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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

STRUCTURE AND PHYSICAL PROPERTIES OF Si-PS AND Si-PVC POLYMER NANOCOMPOSITES

Specialty: 2206.01 – Molecular Physics

Field of science: Physics

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Baku – 2025

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GENERAL DESCRIPTION OF WORK

Relevance of the topic and the degree of its elaboration. With the rapid progress of nanotechnology, the development of novel polymer nanocomposites with advanced functional characteristics has become one of the priority directions in molecular physics and materials science. Polymer-based nanocomposites, particularly those modified with inorganic nanoparticles, are of great significance due to their numerous advantages, such as enhanced mechanical strength, thermal stability, optical transparency, and tunable conductivity, which open up broad prospects for practical applications. Thermoplastic polymers, which are widely employed in industry, are selected as the primary matrices owing to their stable chemical structure and favorable technological processability. Modification of these polymers with various functional nanoparticles results in the formation of composite structures that exhibit novel physical properties and, therefore, represent attractive research objects from the standpoint of multicomponent systems.[1]

The investigation of structure–property relationships in nanoparticle-modified polymer matrices is of particular importance, since nanoparticles play a decisive role both through quantum size effects and surface activity. The emergence of diverse interactions in such systems leads to structural transformations that exert a significant influence on their molecular properties. Hence, a comprehensive study of the morphological, structural, spectroscopic, thermal, and optical properties of nanocomposites, as well as a systematic analysis of how these properties depend on nanoparticle concentration, is of great scientific necessity. Structural modifications within nanocomposites, including phase transitions, can be effectively revealed by employing a variety of experimental methods. In molecular physics, the investigation of such multicomponent systems is of great importance, as it enables the elucidation of the relationship between the microscopic structure of matter

[1]Kurien, R.A. A comprehensive review on the mechanical, physical, and thermal properties of abaca fibre for their introduction into structural polymer composites / R.A.Kurien, D.P.Selvaraj, M.Sekar [et al.] // Cellulose, – 2023. Aug.; v. 30, № 14, – p. 8643-8664.

and its macroscopic properties.[2]

Over the past decade, the use of polymers modified with nanoparticles has expanded significantly across many industrial sectors. Among the polymers of practical importance and industrial relevance, polystyrene (PS) and polyvinyl chloride (PVC) occupy a special place. Both polymers are widely employed in various industries-including construction, automotive, electrical engineering, and medicine-owing to their high chemical and mechanical resistance, simple and cost-effective production technology, and ease of processing. Silicon (Si) nanoparticles, on the other hand, are widely utilized in electronics, photonics, sensor technologies, biomedicine, and energy storage systems due to their universal semiconductor characteristics, such as an optimal band gap, high melting temperature, and the ability to form a stable oxide layer on their surface. In this context, PS- and PVC-based nanocomposite materials modified with Si nanoparticles represent a highly relevant subject of investigation, both for fundamental scientific research and for industry-oriented applications.[3]

It should be emphasized that the investigation of the physical and physicochemical properties of polymer-based nanocomposite systems, as well as the study of the molecular mechanisms of structural formation and interaction processes occurring in such systems, holds great significance in molecular physics, physical chemistry, nanotechnology, and materials science. The entire set of physical and physicochemical characteristics of nanoparticle–polymer systems is determined by the interactions arising between the molecules (atoms) of the system's components, and explaining the mechanisms underlying the variation of these properties remains a considerable challenge. Although a substantial body of research has been conducted in this field, there is still a strong demand for further studies. PS and PVC have been the subject of intensive investigation for many years. However, certain

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[2]Guedri, A. Synthesis, characterization, structural, and optical properties of polyvinyl Chloride/Zinc oxide nanocomposite films for photocatalysis application / A.Guedri, M.Zaabat, B.Boudine [et al.] // Journal of Inorganic and Organometallic Polymers and Materials, – 2020. May; v. 30, № 12, – p. 4884-4894.

[3]De Souza Neto FN, Ferreira GR, Sequinel T, et al. Polymeric nanocomposites for automotiveapplication. Amsterdam: Elsevier eBooks, 2023, pp. 473–506. DOI: 10.1016/b978-0-323-91611-0.00009-8.

gaps and shortcomings persist in this direction. In particular, comparative studies on nanocomposites derived from both PS and PVC polymer matrices are scarcely represented in the literature. A review of scientific publications indicates the necessity for purposeful, systematic, and comprehensive research employing modern and informative methods. The present dissertation is devoted to this highly relevant problem-namely, the study of the structure and physical properties of PS- and PVC-based polymer nanocomposite materials modified with Si nanoparticles.

The object and subject of the research. The object of the research is polymer nanocomposite materials based on PS and PVC, modified with different concentrations of Si nanoparticles ($C'_{Si} = 1.5\%$, $C''_{Si} = 3\%$). The subject of the research is the analysis of the morphological, structural, spectroscopic, thermal, and optical properties of these nanocomposite materials from the perspective of molecular physics.

Purpose and objectives of the research. The main purposes of the dissertation was to obtain PS- and PVC-based polymer nanocomposite materials modified with Si nanoparticles, which possess wide application potential, and to carry out a comprehensive study of their structure and physical properties using modern experimental methods. The research also seeks to investigate the influence of certain external factors (such as concentration, temperature, etc.) on the studied systems, to determine the molecular mechanisms underlying these effects, and to achieve purposeful modification of the nanocomposite materials' properties in accordance with their potential application areas.

To achieve this goal, the following problems were solved:

– Development of the technology and determination of the optimal processing conditions for the fabrication of novel PS- and PVC-based polymer nanocomposites modified with Si nanoparticles;

– Investigation of the internal structure, surface morphology, and degree of nanoparticle dispersion within the polymer matrix using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as well as the crystalline structure, phase composition, and crystallite size using X-ray diffraction (XRD);

– Examination of the molecular structure and structural characteristics of the nanocomposites by infrared (IR) and Raman spectroscopy;

– Study of the thermal and thermodynamic properties through thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC);

– Determination of the kinetic and thermodynamic characteristics of thermal degradation;

– Investigation of the optical properties by spectroscopic ellipsometry.

Research methods. The research employed the following experimental methods: scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), infrared (IR) spectroscopy, Raman spectroscopy, thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and spectroscopic ellipsometry. Using these experimental techniques, the morphological, structural, spectroscopic, thermal, and optical properties of the studied samples were comprehensively examined.

Main provisions submitted for the defense.

1. Modification of the flexibility of the polymer chains resulting from the incorporation of Si nanoparticles into the PS and PVC polymer matrices.

2. Dependence of the thermal stability, thermal degradation rate, and glass transition temperature of Si-PS and Si-PVC polymer nanocomposites on the concentration of Si nanoparticles.

3. Structural characterization of Si-PS and Si-PVC polymer nanocomposites as a function of Si nanoparticle concentration.

4. Variation of the refractive index and extinction coefficient of Si-PS and Si-PVC nanocomposites with Si nanoparticle concentration.

5. Determination of the dependence of the refractive index of Si-PS and Si-PVC nanocomposites on the temperature–time regime of crystallization.

Scientific Novelty of the Research. For the first time in this study:

1. Based on the results of SEM, TEM, and XRD analyses, the internal structure, surface morphology, dispersion degree, crystalline structure, phase composition, and crystallite size of PS- and PVC-based polymer nanocomposites modified with Si nanoparticles were determined.

2. According to the results of IR and Raman spectroscopy, the mo-

lecular structure and structural features of the nanocomposites were investigated.

3. On the basis of TGA, DTA, and DSC data, the thermal and thermodynamic properties of the nanocomposites were comprehensively analyzed.

4. Using the Coats–Redfern method applied to the TGA experimental data, the kinetic and thermodynamic characteristics of thermal degradation (conversion degree, activation energy, Gibbs free energy of activation, enthalpy of activation, and entropy of activation) of the nanocomposites were determined.

5. According to spectroscopic ellipsometry results, the optical properties of the nanocomposites (refractive index and extinction coefficient) were systematically analyzed.

Theoretical and practical significance of the research. The synthesis of polymer-based nanocomposite materials, the investigation of their structure and physical properties, the acquisition of experimental data in such systems, and the determination and evaluation of polymer macromolecule conformations are critically important for the search for prospective new materials that are cost-effective, environmentally safe, and durable for long-term use. Such materials open new possibilities for practical applications in electronics, optoelectronics, sensors, protective coatings, and biomedical fields. Therefore, the research conducted in this dissertation holds both theoretical significance, from the perspectives of molecular physics and nanophysics, and certain practical relevance.

Approbation and application. The main provisions and results of the dissertation have been discussed and published in the materials of the following conferences: 1) Modern Problems of Physics and Astronomy, 2022, Baku State University, Baku; 2) 8th International Conference, Modern Trends in Physics, November 30 – December 01, 2023, Baku State University, Baku; 3) 3rd International Scientific and Practical Conference, Modern Directions and Movements in Science, October 26–28, 2023, №176, Luxembourg, Grand Duchy of Luxembourg; 4) Modern Problems of Physics and Astronomy, 2024, Baku State University, Baku; 5) 5th International Scientific and Practical Conference “Science and Education in Progress”, March 26 – 28, 2025, Dublin, Ireland.

The materials of the dissertation have been published in 6 articles (3 of which are indexed in Web of Science and Scopus databases, and 3 in national journals), 4 conference proceedings (1 international and 3 national), and 2 theses (international) in local and foreign journals.

The name of the institution where the dissertation was completed. The dissertation was carried out the Departments of Optics and Molecular Physics and Chemical Physics of Nanomaterials at Baku State University.

Structure, volume, and main content of the dissertation. The volume of the dissertation is 152 pages. The work, including 58 figures and 9 tables, consists of an introduction, 4 chapters, a conclusion, and also list of literature from 195 sources, a list of abbreviations and symbols. The total volume of the dissertation in symbols (excluding spaces in the text, figures, tables, graphs and the list of references) is 182 920 characters (including an introduction – 13 258 characters, chapter I – 50 887 characters, chapter II – 32 677 characters, chapter III – 54,958 characters, chapter IV – 29 293 characters, conclusion – 1 847 characters).

CONTENT OF THE WORK

The introduction explains the relevance of the topic, defines the objectives and scientific novelty of the study, highlights the main provisions presented for defense, provides information on local and international conferences where the research results were discussed, and demonstrates the scientific and practical significance of the dissertation, along with a brief summary of its chapters.

The first chapter is of a review nature and presents a concise summary of the work related to the microscopic, spectroscopic, optical, mechanical, and thermal properties of Si-PS and Si-PVC composite systems.

The second chapter is devoted to the synthesis technology of inorganic nanofillers and organic polymer-based nanocomposites, as well as a discussion of the research methods. This chapter details the selection of research objects and their synthesis technology, the investigation of the molecular structure of polymer nanocomposites using various experimental techniques-Scanning Electron Microscopy (SEM and TEM), X-ray Diffraction (XRD), Infrared (IR) and Raman Spectroscopy, Simultaneous Thermal Analysis (TGA, DTA, and DSC), and

Spectroscopic Ellipsometry-and also provides a detailed explanation of the determination of the kinetic and thermodynamic characteristics of thermal degradation.

In the third chapter, the Si-PS composite system is systematically studied in terms of its structure, interphase interactions, optical and thermal-physical properties, and kinetic and thermodynamic parameters, depending on the filler concentration and the temperature-time crystallization regime. EDS (SEM) analysis confirmed the high chemical purity of the Si nanoparticles. TEM images provided information on their size and morphology. It was found that the smallest Si nanoparticles range between 10–20 nm (Figure 1a). XRD analysis confirmed that the particles have a polycrystalline structure. The diffraction peaks observed at 2θ angles of 28.40, 47.20, 56.05, 69.10, and 76.30° correspond to the Miller indices [111], [220], [311], [400], [331], and [422], indicating a diamond-type crystal lattice (Figure 1b). Changes in the morphology of PS upon the incorporation of Si nanoparticles were also studied using SEM and TEM methods. As shown in Figure 2a, TEM images of the Si-PS composite system revealed interphase interactions between PS and Si and demonstrated the presence of physical contact, with clearly distinguishable polymer–filler boundaries.

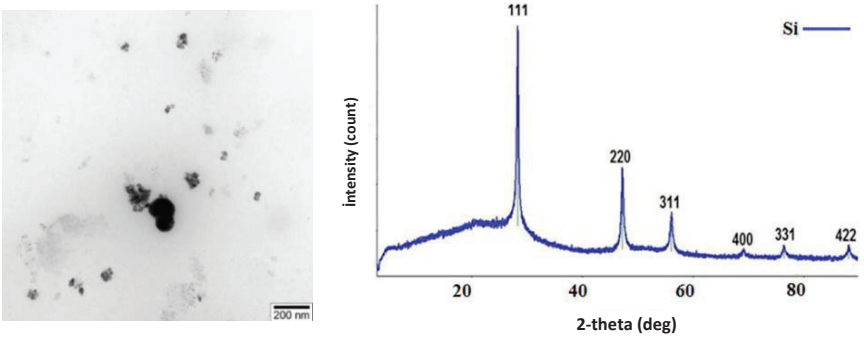
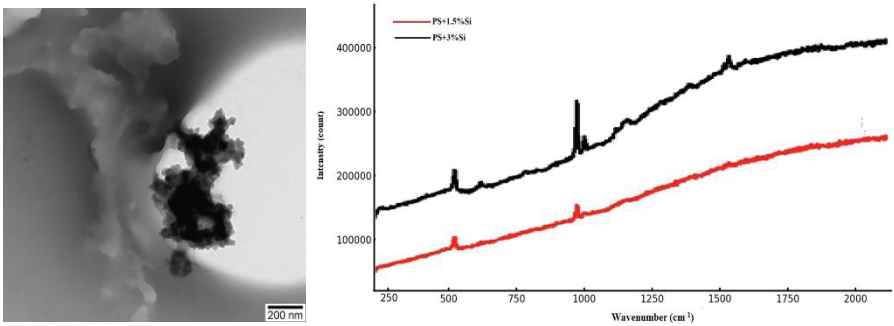


Figure 1. TEM (a) and XRD (b) images of pure Si nanoparticles



a) **b)**

Figure 2. TEM (a) and Raman spectra (b) of the Si-PS composite system

In Figure 2b, the Raman spectra of the Si-PS nanocomposite system at two different silicon concentrations (C'_{Si}=1.5%, C''_{Si}=3%) are presented. It is well known that spectroscopic methods allow for the determination of the molecular structure, chemical bonds, and interphase interaction characteristics of nanocomposite systems. Analysis performed in the 250–2000 cm^{-1} range using Raman spectroscopy revealed the molecular structural features and interphase interactions of the Si-PS system. The absorption band at 520 cm^{-1}, corresponding to the valence vibrations of the Si–Si bond, was observed. Polystyrene is composed of a main chain and phenyl side groups. The π-electrons of the phenyl ring generate strong signals in the Raman spectrum. With an increase in Si concentration from 1.5% to 3%, in addition to the 520 and 1001 cm^{-1} bands, new peaks at 1150 cm^{-1} (C–H stretching) and 1500 cm^{-1} (CH_2 bending) were recorded. The emergence of these new peaks confirms the nanoparticle–polymer interaction. It is assumed that these peaks arise due to induced dipoles in the polystyrene polymer, generated by the permanent dipole effect of silane groups present on the surface of the Si nanoparticles. Furthermore, in this chapter, the structure of the Si-PS composite system was also studied using FTIR and XRD methods. XRD analysis indicated that when polycrystalline Si is added to amorphous polystyrene, PS retains its amorphous structure. Measurements in the FTIR region revealed peaks at 694, 835, 905, and 1026 cm^{-1}, associated with the silane groups on the Si surface. It was confirmed that Si nanoparticles interact with the polymer matrix

only physically. The main absorption bands of the polystyrene matrix were observed at 3022, 2919, 2850, 1602, 1490, and 1450 cm^{-1}, corresponding to the vibrations of aromatic C–H and CH_2 groups and the stretching of C=C bonds. With increasing Si concentration in the polystyrene matrix, changes in the position, shape, and intensity of absorption bands in the FTIR spectrum are attributed to the conformational diversity arising from the polymer's atactic stereochemical structure and amorphous nature.

The concentration-dependent thermal properties of the Si-PS nanocomposite were studied using Simultaneous Thermal Analysis (TGA, DTA, and DSC). Figure 3 shows the mass–temperature curves for pure PS and the Si-PS nanocomposite, indicating that pure polystyrene loses 50% of its mass at 434.31°C and its entire mass at 462.5°C. In the Si-PS nanocomposite, the decomposition temperatures increase with the nanoparticle concentration. For Si(1.5%)-PS, $T_{s0\%}$ and $T_{son\%}$ were observed at 435.18°C and 442.12°C, respectively, while for Si(3%)-PS, they were 438.47°C and 481.85°C. This increase is explained by the fact that Si nanoparticles create a diffusion barrier within the polymer matrix, promote homogeneous heat distribution, and limit the release of pyrolytic products, thereby slowing down the decomposition process.

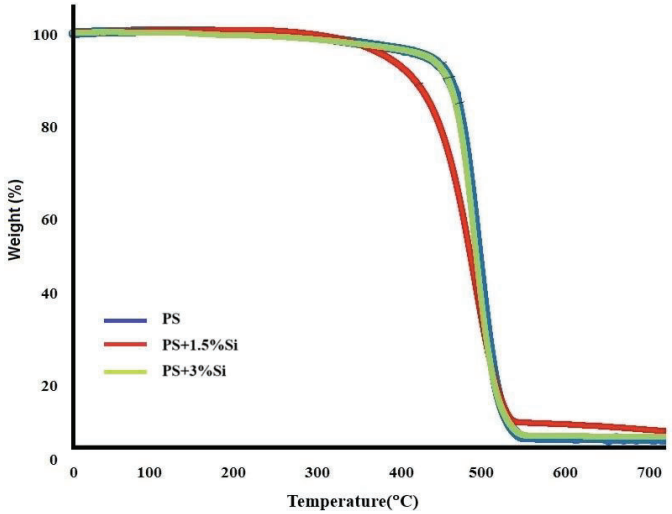


Figure 3. TGA curves of pure PS and Si-PS composite systems

DTA analysis also confirms that the addition of Si delays the degradation of PS. The maximum rate of thermal degradation of pure PS was -42.460 mg/min, whereas for the sample with 3% Si, this value decreased to -35.099 mg/min. This reduction is attributed to the nanoparticles restricting chain mobility, regulating heat transfer, and consequently enhancing the thermal stability of the material. DSC analysis further confirmed that with increasing Si concentration in PS, the glass transition temperature shifts toward higher temperature regions[4].

The thermal decomposition kinetics of PS and Si-PS composite samples were investigated using the Coats–Redfern method, and the dependence of the polymer's kinetic and thermodynamic parameters on the degree of conversion (α) was analyzed. As seen from the Ea(α) dependence shown in Figure 4a, the addition of Si nanoparticles led to a decrease in the observed activation energy compared to pure polystyrene. In the pure PS sample, a slight increase in activation energy is observed as the conversion degree increases, reaching a maximum value of 264.9 kJ/mol at α = 0.4. Subsequently, although the conversion degree continues to increase, the activation energy decreases. The fact that the thermal degradation of polystyrene does not proceed with a constant activation energy indicates that the energy required varies at different stages of the process.

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[4]Shirinova, H. Preparation, characterization and thermal properties of the PS+Si based polymer nanocomposites / H.Shirinova, A.Surkhayli, B.Pashayev [et al.] // Journal of Thermoplastic Composite Materials, – 2025. Sep.; v. 38, № 5, – p. 1785-1798.

a constant activation energy indicates that the energy required varies at different stages of the process. With the incorporation of Si nanoparticles, a reduction in activation energy is observed across all degrees of conversion. TGA results indicate that the inclusion of Si nanoparticles enhances the thermal stability of the nanocomposite. However, the decrease in activation energy may be related to a reduction in microkinetic barriers. Although the addition of Si nanoparticles confers higher thermal stability to the PS system at the macroscopic level, at the microscopic scale, the surface of the Si nanoparticles alters the mechanism of free radical formation that occurs during the thermal degradation of polystyrene.

When Si nanoparticles are incorporated into polystyrene, the silane groups on their surface partially alter the electron density of C–C and C–H bonds, generating an inductive effect and weakening the bonds. Notably, the effect of Si nanoparticles is most pronounced during the initiation stage of degradation. The primary changes observed upon the addition of Si occur at low degrees of conversion, i.e., during the initial stage of the process, which corresponds to the initiation phase of degradation. As the degree of conversion increases, the difference in activation energies decreases and approaches zero. Thus, Si nanoparticles primarily reduce the activation energy during the early stage of conversion due to the inductive interaction between the silane groups on the Si surface and the polystyrene matrix. This observation is consistent with the results obtained from Raman spectroscopy.

A similar trend is observed for the activation enthalpy. $\Delta H^{\#}$ remains positive in all cases, indicating that the process is endothermic; however, the presence of Si reduces the amount of heat required for the reaction to proceed. For pure PS, the maximum $\Delta H^{\#}$ is 259.09 kJ/mol at $\alpha = 0.40$, and the minimum value is 78.84 kJ/mol at $\alpha = 0.98$. When 1.5% Si nanoparticles are added, the maximum enthalpy decreases to 240.60 kJ/mol at $\alpha = 0.475$, and the minimum $\Delta H^{\#}$ is 95.27 kJ/mol at $\alpha = 0.98$. In the system containing 3% Si, the maximum $\Delta H^{\#}$ further decreases to 198.85 kJ/mol at $\alpha = 0.525$, while the minimum remains 78.97 kJ/mol at $\alpha = 0.98$. This behavior is explained by the increased ordering of the system and the restricted mobility of the polymer chain segments as the nanoparticle concentration rises (Figure 4b).

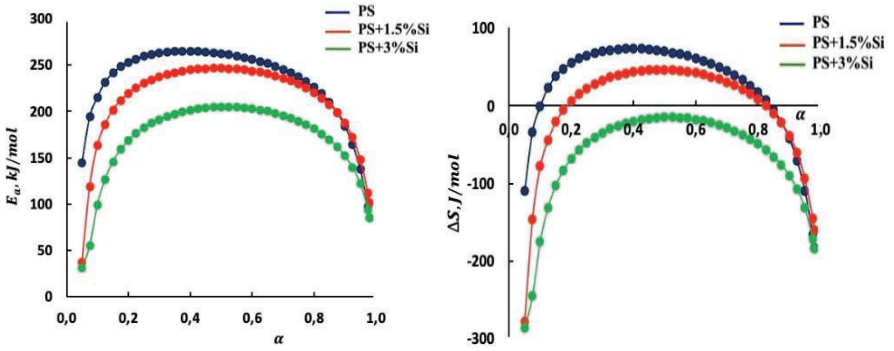

Figure 4. Dependence of Ea(α) (a) and $\Delta S^{\#}$(α) (b) for pure PS and Si-PS composite systems

For the sample with 1.5% Si, the minimum $\Delta G^{\#}$ is 207.49 kJ/mol at α = 0.625, and the maximum $\Delta G^{\#}$ is 214.40 kJ/mol at α = 0.98. When the Si concentration reaches 3%, the minimum $\Delta G^{\#}$ occurs at α = 0.45 with a value of 209.20 kJ/mol, and the maximum is 217.24 kJ/mol at α = 0.98.

For the Si-PS composite system, the refractive (n) and extinction (k) coefficients were studied in the 200–1200 nm range using spectroscopic ellipsometry. The analysis indicates that increasing the Si content in Si-PS nanocomposites from 1.5% to 3% results in only slight increases in the refractive and extinction coefficients in both the normal and anomalous dispersion regions.

This chapter also investigates the effect of different temperature–time crystallization regimes on the structure of the Si-PS system. SEM analysis shows that during slow cooling, more time is available for the polymer chains to reach thermodynamic equilibrium, resulting in a more ordered morphology. In contrast, samples obtained via rapid cooling exhibit heterogeneous structures, which is explained by the high cooling rate impeding the homogeneous distribution of Si nanoparticles among PS chains and preventing the formation of an ordered chain structure. XRD analysis further confirms that as the cooling rate increases, the fraction of the amorphous phase in the system also increases. TGA results indicate that the T_{50}% values for samples cooled in water and liquid nitrogen are very close (435.18°C and 433.29°C,

respectively) and are higher than those for the sample obtained under slow cooling (426.08°C). According to DSC analysis, the glass transition temperature (Tg) of the sample rapidly cooled in liquid nitrogen is higher, which is attributed to the restriction of chain mobility by the nanoparticles[5].

Kinetic and thermodynamic parameters of Si-PS composites synthesized under different temperature-time (TT) conditions were analyzed using the Coats–Redfern method, showing that the cooling rate significantly affects the material's stability and degree of structural ordering. Lower parameter values observed under slow cooling are associated with weaker interactions between polymer segments, which increase chain mobility and reduce the energy barrier. In this case, the structure is less stable; however, sufficient time is available for the molecules to reach thermodynamic equilibrium, so local ordering is partially preserved.

In the fourth chapter, the thermal and optical properties, structure, and thermal decomposition kinetics of the Si-PVC composite system were analyzed depending on the filler concentration and different TT conditions. Similar to the Si-PS system, the structure of the Si-PVC system was investigated using a series of microscopic and spectroscopic methods. SEM analyses of the Si-PVC system revealed that Si nanoparticles not only penetrate the polymer matrix but also form aggregates on the surface, altering its morphology. This behavior is associated with the partial crystallinity and polar nature of the polymer.

The structure of the Si-PVC composite system was further analyzed using X-ray diffraction, and the results are presented in Figure 5. XRD analysis confirms that PVC possesses an approximate crystallinity of 10%. Upon the addition of Si, the double peak observed around 20° broadens, indicating that the nanoparticles are located within the amorphous phase of the polymer and act as structural centers.

According to Raman spectroscopy, as the concentration of Si nanoparticles increases, the intensity of the characteristic bands observed in the 1100–1600 cm^{-1} range, which are specific to PVC, also increases.

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[5]Shirinova, H. Optimizing thermal behavior in HIPS/silicon nanocomposites: The role of cooling rates / H.Shirinova, A.Surkhayli, B.Pashayev [et al.] // Journal of Elastomers & Plastics, – 2025. Mar.; –p.1–17.

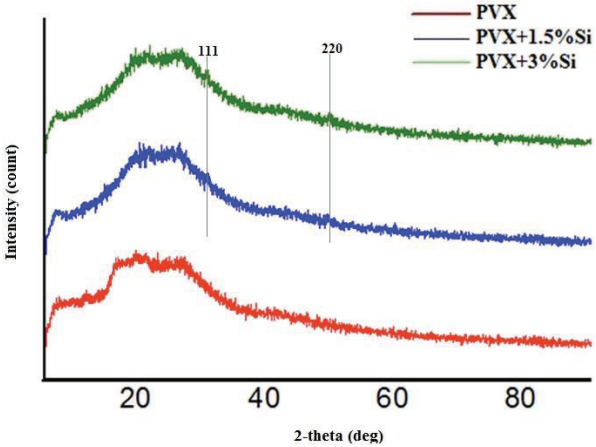

Figure 5. RD spectra of pure PVC and Si–PVC composite system

This indicates the presence of physical interactions between PVC and Si nanoparticles. To investigate the nature of these interactions more precisely, infrared spectroscopy was employed (Figure 6). When Si nanoparticles are incorporated into PVC, particularly in the 700–850 cm^{-1} region, noticeable changes are observed. At a concentration of 1.5% Si, a sharp absorption band corresponding to the deformation vibrations of the C–Cl bond is recorded at 730 cm^{-1}. This is related to chain flexibility and suggests that the polymer chain remains elastic. However, when the Si concentration reaches 3%, the intensity of the absorption band at 730 cm^{-1} decreases, while a new absorption band appears at 840 cm^{-1} corresponding to the stretching vibrations of the C–Cl bond. These changes demonstrate that the Si nanoparticles reduce chain flexibility and enhance the rigidity of the C–Cl bonds. Since IR spectroscopy is sensitive to dipole-dipole interactions, it is assumed that polar silane groups on the surface of Si nanoparticles interact predominantly with the polar –C–Cl bonds of PVC through dipole–dipole, i.e., orientation-type interactions.

In addition, the concentration-dependent thermal properties of the Si–PVC composite system were investigated, and it was found that the incorporation of Si nanoparticles and the subsequent increase in their concentration enhance the thermal stability. Specifically, in the initial decomposition stage, the temperature corresponding to 50% mass loss for pure PVC is 318.14°C, while for the final decomposition stage it is

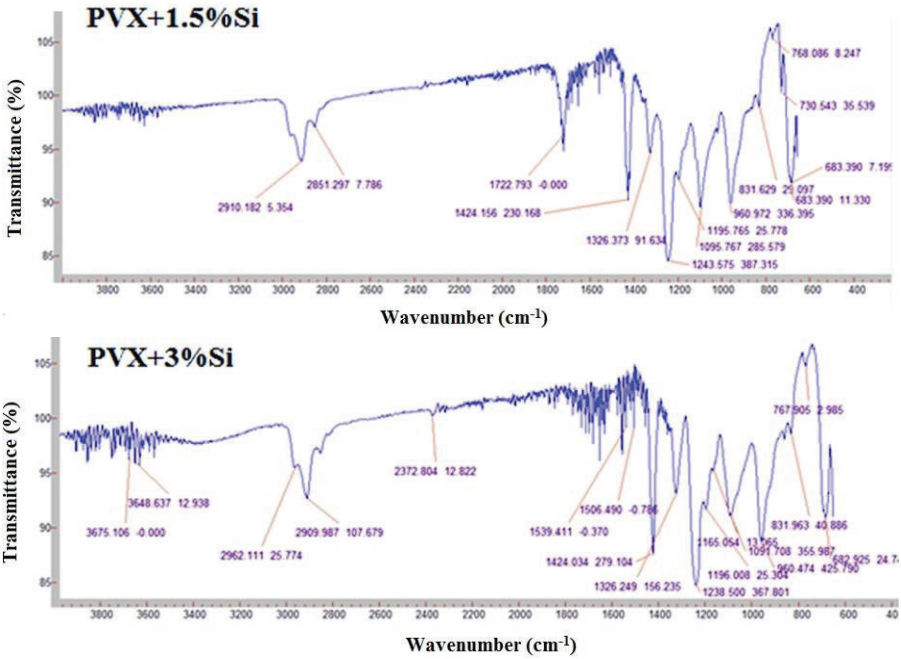

Figure 6. IR spectra of the Si–PVC composite system

490.45°C. The addition of 1.5% Si increases the T_{50}% temperature by approximately 60°C, reaching 547.52°C. This delays the degradation of the main polymer backbone, causing decomposition to occur at higher temperatures. This effect is attributed to the homogeneous heat distribution provided by Si nanoparticles and the reduction of free volume. However, at 3% Si concentration, aggregation occurs, which lowers T_{50}% to 513.39°C. This phenomenon is associated with the formation of clusters due to the polar and partially crystalline structure of PVC as the nanoparticle concentration increases. DTA results confirm that, while the maximum rate of thermal degradation for pure PVC is –15.685 mg/min, it decreases to –10.578 mg/min and –12.315 mg/min for samples containing 1.5% and 3% Si, respectively (Figure 7). In the second stage, however, the maximum degradation temperature and rate remain nearly unchanged (447–451°C and 4–6 mg/min), since this stage is primarily associated with the decomposition of the polymer backbone, where the influence of Si nanoparticles is minimal. DSC analysis further reveals that the glass transition temperature of pure

PVC is 73°C, whereas for the 3% Si sample it increases to 87°C. This shift is explained by the restricted mobility of polymer chains and the enhanced structural rigidity induced by the nanoparticles[6].

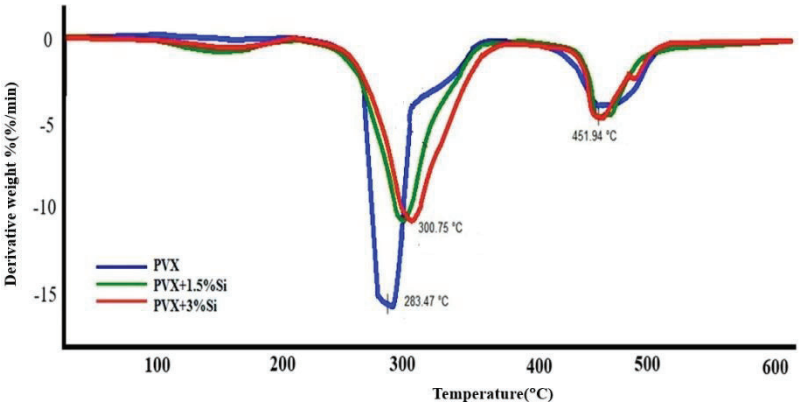

Figure 7. DTA curves of pure PVC and the Si–PVC composite system

Kinetic analyses conducted for the Si–PVC composite system reveal that, in the case of pure PVC, the activation energy reaches its maximum value of 271.99 kJ/mol at a conversion degree of $\alpha = 0.050$. Similar to the Si–PS system, a reduction in the calculated activation energy is also observed for the Si–PVC nanocomposite compared to the neat polymer. This indicates that although thermal stability increases at all concentrations, the degradation process becomes kinetically more favorable at lower concentrations. The most pronounced difference between the activation energies of PVC and Si–PVC nanocomposite is observed at low conversion values, while beyond $\alpha = 0.6$ the difference completely disappears. It is well known that, at low conversion degrees, the primary degradation of PVC is associated with dehydrochlorination. It is assumed that the silane groups on the surface of silicon nanoparticles polarize the C–Cl bond, thereby facilitating HCl elimination and leading to the observed decrease in the activation energy corresponding to this stage.

[6]Shirinova, H.A., Surkhayli, A.E., Pashayev, B.G. Fabrication, characterization and thermal properties of PVC+Si based polymer nanocomposites // Composite Interfaces, – 2025. Feb.; – p. 1-16.

The activation enthalpy ($\Delta H^{\#}$) follows the same trend. In contrast, the Gibbs free energy ($\Delta G^{\#}$) exhibits no significant dependence on the degree of conversion. Regarding entropy ($\Delta S^{\#}$), pure PVC shows a high positive value of 178.70 J/mol·K at α = 0.050, which decreases sharply as the reaction progresses, reaching –358.16 J/mol·K at α = 0.700. For the samples with 1.5% and 3% Si, the maximum $\Delta S^{\#}$ values were –164.62 and –148.56 J/mol·K, respectively, while the minimum values were –339.58 and –329.02 J/mol·K.

In the energy dependence of the refractive index, anomalous dispersion was observed near the absorption edge for nanocomposites prepared at both concentrations. In this spectral region, the refractive index of the Si(1.5%)–PVC nanocomposite was determined to be n = 1.665, while that of the Si(3%)–PVC nanocomposite was n = 1.655. In the case of the Si(3%)–PVC nanocomposite, light scattering occurs not in a homogeneous optical medium but in regions with locally varying density, due to the defects introduced into the supramolecular structure of the polymer by the filler. This leads to a decrease in the effective optical density and, consequently, to a reduction in the refractive index.

The extinction coefficient, however, exhibited a different trend with increasing concentration, showing an increase in both the normal and anomalous dispersion regions (Figure 8). All these results can be attributed to the intensified aggregation at 3% concentration, reduced dispersity, and the formation of defects in the supramolecular structure of the polymer within the Si–PVC composite system.

The Si–PVC composite samples were investigated under different cooling modes. SEM images reveal that slow cooling leads to a more ordered and compact structure. The structure of the Si–PVC composite system obtained under different cooling modes was also studied by XRD. In the slow-cooling regime, the diffraction peaks appear sharper, while broader diffraction patterns are observed for water- and liquid-nitrogen-cooled samples. With increasing cooling rate, the fraction of the amorphous phase in PVC increases, since, according to free-volume theory, Si nanoparticles fill the interchain voids, thereby reducing free volume and restricting molecular mobility. Consequently, under slow- and water-cooling modes, chain segments are able to overcome kinetic barriers, adopt more stable conformations, and arrange themselves in a more ordered fashion.

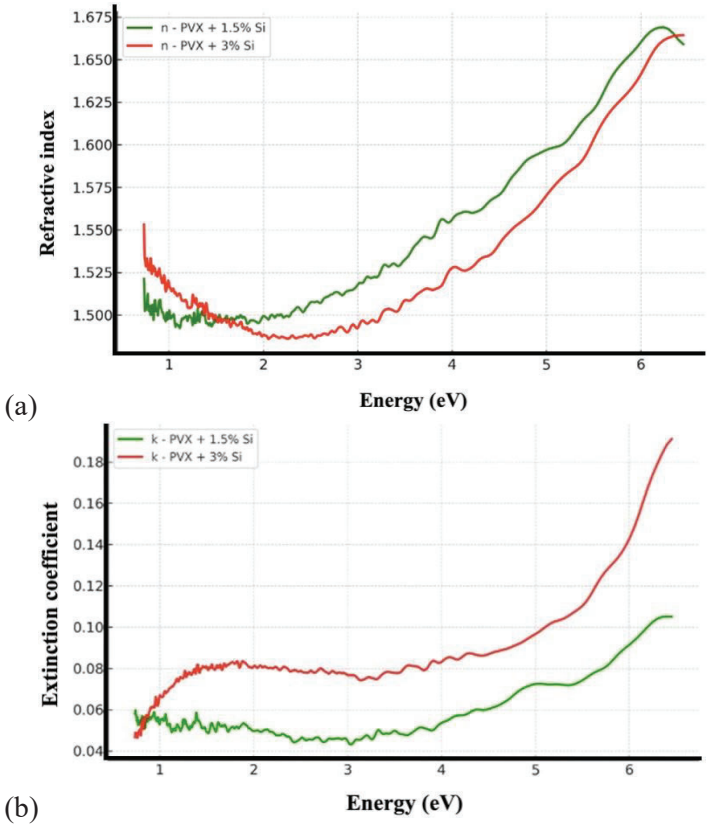

Figure 8. Dependence of the refractive index (a) and extinction coefficient (b) on incident photon energy for the Si–PVC composite system

The thermal properties of the Si–PVC system under different cooling modes were also examined. TGA results show that the highest thermal stability is achieved in the water-cooled sample: the temperature corresponding to 50% mass loss is 329.3°C, and the final decomposition temperature is 547.52°C. For liquid-nitrogen cooling, the corresponding values are 313.4 and 484.85°C, while for slow cooling they are 320.5 and 481.29°C. According to DTA analysis, the maximum degradation rate in the water-cooled sample is –10.578 mg/min, whereas in the liquid-nitrogen-cooled sample it is higher, –13.645 mg/min. This behavior is attributed to the inability of polymer chains to fully relax during rapid cooling, leading to their instantaneous stabilization. In contrast, in the slow-cooling regime, the maximum de-

gradation rate is –7.545 mg/min, and in the second stage the process proceeds more slowly (–4.5 mg/min) and in a more stable manner.

The glass transition temperature (Tg) and phase transition characteristics of the Si–PVC composite system synthesized under different cooling modes were studied by DSC analysis, and the results are presented in Figure 9. The measurements show that the Tg of the Si–PVC nanocomposite varies significantly depending on the cooling regime. Specifically, the glass transition temperature is 83°C for the nanocomposite obtained under slow cooling, 85°C for the water-cooled sample, and 98°C for the system cooled in liquid nitrogen. Similar to the PS-based composites, the highest Tg in the Si–PVC nanocomposite is observed for the liquid-nitrogen-cooled sample. In contrast, for PVC-based nanocomposites, the Tg values of the water-cooled and slow-cooled samples are very close to each other. The Tg depends on the chemical composition and chain structure of the polymer. Since PS is completely amorphous, the Tg values of the samples obtained under slow- and water-cooling modes differ markedly. However, because PVC is partially crystalline, this difference is considerably smaller.

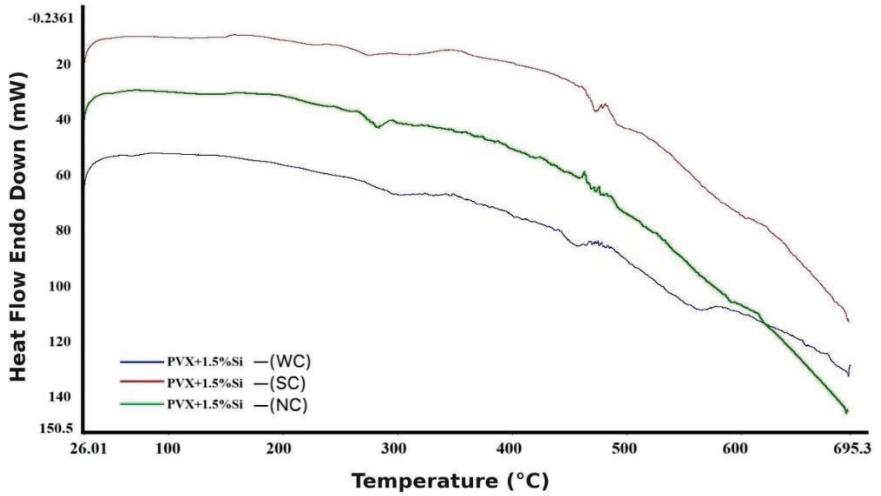

Figure 9. DSC curves of the Si–PVC composite system synthesized under different cooling modes

The thermal degradation of Si–PVC composite samples obtained under different cooling modes was investigated using the Coats–Redfern method, and the kinetic parameters were calculated. The highest activation energy was observed for the water-cooled samples. This behavior is associated with stronger interactions between polymer chains and the restriction of molecular mobility. In this case, Si nanoparticles are distributed homogeneously but do not play a major structuring role; instead, the dominant interactions arise among polymer segments themselves. For the slow-cooled samples, polymer chains are arranged more regularly around Si nanoparticles, forming localized crystalline regions, whereas rapid quenching in liquid nitrogen results in an amorphous and disordered structure.

Figure 10 presents the dependence curves of $\Delta G^{\#}(\alpha)$ and $\Delta H^{\#}(\alpha)$ for the Si–PVC composite system. As seen from the graph, the optimal molecular structure is formed during water cooling, which is confirmed by both the higher activation energy and enthalpy ($\Delta H^{\#}$). According to the $\Delta G^{\#}$ analysis, its relatively lower values under slow cooling indicate reduced system stability, whereas the higher $\Delta G^{\#}$ values in water- and liquid-nitrogen-cooled samples demonstrate the formation of more stable structures. The entropy parameter ($\Delta S^{\#}$) shows the lowest values under slow cooling, reflecting a more ordered internal structure. In contrast, under water and liquid nitrogen cooling, $\Delta S^{\#}$

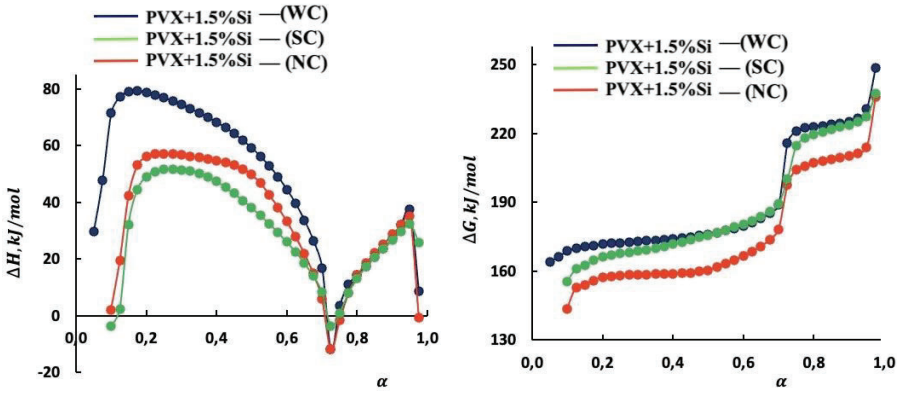

Figure 10. Dependence of $\Delta H^{\#}(\alpha)$ and $\Delta G^{\#}(\alpha)$ on the degree of conversion for the Si–PVC composite system synthesized under different cooling modes

exhibits higher values. In particular, in the liquid-nitrogen regime, this effect is attributed to the partial disruption of the existing crystalline phase due to rapid cooling.

Spectroscopic ellipsometry analysis shows that, depending on the cooling regime, the highest refractive index of the Si–PVC system is observed in the liquid-nitrogen-cooled samples. This phenomenon is related to the molecular structure of PVC, since during rapid cooling the dipole–dipole interactions of C–Cl bonds are enhanced, chain segments are compacted through electrostatic attraction, and the local optical density increases. As a result, the refractive index rises. Conversely, the extinction coefficient is lower in this case, because the dense and homogeneous structure reduces light absorption and scattering, thereby improving optical transparency. Under slow cooling, however, the chains undergo relaxation, and irregular transitions form between local crystalline and amorphous regions. This heterogeneity impedes light propagation, increases internal losses, and raises the extinction coefficient.

CONCLUSIONS

1. Polymer nanocomposite materials based on PS and PVC, modified with Si nanoparticles at different concentrations (C'_{Si} = 1.5%, C''_{Si} = 3%) and synthesized under various crystallization temperature–time (CTT) regimes (rapid quenching in liquid nitrogen, cooling in water at 0°C, and slow cooling in air), were obtained.

2. SEM, TEM, and XRD studies revealed that Si nanoparticles penetrate into the bulk of the PS and PVC polymer matrices, leading to the formation of effective interfacial interactions at the polymer–nanoparticle boundary.

3. Investigations conducted by IR and Raman spectroscopy demonstrated that Si nanoparticles induce different types of interactions with the polymers: induction-type interactions with the PS matrix and orientation-type interactions with the PVC matrix, owing to the presence of silane groups on the nanoparticle surface.

4. Results of synchronous thermal analysis showed that increasing the concentration of Si nanoparticles enhances the thermal stability of Si-PS and Si-PVC nanocomposites, reduces the degradation rate, and

raises the glass transition temperature. The dispersed nanoparticles restrict the release of volatile products during pyrolysis, thereby slowing down the degradation process.

5. Using the Coats–Redfern method, the kinetic and thermodynamic parameters (α, E_a, $\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$) of Si-PS and Si-PVC nanocomposites were calculated. Analysis of the dependencies indicated that incorporation of Si nanoparticles into the polymer matrices leads to a more structured system. However, this effect is nonlinear with respect to concentration: it reaches a maximum at 1.5% Si, but diminishes at 3% due to aggregation phenomena.

6. Spectroscopic ellipsometry results demonstrated that, in both normal and anomalous dispersion regions, the refractive index of the Si-PVC nanocomposite exhibits a stronger dependence on Si nanoparticle concentration compared to the Si-PS system. Furthermore, the dependence of the refractive index on the crystallization temperature–time regime was established: the Si-PS nanocomposite quenched in liquid nitrogen exhibited the lowest refractive index, whereas the Si-PVC nanocomposite obtained under the same conditions showed a comparatively higher refractive index.

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The defense will be held on **29 October 2025** at **15^{00}** at the meeting of the Dissertation council ED 2.19 of Supreme Attestation Commission under the President of the Republic Azerbaijan operating at the Baku State University.

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Abstract was sent to the required addresses on 22nd september 2025.

Signed for print: 17.09.2025
Paper format: 60×84 1/16
Volume: 35 147 characters
Number of hard copies: 20 units