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Environmental friendly decorative electroless copper plating on Acrylonitrile Butadiene Styrene plastics

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ABSTRACT

In the present research work, a new environment friendly electroless copper plating process, copper coating has been successfully achieved on acrylonitrile butadiene styrene (ABS) plastics by using a typical alkaline bath solution. A durable bright copper deposition on the ABS plastic was studied by the non-electrolytic process using alkaline copper(II) nitrate bath and gold chloride activator. The electroless copper plating was carried out by studying the impact of different factors such as variation of bath concentration, variation of plating time and variation of temperature. The optimum conditions of smooth surface coverage of quality grade coating were found to be plating time of 15 min, concentration of copper(II) nitrate as 2% (w/v) and the temperature of 60 ° ± 2 °C. This study suggests that electroless copper plating on acrylonitrile butadiene styrene polymers be used for coating applications in engineering, aircraft, oil and gas, construction, electronics, and a number of other fields based on the results achieved.

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INTRODUCTION

Metallization of plastics is general uses nowadays in many related to technology sectors from the manufacture of printed circuitsin electronics to ornamental coatings generally manufacturing (Zhang *et al.*, 2014). Electroless plating and electroplating are two different types of plating processes. Electroless plating slightly deposits an electrically conductive metallic layer on the separating ABS substrate, also, preparing the face for latterly adherent electroplated grade coating. The electroplating step, with the help of current, builds fresh consistence of essence like copper, nickel, or chrome, indeed as and when needed by the part or for finishing functions (Olivera *et al.*, 2016 & Teixeira and Santini, 2005). Plastic substances are generally plated so as to achieve graces of the metals to the polymer substrate (Wang *et al.*, 2013). Decorative plating of plastic impacts the physical and chemical properties of the plastic directly (Snyder, 2007). They need to be used substantially due to some unique graces, like light weight. It's been used for electric insulation, erosion resistance, heat insulation, and sound insulation, and it's been used for a while, and their marketable significance is adding , particularly concerning top quality products (Munteanu *et al.*, 2011).

The copper plating of ABS(acrylonitrile butadiene styrene) plastics deposits a coat of copper on the ABS plastics by means of the electroless deposit process. The main principle of this system is to conduct the physical and chemical properties of the copper onto the surface of the ABS plastic. Copper's elemental quality as a essence coating on ABS plastic is that it may be used for both decorative and functional purposes. The thermoplastic ABS is made by copolymerizing styrene and acrylonitrile with polybutadiene. Plastic materials that have been plated can be used for a longer period of time. In particular, ABS plastic is very suitable for this work (Tang *et al.*, 2009). Electroless plating utilizes an easier method. The component is treated chemically to remove oils and different corrosive elements, and is then activated with an acid etch or proprietary solution (Uraz *et al.*, 2019). Electroless plating is the main purpose of the electroplating process. During this portion, the plastic raw material features a conductive actions. It provides homogeneous order, persistence, and like viscosity. It's nonmagnetic, and there's no impressed entry piece under deformation or extension due to the advanced stretching rate. The change from the electroless plating to the electroplating is about strength. Electroless plating doesn't need electricity. So the plating film appears with an unwavering structurepper's introductory quality as a essence coating on ABS plastic. (Uraz, 2020).

Among metal coating ways, electroless metal plating is the most popular way to produce metal- covered materials. Because electroless plating has blessings in terms of coherent metal deposit, excellent conductivity, and applicability to complicated-structured materials or nonconductors. It's applied to utmost polymer substrates. The conductor system has been reported to do because of a admixture of partial electrode oxidation and reduction processes. The electroless plating methodology consists basically of a series of pretreatments, like etching, sensitization and activation. The former, is an necessary system that handing the substrate with depressions and in some cases, changed chemistry that improves the wettability of the face and generally renders a hydrophobic face hydrophilic. Chemical etching is typically well- known pickling the system that has been applied to numerous kinds of polymers for metallization, similar as ABS and so on (Domenech *et al.*,2003). Electroless plating baths generally contain a metal ion source, reducing agents, complexifying agents, a stabilizer, a buffering agent, and a wetting agent, with temperature and pH controlled as experimental parameters (Sudagar *et al.*, 2013). Electroless copper plating has been extensively used in Printed Circuit Board(PCB) manufacturing to deposit a copper layer onto dielectric materials(similar as epoxy resin- based polymers) (Azar *et al.*, 2022).

Electroless copper plating is a system of reduction of Cu^{2+} ions on the face of colorful dielectric materials and semiconductors so as to get ornamental and functional copper coatings. These coatings have set up wide operation for the conformation of conductive patterns, wiring openings within the system of producing printed circuit boards and integrated circuits, as well as for a variety of other operations in electrical engineering and electronics. For the electroless deposit of copper, formaldehyde(or its derivations) has traditionally been employed as a reducing agent in electrolytes, furnishing both a high deposit rate and excellent mechanical properties of the formed copper coatings (Georgieva *et al.*, 2021, Luo *et al.*, 2014, Tang *et al.*, 2008). Furthermore, this process has several advantages, including i) high selectivity, ii) uniform thickness over the entire object to be plated, especially complex geometry objects, iii) uniform physical and mechanical properties, iv) high rate of deposition for commercial applications by changing the solution composition, pH, and temperature, v) deposition on non-conducting surfaces, and vi) high process throughput, and vii) very economic cost of tools and materials. (Ghosh, 2019).

The main goal of this study is to optimise the composition and mode of operation of a new environmentally friendly solution for electroless deposition of thin copper layers over ABS plastic and determining the best plating conditions.

OBJECTIVES OF THE STUDY

The objectives of the present work comprised (i) to study the electroless copper plating on ABS plastic by using the nitrate bath, and (ii) to study the optimum concentration of copper(II) nitrate, plating time and temperature for electroless copper plating.

MATERIALS AND METHODS

The electroless copper plating on ABS plastic material experiments were fulfilled. The experimentations correspond of four way: preparing the chemicals and materials, etching, plating and the analysis of samples. The investigated parameters were concentration of copper(II) nitrate, plating time,and plating temperature.

Pre-treatment Techniques for Electroless Plating

Acrylonitrile butadiene styrene (ABS) substrates with a thickness of 0.20 cm and an area of 5 cm × 2.5 cm were used as substrate for the measurement of deposition rate. Before deposition, the ABS substrates were pre-treated by polishing, cleaning, etching, neutralising and activation processes. In the polishing process, water-proof abrasive paper was used for removing the scale, paint and like incrustation from the plastic surface. After the operation, the ABS plate was washed with distilled water and dried.

In the cleaning process, the alkaline cleaning solution was prepared by dissolving 15 g of sodium hydroxide, 20 g of sodium carbonate decahydrate and 10 g of detergent in 1 L of distilled water. Firstly, the test pieces were cleaned with hot water for 15 min. Then the test pieces were agitated in 250 mL of hot alkaline solution for about one and a half at 45 °C.

In the etching process, the chromic acid solution was prepared by dissolving 10 g of $K_2Cr_2O_7$ in 20 mL of concentrated sulphuric acid and made up to 100 mL of distilled water. In this process, the cleaned test pieces were immersed in hot chromic acid solution for about one and a half hours. The bath temperature was maintained at 45 °C. After immersing, the cleaned test pieces were usually washed with distilled water.

In the neutralization process, the mild alkaline solution was prepared by dissolving 0.25 g of NaOH in 250 mL of distilled water. After etching, the test pieces were neutralized with 2 M mild alkaline solution. This neutralization step is required to remove a large amount of chromium from the surface. After dipping in the mild alkaline solution, the test pieces were washed with hot distilled water and allowed to dry.

In the activation process, the gold chloride activation solution (0.03 % w/v) was prepared by dissolving the 0.0303 g of $AuCl_3$ in 4 mL aqua regia and made up with distilled water to 100 mL. After neutralization, the neutralization, the test pieces were activated by dipping in the activation solution for about one day at room temperature. After activation, the test pieces were rinsed again with distilled water and dried. And then the test pieces were weighed.

Preparation of Electroless Copper Plating Bath Solution

Copper(II) nitrate (3.75 g) was dissolved in 100 mL distilled water. Then Rochelle salt (7.5 g) was added to copper(II) nitrate solution. After that, (5 g) sodium hydroxide and (2.5 g) sodium bicarbonate are added to this solution. Finally, 25 mL of formaldehyde was added and made up to 250 mL of distilled water. After activation, the plastic pieces are ready for electroless metal plating. The prepared plastic pieces were then dipped into a prepared electroless copper bath solution.

Electroless Plating

Electroless copper plating process was as follows. The apparatus was set up as shown in figure 1. A prepared electroless copper solution was placed in a 250 mL beaker. The beaker was immersed in hot bath water and adjusted the temperature to 60 °C. It was ready for dipping the plastic substrates into the bath solution. During the experiment, the solution was stirred to obtain a uniform coating. After the electroless plating solution was prepared, the test pieces of plastic substrate, which had been activated, were immersed into the prepared bath solution and the solution was stirred. The test pieces were taken out, rinsed with distilled water and dried. Then the test pieces were weighed. Experimental runs were done at various temperatures, various plating times and using various concentrations of copper(II) nitrate. Thickness of copper is determined by using the equation (1) and (2).

$$\text{Thickness of copper} = \frac{\text{deposited mass}}{\text{area} \times \text{density of copper}} \qquad (1)$$

$$= \frac{\text{deposited mass} \times \text{volume of copper}}{\text{area} \times \text{mass of copper}} \qquad (2)$$

Fig. 1. Assembled equipment for the whole electroless copper plating process.

RESULTS AND DISCUSSION

Studies on Pre-treatment of ABS Plastics

In order to ensure a satisfactory adhesion of copper deposite by electroless plating, the surface of the substrate had to be perfectly cleaned free of any trace of grease, dirt, oil and other impurities. After cleaning, it is then etched in acid dip solution. The acid dip or etching process is the initial processing step necessary to give a good metal to plastic adhesion. An acid dip also removes all residual alkaline films from the cleaning procedure. After etching, it is then washed with mild alkaline solution. If much Cr^{6+} remains, it will interfere with the catalytic process. In the activation process, $AuCl_3$ is the most suitable activator for electroless copper plating. Acidified gold chloride is effective when nickel, copper, silver, chromium and iron are deposited. Activation solution are essential because without them the process will not function. Activation can be used quite successfully, without sensitizing, since the reducing agent in the electroless solution affects reduction to the metallic state.

Studies on Use of Electroless Bath Solution

The plastic substrates are ready for electroless copper plating after the above steps are finished. The process is one in which the surface of the substrate is covered with a metallic coating. The solution used was composed of copper ions and a suitable reducing agent. Sodium hydroxide was used to maintain the pH of the solution between 10 and 11. Sodium bicarbonate was used as a stabilizing agent, and formaldehyde was used as the reducing agent. It may well be pH-dependent. It should be capable of reducing divalent copper to metallic copper in an alkaline solution. Rochelle salt (also known as sodium potassium tartrate tetrahydrate) was used as a complexing agent to complex the copper ions, preventing copper hydroxide precipitation in electroless copper solutions. Initially, the gold is the catalyst that helps precipitate Cu0 on the substrate surface when the reaction is proceeding autocatalytically.

Determination of Optimum Concentration of Copper(II) Nitrate

Table 1 shows the effect of the thickness with regards to the concentration of copper(II) nitrate from 1% to 5%. Figure 2 shows that as the concentration of copper(II) nitrate increases, the thickness of the deposited layer increases, up to 2%. However, if the concentration of copper(II) nitrate is greater than 2 %, the thickness of the layer begins to decrease, and it does not produce a smooth, bright copper surface layer. Therefore, it can be concluded that the best-deposited layer can be formed with up to 2% w/v or w/w of copper(II) nitrate.

Table 1. Variation of Thickness of Copper Deposit on ABS Plastics with Respect to the Concentration of Copper(II) Nitrate

Operation Conditions:
Bath composition – (1 % to 5 %) $Cu(NO_3)_2.3H_2O$
Temperature - 60 °C ± 2 °C
pH - 11 to 12
Time - 15 min

Concentration of $Cu(NO_3)_2.3H_2O$ (% w/v)	1	2	3	4	5
Thickness × 10^{-5} (cm)	1.25	2.61	3.32	4.72	5.22

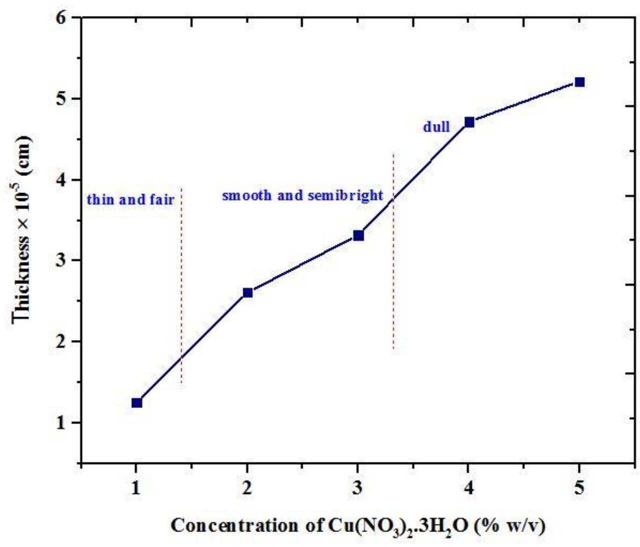

Fig. 2. Relation between thickness and concentration of copper(II) nitrate.

Determination of Optimum Plating Time

The ABS plastics were deposited at various plating times (within 5 to 25 min), and the thickness of copper deposited was calculated and shown in Table 2. Figure 3 shows that as the plating time increases, the thickness of copper deposited increases within 15 min. At that time, the surface's appearance becomes smooth and semibright. However, at the point where the plating time is above 15 min, although the thickness was increased, the dull surface was plated instead of the shiny one.

Table 2. Variation of Thickness of Copper Deposit on ABS Plastics with Respect to Plating Time

Operation Conditions:
Bath composition – (2 %) $Cu(NO_3)_2.3H_2O$
Temperature - 60 °C ± 2 °C
pH - 11 to 12
Time - 5 min to 25 min

Plating time (min)	5	10	15	20	25
Thickness × 10^{-5} (cm)	1.24	3.83	4.34	6.14	8.18

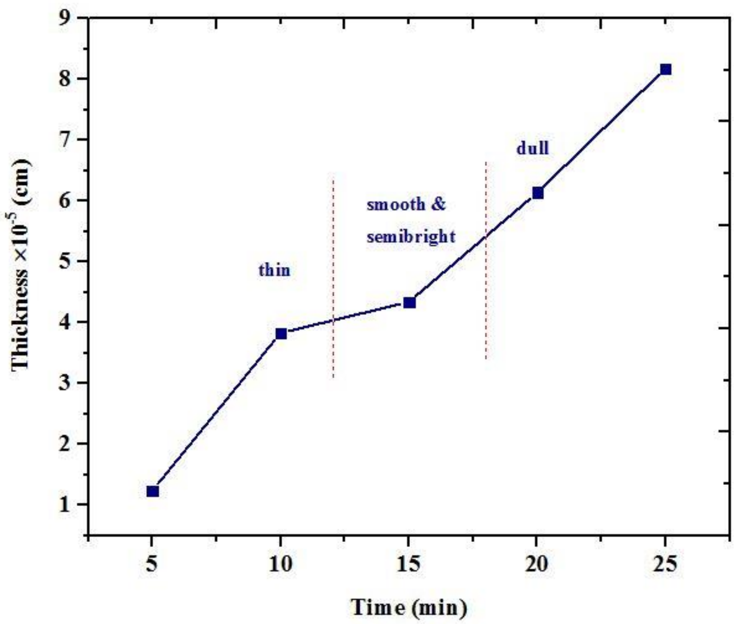

Fig. 3. Relation between thickness and plating time.

Determination of Optimum Temperature

The results are presented in Table 3. The variation of thickness of deposited layer were shown with respect to the various temperature. Figure 4 shows that a quality-grade coating was best achieved with a shining tone and uniform adherent coverage at a temperature of 60 °C. Increasing the temperature promotes the thickness of the deposited layer (within 50 °C to 60 °C). However, at a temperature of about 70 °C, although further increases in copper deposition were obtained, a dull plated surface was observed. At about 80 °C, it was found that the formation of the deposited layer could be peeled off.

Table 3. Variation of Thickness of Copper Deposit on ABS Plastics with Respect to the Bath Temperature

Operation Conditions: Bath composition – (2 %) $Cu(NO_3)_2.3H_2O$ Temperature - 40 °C to 80 °C pH - 11 to 12 Time - 15 min					
Temperature (°C)	40	50	60	70	80
Thickness × 10^{-5} (cm)	1.86	2.64	3.52	4.11	5.69

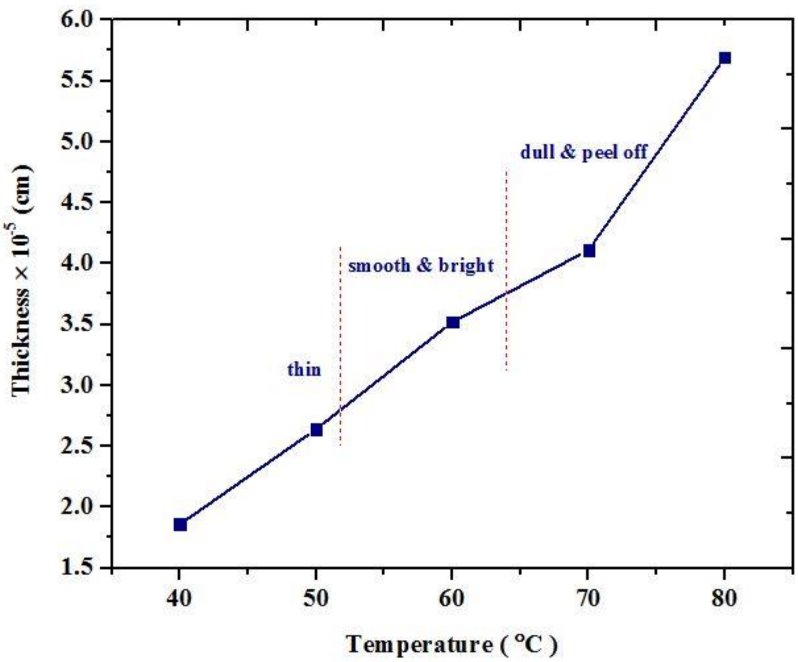

Fig. 4. Relation between thickness and temperature.

Application

Figure 5 shows the application of plastic botton over electroless copper plating. In this process, 2 % $Cu(NO_3)_2.3H_2O$ as the bath concentration, 60 °C temperature, and a 15 min plating time were used. As seen in Figure 5, the shining and uniform adherent coverage of copper was observed.

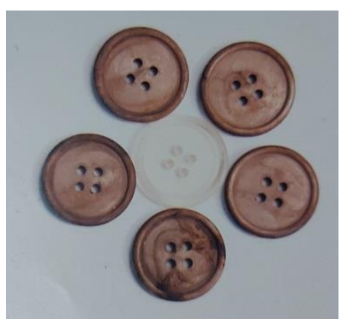

Fig. 5. Electroless plating of copper on plastic button.

CONCLUSION AND RECOMMENDATION

This investigation revealed that the formation of deposited copper layer on ABS plastic depends on the concentration of copper(II) nitrate trihydrate, plating time and temperature. It also indicates that optimum conditions exists with respect to the plating time of 15 min, 2 % (w/v) of $Cu(NO_3)_2$ concentration temperature of 60 ± 2 °C. The apparatus setting is one of the important controlling factors in order to achieve an optimum thickness of the copper deposited layer on the ABS plastic substrates. In addition, the pH of the electroless solution of nitrate bath was in the range of 11 to 12. The decorative appearance of copper deposit was smooth and bright. This decorative electroless copper plating on acrylonitrile butadiene styrene plastics may intend to have a good potential, effective for used to provide protection from wear and abrasion, resistance against corrosion, and add hardness to parts of all conditions. Based on the obtained results, we do recommend that electroless copper plating on acrylonitrile butadiene styrene plastics can also be applied for coatings applications in engineering, aerospace, oil and gas, construction, electronics and several others. It is recommended that this study be shared with the polymer based electrochemical researchers, especially material plating. For future researchers, it is recommended to investigate other factors that could affect the performance level of the electroless copper plating on acrylonitrile butadiene styrene plastics. The same study can also be done in other domains of research work and the other electronic device applied areas that capture the focus of electroless plating.

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REFERENCES

Azar, G.T.P., Danilova, S., Krishnan, L., Fedutik, Y., & Cobley, A. J. (2022). Selective electroless copper plating of ink-jet printed textiles using a copper-silver nanoparticle catalyst. Polymers, 14(3467), 1-21. https://doi.org/10.3390/polym14173467

Domenech, S.C., Lima, J.E., Drago, V., Lima, J. C., Borges, N.G., Avila, A.O.V., & Soldi, V. (2003). Electroless plating of nickel–phosphorous on surface-modified poly(ethylene terephthalate) films. *Applied Surface Science*, 220, 238-250. https://doi:10.1016/S0169-4332(03)00815-8

Georgieva, M., Girginov, C., Petrova, M., Lazarova, D., Dobreva, E., & Kozhukharov, S. (2021). Electroless copper plating of dielectrics from environmentally friendly reducer-free electrolyte. *Transactions of the IMF*, 99(5), 238–245. https://doi.org/10.1080/00202967.2021.1957339

Ghosh, S. (2019). Electroless copper deposition: A critical review. *Thin Solid Films*, *669*, 641-658. https://doi.org/10.1016/j.tsf.2018.11.016

Luo, L.M., Lu, Z.L., Huang, X.M., Tan, X.Y., Ding, X.Y., Cheng, J.G., Zhu, L., & Wu., Y.C. (2014). Electroless copper plating on PC engineering plastic with a novel palladium-free surface activation process. *Surface and Coatings Technology*, 251, 69-73. http://dx.doi.org/10.1016/j.surfcoat.2014.04.005

Munteanu, D., Gabor, C., Constantin, D.G., Varga, B., Adochite, R., Andrei, O.C., Chappe, J.M., Cunha, L., Moura, C., & Vaz, F. (2011). Friction and wear behaviours of Ti (C, O, N) dark decorative coatings. *Tribology International*, 44(7-8), 820-828.

Olivera, S., Muralidhara, H. B., Venkatesh, K., Gopalakrishna, K., Vivek, C. S. (2016). Plating on acrylonitrile–butadiene–styrene (ABS) plastic: a review. *Journal of Materials Science*, 51, 3657–3674. https://doi 10.1007/s10853-015-9668-7

Snyder, D.L. (2007). Decorative chromium plating. *Metal Finishing*, 105(10), 173-181.

Sudagar, J., Lian, J., & Sha, W. (2013). Electroless nickel, alloy, composite and nano coatings – A critical review. *Journal of Alloys and Compounds*, 571, 183–204. https://doi:10.1016/j.jallcom.2013.03.107

Tang, X., Cao, M., Bi, C., Yan, L., & Zhang, B. (2008). Research on a new surface activation process for electroless plating on ABS plastic. *Materials Letters*, *62*, 1089–1091. http://doi:10.1016/j.matlet.2007.07.055

Tang, X.B.C., Han, C., & Zhang, B. (2009). A new palladium free surface activation process for Ni electroless plating on ABS plastic. *Materials Letters*, 63, 840-842. https://doi.org/10.1016/j.matlet.2009.01.006

Teixeira, L.A.C., & Santini, M.C. (2005). Surface conditioning of ABS for metallization without the use of chromium baths. *J Mater Process Technol*, 170(1), 37–41.

Uraz, C. (2020). The electroless metal plating process over ABS plastic by using ionic liquids. *Res. Eng. Struct. Mat.*, 6(1), 45-52. http://dx.doi.org/10.17515/resm2019.91ma0128

Uraz, C. & Özçelik, T.G. (2019). Electroless metal plating over ABS plastic. *Engineering Sciences (NWSAENS)*, 14(2), 63-70. https://doi: 10.12739/NWSA.2019.14.2.1A0432

Wang, W., Ji, S., & Lee, I. (2013). A facile method of nickel electroless deposition on various neutral hydrophobic polymer surfaces. *Appl Surf Sci*, *283*, 309–320. https://doi:10.1016/j.apsusc.2013.06.108

Zhang, H. N., Wang, J., Sun, F. F., Liu, D., Wang, H.Y., & Wang, F. (2014). Study of electroless copper plating on ABS resin surface modified by heterocyclic organosilane self-assembled film. *Bull. Mater. Sci.*, 37(1), 71-76.