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Effect of PbS/CdS Nanoparticles Concentration on Mechanical Properties of PVDF-Based Composites

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Abstract

The aim of this study is to investigate the effect of PbS/CdS nanoparticles concentration on the mechanical properties of polyvinylidene fluoride (PVDF)-based composites. For this purpose, nanocomposite samples with PbS/CdS nanoparticles at 1%, 3% and 5% concentrations were prepared and their tensile strength, Young's modulus and elongation at break were analyzed. The results show that at 1% nanoparticle concentration, the tensile strength increased by 12%, providing a significant improvement in mechanical properties. However, when the concentration increased to 3% and 5%, a decrease in mechanical performance of about 8% was observed due to agglomeration of nanoparticles and structural heterogeneity in the matrix. This study offers new perspectives for the optimization of PVDF-based nanocomposites and their effective use in industrial applications.

Keywords: PVDF, Nanocomposite films, PbS/CdS nanoparticles, Young's modulus, mechanical properties
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1. Introduction

Polyvinylidene fluoride (PVDF)-based nanocomposites have a wide range of applications in modern technologies due to their unique piezoelectric, dielectric and mechanical properties. These materials have attracted great interest in areas such as sensors, energy storage devices, flexible electronics and biomedical applications [2]. The mechanical strength and elasticity of PVDF can be significantly improved by

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the addition of nanoparticles, which makes its use in functional applications more effective [10]. The integration of nanoparticles into polymer matrices not only increases the mechanical strength, but also optimizes properties such as thermal stability and electrical conductivity [16]. In recent years, various nanoparticles have been widely studied to improve the properties of PVDF-based composites. For example, carbon nanotubes (CNTs) and graphene oxide have been effective in enhancing the mechanical strength and electrical conductivity of PVDF [3,15]. Nanoparticles such as TiO2 and ZnO have improved the mechanical properties of PVDF as well as its functionality for sensing and energy harvesting applications [11,14]. Materials such as silica (SiO2) and BaTiO3 have also been used to enhance the mechanical strength and biocompatibility of PVDF-based composites [1,8]. However, these studies have focused on the more studied nanoparticles, and semiconducting nanoparticles, especially lead sulfide (PbS) and cadmium sulfide (CdS), have been less studied in terms of their effects on mechanical properties in polymer matrices [6]. Although PbS and CdS nanoparticles have been studied for their optical and electronic properties, there is limited information on their effects on mechanical properties in polymer matrices [12]. For example, PbS nanoparticles have increased mechanical strength in polystyrene matrices [4], while CdS has improved both mechanical and thermal properties in PMMA [9]. However, the effect of these nanoparticles on the mechanical properties in PVDF matrix, especially how their concentration affects these properties, has not yet been studied in depth. Previous studies on the effect of nanoparticle concentration on mechanical properties have shown that strength increases at optimal concentrations, but properties deteriorate due to agglomeration at high concentrations [20]. To address this research gap, this study systematically analyzed the effect of PbS/CdS nanoparticle concentration on the mechanical properties of PVDF-based composites. The aim of the study is to evaluate the effects of PbS/CdS nanoparticles at different concentrations on mechanical strength, elasticity, and stiffness in PVDF matrix and to determine the optimal conditions for potential applications of these composites in fields such as sensors and energy storage.

2. Experimental Methodology

In this study, polyvinylidene fluoride (PVDF, Mw ≈ 534,000, Aldrich Chemistry) was used as the main polymer matrix. For the synthesis of PbS and CdS nanoparticles, lead acetate ($Pb(CH_3COO)_2$, 99%, Aldrich Chemistry), cadmium acetate ($Cd(CH_3COO)_2$, 99%, Merck), and sodium sulfide (Na_2S, 99%, Aldrich Chemistry) were obtained. Dimethylformamide (DMF, ≥99%, Merck) was used as the solvent for the preparation of the composites. All chemicals were used without further purification.

PbS and CdS nanoparticles were synthesized by chemical precipitation. For PbS, 0.02 mol $Pb(CH_3COO)_2$ was dissolved in distilled water (100 mL) and 0.02 mol Na2S solution (100 mL) was slowly added. The mixture was stirred at 60°C for 1 h with a magnetic stirrer (500 rpm). The resulting precipitate was separated by centrifugation (8000 rpm, 10 min), washed three times with distilled water and dried in a vacuum oven at 80°C for 12 h. CdS nanoparticles were synthesized in a similar manner: 0.02 mol $Cd(CH_3COO)_2$ was dissolved in distilled water, 0.02 mol Na2S was added and stirred at 60°C for 1 h. The precipitate was separated and dried in the same manner.

PVDF-based nanocomposites were prepared by solvent casting. PVDF was dissolved in DMF at a concentration of 10% (w/v) and stirred at 60°C for 4 h with a magnetic stirrer (600 rpm). PbS and CdS nanoparticles were added in different proportions (1%, 3%, 5%) relative to the PVDF mass. The mixture was dispersed for 30 minutes using an ultrasonic homogenizer (Sonics Vibra-Cell, 500 W, 20 kHz, 70% amplitude). Then, the solutions were poured onto glass plates and dried in a vacuum oven at 80°C for 12 hours. The obtained films were approximately 0.1 mm thick.

The surface morphology of the nanocomposites was examined using a scanning electron microscope Zeiss Auriga (Germany) to analyze the dispersion and size of the nanoscale titanium oxide particles in the polymer matrix. Scanning was performed at an accelerating voltage of 30 kV

Tensile tests of the nanocomposites were carried out in displacement control mode, using a Zwick/Roell Z010 (Zwick/Roell GmbH, Germany) according to the UNI EN ISO 527-2 standard. For tensile measurements, 1BA type samples were used. A contact extensometer with a base length of 30 mm was used to determine Young's modulus.

Tensile strength, strain at break, and Young's modulus were calculated from the stress–strain curves. The measurements were performed at room temperature, at least five samples were tested for each sample group, and the results are presented as mean values and standard deviations. Samples intended for mechanical characterization were cut from films prepared in the form of sheets with a thickness of 100–200 µm. The mechanical properties of the nanocomposites were measured with a universal testing machine (Instron 5567). The tensile test was performed according to the ASTM D638 standard. The samples were stretched at a speed of 5 mm/min, and 5 samples were tested for each concentration. The average values and standard deviations were statistically calculated. All experiments were repeated at least three times to ensure reproducibility of the results.

3. Results and Discussion

Figure 1 shows the surface morphology of the PVDF+PbS/CdS nanocomposite at 3,000x magnification, revealing bright spots. The distinct PbS/CdS particles embedded in the polymer matrix indicate a relatively uniform distribution, which is beneficial for enhancing the composite's properties.

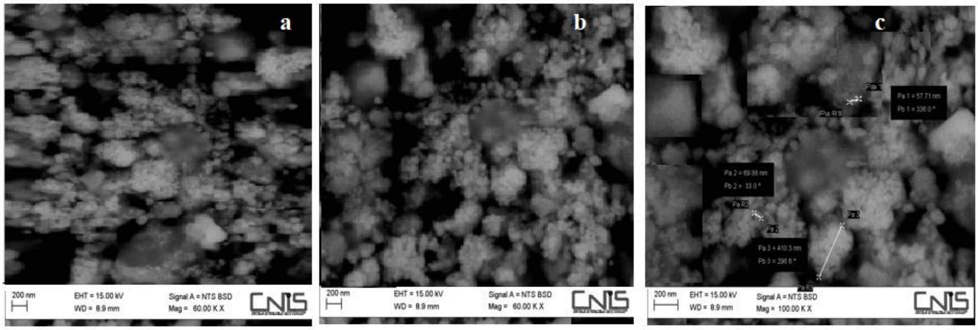

Figure 1. SEM images of PVDF+PbS/CdS nanocomposites a-1%, b-3%. C-5%.

In this study, the stress-strain diagram of PVDF-based nanocomposite materials was investigated. PbS/CdS nanoparticles were added to the composite samples at different concentrations (1%, 3% and 5%) and the mechanical properties of the obtained samples were experimentally studied.

For this purpose, stress-strain diagrams were drawn for each sample and a comparative analysis was performed (Figure 2). In the pure PVDF sample, the maximum stress was approximately 30 MPa, and the relative elongation was ~20%. This result indicates that PVDF has a high elastic capacity. In the nanocomposite sample containing 1% PbS/CdS, the maximum stress increased to ~36 MPa, but the elongation value decreased to 10%. This indicates that the nanoparticles were homogeneously distributed in the matrix and increased the strength of the material. In the sample with 3% PbS/CdS added, the stress decreased slightly and stabilized around 30 MPa, and the elongation was ~7%. This can be explained by the fact that the particles

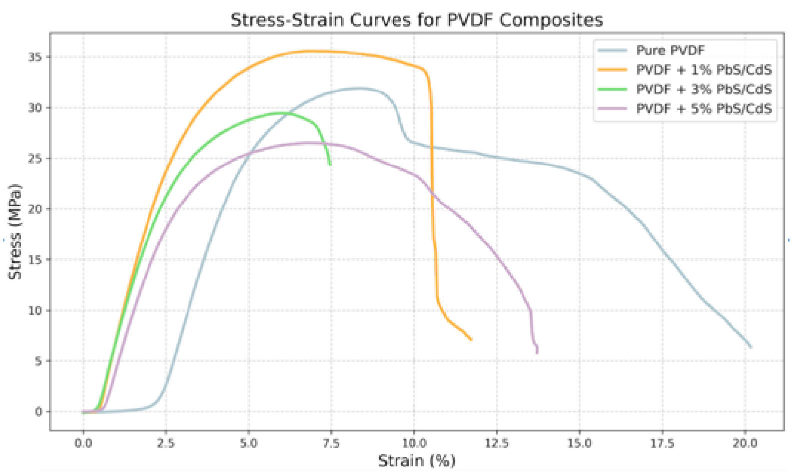

Figure 2. Stress-strain diagram of PVDF and PVDF + (1%, 3%,5%) PbS/CdS composites

have already started to agglomerate somewhat. In the 5% PbS/CdS composite, the maximum stress was recorded at 25–26 MPa and the strain was even lower (~6.5%). This is associated with the fact that the high concentration of nanoparticles aggregates with each other, causing cracks and weak spots. In conclusion, the analysis of the stress-strain diagrams showed that the concentration of 1–3% PbS/CdS in the PVDF matrix is optimal for improving the mechanical properties. However, concentrations above 5% lead to a decrease in the strength of the material.

The tensile stress (TS), Young's modulus (YM) and elongation at break obtained as a result of the experiments are summarized in Table 1. As can be seen from the table, the addition of PbS/CdS nanoparticles to the PVDF matrix had a significant effect on the mechanical properties of the composites. In particular, at a concentration of 1%, maximum tensile strength and Young's modulus were observed.

Table 1.

Sample	**Tensile strength (MP)**	**Young's modulus (GPa)**	**Elongation (%)**
Pure PVDF	31.89	1.12	841.33
PVDF +1% PbS/CdS	35.57	1.38	685.03
PVDF +3% PbS/CdS	29.44	1.23	602.05
PVDF +5% PbS/CdS	26.48	1.12	686.91

At concentrations of 3% and 5%, a decrease in the elongation of the material and a relative weakening of the tensile strength were observed. These changes are associated with the degree of dispersion and agglomeration tendency of the nanoparticles.

Experimental results have shown that the addition of PbS/CdS nanoparticles to the PVDF matrix has a significant effect on its mechanical properties. The obtained stress-strain diagrams show that the tensile strength and Young's modulus increased at 1% and 3% PbS/CdS concentrations. This is associated with the homogeneous dispersion of nanoparticles in the matrix and the increase in the load transfer effect at the particle-matrix interface [21, 22]. The maximum tensile strength observed in the 1% PbS/CdS composite indicates that this concentration creates an optimal reinforcement effect. Previous studies have also shown that the addition of nanofillers at low concentrations significantly improves the mechanical properties of the polymer matrix [21, 24]. In contrast, a decrease in both tensile strength and strain values was observed in the sample with 5% PbS/CdS added. This is explained by the agglomeration and crack nucleation of high-concentration nanoparticles [23, 25]. These results are also consistent with the trends noted by other authors in PVDF and other polymer systems [26-28].

In particular, a significant increase in tensile stress and Young's modulus was observed at a concentration of 1% PbS/CdS, which was explained by the effective dispersion of the particles in the PVDF matrix. Although the reinforcing effect was preserved to some extent at a concentration of 3%, a decrease in the degree of elasticity occurred. In the sample containing 5% PbS/CdS, an overall weakening of the mechanical properties was observed due to agglomeration and weak interface.

4. Conclusion

In this study, the effect of adding PbS/CdS nanoparticles to the PVDF polymer matrix at different concentrations on the mechanical properties was studied. The results obtained showed that the addition of nanoparticles to the polymer significantly improves the tensile strength and elastic modulus of the material.

The results show that the mechanical properties of PVDF-based nanocomposites can be effectively improved when the optimal concentration of PbS/CdS nanoparticles is in the range of 1–3%. This study provides an important scientific basis for the development of more functional and robust polymer nanocomposites in the future.

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