Research Article

Synthesis and Characterization of Ag_2S Layers Formed on Polypropylene

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Silver sulphide, Ag_2S , layers on the surface of polypropylene (PP) film was formed by chemical bath deposition method (CBD). Film samples were characterised by X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction analysis (XRD). The surface morphology, texture, and uniformity of the silver sulphide layers were formed on PP surface dependent on the number of polymer immersions in the precursor solution. XPS analysis confirmed that on the surface of the polypropylene film, a layer of Ag_2S was formed. ATR-FTIR and FTIR spectra analysis showed that the surface of Ag_2S layers is slightly oxidized. All prepared layers gave multiple XRD reflections, corresponding to monoclinic Ag_2S (acanthite). The Ag_2S layer on polypropylene was characterized as an Ag^+ ion selective electrode in terms of potential response and detection limit. The electrode was also tested as an end-point electrode for argentometric titration of thiamine hydrochloride.

1. Introduction

Polymers modified by thin electrically conductive or semi-conductive films of binary inorganic compounds, particularly of metal chalcogenides [1–4] represent a new class of materials—composites. The application of these composites is determined by their properties, whereas the latter depend significantly on the preparation method, even the chemical composition and structure of composites slightly change [5, 6].

In the last few years, there is a growing interest in Ag_2S films because of their unique electrical [7, 8], optical [9], photovoltaic [10], and thermoelectric properties [11, 12].

These unique properties suggest potentially broad applications of Ag_2S films in various devices such as solar cells, super ionic conductors and semiconductors, photo detectors, photo thermal conversion, electroconductive electrodes, microwave shielding coating, gas sensors functioning at temperatures tending to room temperature, polarizer's of

infrared radiation, and active absorbents of radio waves [5, 6, 13–15].

The properties of Ag_2S films can be successfully utilized by deposition its layers (either by in situ or ex situ methods) onto polymer surface, since a polymer can be easily designed into almost any shape required by a particular application. Additionally, the polymer can also act as the controlled environment for the growth of the film layers. Furthermore, the Ag_2S /polymer composites may exhibit new properties that differ from those of single Ag_2S films, arising from the spatial orientation and network arrangement. Therefore, the ability to prepare such composites on a large scale is an important goal of materials science.

The properties of Ag_2S /polymer composites are very sensitive to preparation technique and significantly depend on the nature of polymer on which Ag_2S layers are formed. Recently, there have been a number of papers suggesting different methods for the incorporation of silver sulphide nanocrystals in different polymer matrices and their characterization. The well-dispersed Ag_2S nanoparticles

incorporated in polyvinylpyrrolidone (PVP)/fibre matrices using the electrospinning technique [16]. Kumar et al. [17] have applied a sonochemical method for the preparation of Ag_2S nanoparticles in the presence of polyvinyl alcohol. Composite thin films consisting of nanosized Ag and Ag_2S particles dispersed in nylon 11 thin films have been prepared by using a thermal relaxation technique [18]. Wang et al. developed a gas/solid reaction method based on surface initiated atom transfer radical polymerization (ATRP) for fabricating nanoparticles/polymer composite thin films, while preventing the aggregation of nanoparticles; thus the reaction may happen on the surface of composite thin films [19].

This present study focuses on the deposition of Ag_2S layers on the polypropylene (PP) by the chemical bath deposition method (CBD). PP film is characterized by many excellent properties than other polymers. This is a low density, high thermal resistance, high strength at high flexibility, resistance to cracking under stress and a very good chemical stability [20].

The CBD method is relatively simple and inexpensive, and highly reproducible technique. The technology is based on slow controlled precipitation of the Ag_2S through the reaction between Ag^+ and sulphur compounds as the sulphur source.

In the past decade, Ag_2S thin films by CBD method have been successfully prepared on silica [21], glass [22], biopolymer matrix [23], indium doped tin oxide (ITO) film [24], and polyamide (nylon) surfaces [25].

The sulphur precursors were usually thiourea [24], the elemental sulphur dissolved in a concentrated NaOH solution [26], thioacetamide [27], sodium sulphide [25], sodium thiosulphate [3], dimethylthiourea [6] and toxic carbon disulphide (CS_2) in ethanol [28]. The most pronounced role in the formation of the Ag_2S particles and consequently deposits has been played by the complexing agents. An ethylenediaminetetraacetate disodium salt (EDTA) [8] and ammonia solution [21] acting as a complexant for Ag ions or as a catalyst is usually employed to control the reaction rate. The commonly accepted underlying mechanism involves alkaline solution (pH 6–10) as ammonia for pH adjustment [8] and higher temperature 30–80°C [21].

However, the adding of complexing agent increases experimental parameters whereas the nonaqueous medium is expensive or toxic generally.

In this paper we report on the depositing of Ag_2S layers by CBD from an acidic aqueous solution containing silver nitrate and an excess of sodium thiosulphate at 20°C temperature. The replacement of complexing agents with excess of sodium thiosulphate results to the simpler reaction mechanism. A reaction mechanism for depositing continuous Ag_2S layer has been examined, and the optimal precursor's concentrations in solution are suggested. The chemical composition, structural, and morphological properties of Ag_2S layer formed on polypropylene surface have been investigated. The Ag_2S layer formed on polypropylene was also tested as an indicator electrode for argentometric titration of thiamine hydrochloride (vitamin B_1).

2. Experimental

15 mm × 70 mm size samples of nonoriented isotactic polypropylene (PP) film of 150 μm thicknesses (Proline X998, KWH Plast, Finland) were used for the experiments.

Before Ag_2S formation process, the hydrophobic PP sample requires a previous surface treatment process in order to facilitate its adhesion properties. Polymer was treated for 25 min at 90°C with etching solution ($\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (1:1), saturated with CrO_3). The formation of Ag_2S layers on PP was carried out in the glass reactor. Etched PP films were immersed for 40 min in aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (0.2 mol/dm³) and AgNO_3 (0.08 mol/dm³) solutions at 20°C with pH 2.3. Then obtained samples were removed from reaction solution, rinsed with distilled water and dried at room temperature. The Ag_2S /PP samples were subjected for repetitive immersions in order to increase Ag_2S amount. The Ag_2S /PP samples were repeatedly immersed in the freshly prepared reaction solution. The immersions procedure was repeated for 5 times.

Distilled water, and analytically pure $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, AgNO_3 , reagents were used to prepare reaction solutions.

Solutions' pH was measured by using pH-meter WTW330, with combinative glass and Ag/AgCl electrode and temperature meter WTW SenTix 41 (Germany).

Before the chemical analysis, samples of PP strips plated with Ag_2S films have been mineralized. Samples were treated under heating with 6 mol/dm³ nitric acid to oxidize sulphur compounds to sulphates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. The resulting solution was poured into a 25 cm³ flask and made up to the mark with distilled water. Then the 5 cm³ of this solution was taken for the sulphur concentration determination, and remaining part was used to determine the silver concentration.

Sulphur concentration in the silver sulphide layer was determined turbidimetrically [29]. Sulphate ions in the range from 1 mg/dm³ to 15 mg/dm³ may be readily determined by utilising the reaction with barium chloride in a solution slightly acidified with hydrochloric acid to give barium sulphate. A glycerolethanol solution helped to stabilise the turbidity of the barium sulphate suspension. The measurement of the intensity of the transmitted light as a function of the concentration of the suspension of BaSO_4 was carried out with a GENESYS 20 spectrophotometer (Thermo Spectronic, UK), at a wavelength $\lambda = 400$ nm. The standard deviation of the method with the photometric procedure in the range of concentrations from 5 mg SO_4^{2-} dm³ to 10 mg SO_4^{2-} dm³ was $\pm 8\%$.

Silver concentration was determined with an atomic Perkin-Elmer absorption meter 503 ($\lambda = 328$ nm). The sensitivity of the method is 0.06 $\mu\text{g}/\text{cm}^3$ for 1% Ag absorption.

The content of silver and sulphur was expressed as $\mu\text{mol}/\text{cm}^2$. Three samples of each PP strip plated with Ag_2S film have been used to determine the concentration of silver and sulphur.

The scanning electron microscope (SEM) Quantax 200 with a detector X Flash 4030 (Bruker AXS Microanalysis

GmbH, Germany) was applied for the obtained Ag₂S layers surface analysis.

The surface morphology of the films was investigated using an atomic force microscope (NANOTOP-206, Microtestmachines, Belarus). An ULTRASHARP Si cantilever (force constant 5.0 N/m, curvature radius less than 10 nm) was used. The measurements were performed in the contact mode. The AFM characteristics: maximum scan field area up to 15 × 15 microns, measurement matrix up to 512 × 512 points. The image processing and the analysis of scanning probe microscopy data were performed using a Windows-based program (Surface View version 2.0).

XPS measurements were performed with a Vacuum Generator (VG) ESCALAB MKII spectrometer. The non-monochromatic Al K α X-ray radiation ($h\nu = 1486.6$ eV) was used for excitation. The Al twin anode was powered at 14 kV and 20 mA. The photoelectron takeoff angle with respect to the sample surface normal was 90°, and XPS spectra of Ag 3d_{5/2}, S 2p_{3/2}, and O 1s were taken at a constant analyzer energy mode (at 20 eV pass energy). The base pressure in the working chamber was kept below 5×10^{-7} Pa. The spectrometer was calibrated relative to Ag 3d_{5/2} at 368.0 ± 0.1 eV and Au 4f_{7/2} at 83.8 ± 0.1 eV. The quantitative elemental analysis was done by estimating peak areas and taking into account empirical sensitivity factors for each element [30]. A standard program was used for data processing (XPS spectra were treated by a Shirley-type background subtraction and fitted with mixed Gaussian-Lorentzian functions). Binding energies were referenced to the C 1s (284.5 eV) on unsputtered surfaces. All samples were scanned as received—without ion beam surface cleaning procedure. Assignment of the signals to specific structures or given oxidation state of elements analysed was done by comparison with data reported by NIST Standard Reference Database 20, Version 3.5 [31] and to the literature references.

The changes in chemical structure and binding configuration of a thin layer were analyzed by attenuated total reflectance (ATR) spectroscopy, since ATR spectroscopy is an often chosen technique as it may be used to obtain the spectra of the surfaces of the adhesive sides of a sample. ATR-FTIR spectra were recorded in the wavenumber range 4000–600 cm⁻¹ by the compensation method. In the 600–100 cm⁻¹ spectral region, were recorded FT-IR spectra. Ag₂S deposits were scraped with a nonmetallic scraper, and then scrapings were solid mixed with CsI, modulated into pellets and subjected to FT-IR spectroscopy. Spectra were recorded on a *Perkin Elmer FT-IR Spectrum GX* spectrophotometer (USA) by averaging 64 scans with a wave number resolution of 1 cm⁻¹ (0.3 cm⁻¹) at room temperature.

X-ray diffractometry was carried out under a Bragg-Brendan circuit on a diffractometer (Dron-6, Russia) using Cu K α ($\lambda = 0.154178$ nm) radiation, 30 kV voltage, and 30 μ A current. The scanning range was $2\theta = 22$ – 60° . The scanning speed was 1°·min⁻¹. Results were registered in *in situ* mode with a computer, and X-ray diffractograms of samples were treated using the Search Match, Xfit, ConvX, Dplot95, and Photo Styler programs.

Potentials were measured by using modified micro-processor HI 2200 (Hanna Instruments USA) relative to the reference Ag, AgCl/KCl_(sat.) electrode. The indicator electrodes were Ag₂S/PP samples. The potentiometric measurements were made with the following electrochemical cell Ag/AgCl/KCl_(sat.)//sample solution/Ag₂S/PP/Ag. The Ag₂S/PP electrode was soaked in 0.01 mol/dm³ AgNO₃ solution for 2 h before each measurement.

The 0.100 g amount of vitamin B₁ (thiamine hydrochloride CAS RN67-03-8) powder was dissolved in 20 cm³ of water. The resulting solution was poured into a 100 cm³ volumetric flask and made up to the mark with distilled water. 50 cm³ of the sample solution containing 50 mg of thiamine was transferred into a beaker, 10 cm³ of distilled water or 10 cm³ of 1 mol/dm³ NaOH was added, and resulting solution was titrated with 0.01 mol/dm³ silver nitrate solution in 0.5 cm³ increments using Ag₂S/PP membrane electrode. The end point of the titration was determined from the Gran plots.

3. Results and Discussion

3.1. Ag₂S Layers Formation Mechanism on a PP Film in Chemical Bath Deposition Process. The silver sulphide layers may be deposited on the PP films by immersing polymer in aqueous solutions of silver nitrate (AgNO₃) and sodium thiosulphate (Na₂S₂O₃). When a soluble sodium thiosulphate reacts with a silver nitrate, insoluble silver thiosulphate, Ag₂S₂O₃, (the solubility product for Ag₂S₂O₃ is $K_{sp} = 1 \times 10^{-13}$ [32]) is formed by reaction

Ag₂S₂O₃ is comparatively unstable and hydrolyzes to release Ag₂S into the reaction solution:

The initial experiments indicated that the usage of 0.2–0.1 mol/dm³ AgNO₃ and 0.2–0.1 mol/dm³ Na₂S₂O₃ solutions for Ag₂S layers depositing on PP, results in quick settle of Ag₂S precipitates on reactor bottom and layers on polypropylene could not be formed. Therefore, the slow precipitation of silver sulphide particles is essential for the formation of the layers on polymer surface.

In order to diminish the rate of silver sulphide formation process, the silver ions were complexed by thiosulphate ions. When the sodium thiosulphate solution was added into the aqueous silver nitrate solution, silver ions were coordinating with some thiosulphate groups, resulting in the relatively high silver ions concentration around these groups. In the presence of thiosulphate excess, the soluble [Ag₂(S₂O₃)₂]²⁻, [Ag₂(S₂O₃)₃]⁴⁻ and [Ag₂(S₂O₃)₄]⁶⁻ complexes are formed.

In nitric acid solution, these complexes decomposed, and they slowly released S²⁻ ions combined with the Ag⁺ ions to form a very insoluble Ag₂S (the solubility product for Ag₂S is $K_{sp} = 7.2 \times 10^{-50}$ [32]) nuclei on some special sites of PP.

Simultaneously, the side reactions are also possible.

TABLE 1: Chemical composition of Ag_2S layers formed in PP matrices, depending on the film immersions time.

Parameter	Immersion time, min		
	40	120	200
Silver concentration $c_{\text{Ag}}, \mu\text{mol cm}^{-2}$	1.312 ± 0.005	2.970 ± 0.006	3.779 ± 0.004
Sulfur concentration $c_{\text{S}}, \mu\text{mol cm}^{-2}$	0.937 ± 0.007	1.485 ± 0.008	2.065 ± 0.006

The thiosulphate can react with nitric acid forming thiosulphuric acid by reaction:

The formed thiosulphuric acid may slowly decompose, and the new structural units such as elemental sulphur appear:

Elemental sulphur can dissolve in nitric acid by reaction:

Silver nitrate and sulphur acid can react to form silver sulphate:

The incorporation of impurities such as a silver sulphate and sulphur is quite possible in the bulk Ag_2S layer.

It was found that the 0.08 mol/dm^3 AgNO_3 and 0.20 mol/dm^3 $\text{Na}_2\text{S}_2\text{O}_3$ solutions are the most suitable for the formation of silver sulphide layers on polypropylene surface at pH 2.3 and 20°C temperature.

3.2. Chemical Analysis of Ag_2S Layers. As mentioned above, the preparation method influences the composition and properties of sulphide layers. Therefore, the initial stage of the work was aimed to establish the chemical composition of the deposited silver sulphide.

The chemical composition of silver sulphide layer obtained for different PP film immersion time in 0.08 mol/dm^3 AgNO_3 and 0.20 mol/dm^3 $\text{Na}_2\text{S}_2\text{O}_3$ solutions at 20°C is presented in Table 1. The molar ratios of silver to sulphur show that the stoichiometric silver sulphide and nonsulphide sulphur can coexist in synthesised layers.

3.3. Morphology of Ag_2S Layers. Figure 1 shows the representative SEM images of an Ag_2S layers on PP surface formed after 5 immersions (40 min each) of polymer in precursor solution. The sulphide surface exhibits nonhomogeneous morphology. The irregularly shaped grains join to form different sized islands on PP surfaces. The maximum size of islands is $19.5 \times 47 \mu\text{m}$ and the smallest $7.8 \times 8 \mu\text{m}$. The large number of micro bumps and irregularly spread clusters are also visible.

The AFM images of Ag_2S layers on PP surface are shown in Figures 2 and 3. The Ag_2S layer exhibits a grain-type surface morphology; however, the size of grains, like

FIGURE 1: SEM image of Ag_2S layer formed on etched PP surface which was immersed in $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3$ solution 5 times at 20°C .

the roughness of layer depends on the number of polymer immersion time in precursor solution.

When the polymer was immersed for 1 cycle in precursor solution, the irregular growth of different shaped grains is observed (Figure 2). The height of grains changed from 36 nm to 108 nm, and the average width was about 148 nm. In the local regions of layer surface, some of grains coalesce forming aggregates. The width of aggregates changed from 0.54 to $0.97 \mu\text{m}$. The maximum height of the aggregates was about 138 nm. The appreciable numbers of bumps is also observed on polymer surface (Figures 2(a) and 2(b)). The root mean square roughness (R_q) was 25.9 nm, while an average roughness (R_a) was about 20.2 nm. The R_q value is greater than R_a , which support the rough morphology of Ag_2S layer surface.

The increase of polymer immersions times of in precursor solution leads to PP surface fulfillment. When the number of immersions was increased up to 5 (Figure 3), the rather large agglomerates composed of the different size particles are observed on surface. The width of aggregates changed from 0.56 to $1.6 \mu\text{m}$. The maximum height of the aggregates increased up to 162 nm. On the other hand, in the regions surrounding aggregates, the numerous grains are still observed. The width of grains varied from 28 to 200 nm, while the height of grains equaled to 46–48 nm. The parameters R_q and R_a are of higher magnitudes, namely, about 33.8 and 25.5 nm, respectively, suggesting a rather rough surface.

3.4. XPS Analysis of Thin Ag_2S Layers. Ag_2S layers deposited on PP surface were examined by XPS measurements. The core

TABLE 2: XPS results derived from the curve fitted deconvoluted spectra.

Immersion time, min	Element	Atomic percentage, %	Binding energy, eV	NIST data	Oxidation state	Attribution to structural element found in	Relative percentage, %
40	Ag 3d _{5/2}	33.33	368.5	368.1		Ag ₂ S	
				368.4	+1	Ag ₂ O	100
				368.3		Ag ₂ SO ₄	
	S 2p _{3/2}	22.23	160.8	160.7	-2	Ag ₂ S	62.90
			163.0	163.1	0	-S-S-	23.65
			168.8	168.6	+6	S(VI)-O	13.45
			531.0	530.9		Ag-O	18.55
	O 1s	44.44	532.1	532.0	-2	Ag ₂ SO ₄	46.52
			533.3	533.3		O ₂ (adsorbed)	34.93
120	Ag 3d _{5/2}	50.70	368.2	368.1		Ag ₂ S	
				368.4	+1	Ag ₂ O	100
				368.3		Ag ₂ SO ₄	
	S 2p _{3/2}	24.67	161.0	160.7	-2	Ag ₂ S	69.98
			163.3	163.1	0	-S-S-	16.65
			168.4	168.6	+6	S(VI)-O	13.37
			531.2	530.9		Ag-O	16.77
	O 1s	24.63	532.0	532.0	-2	Ag ₂ SO ₄	65.60
			533.4	533.3	-2	O ₂ (adsorbed)	17.63
200	Ag 3d _{5/2}	40.68	368.0	368.1		Ag ₂ S	
				368.4	+1	Ag ₂ O	100
				368.3		Ag ₂ SO ₄	
	S 2p _{3/2}	22.18	160.8	160.7	-2	Ag ₂ S	60.50
			163.0	163.1	0	-S-S-	23.16
			168.8	168.6	+6	S(VI)-O	16.34
			530.8	530.9		Ag-O	16.08
	O 1s	37.17	531.9	532.0	-2	Ag ₂ SO ₄	68.93
			533.3	533.3		O ₂ (adsorbed)	14.99

levels S 2p, Ag 3d_{5/2}, and O 1s spectra were measured. During formation of the Ag₂S layer on the surface of polypropylene, all processes proceed in an open medium; therefore, it is not possible to avoid ambient effects. Since the surface of this layer is active, it adsorbs oxygen, water, and other contaminants [33, 34]. The sulphide layer on the PP surface is non-homogeneous (Figure 1) enabling an easy contact of the atmospheric oxygen with silver and sulphur ions. Therefore, the composition of the Ag₂S layer on the surface can differ from the chemical composition of the entire layer. It is necessary to emphasize that the XPS method investigates a very thin (up to few nm) surface layers.

The analysis of experimental XPS data shows that the composition of Ag₂S layers formed at different immersion times is rather similar. They consist of silver, sulphur, and oxygen in various combinations (Table 2).

The S 2p_{3/2} spectra for film samples show three peaks at about 160.8, 163.0, and 168.8 eV.

According to the NIST XPS data base [31], the S 2p_{3/2} peak at 160.8 eV is assigned to Ag-S-Ag bonding of Ag₂S,

and the S 2p_{3/2} peak at 163.0 eV is assigned to -S-S-bonding. The latter is about from 13.77 to 23.66% of S 2p_{3/2} peak (Table 2), depending on the immersion time. This peak probably resulted from the chemisorbed sulphide nanoparticles, rather than the incorporation of elemental sulphur, since the S 2p_{3/2} peak occurs above 164.0 eV [35]. A spectral line at higher energies of about 168 eV originates from oxidized sulphur [36]. For all samples, the higher energy S 2p_{3/2} peak position at 168.8 eV well coincides with the known Ag₂SO₄ position (168.6 eV) [31]; therefore, we assign this peak to sulphur(VI) bond to oxygen.

According to the literature data, Ag 3d_{5/2} core level, located at 368.3 eV, corresponds to binding energy of metallic silver [37], while the line at lower energies of 367.8 eV indicates the presence of Ag⁺ [38, 39]. The peaks of Ag 3d_{5/2} at 368 eV and S 2p_{3/2} at 161.2 eV are the characteristic binding energies for the Ag₂S [26], whereas the Ag 3d_{5/2} line for Ag bounded to sulphur has been reported at 368.9 eV [40]. The Ag 3d_{5/2} component with binding energy of 367.9 eV was reported for Ag₂O [41], while for AgO, it shifted by

FIGURE 2: AFM image of Ag_2S layer on etched PP surface immersed for 1 time in $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3$ solution at 20°C : (a) 2D topography; (b) 3D topography.

FIGURE 3: AFM image of Ag_2S layer on etched PP surface immersed for 5 times in $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3$ solution at 20°C : (a) 2D topography; (b) 3D topography.

0.5 eV to value of 367.4 eV [42]. Summarising analysis data of experimental $\text{Ag } 3d_{5/2}$ peak detected in the range between 368.5 to 368.0 eV (Table 2), it is difficult to distinguish between Ag–O–Ag and Ag–S–Ag bond position. However, concerning the $\text{S } 2p_{3/2}$ core levels (Table 2), it can be noted that the majority of the sulphur is in the S^{2-} state, confirming that the obtained layers are indeed Ag_2S .

The XPS spectrum for O 1s can be deconvoluted into free different contributions with binding energies at around 531.0, 532.0, and 533.3 eV (Table 2). The peak at around 533.3 eV on the high binding energy side of the O 1s region

was ascribed to the atmospheric oxygen adsorbed on the layer surface. The peak with binding energy of 529.5 eV was reported for Ag_2O [41]. Two peaks at 528.7 and 531.0 eV are observed in the O 1s spectrum of AgO [43]. The presence of component at 531.0 eV in all studied O 1s spectra confirms that the silver sulphide surface layer oxidized.

3.5. ATR-FTIR Analysis of Ag_2S Layers. Seeking to investigate the changes of the chemical composition of the untreated PP, etched PP, and PP samples, coated with a layer of silver sulphide, ATR-FTIR spectra (Figure 4) were recorded.

FIGURE 4: (a) ATR-FTIR spectra of untreated polypropylene (1), etched PP (2), and etched PP samples covered with Ag₂S layer after 5 immersions in AgNO₃/Na₂S₂O₃ solution at 20°C: (3); (b) FTIR spectrum of scrapped Ag₂S deposits.

FIGURE 5: X-ray diffractograms of the Ag₂S layers formed on PP in 0.08 mol/dm³ AgNO₃ and 0.20 mol/dm³ Na₂S₂O₃ solutions at 20°C for different immersions time, min: 1: 40; 2: 140; 3: 200.

Figure 4(a) shows ATR-FTIR spectra of untreated (curve 1), etched polypropylene film (curve 2), and PP samples, coated with a layer of silver sulphide (curve 3) in the range of 4000 to 600 cm⁻¹, and Figure 4(b) displays FTIR spectrum of PP samples, coated with a layer of silver sulphide in the range of 600 to 100 cm⁻¹.

The PP sample ATR-FTIR spectrum (Figure 4(a), curve 1) displays absorption peaks which coincide well with the reported literature data [44]. In polypropylene spectrum, moderate absorption peaks of deformation vibrations of the plane methylene group arise in the spectral range of 1445 to 1485 cm⁻¹, and methyl groups vibrations are registered in range of 1430–1470 cm⁻¹ or 1365 to 1395 cm⁻¹. These peaks in our spectrum appear at 1451 cm⁻¹ and 1375 cm⁻¹, respectively. A broad and intense band at around 2915 cm⁻¹ was

attributed to vibrations of CH bands. The absorption features at 840, 1000, and 1170 cm⁻¹ are characteristic vibrations of terminal unsaturated CH₂ groups present in isotactic PP [44]. These characteristic features in our experimental spectrum are observed at 840, 990, and 1165 cm⁻¹ (Figure 4(a), curve 1).

ATR-FTIR spectrum of etched PP sample (Figure 4(a), curve 2) shows some changes. The characteristic peaks sharply diminish, and a new signal appears at 1719 cm⁻¹. This signal is probably due to superposition of signals at 1710 and 1724 cm⁻¹, characteristic of carboxylic and carboxylic stretching vibrations, respectively [45]. The spectrum of etched PP confirms that the oxidizing pretreatment of polypropylene increases surface hydrophilicity. Better hydrophilic characteristics of PP surface induce electrostatic

FIGURE 6: Change of $\text{Ag}_2\text{S}/\text{PP}$ electrode potential with Ag^+ ion concentration, mol dm^{-3} . Electrode prepared in 0.08 mol/dm^3 AgNO_3 and 0.20 mol/dm^3 $\text{Na}_2\text{S}_2\text{O}_3$ solutions at 20°C for different immersions time, min: 1: 140; 2: 200.

interactions between the charged sites of the polymer and the sulphide particles, providing its adhesion to the polymeric surface.

The ATR-FTIR spectrum of PP samples covered with Ag_2S layers (Figure 4(a), curve 3) shows that the intensity of peaks, characterising etched PP, decreased, and two new broad vibration bands at 1137 cm^{-1} and 640 cm^{-1} appeared. On the grounds of the literature data [46–48], the bands in the range of the wavenumbers $1000\text{--}1250 \text{ cm}^{-1}$ correspond to vibration frequencies of the S–O band: in the range of $1186\text{--}1224 \text{ cm}^{-1}$, it corresponds to the asymmetric valence S–O vibrations, $\nu_{\text{as}}(\text{S-O})$, while the peaks corresponding to the symmetric valence S–O vibrations, $\nu_{\text{s}}(\text{S-O})$, appear in the interval of $1018\text{--}1095 \text{ cm}^{-1}$. According to the reported data [47], the sulphates vibration modes arise in the wavenumber range of $1080\text{--}1130 \text{ cm}^{-1}$ and $610\text{--}680 \text{ cm}^{-1}$. The scissoring vibration mode of the O–S–O group occurs as a strong band between $400\text{--}650 \text{ cm}^{-1}$ [49].

Therefore, the peak of 640 cm^{-1} to the symmetric deformation of O–S–O vibrations, $\delta_{\text{s}}(\text{O-S-O})$, and the peak of 1137 cm^{-1} corresponds to the asymmetric deformation of O–S–O vibrations, $\delta_{\text{as}}(\text{O-S-O})$.

The broad absorption band maximum at 237 cm^{-1} observed in FTIR spectrum (Figure 4(b)) corresponds to characteristic vibrations of Ag–S and is in good agreement with reported data for Ag_2S [48, 50].

3.6. XRD Analysis of Thin Ag_2S Film Layers. The deposited Ag_2S layers were subjected to X-ray diffractometry to investigate the crystallographic structure of these layers. Structural studies of the Ag_2S deposits on polypropylene are limited by the crystallinity of the PP film itself. The intensity of its peaks exceeds the intensity of silver sulphide peaks several times in $2\theta \leq 20^\circ$. Therefore, XRD diffractograms of samples were recorded in the 2θ range between 22 and 60° .

Figure 5 presents the X-ray diffraction pattern of the as-prepared $\text{Ag}_2\text{S}/\text{PP}$ composites. The phase composition was determined by comparing $\text{Ag}_2\text{S}/\text{PP}$ composites XRD diffraction patterns with those of known minerals.

FIGURE 7: Potentiometric curves for the titration of 0.0024 mol/dm^3 thiamine with 0.01 mol/dm^3 silver nitrate solutions in alkaline medium using $\text{Ag}_2\text{S}/\text{PP}$ layer as an indicator electrode. Electrode prepared in 0.08 mol/dm^3 AgNO_3 and 0.20 mol/dm^3 $\text{Na}_2\text{S}_2\text{O}_3$ solutions at 20°C for 200 min.

Diffraction pattern gave dominant peaks 2θ at 26.189° (the crystallographic planes (111), 29.063° (012), 31.820° (120), 33.666° (121), 34.743° (112), 36.806° (022), 37.6° (200), 40.798° (031), 43.47° (130), 46.28° (202), and 53.21° (004)) and showed the polycrystalline nature of the prepared Ag_2S layer. The diffraction patterns were indexed to the monoclinic Ag_2S phase and are in good agreement with the reported data for $\alpha\text{-Ag}_2\text{S}$ (acanthite) (JCPDS Card File: 00-014-0072).

3.7. Application of $\text{Ag}_2\text{S}/\text{PP}$ Layers for Potentiometric Measurements. To assess the practical applicability of the prepared silver sulphide layer on polypropylene films, an attempt was made to test $\text{Ag}_2\text{S}/\text{PP}$ composite as an Ag^+ ion selective electrode.

For analytical applications, the response time of a sensor is an important factor. The average time to reach a potential within $\pm 1 \text{ mV}$ of its final equilibrium value was measured after successive immersion of the $\text{Ag}_2\text{S}/\text{PP}$ composite electrode in a series of AgNO_3 solutions of different concentration, each having a 10-fold increase in Ag^+ ion concentration from 1.0×10^{-8} to $1.0 \times 10^{-2} \text{ mol/dm}^3$. The ionic strength of solutions was 0.1 mol/dm^3 . The static response time for $\text{Ag}_2\text{S}/\text{PP}$ composite electrode obtained was 20 s for $1 \times 10^{-2} \text{ mol/dm}^3$ Ag^+ ion concentration, while at lower concentrations the response time increased up to 60 s.

A linear potential response was obtained in the concentration range from 1×10^{-2} to $1 \times 10^{-5} \text{ mol/dm}^3$ (Figure 6). The change in slope per decade change in Ag^+ ion concentration was found to be slightly lower than that of 25.6 mV decade for a theoretical Nernstian response, which is the expected value for a univalent ion. A potential deviation from linear behaviour was observed in the concentration range below $1 \times 10^{-6} \text{ mol/dm}^3$.

The $\text{Ag}_2\text{S}/\text{PP}$ composite electrode was also tested as an end-point indicator electrode in potentiometric titration involving Ag^+ ions. The method can be applied for the determination of thiamine hydrochloride.

In highly alkaline medium, thiamine undergoes chemical transformation and loses two protons through two distinct

dissociation steps. The reaction occurs through intramolecular addition of the amino group of thiamine to the thiazolium ring with loss of first proton, accompanied by opening of the thiazole ring and loss of a second proton [51]. These

protons can be replaceable by Ag^+ ions. In presence of sodium hydroxide, the silver ions do not react with free chloride but react with thiols only [52].

The solubility product of AgOH ($K_{\text{sp}} = 2 \times 10^{-8}$) is higher than that of AgCl ($K_{\text{sp}} = 1.78 \times 10^{-10}$); therefore, the precipitation of AgCl would be suppressed by the addition of NaOH excess. In alkaline medium, $\text{Ag}_2\text{S}/\text{PP}$ does not respond to HO^- ions; hence, this electrode can be used as an indicator electrode for the determination of thiamine content in vitamin B_1 .

The potentiometric titration curves of 0.0024 mol/dm^3 thiamine with 0.01 mol/dm^3 silver nitrate in alkaline medium are shown in Figure 7. There is a clear potential break (Figure 7) corresponding to the consumption of 0.78 mole of silver nitrate per mole of thiamine.

4. Conclusions

Ag_2S layers were successfully prepared at 20° temperature on polypropylene (PP) immersed in a bath containing the aqueous solutions of 0.08 mol/dm^3 silver nitrate and 0.2 mol/dm^3 sodium thiosulphate solution. The surface morphology, texture, and uniformity of the silver sulphide layers formed on PP surface dependent on the number of polymer immersions in the precursor solution. Chemical and X-ray photoelectron spectroscopy analyses confirmed a formation of silver sulphide on polypropylene surface. ATR-FTIR and FTIR spectra analysis showed that the surface of Ag_2S layers is slightly oxidized. The XRD studies indicated that the deposited layers were polycrystalline with monoclinic (acanthite) crystal structure. The $\text{Ag}_2\text{S}/\text{PP}$ sensor exhibited low detection limit and therefore, are promising as indicating electrode in argentometric titration of vitamin B_1 as well as a sensor for determination of silver ions.

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