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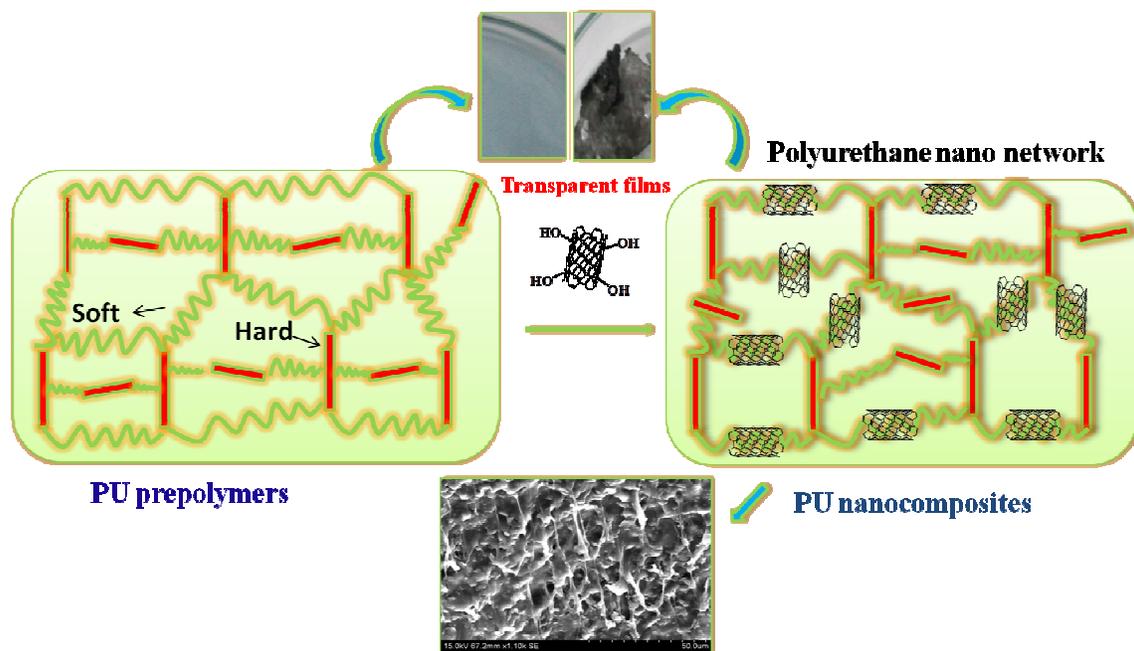
Augmentation of properties on sparingly loaded nanocomposites *via* functionalized single-walled carbon nanotubes by covalent approach

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Polymer nanocomposites are developed as transparent films by the covalent addition of polyurethane (PU) prepolymers to the functionalized carbon nanotubes, [OH]_n-SWCNTs for the first time *via* an efficient route using mild reagents, added in trace loadings. These PU nanocomposites, distributed uniformly *via* covalent bond between SWCNTs and polyurethane network, enhanced mechanical, thermal and conductivity (10^{-4} S cm⁻¹) properties. An anomalous behaviour in magnetic property is observed and characterized with these PU nanocomposites by vibrating sample magnetometer (VSM) at ambient temperature.



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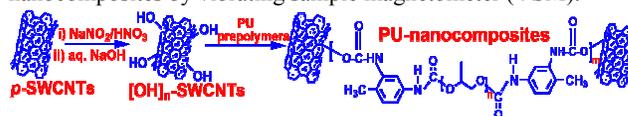
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Polymer nanocomposites are developed as transparent films by the covalent addition of polyurethane (PU) prepolymers to [OH]_n-SWCNTs functionalized for the first time via an efficient route using mild reagents, added in trace loadings. PU nanocomposites, distributed with SWCNTs, enhanced mechanical, thermal and conductivity (10⁻⁴ S cm⁻¹) properties.

It is ubiquitous to develop polymer nanocomposites¹ using carbon nanotubes,² multi-walled carbon nanotubes and single-walled carbon nanotubes towards various applications,³⁻⁵ by diverse methods such as solution and melt mixing, non-covalent, grafting, *in situ* polymerization, etc.⁶⁻⁸ Song and Hesheng co-worker have reported the synthesis of PU nanocomposites using SWCNTs by two step *in situ* polymerization.^{9,10} In our previous report, pristine SWCNTs was used to develop PU nanocomposites by non-covalent method¹¹ and recently published on castor oil based PU/silica nanocomposites.¹² As such SWCNTs have extraordinary thermal, electrical and mechanical properties, their dispersion into PU network can pave a new avenue to promote their properties to use in electronics and automobiles.⁵ Currently, PU nanocomposites are synthesized upon the reaction between PU prepolymers and [OH]_n-SWCNTs via covalent approach, the SWCNTs attached by covalent bond are susceptible to transmit their unique properties into PU networks. To facilitate the reaction between isocyanates group on prepolymers and SWCNTs, a facile method has been developed for the first time to obtain [OH]_n-SWCNTs from *p*-SWCNTs by modifying a synthetic route used for the conversion of fullerenes into fullerlenols.¹³ In step I, *p*-SWCNTs were converted into [NO₂]_n-SWCNTs by radical addition of gaseous nitro radical generated from the mixture of sodium nitrite and conc. HNO₃, followed by aqueous alkaline treatment of [NO₂]_n-SWCNTs afforded [OH]_n-SWCNTs in good yield, as given in scheme 1 (Experimental procedure and Fig. S2 are given in ESI).

In previous literature, polymer nanocomposites revealed the enhancement of mechanical, thermal and conductivity properties, prominently due to the incorporation of carbon nanotubes⁶ into polymer matrix in the range of 0.5 to 10 wt. % and once ultrasmall loadings of SWCNTs used to study mechanical properties.¹⁴ Herein, mildly functionalized [OH]_n-SWCNTs covalently added in trace loadings (0.01, 0.05, 0.1 and 0.3 wt. %) to prepolymers, without compromising its unique properties as shown in Fig. 1. To develop such PU nanocomposites, *in situ* addition of [OH]_n-SWCNTs into the composition of PU

prepolymers, formulated from poly(propylene glycol) [PPG] and 2, 4' - toluene diisocyanate (TDI) in the presence of catalysts, Cu(I)Br and *N, N, N', N'', N'''*- Pentamethyldiethyentriamine (PMDETA) in THF under stirring at 65 °C, as given in ESI (Fig. S1). Compositions of PU control and PU nanocomposites were casting into stiff and transparent films, characterized by ATR-IR, UV-*vis* DRS (Fig.S15), Confocal Raman, Solid state ¹³C NMR, DSC, TGA, Optical microscopy, SEM and tensile strength. In this sort of films, [OH]_n-SWCNTs are covalently bonded uniformly on PU network, which excluded the agglomeration of SWCNTs. Indeed, thermal, mechanical and conductivity studies, the non-trivial magnetic characterization was conducted to illustrate the anomalous behaviour in magnetic properties of PU-nanocomposites by vibrating sample magnetometer (VSM).



Scheme 1 Functionalization of *p*-SWCNTs into [OH]_n-SWCNTs followed by reaction with PU prepolymers to afford PU nanocomposites.

To explore the conductivity properties, Impedance spectroscopy (Hewlett Packard 4284A precision LCR meter) and two-probe resistance (Keithley 2400 source meter) were used to measure conductivity and resistivity on control and PU nanocomposites. Conductivity data were collected on PU nanocomposites films of thickness (1.5 mm) to collect real (*Z'*) and imaginary (*Z''*) values from Impedance spectroscopy, as shown in Fig. 1a.

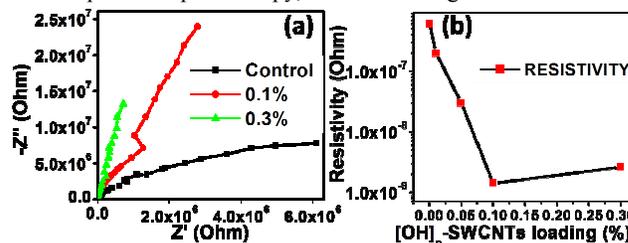


Fig. 1 a) Enhancement of conductivity due to the increase in SWCNTs loadings, b) Conquest of resistivity with increase in loading of SWCNTs.

PU nanocomposites films (0.3 and 0.1 wt. % of [OH]_n-SWCNTs) exhibit the enhanced conductivity (0.3 wt. % : $\sigma = 6.35 \times 10^{-4}$ S cm⁻¹, 0.1 wt. % : $\sigma = 2.37 \times 10^{-5}$ S cm⁻¹), as compared to the conductivity of the control PU film ($\sigma = 2.98 \times 10^{-6}$ S cm⁻¹), conductivity values are increased by one order gradually among

these three samples, control and PU nanocomposites (0.1 and 0.3 wt. % loadings). Conductivity values reported with current work are higher than PU nanocomposites with 2 wt. % of SWCNTs from another report.¹⁵

On the other hand, the reduction in resistivity in this case is reported as a plot (wt. % of [OH]_n-SWCNTs vs. resistivity) in Fig. 1b, according to the increase of [OH]_n-SWCNTs. Even if the least quantity (0.01 and 0.05 wt. % of [OH]_n-SWCNTs) of SWCNTs covalently linked into polymer network, the resistivity is reduced from 10⁻⁷ to 10⁻⁸ Ω, and it reduced further from 10⁻⁸ to 10⁻⁹ Ω while the resistivity measured for the PU nanocomposites films with 0.1 and 0.3 wt. %. Both conductivity and resistivity values matches to reveal the enhancement of conductivity, the order of increase in conductivity as well as order of reduction in resistivity on these samples occur due to the incorporation of different loadings of [OH]_n-SWCNTs.¹⁶

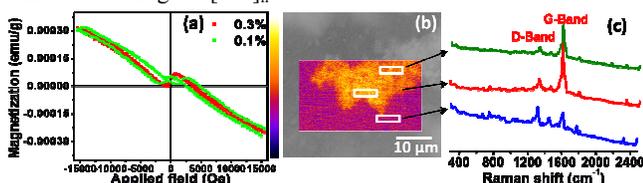


Fig. 2 a) VSM depicts diamagnetism of PU nanocomposites (0.1 and 0.3 wt. %), b) Confocal image probe focused on PU nanocomposites (0.3 wt. %) and c) Raman spectra correspond to three spots on confocal region.

The magnetic study was performed on the basis of anomalous feature noticed during solid state NMR sample preparation, films cut into petite pieces found to attract on magnet. This feature was observed without encapsulation of ferromagnetic metals (Fe, Co or Ni), prompted us to study the magnetic properties of these samples by VSM. In this context, the observed curves profile in Fig. 2a clearly depicts the typical diamagnetic property of SWCNTs.¹⁷ The identical types of curves were noticed for both samples, irrespective of the quantities of SWCNTs loading, increased from 0.1 to 0.3 wt. %. However, the off-centre displacement of magnetization curve is observed in this graph, which indicated the interaction of electrons on PU nanocomposites with the applied field. Conventionally, metals generate flux while subjected to the applied magnetic field.¹⁸ Presumably, there is emergence of flux in these materials occurred due to the presence of trace proportion of metallic carbon nanotubes embedded into the polymer matrix and it may have revealed due to the exposure of interfacial layers between PU matrix and SWCNTs.

The narrow region of PU nanocomposites film has been focused to collect confocal Raman images to view the distribution of SWCNTs under colour contrast, where Raman spectra were collected randomly on three different spots to probe the interaction of SWCNTs with PU network,¹⁹ as shown in Fig. 2b. Raman bands shown in Fig. 2c appear broader and shifted to upfield frequencies, G band around 1594 cm⁻¹ and D band around 1459 cm⁻¹, whereas amides I, II and III bands are at 1778, 1539 and 1535 cm⁻¹, respectively. The shift in frequencies is occurred due to the proper dispersion of SWCNTs and their π-π interaction with PU network.¹⁵ Raman frequencies observed on confocal regions and spectra collected on control and PU nanocomposites also absorbed in same frequencies range, as given in ESI (Fig. S12). D band at 1454 cm⁻¹ and G band at 1589 cm⁻¹, whereas N-

H stretch of amide I (1776 cm⁻¹), amide II (weak, 1538 cm⁻¹) and amide III (strong, 1323 cm⁻¹) with respect to amide link of urethane and aromatic moiety of TDI is seen at 1619 cm⁻¹.

ATR-IR spectra of control and PU nanocomposites samples supported the existence of urethane link¹⁰, axial stretching vibration of -NH is noticed at 3352 cm⁻¹ and C=O frequency at 1710 cm⁻¹. The C-H symmetric stretching vibrations of methyl group observed at 2968 cm⁻¹ and strong absorption frequency at 1190 cm⁻¹ arisen due to C-O-C of PPG. Aromatic ring stretch is noticed at 1592 cm⁻¹ and aromatic out of plane bend frequency at 772 cm⁻¹, as shown in Fig. 3a.

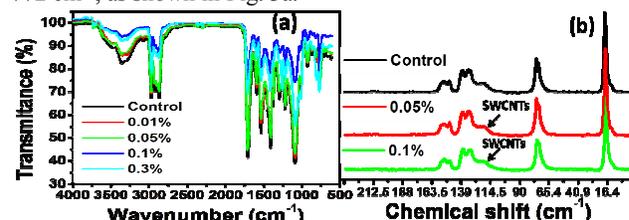


Fig. 3 a) ATR-IR of control and PU-nanocomposites films, b) Solid state ¹³C NMR spectra of control and PU-nanocomposites (0.05 and 0.1 wt. %).

Solid state ¹³C NMR for these samples were collected from Bruker 400 MHz and the set of spectra is shown in Fig. 3b. Control and PU nanocomposites have been inferred from their broad signals urethane bonds²⁰ due to addition of isocyanate to hydroxyl group are shown between 159-148 ppm, peaks in the range of 136-121 ppm are assigned for aromatic carbons of TDI, signal around 76-71 ppm is attributed to the carbon moiety of PPG backbone and the upfield chemical shift, 21-16 ppm is appeared for methyl groups of TDI as well as PPG. All these spectra exhibit identical pattern of peaks except the minor peak at 121 ppm, which is not visible in control film, it corroborates the presence of sp² hybridized carbon centres of [OH]_n-SWCNTs bonded to the polymer nanocomposites.²¹ The chemical structure deduced from ¹³C NMR data matches with the interpretation already done with ATR-IR and Raman spectra.

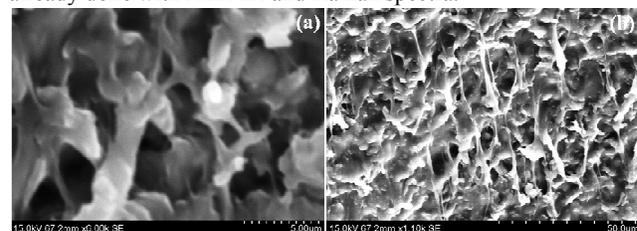


Fig. 4 SEM images of cross-linked view on PU matrix tethered with SWCNTs a) high magnification (6 K) and b) low magnification (1.10 K)

SEM images of the cured film (0.3 wt. %) sputtered with gold have been recorded at acceleration voltage of 15 kV to examine its morphology. Both low and high magnification images collected from SEM are shown in Fig. 4, dark contrast region represents the polymer network, where SWCNTs are entangled uniformly. Likewise, the bright contrast corresponds to SWCNTs, those appear intact and free from agglomeration. The interface between PU matrix and SWCNTs is evidently visible around the entire region on PU nanocomposites.

Thermal characterization by TGA and DSC provides information on improvement of thermal property due to addition of SWCNTs. TGA plot shows onset degradation temperature above 270 °C and peak temperature above 420 °C with respect to degradation of polymeric samples. Even the trace loadings of SWCNTs into PU

matrix enhanced their thermal stability, compared to the peak temperature of control sample (420 °C), peak temperature of PU nanocomposites samples (0.01 wt. %: 436 °C, 0.05 wt. %: 443 °C, 0.1 wt. %: 448 °C and 0.3 wt. %: 451°C) exhibit shift in degradation temperature, as shown in Fig.5a.

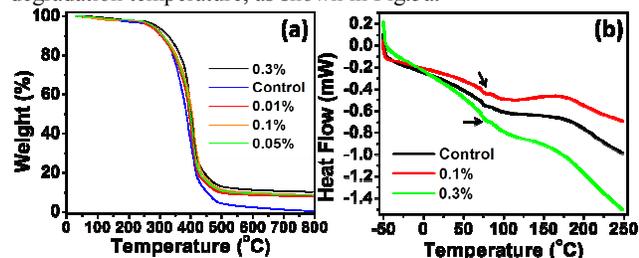


Fig. 5 a) TGA Thermograms obtained for different wt. % of SWCNTs, b) DSC for control and PU nanocomposites (0.1 and 0.3 wt. %).

DSC thermograms obtained for the samples, control and PU nanocomposites with loadings, 0.1 and 0.3 wt. % were compared in Fig. 5b. T_g value for the control film is at 76 °C, whereas the sample containing 0.3 wt. % of SWCNTs is noted at 77 °C and the sample containing 0.1 wt. % of SWCNTs does not show much variation from the control sample.²² DSC profile did not show any melting peak with any of these samples up to 250 °C. Thermal properties illustrated the improvement in thermal conductivity due to the facilitation of heat transport by SWCNTs, which incorporates thermal stability on nanocomposites film, since there is homogeneous dispersion of SWCNTs achieved in polymer matrix.¹⁰

Table 1 Tensile strength of control and PU nanocomposites.

S. No.	Wt. % of SWCNTs	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile strain (mm/mm)	Tensile stress (MPa)
1.	Control	8.5	6.3	136.8	1.36	8.5
2.	0.05	8.9	4.9	182.3	1.82	8.9
3.	0.1	9.3	5.0	184.8	1.83	9.2
4.	0.3	10.4	9.8	104.3	1.06	10.4

Tensile strength was tested²³ for these uniform thickness film samples to investigate their mechanical properties, as shown in Table 1. As compared to the tensile strength of control sample in entry 1, PU nanocomposites in entry 2, 3 and 4 shows gradational improvement in tensile strength with respect to increase in SWCNTs loading.⁹ The highest Young's modulus value is observed for the entry 4 (0.3 wt. % of SWCNTs). Samples in entry 3 and 4 deduced to exhibit improvement in plastic behavior, since the stress-strain curve passes through the strain hardening region, which is above the steady state and critical stress, as shown in ESI (Fig. S13).

In summary, we have developed a facile synthetic route to transform *p*-SWCNTs into $[OH]_n$ -SWCNTs in good yield. PU nanocomposites are formed as films by unique approach, *in situ* addition of $[OH]_n$ -SWCNTs in trace quantities to PU prepolymers with isocyanate group. Covalently attached $[OH]_n$ -SWCNTs on PU prepolymers improved their desired properties due to uniform dispersion, without agglomeration. The upfield shift in Raman spectra envisaged the dispersion and π - π interaction among PU and SWCNTs. Even the sparingly added $[OH]_n$ -SWCNTs attributed to enhance the conductivity of control sample and reduced its resistivity. VSM study redefined the diamagnetic property of $[OH]_n$ -SWCNTs with mild magnetic flux arisen from

the ultrafine fraction of metallic SWCNTs. DSC and TGA profile exhibited the improvement in thermal stability of polyurethane and tensile strength is enhanced according to the increase in SWCNTs, its tensile profile proved to exhibit plastic behaviour.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Materials, synthesis and characterization of $[OH]_n$ -SWCNTs, control PU and nanocomposites films. FTIR, Raman, TGA and DSC of $(OH)_n$ -SWCNTs. TG/DTG, UV-vis DRS, photographs, optical images and tensile profiles of control and PU nanocomposites. See DOI: 10.1039/b000000x/

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