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Augmentation of properties on sparingly loaded nanocomposites *via* functionalized single-walled carbon nanotubes by covalent approach

Adhigan Murali, Senthil A. Gurusamy-Thangavelu,* Sellamuthu N. Jaisankar* and Asit B. Mandal*

Polymer Division, Council of Scientific and Industrial Research (CSIR)- CLRI, Adyar, Chennai, 600 020, India.
Tel.: +91-44-24422059/24910846, Fax: +91-44-24911589/24912150 E-mail: senthil@clri.res.in; snjsankar@clri.res.in; snjaio@yahoo.com; abmandal@hotmail.com

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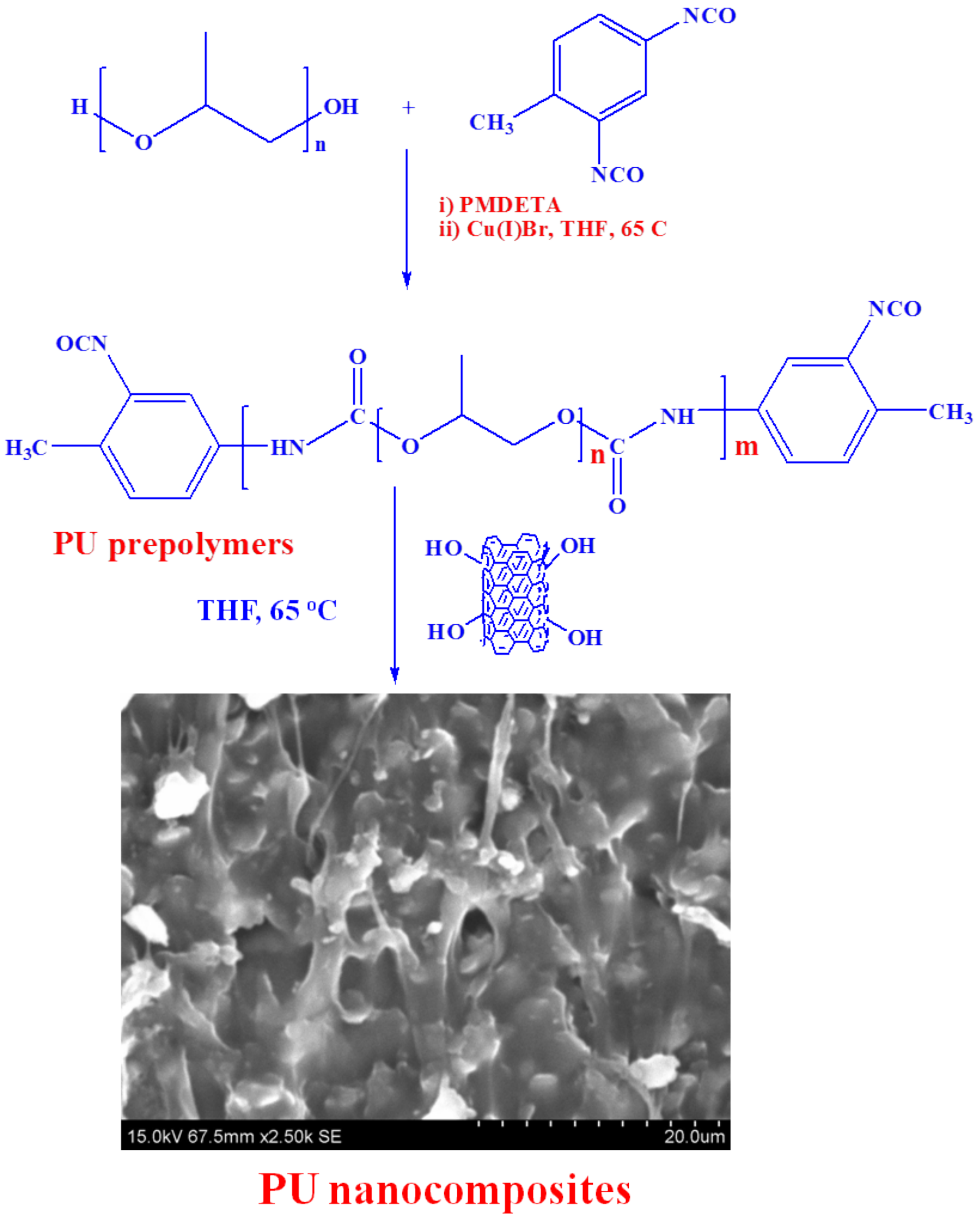

Fig. S1 Covalent addition of $[OH]_n$-SWCNTs to PPG and TDI based PU.

EXPEREMENTAL METHODS

Materials

Poly(propylene glycol) (PPG, average M_n ~2000), 2, 4'- toluene diisocyanate (TDI, 80 %), copper (I) bromide [Cu(I)Br, 98 %], *N*, *N*, *N′*, *N″*, *N″*-Pentamethyldiethyentriamine (PMDETA, 99 %) and single-walled carbon nanotubes (carbon >90 %, ≥70 % carbon as SWCNTs, 0.7-1.3 nm diameter) were procured from Aldrich, USA. Sodium nitrite ($NaNO_2$), nitric acid (69-72 %) and THF were purchased from Merck. Freshly distilled THF was used in all reactions after stored for overnight in sodium hydroxide. Poly(propylene glycol) was heated in rotary evaporator at 80 °C for 1 h before attempt to use in PU prepolymers/PU nanocomposites reactions.

Synthesis of $[NO_2]_n$-SWCNTs from pristine SWCNTs

Pristine SWCNTs (90 mg, black color flabby solid) suspended in dry toluene (45 ml) was subjected to sonication in probe sonicator (Probe sonicate sonics VCX 750, 750 W, 20 KHz, 60 % amplitude, Sonics & Materials Inc., Newtown, USA) for 30 minutes before transferring the suspension into 100 ml two necked round bottom flask A.

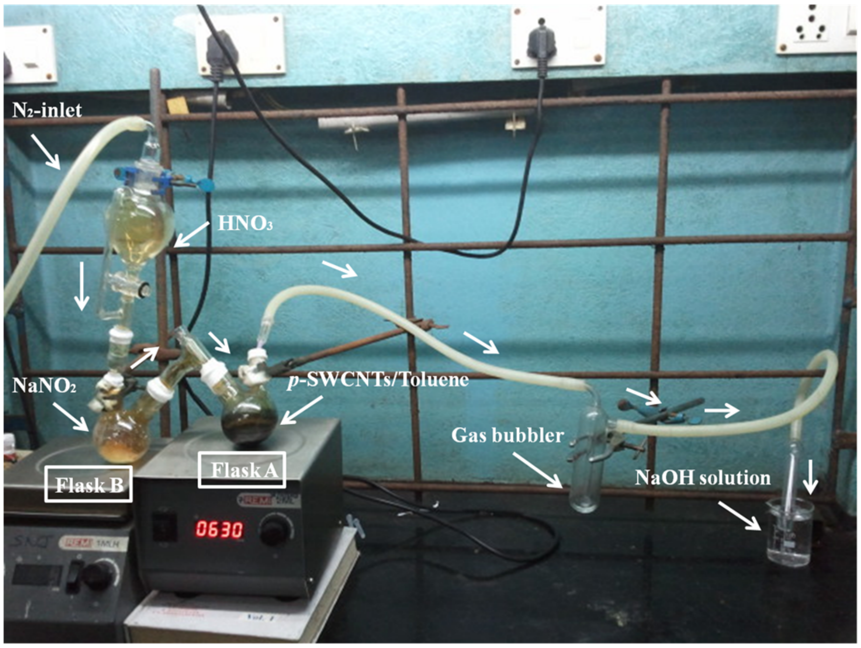

Fig. S2 Experiment assembled for the functionalization of $[NO_2]_n$-SWCNTs by radical addition.

Another 100 ml two necked round bottom flask B charged with $NaNO_2$ (12 g, 174 mmol) was equipped with pressure equalizer funnel filled with conc. HNO_3 (12 ml) and connected with flask A through a ground joint connection bent (to exchange NO_2 gas radicals). To the above experimental set up, outlet joint was connected to sodium hydroxide (2N) solution to bubble any excess gas and N_2 gas inlet was connected from the top of equalizer funnel to purge out oxygen. After N_2 gas purged out, conc. HNO_3 was added drop wise into flask B to liberate NO_2 radical as brown gas and it passed through glass bent to flask A containing stirred suspension of SWCNTs in dry toluene. The stirring was continued for 8 h and any excess brown gas (NO_2 radicals) remained in the flask A was purged out with N_2 before proceed to further work up. Toluene was evaporated from the reaction mixture and the crude solid product was suspended in hexane (20 ml) and centrifuged at 10,000 rpm for 10 min. The above centrifuge process was repeated three times and covered with pierced aluminum foil to evacuate under high vacuum oven kept at 50 °C. After cooled down this oven to ambient temperature, flabby solid sample was weighed, 78 mg. FTIR sample was prepared for the above product using KBr pellet and the data collected from the FTIR laboratory spectrometer ABB MB3000.

Synthesis of $[OH]_n$-SWCNTs from $[NO_2]_n$-SWCNTs

A clean dry boiling tube was charged with $[NO_2]_n$-SWCNT (75 mg) and NaOH (5 ml, 3N solution in deionized water) was added before subjected to sonication for 20 min. After sonication, reaction mixture was stirred in hot oil bath at 50 ˚C for 4h. The reaction mixture was brought down to ambient temperature before addition of methanol (16ml) to precipitate the crude black solid product. The crude solid was washed twice with deionized water (20 ml) to wash off any alkaline residue and dried under vacuum at 50 °C for 5 h to obtain $[OH]_n$-SWCNTs (66 mg). FTIR was collected for this sample to identify characteristic peaks correspond to hydroxyl functionalized SWCNTs.

Synthesis of PU prepolymers film (control)

Synthesis of prepolymer was performed in a three necked round bottom flask equipped with a mechanical stirrer under nitrogen atmosphere, flask was charged with Cu(I)Br (2 mg) prior to the addition of poly(propylene glycol) (4.5 g, 0.00225 M) and 2, 4 - toluene diisocyanate (TDI, 2.5 ml, 0.0139 M) at ambient temperature. To the above stirred reaction mixture, PMDETA (0.025

g, 0.000144 M) and dry THF (3 ml) was added before heated up to 65 ºC in oil bath. The reaction was continued at 65 ºC for 2 h, dry THF (3 ml) was added periodically every 15 min to avoid gel formation. This viscous reaction mixture was removed from the oil bath and transferred carefully under hot condition to petri dish evenly to form a transparent film with uniform thickness (1.5 mm). Curing process was carried out at ambient temperature for a week.

Synthesis of PU nanocomposites film

PU nanocomposites were prepared from PU prepolymer and $[OH]_n$-SWCNTs. To the above stirred viscous mixture, suspended $[OH]_n$-SWCNTs (0.021 g, 0.3 wt. %, after sonication for 15 min) in dry THF (10 ml) was added and stirred further at 65 °C for 30 min. The viscous reaction mixture turned to dark color upon addition of SWCNTs and removed from oil bath to transfer under hot condition to petri dish to recover film after curing at ambient temperature. The identical procedure was followed to develop PU nanocomposites, $[OH]_n$-SWCNTs loadings [0.007 g (0.1 wt. %), 0.0035 g (0.05 wt. %) and 0.0007 g (0.01 wt. %)] were suspended in THF to formulate other three films.

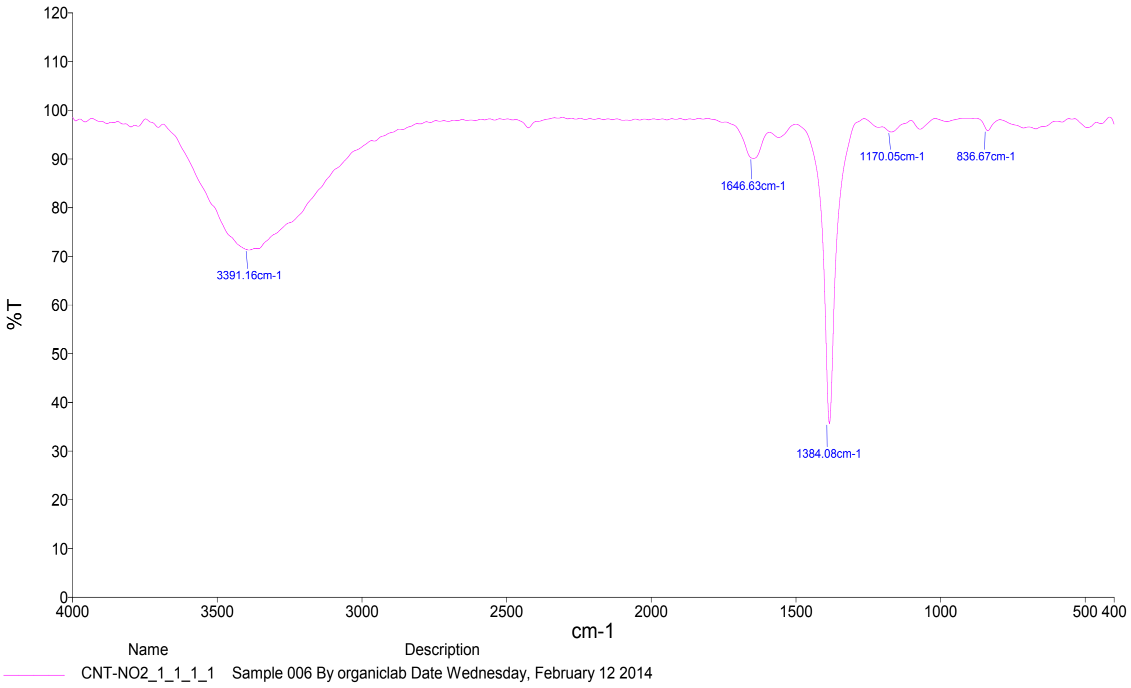

Fig. S3 FTIR spectrum of functionalized $[NO_2]_n$-SWCNTs.

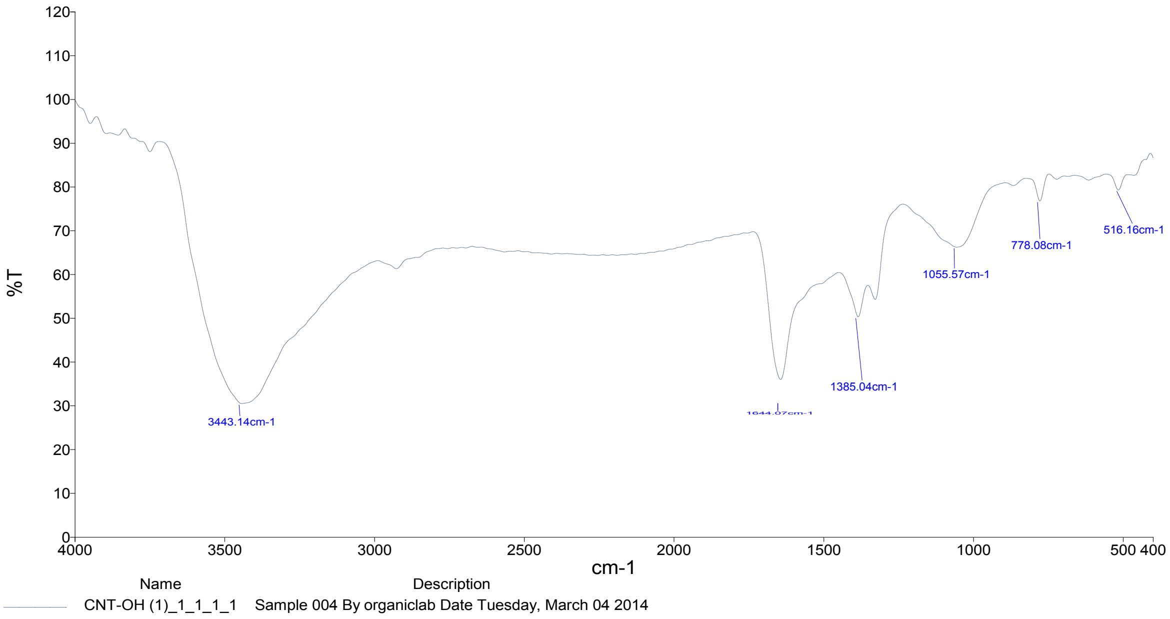

Fig. S4 FTIR spectrum of functionalized $[OH]_n$-SWCNTs.

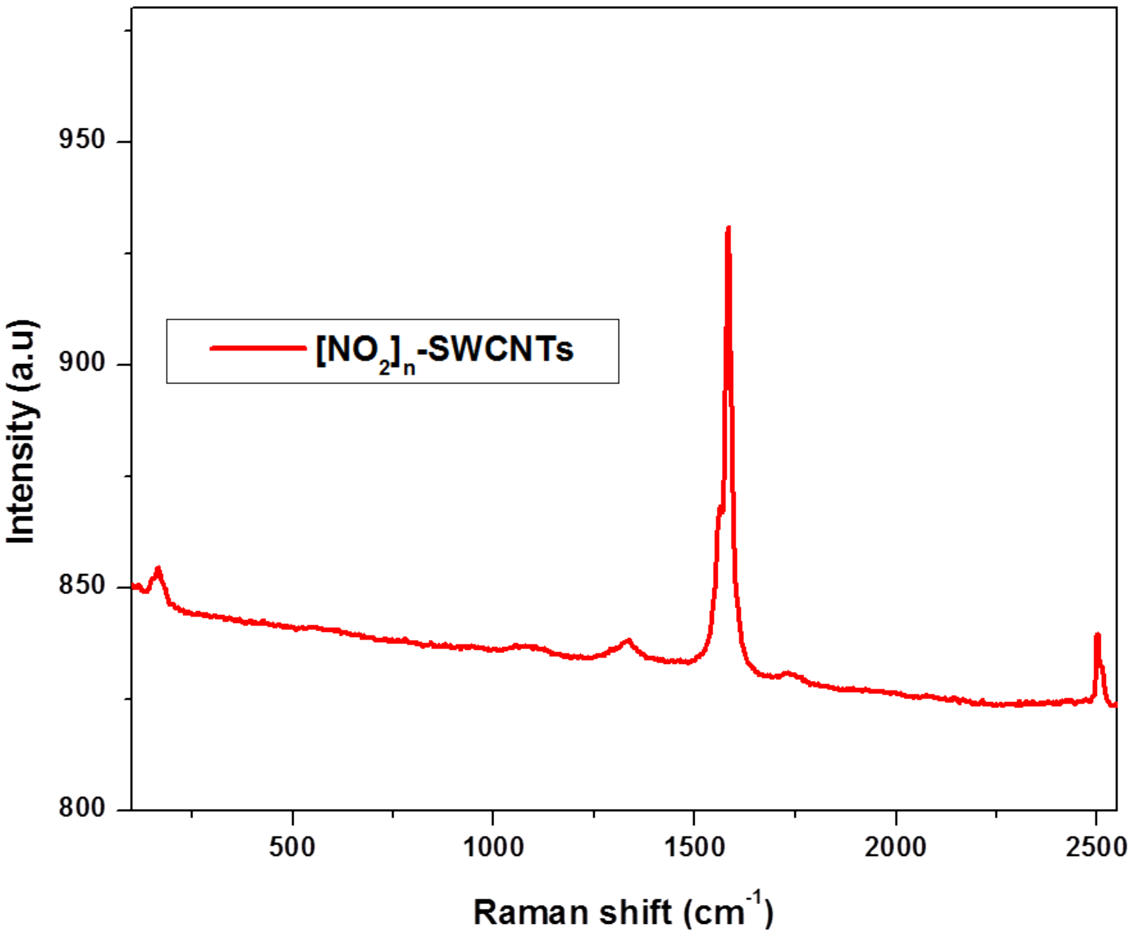

Fig. S5 Raman spectrum of functionalized $[NO_2]_n$-SWCNTs.

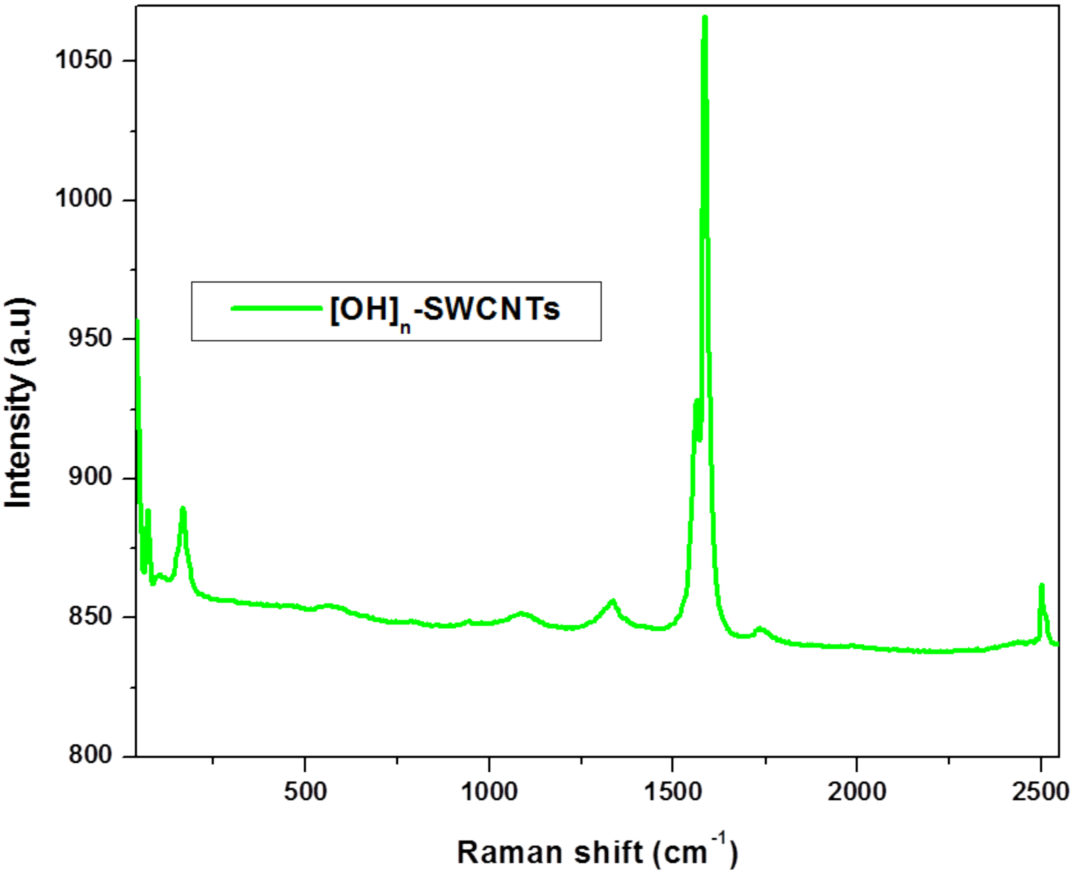

Fig. S6 Raman spectrum of functionalized [OH]$_n$-SWCNTs.

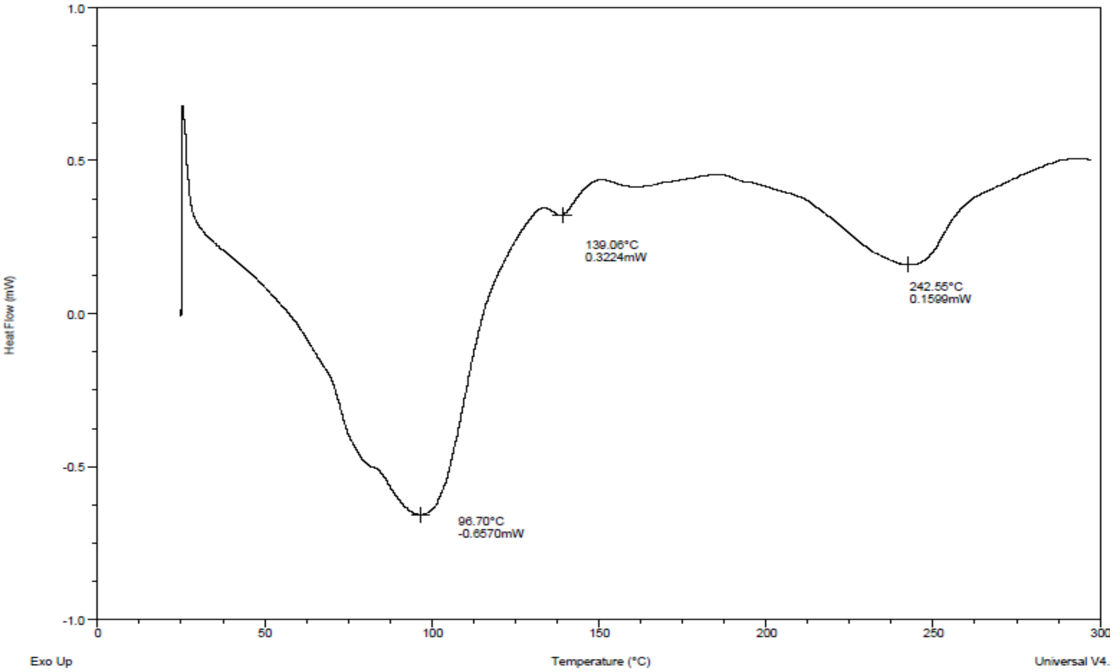

Fig. S7 DSC thermogram of functionalized $[NO_2]_n$-SWCNTs.

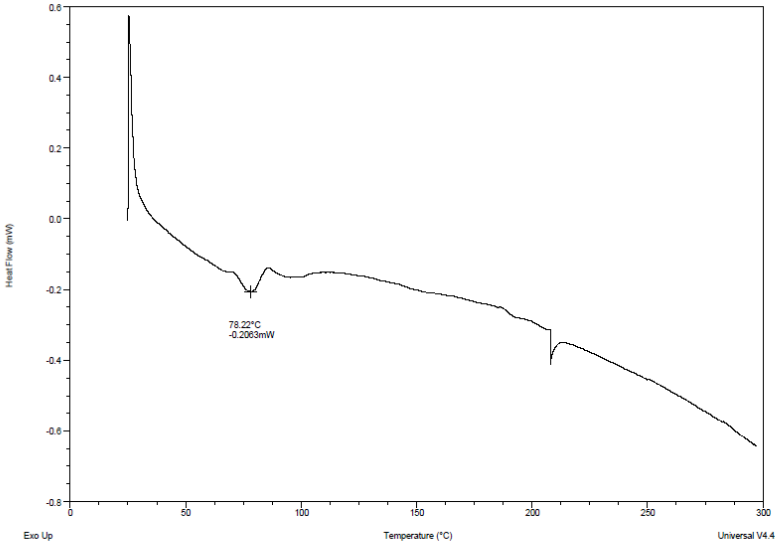

Fig. S8 DSC thermogram of functionalized $[OH]_n$-SWCNTs.

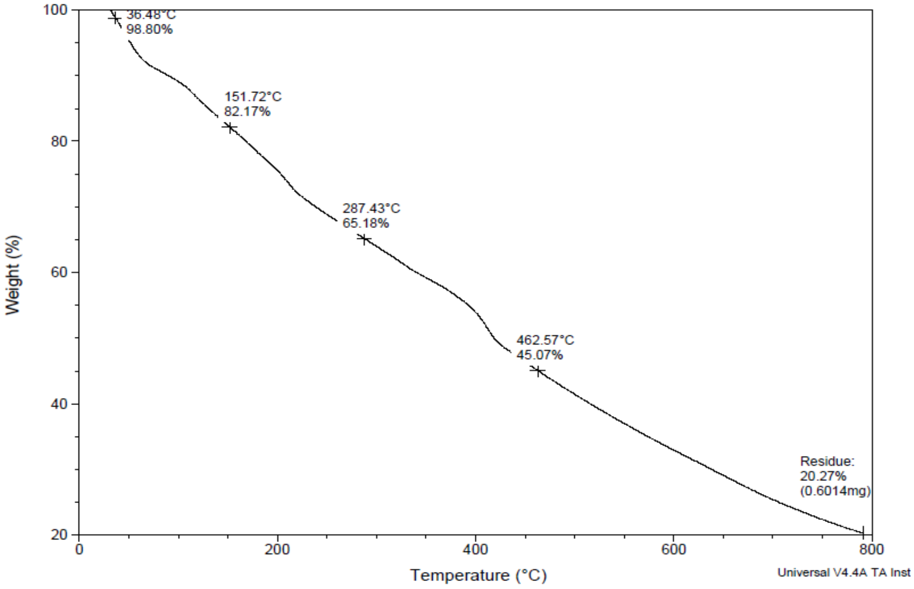

Fig. S9 TGA thermogram of functionalized $[NO_2]_n$-SWCNTs.

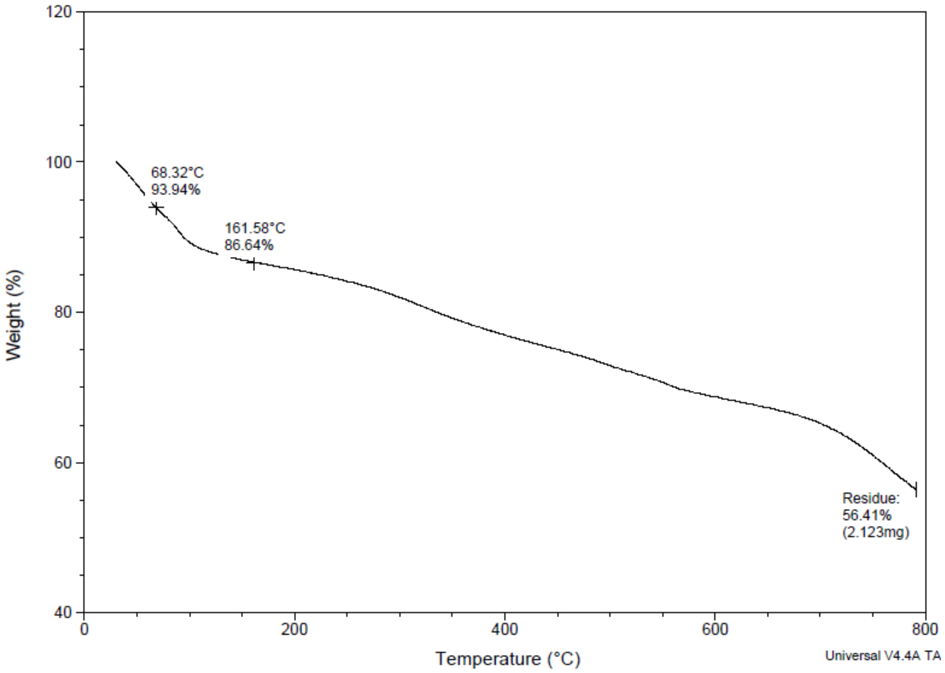

Fig. S10 TGA thermogram of functionalized $[OH]_n$-SWCNTs.

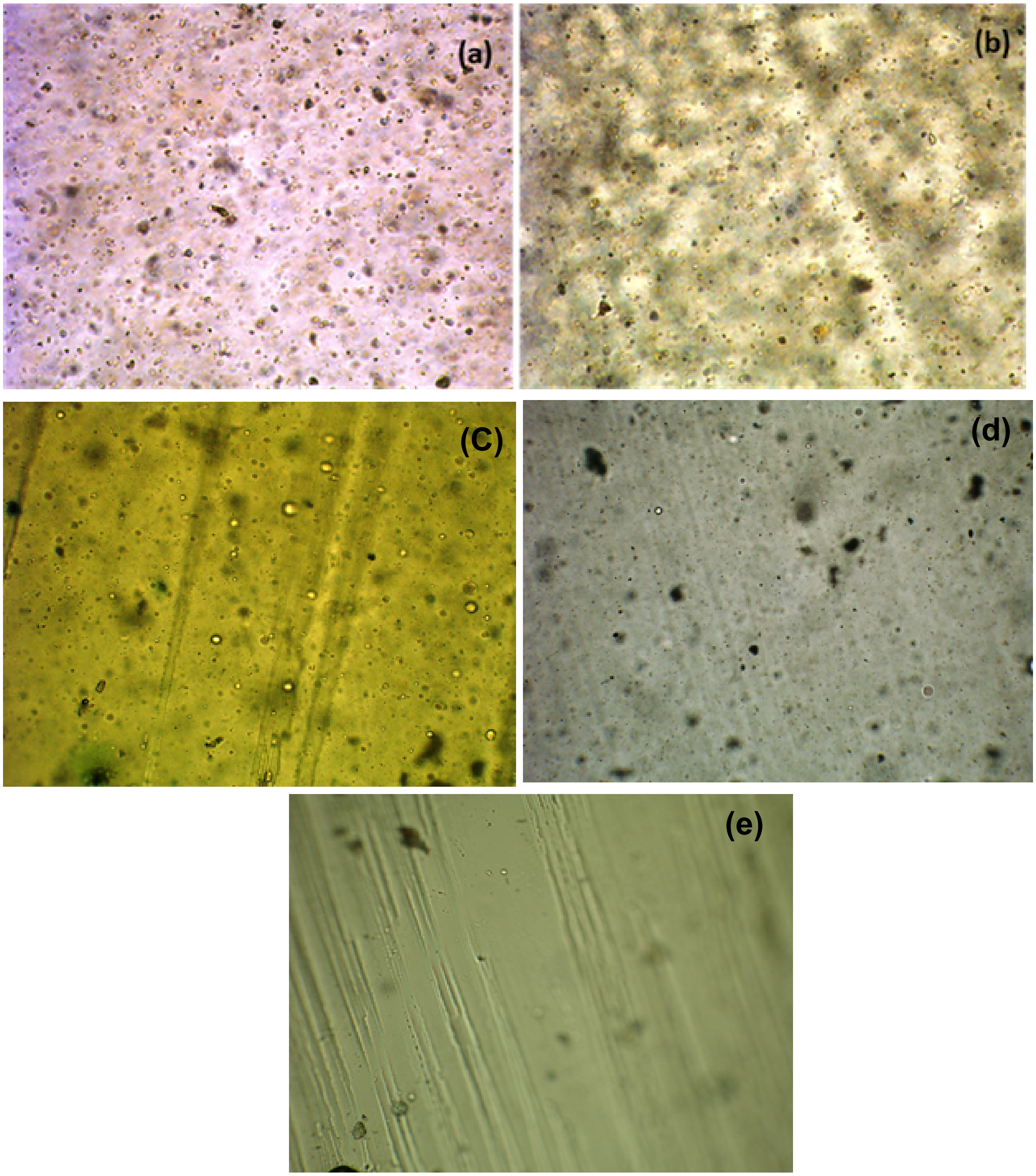

Fig. S11 Optical microscopy images of PU nanocomposites [(a) 0.3 % (b) 0.1 % (c) 0.05 % (d) 0.01 % loading (e) control] films (100X).

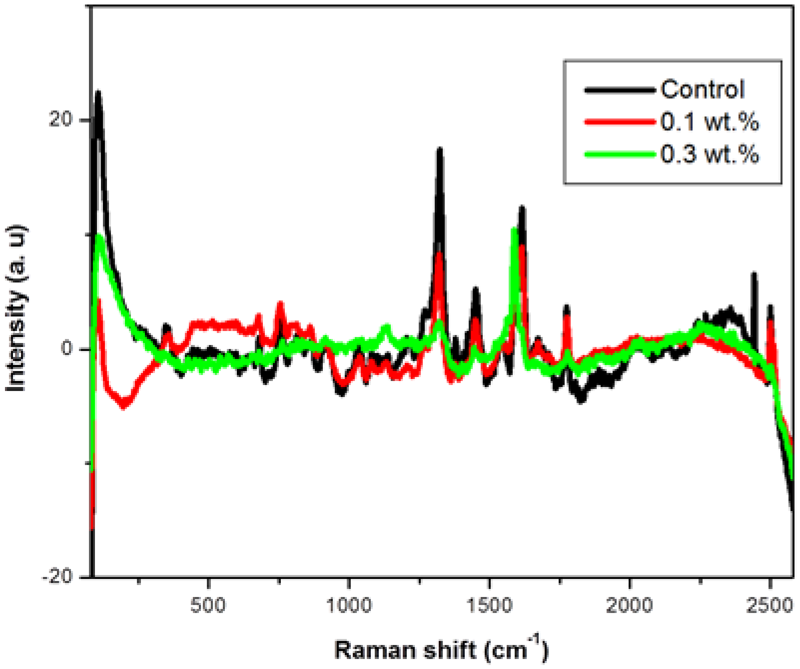

Fig. S12 Raman spectra of PU and PU nanocomposites at different loadings.

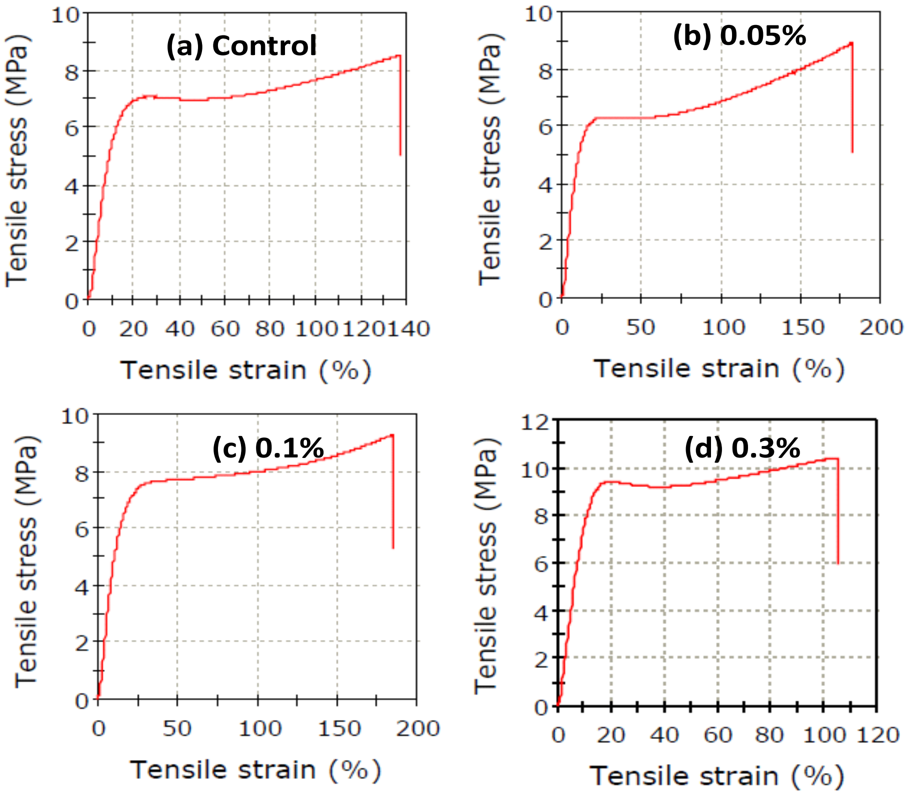

Fig. S13 Tensile profiles of control and PU nanocomposites at different wt. % of loadings.

The first one third region of the tensile profile provides information about elastic deformation and the remaining region corresponds to ductile deformation.[1] The yield values (0.1 wt. %: 7.8 MPa and 0.3 wt. %:9.3 MPa) noticed for the samples containing 0.1 and 0.3 wt. % of SWCNTs is existing above the control sample value (6.9 MPa). Samples in entry 3 and 4 deduced to exhibit plastic behavior, since the stress-strain curve passes through strain hardening region, which is above the steady state and critical stress.

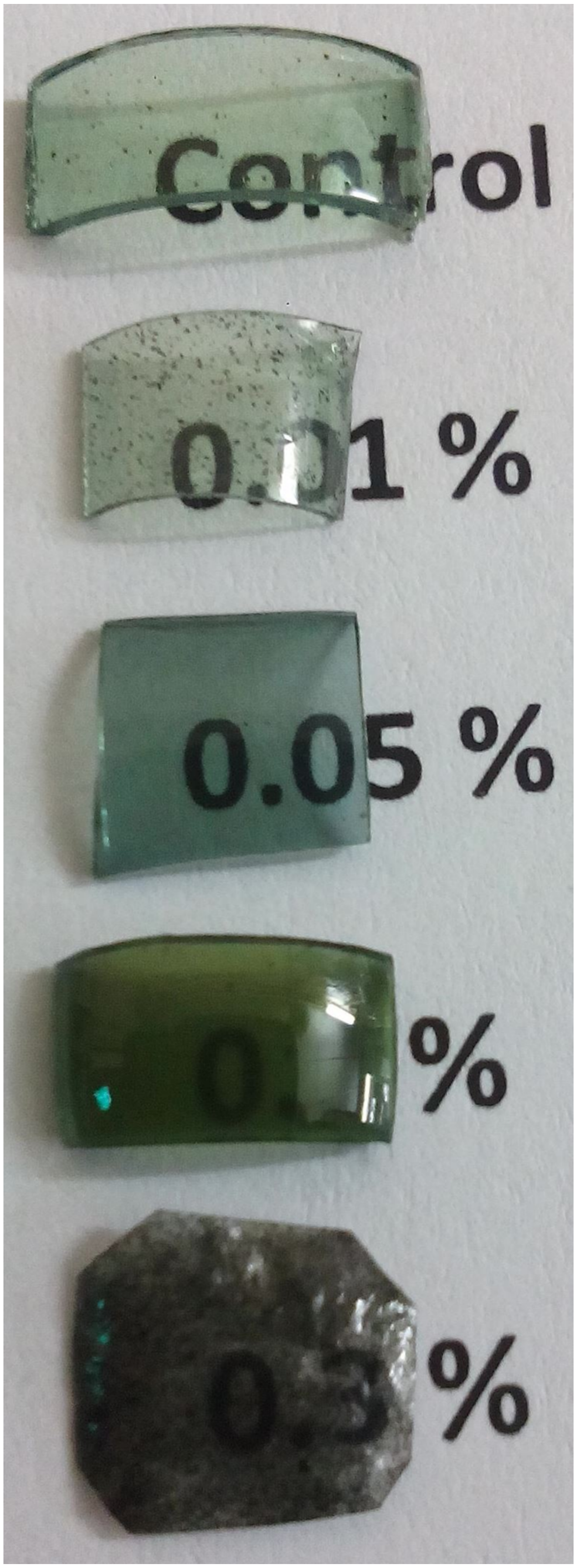

Fig. S14 Transparent images of PU control and PU nanocomposites films.

Optical microscopic images (Fig. S11) of PU and PU nanocomposites films reveal the transparency as well as the intensification in distribution of $[OH]_n$-SWCNTs. However, the degree of transparency of PU nanocomposites films appears slightly cloudy upon loading (0.01 % to 0.3 %) of $[OH]_n$-SWCNTs (Fig. S14).

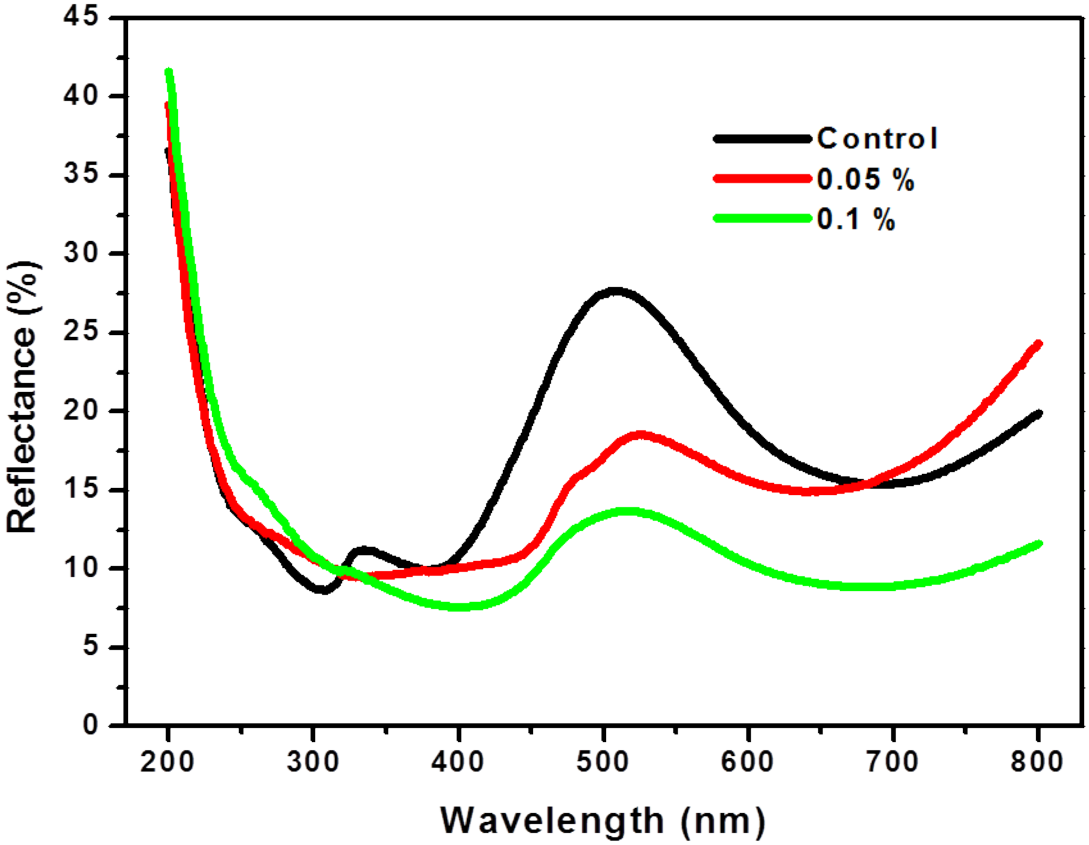

Fig. S15 UV–*vis* DRS spectra of PU control film and PU nanocomposites films.

Control PU film and PU-nanocomposites films (0.05 and 0.1 %) were characterized by UV-visible diffuse reflectance spectra to support the film samples are transparent in visible region as shown in Fig. S15. In UV wavelength region, the spectral data of these films are appeared to be similar and overlap with each other. There is appreciable variation among the spectra in visible wavelength region, highest percentage of value is observed in graph to support the maximum transparency in case of PU control film and drops eventually with respect to the increase in loading of $[OH]_n$-SWCNTs in PU nanocomposites films (0.05 and 0.1 %).

TG/DTG Analysis

The thermal stability is provided in terms of degradation time profile. The degradation time (9.02-14.88 min.) derived from derivative thermogravimetric (DTG) curve (Fig. S16-S20) is incorporated, where linear increase in degradation time is provided correspond to control PU and PU nanocomposites films loaded with $[OH]_n$-SWCNTs. The DTG derivative curve corresponds to each of the above TGA data carried out under slower rate of heating (10 °C/min.) is shown in Fig. S16-S20, which depict the improved resolution of degradation time compared to that of previous set of data (Fig. 5a) given in main manuscript, collected under heating rate (20 °C/min.).

In particular, the peak of the first derivative curve is known as the first derivative peak temperature (T_p), where maximum change in rate of weight loss occurred ahead of degradation temperature.[2] The T_p of the first derivative DTG curve is combined with all descending TGA profile display the corresponding weight loss occurred over the linear temperature ramp (25 to 800 °C). In case of TG/DTG data (Fig.S16-S20), the significant shift in T_p and increase in degradation time attributed to the enhancement of thermal stability of PU nanocomposites film samples with different loadings (0.3 %, 386.8 °C ; 0.1 %, 383.4 °C ; 0.05 %, 378 °C ; 0.01 %, 378.2 °C) compared to control PU film sample (370.8 °C) infers the gradational enhancement of thermal stability due to the covalent addition of $[OH]_n$-SWCNTs on PU prepolymers.

The hard segments degrade prior to soft segments in PU samples composed of variable proportion of hard and soft segments according to the components used in PU formulation.[3] The above samples are comprised of minimum fraction of hard segment and larger amount of soft segment, identified from the TG/DTG curve where hard and soft segment degrades around 250 and 400 °C respectively.

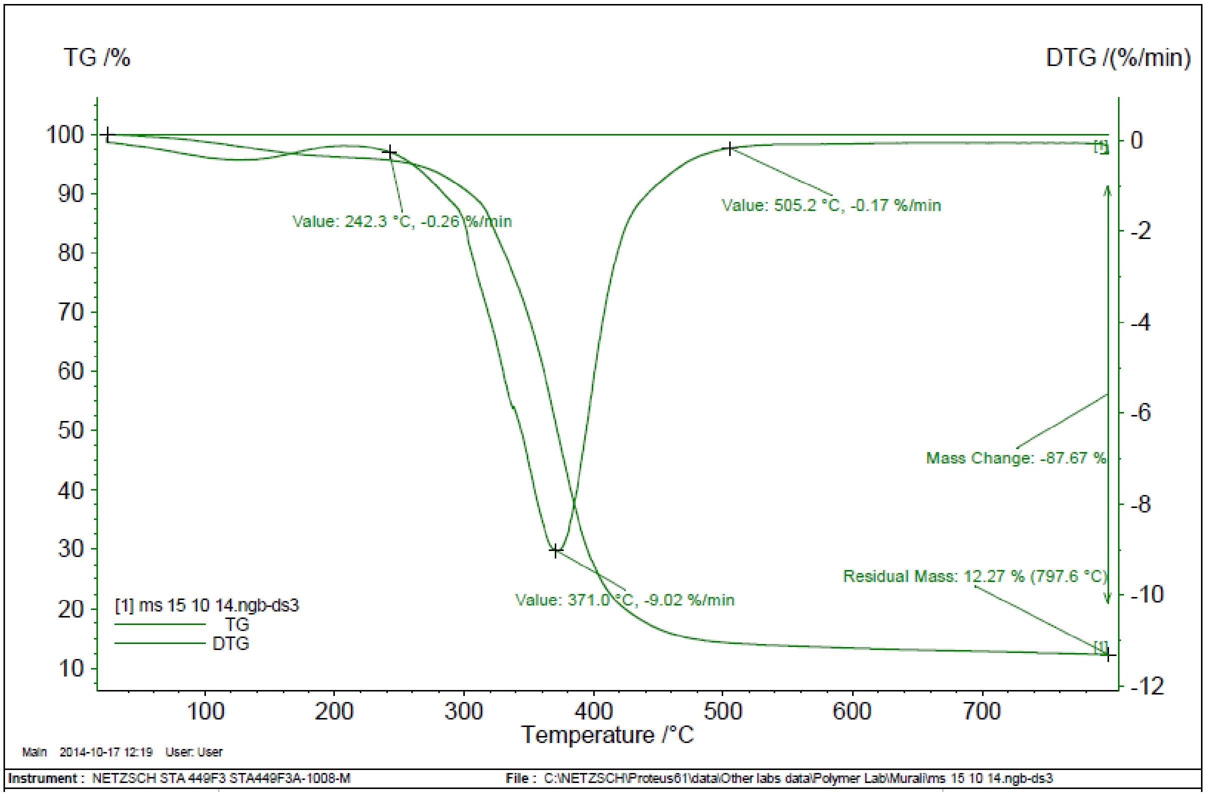

Fig. S16 TG/DTG curve of control PU film.

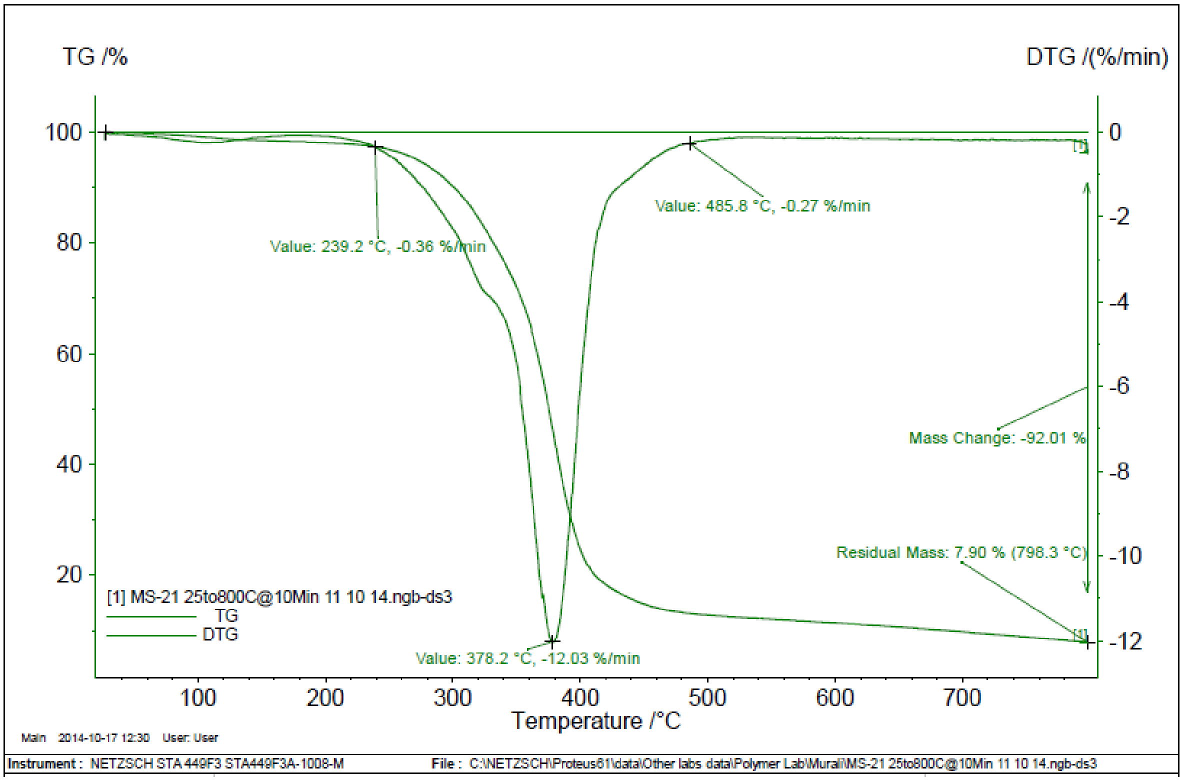

Fig. S17 TG/DTG curve of PU nanocomposites film (0.01 %).

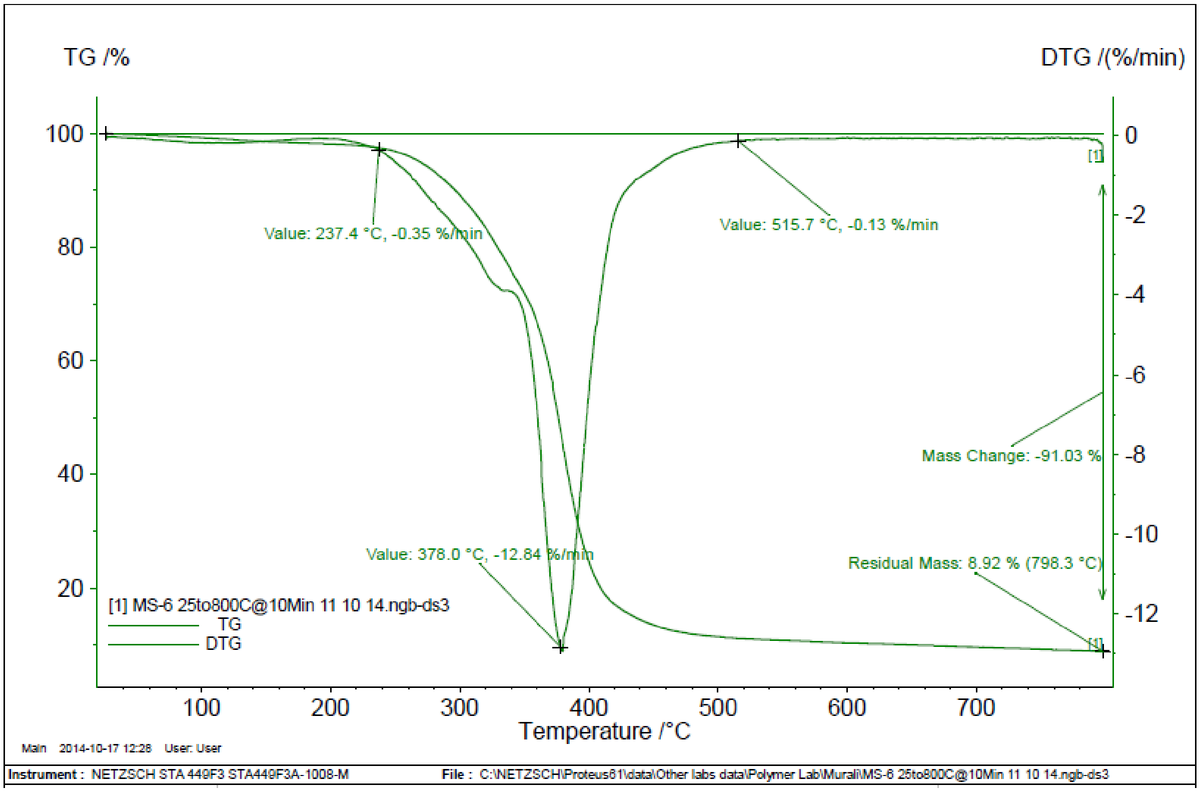

Fig. S18 TG/DTG curve of PU nanocomposites film (0.05 %).

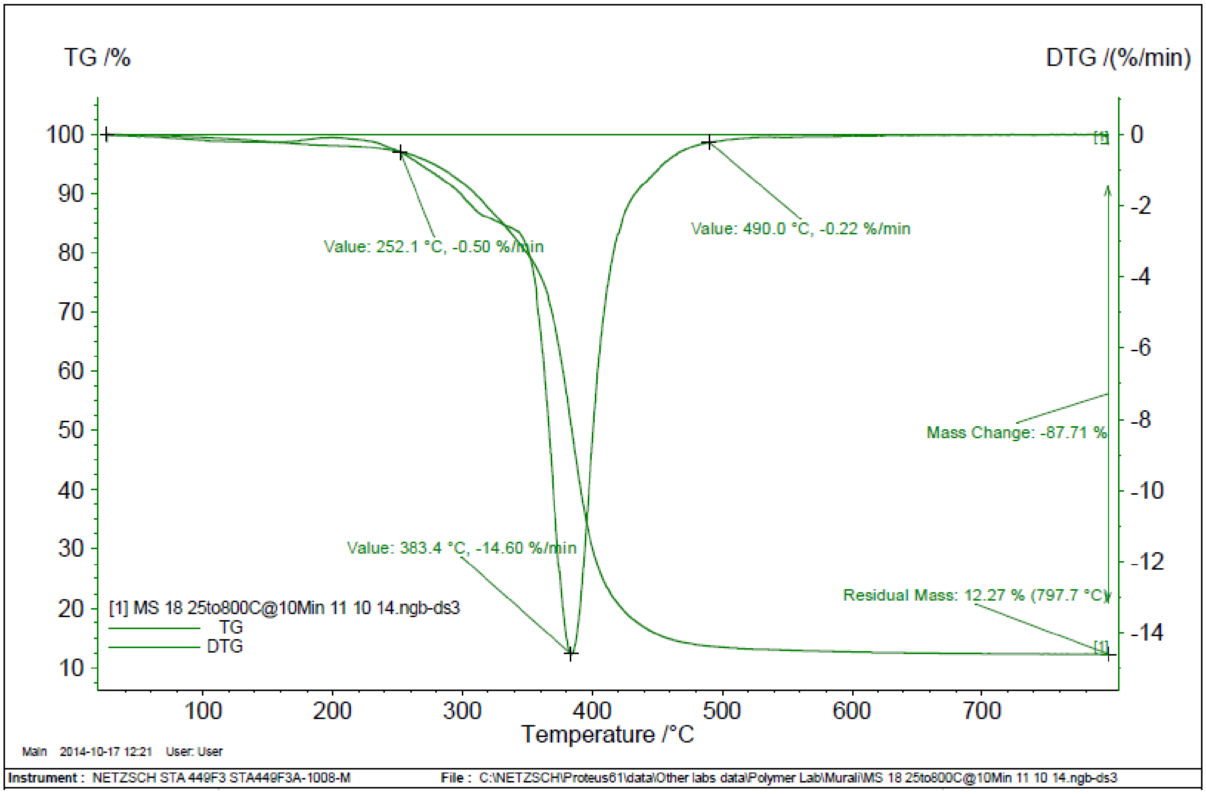

Fig. S19 TG/DTG curve of PU nanocomposites film (0.1 %).

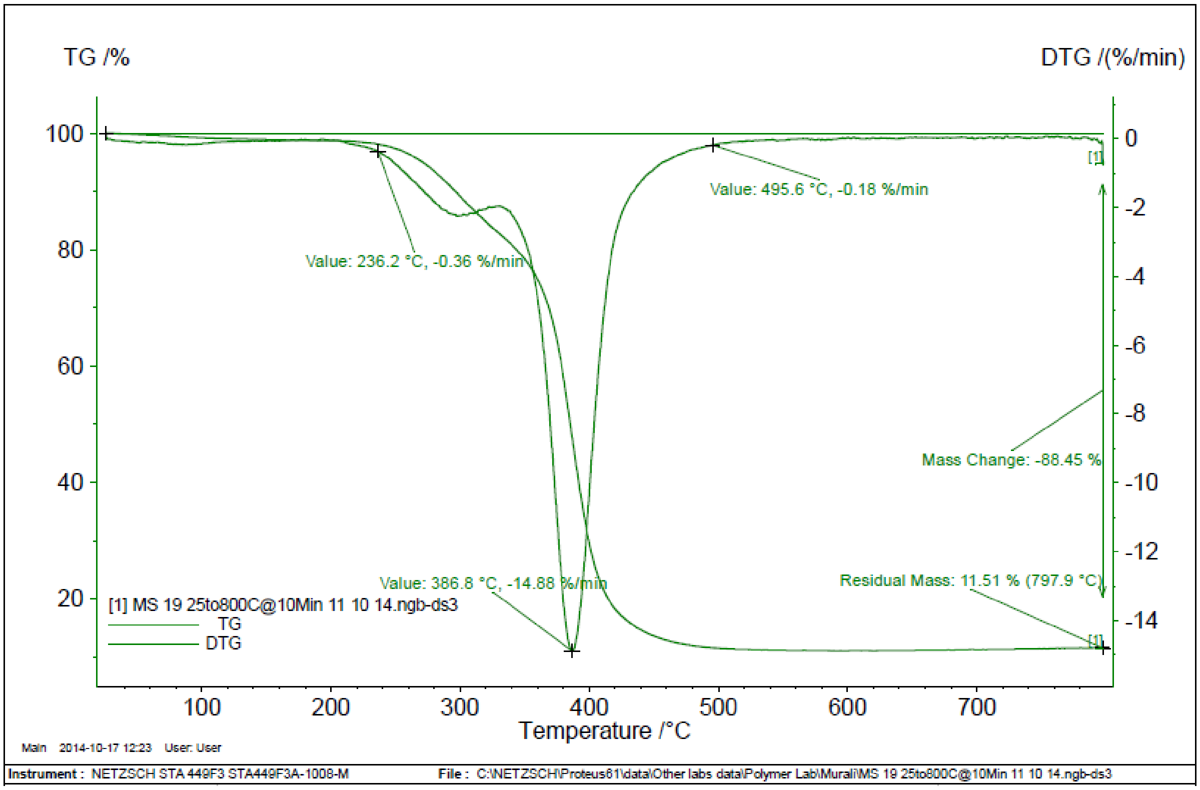

Fig. S20 TG/DTG curve of PU nanocomposites film (0.3 %).

References:

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2. F. Coutinho and M. C. Delpech. *Polym. Degrad. Stabil*, 2000, **70**, 49.
3. G. Trovati, E. A. Sanches, S. C. Neto, Y. P. Mascarenhas and G. O. Chierice. *J. Appl. Polym. Sci.*, *2010*, **115**, 263-268.