property of the encapsulant is the thermal stability, as it has to withstand a harsh environment while protecting the OPV devices. The thermal stability can be gauged by carrying out differential thermal analysis (DTA). The thermal analysis was carried out for four composites, namely 5% Saran, 5% Saran with 0.5% BN-NT, 10% Saran and 10% Saran with 1.5% BN-NT. The DTA plots for each of the samples are given in figure 6. The enthalpy of the sample is related to the area under the curve in the DTA plot. It is not possible to directly relate the data to the thermal conductivity of the sample but a qualitative idea of the thermal conductivity and the enthalpy can be obtained from the area under the curve in this plot. The areas under the curves for the different samples are given in table 2.

It is evident from the curves in figure 6 and table 2 that the enthalpy increases with the BN-NT loading and becomes very significant for the last case where we have 1.5% BN-NT loading in the composite. This shows that we can enhance the thermal stability of the encapsulant by using a composite instead of pure Saran as the encapsulant.

#### 4. Conclusions

In summary, we have developed a novel polymer nanotube composite for organic photovoltaic packaging based applications, which shows excellent transparency in the visible region, good barrier properties and good thermal stability. This work gains importance as only a few options appear currently feasible for encapsulant materials. In this regard, employing a polymer composite can significantly improve the device life

and, hence, the commercial utility of the organic photovoltaic devices.

#### Acknowledgments

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