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Strengthening of $\beta$ polymorph in PVDF/FLG and PVDF/GO nanocomposites

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Abstract

The nanocomposites of PVDF/FLG and PVDF/GO are prepared using the solution casting method for varying concentrations of FLG and GO from 0.1 to 1 wt% in PVDF matrix. The effect and dispersion of FLG and GO are observed with help of Scanning electron microscopy (SEM) and x-ray diffraction confirming the good dispersion of FLG and GO in the matrix. The samples are also characterized for thermal and mechanical properties using Differential scanning calorimetry (DSC) and universal testing machine (UTM). FLG and GO nanofillers seemed to increase the tensile strength from 10 MPa to 20 MPa and variation in crystallinity to get maximum output in terms of $\beta$ phase which can be utilized for piezoelectric and pyroelectric behavior of PVDF polymer.

Introduction

Polyvinylidene fluoride (PVDF) has five polymorphs in its crystalline structure named $\alpha$, $\beta$, $\delta$, $T$ and $\epsilon$ [1]. It has broad applications in terms of piezoelectric and pyroelectric behavior [2]. Most applicable polymorphs in crystalline structure are $\alpha$ and $\beta$ in which $\beta$ phase contains Trans-Trans (TT) with orthorhombic unit cell which can be achieved using nucleating effect of suitable nanofiller in PVDF matrix [3]. This $\beta$ phase is highly active for piezoelectric and pyroelectric applications. On the other hand, $\alpha$ phase is Trans-Gauche-Trans-Gauche (TGTG) chain conformation having monoclinic unit cell, and can be obtained by crystallization from melt [3]. The availability of different crystalline structures in PVDF is due to similar atomic radii of fluorine and hydrogen in monomer unit which results in chain polarization [4]. $\beta$ phase of PVDF Trans-Trans (TT) conformation results in hydrogen and fluoride on opposite corners of polymer backbone which produce a net non-zero dipole moment [5]. It makes PVDF to be used in optical, electrical, sensors and transducers applications [6, 7]. There are several approaches to get $\beta$ phase in PVDF. One of them is by applying specific conditions to customize the crystal structure. It includes crystallization by melting under pressure [8, 9] or under special conditions [10]. Stretching of melt crystallized films biaxially or uniaxially [9, 10]. Another method is by introducing external nucleating agent in structure to get ultimate results like Carbon nanotubes (CNT’s) [8], graphene nanosheets [11] and clay [12] can be used to get $\beta$ phase in PVDF. It is necessary that filler surface adsorb PVDF chains due to which PVDF-filler interface causes transition of $\alpha$ phase (TGTG) to $\beta$ phase (TT). It is suggested to use those fillers having carbonyl groups because of higher compatibility with fluorine in the PVDF [13]. It gives uniform distribution of nanofiller and ultimately produces competitive candidate for piezoelectric and pyroelectric applications. Graphene is a single layer graphite that is an attractive candidate for use as a nanofiller in PVDF matrix to get improved properties for specific applications. It has considerable thermal, electrical and mechanical properties. It is available in different forms based upon the synthesis technique. It is a single layer of carbon atoms obtained by exfoliation or oxidation of graphite [14]. Graphene oxide (GO) contains oxygen groups on surface. These groups are in the form of hydroxyl and carboxyl groups [14, 15] which induce hydrophilic nature to this nanofiller [16, 17]. Secondly GO has more stability because of oxygen groups on
surface. While few-layered graphene is lacking with these properties. Due to this reason, GO is more focussed in the research. This property of GO leads to successful exfoliation of bulk graphite oxide by sonication in water [14]. PMMA-modified graphene sheets are utilized as a nucleating agent for β phase in PVDF or modified graphene nanocomposite by Nayek et al. PMMA contains carbonyl group is used with graphene. Moreover Few-layered–graphene also being used in many other applications as well like vapour phase separation, sensors, energy storage devices, and piezoelectric devices [18–22].

In PVDF/graphene nanocomposites, it is observed graphene is less interactive to PVDF [23]. It is also observed that thermally reduced graphene oxide in PVDF produces both α and β phases in PVDF matrix [24]. Oxygen-containing groups in graphene oxide become reduced in thermal reduction process. Due to insufficient groups on graphene oxide cause incomplete transition of β phase. Because of higher potential in graphene, it is necessary to have fully β phase polymorph in PVDF/graphene nanocomposite films. Dimethylformamide (DMF) is chosen as a suitable solvent for the solubility of PVDF. Graphene in DMF can be dispersed to get nanocomposite films by solution casting method [11]. Different concentrations of graphene in two forms named as few-layer graphene and graphene oxide are used individually to optimize the β phase in PVDF matrix. It is also characterized for thermal, mechanical and morphological features. The dispersion of graphene is also discussed for these nanocomposite films.

This research will provide the utilization of piezoelectric and pyroelectric properties of PVDF using graphene-based nanofillers in PVDF matrix. Due to higher difference in melting (∼168 °C) and glass transition (∼−40 °C) temperature of PVDF polymer, it is difficult to control film synthesis parameters to avoid shrinkage. Graphene-based nanofillers show higher nucleating effect with lower weight percent as compared to other nanofillers. Due to lower weight percent and higher output, these nanofillers can be best candidate for getting β phase of PVDF.

**Experimental**

**Materials**

Dimethylformamide (DMF) was bought from Fluka Co. USA and Polyvinylidene fluoride (PVDF) from Sigma Aldrich Co. USA.

**Sample preparation**

FLG and GO were fabricated by Modified Hammers Method. Films of PVDF/GO were prepared by solution casting method, Firstly, PVDF dissolved in DMF solvent at a temperature of 40 °C with the help of magnetic stirrer for 12 h. Then weighed the concentration of GO dispersed in the solution by mixing for 12 h followed by 1 h sonication process. In last step, obtained solution poured into glass petri dish at room temperature and placed in the vacuum oven for drying at 50 °C. It takes 12 h for complete drying of films under these conditions. The same procedure was adopted for PVDF/FLGs films. For the characterization, dried films were cut as per the requirement of the test. The solution casting method was used to prepare nanocomposites as it is the best suited, economic, fast and easy method for lab-scale experimentations also it gives maximum dispersibility of nanofiller than any other lab-scale method.

**Characterization techniques**

*X-ray diffraction (XRD)*

It was done using Cu Kα Radiations (λ = 0.15418 nm) with a scan rate of 2° min⁻¹ over the range 2θ = 5°–80°. It was conducted on room temperature using Theta-Theta instrument by STOE-Germany.

*Scanning electron microscopy (SEM)*

Morphologies of PVDF/FLG and PVDF/GO nanocomposite films having weight percent from 0.1 to 1 for both nanofillers are observed. For that purpose, JOEL JSM-6490A Analytical Scanning Electron Microscope was used. Sample preparation includes the dipping of composite films in liquid nitrogen for the cryogenic crack to occur for getting fresh surface. In the next step, they were gold plated (∼250 Å) using JOEL JFC-1500 Ion sputtering device. In last step samples were mounted on aluminum stubs.

*Differential scanning calorimetry (DSC)*

It was done on DSC-6000 by Perkin’s Elmer. Samples were dried in a vacuum oven before putting them in stainless steel pans for DSC measurements. The weight of each sample kept constant at 5 mg and scanning rate was 10 °C min⁻¹. Measurements were taken between −40 °C to 200 °C.
Tensile mechanical properties
The tensile properties of nanocomposite films were determined using Trapezium-X universal Testing Machine (AG-20KNXD Plus) manufactured by Shimadzu Corporation at a crosshead speed of 5 mm per minute (ASTM D882). Cutting of these samples was done using hand cutter (ASTM D6287). To avoid notches and roughness of the surface, samples were cut carefully. All the samples were tested at room temperature and atleast 5 individual determinations were used to obtain an average value.

Results and discussion

X-ray diffraction
Figure 1 (a) shows the XRD patterns of Polyvinylidene fluoride (PVDF) with two phases α and β. Nanofillers few-layered graphene and graphene oxide used separately in the same PVDF matrix can also be seen with their characteristic peaks on their respective planes.

PVDF has α phases at 2θ angles of 18.4 and 26.6 at planes (100) and (021) [25] while β phase respond at two planes (110) (200) with 2θ angle 20.4 [25]. The characteristic peak of few-layer graphene is at 2θ angle of 26.8 and graphene oxide at 9.8 on (002) and (001) planes respectively [26].

Figure 1 (b) presents the PVDF/FLG composite systems having weight percent of nanofiller ranging from 0.1 to 1. With the addition of FLG in PVDF matrix we can observe matrix becoming enriched with β phase and we get this trend till 0.5 weight percent of FLG. Above this weight percent α phase start appearing again which might be result of agglomeration in matrix leading to decreased chain confinement. The intensity of α phase is minimum at 0.3 weight percent which has good dispersion of nanofiller in the matrix.

Figure 1 (c) shows the PVDF/GO composite system having the same weight percent as being used for FLG. In this case we observed immediate response of adding GO in PVDF. The intensity of β phase become stronger even at 0.1 weight percent of GO which continues with increasing weight percent. It is because of strong compatibility between carbonyl groups in GO and fluorine in PVDF due to which there is no individual characteristic peak of GO in this composite system. For this system, good dispersion is also achieved at 0.3 weight percent which is confirmed with maximum intensity of β phase as compared to other weight percent of GO.

It seems from the graph from figure 1 (c) that the peak intensity of 0.5 wt% is less than 0.3 wt% and 1 wt% GO. Peak intensity within a single pattern indicates the ratio of that phase present in the sample. It cannot be compared with other graphs with respect to its intensity. The presence of peak indicates that this phase exists in that material but didn’t indicate the amount when compared with other graphs.

Scanning electron microscopy
Dispersion of few-layer graphene and graphene oxide in PVDF matrix and its effect on morphology was studied using this technique. Figure 2(a) represents the plain plateau of PVDF matrix at scale of 1 μm. We can see dispersion of nanofillers with 1 weight percent for FLG and GO in the matrix as brighter points in figures 2(b) and (c) respectively [11]. The difference in densities reflects in the form of brightness in SEM images. FLG at 1 weight percent (figure 2(b)) is showing higher agglomeration as compared to GO (figure 2(c)) in the same matrix. GO is more uniformly distributed with only few stackings in PVDF matrix. It has stronger compatibility of functional groups which is already confirmed by XRD analysis.
Differential scanning calorimetry

Thermal properties of both nanocomposite systems (PVDF/FLG, PVDF/GO) and their relation to crystalline structure were characterized by this technique.

Figure 3(a) shows the heating thermograms of DSC for PVDF/FLG composites. The concentration of nanofiller is same as in case of XRD. A low temperature melting peak is attributed to $\alpha$ phase of PVDF\textsuperscript{[11]} while higher temperature melting peak is for $\beta$ phase of PVDF\textsuperscript{[11]}. At 0.3 weight percent of FLG in PVDF matrix, we get only one peak of melting at 166.9 $^\circ$C which is of beta phase. It is already confirmed from XRD analysis that we have maximum intensity of beta phase at 0.3 weight percent of FLG. For higher concentrations above 0.3, $\alpha$ phase starts appearing again due to which second peak is there for higher weight percent of FLG.

Based on these observations we can see nanocomposite with 0.3 weight percent of FLG has the highest melting temperature in contrast to other concentrations of nanofiller.

Figure 3(b) illustrates the heating thermograms of PVDF/GO nanocomposites. As we know from XRD analysis this composite system gets the $\beta$ phase immediately at lower concentrations of GO. For all the concentrations of GO we have only $\beta$ phase\textsuperscript{[27]}. It can be seen from the DSC heating curves, there is single peak.
of melting for all the concentrations between 0.1 to 1 weight percent of GO. Due to this reason, we observe small variations in melting temperatures of all concentrations ranges between 163.9 to 165.7 °C (Table 1).

In the same way cooling behaviors of both these systems are also observed after this heating. Samples are cooled down at the same rate and following curves are obtained.

Figure 3(c) shows the PVDF/FLG system. The crystallization peak is shifting as compare to pure PVDF. We can see maximum peak shift for 0.3 weight percent of FLG in this system because of single β phase at this concentration. It has maximum crystallization temperature of 138.3 °C (Table 1) among other concentrations of FLG in PVDF. The introduction of α phase lowers the transition temperature which can be observed for concentrations above and below 0.3 weight percent of FLG in PVDF matrix.

Figure 3(d) demonstrates the cooling behavior of PVDF/GO nanocomposite system. It has stronger compatibility of GO with PVDF which results in single β phase with all concentrations of GO between 0.1 and 1

| Sample            | Tm (°C) | Tc (°C) |
|-------------------|---------|---------|
| Pure PVDF         | 163.9   | 136.2   |
| PVDF-FLG-0.1      | 164.2   | 135.8   |
| PVDF-FLG-0.3      | 166.9   | 138.3   |
| PVDF-FLG-0.5      | 165.5   | 137.7   |
| PVDF-FLG-1        | 164.2   | 136.5   |
| PVDF-GO-0.1       | 165.7   | 137.8   |
| PVDF-GO-0.3       | 164.8   | 136.8   |
| PVDF-GO-0.5       | 165.6   | 136.8   |
| PVDF-GO-1         | 164.6   | 136.8   |
weight percent. It does not show any remarkable change in transition temperature with varying concentration of GO.

To calculate the percentage of crystallinity [11] of both these systems following formula is used in which \( \Delta H_m \) is calculated from DSC thermograms for each concentration while \( \Delta H_{100} \) is a constant value of 100% crystalline PVDF which is 104.7 J g\(^{-1}\) [28]. Figures 4(a) and (b) shows the percentage of crystallinity for both these systems. Concentrations with stronger \( \beta \) phase are showing a higher percentage of crystallinity which is 0.3 weight percent for FLG and 0.5 weight percent for GO.

\[
\text{Crystallinity (\%)} = \frac{\Delta H_m}{\Delta H_{100}} \times 100
\]

In the case of PVDF/FLG crystallinity raised to 11% as compared to pure PVDF having 42% crystallinity. This percentage dropped back to 46% at 1 weight percent of FLG in PVDF. In contrast GO in PVDF enhances crystallinity to 11% i.e. 53% at 0.5 weight percent. This percentage of crystallinity decreased to 50% at 1 weight percent of GO in PVDF.

GO has more ability to strengthen the \( \beta \) phase in the PVDF matrix because of functional groups. FLG, on the other hand, shows \( \beta \) phase at 0.3 weight concentration having maximum crystallinity in the nanocomposite. It can be considered \( \beta \) phase is more crystalline as compared to \( \alpha \) phase of PVDF. Those concentrations of nanofillers having dominant \( \beta \) phase in PVDF matrix are showing higher percentage of crystallinity which are 0.3 and 0.5 weight percent in case of FLG and GO respectively.

It is evident from figures 4(b) that crystallinity is decreased for 0.3 wt% GO sample. GO is functionalized graphene sheet and have more compatibility with more matrix and so it showed maximum dispersion. As there was no agglomeration and every single particle of GO is well dispersed in polymer matrix and due to intercalation effect, it restrict most of the polymer chains. Due to the constraining effect of GO on polymer chains, crystallinity decreases as chains cannot move and orient to gain order and crystallization due to the presence of GO.

**Tensile properties**

FLG and GO also induce mechanical features to the PVDF matrix which can be confirmed using stress-strain curves. Figures 5(a) and (c) shows the stress-strain curves for PVDF/FLG and tensile strengths of each concentration in the nanocomposite system. With the addition of nanofillers PVDF matrix get increment in the ability to withstand stress applied to it. Initially pure PVDF has 10.75 N mm\(^{-2}\) tensile strength which increased to 13.5 N mm\(^{-2}\) at 1 weight percent of FLG. There can be some entanglement of chains or non-uniform dispersion of FLG at 0.5 weight percent leads to decline in tensile strength. Figures 5(b) and (d) are the stress-strain curves and tensile strength of PVDF/GO nanocomposites. We can observe GO has more ability for enhancing mechanical properties of PVDF matrix. Tensile strength, in this case, reached to 20 N mm\(^{-2}\) at 1 weight percent of GO which is almost double than pure PVDF.

Young’s modulus [27] or elasticity of both systems has an increasing trend shown in figure 6(a) for PVDF/FLG and PVDF/GO. Both systems can bear stress with minimum strain induced in them. Tensile properties have inverse relation with strain at break. In both systems, tensile properties are increasing which ultimately give decreasing trend in case of strain at break for both nanocomposite systems shown in figure 6(b).

As described earlier, GO is well dispersed in the PVDF matrix in 0.3 wt% concentration and restrict most of the polymer chains. When force is applied, these chains cannot move from their position due to the constraining effect caused by the GO and hence very less strain is produced in comparison to 0.5 wt% and 1 wt% GO as there is agglomeration that cause minimum constraining effect on polymer chains and chains can freely move when
external stress is applied. Same is the case for FLG 0.3 wt% sample. 1 wt% FLG sample also shows very little strain, this may be because of very high agglomeration also proven by SEM. This high agglomeration causes empty spaces around the agglomerates and creates a stress concentration point where the stress goes beyond the actual applied stress and so the material fracture at that point.

With the addition of both nanofillers in the PVDF matrix, we get improvement in tensile properties. Graphene oxide has very high intrinsic mechanical properties and exceptionally high surface area making them a good nanofiller for enhancing the mechanical properties of PVDF matrix. As compared to FLG we get more good dispersion and compatibility in case of GO because of oxygen-containing group on its nanosheets. It results in good interfacial stress transfer efficiency. It restricts the polymer chain mobility and so improve the polymer nanocomposite mechanical properties.
Overall, the tensile properties of both systems increased by introducing GO and FLG in PVDF matrix. GO has a stronger impact because of higher compatibility with PVDF.

**Conclusion**

Nanocomposites of PVDF with few-layered graphene (FLG) and Graphene oxide (GO) are successfully synthesized by solution casting method which is confirmed by morphological and crystal structure of both systems with the help of SEM and XRD analysis respectively. GO has carbonyl groups which can make stronger bonding with fluorine in PVDF. It results in dominant $\beta$ phase in PVDF which is also more crystalline than $\alpha$ phase. DSC analysis confirms the variations in transition temperatures based on FLG and GO concentrations in PVDF matrix. In case of FLG, 0.3 weight percent is ideal to get maximum intensity of $\beta$ phase while GO has maximum $\beta$ phase at 0.5 weight percent. This $\beta$ phase show crystallinity of 53% which has piezoelectric applications of PVDF. Properties addition to PVDF polymer is directly related to adsorption of polymer chains on nanofilbers FLG and GO. From these results, we can conclude GO is compatible for PVDF polymer to get $\beta$ phase having versatile applications with low-cost manufacturing technique.

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