INVESTIGATION OF INFRARED AND RAMAN SPECTRA OF POLYMER NANOCOMPOSITES BASED ON POLYCRYSTALLINE SILICON NANOPARTICLES

A.E. SURKHAYLI, H.A. SHIRINOVA, B.G. PASHAYEV, A.H. KARIMOVA, S.G. NURIYEVA, L.R. GAHRAMANLI
Baku State University, Faculty of Physics
E-mail: h.shirinova@bk.ru mob:0515920078

In the presented work, PVC+Si polymer nanocomposites were prepared and the structure of the obtained nanocomposites was studied via microscopic and spectroscopic techniques. The SEM analysis confirmed that the morphology of the nanocomposite is not smooth and that defects, cracks, and roughness appear in the structure of the polymer with the addition of nanoparticles. XRD studies confirmed that the PVC+Si system has an amorphous structure. A comparison of absorption spectra of pure PVC and PVC+Si nanocomposite in the infrared region showed that there are weak physical interactions between PVC polymer and Si nanoparticles. The Raman spectrum provides proof that the silicon nanoparticles have been effectively incorporated into the PVC matrix, where they are interacting and establishing the bonding features of the silicon-based structure. The proper dispersion and interaction of the silicon nanoparticles with the polymer depend on this interaction.

Keywords: Raman scattering, IR spectroscopy, polyvinyl chloride, silicon nanoparticles
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INTRODUCTION

Polymer nanocomposites have attracted great interest in science due to the significant improvement of their properties with the addition of tiny amounts of nanoparticles compared to traditional composite systems. The slight addition of nanoparticles considerably enhances the properties of polymers and, in some cases, leads to a unique combination of rare and specific characteristics. Polymer materials are widely used in various optoelectronic applications such as optical fibers, optical waveguides, and optical storage systems due to their lightweight, high elasticity, low production temperature, and cost efficiency [1-2]. Among polymers, polyvinyl chloride (PVC) is considered one of the main thermoplastic polymers, along with other commercially important polymers like polyethylene and polystyrene [3]. At the same time, PVC is one of the most widely produced synthetic polymers globally, ranking among the top due to its broad application areas and its acceptance as an indispensable material that is inexpensive and recyclable [4-5]. Literature reviews indicate that PVC is also the second-largest polymer produced worldwide by volume, commonly used in products such as flooring, blood bags, bottles, cables, packaging, medical tubing, credit cards, and artificial leather [6].
Additionally, PVC is used in various sectors of industry, as well as in different applications due to its antibacterial properties. Many studies have focused on the incorporation of photocatalysts into PVC to investigate photodegradation mechanisms. This is related to PVC's ability to degrade easily and prevent the formation of dioxins under natural conditions [7]. Recent research in the field of PVC modification with nanoparticles shows that further enhancement of this material's properties makes it suitable for a wide range of technological applications. Furthermore, as we know, silicon is one of the key elements due to its wide range of applications and many valuable properties. According to research, many limitations of modern electronic devices can be overcome through the integration of photonics with electronics. For this, silicon-based materials are widely used. Silicon is an essential element utilized in various optical functions such as light sources, amplifiers, waveguides, modulators, memory devices, and detectors [8]. In addition, the literature emphasizes the properties of nanoparticles, particularly materials that can be used as amplifying systems, in numerous articles. Among these materials are Si, C, Ge, and other nanostructures. Articles discussing the amplifying properties of Si nanostructures observed through Raman spectroscopy have been reviewed. Undoubtedly, every effort made to determine the mechanisms of radiation absorption, scattering, or emission enhancement is highly valuable, especially concerning energy production. Due to practical and economic reasons, particles in the range of approximately a hundred nanometers are important, as this size eliminates issues related to quantum confinement and momentum expansion [9]. Therefore, the synthesis and structural investigation of silicon-based polymer nanocomposites using various methods has garnered significant interest. Although many scientific studies have been conducted on silicon and PVC individually, there are still nuances that remain unclear and require further research, sparking the interest of scientists.

Considering these aspects, this research article utilizes silicon nanoparticles as an inorganic filler and PVC polymer as the matrix, and the Raman and infrared spectra of the resulting films were analyzed. From the literature, it is known that Raman spectroscopy provides valuable information about the chemical composition and structure of a sample. Silicon is widely used as a reference material for Raman spectroscopy due to its unique properties, highlighting the significance of this research. For PVC-based polymer nanocomposites, Raman spectroscopy is used to demonstrate how the addition of nanomaterials

131, H.Javid ave, AZ-1073, Baku
Institute of Physics
E-mail: jophphysics@gmail.com

affects the polymer's structure and molecular vibrations. Similarly, infrared (IR) spectroscopy is a widely applied analytical method for studying the molecular structure and composition of polymers and nanocomposites. The IR spectrum of PVC-based polymer nanocomposites reflects changes in the functional groups of the polymer due to the addition of nanomaterials to the polymer matrix. These changes depend on the composition of the nanocomposite, the type, and the amount of nanomaterial included.

MATERIAL

The PVC polymer used has a density of 1.4 g/cm³ and was produced by Iran's Petrochemical Company. The solvent used is high-purity tetrahydrofuran (THF) with a purity of 99.9%. The nanofiller is silicon with particle sizes of approximately 50 nm.
Silicon nanoparticles were synthesized by the thermal carbon reduction of silicon oxide. The nanoparticles obtained from rice husks were ground and dried, while the carbon materials were derived from lignocellulosic raw materials. The synthesis process was conducted in a Linn High Therm HT-1800-Vac furnace at 2100°C in the presence of silicon dioxide and carbon [10].

SYNTHESIS OF NANOCOMPOSITES

Polymer nanocomposites were obtained by combining mechanical stirring of solutions using a magnetic stirrer and hot pressing methods, where the mixture was intensively stirred for 1 hour until a homogeneous solution was achieved. PVC powders were dissolved in tetrahydrofuran (THF), an organic solvent, at room temperature, and then Si nanoparticles were added to the polymer solution. The resulting polymer and nanoparticle mixture was poured into Petri dishes and left for 24 hours to allow the solvent to evaporate. These billets were hot-pressed at the melting temperature of PVC under 10 MPa pressure and then cooled in water at room temperature to produce samples with a thickness ranging from 90 to 110 mkm and a diameter of 4 cm. The nanocomposite sheets were obtained with a nanoparticle concentration of 3%.

METHODOLOGY

The morphology of the samples was examined using a Vega Tescan microscope. X-ray diffraction (XRD) was performed at room temperature on a Rigaku Mini Flex 600 XRD diffractometer. In all cases, Cu Kα radiation was used, with a Cu X-ray tube operating at a current of 15 mA and a voltage of 30 kV. The samples were scanned in a 2θ angle range of 20°–70°. The IR spectra of the samples were recorded using an FT-IR Varian-3600 Excalibur Series spectrometer, which allows the recording of spectra in the range of 4000-400 cm^{-1}. The Raman spectra of the samples were obtained using a Renishaw inVia Raman Microscope.

RESEARCH

The SEM image of the PVC+3%Si nanocomposite is shown in Figure 1. Based on the SEM images, it is possible to gain an understanding of the morphology of the nanocomposite. The SEM analysis confirmed that the morphology of the nanocomposite is not smooth, that defects, cracks, and roughness appear in the structure of the polymer with the addition of nanoparticles.

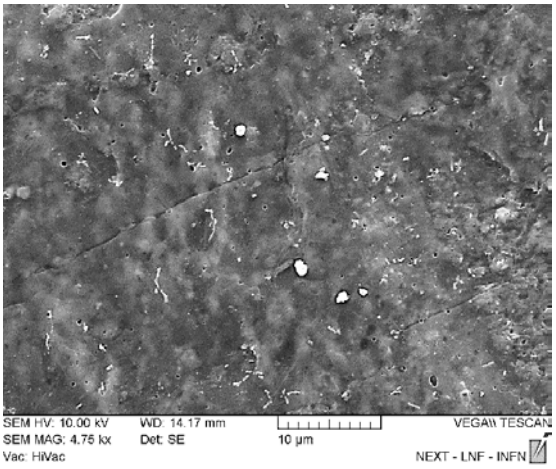

Fig. 1. SEM image of the surface of the PVC+3%Si nanocomposite.

Figure 2 demonstrates X-ray diffractogram of the PVC+3%Si nanocomposite. It is known that polyvinilcloride is amourphous polymer with reflaction pattern at 2θ ~18º, 24º and 40º. Furthermore, silicon nanoparticles characteristic XRD pattern located in the 28,46 º-60 º region of the 2theta value.

In Figure 3, the infrared (IR) spectra of pure PVC and PVC+3%Si polymer nanocomposite are presented. The peaks located in the range of 600-700 cm^{-1} in Figures 3a and 3b correspond to the vibrations of the C-Cl bond in the PVC polymer. The peaks corresponding to PVC in the frequency range of 1000-1100 cm^{-1} are associated with the vibrations of the C-C bond. Additionally, the peaks around 1250 cm^{-1} are attributed to the C-H bond near Cl, while the peaks around 1400 cm^{-1} are associated with aliphatic C-H bonds. The peaks depicted in the range of 2800-3000 cm^{-1} also characterize the vibrations of the C-H bond [11-14].

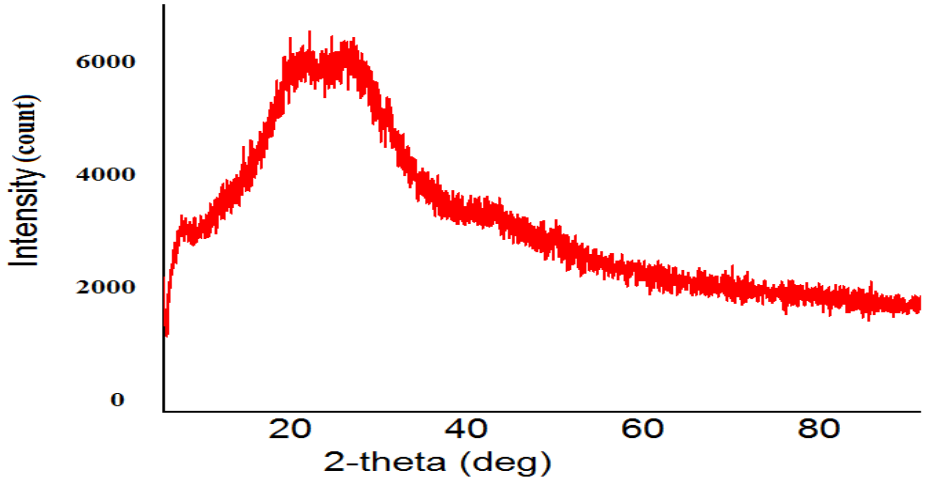

Fig. 2. X-ray diffractogram of the PVC+3%Si polymer nanocomposite.

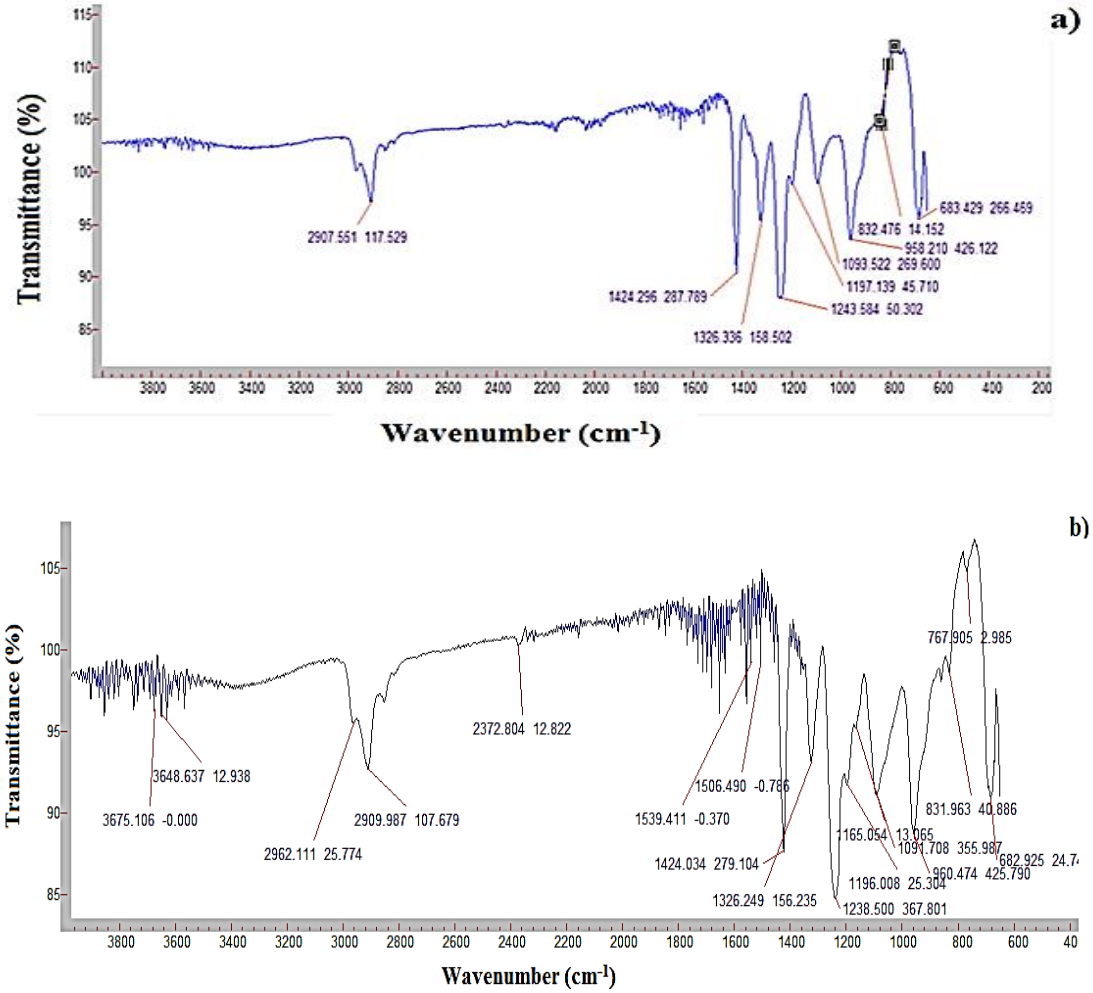

Fig. 3. IR spectra of pure PVC and PVC+3%Si nanocomposite: a) Pure PVC, b) PVC+3%Si

According to the literature review, characteristic peaks for silicon nanoparticles were observed at 670, 798, 808, 960, 1023, and 1100 cm^{-1}, corresponding to the vibrations of Si–C, Si–O, and Si–O–Si bonds, respectively. The peak at 1638 cm^{-1} is attributed to the O-H bond vibrations of physisorbed water molecules, indicating that these silicon nanocrystals are partially oxidized. Meanwhile, the peaks observed in the range of 1562 and 1296 cm^{-1} are associated with the C-O-C bond, the peak at 1424 cm^{-1} corresponds to the C-H bond, and the peaks around 3450 and 1630 cm^{-1} correspond to the SiO–H bond vibrations [15-18]. Comparison of absorption spectra of pure PVC and PVC+Si nanocomposite in the infrared region showed that there are weak physical interactions between PVC polymer and Si nanoparticles.

In Figure 4, the Raman spectra of PVC+3%Si nanocomposites at various frequency ranges are

presented. In Figure 4a, the spectra recorded in the low-frequency range of 250-2000 cm^{-1} are shown, while in Figure 4b, the spectra in the high-frequency range of 2200-3600 cm^{-1} are depicted. Upon examining the Raman spectra in the low-frequency range shown in Figure 4a, an intense peak is observed in the range of 500-600 cm^{-1}. According to the literature review, the peak observed around 520 cm^{-1} is primarily associated with Si-Si vibrations [19]. Additionally, it is known that vibrations corresponding to the C-Cl bond are also observed in the 500-600 cm^{-1} range. It is believed that the main peaks observed in this range are predominantly related to silicon, although the C-Cl bond vibrations also overlap in this region.

In Figure 4b, an intense peak is observed at 3100 cm^{-1} in the Raman spectra recorded in the high-frequency range of 2200-3600 cm^{-1}. The literature review indicates that these peaks correspond mainly to the spectral lines of the PVC polymer. Peaks observed in the Raman spectrum in the range of 3000-3200 cm^{-1} are most commonly associated with C-H bond vibrations. Specifically, they are characteristic of C-H bonds associated with sp^2 hybridized carbon atoms (aromatic or alkene). Additionally, this range may also be related to vibrations of sp C-H bonds, hydroxyl groups (O-H), or amines (N-H). O-H vibrations are observed as broad and more diffuse peaks in the range of 3200-3600 cm^{-1}. Furthermore, peaks corresponding to C-C vibrations are observed at 1200 cm^{-1}, while C-H bond vibrations are observed in the range of 1400-1500 cm^{-1}[20-23].

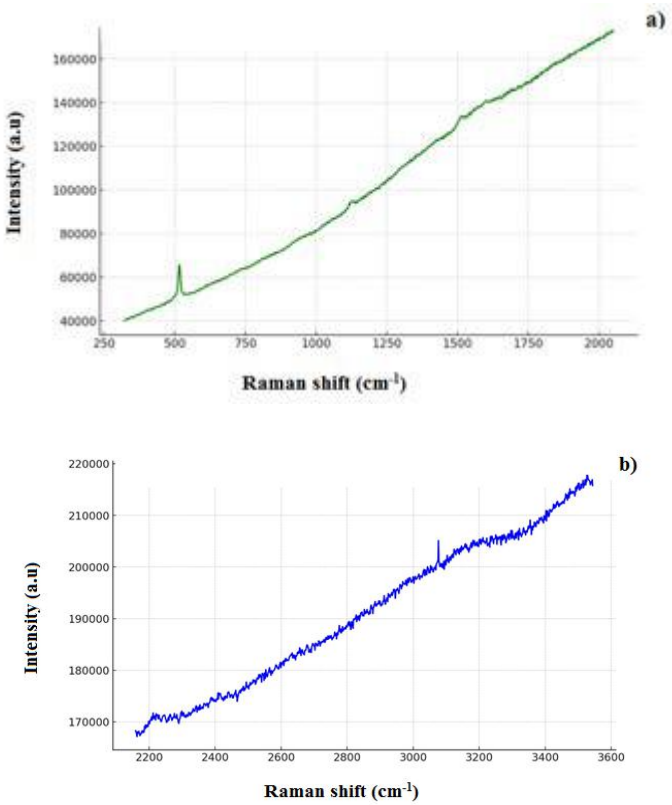

Fig. 4. Raman spectra of PVC+3%Si nanocomposite in low and high frequency ranges: a) Low frequency range (250-2000 cm^{-1}), b) High frequency range (2200-3600 cm^{-1})

CONCLUSION

The work that was presented involved the preparation of polyvinylchloride and silicon-based polymer nanocomposites. The morphology and structure of the final nanocomposites were examined using spectroscopic and microscopic methods. The SEM study verified that the inclusion of silicon nanoparticles causes flaws, fissures, and roughness to emerge in the polyvinylchloride structure, resulting in a non-smooth nanocomposite morphology. The amorphous structure of the PVC+Si system was verified by XRD investigations. The introduction between silicon nanoparticles and polymer matrix was investigated by Infrared and Raman spectroscopic methods. The infrared absorption spectra of the PVC+Si nanocomposite and pure PVC were compared, and the results indicated that the PVC+Si polymer and Si nanoparticles have weak physical introduction. The presence of Si nanoparticles embedded in the PVC matrix, interacting and producing bond properties of a Si-based structure, is confirmed by the Raman spectrum. Ensuring optimal dispersion and contact between the silicon nanoparticles and the polymer is contingent upon this interaction.

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