

Study of Optical, Thermal, Mechanical and Microstructural Properties of Fullerene/Poly (vinylidene fluoride) Polymer Nanocomposites

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Received: 14.12.2021; Accepted: 1.02.2022; Published: 25.03.2022

Abstract: Fullerene (C₆₀)/ poly (vinylidene fluoride) PVDF polymer nanocomposites (PNCs) films were prepared using a solution casting route. The optical, microstructural, thermal, and mechanical properties of pure PVDF and C₆₀-PVDF polymer nanocomposite films were studied using UV-Visible & Fourier Transform infrared (FTIR) spectrophotometer, X-ray diffractometer, Thermo-gravimetric analyzer, Tensile tester, and Field emission scanning electron microscope. An absorption band near 350 nm in the absorption spectrum shows the presence of C₆₀ nanoparticles in the PNC film. In the FTIR spectrum, the presence of vibrational bands near 510 and 840 cm⁻¹ suggest the development of β-phase of PVDF in PNC films. An increase in the degradation temperature from 444 °C in pure PVDF to 506 °C in PNC with 0.5 wt% C₆₀ is ascribed to cross-linking occurring between C₆₀ and polymer in PNC films. Both thermal conductivity and Young's modulus vary non-linearly with C₆₀ content in PNC films. Microscopic image shows agglomerated C₆₀ particles of diameter ~550 nm, which were cross-linked to PVDF particles.

Keywords: solution casting; polymer nanocomposites; cross-linked structure; degradation temperature; Young's modulus.

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1. Introduction

Since the discovery of piezoelectric actions in poly (vinylidene fluoride) PVDF by Kawai in 1969 [1], semi-crystalline polymer and its copolymer have been investigated much these days [2-7]. Amongst various polymers, PVDF, in particular, has many advantageous features like low cost, flexibility, long-term stability, solubilization in many solvents, hydrophobicity, easy castability, excellent mechanical strength, good aging resistance, high chemical selectivity, large polarization, etc. as compared to many known technological polymers like poly (acrylonitrile), poly(tetrafluoro ethylene), polyimide, polysulfone, etc. [2-7]. Owing to possession of improved properties, PVDF finds applications in various fields like sensing [2-6], energy harvesting [5,8-13], biomedical [6,9,14,15], nonlinear optics [16], water treatment [17,18], electromagnetic field shielding [19,20], distillation [17,18,21,22] and ultrafiltration [17,18]. PVDF is a fluoropolymer consisting of -(CH₂CF₂)- repeating unit. The repeating unit can exist in two conformations, i.e., Gauche (G) and Trans (T). Based on chain conformations, internal rotation about the C-C chain, and steric hindrance, PVDF polymer can exist in five crystalline forms α, β, γ, δ, and ε. Out of these five forms, 'α' is the most stable crystalline form but possesses no net dipole moment as it follows a TGTGTG... sequence about

the main backbone chain. The all Trans (TTTTT...) conformational sequence results in electro-active β -phase are of immense technological importance, especially in sensing due to the exposition of strong piezoelectricity on account of spontaneous polarization [8-13].

Several techniques were adopted by researchers to increase the percentage of β -phase in the PVDF are mechanical stretching [23-25], polymer blending [24,26,27], electrospinning [24,28,29], spin coating [24,30], sonication [8,31-35], addition of nanofillers [2,3,9-12,14-16,20,24], etc. However, polymer nanocomposites (PNCs) obtained by adding nano-fillers to PVDF polymer attract much attention due to their multifunctional properties like optical, electrical, thermal, mechanical, biological, etc. [9-12,14-16,20]. Various literature shows that diverse types of fillers in the form of metal oxides, transition metal oxides, carbon nanostructures (fullerene C₆₀, carbon nanotube (CNT), graphene), ferrites, clay, etc. are tried by the researcher to enhance the dielectric, thermal, mechanical properties, etc. by increasing the percentage crystallinity of β -phase in PVDF [9-12,14-16,20,24]. Xiao *et al.* [31] reported an enhanced thermal conductivity (K-value) in PVDF/Boron Nitride (BN) composites in the presence of CNT. They reported a K-value of 1.30 Wm⁻¹K⁻¹ in PVDF/BN (20 wt%)/CNT (2 wt%) composite, and K-value increases almost linearly with BN-content (1-20 wt%). Mandal and Nandi [32] studied the effect of CNT addition on the thermal and mechanical properties of polymethyl methacrylate (PMMA). They reported that the formation of hard composite material causes an increase in thermal stability, tensile strength, and Young's modulus of PMMA/CNT composite. In an article, Zhou *et al.* [34] reported that the K-value in PVDF/Ni composite is significantly enhanced due to the high K-value of nickel metal. Georgousis *et al.* [35] reported that at higher loading of CNT (6 and 8 wt%) the yield stress increases marginally relative to the pristine PVDF owing to enhancement in the β -phase.

In recent times, carbon nanostructure-based spherical filler like C₆₀ is also attracting much attention due to its excellent optical, biological, rheological, and thermal properties [36-46]. Fullerene is chosen because many researchers report that C₆₀ can alter the properties of the polymer via the transformation of α to β -phase in PVDF [8-10,12,18,33,47,46]. Vukicevic *et al.* [8] have reported that C₆₀ nanoparticles (NPs) increase the polymer's melting point by drastically reducing chain mobility. In an article, Zhang *et al.* [9] reported that they had fabricated β -form of PVDF in the presence of C₆₀ using a twin-screw extruder. They succeeded in forming nanowires of PVDF assisted by C₆₀ in C₆₀/PVDF nanocomposites. Kim *et al.* [18] developed C₆₀/PVDF membranes via a solution casting route that is useful for microfiltration and characterized their mechanical strength, hydrophilicity, and antifouling properties. The Young's modulus of C₆₀/PVDF PNC can be increased up to 1550 MPa upon addition of as small as 0.2 wt% C₆₀ [25]. They also reported that Young's modulus varies non-linearly with C₆₀ content. Zeuv *et al.* [47] reported that Young's modulus and tensile strength of Polyaniline/C₆₀ PNC could be improved by 20% by doping of 0.02-0.08 wt% C₆₀. According to their report, Young's modulus varies non-linearly with C₆₀ content and can give 3.0 GPa at a loading of 0.04 wt%. In epoxy/C₆₀ PNC, Young's modulus can be increased up to 20% by loading of 0.12 wt% C₆₀ [48].

The present work aims to link C₆₀ with PVDF via non-covalent interaction and develop PVDF/C₆₀ nanocomposite films via a solution casting route. In this study, the development of PNC films was discussed using N-methyl pyrrolidone (NMP) solvent. As far as my knowledge is concerned, it is of the first kind to develop PVDF/C₆₀ nanocomposite films using NMP as a common solvent for both materials. The effect of C₆₀ NPs on the optical, microstructure, thermal and mechanical properties have been investigated.

2. Materials and Methods

PVDF powder (average Molecular weight ~534,000) was purchased from Sigma-Aldrich (is now Merck). Fullerene C₆₀ (99.9 % purity) and the solvent N-methyl pyrrolidone (NMP) were purchased from Alfa Aesar and Sigma-Aldrich. All these raw materials were used as such in developing PNCs.

At first, C₆₀ power was submerged in NMP solvent, and the mixture was stirred with a stirrer maintained at 1500 rpm for 20 min to prepare C₆₀ solution. Then, PVDF (3g) was immersed in 100 mL NMP, and the mixture was stirred using an electrical stirrer maintained at 70 °C and 3000 rpm for 2 h to prepare PVDF solution. The PVDF solution was allowed to cool to RT. The different volume of C₆₀ solution was added to a fixed volume (5 mL) of PVDF solution to develop C₆₀/PVDF nanofluids of various C₆₀ contents in NMP. In this manner, I prepared four NFs of different C₆₀ contents. The NFs were poured into four glass sheets and placed in a vacuum oven maintained at 120 °C for 5 h to remove the solvent. After removing the solvent, the nanocomposite films were peeled off from the sheets and obtained PNCs films were stored in desiccators for experimental analysis.

Absorption spectra of PNCs films were measured under identical conditions on a Perkin–Elmer double beam spectrophotometer (LAMBDA 1050). Infrared (IR) spectra have been studied with a Thermo Nicolet Corporation FTIR spectrometer (Model NEXUS-870). The X-ray diffraction (XRD) patterns of PNCs were obtained from a diffractometer made in Germany (Rigaku D/MAX-r.) with 2θ ranging from 5 to 60°, using Cu Kα radiation ($\lambda = 1.5406$ Å) at room temperature. Images of PNCs films were studied with a Field Emission Scanning Electron Microscope (FESEM) of ZEISS SUPRA–40. The thermal conductivities of the composites were measured using an LFA 447 Nano Flash (NETZSCH, Germany). A sample with a diameter of 12.6 mm was used for finding thermal conductivity value. Using the relationship $C = \alpha t_{50}/d$, the thermal diffusivity (α) can be calculated. Here, C is a dimensionless constant, t_{50} denotes the time to get one-half of the maximum temperature, and d denotes sample thickness. Now, thermal conductivity can be calculated using the equation $K = \alpha \times C_p \times \rho$, where K, ρ , and C_p represent thermal conductivity, bulk density, and specific heat of composites, respectively. Thermogravimetric analysis (TGA) was performed on a TGA 209 F3 (NETZSCH, Germany). The samples weighing nearly 10 mg were placed in the instrument, and measurements were performed under an N₂ gas atmosphere with a heating rate of 10 °C/min. The mechanical properties of the films were measured using universal testing machines UTM (INSTRON Instruments) following the ASTM D638-10 standard, taking an average of five measurements per reported value with the standard deviation under 65%. The extension rate was kept at ~10 mm/min. The dimensions of the film used were ~2cm × 5cm × ~200–250 μm (width × length × thickness).

3. Results and Discussion

3.1. Electronic and vibrational spectroscopy.

The electronic absorption spectra of C₆₀/PVDF PNCs films with C₆₀ content (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.5 wt% in the wavelength range (240–740 nm) are given in Fig. 1. As the peaks are broad, de-convolution was done (for sample-3) to split the broad peak into two peaks. The two peaks, one near 290 nm and the other near 350 nm, were seen after de-convolution. The de-convoluted spectrum is placed in the inset of Fig. 1. The two peaks were

from the C₆₀ band [39,40]. PVDF usually gives a band near 200 nm [16]. The nonpresence of this band near 200 nm shows that C₆₀ is successfully incorporated into the PVDF matrix in PNCs. Also, it was found that the peak maximum is shifting to a higher wavelength (i.e., from 286 nm in 0.1 wt% C₆₀ to 298 nm in 0.5 wt% C₆₀) upon the incorporation of more and more C₆₀ into the polymer matrix. This result suggests that some interaction (maybe charge transfer type) occurs between C₆₀ and PVDF polymer [42-46,49].

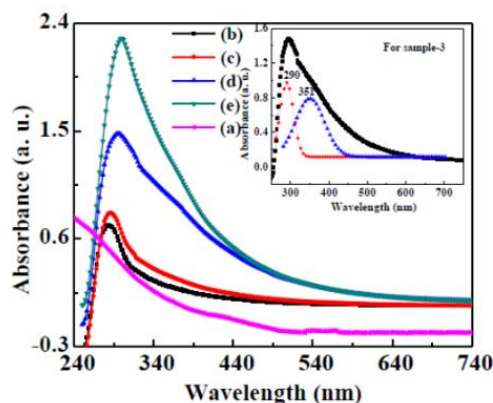


Figure 1. Absorption spectra of C₆₀-PVDF PNCs: (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.5 wt% C₆₀. Inset shows deconvolution of a broad absorption into two bands.

In order to identify the various crystalline polymorphs in PNCs film, we studied the vibrational spectra (Fig. 2) of C₆₀/PVDF PNCs films with C₆₀ content (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.5 wt%. The selective bands at 1268, 966, 831, 786, 755, 607, 523, 502, and 481 cm⁻¹ which were assigned in Fig. 2 are recognized as α or β -phase in PNCs containing 0.5 wt% C₆₀ (see the Table 1 for polymorph type and band assignment) [8,9,35]. No such band was seen in pure PVDF film (Fig. 3). This clearly shows that C₆₀ NP induces crystallinity in PVDF matrix. Further red-shift (i.e., wavenumber decreases to lower value upon adding C₆₀ into PVDF) in these bands in the presence of C₆₀ suggest charge transfer type interaction between carbon NP and fluoro-polymer via C₆₀---F-atom [42-46,49]. This band shift also suggests cross-linking between C₆₀ and PVDF polymer [48].

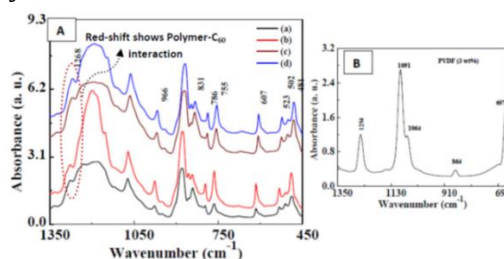


Figure 2. FTIR spectra of (A) C₆₀-PVDF PNCs and (B) pure PVDF.

Table 1. Assignments of vibrational bands.

Sl. No.	Band Position (cm ⁻¹)	α/β -phase assignment [8,9,35]
1	1268	β
2	966	α
3	831	β
4	786	α
5	755	α
6	607	α
7	523	α
8	502	β
9	481	β

3.2. XRD and microstructures.

XRD patterns of pure PVDF and C₆₀-PVDF PNC films are shown in Fig. 3. For the pure PVDF film, the diffraction lines corresponding to 2θ angles were found at 18.02 and 20.2. This shows that PVDF film is a little crystalline in nature. As per the referred diffraction data, the reflection of polymer with 0.5 wt% C₆₀ at 2θ angles 17.83, 20.6, and 36.34 are ascribed to α , β , and β -phase, respectively. Whereas no such peak was seen in pure PVDF. This suggests that C₆₀ NPs help crystallize the polymer [8,9,11].

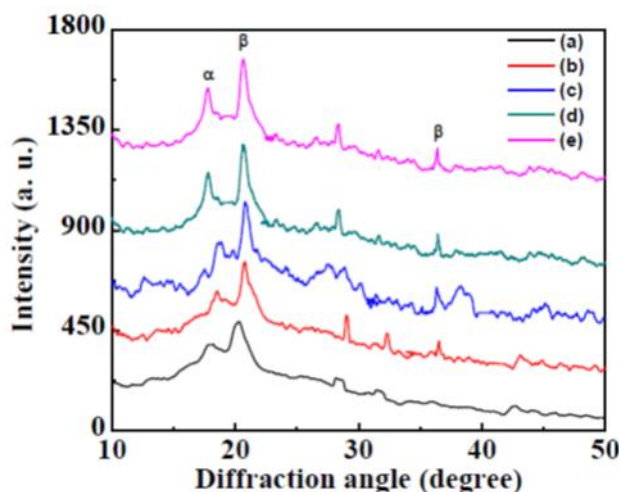


Figure 3. Diffraction patterns of C₆₀-PVDF PNCs: (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.5 wt% C₆₀.

Fig. 4 displays the FESEM images of pure PVDF and C₆₀-PVDF PNC film. The FESEM image of pure PVDF film (Fig. 4a) shows spherical particles (~450 nm) of PVDF polymer. In Fig. 4b, the image shows agglomerated C₆₀ particles of ~550 nm, which were cross-linked to PVDF particles. Fig. 4c shows a magnified image of the C₆₀ nanocluster.

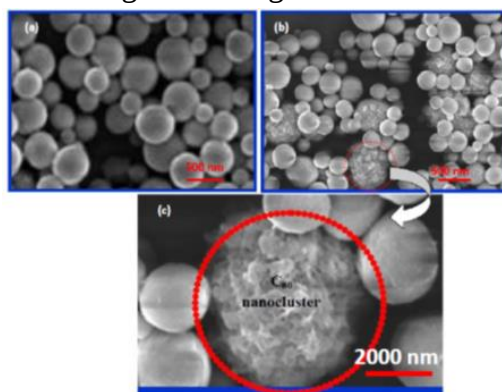


Figure 4. FESEM image of (a) Pure PVDF film; (b) C₆₀-PVDF PNC film with 0.3 wt% C₆₀ and (c) magnified image of the selected portion of Fig. 4b.

3.3. Thermal properties of C₆₀-PVDF PNC films.

The thermal stability of PNC films was studied from TGA curves. Fig. 5a shows the TGA curves for pure PVDF film and C₆₀-PVDF PNC films. All TGA curves show a single degradation temperature. The PVDF polymer is almost thermally stable up to 378 °C. After this temperature, PVDF polymer matrix degrades at a rapid rate. As seen from the TGA thermograms of PNCs films, the temperature at which the PNCs starts degrading drastically increases upon more and more addition of C₆₀ NPs into the polymer matrix [32,50].

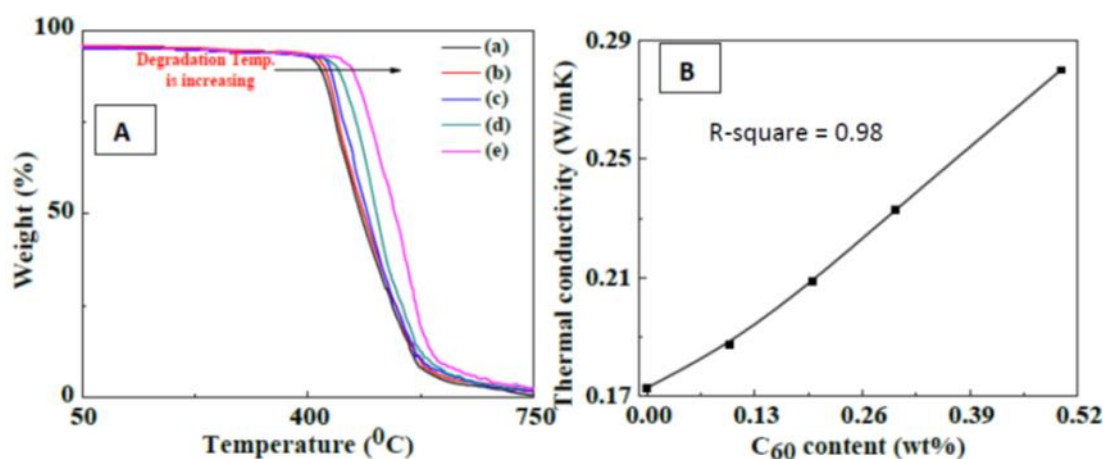


Figure 5. (A) TGA curves of C₆₀-PVDF PNCs: (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.5 wt% C₆₀ and (B) Variation of K-value Vs C₆₀ content in C₆₀-PVDF PNCs.

The degradation temperature has increased from 444 °C (pure PVDF) to 506 °C (PNC with 0.5 wt% C₆₀). The result reveals that the cross-linking occurs between C₆₀ and polymer, helping PNCs sustain thermal degradation. Also, it suggests that % cross-linking increases upon the addition of more and more carbon NPs into the matrix.

Thermal conductivity (K) values with and without filler were measured. K-value vs. wt% of C₆₀ plot (Fig. 5b) shows that C₆₀-PVDF PNC films exhibit enhanced K-value compared to pure PVDF film. The K-value varies non-linearly with C₆₀ content. Xiao *et al.* [31] and Cao *et al.* [52] have reported a similar nonlinear relationship between K-value and filler content. The K-value of PNC with 0.5 wt% C₆₀ is 0.28 W mK⁻¹, and this value is ~61% higher than pure PVDF film (0.172 W mK⁻¹). The enhanced value of K in PNC films is ascribed to the formation of thermal conductivity path by developing cross-linked structure in the PNC films, as seen from the FESEM image (Fig. 4) [31,52].

3.4. Mechanical properties of C₆₀-PVDF PNC films.

The stress-strain % plot of pure PVDF and PNC films is shown in Fig. 6A. The strain % at break decreases with an increase in C₆₀ content. The result is due to incorporating more and more carbon NPs into the polymer matrix. These NPs cross-link the polymer molecule and make the matrix rigid, decreasing the plasticity of PNC films. Upon increasing the C₆₀ content to 0.5 wt% in PCN film, the strain % decreases nearly 200% relative to pure PVDF.

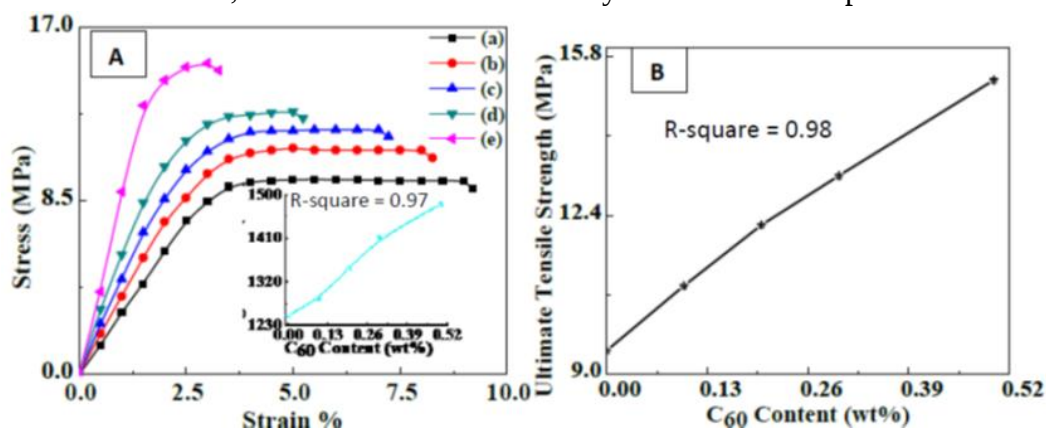


Figure 6. Variation of (A) stress Vs strain % of C₆₀-PVDF PNCs: (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.5 wt% C₆₀, and (B) Ultimate tensile strength Vs C₆₀ content. Inset in Fig. 6A shows the variation of Y-value Vs C₆₀ content.

Fig. 6B shows the variation of ultimate tensile strength against C_{60} content in pure PVDF and PNC films. From the plot, it is found that tensile strength varies non-linearly with C_{60} content. Relative to the pure PVDF, the ultimate tensile strength increases by 62% in PNC film consisting of 0.5 wt % C_{60} . This result is due to the formation of carbon nano-filler's cross-linked structure in PNC films. As it can be seen from the inset of Fig. 6A that Young's modulus (Y) gradually increases with C_{60} content. These two parameters also vary non-linearly with each other, upon increasing the C_{60} content to 0.5 wt% in PCN film, the Y-value increases by nearly 18% concerning pure PVDF.

4. Conclusions

C_{60} -PVDF PNCs films were developed via a solution casting route and studied their optical, microstructural, thermal, and mechanical properties. The UV-Vis spectra show the incorporation of C_{60} into the polymer matrix. XRD patterns and FTIR spectra suggest an enhancement in % crystallinity of PVDF polymer via the formation of α and β -phase in PNC films. The composites' thermal and mechanical properties increase with increasing C_{60} content due to the formation of cross-linked microstructures. The developed polymer nanocomposites may find useful in bio-sensing and microfiltration.

Funding

This research received no external funding.

Acknowledgments

The kind help from the Silicon Institute of Technology is highly acknowledged.

Conflicts of Interest

The authors declare no conflict of interest.

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