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Syndiotactic Polystyrene / Fullerene Composites: Elucidation of Structural Aspect

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Summary: Syndiotactic polystyrene (sPS), an attractive polymer due to its wide range of application, forms polymer-solvent intercalates with a large variety of solvent molecules ranging from liquids to solids. Recently, it has been realized that sPS intercalate prepared from SPS/naphthalene gel is more promising of making meso-porous materials. Here, the composite of sPS/fullerene have been prepared by taking advantage of sublimation of naphthalene. The different techniques as like XRD, SEM, HRTEM, FT-IR, DSC, TGA etc have been employed to characterized sPS/fullerene composite. XRD investigation shows the presence of δ form sPS in the composite. SEM and HRTEM reveal the fibrillar network with fringe like structure in presence of fullerene only and the average diameter of fibril has increased as compared to pure sPS fibrils. The conductivities of these fibrils have been increased with increasing amount of fullerene.

Keywords: conductivity; fullerenes; nano fiber; polymer-solvent complex; syndiotactic polystyrene

Introduction

In the last decade, syndiotactic polystyrene (sPS) has received considerable attention not only its high melting temperature, fast crystallization rate, low dielectric constant, low specific gravity and good chemical resistance[1] but also its tremendous affinity to form polymer-solvent complex, that is visualized for good technological application, with solvents ranging from liquid from solid at room temperature. In the solid state, sPS, having a very complex polymorphic behaviour, can be described into two crystalline forms, α and β, with all trans conformation with identity period 0.51 nm and two, δ and γ, containing 2_1 helical chain conformation with a identity period of 0.78 nm.[2] Due to the formation of the solvent induced crystalline δ form sPS has a tendency to form polymer-solvent crystallosolvates or chlathrate type compound with a wide range of solvents like benzene,[3] toluene,[4] chloroform,[5] decalin,[6] dichloroethane[7] and even in solid solvent like benzophenone,[8] naphthalene[9] etc. The easy way to form sPS chlathrate has recognized recently to prepare porous material,[10] gas sensors,[11–13] chiro-optical materials.[14]

On the other hand, fullerene (C_{60}) has attracted the great interest because of its high symmetry, novel π-conjugated systems, and unique chemical and physical properties. It has potential applications in hetero-junction solar cell[15] as well as medical sciences.[16] Conventional sublimable solid solvents such as naphthalene, ferrocene and camphor finely dissolve fullerene (C_{60}) in the solution state to form the superstructure.[17] In this contribution, the composite of sPS/fullerene have been

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prepared by taking advantage of sublimation of naphthalene.

Experimental Part

Materials

The syndiotactic polystyrene (sPS) sample was synthesized by using a method devised by Zambelli and co-workers.[18] The content of syndiotactic triads as characterized by ^{13}C- NMR was found to be over 99%. The molecular weight characterization of these samples was performed by SEC in dichlorobenzene at 140 °C and yielded the following values: $M_w = 1.0 \times 10^5$ g/mol with $M_w/M_n = 4.4$ for sPS. Naphthalene was purchased from Sigma-Aldrich and Fullerene (C_{60}, 99.5%) was purchased from Materials and Electrochemical Research Corporation, USA and both were used as received without further purification.

Preparation of Composites

Required amount of sPS, C_{60} and naphthalene (as indicated in Table 1) were taken in hermetically sealed test tube and heated around 120 °C for 10min to homogenize the solution. After cooling it to room temperature all samples were transformed into gel. All the further characterizations were carried out with the dried samples which were prepared by keeping these samples in vacuum at room temperature for one week.

Instrumentation

Thermogravimetric analysis (TGA) of the dried sPS/C_{60} composites were done with TA thermal analysis system at heating rate 10 °C/min under N_2 environment. The FTIR spectra were recorded in an FTIR-8400S instrument (Shimadzu) using the KBr pellets of the dried sPS/C_{60} composites. The differential scanning calorimetry (DSC) of the sPS/C_{60} samples (as-prepared) were made in a Perkin-Elmer Differential Scanning Calorimeter (Diamond DSC-7) with Pyris Software. The samples (~10 mg) were taken in 'volatile sample' pan that were hermetically sealed. The system was heated from 20 to 280 °C at the heating rate 10 °C/min under a nitrogen atmosphere. The sample was then kept at 280 °C for 5 min and cooled to 20 °C at the cooling rate of 5 °C/min and that was kept for 10 min. Then, the samples were again heated to 230 °C at the heating rate 5 °C/min. The enthalpy values were obtained from the peak area using the Pyris software. The weight of the sample was checked after each experiment and instrument was calibrated with indium before each set of experiments. The wide-angle X-ray diffraction (XRD) experiments were performed with the dried sPS/C_{60} composites in a Bruker AXS diffractomer (model D8 Advance) using a Lynx Eye detector. The instrument was operated using CuKα radiation ($\lambda = 1.54$ Å), at 40 kV voltage and at a 40 mA current. The sample was scanned in the range (2θ) 2-40° at the scan rate 1 s/step with a step width of 0.02°.

The thin films of the sPS-C_{60} composite samples on a glass cover slip were dried in vacuum at room temperature and were coated with platinum by sputtering technique under argon atmosphere and observed under FE-SEM (Jeol JSM-6700F) operating at 5 kV in secondary electron mode. The TEM micrographs of the sPS/C_{60} composite samples were made by taking one drop of sol on the carbon coated copper grid and after cooling dried in vacuum at room temperature. The micrographs were taken

Table 1.
Preparation of composites.

Sample ID	sPS wt.(mg)	C60 (mg)	Naphthalene (mg)	% w.r.t sPS (w/w)	% w.r.t C60 (w/w)
sPS-C60-1	95.00	5.00	1000.0	8.6	0.454
sPS-C60-2	90.00	10.00	1000.0	8.18	0.909
sPS-C60-3	80.00	20.00	1000.0	7.27	1.818
sPS-1	100.00	—	1000.0	9.09	—

from a high resolution transmission electron microscope (JEOL, 2010EX) operated at an accelerated voltage of 200 kV. The diameter of fiber was measured using photoshop software and taking average from different spots.

The dc conductivity of the dried sPS/C_{60} composites were measured by a two-probe method using an electrometer (Keithley model - 617). The pellets (thickness ~0.15 mm) of the samples were made by pressing the dried sPS/C_{60} composites. These pellets were then connected to the electrometer through a copper wire using silver paste. The resistance (R) was measured, and the conductivity (σ) was calculated from the equation $\sigma = l/R \times A$ where 'l' is the thickness and 'A' is the cross-sectional area of the pellets.

UV-Vis spectroscopy all samples were studied with Hewlett-Packard UV-Vis spectrophotometer (model 8453). UV-vis spectroscopic analysis was done by dissolving all dried sPS/C_{60} composite samples in toluene solvent along with a known concentration toluene solution of C_{60}. From the absorbance values, the concentration of C_{60} in all dried sPS/C_{60} composite samples were calculated.

Results and Discussion

Thermogravimetric analysis of all dried samples is presented in Figure 1. The pristine $C_{60,}$ it shows only one stage of thermal degradation at around 600 °C and in case of only sPS-1 two stages of thermal degradation are evident. Usually, in all dried sPS/C_{60} composites three distinct stages of thermal degradation are shown. The first degradation around 85–120 °C is for intercalated naphthalene molecules and second is around 350–450 °C due to the degradation of the sPS polymer. The third event, i.e., the higher temperature degradation arises from the degradation of fullerene moieties. With increasing the fullerene weight percentage, the weight loss in fullerene degradation region is increased. From the weight loss of three different degradation regions the weight percent of intercalated naphthalene, sPS and attached C_{60} have been calculated in three sPS-C_{60}/naphthalene samples. It results that 10% (*w/w*) naphthalene is present in all samples and 5, 8 and 10% (*w/w*) fullerene and 85, 82 and 80% (*w/w*) sPS are present in sPS-C_{60}-1, sPS-C_{60}-2 and sPS-C_{60}-3, respectively.

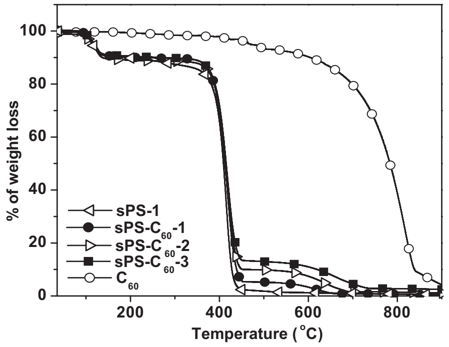

Figure 1.
TGA plots of fullerene, sPS-1 and all dried sPS/C_{60} composites.

To evaluate the (*w/w*) % of fullerene present in the all dried sPS/C_{60} composite samples, we have also done the UV-Vis spectroscopic analysis of toluene solution of all dried sPS/C_{60} composites. The UV-Vis spectroscopic technique reveals that 4.9, 8.1 and 9.6% (*w/w*) fullerene is present in sPS-C_{60}-1, sPS-C_{60}-2 and sPS-C_{60}-3 respectively. These values are close proximity to the values obtained from TGA data.

Typical DSC thermograms of sPS/C_{60} as-prepared samples obtained at 5 °C/min are shown in Figure 2. Two domains can be distinguished; a low-temperature region, typically near 82 °C, where the melting endotherm is related to the only naphthalene, and a high-temperature region dealing with thermal events related to the polymer. The melting temperature of the polymer domain of gel samples are little bit of lower than that of the sPS only (126 °C) under identical experimental condition.[9] All these values of melting temperature and their △H values are given in the Table 2.

Surface morphology of the composite samples was observed by the FE-SEM and

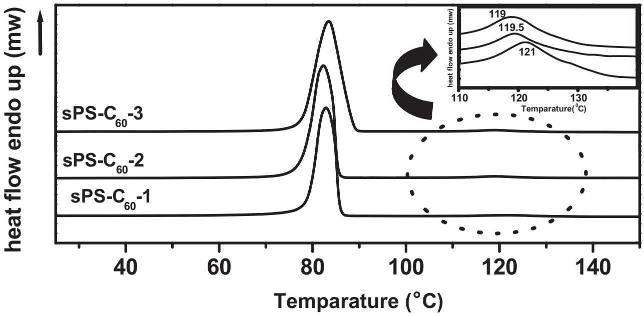

Figure 2.
Typical DSC traces of as-prepared samples in second heating. In the inset the region between 90-140°C are given.

Table 2.
Thermal properties of dried sPS/C_{60} composites.

Samples	T_m for naphthalene (°C)	△H (J/g)	T_m for sPS (°C)	△H (J/g)
sPSC_{60}-1	82.93	115.85	121.34	3.0657
sPSC_{60}-2	82.58	126.77	119.32	3.0206
sPSC_{60}-3	83.09	130.80	119.32	2.8098

TEM image. Morphology observed by FE-SEM reveals a fibrillar network for sPS-1 in dried condition as reported previously.[9] This network type morphology retains in case of all sPS/C_{60} samples (Figure 3). The diameter of the sPS-1 nanofiber is 30 nm and it is increased to 48 nm, 50 nm and 55 nm in sPS-C_{60}-1, sPS-C_{60}-2 and sPS-C_{60}-3 nanofiber respectively. The diameter of the fibre is gradually increased from sPS-C_{60}-1 to sPS-C_{60}-3 with increasing percentage of fullerene in the composite. This increasing is due to the supramolecular attachment of fullerene to the sPS polymer by π-π interaction with benzene group of sPS.

Under HRTEM investigation of sPS-C_{60}-3 sample, it gives the nano fibrillar structure and the crystal lattice fringes are clearly seen as stripes (Figure 4). The diameter of the fringes is determined by Image-J software and it is estimated to be 0.8 nm. These long range ordering crystal fringes are the clear evident for the attachment of fullerene moiety with the polymer chain.

Typical X-ray diffraction pattern of the dried sPS/C_{60} composite systems are shown in Figure 5. Two important reflections at $d = 1.19$, 0.85 nm are for δ form sPS and these values get a little bit of enhancement than our previously reported sPS/naphthalene system.[10] This is due to the anchoring of fullerene unit to the sPS polymer chain. The characteristic eight reflections indexed as the (111), (220), (311), (222), (331), (420), (422) and (511)/(333) are originating from the fcc arrangement of C_{60} (corresponding d values are given in Figure 5). From the diffraction studies, it is evident that C_{60} can easily incorporate within the crystalline lattice of sPS through the π-π interaction between benzene and fullerene.

In FTIR spectroscopy (Figure 6), sPS-1 shows the strong band for 2_1 helical conformations of sPS at 568 cm^{-1} along with the typical polystyrene tacticity band at 1068 cm^{-1} and C=C stretching band at 1446 and 1492 cm^{-1} and aromatic and aliphatic C-H stretching at 3017 and 2923 cm^{-1} respectively. In all three dried sPS/C_{60} composite samples characteristic bands for fullerene are seen at 530, 576 and 1176 cm^{-1}. The bands for C=C stretching reduces to 1490, 1488 and 1486 cm^{-1} in sPS-C_{60}-1, sPS-C_{60}-2 and sPS-C_{60}-3, respec-

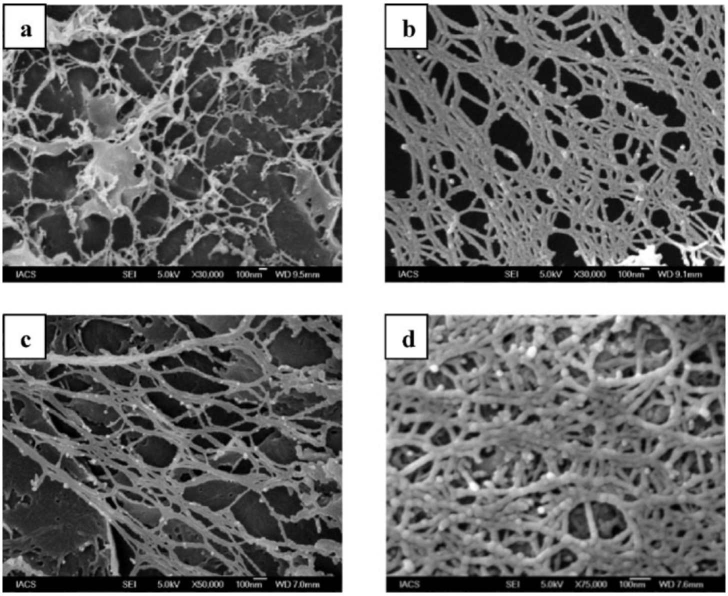

Figure 3.
FE-SEM images of the dried composite samples. (a) sPS-1, (b) sPS-C_{60}-1, (c) sPS-C_{60}-2 and (d) sPS-C_{60}-3.

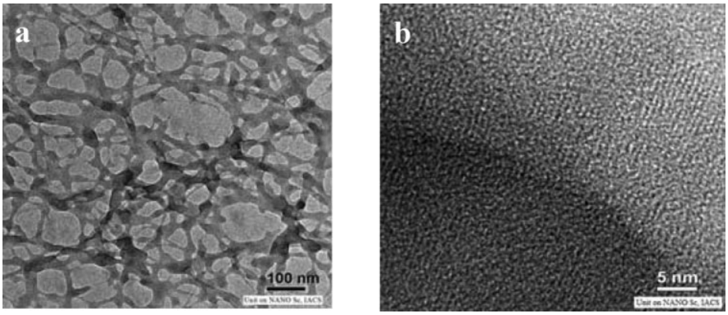

Figure 4.
HR-TEM images of the dried gel sample. (a) sPS-C_{60}-3, (b) Lattice fringe pattern of sPS-C_{60}-3.

tively. This slight reduction of stretching frequency is due to attachment of C_{60} to the benzene group of sPS chain. This statement is strongly supported by the mighty enhancement of aromatic C-H stretching frequency to 3022, 3024 and 3025 cm^{-1} in sPS-C_{60}-1, sPS-C_{60}-2 and sPS-C_{60}-3, respectively. The anchoring of C_{60} to the sPS chain also affects the environment of aliphatic C-H bond which is clearly evident from the reduction of aliphatic C-H stretching frequency in three dried sPS/C_{60} composite samples. For the same reason the frequency of tacticity band of sPS shows a slight reduction in three sPS/C_{60} samples from the original sPS-1 sample (indicated by arrow in Figure 6). In every case the bands at 471 and 746 cm^{-1} are for naphthalene.

The dc conductivity study of all dried composite samples shows a gradual increase of conductivity with increase of fullerene weight percentage in sPS/C_{60} composite samples. The log σ_{dc} vs. *w/w* % of fullerene in all dried gel samples are presented in Figure 7. This enhancement of

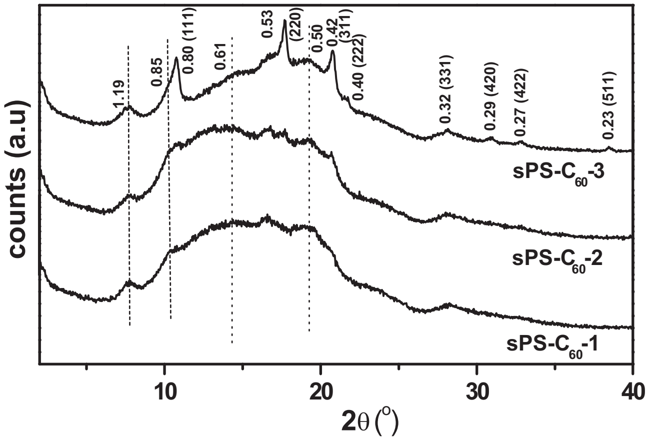

Figure 5.
X-ray diffraction pattern of sPS-C_{60}/naphthalene dried gels. Corresponding reflection planes of C_{60} and all *d* values are given in nm unit.

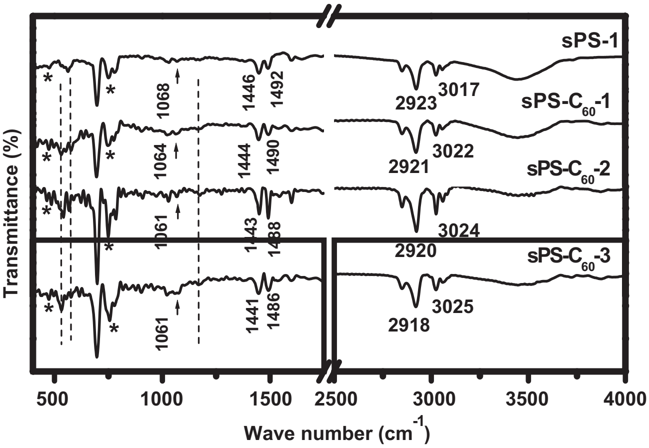

Figure 6.
FTIR spectroscopy of sPS and dried sPS/C_{60} composite. Dotted lines show the bands for fullerene and (*) for the strong naphthalene band.

the electronic property of sPS polymer chain is attributed to the anchoring of conducting fullerene unit by π-π interaction with the benzene of sPS chain. This is clear evidence of entrapment of fullerene between two successive benzenes is sPS chain.

Conclusion

Syndiotactic polystyrene-C_{60} composites are prepared by utilizing the concept of polymer-solvent complex. The composites are characterized successfully with help TGA, FT-IR and diffraction studies. XRD and FTIR studies indicate not only the formation of 2_1 helix of sPS in the composite but also anchoring of fullerene by π-π interaction between benzene moiety of sPS and fullerene. The morphology of composites as investigated by FESEM and TEM is fibrillar in nature and the fibrillar diameter increases with increasing concentration of C_{60}. The attachment of fullerene

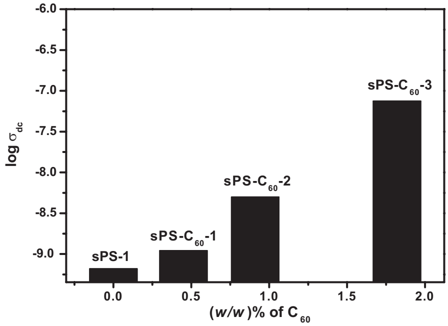

Figure 7.
log σ_{dc} vs. initial (*w/w*) % of fullerene histogram in all dried composite samples.

affects on the thermodynamic and electronic properties of the polymer. Polymer conductivity is increased with gradual increase of fullerene.

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