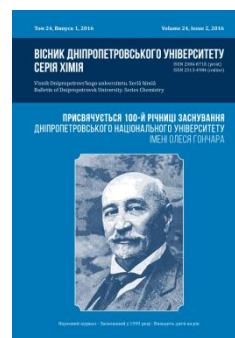




Вісник Дніпропетровського університету. Серія Хімія  
Bulletin of Dnipropetrovsk University. Series Chemistry

*p*-ISSN 2306-871X, *e*-ISSN 2313-4984  
journal homepage: <http://chemistry.dnu.dp.ua>



UDC 541.135; 544.6.018.462

## STYROMAL BASED POLYMER FILMS MODIFIED WITH COPPER MICROPARTICLES

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*Received 16 September 2016; revised 29 October 2016; accepted 7 December 2016; available online 31 December 2016*

### Abstract

A method for the synthesis of polymeric film based on a copolymer of styrene and maleic anhydride (stiromal) and oligodiol was suggested. Block copolymer of ethylene glycol and propylene glycol was used as oligodiol. It was shown that synthesized materials have moderate water swelling capacity in and ion-exchange properties. Static exchange capacity in 0.1 mol/L NaOH aqueous solution is within the interval of 1.44–1.76 mmol/g. At air-dry state films have a tensile strength of 4–6.6 MPa and an elongation at break tensile 38–61 %. The effect of stiromal molecular weight and oligodiol type, and conditions of film formation on ion-exchange and physical-mechanical properties of the films was studied. The synthesized material appeared to be able to sorb  $\text{Cu}^{2+}$ -ions from neutral and acidic solutions. The distribution coefficient in case of sorption from slightly acidic solution with  $\text{Cu}^{2+}$  concentration of 50 mg/L was 48–50. Composite material with a metal submicroparticles uniformly distributed in the polymeric matrix was obtained by chemical reduction of copper ions sorbed. It was found that the film acquires electric conductivity, as a result of filling of metal particles, which allows copper electrodeposition on the film surface.

*Keywords:* polymeric composite material; polymeric matrix; styromal; oligodiol; static exchange capacity; sorption of  $\text{Cu}^{2+}$ -ions; copper microparticles; electroplating.

## ПОЛІМЕРНІ ПЛІВКИ НА ОСНОВІ СТИРОМАЛЮ, МОДИФІКОВАНІ МІКРОЧАСТИНКАМИ МІДІ

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### Анотація

Запропонована методика синтезу полімерних плівкових матеріалів на основі кополімеру стиролу і малеїнового ангідриду (стиромалю) та олігодіолу. В якості олігодіолу використовували блоккополімер етиленгліколю та пропіленгліколю. Показано, що синтезовані матеріали помірно набрякають у воді та мають іонообмінні властивості. Статична обмінна ємність в 0.1 N водному розчині NaOH має значення 1.44–1.76 мекв/г. У повітряно-сухому стані плівки мають розривну міцність 4–6.6 МПа та відносне розривне подовження при розтягу 38–61 %. Досліджено вплив молекулярної маси стиромалю, типу олігодіолу та умов плівкоутворення на іонообмінні і фізико-механічні властивості плівок. Синтезований матеріал виявив здатність сорбувати іони  $\text{Cu}^{2+}$  з нейтральних і кислих розчинів. Коефіцієнт розподілу при сорбції зі слабкого розчину з концентрацією йонів  $\text{Cu}^{2+}$  50 мг/л мав значення 48–50. Шляхом хімічного відновлення сорбованих іонів Купруму отримано композиційний матеріал з субмікрочастками металу, рівномірно розподіленими в полімерній матриці. Виявлено, що в результаті наповнення частками металу плівкові матеріали набувають електропровідності, достатньої для нанесення на їх поверхню гальванічного мідного покриття.

*Ключові слова:* полімерний композитний матеріал; полімерна матриця; стиромаль; олігодіол; статична обмінна ємність; сорбція іонів  $\text{Cu}^{2+}$ ; мікрочастинки міді; гальванічне покриття.

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doi: 10.15421/081612

## ПОЛИМЕРНЫЕ ПЛЕНКИ НА ОСНОВЕ СТИРОМАЛЯ, МОДИФИЦИРОВАННЫЕ МИКРОЧАСТИЦАМИ МЕДИ

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### Аннотация

Предложена методика синтеза полимерных плёночных материалов на основе сополимера стирола и малеинового ангидрида (стиромалея) и олигодиола. В качестве олигодиола использовали блоксополимер этиленгликоля и пропиленгликоля. Показано, что синтезированные материалы имеют умеренную набухаемость в воде и обладают ионообменными свойствами. Статическая обменная ёмкость в 0.1 N водном растворе NaOH имеет значения 1.44–1.76 мэкв/г. В воздушно-сухом состоянии плёнки имеют разрывную прочность 4–6.6 МПа и относительное разрывное удлинение при растяжении 38–61 %. Исследовано влияние молекулярной массы стиромалея, типа олигодиола и условий пленкообразования на ионообменные и физико-механические свойства плёнок. Синтезированный материал показал способность сорбировать ионы  $\text{Cu}^{2+}$  из нейтральных и кислых растворов. Коэффициент распределения при сорбции из слабокислого раствора с концентрацией  $\text{Cu}^{2+}$  50 мг/л имел значения 48–50. Путём химического восстановления сорбированных ионов меди получен композиционный материал с субмикрочастицами металла, равномерно распределёнными в полимерной матрице. Обнаружено, что в результате наполнения частицами металла плёночные материалы приобретают электропроводность, достаточную для нанесения на их поверхность гальванического медного покрытия.

*Ключевые слова:* полимерный композиционный материал; полимерная матрица; стиромаль; олигодиол; статическая обменная ёмкость; сорбция ионов  $\text{Cu}^{2+}$ ; микрочастицы меди; гальваническое покрытие.

### Introduction

Conductive polymers are perspective type of modern composite materials. They consist of polymeric matrix and conductive filler distributed therein. Metal, technical carbon, conductive fibers etc. are usually used as conductive filler [1–3]. These compositions can be used as antistatic materials, flexible heaters, contact materials for electronic equipment, cable sheathing, electromagnetic shielding, conductive adhesives etc. [4–6]. Despite intensive research in the field of polymeric materials with different forms of conduction, many problems need to be solved. Specifically, it is of interest to reveal the effect of chemical structure, polymeric matrix topology and nature of the filler as well as mixing procedure on material properties.

The polymeric matrixes based on copolymers of styrene with maleic anhydride (styromals) are worth noticing. The presence of reactive anhydride cycles in the macromolecular chains offers extensive opportunities for chemical modification of the polymer [7; 8]. Particularly, branched and crosslinked structures can be obtained basing on styromals as well as functional groups, such as ion exchange groups, can be added to the structure of copolymers.

Electrical conductivity is usually provided to polymeric materials by injection of dispersed metal fillers using advanced chemical and electrochemical techniques when dispersed phase is formed directly in the polymer [9–12].

The aim of this investigation was to ascertain the possibility of creation a composite material based on styromal that filled with submicron copper submicron particles, which has electrical conductivity and acceptable physical and mechanical properties. The main approach includes sorption of  $\text{Cu}^{2+}$ -ions on ion-exchange polymeric matrix and their consequent reduction with formation of metal microparticles.

### Experimental Section

The following chemicals were used for the synthesis of polymeric matrixes:

- styrole and maleic anhydride copolymers SMA 3000 and SMA 1000 produced by ATOFINA ChemicalsInc and also synthesized by the method mentioned below (SM-1 and SM-2);
- oligodiols produced by BASF: block-copolymers of ethylene glycol and propylene glycol of Pluronic PE brand, and oligoethylene glycol Pluriol P900.

Styromal synthesis was carried out using styrole produced by Dow Chemical Company maleic anhydride according to State Standard 11153-75 and benzoyl peroxide Luperox A75 produced by Arkema. Styrole was used after preliminary distillation under vacuum. Maleic anhydride was re-crystallized from acetone. Benzoyl peroxide was preliminarily dried on filter paper during 24 h at room temperature. Solvents (benzene and ethylacetate AR) were used without preliminary conditioning. 9.8 g of maleic anhydride and 200 mL of solvent

(benzene or benzene and ethyl-acetate mixed 3:1 by volume) were loaded into laboratory glass reactor equipped with stirring unit with hydrolock and thermometer. The mass was heated to 40–45 °C and stirred until anhydride completely dissolves. Next, 0.2 g of benzoyl peroxide and 10.4 g of styrene were added. The mass was brought to a boil and was stirred during 2 h. White polymer sediment was formed. After cooling down the product was separated from stock solution using Nutsche filter and dried in vacuum oven at 50 °C up to constant mass.

Polymeric matrixes were synthesized with their simultaneous forming as elastic transparent films using curtain coating method. In order to do this, separated solutions of styromal and oligodiol in ethyl-acetate, tetrahydrofuran, acetone, and their mixes were made. Next, correspond solutions were mixed and thermostated in a closed container during 1 h at 40 °C, and poured on horizontal adhesive underlying. Reaction mass was applied in the way to receive a film of 0.30–0.35 mm thick. Applied layer was kept in usual conditions for 24 h, and next it was subjected to thermal processing in the interval of 70–110 °C, raising temperature for 10 °C by every hour.

Viscosity-average molecular weight of styromale samples was calculated using Mark–Kuhn–Kuvink formula:

(1)

Value of characteristic viscosity  $[\eta]$  was defined for diluted acetone solutions at  $30 \pm 0.05$  °C using Ostwald viscosimeter with 0.63 mm diameter of the capillary. Formula coefficients were taken from [8]:  $K = 8.69 \cdot 10^{-5}$ ,  $\alpha = 0.7$ .

In order to determine the statistic volume capacity (SVC) analytic sample of the polymeric film (approximately 0.5 g) was immersed into 100 mL 0.1N KOH, and kept for 24 h. Then aliquote of was titrated using 0.1 mol/L HCl.

Swelling ratio ( $W$ ) of film material was determined by the relative surface increasing for the 15×15 mm sample after keeping it in distilled water for 24 h at 23 °C.

Sorption capacity of polymer films by  $\text{Cu}^{2+}$  ions ( $SC_{\text{Cu}}$ ) was determined in aqueous  $\text{CuSO}_4$  solution that contains 50 mg/liter of  $\text{Cu}^{2+}$ -ions and 1 mol/L of  $\text{H}_2\text{SO}_4$ . Samples of film material with the size of 10×20 mm were dipped into 10 mL of the solution and kept there for 12 h. Amount of sorbed ions was detected by spectrophotometric analysis using photocolormeter KFK-3 [13].

Tensile strength ( $\sigma$ ) and specific fracture elongation under the tension ( $\epsilon$ ) were determined using tensile machine FP 10 according to State Standard 14236-81.

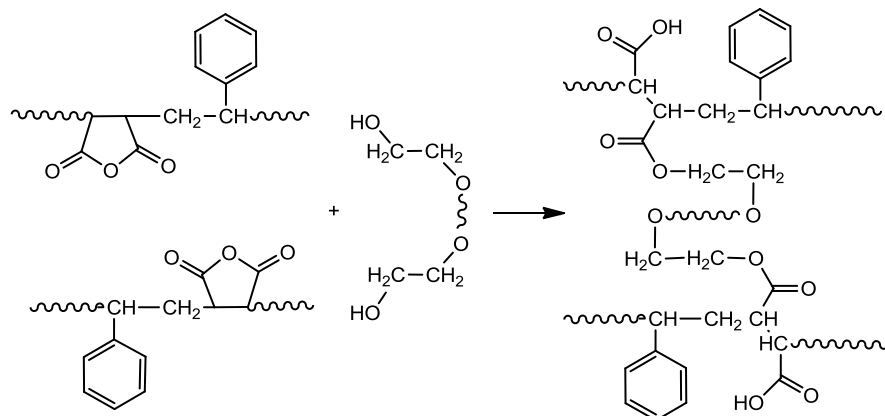
Filling of polymeric matrix with copper nucleus was carried out using two methods. According to the first method films were kept for 24 h in the solution of copper salt (acetate, sulfate or pyrophosphate) with monoethanolamine or diethanolamine as reducing agent with afterbaking at 90–120 °C during 5 h. According to the second method films were kept sequentially in saturated copper salt solution (acetate or sulfate) and solution of sodium borohydride.

Electrical resistance of polymer films was measured using digital multimeter DT 9208A on the length 1 cm. Copper electroplating on the surface of film samples was carried out in the solution of 0.1 mol/L  $\text{CuSO}_4$  and 1 mol/L  $\text{H}_2\text{SO}_4$  at current density 1–2 mA/cm<sup>2</sup>.

Microstructure of obtained composite material was studied using metallographic microscope MIM-7 at 500x optical zoom.

## Results and Discussion

Spatially structured polymeric matrix from styromal and oligodiol formed according to the principle circuit:



Search for optimal composition of reaction mixture was carried out to ascertain probability and conditions of obtaining of the films with acceptable physical-mechanical properties. Type

of styromal, oligodiol and solvent as well as their ratio were selected.

Characteristics of used derivative compounds are shown in the [Table 1](#).

Table 1

Characteristics of derivative components for film synthesis							
Styromal				Oligodiol			
Label	$[\eta]$ , cm <sup>3</sup> /g (acetone, 30 °C)	Acid number, mg KOH/g	Label	g/mol	Mass of polyoxy- propylene block, g/mol	Viscosity by Brookfield (23 °C, 60 rev./min), mPa·s	
SMA 1000	2.6	2300	PE 6400	2900	1750	1000	
SMA 3000	4.3	4400	PE 9200	3650	2750	900	
SM-1*	37.7	83000	PE 10100	3500	3250	800	
SM-2*	58.5	150000	P 900	900	–	170	

\* Product SM-1 was obtained in benzene; product SM-2 was obtained in mixture benzene/ethyl acetate

Setting the anhydride/hydroxyl ratio of 1:0.5 and using ethyl-acetate as a solvent was discovered as the most appropriate option for condensation of SMA 1000, CM-1 and CM-2 with PE 6400. Transparent elastic films with moderate swelling degree (in water) were obtained. Usage of SMA 3000 and P 900 in different combinations together and with other reagents results with fragile product. Applying PE 9200 and PE 10100 yields sticky rubbery materials that become jelly in the water media. Increasing or decreasing the styromal/oligodiol ratio in relation to mentioned above leads to increasing of rigidity or stickiness correspondingly.

Increasing of styromal molecular mass has positive effect on the mechanical strength characteristics of the films as well as on swelling degree ([Table 2](#)). *SVC* values of P-1 and P-2 film materials slightly exceed estimated value (1.62 mEq/g) on the assumption of full conversion of oligodiol hydroxyl groups during polycondensation. Except incomplete conversion it could be attributed to the presence of polyoxyalkene chains in the structure. Nevertheless, sufficient decreasing of *SVC* value appears for the P-3 sample. It could be explained by the formation of sterically inhibited conformations with the increasing of molecular mass of the initial styromal.

Table 2

Characteristics of the films based on styromal and PE 6400

Key	Type of styromal	$\epsilon$ , %	$\sigma$ , MPa	<i>SVC</i> , mEq/g	<i>W</i> , %	Specific volume, cm <sup>3</sup> /g
P-1	SMA 1000	58.3	4.0	1.71	90	2.24
P-2	CM-1	60.8	5.7	1.76	62	1.76
P-3	CM-2	38.3	6.6	1.44	44	1.48

Examination of sorption capacity of the films with relation to Cu<sup>2+</sup> ions shows that sorption efficiency stays significantly high even in case of low sorbate concentration (50 µg/mL). This is evidenced from the calculations of distribution factor (*K*) that shows ratio between sorbed ion in sorbent and sorbate at equilibrium condition. After 70 hours of experiment this factor becomes 21.5 for P-1, 41 for P-2 and 48 for P-3. Volumetric coloring of the films also was also clearly observed. Nevertheless, sorption rate was low. Furthermore, acidic media sufficiently inhibits ion exchanging process between polymer matrix and solution as shown on [Fig. 1](#). During 70 h of sorption *K* values become 4.5–11 for samples P-1–P-3 that is several times less than in case of moderate acidity.

Films saturated with Cu<sup>2+</sup>-ions were found deficient in conductivity to be further modified galvanically. So, modification was obtained with the application of chemical reduction of Cu<sup>2+</sup>-ions directly within polymer matrix. Depending on total determined properties the film P-3 was used to obtain metal-polymer composition.

Method that includes exposing the sample in 0.5 mol/L CuSO<sub>4</sub> and NaBH<sub>4</sub> solutions was discovered as the most appropriate among all tested methods of chemical modification to obtain copper particles within the polymer matrix. Final copper-containing compositions have the form of dark-brown films. Their electrical impedance is 120–150 MOhm/cm. Copper microparticles could be seen by microscopic investigation ([Fig. 2](#)).

The possibility of galvanic metallization of obtained compositions was examined by electrodeposition of copper layer from sulphate electrolyte that contains 0.1 mol/L CuSO<sub>4</sub>, 1 mol/L H<sub>2</sub>SO<sub>4</sub>. Whilst current contact jaw matched width of the sample and the current

density was set minimal (1–2 mA/cm<sup>2</sup>). It was found that copper coating was formed on the

surface as well as within the volume of the film during the electrolysis.

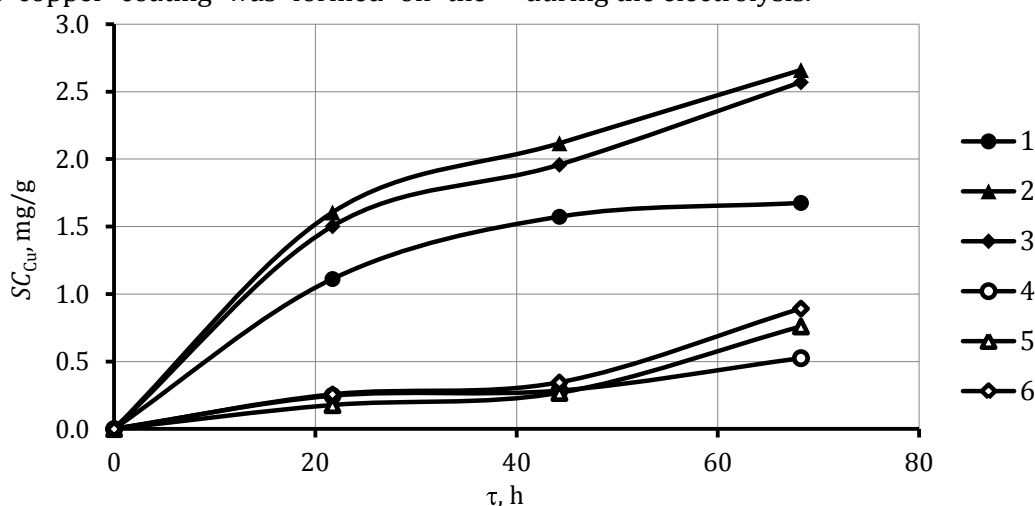


Fig. 1. Sorption capacity by Cu<sup>2+</sup>-ions ( $SC_{Cu}$ ) versus time of sorption for films P-1 (1, 4), P-2 (2, 5), P-3 (3, 6) aqueous 50  $\mu\text{g}/\text{mL}$  CuSO<sub>4</sub> solution (1–3) and with the presence of 1.0 mol/L H<sub>2</sub>SO<sub>4</sub> (4–6)

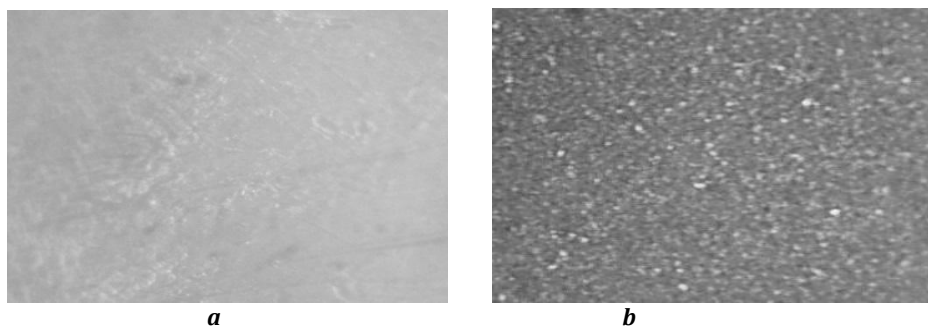


Fig. 2. Samples micrographs (500x): *a* – polymer matrix, *b* – obtained composite material

## Conclusions

Therefore, methods of obtaining polymeric films that could be used as a matrix for production of electroactive composite materials was developed. It was shown that synthesized ionogenic polymer film materials based on styromal and block copolymer of ethyleneglycol and propyleneglycol can sorb Cu<sup>2+</sup>-ions from water solutions. It was found that after reduction of sorbed Cu<sup>2+</sup>-ions obtained polymeric materials characterized by conductivity that is enough to electrodeposition of copper coating.

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