

## Effect of Fullerene ( $C_{60}$ ) on Vibrational Spectra, Hydrodynamic Diameter, Zeta Potential and Microstructures of $C_{60}$ /Poly(vinyl pyrrolidone) Nanofluids in Aqueous Medium

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In this article, we discussed the effect of fullerene ( $C_{60}$ ) content on the optical, electrokinetic and microstructural properties of poly(vinyl pyrrolidone)  $C_{60}$ :PVP nanofluids in water. Vibrational spectra reveal a charge transfer type interaction that exists between poly(vinyl pyrrolidone) and  $C_{60}$  results in an enhancement in vibrational band intensity in some of the selective bands of poly(vinyl pyrrolidone) molecule. Photoluminescence spectra show a decrease in the light intensity of poly(vinyl pyrrolidone) upon addition of  $C_{60}$  due to donor-acceptor type interaction. Dynamic light scattering study show that the hydrodynamic diameter of  $C_{60}$  assemblies varies non-linearly with  $C_{60}$  content. Polydispersity index values evident a well dispersed structures of  $C_{60}$  assemblies with poly(vinyl pyrrolidone) in water. Both zeta potential and surface conductivity values are also varies nonlinearly with  $C_{60}$  content in the nanofluids. Micrographs in  $C_{60}$ :PVP nanofluids shows well ordered self assembled nanostructures.

**Keywords:** Fullerene, Poly(vinyl pyrrolidone), Nanofluids, Dynamic light scattering, Zeta potential, Surface conductivity.

### INTRODUCTION

Development of functional nanostructures in one, two, and three dimensions *via* self-assembly is governed by both particle-particle and particle-substrate or particle-template interactions. Nanoparticles containing micro and nanoporous structure of well connectivity are of practical applications in various field like catalysis, drug delivery, sensors, pigments and optics [1-5]. In these days, lot of research work is going on the polymer assisted self-assembly of nanoparticles of controlled shape and size *via* solution phase synthetic route. Polymer mediated self-assembly is reported to result in highly controlled assembly of nanoparticles of desired thickness and dimensions required for many applications. In this regard, various functional polymers such as poly(vinyl pyrrolidone), poly(ethylenimine), poly(ethylene glycol), polystyrene, *etc.* are used not only as encapsulant for the nanoparticles but also helps in layer-by-layer self-assembling process. It is reported that polymer assisted self assemblies retain the optoelectronic properties of nanoparticles [5-10].

Among the various nanomaterials, carbon nanoparticles like fullerene ( $C_{60}$ ) found to undergo self-assembling process

using non-covalent interaction to form supramolecular architectures useful for optoelectronic applications [6-13].  $C_{60}$  is considered as one of the most studied carbon nanoparticles owing to its excellent chemical, optical and optoelectronic characteristics. Owing to execution of low reorganization energy, accelerated forward and decelerated backward electron transfer process and excellent charge carrier mobility, this spherical nanostructure is gathering much attention in developing numerous next generation electronic devices [6-10]. In this regard, various techniques such as liquid-liquid interfacial precipitation, template assisted dip and drop drying processes, *etc.* are used in developing self-assembled  $C_{60}$  nanostructures of various dimensions and thickness [6-9]. In present study, we report on the effect of fullerene ( $C_{60}$ ) content on the optical and electro-kinetic parameters of poly(vinyl pyrrolidone) in correlation to microstructures of  $C_{60}$ :PVP nanofluids.

### EXPERIMENTAL

Both raw materials *i.e.*, fullerene ( $C_{60}$ ) and poly(vinyl pyrrolidone) used in synthesis of nanofluids were purchased from Alfa-Aeser and used as such without any chemical modifi-

cation. For spectral analyses, Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Corporation, Model NEXUS-870) in attenuated total reflectance mode to study the vibrational spectra of synthesized nanofluids. Zeta potential ( $\xi$ ), surface conductivity ( $\sigma_{sc}$ ), hydrodynamic diameter ( $L_{hd}$ ) and polydispersity index (PDI) was measured using Malvern apparatus. A scanning electron microscope (SEM) of Oxford model Leo1550 was used to study size and shape of nanocrystals in the composite films.

**General procedure:** At first we prepared (a) poly(vinyl pyrrolidone) solution of 1.1 M concentration and (b) fullerene (C<sub>60</sub>) solution of 1.39 mM concentration which were named as sample-1 (S-1) and sample-2 (S-2), respectively. Then we added different volumes of S-1 to five different batches of S-2 in order to prepare five nanofluids. In order to prepare nanofluids, the mixture solutions were stirred using magnetic stirrer at room temperature and then sonicated at 50 °C for 20 min. The frequency of sonicator was fixed at 20 kHz and power at 250 W. Then nanofluids were kept in vacuum oven maintained at 3 kPa pressure. The temperature was maintained at 110 °C for a period of ~10 h. Thus, nanocomposite films of PVP-coated C<sub>60</sub> were obtained. The nanofluids were obtained by adding deionized water to PVP-surface modified films and then sonicated at 50 °C for 15 min.

## RESULTS AND DISCUSSION

**Vibrational study of C<sub>60</sub>:PVP NFs:** The vibrational spectra of C<sub>60</sub>:PVP nanofluids consisting of (a) 0, (b) 2, (c) 4, (d) 10, (e) 20, and (f) 30  $\mu$ M C<sub>60</sub> were studied in water to have an idea about how the incorporation of C<sub>60</sub> alters the spectra of poly(vinyl pyrrolidone). The results shows some interaction occurs with C<sub>60</sub> molecule *via* reactive C=O moieties of PVP molecules. As it is seen from the spectra in Fig. 1 that C<sub>60</sub> induces a marked change in the phonon bands in the local vibrations in pyrrolidone groups of PVP molecules, indicated that it promptly interacts with PVP in C<sub>60</sub>:PVP complex. The interaction is minimum owing to steric considerations [10-15]. For illustration,  $\nu$ (C=O) stretching at 1645 cm<sup>-1</sup>,  $\nu$ (C-N)

stretchings at 1497 and 1295 cm<sup>-1</sup>,  $\nu$ (C-H<sub>2</sub>) bending at 1466, 1449, 1433, and 1321 cm<sup>-1</sup>, and C-H in-plane bending at 1372 cm<sup>-1</sup> vibration bands in pyrrolidone ring of PVP molecules have perceived considerably enhanced intensities in the presence of C<sub>60</sub> molecules. As it is evident with dramatically promoted band intensities, both C-N and C=O sites of >N-C=O moieties of PVP share maximum interactions with C<sub>60</sub> molecules.

A maximum red-shift as much as 8 cm<sup>-1</sup> incurs from a  $\nu$ (C=O) stretching at 1645 cm<sup>-1</sup> in a virgin sample to 1637 cm<sup>-1</sup> in the complex. The other vibrations hardly shift by 1-3 cm<sup>-1</sup>. The variation in the integrated band intensity ( $I_{int}$ , value) of C=O stretching band of PVP molecules against C<sub>60</sub> content in C<sub>60</sub>:PVP nanofluids prepared in water was also studied. From Fig. 1b, it is seen that  $I_{int}$ , value acquires a maximum value at a critical dosage  $C_{p1} = 10.1 \mu$ M C<sub>60</sub> due to percolation effect [15].

**DLS and zeta potential of C<sub>60</sub>:PVP nanofluids:** The DLS spectra of C<sub>60</sub>:PVP nanofluids prepared in an aqueous medium. A single DLS band is shown in a bare PVP solution also in water (Fig. 2). When as small C<sub>60</sub> dosage as 2.0  $\mu$ M is added to PVP solution, the DLS band has splits into two well-separated bands in two effective  $L_{hd}$  values (15.6 and 258.3 nm). The first Band-1, which is reasonably broad (FWHM ~305 nm), attributes to primarily bare PVP molecules dispersed in a solution in water. The band-2, which is reasonably sharper (FWHM ~20.3 nm), arises in PVP-surface modified C<sub>60</sub> rearranged in joint assemblies. As a matter of fact, it results in a manifested intensity near 16 nm along with a satellite band (band-3 as it is marked with an arrow) emerged at a reasonably smaller  $L_{hd} = 8.2$  nm value. This band-3 is well resolved in the subsequent samples of reasonably C<sub>60</sub> larger dosages and arises from the C<sub>60</sub> core embedded in PVP in small clusters [14,15].

As given in Table-1, an average  $L_{hd}$  value 24 nm is estimated from the total band profile, with a PDI 0.544, in a 2  $\mu$ M C<sub>60</sub> doped PVP of 40.0 g/L in water. Such a moderate  $L_{hd}$  value signifies that PVP grafts over C<sub>60</sub> of small entities dispersed in water. When C<sub>60</sub> content is increased to as large as 30.0  $\mu$ M in a sample f (Fig. 2), three DLS bands are displaced well-separated apart in three different  $L_{hd}$  values 472, 25 and 6.5 nm, with a

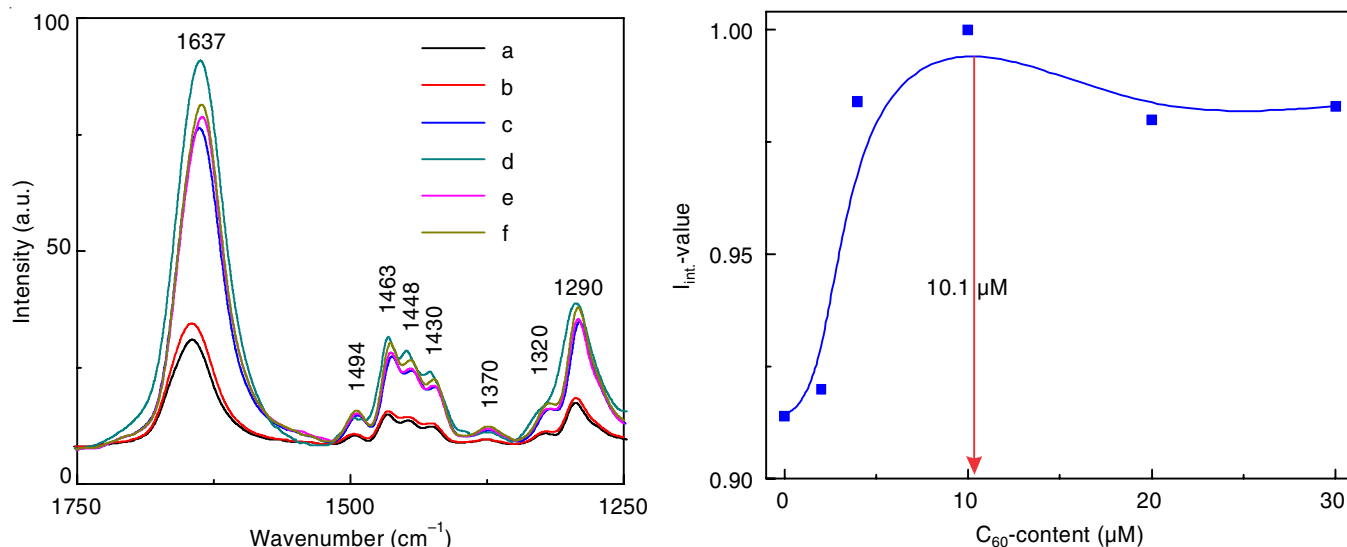


Fig. 1. (a) FTIR bands in C<sub>60</sub>:PVP nanofluids consisting of (a) 0, (b) 2, (c) 4, (d) 10, (e) 20, and (f) 30  $\mu$ M C<sub>60</sub> with 40.0 g/L PVP in water and (b) The variation of  $I_{int}$ -value in the C=O stretching band with C<sub>60</sub>-content in the grafted C<sub>60</sub>:PVP nanofluids in water

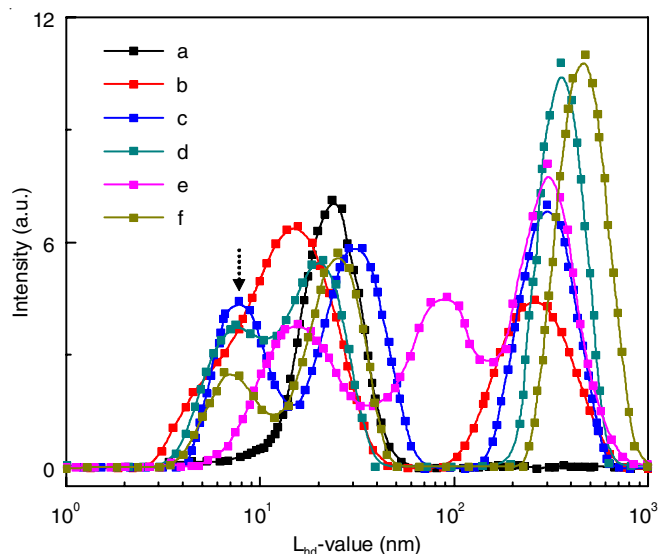


Fig. 2. Distribution of  $L_{hd}$ -values in  $C_{60}$ :PVP nanofluids consisting of (a) 0, (b) 2, (c) 4, (d) 10, (e) 20, and (f) 30  $\mu M$   $C_{60}$  NPs in 40.0 g/L PVP in water

TABLE-1 VALUES FOR $L_{hd}$ , PDI, $\xi$ , AND $\sigma_{sc}$ DETERMINED IN $C_{60}$ :PVP NANOFLUIDS FROM DLS AND ZETA POTENTIAL IN WATER				
$C_{60}$ -content ( $\mu M$ )	$L_{hd}$ -value (nm)	PDI-value	$\xi$ -value (mV)	$\sigma_{sc}$ -value (mS/cm)
0	20	0.271	(-) 7.10	0.043
2	24	0.544	(-) 18.0	0.150
4	67	0.463	(-) 18.8	0.183
10	178	0.296	(-) 21.4	0.230
20	151	0.476	(-) 11.4	0.192
30	182	0.506	(-) 8.30	0.064

pretty large average  $L_{hd}$  value 181.5 nm and a large PDI 0.506 as well. The prominent first band-1, which is attributed to PVP encapsulated  $C_{60}$  clusters, revealed an intense band. The other two bands (band-2 and band-3) which share 51 and 22 % peak intensity of the first band could arise in PVP molecules dispersed in a solution and those which bridge a surface-interface on

$C_{60}$  nanosurfaces, respectively. It is quite possible that both the interface and the  $C_{60}$  core scale over the same size. In this case, they could appear in same band-3. In a case, a relative PVP-content is not so large it cannot form a thick PVP layer over  $C_{60}$  in core-shell particles and it would not appear in such a large  $L_{hd}$  value. The  $L_{hd}$  values span over a wide spectrum 20-182 nm with PDI indices extending over 0.271 to 0.506 in the  $C_{60}$ :PVP nanofluids prepared in water. These results brief an effectively wider distribution of flocculates as compared to those of prepared in *n*-butanol [14]. As expected, a difference arises primarily due to stronger interaction with water molecules than those in *n*-butanol.

The variations in hydrodynamic diameter ( $L_{hd}$ ) and poly-dispersity index (PDI) values with  $C_{60}$  content in the  $C_{60}$ :PVP nanofluids in water were also studied. As the results are shown in Fig. 3, both these parameters vary non-linearly with  $C_{60}$  content over the region covered in this experiment. By increasing the  $C_{60}$  content, the  $L_{hd}$  value varies through a maxima at a specific 12.0  $\mu M$   $C_{60}$  content as a result of percolation effect in a cross-linked structure. In contrast, the PDI-value displays a minima near 10.7  $\mu M$   $C_{60}$ , which demonstrates that  $C_{60}$  rearranges with PVP in a narrow size distribution.

To understand the nature of the charge-types accumulated onto the  $C_{60}$  nanosurfaces and in developing the formalism of the long term stability of the  $C_{60}$ :PVP NFs we prepared in water, we studied the zeta potential ( $\xi$ -value) distributions in the  $C_{60}$ :PVP NFs which consist of selective dosages of (a) 0, (b) 2, (c) 4, (d) 10, (e) 20 and (f) 30  $\mu M$   $C_{60}$  in a fixed 40.0 g/L value of PVP dissolved in water. As can be seen from the results compared in Fig. 4 for the different samples, a bare PVP solution without having any  $C_{60}$  inclusion exhibits only a single zeta band (FWHM  $\sim 9$  mV) at an average  $\xi$ -value (-) 7.1 mV with  $\sigma_{sc}$ -value 0.043 mS/cm in sample (a).

Upon addition of a merely 2.0  $\mu M$  of  $C_{60}$  molecules to this sample, a relatively broader band (FWHM  $\sim 11$  mV) appears at a manifested average  $\xi$ -value (-) 18.0 mV along with a significantly enhanced  $\sigma_{sc}$ -value 0.15 mS/cm. Such a large  $\xi$ -value can arise if and only if small  $C_{60}$  clusters retain on association to the PVP molecules in this sample consistent with a marginally increased  $L_{hd} = 24$  nm in the DLS spectrum described

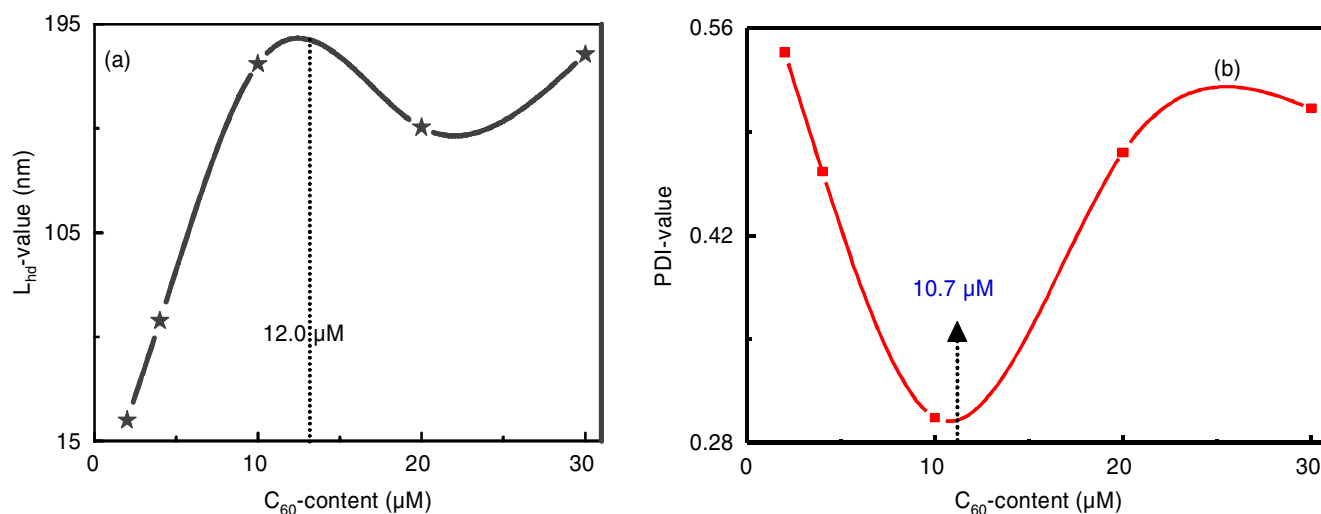


Fig. 3. Variations in (a) average  $L_{hd}$ -value and (b) PDI-index in PVP surface modified  $C_{60}$  clusters with  $C_{60}$ -content in the  $C_{60}$ :PVP nanofluids in water

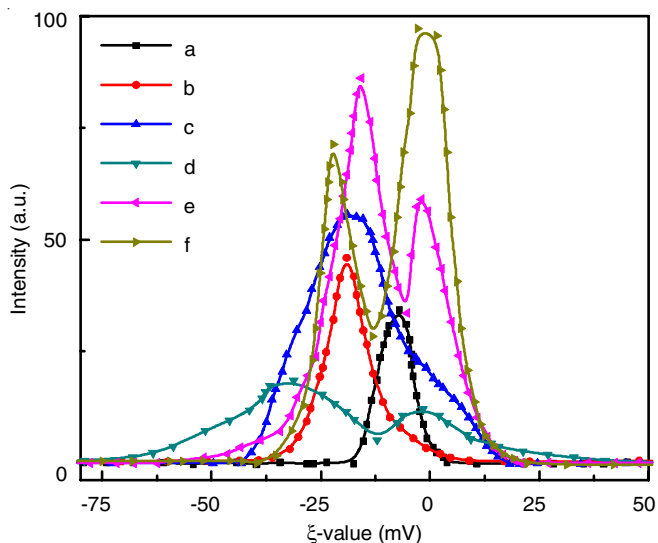


Fig. 4. Distribution of  $\xi$ -values in C<sub>60</sub>:PVP NFs consisting of (a) 0, (b) 2, (c) 4, (d) 10, (e) 20, and (f) 30  $\mu\text{M}$  C<sub>60</sub> molecules in water

above. The C<sub>60</sub> nanosurfaces in such small C<sub>60</sub> clusters adsorb concomitantly large numbers of reactive PVP molecules over them to give rise an enhanced number of  $n$ -electrons from the C=O and C–N moieties of a surface PVP layer which renders an electron transfer to the C<sub>60</sub> in joint C<sub>60</sub>-PVP assemblies [10,14,15].

A significantly large doping such as 30  $\mu\text{M}$  C<sub>60</sub> of a polymer solution of 40 g/L PVP in water in sample (f) gives rise to a zeta distribution of two well-separated bands at (-) 2.21 and (-) 21.3 mV. The first  $\xi$ -band is prominent of sharing about 67 % integrated intensity in the two bands. Eventually, primarily the C<sub>60</sub> molecules which are encapsulated in PVP molecules in a stable surface layer exhibit this band. The other  $\xi$ -band ascribes to PVP molecules which are merely dispersed *via* solvent H<sub>2</sub>O molecules in the C<sub>60</sub>:PVP nanofluids. According to it, an average  $\xi$ -value (-) 8.3 mV is estimated from the observed  $\xi$ -band profile, with a pretty decreased  $\sigma_{\text{sc}} = 0.064$  mS/cm value on the flocculates are grown-up largely to  $L_{\text{hd}} = 182$  nm. Such large C<sub>60</sub> clusters developed in this sample are

the major source of performing a reasonably small  $\xi$ -value and a small  $\sigma_{\text{sc}}$  as well. Expectedly, such large C<sub>60</sub> clusters adsorb proportionately smaller number of PVP molecules over them in the form of a C<sub>60</sub>-PVP complex, which give rise to a merely surface limited PVP  $\rightarrow$  C<sub>60</sub>  $n$ -electron transfer over the C<sub>60</sub> surfaces in a core-shell C<sub>60</sub>:PVP structure. In general, a water medium is shown of promoting the  $\xi$ -value in these C<sub>60</sub>:PVP nanofluids by 20-50 % in comparison to those shown in  $n$ -butanol, especially over effectively small  $\leq 10$   $\mu\text{M}$  C<sub>60</sub> dosages. No much difference is observed over larger C<sub>60</sub> dosages, which are not so effective in controlling an average  $L_{\text{hd}}$ -value in an aqueous medium grafted with polymer PVP molecules. The aqueous NFs offer nearly two times larger  $\sigma_{\text{sc}}$ -values than those made in an organic solvent such as  $n$ -butanol [14]. Furthermore, we also studied variations in the  $\xi$  and  $\sigma_{\text{sc}}$ -values in the C<sub>60</sub>:PVP NFs in water as a function with C<sub>60</sub>-content. As it is illustrated with the plots (Fig. 5), both these parameters show two distinct peaks, one at 3  $\mu\text{M}$  C<sub>60</sub> and other at 11  $\mu\text{M}$  C<sub>60</sub>. A maximum  $\xi$ -value acquired at 11  $\mu\text{M}$  C<sub>60</sub> results from adsorption of relatively large number of PVP molecules on the C<sub>60</sub> nanosurfaces *via* the  $n$ -electron rich C=O and C–N moieties (PVP) of a surface layer. As given in Table-1, relatively smaller  $\xi$  and  $\sigma_{\text{sc}}$ -values perceived in the samples (e) and (f) in comparison to a sample (d) is attributed to a reasonably decreased value of the PVP to C<sub>60</sub> molar ratio.

**Microstructures in C<sub>60</sub>-PVP NFs:** Typical FESEM images in Fig. 6(a,b) taken from the NFs consisting of 10 and 20  $\mu\text{M}$  C<sub>60</sub> doping in 40.0 g/L PVP clearly reveals that PVP assisting C<sub>60</sub> NPs in assembling in strips or bars form. The thickness of bars/strips lies in the range 10-20 nm. An increased C<sub>60</sub>-content such as 20  $\mu\text{M}$  has promoted self-assembling but results in C<sub>60</sub>-PVP sheets of relatively larger thickness owing to lowering in PVP:C<sub>60</sub> molar:ratio. FEM images shows that C<sub>60</sub> NPs are cross-linked to each other *via* PVP and results in formation of nano-bars/strips of various thickness.

## Conclusion

Introduction of C<sub>60</sub> into PVP polymer alters the vibrational band (both position & intensity), hydrodynamic length, PDI,

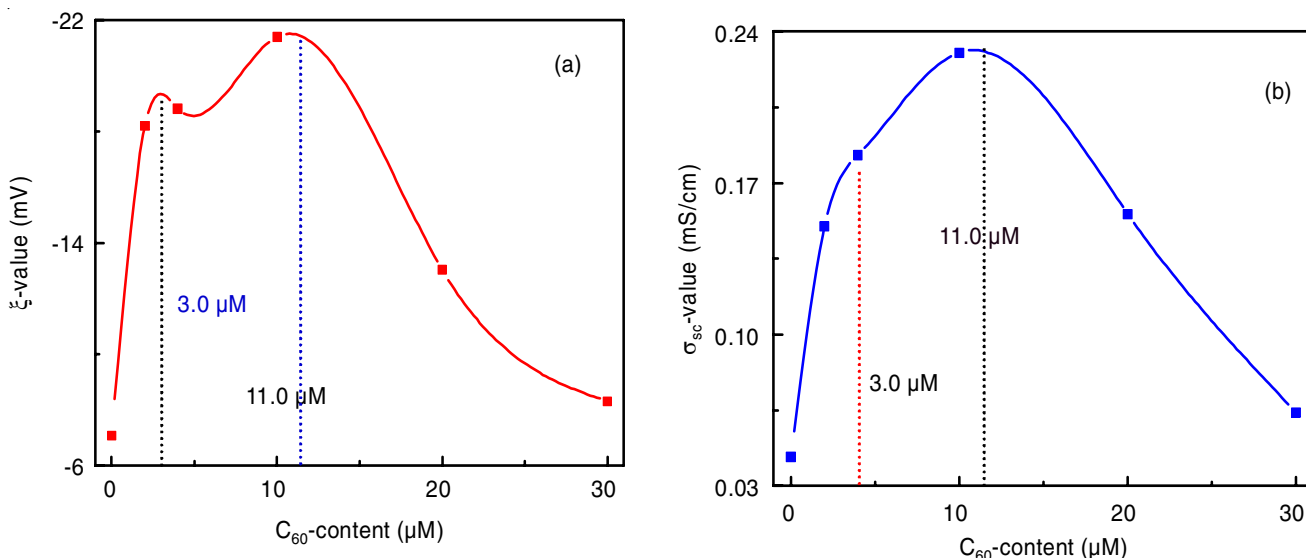


Fig. 5. Variations in (a)  $\xi$ -value and (b)  $\sigma_{\text{sc}}$ -value with the C<sub>60</sub>-content in the C<sub>60</sub>:PVP NFs in water, with a fixed 40 g/L PVP in all the samples

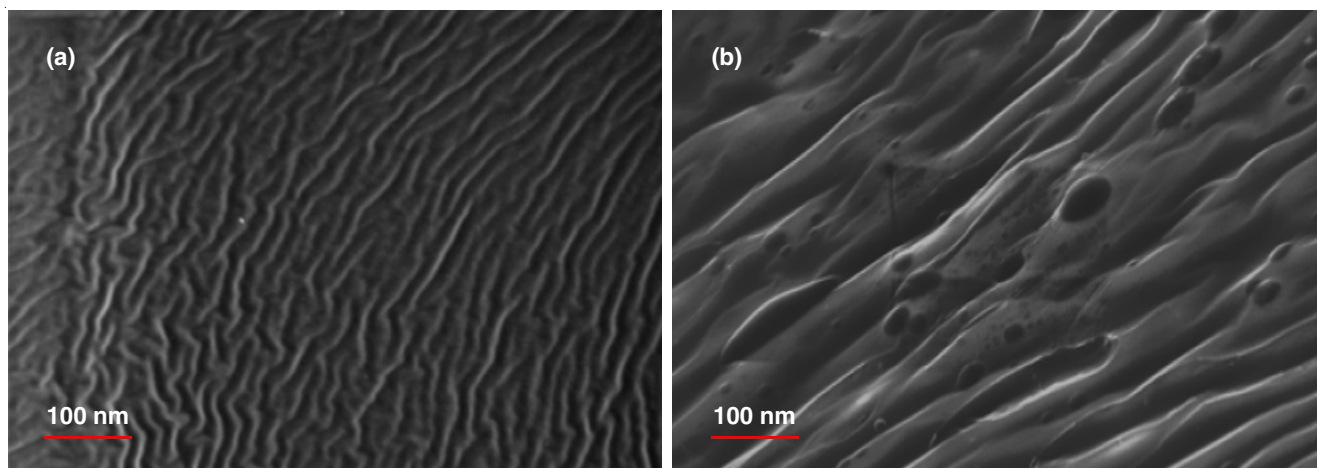


Fig. 6. SEM micrographs of  $C_{60}$ :PVP NFs consisting of (a) 10 and (b) 20  $\mu M$   $C_{60}$

zeta potential of the host material. Shift in the position of  $>C=O$  band of PVP in presence of  $C_{60}$  confirms the interaction between them. Negative zeta potential results from accumulation of non-bonding electrons of PVP on the surface of  $C_{60}$ . Micrographs suggests assembling of  $C_{60}$  in bar or strip form *via* PVP molecule.

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#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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