Composites Science and Technology 71 (2011) 397–405

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Structure–property relationship of SELF-sustained homogeneous ternary nanocomposites: Key issues to evaluate properties of rrP3HT wrapped MWNT dispersed in TPU

Suparna Saha [b], Jyoti Prakash Singh [a], Uttam Saha [a], Thako Hari Goswami [a,*], K.U. Bhasker Rao [a]

[a] Electronics and Smart Materials Division, Defence Materials and Stores Research and Development Establishment, DMSRDE P.O., G.T Road, Kanpur 208 013, India
[b] Department of Polymer Science & Technology, University of Calcutta, 92 A.P. C Road, Kolkata 700 009, India

ARTICLE INFO

Article history:
Received 17 September 2010
Received in revised form 1 December 2010
Accepted 6 December 2010
Available online 14 December 2010

Keywords:
A. Nanocomposites
A. Carbon nanotubes
B. Thermal properties
B. Mechanical properties
D. Scanning electron microscopy (SEM)

ABSTRACT

An interesting correlation between nature of wrapping, wrapping thickness and crystallinity of regioregular poly(3-hexyl thiophene) (rrP3HT) wrapped multi-walled nanotube (MWNT) arises due to different loading of rrP3HT and their combined effect on the properties of a ternary system prepared by uniform dispersion of wrapped CNT into thermoplastic polyurethane (TPU) are highlighted in the article. Data accumulated through different techniques demonstrate that 2.5 wt.% of rrP3HT with 0.5 wt.% of MWNT can be the ideal ratio of filler to achieve highest properties in these stable self-sustained homogeneous composites. Wrapping of rrP3HT on the wall of CNT through π–π and/or CH–π interaction is ascertained from shifting in peak position and I_{asym}/I_{sym} ratio of C=C bond of rrP3HT in FTIR spectroscopy. Strong quenching of fluorescence intensity of rrP3HT in composite further support π–π interaction between rrP3HT and CNTs. SEM micrograph of rrP3HT/TPU blends suggest uniform globular dispersion of polythiophene into TPU matrix without any separate phase domain and addition of CNTs considerably reduce globule size. Single Tg(~-40 °C, DMA, DSC, TMA) clearly ascertain the miscibility of composite. An 'order to order transition' through coil to rod transformation leads to strong, sharp red shifting ($\sim$150 nm shift compared to pristine rrP3HT) in emission peaks of rr-poly (3-hexylthiophene) in blends. Further red shifting and highest quenching is observed in case of 2.5% rrP3HT loaded ternary system whereas blue shifting and quenching in case of 0.5 wt.% (non-uniform wrapping) and 5 wt.% (agglomerates) rrP3HT loading.

1. Introduction

Discovery of highly conductive π-conjugated polymers makes the pathway for developing next generation semi-conducting materials for electronic and optical devices owing to their excellent solubility and processability. Correct molecular engineering during synthesis of these polymers can tune the optical and electronic properties. Poly (alkyl-thiophenes) in particular regioregular poly (3-hexylthiophene) (rrP3HT) [1] has been the focus of great attention due to its relatively high chemical stability in ambient conditions, excellent solubility in variety of solvents and high conductivity. Conductivity of these polymers depends on the head–tail (H–T) regioregularity of the chain; higher the regioregularity higher is the conductivity. On the other hand, processing condition has role to play; solvent-casted samples have one order higher conductivity than melt-cooled samples whereas spin-coated samples have two orders higher conductivity than that of solvent-cast film. Mobility of rrP3HT in the organic field effect transistors (OFETs) has reached the values of 0.01–0.2 $cm^2 V^{-1} s^{-1}$ [2]. Electronic band gap of polythiophenes falls within the visible region of electromagnetic spectrum and photoluminescence property can be tuned in its nanocomposites by different procedures [3]. It is now well known that optoelectronic properties of P3HT films are highly sensitive to microstructure and film morphology which depend on various materials and process variables viz., solvent type, temperature, film-casting technique, P3HT average molar mass and polydispersity. Certainly, first important consideration during tailoring of electronic properties of P3HT materials is to determine the effect of regioregularity and molar mass of the polymers.

Unique physical, mechanical (high modulus) properties and high electrical/thermal conductivity [4,5] of CNTs holds the potential to improve the host material's mechanical, electrical and thermal properties by orders of magnitude well above the performance possible with traditional fillers. A better understanding of the interaction between polymers and nanotube is still a critical factor to allow an optimization of polymer–nanotubes compositions to

---

* Corresponding author. Fax: +91 5122450404.
E-mail address: thgoswami@yahoo.co.uk (T.H. Goswami).

0266-3538/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2010.12.005

have composite materials with improved performances. Key issues for producing superior CNT nanocomposites are however: (i) appropriate %weight ratio of conducting polymers to CNT to obtain uniform wrapping; (ii) homogeneous dispersion of wrapped CNTs in polymeric matrix; and (iii) strong interfacial interaction to affect efficient load transfer from polymeric matrix to CNTs. Difficulty in processing due to insolubility may however be overcome by wrapping the carbon nanotube with polymer, which renders them soluble in common solvents [6]. Recently, direct polymerization of monomers in functionalized CNT has received great attention to prepare polymer wrapped CNTs [7,8].

Blending of thermoplastic polyurethane (TPU) with polythiophenes/carbon nanotubes enables to combine its mechanical properties with the transport and optical properties of conjugated polymers [9,10]. It motivates to develop low-cost fluorescent conductive material to be used as chemi-resistive sensor [11]. Composite nanofibers and films made from solution of the homogeneously dispersed SWNTs in PU have received substantial attention in recent time [12,13].

In this work, primary goal is to achieve optimal conditions to obtain uniform homogeneous blend without interfering physical property of P3HT. Thermoplastic properties of polyurethane enabled the self-sustained P3HT/TPU films to be stretched in order to induce a higher chain alignment of P3HT [10]. Optical properties of these P3HT/TPU films show that P3HT conjugation length is increased substantially and the material has potential for application in opto-electrical devices. Another goal is to prepare a stable dispersion of CNT (fixed concentration, 0.5 wt.%) in the blend of TPU-rrP3HT. Two issues concerning TPU–P3HT–CNT nanocomposites have been addressed in this work: (i) the nature of polymer–CNT interaction; wrapping or not, phase structure and crystallinity of the bulk material; and (ii) establishment of optimized structure–property relationship as a function of concentration ratio between P3HT and CNT to achieve highest value. Investigations of photophysical properties of binary and ternary systems provide a clear structure–property relationship with respect to rrP3HT–CNT concentration ratio and nature of wrapping.

2. Results and discussion

2.1. Selection of materials and preparation of composite

Among the Shape Memory Polymers (SMPS), commercial grade thermoplastic polyurethane under the trade name Desmopan (DP 9380A) is extensively studied for its excellent shape memory effects. The host matrix, Desmopan, find broad application in temperature sensing elements [14,15]. These polymers have good elasticity and strength and depending on the nature and amount of polyol, isocyanates and chain extender used, elasticity and strength will vary.

rrP3HT (>99% regioregularity), a highly ordered semi-crystalline material, is believed to conduct current through chain transport in the crystalline region and through hoping or tunnelling processes in the amorphous region [16]. Presence of TPU/CNTs induces chain alignment of folded coil structure of rrP3HT in the direction of TPU/CNTs chain length. Combined effect (orderisity and conjugation length) has substantial influence to lower the band gap of the composite.

Three P3HT–TPU blend samples containing 0.5, 2.5, and 5 wt.% of rrP3HT (PH1, PH2, PH3) are prepared by mixing appropriate amount of rrP3HT with TPU. About 2 h stirring is required to dissolve TPU into THF (40 ml) and the solution is then mixed with rrP3HT under inert atmosphere in stirring condition (~6 h) to produce homogeneous mixture. Solution casted films are dried under vacuum at room temperature for more than 1 week in inert atmosphere. Typical thickness of these films is of the order of 220 μm.

To prepare ternary nanocomposites (PHC1, PHC2, PHC3), a given amount of rrP3HT (0.5, 2.5, and 5 wt.%) and CNT (0.5 wt.%) is sonicated under inert atmosphere using probe sonicator for 1 h 30 min in THF solution. Mechanical energy provided during sonication overcomes the vander-waals interaction in the NT bundles leading to NT exfoliation and allows P3HT molecules to adsorb or wrap onto the surface of NT walls [17]. This P3HT wrapped NT solution can be easily dispersed into TPU solution. The resulting mixture is further stirred for 5 h under inert atmosphere to get a stable dispersion with minimal nanotube aggregation. Solution casted films are dried under vacuum at room temperature for more than 1 week. Thickness of the films is of the order of 400 μm.

2.2. Morphology

Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images of the MWNT samples confirm the distribution of length (1–1.5 μm) and diameter (100 nm) [18]. Carbon purity (>85%) and metal oxide impurity (<5%) is confirmed by thermo-gravimetric analysis. Early information about polymer–CNT interface and nature of polymer coating on CNT surface suggest a distinct tendency for polymer chain alignment of rod segments in the direction of CNT main axis and a region of aligned rod-like self-assembly of P3HT chains [19,20].

Typical surface images of TPU/rrP3HT blends are presented in Fig. 1a–c and corresponding CNT–nanocomposites are presented in Fig. 1d–f. Surface images of TPU/rrP3HT blends indicate smooth homogeneous surface at low loading of P3HT (0.5 wt.% loading of P3HT, Fig. 1a). Increase of P3HT loading (2.5 wt.% loading of P3HT, Fig. 1b) in the matrix produce morphology of globular aggregates of P3HT dispersed uniformly all over the blend surface. On further increase of P3HT loading (5 wt.% loading of P3HT, Fig. 1c), globule size of P3HT is also increased. No separate phase domain of P3HT is however observed in any of the above the matrix. This is an excellent improvement in respect of blend homogeneity (single Tg, obeying Fox equation, through DMA, DSC, TMA clearly ascertain the miscibility of composite) compared to earlier result where a hetero-phase blend with separate micro-domain of P3HT is reported [9]. Fine dispersion of CNT in TPU/rrP3HT blends considerably reduce the aggregates size of P3HT globule in 5 wt.% loaded P3HT nanocomposite (Fig. 1f), whereas in low loaded P3HT (up to 2.5 wt.%) globular aggregates of P3HT is disappeared (Fig. 1d and e). Average diameter of conducting polymer wrapped CNT are measured through software calculation of SEM images. Nature of wrapping and wrapped thickness depends on the amount of P3HT; 2.5 wt.% of P3HT records highest thickness of 220 nm whereas 5 wt.% P3HT shows the lowest thickness (117 nm). An in-between thickness of 140 nm is observed in case of 0.5 wt.% loaded P3HT. These values give a definite relationship between nature of wrapping/wrapping thickness and initial amount of P3HT loading. From experimental data, it is apparent that initial concentration of polymer is insufficient to cover up entire CNT surface uniformly at low loaded P3HT whereas agglomeration of polymer on the surface of CNT is the possible reason for observed lowest wrapping thickness in case of highest loaded P3HT (5 wt.%). In the present case, 2.5 wt.% of P3HT is observed to be optimum. Physical verification of samples also supports wrapping mechanism. It is well known that pure rrP3HT is easily precipitated out on addition of poor solvent (methanol). Dispersed composite solution is found to be too stable to precipitate out at all on treatment with methanol even after a week. This observation is first indication of a strong interaction between CNT and conducting polymer that disturbed self-organization of the pristine rrP3HT and induces a new structural alignment of rrP3HT in the direction of CNT-chain [19]. It appears that modified self-assembly of conducting polymer in CNT composites minimised the interfacial surface