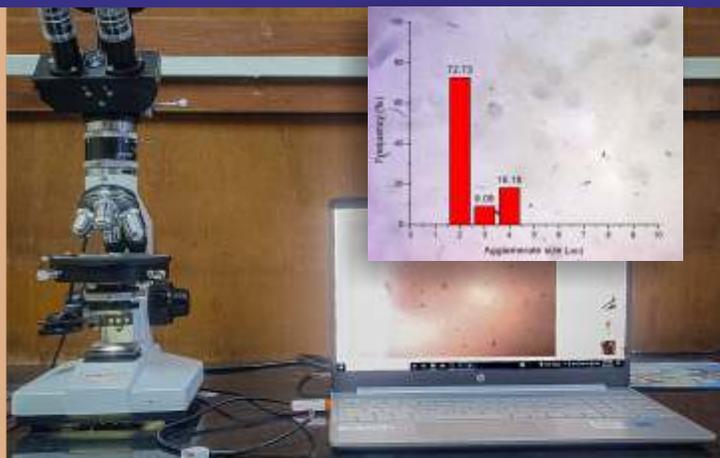


Dispersion Studies of Single Wall Carbon Nanotubes in Polyacrylonitrile



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Abstract

With the increasing demand for advanced materials in the world, carbon nanotubes (CNT) have always been the first choice for material properties enhancement but their uniform dispersion is a big challenge for obtaining desired results in various applications. The recent developments of CNT and Polyacrylonitrile composite show that they not only act as a good reinforcing agent but also as property enhancers of carbon fibres produced from it. However, agglomerate size and dispersion of CNT play an important role in resultant carbon fibres, since big agglomerate size results in a defect in fibre. In this research work, we are reporting the dispersion of ultrasonicated single wall carbon nanotubes in polyacrylonitrile dope solution by mechanical stirring. Significant improvement in the properties of polyacrylonitrile was obtained due to the effective dispersion of single carbon nanotubes which were characterized by optical microscopy, Brookfield viscosity measurement, and solvent resistance test.

Key Words:

Polyacrylonitrile, Single walled carbon nanotubes, microscopy, nano-composite, CNT dispersion.

1. Introduction

Carbon nanotubes (CNT) are one of the best reinforcing agents used for making high end products. It is well known that CNT also acts as a nucleating agent for polymer crystallization [1]. This behavior has been observed with many polymers like Polypropylene, Polyethylene, Nylon, Polyacrylonitrile (PAN), etc., [1-4]. Being a precursor for carbon fibre production, PAN has significant importance than the other polymer nano-composite. CNT in PAN matrix not only acts as a nucleating agent but also behaves like the template to form a graphitic structure at the carbonization stage [5].

The addition of multiwall carbon nanotubes (MWCNT) and single wall carbon nanotubes (SWCNT) in PAN has been reported by several research groups. Though the dispersion of MWCNT is better than SWCNT resultant performance of SWCNT reinforced showed better performance than MWCNT, because of its low diameter of few nano-meter and greater surface area [6]. This increases the effective number of CNT present along the axis of carbon fibre which affects the carbon fibre modulus and tensile strength. The presence of more CNT oriented along the direction of the fibre axis results in better mechanical properties of the resultant carbon fibre which is greatly related to the dispersion of the CNT in

the PAN matrix. Better dispersion of CNT in PAN not only gives them a more effective number of CNT along the carbon fibre axis but also gives more surface area to PAN polymer chains for nucleation and increase in strength.

Though the addition of a single wall carbon nanotube in the PAN matrix has many benefits but finding a suitable solvent for both is a very tough task. PAN being polar and SWCNT being non-polar, complete dispersion of SWCNT is always a challenge in any PAN dissolving solvents [7]. Arias-Monje et al, reported 2-3 times better mechanical strength in 15wt% CNT reinforced carbon fibre than virgin PAN carbon fibre [8]. Loading of that high amount of CNT had surely made the carbon fibre stronger but limited its use for industrial application.

For industrial application purposes, similar strength is required for low CNT loading as low as 1wt% which will make it high-performance carbon fibre. The same can be achieved by functionalizing the CNT which will provide better dispersion of nanotubes in the PAN matrix [9]. Quan et al, has investigated the dispersion of amine-functionalized CNT in PAN matrix against the virgin CNT [10]. Due to amine-functionalization, surface cohesion energy of nanotubes was greatly reduced which allowed better dispersion and interaction of CNT with PAN polymer chains but its effect on resultant carbon fibre is still unknown.

Since, producing carbon fibre from PAN involves various reactions like oxidation, cyclization, dehydrogenation and finally, carbonization and effect of functionalization is still undiscovered in these processes.

In this study, we proposed a combination of ultrasonication and mechanical stirring for dispersion of SWCNT in PAN matrix where Dimethyl acetamide (DMAc) was used as a common solvent. Dispersion of SWCNT in PAN is characterized by Optical microscopy, Brookfield viscosity, Opaqueness of PAN/SWNT composite films, and Solvent resistance test.

2. Experimental:

2.1 Material

Polyacrylonitrile was procured from Technorbital Advance Materials Pvt Ltd of molecular weight 116000g/mol. SWCNT was procured from AdnanoTechnologies Pvt Ltd with a purity of 99%. Dimethyl Acetamide was procured from Venus Trading Corporation, of commercial grade.

2.2 The procedure of making PAN-SWNT composite

Stock solution preparation of PAN in DMAc:

Before proceeding with solution making, PAN polymer was dried in a vacuum oven @ 50°C overnight to remove residual moisture content. The solutions of PAN in DMAc in the concentration of 15wt% were prepared by dissolving 225g of dried PAN in 1000 ml of DMAc respectively. All solutions were prepared under a hot bath by maintaining 55±2°C bath temperature and mechanical stirring at 500 rpm. Mixing was done until PAN was completely dissolved.

SWCNT stock solution preparation:

Concerning PAN concentration suitable amount of SWCNT was added to 50 ml DMAc to obtain 0.1 wt%, 0.2 wt%, 0.5wt%, and 1wt% PAN/SWCNT composite solution. After the addition of SWCNTs in DMAc in the respective amount, it is subjected to ultrasonication for 4 hours.

PAN-SWCNT composite preparation:

Respective composite solutions were prepared by mixing the PAN solution and SWCNTs solution in a mechanical stirrer

@ 3000rpm for 6 hours and samples from each composite sample were drawn after every 2 hours of mixing time for Optical microscopy.

3. Characterization

3.1 Optical Microscopy:

Optical microscopy was done with an Almicro optical microscope (model P12). Samples for microscopy were drawn at the interval of 2 hours sonication, 4 hours sonication, 2 hours shear mixing, 4 hours shear mixing, and 6 hours shear mixing respectively. The analysis of agglomerate size was done by Biohazard v4.0 software (Microscope software) for calculation.

3.3 Brookfield Viscosity:

Brookfield viscosity of all samples was measured with BrookfieldSynchro-Lectric Viscometer (ModelLVF), made by Brookfield engineering laboratories Inc, Stoughton, Massachusetts at the speed of 3-30 rpm with spindle numbers 3 and 4 at 35°C.

4. Result and discussion:

4.1 Optical microscopy

Ultrasonication is a very effective and powerful tool in breaking the SWCNT agglomerate size but uniform dispersion with only sonication is very difficult to obtain. Employing the combined technique for agglomerate size reduction and dispersion was effectively achieved with sonication and shear mixing. The vibration produced during sonication of SWCNT in DMAc decreases the cohesion energy between SWCNT agglomerates gradually but complete dispersion with sonication alone will take a very long time. The SWCNT dispersion will remain stable under the influence of sonication only, on the removal of vibration energy from sonication these SWCNT will again tend to combine and form agglomerates. Thus, shear mixing of the SWCNT/DMAc in PAN/DMAc dope solution allowed PAN polymer chains to penetrate in the sites of SWCNT agglomerate which were opened by sonication. The drastic reduction in the agglomerate size just after 2 hr of shear mixing gives evidence the PAN polymer chains are very effective in dispersing and keeping the SWCNT stable in the composite solution. Figure 1a)-1d), represents the Optical microscopy images of PAN/SWCNT solution at various stages.

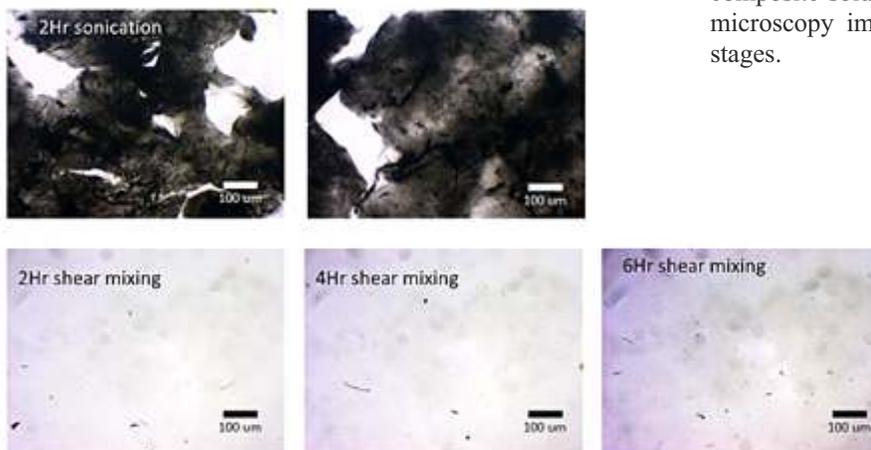


Figure 1a) Optical images of 0.1wt% SWCNT in PAN at various stages

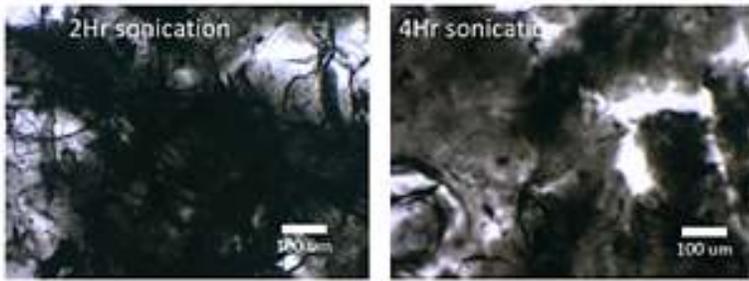


Figure 1b) Optical images of 0.2wt% SWCNT in PAN at various stages

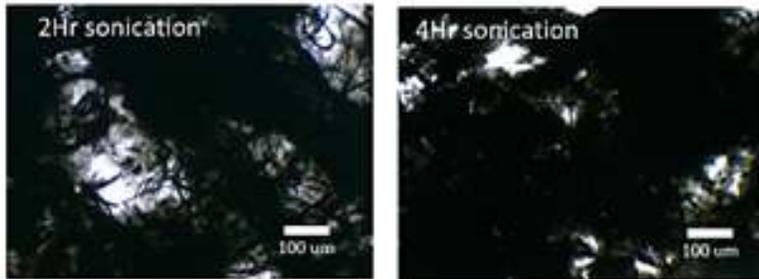
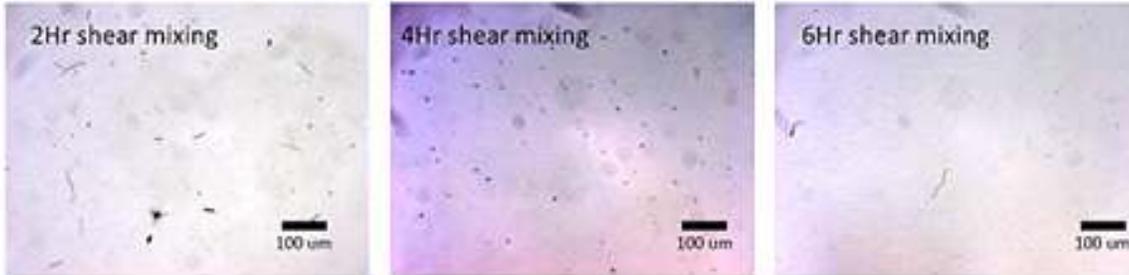


Figure 1c) Optical images of 0.5wt% SWCNT in PAN at various stages

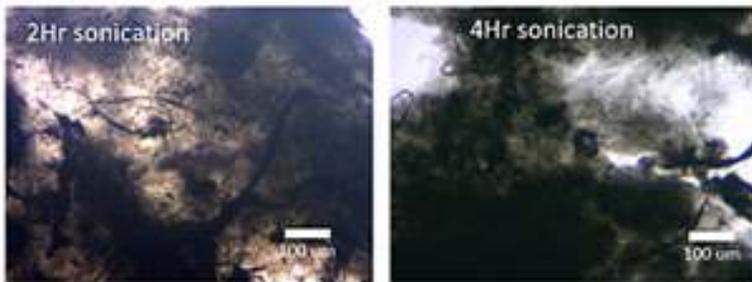
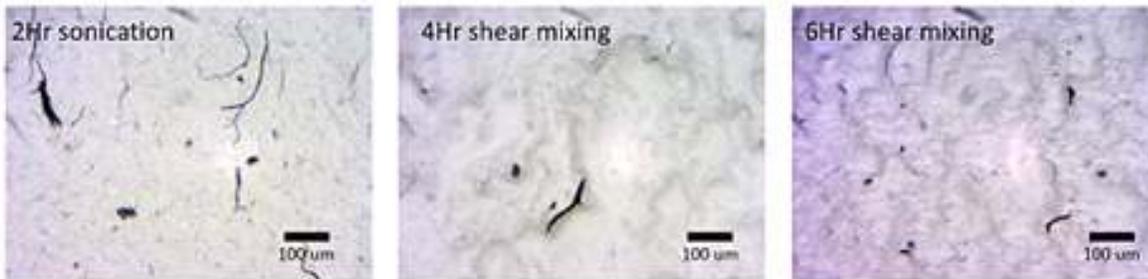
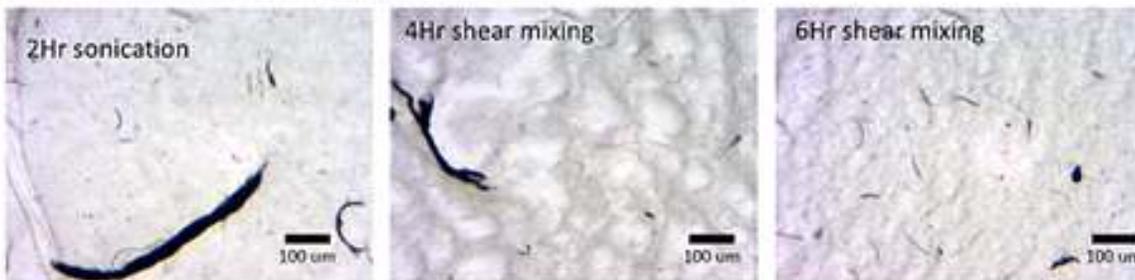


Figure 1d) Optical images of 1wt% SWCNT in PAN at various stages



Along with agglomerate size reduction and agglomerate size gives more information on the dispersion of the SWCNT in the PAN matrix. Agglomerate size distribution here is doing the same work as polydispersity index in the case of polymer. Agglomerate size distribution represents the presence of different sizes of SWCNT agglomerates present in the PAN matrix where its value closure to 1 indicates the presence of all similar sizes of agglomerates in SWCNT/PAN. Calculation of both agglomerate size and agglomerate size distribution is done as per given below equation 1, equation 2, and equation 3:

- Number average Agglomerate size (A_n):

$$A_n = \frac{\sum_n^i N_i A_i}{\sum_n^i N_i} \dots(1)$$

- Size average agglomerate size (A_s):

$$A_s = \frac{\sum_n^i N_i A_i^2}{\sum_n^i N_i A_i} \dots(2)$$

- Agglomerate size distribution = $\frac{A_s}{A_n} \dots(3)$

Where N is the number of agglomerate particles

A is the size of respective agglomerate particles

With optimized sonication and shear mixing, all PAN/SWCNT composites attained ~1 Agglomerate size distribution which indicates homogeneous network formed by SWCNT and also represents PAN behavior as a kinetic stabilizer for SWCNT (as shown in Figure 2).

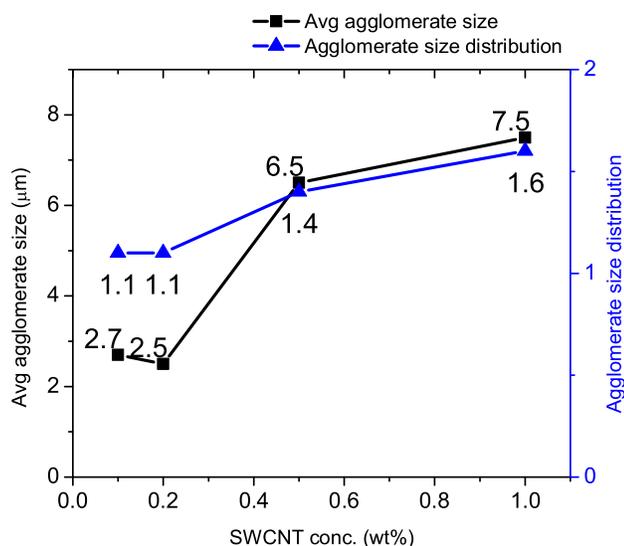


Figure 2: Effect of SWCNT concentration on the agglomerate size reduction and agglomerate size distribution after 4 hours ultrasonication and 6 hours shear mixing.

Though uniform dispersion of SWCNT bundles was achieved with the combination of ultra-sonication and shear mixing agglomerate size was found to be increasing with

SWCNT concentration in PAN matrix. The smaller agglomerate size in C1 PAN/SWCNT composite can be attributed to the low concentration i.e., 0.1 wt% of SWCNT, since a greater number of PAN polymer chains were present to interact with SWCNT and making more favorable conditions in preventing SWCNT aggregation and de-bundling.

4.2 Brookfield viscosity

Brookfield viscosity is the resistance to flow of a polymer solution under shear rate which is directly related to the molecular weight, degree of entanglement, and interactions between polymer chains. Figure 3 represents the Brookfield viscosity data PAN and PAN/SWCNT composite solution.

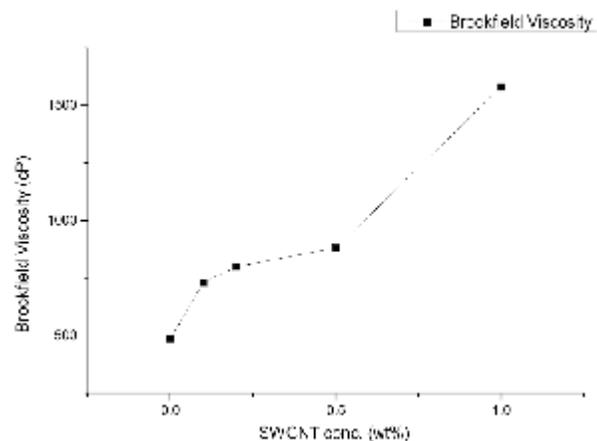


Figure 3: Effect of SWCNT concentration on Brookfield viscosity with images showing opaqueness of films prepared with respective PAN/SWCNT composite solution

As shown in the figure with increasing the SWCNT in PAN matrix films are becoming opaque and also the viscosity of the PAN/SWCNT solution is increasing with SWCNT content. This result also conforms with the optical microscopy results which represent uniform dispersion of SCWNT in PAN matrix. The drastic increase in viscosity was observed for 0.1 wt% and 1wt% SWCNT addition which represents the uniform dispersion of SWCNT was stabilized by PAN polymer chains where they are interacting and wrapping the SWCNT and preventing its aggregation. Further, it also shows PAN polymer chains also act as a stabilizing agent which is reducing the surface cohesion energy of SWCNT agglomerates. Table 1 represents the detailed data of Brookfield viscosity of respective PAN and PAN/SWCNT composite solutions.

Table 1: Brookfield viscosity of PAN and PAN/SWCNT composite solution

S. No	15% PAN Solution (ml)	CNT Conc. (%)	Brookfield Viscosity (cP) at 35°C
1	200	0	485
2	200	0.10%	730
3	200	0.20%	800
4	200	0.50%	880
5	200	1.00%	1580

4.3 Solvent resistance test

A solvent resistance test was done to study the interaction between PAN and SWCNT. All the composite films i.e., pristine PAN as well as PAN/SWCNT films were kept in Dimethylformamide (DMF) solvent for 1 hr at the controlled temperature of 25°C. We observed DMF acted as a strong solvent for completely dissolving PAN polymer, however, PAN/SWCNT composite showed resistance towards the complete dissolution in DMF solvent. It can be related to the strong interactions between PAN polymer chains and SWCNT. A similar effect can be seen when SWCNT concentration in PAN increased from 0.1 wt% to 1wt% where an increase in SWCNT concentration residual weight after the test period was observed increasing in PAN/SWCNT composites films (as shown in Figure 4 and Table 2).



Figure 4: PAN and PAN/SWCNT dried composite films in DMF, (left to right): PAN, 0.1wt%, 0.2wt%, 0.5wt% and 1wt% SWCNT respectively

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Table 2: Solvent resistance test

S. no.	Sample	SWCNT conc. (wt%)	DMF resistance		
			Before wt (mg)	After wt (mg)	wt loss (%)
1	PAN	0	102.1	0	100.00
2	C1	0.1	127.5	96.3	24.47
3	C2	0.2	115.5	90.8	21.39
4	C3	0.5	125.6	106.8	14.97
5	C4	1.0	113.5	100.8	11.19

As indicated from the optical microscopy and Brookfield viscosity, the uniformly formed network of SWCNT in PAN is not only restricting the penetration of DMF in composite films but also keeping PAN polymer chains strongly attached on the SWCNT surface. This effect is said to be very prominent on just the initial introduction of carbon nanotube in the PAN matrix.

5. Conclusion:

Dispersion of SWCNT in PAN matrix was successfully obtained from ultrasonication and mechanical stirring. Optical microscopy results show mechanical stirring aids in reducing the agglomerate size by more than 10 times. Though the near 1 value of agglomerate size distribution was obtained in all PAN/SWCNT composite solutions agglomerate size increased with an increase in SWCNT concentration. Brookfield viscosity and physical images of PAN/SWCNT solution also show uniform dispersion of SWCNT in the PAN matrix. Solvent resistance test and drastic increase in Brookfield viscosity show good interaction between PAN polymer chains and SWCNT.