The Journal of Chemical Technology and Metallurgy started originally in 1954 as Annual Journal of the former Higher Institute of Chemical Technology. It ran in Bulgarian. In 2000 its name was changed to Journal of the University of Chemical Technology and Metallurgy. It was published quarterly in English. Since 2013 it has run bimonthly as Journal of Chemical Technology and Metallurgy.

Honorary Editor
R. Dimitrov

Editor-in-Chief
B. Koumanova

University of Chemical Technology and Metallurgy,
8 Kl. Ohridski blvd., 1756 Sofia, Bulgaria
Tel: (+ 359 2) 8163 302, E-mail: journal@uctm.edu

Editorial Board

S. J. Allen
Queens University of Belfast, UK

D. Angelova
University of Chemical Technology and Metallurgy, Bulgaria

M. Bojinov
University of Chemical Technology and Metallurgy, Bulgaria

J. Carda
University Jaume I, Castellon, Spain

G. Cholakov
University of Chemical Technology and Metallurgy, Bulgaria

V. Dimitrov
Bulgarian Academy of Sciences

N. Dishovsky
University of Chemical Technology and Metallurgy, Bulgaria

S.J.C. Feyo de Azevedo
Universidade do Porto, Portugal

M. Jitaru
University “Babeș -Bolyai”, Cluj-Napoca, Romania

S. Kalcheva
University of Chemical Technology and Metallurgy, Bulgaria

F. Keil
Hamburg University of Technology, Germany

T. Konstantinova
University of Chemical Technology and Metallurgy, Bulgaria

M. Kucharski
AGH University of Science and Technology, Krakow, Poland

J.M. Le Lann
Institut National Polytechnique, Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, Toulouse, France

A. Mavrova
University of Chemical Technology and Metallurgy, Bulgaria

D. Mehandjieva
Bulgarian Academy of Sciences

V. Meško
International Balkan University, Skopje, Macedonia

L. Mörl
University “Otto-von-Guericke”, Magdeburg, Germany

B. Nath
European Centre for Pollution Research, London, UK

D. Pavlov
Bulgarian Academy of Sciences

L. Petrov
Bulgarian Academy of Sciences

D.C. Shallcross
The University of Melbourne, Australia

M. Simeonova
University of Chemical Technology and Metallurgy, Bulgaria

V. Stefanova
University of Chemical Technology and Metallurgy, Bulgaria

D. Stoilova
Bulgarian Academy of Sciences

N. Tsarevsky
Southern Methodist University, Dallas, Texas, USA

I. Turunen
Lappeenranta University of Technology, Finland

S. Vassileva
University of Chemical Technology and Metallurgy, Bulgaria

S. Velea
University of Chemical Technology and Metallurgy, Bulgaria

L. Vezenkov
University of Chemical Technology and Metallurgy, Bulgaria

Ž. Živković
University of Belgrade, Technical Faculty, Bor, Serbia

Technical secretary: S. Georgieva

The annual subscription (for 6 issues) is 350 €, including postage, handling and packaging charge.

©UCTM, 2005. All rights reserved. Reproduction in part or whole without permission is strictly prohibited.
Prepress and design: A. Staneva; Printing: S Print Ltd., Sofia
# TABLE OF CONTENTS

Effect of the modified solid product from waste tyres pyrolysis on the properties of styrene-butadiene rubber based composites  
Nedialko Delchev, Petrunka Malinova, Mihail Mihaylov, Nikolay Dishovsky...............................................................525

In-situ preparation of Polyamide-6/polypropylene glycol copolymers with mineral fillers  
Petko Krastev, Roza Mateva..........................................................................................................................................535

Effects of temperature and concentration dependent viscosity on onset of convection in porous media  
Fatemeh Bahadori, Sima Rezvantalab...............................................................................................................................541

Laue functions model vs Scherrer equation in determination of graphene layers number on the ground of XRD data  
Beti Andonovic, Misela Temkov, Abdulakim Ademi, Aleksandar Petrovski, Anita Grozdanov,  
Perica Paunović, Aleksandar Dimitrov ........................................................................................................................545

Kinetics of borohydride electrooxidation: revisited  
Sasha Kalcheva, Ivan Kanazirski...................................................................................................................................551

Electrochemical studies of metal complexes of malonyl dihydrazide  
K. Ramana Kumar, A. Raghavendra Guru Prasad, V. Srilalitha, Y.N. Spoorthy, L.K. Ravindranath..............................................559

Electronic and infrared spectral studies on the poly(propyleneamine) dendrimers peripherally modified with 1,8-naphthalimides  
Desislava Staneva, Ivo Grabchev, Pavlina Mokreva........................................................................................................569

Sensor activity and logic behaviour of some 2-aminoterephthalic derivatives  
Polya Miladinova, Nikolai Georgiev...................................................................................................................................577

Compensation effect in the kinetics of thermal aging of semi chemical pulp  
Rumyana Boeva, Greta Radeva........................................................................................................................................585

Study of the complex equilibrium between titanium (IV) and tannic acid  
Andriana Surleva, Petya Atanasova, Tinka Kolusheva, Latinka Costadinova........................................................................594

Solvatochromism of homodimeric styryl pyridinium salts  
Stanislava Yordanova, Ivan Petkov, Stanimir Stoyanov....................................................................................................601

Electric-arc-carbothermic processing of agglomerated waste dispersal materials from ferrous metallurgy  
Daniela Grigorova, Maxim Marinov, Rossitza Paunova......................................................................................................610
Utilization of waste powder and sludge in iron ore sintering process
Daniela Grigorova, Tsvetan Tsanev, Maxim Marinov.................................................................615

Research of influence equal channel angular pressing on the microstructure of copper
Sergey Lezhnev, Irina Volokitina, Toncho Koinov........................................................................621

Guide for Authors..............................................................................................................................631
EFFECT OF THE MODIFIED SOLID PRODUCT FROM WASTE TYRES PYROLYSIS ON THE PROPERTIES OF STYRENE-BUTADIENE RUBBER BASED COMPOSITES

Nedialko Delchev¹, Petrunka Malinova², Mihail Mihaylov², Nikolay Dishovsky²

¹ Polymermetal Ltd., Haskovo, Bulgaria
² University of Chemical Technology and Metallurgy, 8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: m_c_mihaylov@uctm.edu

ABSTRACT

Being resistant to moisture, oxygen, ozone, solar radiation, microbiological degradation, etc., waste car tyres and their deposition present a great environmental problem. Pyrolysis is an environment-friendly process for their recycling. This paper presents data referring to the study of the effect of the solid product from waste tyres pyrolysis on the properties of styrene-butadiene rubber (SBR) based composites. It is found that the further modification of the pyrolysis carbon black decreases two times the ash content and six times the zinc oxide concentration in the ash but the curing characteristics of the investigated SBR based compounds remain unaffected. The values of the modulus 100, the tensile strength and Shore A hardness of vulcanizates containing modified pyrolysis carbon black increase, while the elongation at break and the residual elongation decrease slightly. The effects observed are related to the decreased ash content of the pyrolysis carbon black following the modification as well as to the increased silicon oxide concentration in the remaining ash.

Keywords: rubber, waste tyre, carbon black, pyrolysis.

INTRODUCTION

Being resistant to moisture, oxygen, ozone, solar radiation, microbiological degradation, etc., waste car tyres and their deposition present a great environmental problem. On the other hand, that waste is flammable and its uncontrolled combustion endangers further the environment.

The different methods for waste tyres reuse involve:
- Recovery of the used tyres;
- Mechanical grinding/shredding (obtaining of rubber powder);
- Obtaining a rubber reclaim;
- Devulcanization;
- Pyrolysis, etc.

Pyrolysis is the process of thermal destruction of organic materials. It proceeds in absence of oxygen at temperatures in the range from 500°C to 800°C. The waste tyres subjected to pyrolysis (directly or having undergone some preliminary treatment) are heated gradually starting from an ambient temperature to 700°C-800°C at constant purging by nitrogen, carbon dioxide and/or water vapour [1]. There is a renewed interest to pyrolysis as a method for recycling and reuse of waste tyres because it is an environmentally friendly process yielding useful products. The latter include pyrolysis oil (40 - 60
%, solid carbon residue (30 – 40 %), steel and gaseous products [2]. Each of those products can find various industrial applications. For instance, the pyrolysis oil, which is a complex mixture of organic components, can be used as a plasticizer in rubber industry, as diesel oil [2 - 5] or as a carbon black source [6]. The application of the pyrolysis products in the former two cases is hampered by the high carbohydrates concentrations [7 - 10]. The gaseous products contain \( \text{H}_2, \text{H}_2\text{S}, \text{CO}, \text{CO}_2, \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{etc} \). They can be used as the energy source required for the pyrolysis proceeding [2]. The solid product of waste tyres pyrolysis (called also pyrolysis carbon black) includes carbon black (80 - 90 %) and inorganic substances (10 - 20 %) which are always present in the rubber compounds used to manufacture car tyres. The briquetted product can be burnt in industrial furnaces. Though being very caloric, containing ca 20-25% of ash, it is not lucrative. It is hypothesized that the pyrolysis carbon black can entirely or partially replace the conventional carbon black in rubber industry following a subsequent mechanical or chemical treatment. That product may be quite effective in manufacturing less demanding rubber items such as floorings for various usages, isolation stall mats, hit resistant coatings, etc.

The present paper aims at presenting the investigations on the effect of the modified solid product from waste tyres pyrolysis on the properties of composites based on styrene-butadiene rubber (SBR).

**EXPERIMENTAL**

**Materials**

The investigations were performed on 1500 type styrene-butadiene rubber (Ravaflex SBR 1500) supplied by Ravago Group. It is a copolymer of styrene (23,5%) and butadiene and is easily processed. The solid pyrolysis product was obtained in accordance with the procedure described in [1].

**Modification of the solid pyrolysis product**

The solid pyrolysis product was placed in a round bottom flask and hydrochloric acid (5 %) was added at a ratio of 1:4. The mixture was boiled under a reflux condenser for 20 min. Then the product was washed with distilled water over a buchner funnel till obtaining a clear filtrate, which gave no white residue in presence of silver nitrate. A strong odour of hydrogen sulphide was evolved during the modification indicating that the sulphur and sulphur-containing compounds were removed from the carbon black. The modification of the solid pyrolysis product was performed to reduce its ash content being one of its drawbacks. The solid pyrolysis product will be further referred to as pyrolysis carbon black.

**Rubber compounds**

Four SBR based compounds containing virgin and modified pyrolysis carbon black were prepared. Their formulations are presented in Table 1. Aiming an objective comparison, the added amount of pyrolysis carbon black was estimated on the ground of the carbon (active substance) content, i.e. the compensated ash content which was determined in advance. Thus 60 g and 83.3 g of virgin pyrolysis carbon black in compounds denoted by SBR 1 and SBR 2 correspond to 50 g and 70 g conventional carbon black, respectively. While 54.7 g and 76.6 g of modified pyrolysis carbon black in compounds denoted by SBR 3 and SBR 4 correspond to 50 g and 70 g conventional carbon black, correspondingly.

**Preparation and vulcanization of the rubber compounds**

The rubber compounds were prepared using an open two-roll laboratory mill (L/D 320x160 and friction of 1.27) according to a specific recipe and blending regime. The speed of the slow roll was 25 rpm.

The rubber was plasticized on the rolls for several minutes prior to adding the ingredients.

The mill had to be cooled at each blending cycle to avoid compounds sticking onto the rolls. The blend was cut diagonally when the ingredients were absorbed in the rubber matrix and the strap prepared was transferred to the opposite side of the steam-roller. Then the compound was homogenized by making a roll and driving it through a narrow shank. The compounds obtained in the form of a sheet were kept for 24 prior to the vulcanization proceeding.

The specimens were vulcanized on an electrically heated hydraulic press at 10,0 MPa and 160°C according to the optimums of each rubber compound that were determined using an moving die rheometer (MDR 2000).

**Experimental Methods**

**Characterization of the virgin and modified pyrolysis carbon black**
**Determination of the losses on heating performed according to ISO 15651/2-91**

1. The weighing glass vessel and its lid were dried separately in a drying oven for 30 min at 105 ± 2°C and subsequently transferred to a dessicator to cool to an ambient temperature. Then they were weighed with an inaccuracy < 0.1 mg.

2. About 2 g of pyrolysis carbon black were weighed in a glass vessel with an inaccuracy < 0.1 mg.

3. The uncovered weighing glass vessel containing the sample and its lid were dried in a drying oven for 1 h at 105 ± 2°C.

4. The weighing glass vessel was covered with the lid and transferred to the dessicator. Its lid was removed again and it was cooled to an ambient temperature. Then the lid was put on and the vessel was weighed with an inaccuracy < 0.1 mg.

The weight loss on heating was calculated in % according to the formula:

\[
\frac{m_1 - m_2}{m_1 - m_0} \times 100, \%
\]

where \(m_0\) is the weight of the weighing vessel (g), \(m_1\) is the total weight of the weighing vessel with the lid and the sample prior to the heating (g), while \(m_2\) is the total weight of the weighing vessel with the lid and the sample after the heating (g).

**Determination of the ash content according to ISO 15651/3-91**

1. The crucible and its lid were put into a muffle furnace set at 550 ± 25°C for 1 h, then transferred to a dessicator and cooled to an ambient temperature. It was weighed with an inaccuracy < 0.1 mg.

2. A pyrolysis carbon black sample of a mass > 2 g was dried in a drying oven for 1 h at 105 ± 2°C.

3. About 2 g of the pyrolysis carbon black sample were put into the preheated crucible and weighed with an inaccuracy < 0.1 mg.

The ash content was calculated according to the formula:

\[
\frac{m_2 - m_0}{m_1 - m_0} \times 100, \%
\]

where \(m_0\) was the weight of the crucible with its lid (g), \(m_1\) was the weight of the crucible with its lid and the sample loaded (g), while \(m_2\) was the weight of the crucible with its lid and the ash obtained (g).

**Determination of dibutyl phthalate absorption (oil absorption number) according to ISO 9665-76**

The tested pyrolysis carbon black (0.5 g weighed with an inaccuracy < 0.001 g) was placed in a porcelain mortar and several drops of dibutyl phthalate (DBP) were added using a microburette. The mixture was ground carefully with the pestle till the disappearance of DBP oil stains on the mortar or on the plate surface. In fact the introduction of DBP continued till all carbon black could be gathered on the pestle. The absorption of DBP (X) in ml/100 g, was calculated according to the formula:

\[
X = \left( \frac{V}{G} \right) \times 100
\]

where \(V\) was the quantity of absorbed DBP (ml), while \(G\) was the weight of the pyrolysis carbon black sample (g).

**Determination of the iodine number by the titration method according to ISO 15651/1-91**

The pyrolysis carbon black sample, already preliminary dried, was weighed and stirred intensively with a certain amount of iodine solution of a predetermined concentration. Then the solid was separated by centrifugation, while the residual solution was titrated with a solution of sodium thiosulfate of a certain concentration.

The iodine number IAN per 1 mg iodine, i.e. the iodine adsorbed by 1 g of pyrolysis carbon black (with an inaccuracy < 0.1 mg/g) was calculated by the formula:

\[
IAN = \left( \frac{V_i - V_s}{5} \frac{C_i}{4m} \right) \times 158.6 \left( \frac{V_s - V_i}{C_i} \right) \frac{C_i}{m}
\]

where \(V_i\) was the volume of sodium thiosulfate solution used to titrate the iodine solution in the blank sample (ml), \(V_s\) was the volume of sodium thiosulfate solution used to titrate the iodine solution in the sample (ml), \(C_1\) was the concentration of sodium thiosulfate solution (mol/dm³), while \(m\) was the weight of pyrolysis carbon black sample (g).

**Determination of the specific surface area according to Klyachko-Gurvich method**

The solid body specific surface area was determined
by Klyachko-Gurvich method. The method is based on the dependence of macromolecular surface on the volume of the gas needed for its formation in m\(^2\). The dependence is linear in accordance with the BET theory. The latter shows that a linear section of the adsorption isotherm starts to outline with the formation of a monomacromolecular layer on the adsorbent surface.

The determination of the specific surface area by this method involves measuring the decrease of the adsorbate pressure (that of the gaseous nitrogen) due to its adsorption on the surface of a given specimen at a constant temperature (in this case -196°C referring to the liquid nitrogen temperature) in a system of a fixed volume.

Fig. 1 presents the equipment used.

The specific surface area was determined in accordance with:

\[
S_0 = f(\Delta P - \Delta P_0)
\]

where \(\Delta P\) was the decrease of the adsorbate pressure due to the adsorption of the sample and the ‘dead’ volume of the apparatus at \(-196^\circ C\), \(\Delta P_0\) was the decrease of the adsorbate pressure due to the ‘dead’ volume of the apparatus. It is worth adding that

\[
\Delta P_0 = f(m,d)
\]

where \(m\) was the sample mass, while \(d\) was the sample density. The specific surface area was defined by:

\[
S = S_0 / m, \text{ m}^2/\text{g}
\]

**Characterization of the ash content of the virgin and modified carbon black by a full silicate analysis (an weight analysis, AAS, ICP-OES)**

Average samples of virgin and modified carbon black were prepared by grinding to obtain particles of a size < 100 \(\mu m\).

Heating losses were determined by weighing the samples placed in platinum crucibles. Analytical scales were used. The crucibles were heated in a muffle furnace at 1000°C for 1 h. The losses on heating were determined by the balance of the samples weight before and after the heating.

Silicon dioxide amount was determined by the weighing method. The samples were placed in platinum crucibles and decomposed by melting in presence of potassium-sodium carbonate. The melt still hot was dissolved in dilute hydrochloric acid. The sediment was filtered off from the solution and subsequently washed with dilute hydrochloric acid and water. The sediment and the filters were put in a platinum crucible preheated to a constant weight in a muffle furnace at 1000°C for 1 h. The residues were in fact pure \(\text{SiO}_2\). They were weighed and the percentage amount of the component was calculated taking into account that of the reference sample. The solution left after melt removal was transferred to a measuring cylinder to be used in determining the metals content by ICP-OES spectrometric analysis.

The samples were additionally dissolved in a mixture of acids (HF, \(\text{HClO}_4\), \(\text{HNO}_3\)) aiming the determination of the alkali metals content. They were placed in platinum pans and heated slowly in a sand bath. The dry residue was dissolved in dilute hydrochloric acid and the solution obtained was transferred to a measuring cylinder. The amount of Mg, Ca, Cu, Fe, Zn, Al, Pb, Ti was determined by ICP-OES method using a Prodigy high dispersion ICP-OES spectrometer (Teledyne Leeman Labs) of dual view configurations (radial/axial) and 0.007 nm resolution. The amount of Na and K was estimated by AAS using a Perkin Elmer 5000 atomic absorption spectrophotometer working in an emission regime (acetylene/air flame, K wavelength of 766.5

Table 1. Formulations of SBR compounds filled with virgin (non-modified) and modified pyrolysis carbon black (phr).

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>SBR 1</th>
<th>SBR 2</th>
<th>SBR 3</th>
<th>SBR 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Styrene-butadiene rubber SBR 1500</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2. Zinc oxide</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3. Stearic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4. Non-modified pyrolysis carbon black</td>
<td>60.0</td>
<td>83.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5. Modified pyrolysis carbon black</td>
<td>-</td>
<td>-</td>
<td>54.7</td>
<td>76.6</td>
</tr>
<tr>
<td>6. N-Tert-Butyl-2-Benzothiazole Sulfenamide</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>(TBBBS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Sulphur</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
</tbody>
</table>
nm, Na wavelength of 589.0 nm).

The spectral results referring to the components concentrations were recalculated as oxides.

**Determination of the vulcanization characteristics**

The vulcanization characteristics of the rubber compounds were determined on an MDR 2000 moving die rheometer (Alpha Technologies) according to ISO 3417:2010.

A sample of the rubber compound was placed in a hermetic chamber at pressure lower than that initially determined. It was kept constant at high temperatures. The piston rod penetrated the sample and oscillated at small rotation amplitude (the oscillation angle was 0.5°). That caused shear deformation of the sample. The torque moment required for the disk oscillation depended on the deformation resistance (shear modulus) of the rubber. The torque moment was recorded graphically as a function of time.

**Determination of the mechanical properties of the vulcanizates obtained**

**Shore A Hardness**

Shore A hardness of the samples was determined 24 h after the vulcanization on a Mitotoyo portative hardness testing machine according to ISO 7619:2012. The hardness was determined by the penetration of a tester into the material under conditions previously set.

**Determination of the stress-strain properties**

Double sided belts were cut from the rubber samples on a plate punching machine 24 h after the vulcanization. The belts were measured by a micrometer with precision of 0.01 mm. The determination of modulus 100 and modulus 300, the tensile strength, the elongation at break of the vulcanizates studied were determined on a dynamometer at a 500 mm/min speed of the wedge action jaws according to ISO 37:2008.

**Determination of the residual elongation**

The residual elongation in the treated part of the samples was measured at least 1 min after the break. The two parts of the broken belt were reconnected and the length of the treated part was measured. The residual elongation was calculated by the formula:

\[
\varepsilon_r = \left[\left(\ell_2 - \ell_0\right)/\ell_0\right] 100 \quad (8)
\]

where \(\varepsilon_r\) was the residual elongation (%), \(\ell_0\) was the initial belt length (before tensioning), while \(\ell_2\) was the elongation observed 1 min after the release.

**Determination of accelerated heat ageing resistance**

The accelerated heat ageing resistance was determined according to ISO 188:2009 for 72 h at 100°C in a thermochamber ventilated by forced air convection. The aging coefficients were calculated by the formula:

\[
K = \left[\left(B - A\right)/A\right] 100 \quad (9)
\]

where \(B\) was the parameter value prior to aging, while \(A\) was the parameter value found after the aging. It is worth adding that the negative value of the aging coefficient (%) is indicative of aggravated mechanical properties.

**RESULTS AND DISCUSSION**

**Characterization of virgin and modified pyrolysis carbon black**

The results from the investigation of the properties of virgin and modified pyrolysis carbon black are summarized in Table 2.

The comparison of the properties of pyrolysis carbon black prior to and after the modification reveal that:

- The losses on heating of pyrolysis carbon black

<table>
<thead>
<tr>
<th>Properties</th>
<th>Virgin pyrolysis carbon black</th>
<th>Modified pyrolysis carbon black</th>
</tr>
</thead>
<tbody>
<tr>
<td>Losses on heating, %</td>
<td>1.45</td>
<td>1.78</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>16.2</td>
<td>8.6</td>
</tr>
<tr>
<td>Dibutyl phthalate absorption (oil number), ml/100 g</td>
<td>120</td>
<td>127</td>
</tr>
<tr>
<td>Iodine adsorption (iodine number), mg/g</td>
<td>182</td>
<td>171</td>
</tr>
<tr>
<td>Specific surface area, m²/g</td>
<td>137.95</td>
<td>120.85</td>
</tr>
</tbody>
</table>
change slightly upon modification mainly because of moisture and other volatile substances presence. The losses on heating are less than 1.8%.

- The ash content obtained after the modification is almost two times lower - 16.2% prior to and 8.6% after modification, correspondingly. Taking into consideration the main purpose of the treatment, it can be concluded that the goal is achieved.

- The modification does not affect the structure of pyrolysis carbon black because the oil number values of virgin and modified pyrolysis carbon black are close. The same is valid for the specific surface area and the iodine number, i.e. the modification results predominantly in decrease of the ash content of pyrolysis carbon black. The latter was subjected to additional analyses expecting further decrease of its content. The results from the weight analysis, AAS and ICP-OES are summarized in Table 3. The latter shows that ZnO content in pyrolysis carbon black is almost six times lower after its treatment with hydrochloric acid, which in turn verifies the conclusion that the main purpose of the modification was achieved. The content of SiO₂ is the highest in the ash of modified pyrolysis carbon black as it does not react with hydrochloric acid. In fact SiO₂ is present as the material subjected to pyrolysis included “green tyres” as well. It is known that they use silicon dioxide but not carbon black as filler. Another reagent, such as hydrofluoric acid, is required to remove SiO₂ but in fact its removal is not a must in case of pyrolysis carbon black as it is active filler. An option would be to introduce some silane coupling agent to the rubber mixture like it is usually done when filling with fresh silicon dioxide is carried out. Silane bifunctional nature improves the elastomer-filler interaction. On the other hand, the significantly decreased zinc oxide amount in the ash can be considered a significant success. The decrease of zinc oxide concentration in rubber compounds is a challenge worldwide because of zinc ions ecotoxicity. The greatest concentration decrease results from the modification in case of Na₂O, K₂O, Fe₂O₃, MgO and CaO. There are no changes in the concentration of TiO₂ and PbO.

### Curing characteristics of the rubber compounds comprising virgin (non-modified) and modified pyrolysis carbon black

The vulcanization isotherms of the SBR based compounds containing various amounts of virgin (SBR 1 and SBR 2) and modified (SBR 3 and SBR 4) pyrolysis carbon black are shown in Fig. 2. It is seen that they have an identical curve pattern. A wide plateau of
vulcanization (equilibrium torque curves) is outlined, which in turn indicates that the compounds are suitable for thick-wall items manufacture. The compounds containing virgin and modified pyrolysis carbon black of an amount equal to 50 phr carbon black show overlapping isotherms, unlike those referring to amounts equal to 70 phr. The most important fact is that the usage of modified pyrolysis carbon black does not worsen the curing characteristics of the compounds, i.e. there is no reason to exclude the pyrolysis solid product as filler.

The curing characteristics (minimum torque - $M_L$, maximum torque - $M_H$, as well as the difference between them – $\Delta M$; the thermoplastic interval - $t_{SP}$; optimum curing time - $t_{90}$; curing rate – $V_c$) of the studied SBR based compounds obtained at 160°C are presented in Table 4. The latter shows that the values of the vulcanization pa-

Table 3. Ash content data as obtained from weight, AAS and ICP-OES analyses.

<table>
<thead>
<tr>
<th>Substances</th>
<th>Content, %</th>
<th>Virgin pyrolysis carbon black</th>
<th>Modified pyrolysis carbon black</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>38.80</td>
<td>87.32</td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.77</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.31</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.50</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Na2O</td>
<td>2.41</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>K2O</td>
<td>5.65</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.53</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>TiO2</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>46.10</td>
<td>7.22</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>0.19</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Losses on heating, 1000°C</td>
<td>4.69</td>
<td>2.83</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Curing characteristics of the studied SBR based compounds obtained at 160°C.

<table>
<thead>
<tr>
<th></th>
<th>$M_L$, dNm</th>
<th>$M_H$, dNm</th>
<th>$\Delta M$, dNm</th>
<th>$t_{SP}$, min</th>
<th>$t_{90}$, min</th>
<th>$V_c$, %/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1</td>
<td>4.54</td>
<td>31.48</td>
<td>26.94</td>
<td>1:44</td>
<td>10:28</td>
<td>12.8</td>
</tr>
<tr>
<td>SBR 2</td>
<td>8.06</td>
<td>41.52</td>
<td>33.46</td>
<td>1:02</td>
<td>10:50</td>
<td>10.8</td>
</tr>
<tr>
<td>SBR 3</td>
<td>4.56</td>
<td>32.00</td>
<td>27.44</td>
<td>1:44</td>
<td>10:57</td>
<td>11.8</td>
</tr>
<tr>
<td>SBR 4</td>
<td>9.13</td>
<td>47.38</td>
<td>38.25</td>
<td>1:05</td>
<td>10:54</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table 5. Mechanical properties of the SBR based composites filled with virgin and modified pyrolysis carbon black.

<table>
<thead>
<tr>
<th></th>
<th>SBR 1</th>
<th>SBR 2</th>
<th>SBR 3</th>
<th>SBR 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus 100, MPa</td>
<td>3.2</td>
<td>5.2</td>
<td>3.6</td>
<td>6.3</td>
</tr>
<tr>
<td>Modulus 300, MPa</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength, $\sigma$, MPa</td>
<td>12.2</td>
<td>11.8</td>
<td>12.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Elongation at break, $\varepsilon_{100}$, %</td>
<td>305</td>
<td>227</td>
<td>284</td>
<td>198</td>
</tr>
<tr>
<td>Residual elongation, $\varepsilon_{25}$, %</td>
<td>8</td>
<td>5</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Shore A Hardness, relative units</td>
<td>69</td>
<td>78</td>
<td>71</td>
<td>80</td>
</tr>
</tbody>
</table>
Parameters increase at higher filler amounts, regardless of the presence or absence of modification, i.e. the pyrolysis carbon black has no effect on the vulcanization process.

**Mechanical properties of the SBR based composites filled with virgin and modified pyrolysis carbon black**

The mechanical properties of the SBR based vulcanizates are summarized in Table 5. It is seen that the values for the modulus 100 ($M_{100}$) of all studied SBR based vulcanizates increase at higher filler amounts. The increase of $M_{100}$ values of vulcanizates containing less filler is smaller (11%) in case of modification, while that of vulcanizates containing higher filler amounts is more pronounced (17.5%).

Modulus 300 ($M_{300}$) is achieved only in case of a sample containing virgin pyrolysis carbon black of an amount equal to 50 phr carbon black.

The slight changes in the tensile strength values demonstrate that the modification of pyrolysis carbon black has a beneficial effect on that property.

The elongation at break decreases with the increase of pyrolysis carbon black amount. It is less than 10% for vulcanizates containing virgin and modified pyrolysis carbon black of an amount equal to 50 phr, while it is 13%, when the amount considered is equal to 70 phr. Hence, the modification of the filler, despite of the slight tendency of decrease, has no significant effect on the values of that parameter.

The residual elongation decreases with the increase of pyrolysis carbon black amount, but does not change with the filler modification.

Shore A hardness values increase slightly with the filler amount increase for vulcanizates containing the same filler. Identical change is observed in case of filler modification.

The results presented show that the values of modulus 100, the tensile strength and Shore A hardness for vulcanizates containing modified pyrolysis carbon black increase slightly when compared to those referring to vulcanizates containing virgin pyrolysis carbon black. Meanwhile, the values of the elongation at break and the residual elongation are slightly lower. This is most probably due to the lower ash content in the modified pyrolysis carbon black and the fact that it consists predominantly of silicon oxide. It should be added that higher values of $M_{100}$ and $M_{300}$ of the tensile strength and hardness of the vulcanizates as well as the lower elongation values are characteristic of all compounds containing silicon oxide.

**Resistance to heat aging**

The heat aging coefficients of the SBR based vulcanizates are presented in Table 6. The heat aging resistance of the vulcanizates containing minimal amounts of virgin and modified pyrolysis carbon black (equal to 50 phr active substance) is improved in regard to the tensile strength and the elongation at break. The tendency remains unchanged with increase of pyrolysis carbon black amount.
Table 6. Changes in the mechanical properties of SBR based vulcanizates following their heat aging at 100°C.

<table>
<thead>
<tr>
<th></th>
<th>K_σ, %</th>
<th>K_{ε1}, %</th>
<th>K_{Sh}, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1</td>
<td>-31.1</td>
<td>-54.4</td>
<td>10.1</td>
</tr>
<tr>
<td>SBR 2</td>
<td>-23.9</td>
<td>-55.5</td>
<td>2.6</td>
</tr>
<tr>
<td>SBR 3</td>
<td>-25.8</td>
<td>-50.0</td>
<td>7.6</td>
</tr>
<tr>
<td>SBR 4</td>
<td>-21.0</td>
<td>-47.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*K_σ* – aging coefficient with regard to tensile strength;
*K_{ε1}* – aging coefficient with regard to elongation at break;
*K_{Sh}* – aging coefficient with regard to Shore A hardness.

The heat aging resistance coefficient with regard to Shore A hardness has positive values for all vulcanizates studied. The modification of pyrolysis carbon black affects the heat aging resistance of SBR based vulcanizates. The change in Shore A hardness values is smaller in case of modified pyrolysis carbon black. Hence those compounds are more aging resistant.

**CONCLUSIONS**

Pyrolysis carbon black obtained from waste tyres pyrolysis is successfully modified by a method designed to decrease the ash content and that of zinc oxide in particular. It is found that the modification introduced decreases two times the ash content and six times the zinc oxide concentration in the ash.

The studies on the curing characteristics, the mechanical properties and the heat aging resistance of SBR based vulcanizates containing virgin and modified pyrolysis carbon black demonstrate that:

- The curing characteristics are not affected by the modification of the pyrolysis carbon black.
- The values of modulus 100, the tensile strength and Shore A hardness for the vulcanizates containing modified pyrolysis carbon black increase, while the elongation at break and residual elongation decrease slightly. The effects observed are related to the decreased ash content in pyrolysis carbon black following the modification as well as to the increased silicon oxide concentration in the remaining ash.
- The modified pyrolysis carbon black has a beneficial effect on the heat aging resistance of the vulcanizates.

Additional decrease of the ash content in case of using pyrolysis carbon black can be achieved by a further modification with another reagent, e.g. hydrofluoric acid. This will result in silicon oxide elimination. Silane can be used instead of the secondary modification as it enhances the interaction between the rubber macromolecules and silicon dioxide. A reinforcement effect is expected. The latter will be the scope of further studies.

**Acknowledgements**

The authors acknowledge the financial support provided by the Operational Programme Development of the Competitiveness of the Bulgarian Economy 2007-2013, Procedure BG161PO003-1.1.06 - Support for Research and Development Activities of Bulgarian Enterprises; Priority Axis I: Knowledge and Innovations Based Economic Development (Contract BG161PO003-1.1.06-0034).

**REFERENCES**


IN-SITU PREPARATION OF POLYAMIDE-6/POLYPROPYLENE GLYCOL COPOLYMERS WITH MINERAL FILLERS

Petko Krastev, Roza Mateva

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: p_krustev_eng@yahoo.co.uk

ABSTRACT

Polyamide-6 /Polypropylene glycol (PPG) copolymers were synthesized via anionic polymerization of ε-caprolactam in the presence of inorganic additives - graphite and boron carbide using isophorone diisocyanate end functionalized PPG prepared in-situ as a macroactivator. Sodium caprolactam was used as an initiator. The influence of the graphite and boron carbide fillers on the degree of conversion was investigated. The copolymers obtained were characterized by $^1$H NMR and FTIR spectroscopies. The charpy impact strength of the composites was evaluated.

Keywords: polyamide-6, copolymers, graphite, boron carbide.

INTRODUCTION

The focus on the sustainable development of industry led in the recent years to the necessity of new materials able to meet the most stringent specifications for mechanical, thermal, electrical properties but reducing the environmental footprint. In many cases engineering plastics, the most common one still being Polyamide-6 (PA-6) and Polyamide 6,6 (PA-6,6) are able to match these requirements due to their high tensile strength, stiffness, high melting point, relatively good impact/chemical resistance and lower weight compared to that of metals. As different applications of these materials have different specifications, the need of modifying their properties for certain end-use is critical. This area of polymer modification is explored extensively and a broad range of commercial modifiers is presented on the market. Modifiers based on rubbers, acrylics, silicones, polyurethanes are developed to improve the impact strength of PA-6. Mineral fillers like glass fibers, carbon nanotubes [1], but also aramid types of polymers are incorporated into the polymer matrix in the course of the final stages of the injection molding process aiming at better tensile strength, temperature properties and dimensional stability. Lubricants like metal stearates or high molecular silicones are usually applied to obtain better processing-melt flow and mold release. Another aspect of properties modification refers to the development of copolymers or polymer blends, the most popular ones being PA-6 and PA-6,6 copolymer, PA-6,6/ Polyphenylene oxide, PA-6 blends with polyolefins, etc. Thus the use of PA-6 in many fields like the production of automotive-under the hood appliances, etc., requiring materials able to withstand high temperatures for extended periods of time, has greatly increased. On the other hand, the continuous increase of the energy costs and the raw materials prices, the concept of light weighting (metal replacement) across the industry as well as the usage of renewable material sources drive the interest towards creating new approaches to polymer materials. One of them, the so called reaction injection molding (RIM) was developed by Monsanto in 1970s and further commercialized by DSM [2]. This process allows producing the final plastic part from ε-caprolactam (ε-CL), polyether prepolymer and in initiator by one-step process. This concept, applicable to PA-6 in particular,
allows significant energy savings. It provides also modification of the properties of the PA-6 aiming to meet certain requirements. This is achieved by introduction to the polymer chain of elastomeric segments such as polybutadiene, styrene-butadiene, polyols, etc. [3, 4]. It is worth adding that the application of the RIM concept to PA-6 copolymerization envisages the formulation of a 3-component system (ε-CL, prepolymer, filler) as PA-6 is usually modified with the introduction of mineral fillers [5, 6]. The behavior of these composite structures has to be investigated as they affect the polymerization process, while their properties depend in turn on the concentrations of the prepolymer and the filler. The present paper reports data on the copolymerization of PA-6 with polypropylene glycol (PPG) in the presence of two mineral fillers- graphite and boron carbide (B\textsubscript{4}C) in view of their possible participation in the RIM process.

EXPERIMENTAL

Materials

The monomer ε-CL (BASF), M\textsubscript{v}=113.16 was dried for 3 days over P\textsubscript{2}O\textsubscript{5} in a vacuum oven at 60°C. The initiator, sodium salt of ε-CL (Na-CL), was synthesized following the procedure described in ref. [7], M\textsubscript{v}=424. Isophorone diisocyanate (5-isocyanate-1-isocyanatomethyl-1,3,3-trimethylcyclohexane) (IF;Merck), methanol (Fluka), toluene (Fluka) were used as received. PPG (Fluka) (average molecular mass of 2000) was kept in a molecular sieve for 10h at 25°C under vacuum. Graphite of particle size (PS) of 20 µm and B\textsubscript{4}C (Fluka) of PS of 15-62 µm were heated at 150°C for 2 min prior to use.

Synthesis

Functionalization of PPG with isophorone diisocyanate

The PPG (1 mol dissolved in 5 ml toluene) was placed into a 250 ml flask equipped with a separating funnel, a reflux condenser, a thermometer, a stirrer and N\textsubscript{2} inlet. Isophorone diisocyanate (2.2 mol) was added dropwise through the separating funnel at vigorous stirring. The reaction was carried out at 50°C for 4 h. FTIR spectra showed that the NCO group absorption band reached a constant value at ν=2269.9 cm\textsuperscript{-1} on the 4-th hour in correspondence with previous studies [8].

Synthesis of PA-6/PPG polymers with graphite and B\textsubscript{4}C

The polymerization was carried out in the bulk at 180°C with the application of:

a) the ampule technique. Functionalized PPG with IF, the monomer ε-CL, additives (Graphite or B\textsubscript{4}C) and ampules were placed into a glass flask under nitrogen atmosphere and melted for 20 min at 120°C by vigorous stirring (Macroactivator preparation in-situ). After mixture homogenization, the temperature was increased to 140°C, then the initiator (Na-CL) was added at vigorous stirring and the melt was forced into ampules by N\textsubscript{2}.

b) the mold casting. The melt was prepared following the procedure described in (a). It was then transferred to an aluminum mold pre-heated at 180°C.

Block copolymers of different ratios of PPG:IF, graphite and B\textsubscript{4}C were prepared. The initiator concentration was equal to 1 mol % in reference to the monomer quantity.

Analyses

Degree of conversion

The polymers obtained were placed into a Soxhlet apparatus, while the non-reacted monomers were extracted with methanol for 8h. The residue formed was dried in vacuum at 60°C until constant weight was reached. The degree of conversion was determined gravimetrically as a ratio of the weights of the polymers prior to and after the extraction. The additives B\textsubscript{4}C and graphite were not removed from the compound in calculating the values as they being insoluble in methanol would not affect the values of the degree of conversion.

\textsuperscript{1}H NMR

The \textsuperscript{1}H NMR spectra were recorded on a Bruker AM400 apparatus operating at 400MHz. The \textsuperscript{1}H NMR analysis of the purified copolymers was performed in a mixture of HCOOH:CDCl\textsubscript{3} (1:1 v/v) using formic acid as an internal standard.

FTIR

The IR spectra of copolymers free from additives and monomers were recorded in the range of 4000 cm\textsuperscript{-1}-450 cm\textsuperscript{-1} using a Perkin Elmer 1600 (FTIR) spectrophotometer with KBr pellets.

Charpy Impact Strength

The impact resistance was measured at room temperature by Charpy pendulum on 50 mm x 4 mm x 6 mm specimens with average notch depth of 0.5 mm.
The distance between the supports was 40 mm, while the pendulum velocity of impact was 2.9 ms\(^{-1}\).

**RESULTS AND DISCUSSION**

It is known that \(\varepsilon\)-CL polymerization is relatively slow and proceeds with a significant induction period. This problem can be overcome by using macroactivators [9]. Thus, the induction period is eliminated and the polymerization occurs within several minutes leading to polymer-monomer equilibrium. Isophorone functionalized PPG was used as a macroactivator aiming the formation of PA-6/PPG/Graphite and PA-6/PPG/B\(_4\)C copolymers. The polymerization mechanism is shown in Fig. 1.

The PPG macroactivator was synthesized in two steps. The first one referred to the functionalization of PPG using isophorone diisocyanate. It was followed by in-situ synthesis of the corresponding N-carbamoylactam proceeded.

Several polymerizations of \(\varepsilon\)-CL varying the PPG-IF and graphite or B\(_4\)C content were carried out. The ratio of the components in the polymerization system was varied in order to investigate the influence of the fillers and the macroactivator on the degree of conversion. The low molecular weight activator acetyl caprolactam (Ac-CL) was used as a reference. As the copolymerization process proceeds with high polymerization rate and degree of conversion, it is attractive to obtain different composite materials of various properties.

The changes in the degree of conversion of PA-6/PPG-IF/graphite copolymers as a function of the PPG-IF and graphite content are shown in Figs. 2 - 4. It is seen that the degree of conversion is very high in most of the cases considered. A lower degree of conversion is obtained for PA-6/PPG-IF/graphite. Its PPG-IF content was the highest.

Similar results were observed for the copolymerization systems based on PA-6/PPG-IF, where B\(_4\)C was used as filler. The influence of B\(_4\)C concentration on the degree of conversion is almost negligible. In fact the macroactivator content is the main factor (Fig. 5).

The PA-6/PPG-IF/graphite as well as the PA-6/PPG-IF/B\(_4\)C copolymers obtained upon extraction of low Fig. 1. Mechanism of activated anionic polymerization (R =PPG-IF).

Fig. 2. Degree of conversion at different percentage of PPG-IF at 5\(^{th}\) min polymerization time.

Fig. 3. Degree of conversion at 10\(^{th}\) min of polymerization with different percentage of PPG-IF co-monomer.
molecular weight products and fillers are investigated by $^1$H NMR and FTIR.

The FTIR spectra (Figs. 6 and 7) show the characteristic bands of PA-6. The absorption at 3299 cm$^{-1}$ refers to N-H Amide I, Amide II, that at 3072 cm$^{-1}$ is determined by the vibrations of N-H bond of Amid II, while those at 1637 cm$^{-1}$ and 1542 cm$^{-1}$ correspond to -C=O in Amide I and N-H + C-N in Amide II, correspondingly. The absorption at 688 cm$^{-1}$ is typical for PA-6. The absorption of the C-O-C stretching vibration at 1119 cm$^{-1}$ is due to the incorporated PPG.

The synthesized copolymers are investigated by $^1$H NMR as well. The results obtained are illustrated in Fig. 8. Peaks at 1.69 ppm, 1.60 ppm (d), 1.39 ppm (s) (-CH$_2$), 2.39 ppm (m) (-CH$_2$-CO-), 3.32 (s) (-CH$_2$-NH-) are outlined. They are typical for PA-6. The peaks recorded at 1.24 ppm (s) (-CH$_3$), 3.65 ppm (s), (-CH$_2$-O), 3.78 ppm (s), (-CH(CH$_3$)-) refer to the PPG block.

All results pointed above provide to conclude that copolymers of PA-6 and PPG are synthesized.

**Charpy Impact Strength**

One of the main disadvantages of PA-6 refers to its effect on the impact strength observed. It is expected that the copolymers obtained will show better mechanical properties. That is why the influence of graphite and B$_4$C additives on the impact strength of the newly prepared copolymers is followed. The results show significantly improved impact strength of the copolymers obtained when compared to that of pure PA-6/PPG ones (Figs. 9, 10). The effect is outlined.
up to 5 % presence of fillers. No performance change is observed on further increase of the latter. Therefore it can be concluded that the optimal filler concentration is 5 mass % in case 3 % PPG is used as a macroactivator.

CONCLUSIONS

Novel composite materials based on activated anionic polymerization of ε-CL and PPG-IF macroactivator are successfully obtained in the presence of mineral fillers - graphite and B₄C. The formation of PA-6/PPG copolymers is verified by FTIR and 'H NMR analysis. It is found that the mineral filler incorporation results in significant improvement of the impact strength.

In case of high concentrations of the macroactivator (10 %), the increase of the graphite content leads to increase of the polymerization rate and yield. This provides to consider it as an active additive, unlike B₄C which is practically inert. On the other hand, at certain levels of loading (3 – 5 %), both fillers contribute to the improvement of the composites impact strength.

REFERENCES

1. D.Yan, G.Yang, Synthesis and properties of homogeneously dispersed polyamide 6/MWNTs nanocom-
EFFECTS OF TEMPERATURE AND CONCENTRATION DEPENDENT VISCOSITY ON
ONSET OF CONVECTION IN POROUS MEDIA

Fatemeh Bahadori, Sima Rezvantalab

Chemical Engineering Department,
Urmia University of Technology,
P.O. Box: 57166-419, Urmia, Iran
E-mail: f.bahadori@che.uut.ac.ir

ABSTRACT

The instability theory is applied to diffusion-convection phenomena in porous media, where the viscosity of the oil varies due to gas dissolution. An important application of this theory refers to the case where the diffusion-convection is employed as an EOR (Enhanced Oil Recovery) technique in oil reservoirs.

This paper presents results on the onset of Rayleigh–Bénard and Darcy–Bénard–Marangoni convective motions of a Boussinesq fluid taking into account its temperature dependent viscosity and surface tension. Numerical simulations are carried out using the Volume of Fluid (VOF) model, while that of Darcy is applied to the mathematical formulation in evaluating the flow structure and the heat transfer in a two-dimensional fluid porous layer. The results obtained show the trend observed by Hashim and Wilson.

Keywords: Rayleigh–Bénard (RB) convection, Darcy–Bénard–Marangoni (DBM) convection, onset of convection.

INTRODUCTION

Darcy–Bénard (DB) convection is a type of natural convection determined by the unstable vertical density difference in a horizontal fluid saturated porous layer heated from below. The DB convection is extensively studied [1 - 3] because of its importance referring to many scientific, engineering and technological applications such as oil and gas recovery and underground contaminant transport.

The buoyancy-induced flow in a cavity when the heat transfer comes from below leads to patterns of convection cells. However, apart from the buoyancy forces, the convective instability can also result from the surface tension at the free surface contact with the gas known as Darcy–Marangoni (DM) convection. The Marangoni convection in a liquid saturated porous media is discussed [4, 5] in details. Rudraiah and Prasad study [6] the effect of Brinkman boundary layer on the onset of convection in a porous layer driven by surface tension gradients. In addition, Nield suggest a composite fluid and porous layer model for the study of Marangoni convection in a porous layer [7]. Desaive, Lebon and Hennenberg investigate [8] the coupled capillary and gravity driven instability in a fluid layer overlying a porous one. Using the Brinkman’s model to describe the flow in the porous medium they determine the critical Rayleigh and Marangoni numbers for the convection onset. Shivakumara et al. [9] obtain an exact solution for the onset of the surface tension driven convection in superposed fluid and porous layers using the Darcy momentum law.

The aim of this paper is to simulate a porous layer saturated with liquid which is subjected to Darcy–Bénard, Darcy–Maragoni and Darcy–Bénard–Maragoni (DBM) convection.

GOVERNING EQUATIONS

A fluid confined in a porous medium is considered with the assumption that the following linear dependencies hold for the density and the viscosity:

$$\rho = \rho_0 \left[1 - \alpha (C_0 - C)\right]$$ (1)

$$\frac{\mu}{\mu_0} = 1 - \beta (C - C_0)$$ (2)
It is assumed that Boussinesq approximation is valid and the fluid density varies linearly with the temperature in the buoyancy force term:

$$\rho = \rho_0 [1 - \alpha_T (T - T_0)]$$

(3)

where \(\alpha_T\) is the thermal expansion coefficient and \(\rho_0\) is the density at \(T = T_0\). The fluid viscosity is assumed to vary linearly with the temperature in correspondence with:

$$\frac{\mu}{\mu_0} = 1 - \beta_T (T - T_0)$$

(4)

Moreover, the surface tension is also a function of temperature

$$\frac{\sigma}{\sigma_0} = 1 - \tau (T - T_0)$$

(5)

The governing equations for the variable viscosity conditions are formulated [10] as follows:

The Continuity equation

$$\nabla \cdot \mathbf{v} = 0$$

(6)

The equations of motion

$$\frac{\mu}{K} \mathbf{v} = -\nabla P + \rho g + \mu \nabla^2 \mathbf{v} + \nabla \mu \cdot \nabla \mathbf{v} + \nabla \left( \nabla \cdot \mu \mathbf{v} \right)$$

(7)

The equation of diffusion

$$\mathbf{v} \nabla C = D_e \nabla^2 C$$

(8)

Wooding defined [11] the Rayleigh number for a viscous liquid of variable density in a porous medium. The relation he advances is:

$$R = \frac{d \rho}{dz} \frac{g K d^2}{\mu D_e}$$

(9)

where \(K\) is the permeability of the porous medium, \(d\) is tube diameter, while \(D_e\) is the effective diffusivity of the dissolved material.

**NUMERICAL DETAILS**

The governing equations were discretized by applying the second-order upwind scheme for the volume fraction and the power law scheme for the momentum and energy equations. The VOF approach was employed to simulate the heat transfer and the fluid flow in the porous media.

As shown in Fig. 1, the simulation area refers to a liquid saturated porous layer of thickness \(L\) and two lateral walls, an impermeable on the left and a symmetrical on the right. The bottom boundary is rigid, while the top surface, which is in contact with the gas, is treated as a free surface. A temperature difference of \(\Delta T\) is maintained between the top and bottom boundaries of the porous layer.

**RESULTS AND DISCUSSION**

The flow structure and the heat transfer due to Darcy-Bénard, Darcy-Maragoni and Darcy-Bénard-Maragoni convection are discussed.

**Streamlines**

Fig. 2 shows the streamlines that are formed due to DB and DBM convection. As it can be seen, the convection loops in case of DBM convection are bigger than those in presence of DB convection, illustrating thus the surface tension effect. In addition, the greater size of DBM convection loops corresponds to a smaller number of loops.

**Heat transfer**

Fig. 3 shows the average Nusselt number calculated for a cavity subjected to heat transfer from bellow. As it is seen, the increase of the thermal Rayleigh number results in increase of the average Nusselt number. In addition, it shows that the highest average Nusselt number is obtained in case of DBM convection. Besides, the Nusselt number obtained in presence of DB convection is higher than that obtained for DM convection.
CONCLUSIONS

Simulation of the onset of convection in a porous layer with concentration and temperature dependent viscosity is carried out. The Darcy model is employed in the mathematical formulation to evaluate the flow structure and the heat transfer in a two-dimensional fluid porous layer.

Over stable curves

Fig. 4 shows typical stability curves for DB and DM convection. These results correspond to the trend reported by Hashim and Wilson [4]. The latter investigation refers to a case which treats the effect of the surface tension as well.

List of symbols

- \( a \)  dimensionless wave number
- \( c \)  concentration of diffusing fluid
- \( D_e \)  effective diffusivity in porous medium
- \( D \)  diffusivity in porous medium
- \( d \)  tube diameter
- \( g \)  gravity constant
- \( g \)  gravity vector
- \( K \)  permeability
- \( L \)  fluid layer thickness
- \( Nu \)  Nusselt number
- \( p \)  pressure
- \( R \)  Rayleigh number
- \( T \)  temperature
- \( w \)  \( z \)-component of the velocity
- \( W \)  dimensionless \( w \)
- \( v \)  velocity vector
- \( z \)  vertical coordinate
- \( Z \)  dimensionless vertical coordinate
- \( \alpha \)  coefficient of concentration expansion
- \( \alpha_c \)  coefficient of thermal expansion
- \( \beta \)  viscosity-concentration dependence factor
\( \beta_T \quad \text{viscosity-temperature dependence factor} \)

\( \mu \quad \text{fluid viscosity} \)

\( \rho \quad \text{fluid density} \)

\( \tau \quad \text{surface tension -temperature dependence factor} \)

\( \sigma \quad \text{surface tension} \)

\textbf{Subscripts}

\( c \quad \text{critical property} \)

\( \text{property at reference concentration} \)

\textbf{REFERENCES}


LAUE FUNCTIONS MODEL VS SCHERRER EQUATION IN DETERMINATION OF GRAPHENE LAYERS NUMBER ON THE GROUND OF XRD DATA

Beti Andonovic, Misela Temkov, Abdulakim Ademi, Aleksandar Petrovski, Anita Grozdanov, Perica Paunović, Aleksandar Dimitrov

Faculty of Technology and Metallurgy, SS Cyril and Methodius University, Skopje, Macedonia
E-mail: beti@tmf.ukim.edu.mk

ABSTRACT

The present study reports data referring to the determination of the layers of graphene samples obtained by electrolysis in aqueous electrolytes and molten salts using a reverse change of the potential applied. The analysis, based on the calculation of 002 XRD peak intensities, is carried out with the application of the Scherrer equation and the Laue functions model. The latter results differ from those obtained on the ground of Scherrer equation but coincide with data obtained by Raman spectroscopy and other methods. This is attributed to the multi-layer structure of the graphene samples studied.

Keywords: graphene, electrochemical production, XRD analysis, layers, Scherrer equation.

INTRODUCTION

Graphene is the building unit of all carbon allotropes [1]. Mechanical exfoliation of graphite, chemical vapor deposition (CVD) on copper film surfaces [2], nanotubes cutting [3], and different electrochemical methods are used for the production of graphene [4, 5]. It can be obtained as monolayer- bi-layer- and multilayer-flakes or sheets [6] depending on the procedure used. The structural characterization of graphene is of outmost importance because its highly unusual properties are largely determined by its structure.

The number of layers in graphene samples can be estimated using XRD data. The latter can be described by the Scherrer equation which is found adequate [7]. But the application of the Laue functions model presents also definite interest as the results it gives are based on the treatment of the graphene thickness distribution. The present study is aimed at the comparative examination of the data obtained with the application of the Scherrer equation the Laue functions model using graphene samples produced electrochemically in aqueous and non-aqueous electrolytes.

Laue functions model in uniform and non-uniform graphene thickness distribution

The XRD pattern is analyzed using the following Laue functions model which includes graphene thickness distribution and certain parameters [8]:

\[
|F|^2 \propto \left| f(\theta) \right|^2 \sum_{j=0}^{N} \beta_j e^{ik\alpha_j} 
\]

where \( F \) is a structure factor, \( N \) is the number of graphene layer, \( f(\theta) \) is an atomic scattering factor which varies from 6.00 to 6.15 e/atom with incident radiation ranging from 2 to 433 KeV, \( k_a = (2\pi d \sin \theta) / \lambda \), where \( d \) is a lattice spacing between \( j \)th and \((j-1)\)th layer, \( \theta \) is an angle between the incident ray and the scattering planes, \( \lambda \) is a wavelength of X-ray, and \( \beta_j \) is an occupancy of \( j \)th graphene layer. The value of \( \beta_j \) is between 0 and 1. The employed equation parameters \( \beta_j \) make it possible to calculate the n-layer graphene regions coverage of the graphene samples produced by the two electrochemical procedures.

Hence XRD intensities of the curves in Fig. 1 (a-d) were calculated thereof.

In Fig. 1 (a-d), theoretical XRD curves are shown,
with intensities calculated using model (1). The values of employed parameters \( \beta_j \) provide an insight into occupations of each of the graphene layers and therefore corresponding coverages. In Fig. 1 (a-c) are shown graphenes with uniform thickness distribution, meaning all \( \beta_j \) parameters are equal and therefore highest layer covering 100 % of the area. Thus the curves represent bilayered graphene with 100 % coverage of the second layer, 3-layered graphene with 100 % coverage of the third layer, and 16 layered graphene with 100 % coverage of the 16-th layer.

In Fig.1d is shown a theoretical XRD curve of multilayered graphene with non-uniform thickness distribution. The employed \( \beta_j \) parameters enable the calculation of each of the \( j \)th layer region occupancy and hence the \( j \)th layer \( d_j \) coverage percentage, where \( d_{i-1} = \beta_{i-1} - \beta_i \), \( i = 2, 3, \ldots, n \). The calculations of the coverages are given in Table 1.

From the results given in Table 1, it is clear that the layers are non-uniformly distributed, where the monolayer graphene part covers 60 % of the structure. The average number of graphene layers is calculated as NGL = 3.312.

**Scherrer equation and graphene layers number in uniform and non-uniform graphene thickness distribution**

The mean dimension of the crystallite perpendicular to the plane of graphene samples \( L_{002} \) can be determined by the familiar Scherrer equation:

\[
L_{002} = \frac{k \cdot \lambda}{\beta \cos \theta}
\]

where \( k = 0.94 \) is the shape factor, \( \beta \) is the full width at half maximum given in radians, \( \lambda \) is a wavelength of X-ray, and \( \theta \) is the angle between the incident ray and the scattering planes. The number of graphene layers \( N \) may be determined from the equation \( L_{002} = (N - 1) d_{002} \), where \( d_{002} \) is the average distance between graphene planes [7].

In Table 2 are given the values for the curves, shown in Fig. 1 (a-d).

In the last two columns in Table 2, one may easily compare the values which are calculated results for number of graphene layers. In the case of uniform distribution of the graphene layers, the results are in good agreement, whereas in the case of non-uniform thickness distribution, the values greatly differ. Studies and
analysis that were performed upon graphene samples obtained by two different electrochemical methods, and which are further presented, show that in the case of non-uniform distribution, model 1 is more reliable method for determining the number of graphene layers.

**Determining graphene layers number for produced graphene samples with non-uniform graphene thickness distribution**

Two graphene samples are analyzed, with the focus on the determination of the graphene layers number. Scherrer equation method and model 1 are compared for obtaining results for the layers number of the graphene samples studied. The graphene samples were prepared by two different electrochemical methods: high temperature electrolysis in molten salt (graphene sample GMSE2) and electrolysis in aqueous solution (graphene sample GAE1), both using non-stationary current regime.

In Fig. 2a, are shown the theoretical curves calculated using model 1, in the case of graphene sample

<table>
<thead>
<tr>
<th>Parameter $\beta_j$: $j=1,2,\ldots,23$</th>
<th>Value</th>
<th>Occupancy of the $j$-th layer in %</th>
<th>Layer $d_j$</th>
<th>Share of the $j$-th layer in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>1</td>
<td>100</td>
<td>$d_1$</td>
<td>60</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>0.4</td>
<td>40</td>
<td>$d_2$</td>
<td>10</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>0.3</td>
<td>30</td>
<td>$d_3$</td>
<td>3</td>
</tr>
<tr>
<td>$\beta_4$</td>
<td>0.27</td>
<td>27</td>
<td>$d_4$</td>
<td>5</td>
</tr>
<tr>
<td>$\beta_5$</td>
<td>0.22</td>
<td>22</td>
<td>$d_5$</td>
<td>2</td>
</tr>
<tr>
<td>$\beta_6$</td>
<td>0.2</td>
<td>20</td>
<td>$d_6$</td>
<td>5</td>
</tr>
<tr>
<td>$\beta_7$</td>
<td>0.15</td>
<td>15</td>
<td>$d_7$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_8$</td>
<td>0.14</td>
<td>14</td>
<td>$d_8$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_9$</td>
<td>0.13</td>
<td>13</td>
<td>$d_9$</td>
<td>2</td>
</tr>
<tr>
<td>$\beta_{10}$</td>
<td>0.11</td>
<td>11</td>
<td>$d_{10}$</td>
<td>2</td>
</tr>
<tr>
<td>$\beta_{11}$</td>
<td>0.09</td>
<td>9</td>
<td>$d_{11}$</td>
<td>2</td>
</tr>
<tr>
<td>$\beta_{12}$</td>
<td>0.07</td>
<td>7</td>
<td>$d_{12}$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{13}$</td>
<td>0.06</td>
<td>6</td>
<td>$d_{13}$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{14}$</td>
<td>0.05</td>
<td>5</td>
<td>$d_{14}$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{15}$</td>
<td>0.04</td>
<td>4</td>
<td>$d_{15}$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{16}$</td>
<td>0.03</td>
<td>3</td>
<td>$d_{16}$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{17}$</td>
<td>0.02</td>
<td>2</td>
<td>$d_{17}$</td>
<td>1</td>
</tr>
<tr>
<td>$\beta_{18}$</td>
<td>0.01</td>
<td>1</td>
<td>$d_{18}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_{19}$</td>
<td>0.01</td>
<td>1</td>
<td>$d_{19}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\beta_{20}$</td>
<td>0.005</td>
<td>0.5</td>
<td>$d_{20}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_{21}$</td>
<td>0.005</td>
<td>0.5</td>
<td>$d_{21}$</td>
<td>0.4</td>
</tr>
<tr>
<td>$\beta_{22}$</td>
<td>0.001</td>
<td>0.1</td>
<td>$d_{22}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_{23}$</td>
<td>0.001</td>
<td>0.1</td>
<td>$d_{23}$</td>
<td>0.1</td>
</tr>
</tbody>
</table>
GMSE2 produced by electrolysis in molten salt at non-stationary current regime. The theoretical curves (1 and 2) are given for comparison to the theoretical curve (3) that exhibits good fitting to the experimental curve. The experimental curve GMSE2 is presented as (4).

In Fig 2b part of the Raman spectrum of sample GMSE2 is given, showing its C-peak. Its position \( \text{Pos}(C) \) is directly connected to the graphene layers number \( N \), and it varies with \( N \) as in the formula [9]:

\[
\text{Pos}(C) = \frac{2\alpha}{\mu} \sqrt{1 + \cos \left( \frac{\pi}{N} \right)}
\]

where \( \alpha = 12.8 \times 10^{18} \text{Nm}^{-1} \) is the interlayer coupling, and \( \mu = 7.6 \times 10^{-7} \text{kg A}^{-1} \) is the graphene mass per unit area.

According to the analysis of the XRD 002 peak and the employed \( \beta_j \) parameters, the \( j \)-layer region coverages are given in Table 3.

The average value for number of graphene layers for graphene sample GMSE2 is calculated as \( \text{NGL} = 2.4 \) for the dominant structure (above 75 %) and \( \text{NGL} = 7.43 \) for the overall structure, by calculations from model 1. Using the Scherrer equation for the number of graphene layers determination, was obtained \( N = 27.7 \).

According to the C-peak position, which is the only value from Raman spectra that directly points the number of graphene layers [9], for sample GMSE2 was calculated \( N = 2.54 \).

Model 1 stands out as the method giving results in accordance to C-peak calculations for graphene layers number.

In Fig. 3 are shown curves, calculated from the model 1, for graphene sample GAЕ1 produced by electrolysis in aqueous solution at non-stationary current regime, for \( \beta_j \neq 1 \), which suggests that the number of graphene layers has a distribution.

The dotted line (1) in Fig. 3 is calculated curve for uniformly distributed monolayer graphene, the line (2) which is narrower than the monolayer graphene line, but broader than the green experimental curve (3) GAЕ1, is calculated curve for a non uniform distribution of graphene layers number for a 3-layered graphene. The line (4) is calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene. There is a noticeable discrepancy with the experimental curve due to its asymmetry. However, as the correlation coefficient is \( \rho = 0.92 \), it provides an insight with a fair accuracy into \( j \)-layer graphene regions share. According to \( \beta_j \) parameters, the coverages of \( n \)-layer graphene regions are calculated (Table 4).

### Table 2. Calculated values for curves shown in Fig. 1a-d from Eq. 2 and model 1.

<table>
<thead>
<tr>
<th></th>
<th>( \theta ) (Deg)</th>
<th>( L_{002} ) (in nm)</th>
<th>( N ) (by ( L_{002} ))</th>
<th>( N ) (by model 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig.1a</td>
<td>12.36</td>
<td>11</td>
<td>7.17</td>
<td>2.9</td>
</tr>
<tr>
<td>Fig.1b</td>
<td>12.36</td>
<td>8</td>
<td>9.86</td>
<td>3.7</td>
</tr>
<tr>
<td>Fig.1c</td>
<td>12.36</td>
<td>1.5</td>
<td>51.6</td>
<td>15.3</td>
</tr>
<tr>
<td>Fig.1d</td>
<td>12.36</td>
<td>1.5</td>
<td>51.6</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Fig. 2. a) Non uniform multilayer distribution for Sample GMSE2 calculated from model 1; b) C-peak position in Raman spectrum for graphene sample GMSE2.
According to these calculations, the dominant structure (above 90%) is few-layered, and the average value for number of sample GAE1 graphene layers is calculated as $N_{GL} = 2.57$ for the dominant graphene structure and $N_{GL} = 4.25$ for the overall graphene structure. According to Scherrer equation the number of graphene layers is $N = 15.3$.

However, considering GAE1 TEM images and GAE1 Raman spectroscopy results (Fig. 4 a, b), model 1 again stands out as a method producing results which are in accordance with TEM images results and Raman spectrum $I_{2D}/I_G$ FWHM ratio. TEM images in Fig. 4 a, clearly indicate high share of few-layer region, particularly monolayer region, whereas from GAE1 Raman spectroscopy in Fig. 4 b, $I_{2D}/I_G = 1.49$, which estimates the number of GAE1 graphene layers as $N \approx 4$. The obtained number $N$ of graphene layers is in accordance with the number obtained by model 1.

**CONCLUSIONS**

This study shows that the accuracy of Scherrer equation method for determining the number of graphene layers by XRD data decreases as the level of non-uniformity of graphene thickness distribution increases. Therefore, another method is involved for determining the average number of graphene layers by XRD data in the studied graphene samples. It is a Laue functions model.

### Table 3. Coverages of $j$-layer GMSE2 graphene regions.

<table>
<thead>
<tr>
<th>Region Coverage</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer region</td>
<td>$\sim 18.75%$</td>
</tr>
<tr>
<td>2 layers region</td>
<td>$\sim 21.25%$</td>
</tr>
<tr>
<td>3-6 layers region</td>
<td>$\sim 3.75%$</td>
</tr>
<tr>
<td>7-8 layers region</td>
<td>$\sim 2.5%$</td>
</tr>
<tr>
<td>9-10 layers region</td>
<td>$\sim 1.25%$</td>
</tr>
<tr>
<td>$&gt; 10$ layers region</td>
<td>$&lt; 25%$</td>
</tr>
</tbody>
</table>

**Table 4. Coverages of $j$-layer graphene sample GAE1 regions.**

<table>
<thead>
<tr>
<th>Region Coverage</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer region</td>
<td>$\sim 40%$</td>
</tr>
<tr>
<td>2 layers region</td>
<td>$\sim 10%$</td>
</tr>
<tr>
<td>3-6 layers region</td>
<td>$\sim 15%$</td>
</tr>
<tr>
<td>7-10 layers region</td>
<td>$\sim 5%$</td>
</tr>
<tr>
<td>$&gt; 10$ layers region</td>
<td>$&lt; 10%$</td>
</tr>
</tbody>
</table>
which includes graphene thickness distribution and the employed parameters allow calculations of graphene j-layer region coverage, thus enabling determination of the graphene layers number.

Graphene samples which are subject of our study are produced by two different methods: high temperature electrolysis in molten salt and electrolysis in aqueous solution, both using non-stationary current regime.

The analysis and comparison of the two methods show that both are in agreement as far as graphene samples that are considered have uniform thickness distribution. However, in non-uniform distribution cases, Laue functions model (model 1) stands out as reliable and in accordance with other methods results. It additionally provides information on graphene samples j-layer occupancies and therefore coverages with a fair accuracy. The results relevant to graphene samples produced by electrolysis in aqueous electrolyte and by electrolysis in molten salts, both using reverse change of the applied potential, have shown that these graphene samples are few-layered.

REFERENCES
8. A. Ruammitree, H. Nakahara, K. Akimoto, K. Soda, Y. Saito, Determination of non-uniform graphene thickness on SiC (0 0 0 1) by X-ray diffraction, Applied Surface Science, 282, 2013, 297-301.
ABSTRACT

The initial steps of sodium borohydride oxidation are studied at PtAu alloy electrodes of Au bulk composition of 20, 40, 60 and 80 at. %. Linear sweep voltammetry is applied at low scan rates in 0.01 M NaBH$_4$ in 1.00 M NaOH. The experiments are performed at four temperature values in the range from 293.2 K to 323.2 K. The data obtained are compared to those referring to Pt and Au as well. The values of the exchange current density and the total number of electrons exchanged are determined following the effect of the temperature applied. The activation energy for the exchange current density is found dependent on the bulk composition of the alloys studied. The lowest value is expected for an alloy of Au bulk content of ca 50 at. %. The dependence on the surface composition is only a tentative one in view of the sensitivity of the reaction studied. Its proceeding requires the presence of four adjacent active centers on the electrode surface whose heats of adsorption are strongly affected by the alloying.

Keywords: borohydride electrooxidation, electrocatalysis, platinum, gold, PtAu alloys.

INTRODUCTION

Sodium borohydride (NaBH$_4$) has hydrogen content of 10.6 mass % and theoretical H-capacity of 10.8 mass % making it one of the most attractive compounds for chemical hydrogen storage [1]. Hydrogen is released through a hydrolysis reaction proceeding in correspondence with:

NaBH$_4$ + 4H$_2$O $\rightarrow$ NaB(OH)$_4$ + 4H$_2$ \hspace{1cm} (1)

The reaction can take place in room conditions but it has to be catalyzed. Sodium borohydride can also be used as a direct fuel [2 - 5] whose hypothetical oxidation reaction is:

NaBH$_4$ + 8OH$^-$ $\rightarrow$ NaBO$_2$ + 6H$_2$O + 8e$^-$ \hspace{1cm} (2)

It is worth noting that if the oxidation of hydrogen produced in reaction (1) is considered, the two processes are formally equivalent. But BH$_4^-$ poor anodic efficiency of the direct borohydride fuel cell (DBFC) is attributed to reaction (1) and which is why the underlying challenge is to find an electrocatalyst that is active towards oxidation while being inert towards hydrolysis.

A large number of fundamental electrochemical studies of BH$_4^-$ oxidation were carried out on Au [6-25] and Pt [7,8, 21, 22, 26-31] of various catalyst morphologies with the application of electrochemical, electroanalytical and surface techniques. Calculations and modeling based on the Density Functional Theory (DFT) were carried out as well. For several years the interest to Au as an anode material in DBFC was much greater...
than that to Pt as it was believed that it catalyzed predominantly the direct $BH^-_4$ oxidation reaction (BOR), while Pt favored the competition between this preferred reaction and the proceeding heterogeneous hydrolysis. It is well recognized that there are uncertainties regarding BOR mechanism on Au. Some of the schemes advanced suggest several EC steps [6, 8, 16], other focus on an overall CE pathway at low reaction overpotentials [11, 17, 22]. It is suggested [12, 22-24, 25] that BOR is limited at low overpotentials by the weak initial adsorption of the $BH^-_4$ ion resulting in a very low surface coverage of $BH^-_4$ and subsequent reactive intermediates.

There are some uncertainties in connection with BOR mechanism on Pt as well. They are determined by the competition between several electrochemical and chemical steps generating hydrogen as a by-product even at pH 14. It is assumed [21, 22, 26] that BOR at Pt starts with destructive chemisorption of $BH^-_4$ to the electrode followed by the ionization of the adsorbed surface hydrogen:

$$BH^-_4 + Pt \leftrightarrow Pt - BH^-_4 + H^+ + 2e^- \quad (3)$$

This low potential direct oxidation at Pt precedes [22] the hydrolysis of $BH^-_4$, which follows CE-type [8] reactions, i.e. the complete oxidation of $BH^-_4$ follows stepwise mechanism. The comparative investigation of BOR on bulk Au and Pt electrodes [21] provides physical evidence of the intermediate species and $H_2$ formation as a function of the electrode potential advancing the knowledge that Pt can be Faradaic efficient, unlike Au, i.e. Pt will outperform Au as an anode material in DBFC.

Binary Pt-based electrocatalysts [32-40] are found to circumvent some of the major problems referring to borohydride oxidation transformation. All results obtained imply synergism in the electrocatalytic activity of PtAu bimetallic systems. The comparative study of the kinetics of borohydride oxidation in the range of the first anodic maximum at Pt, Au and PtAu bulk alloys [40] shows that two-step formation of adsorbed species containing BOH and H proceeds at the alloy surface. The electronic effect determining the performance observed is attributed to decrease of B-H bonding strength when compared to that of unalloyed Pt. In view of the perfect control [30, 31, 41] of the surface morphology, texture and structure required for the juxtaposition of the intrinsic activity of Pt and Au, it looks challenging to follow the effect of the alloys surface composition on the behavior of the alloys studied in the range of the first anodic maximum. This is in fact the aim of the present communication.

**EXPERIMENTAL**

The kinetic study envisaged was carried out following the procedure described in [40]. Linear sweep (LSV) voltammetry was applied varying the scan rate from 0.020 Vs$^{-1}$ to 0.100 Vs$^{-1}$ and the temperature within the interval from 293.2 K to 323.2 K. The electrochemical measurements were performed with an Autolab PGSTAT 30 with a FRA2 module driven by GPE5 4.9 and FRA 4.9 software (EcoChemie, The Netherlands).

Stationary electrodes of PtAu alloy electrodes of Au bulk content of 20, 40, 60 and 80 at. % were used. Comparative investigations were carried out at polycrystalline Pt and Au electrodes as well. Pt or Au mesh counter electrodes and Ag/AgCl (KCl) reference electrode were used. The true electrode surface of the working electrodes was determined at room temperature prior to each experiment in a three-compartment cell containing 1.0 M aqueous solution of NaOH. The working electrode surface had to be pretreated because of the fouling observed [21, 42]. The procedure developed [40] was applied in a second cell of identical configuration and dimensions. The values of the alloys surface composition were within the error range of the method applied.

All experiments were conducted in 0.01M solution of NaBH$_4$ (Merck, p.a.) in 1.0 M NaOH (Merck, p.a.), Bi-distilled water was used. Each of the borohydride solutions was prepared prior to the corresponding experiment to exclude any homogeneous hydrolysis. A third three-electrode electrochemical cell was used.

**RESULTS AND DISCUSSION**

The comparative investigation of the electrodes catalytic performance is carried out on the ground of the exchange current densities observed following the effect of the alloys composition and the temperature applied. The exchange current density, $j_0$, is the product of the electrochemical specific rate constant and a concentration term containing the activities of the oxidizing and reducing species. It is introduced in electrochemical kinetics [43-45] by the rate equation of an electrode reaction:

$$j = nFv = j_0 \left\{ \exp \left( \beta F \eta / RT \right) - \exp \left[ - (1 - \beta) F \eta / RT \right] \right\} \quad (4)$$
where \( \eta \) is the overpotential (\( \eta \) is the difference between the potential \( E \) and the reversible potential \( E_{\text{rev}} \)), \( \beta \) is the symmetry factor, \( \nu \) stands for the chemical reaction rate, while the rest of the symbols have their usual meaning.

At low values of the overpotential (\( |\beta F \eta / RT| \leq 0.1 \)) Eq. (4) can be put [44] into linear form by expanding the exponent and taking only the first two terms:

\[
j(\eta) = \frac{j_0 F}{RT} \eta \tag{5}
\]

This relationship is found valid for a complex electrode reaction including intermediates adsorption. The derivation [44] is done considering the system at a steady state. When several consecutive reactions are involved and the system is at steady state, all steps occur at the same rate (\( v_1^1A_1 = v_2^2A_2 = v_3^3A_3 = \ldots = v_i^iA_i = \text{const} \)). In fact, although all steps in the sequence proceed at the same rate, the affinities of all steps, except the rate-determining one, are near zero, i.e. these steps are considered to be at equilibrium. The rate-determining step has an exchange rate, which is much lower than that of the other steps and affinity, which is much higher. Assuming that the rate-determining step occurs \( \nu \) times per act of the overall reaction, its affinity is given by \( A_i = A / \nu \). This provides to express the net rate, \( \nu \), of the reaction close to equilibrium through:

\[
v = \nu_{\text{rd}} \left( \frac{A}{\nu RT} \right) \tag{6}
\]

where \( \nu_{\text{rd}} \) is the exchange rate of the rate-determining step. Since the affinity \( A \) of an electrode reaction is equal to the electrical energy per mole which is applied to remove the system from its equilibrium, the rate of the overall reaction is given [44] by:

\[
j = \frac{j_0 nF \eta}{\nu RT} \tag{7}
\]

It is seen that Eq. (7) is in fact identical with Eq. (5) derived for a simple one-electron reaction. Furthermore it can be used in this study as the system behaves reversibly at low scan rates. Eq. (7) is applied in the form:

\[
j_p = -\frac{j_0 nF}{RT} E_{\text{p,rev}} + \frac{j_0 nF}{RT} E_p \tag{8}
\]

assuming that \( \nu = 1 \). Eq. (8) shows that \( j_p \) depends linearly on the peak potential \( E_p \) providing to estimate \( j_0 \) from the slope obtained.

The calculations carried out with the application of Eq. (8) are based on LSV profiles recorded at scan rates varying in the range between 0.020 Vs\(^{-1}\) and 0.100 Vs\(^{-1}\) at several temperature values. Fig. 1 illustrates some of the scans recorded. It is evident that the peak current density increases, while the peak potential value shifts in positive direction with scan rate increase at any of the temperature values set. Fig. 1 shows as well that the curves cross each other at potentials prior to that of the peak. It is worth noting that this behavior is observed only in absence of electrode surface fouling which in turn leads to the suggestion that it can be assigned to a non-negligible hydrolysis of BH\(_4^-\) in correspondence with findings [21, 22]. The latter refer to the behavior of Pt rotating disc electrodes. The fit of the experimental data to Eq. (8) is illustrated in Fig. 2.

The estimation of \( j_0 \) requires the introduction of

![Fig. 1 (a). LSV scans recorded at an alloy of Au bulk content of 40 at. % (Au surface content of 9.7 %) at 308.4 K with scan rates of: (1) 0.020; (2) 0.030; (3) 0.040 and (4) 0.050 Vs\(^{-1}\).](image1.png)

![Fig. 1 (b). LSV scans recorded at an alloy of Au bulk content of 60 at. % (Au surface content of 44.9 %) at 299.0 K with scan rates of: (1) 0.020; (2) 0.030; (3) 0.040 and (4) 0.050 Vs\(^{-1}\).](image2.png)
the value of \( n \). The latter gives the total number of electrons exchanged in the process investigated. It is determined on the ground [40 and references therein] of the rate dependence of the peak current density. Much higher scan rates are required. They have been applied and some of the values obtained were reported [40]. The temperature effect on \( n \) is followed on the ground of the temperature dependence of the diffusion coefficient \( D \). Theoretically it is given by an exponential equation of the type \( D = D_0 \exp(-E/RT) \), where \( D_0 \) is the maximum diffusion coefficient, while \( E \) is the activation energy for diffusion usually given varying from 12.6 \( \text{kJ mol}^{-1} \) to 28.1 \( \text{kJ mol}^{-1} \). The values of \( D \) reported in [19], i.e. 2.42x10^{-5} \( \text{cm}^2 \text{s}^{-1} \) at 298 K and 5.00x10^{-5} \( \text{cm}^2 \text{s}^{-1} \) at 338 K, provide to calculate \( E \) in case of \( \text{BH}_4^- \) diffusion. The value found is equal to 15.2 \( \text{kJ mol}^{-1} \), i.e. it falls within the range pointed above. The calculations referring to \( n \) show that the value for Pt changes from 0.9 at 299.2 K to 1 with temperature increase, while that of the alloy containing 60 at. % is 0.8 and changes to 0.9 at the highest temperature applied. The values found for the alloys containing 40 at. % and 80 at. % of Au stay constant with temperature variation. They are 0.4 and 0.6, correspondingly. That obtained for the alloy of Au bulk content of 20 at. % changes from 1.3 to 1.8 with temperature increase. In fact this is the only electrode material studied whose \( n \) value is close to the expected value of 2. It should be added that all values obtained are lower than 1 and 2, correspondingly, because of hydrolysis proceeding [21, 22], but they are in accord with the mechanistic concepts of borohydride oxidation on Pt(111) and Au(111) [23, 24, 29]. They are based on DFT calculated energy diagram of the reactions taking place. Further support is given by investigations [46 - 51] focused on the relation between the surface electronic structure and the reactivity of transition on noble metals and alloys. It is assumed that in case of Pt [29] and most of the alloys studied [40] the anodic peak is determined by the proceeding of:

\[
\text{BH}_4^{aq} + 4^+ \rightarrow \text{BH}^+ + 3\text{H}^+ + e^- \quad (9)
\]

where the symbol (*) denotes adsorption sites or adsorbed species. The potential range of reaction (9) proceeding is obviously too low for most of the electrodes to provide the occurrence of the second step of the 2e-process, i.e.

\[
\text{BH}^+ + \text{OH}^- + * \rightarrow \text{BOH}^+ + \text{H}^+ + e^- \quad (10)
\]

The concepts just outlined are in accord with the first peak potential values reported in [40]. For the alloys of Au bulk content less than 80 at. % they are lower than this for Pt, which in turn is lower than that for Au [8, 19, 21, 22]. These findings are valid for all temperature values studied. They are in correspondence with the data referring to PtAu bimetallic systems examined [2, 32 - 40].
The values of \( j_0 \) determined depend on the surface composition of the electrode materials. Fig. 3 outlines this dependence. It is seen that \( j_0 \) for three of the alloys is close to and slightly less than that for Pt at lower temperatures (Fig. 3a). These values are much smaller than that for Pt at higher temperatures (Fig. 3b). The exchange current density referring to the alloy of Au surface content of 30 % is the highest among those obtained in this study at all temperatures applied.

The results just reported determine the interest towards the temperature effect on \( j_0 \). It can be described [52] by:

\[
j_0 = A c \rho \pi kT \exp \left( \frac{-E_S}{4kT} \right)
\]  

where \( A \) is the frequency factor, \( c \) is the concentration of the reacting ion, \( \rho \) is the density of the electrode material’s electronic states, \( k \) is the Boltzmann constant, while \( E_S \) is the reorganization energy, characterizing the ligands' charging. In fact \( E_S / 4 \) is the activation energy [52] for the exchange current density. Eq. (11) shows that it can be estimated on the ground of the slope of the linear dependence of \( \ln j_0 \) vs. \( 1/T \). Some of the lines obtained in correspondence with Eq. (11) are presented in Fig. 4. The values of the activation energy are calculated. They are found dependent on the bulk as well as on the surface composition of the alloys investigated. The corresponding dependences are illustrated in Figs. 5 and 6. It is worth pointing out that the dependence on the bulk composition is of the form obtained in [40]. The curve presented in Fig. 5 goes through a minimum at Au bulk content of ca 50 at. %. Besides, the activation energy obtained for two of the alloys is less than that of Au. The effect of the surface composition is not so well outlined. Fig. 6 illustrates the relation's tentative character. The curve shown goes through a minimum at Au surface content of 30 %. The latter value is attracting attention as the highest exchange current densities as well as the highest value of the total number of electrons exchanged are found for this particular surface content. The generalization of all facts obtained provides to conclude that the adsorption sites required for the proceeding of reaction (9) are most favorably distributed in case of Au surface presence of ca 30 %. The requirement of four adjacent

![Fig. 3: Dependence of the exchange current density versus the surface composition of the alloy electrodes studied at (a) 298 K; (b) 308 K. The actual temperature values differ slightly but are close to those cited.](image)

![Fig. 4: Temperature dependence of the exchange current density found for PtAu alloys of Au bulk content of 40 at. % (line 1); 60 at. % (line 2); 80 at. % (line 3).](image)
adsorption centers on the electrode surface combined with the alloying effect on the heats of adsorption of these cites can explain the sensitivity of the oxidation reaction studied and hence the scattering of the points around the tentative curve in Fig. 6.

**CONCLUSIONS**

The comparative kinetic investigation of the process determining the first anodic peak of borohydride oxidation at Pt, Au and Pt-Au alloys of Au bulk content of 20, 40, 60 and 80 at. % provides the determination of the corresponding exchange current density taking into consideration the total number of electrons exchanged in the peak’s potential range and the temperature applied. The latter is varied in the range from 293.2 K to 323.2 K. The activation energy for the exchange current density is estimated and the effect of the alloys composition is followed. It is found that the alloys activation energy is lower than that of Pt. The lowest value is expected at Au bulk content of ca 50 at. %. The dependence on the alloys surface composition is only tentatively outlined most probably because of the sensitivity of the surface reaction studied. Its proceeding requires the presence of four adjacent active centers whose heats of adsorption are strongly affected by the alloying.

**Acknowledgements**

The financial support from the University of Chemical Technology and Metallurgy, Sofia, through Project No 10977/ 2012 is gratefully acknowledged.

**REFERENCES**

8. E. Gyenge, Electrooxidation of borohydride on platinum and gold electrodes: implications for direct
30. P.-Y. Olu, B. Gilles, N. Job, M. Chatenet, Influence of the surface morphology of smooth platinum electrodes for the sodium borohydride oxidation


ELECTROCHEMICAL STUDIES OF METAL COMPLEXES
OF MALONYL DIHYDRAZIDE

K. Ramana Kumar¹, A. Raghavendra Guru Prasad², V. Srilalitha², Y.N. Spoorthy³, L.K. Ravindranath³

¹Malla Reddy Engineering College, Hyderabad, A.P., India
²The ICFAI Foundation for Higher Education, Hyderabad, A.P., India
E-mail: guruprasadar@yahoo.co.in
³Sri Krishnadevaraya University, Anantapur, A.P., India

ABSTRACT

The present article deals with the polarographic and cyclic voltammetric investigations on metal (Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III) and Co(III)) complexes with malonyl dihydrazide (MAH). The variables that influence the electrode process were extensively discussed. The sites susceptible for reduction were reported by comparing the results obtained from polarography and cyclic voltammetry.

Keywords: malonyl dihydrazide, metal complexes, polarography, cyclic voltammetry.

INTRODUCTION

Hydrazides are potential therapeutic compounds due to their wide range of biological activities [1 - 3]. The -NH-NH- hydrazide fragment [4 - 6] plays an important role in medicinal chemistry. Earlier work has demonstrated that some drugs show increased activity when administered as metal chelates rather in the form of original organic compounds [7, 8]. Such complexes have an important role in bioinorganic chemistry and redox enzyme systems [9 - 12]. The study of structural and binding features of various metal complexes can play an important role in better understanding of the biological process. Redox properties of a drug can give insight into its metabolic or pharmaceutical activity [13 - 15]. Literature survey reveals that electrochemical studies have been exploited to predict the behavior of ligand and its complexes in biochemistry and medicine [16].

The aim of present work is to study the electrochemical behaviour of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III) and Co(III) metal complexes with malonyl dihydrazide (MAH). The electron transfer mechanism of the metal complexes is investigated with the aid of polarography and cyclic voltammetry. In earlier studies [17], the authors have reported the physico-chemical aspects the metal complexes of MAH.

EXPERIMENTAL

Materials and methods

All chemicals used were of analytical reagent grade obtained from Merck India Limited. pH measurements were made using pH meter Model L1-10 manufactured by ELICO Private Limited, Hyderabad, India. DC Recording Polarograph manufactured by ELICO Private Limited, Hyderabad, India was used for polarographic studies. Cyclic voltammetric unit consists of X-Y recorder (Model RE.0074), PAR 173 potentiostat, PAR 175 universal programmer. A circulating type thermostat manufactured by Toshniwal, Bombay, India with water as the thermostatic liquid was employed to maintain a constant temperature.

General experimental procedure

10 mL of buffer solution and 2.5 mL of metal complex solution (1×10⁻² M), 10 mL of dimethylformamide and remaining volume of distilled water to make the
total volume to 25 mL were taken into a polarographic/cyclic voltammetric cell. Polarograms/cyclic voltammograms were recorded after deaeration of the solution with nitrogen gas. The polarographic maxima in all cases were suppressed by the addition of two drops of 0.001 % gelatin.

RESULTS AND DISCUSSION

Polarographic studies

The interpretation of polarographic waves of metal complexes has been discussed by Lingane [18]. The electrochemical behaviour of complexes of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III) and Co(III) with MAH in aqueous dimethylformamide (40 % v/v) is presented in this article.

Polarographic behaviour of MAH complexes of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Metal complexes under study have displayed a single reduction wave in the pH range 2.1 - 10.1. The half wave potentials were shifted to more negative values with increase in pH. However, the half wave potential values were constant beyond pH 8.1. This indicates that protons were involved in the reduction process. The number of protons (p) was a small non-integer value and thus indicates the surface protonation [19]. The decrease in wave height with increase in pH may be attributed to the decrease in the rate of protonation. This fact further indicates that the protonated form of the electroactive species has undergone reduction. It was observed in solutions of pH 8.1 - 10.1 that the wave heights and the half wave potentials remain constant signifying the electroactive nature of the protonated and unprotonated forms of the depolarizer.

No wave was observed either with buffer solution or with the reagent when they were employed independently. The half wave potentials of complexes were found to be more negative than the simple metal ions (Table 1). The change in half wave potential (E½) with the concentration of the complex may be attributed to the irreversible nature of the electrode process [20].

This fact was further confirmed from the non-integral values of n obtained from the plots of

\[
\log \left( \frac{i}{1+1} \right) \text{ vs } E_{\text{dme}} [21].
\]

The plots are shown in Fig. 1. The values of H/h½ were fairly constant (Table 2). These facts suggest that the complexes undergo diffusion controlled reduction [22].

Effect of temperature

The polarograms of the metal complexes were recorded at 303, 313, 323 and 333 K at pH 4.1 to study the effect of temperature on the half wave potential and the wave height. The complexes exhibited a well defined single cathodic wave at all temperatures studied. Linear relationship between wave height (H) and h½ suggests the diffusion controlled nature of waves at all temperatures.

Wave height increases with increase in temperature and the value of the temperature coefficient lies between 0.762 - 1.38 % deg⁻¹. αn values (α is the transfer coefficient and n is the number of electrons involved) were calculated using Tomes criteria [23]. The decrease in αn values (Table 3) with increase in temperature may be due to decrease in α values and the decrease in α values was due to the increasing difficulty in transfer of electrons with increasing temperature. A decrease in αn value [24 - 27] suggests that the system tends to
become increasingly irreversible.

This was further supported by the fact that the half wave potential values tend to become more negative with increase in temperature. The thermodynamic parameters were evaluated from the equations proposed by Meites-Israel [28], Oldham-Parry [29] and Gaur Bhargava [30]. The diffusion coefficient value required for the calculation of formal rate constant 'K_{f.h}' at different temperatures was calculated from Stoke-Einstein [31] equation. A perusal of the data pertaining to thermodynamic parameters showed that the formal rate constant decreases with increase in temperature and signifies that the electrode reaction was rendered increasingly irreversible with the raise in temperature. This observation has further confirmed the conclusions arrived on the basis of αn values. Thermodynamic parameters namely enthalpy of activation (ΔH')p, heat of activation at constant volume (ΔH'v) and entropy of activation (ΔS') are shown in Table 4. The data pertaining to heterogeneous rate constant K_{f.h} and activation free energy change, ΔG' at typical pH values were shown in Table 1. It was observed from the data that the electrode process was becoming increasingly irreversible with increase in pH and the same was evinced by the decrease in K_{f.h} and increase in ΔG' values with increase in pH [32]. Plots of log K_{f.h} vs 1/T for the polarographic reduction of metal complexes studied by different treatments are presented in Fig. 2.

The sites susceptible for reduction were metal ion, amide (\text{O}–\text{NH}_2) and azomethine group (\text{C}=\text{N}=\text{NH}) in the enolic form. Since the reagent alone was not undergoing reduction in the potential range of study, the reduction waves observed in the case of complexes

Table 1. Polarographic characteristics and kinetic parameters of M-MAH complex (1 × 10^{-3} M).

<table>
<thead>
<tr>
<th>pH</th>
<th>ΔE/ΔpH</th>
<th>Wave height, H (cm)</th>
<th>αn</th>
<th>Number of protons (P)</th>
<th>D=10^{-10} cm² sec⁻¹</th>
<th>I=10⁻¹⁵ cm⁻¹ sec⁻¹</th>
<th>ΔG° K cal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4.1</td>
<td>Mn(II)-MAH</td>
<td>0.34</td>
<td>0.34</td>
<td>0.35</td>
<td>0.36</td>
<td>0.37</td>
<td>0.38</td>
</tr>
<tr>
<td>pH 8.1</td>
<td>Cd(II)-MAH</td>
<td>0.35</td>
<td>0.36</td>
<td>0.37</td>
<td>0.38</td>
<td>0.39</td>
<td>0.40</td>
</tr>
<tr>
<td>pH 4.1</td>
<td>Cu(II)-MAH</td>
<td>0.36</td>
<td>0.37</td>
<td>0.38</td>
<td>0.39</td>
<td>0.40</td>
<td>0.41</td>
</tr>
<tr>
<td>pH 8.1</td>
<td>Zn(II)-MAH</td>
<td>0.37</td>
<td>0.38</td>
<td>0.39</td>
<td>0.40</td>
<td>0.41</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Table 2. Influence of mercury column height (h cm) on wave height (H cm); Medium: Aqueous DMF (40 % v/v); [M-MAH]: 1 × 10^{-3} M.
Polarographic behaviour of Fe(III) and Co(III) complexes of MAH

The polarographic behaviour of Fe(III) and Co(III) complexes of MAH have been studied in the pH range 2.1 to 10.1.

A single well defined wave was observed in the pH range 2.1 - 10.1 and was attributed to the one electron reduction (Table 1) of metal complex. The half wave potential values were shifted to more negative values compared to the shift of half wave potentials of the waves of simple metal ions. The values of H/h \^{1/2} were fairly constant. Linear plots were obtained between the wave height and the concentration of the complex. These facts suggest that the complexes undergo diffusion controlled reduction. The change in half-wave potential (E_{1/2}) with concentration of complex may be attributed to the irreversible behaviour of the electrode process [33]. This fact was further confirmed by the fractional values of n obtained from the log \( \frac{i}{i_d - i} \) vs E_{dme} plots.

The half wave potentials were shifted to more negative values with increase in pH. As specified earlier, the half wave potentials were not altered beyond pH 8.1. These observations reveal that the protons were involved in the reduction process. However, an increase in wave height with increase in pH may be attributed to the electroactive nature of the unprotonated form of the complex species. The wave height remains constant beyond pH 8.1.

It was observed from the data presented in Table 1 that two waves were observed in pH range 6.1 - 10.1. The absence of second wave in the pH range 2.1 - 4.1 may be due to the formation of a species which can be reduced at more negative potentials. The half wave potentials of the second wave become increasingly negative with the increase in pH and with increase in concentration of the metal complex. n value was found to be a non-integer. These facts suggest that the electrode process was irreversible. Constant values of H/h \^{1/2} and the linear relationship observed between log \( \frac{i}{i_d - i} \) vs E_{dme} suggest the diffusion controlled nature of the reduction process. The effect of pH on half wave potential and wave height was similar to that observed for the first wave.

Effect of temperature

The studies pertaining to effect of temperature were carried out in solutions of pH 4.1. The data given in
Table 4 are indicative of similar inferences as in the case of complexes of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II). The negative $\Delta S^*$ values suggest that the activated state has a more stable structure than the initial state.

The number of electrons involved in the reduction process calculated using De Vries and Kroon method [34] was one in the case of first wave and two in the case of second wave. The wave height of the second wave was observed to be double that of the first wave. Hence the sequence of reduction process may be represented as

$$\text{M(III)}-\text{SAH} \xrightarrow{1e} \text{M(II)}-\text{SAH}$$

$$\text{M(II)}-\text{SAH} \xrightarrow{2e} \text{M(0)}$$

**Cyclic voltammetric studies**

The cyclic voltammograms for all the complexes were recorded in solutions of pH 2.1 - 8.1 at the scan rates of 10, 20, 50, 100 and 200 mV/sec.

**Mn(II)-MAH, Zn(II)-MAH and Cd(II) - MAH complexes**

The results obtained in the cyclic voltammetric studies on MAH complexes of Mn(II), Zn(II) and Cd(II) are given in Tables 5 and 6.

A sharp cathodic peak in the case of Mn(II)-MAH complex and a broad peak in the case of Zn(II) and Cd(II)-MAH complexes were observed at all scan rates. The absence of anodic peak in the reverse scan indicates that the reduction process was irreversible [35]. The presence of single cathodic peak in all cases suggests that the reduction process involves two electrons and the same was inferred from the polarographic studies.

Peak potentials were shifted to more negative values...
and the peak currents increase with increase in scan rate. Further, peak potential increase was more pronounced in solutions of pH 8.1 compared to that in solutions of pH 4.1. However a reverse trend was noticed in the case of peak current. The increase in peak current with increase in scan rate indicates that no chemical reaction was taking place in the vicinity of electrode [36].

Nature of the electrode process

The electrode process was found to be diffusion controlled and irreversible under experimental conditions. The diffusion controlled nature of the electrode process was confirmed by following facts.

- The peak current increases with increase in concentration of the depolarizer [38].
- The irreversible nature of the reduction process was confirmed by the following facts:
  - The cathodic peak potentials were independent of scan rates [39] i.e. $i_{\text{pc}}/n^{1/2}$ vs $n$ was a straight line parallel to the scan rate axis as explained by case I of Nicholson and Shain mechanism related to reversible charge transfer.
  - The anodic peak was absent in the reverse scan [38].
  - The value of $(E_{\text{pc}} - E_{\text{pe}})$ being greater than $56.5 \over n \times mV$ [38].

Table 5. The effect of scan rate on peak potential and peak current; [M-MAH] = 1×10⁻³ M; Medium = Aqueous dimethyl formamide (40 % v/v).

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>pH 4.1</th>
<th>pH 8.1</th>
<th>pH 4.1</th>
<th>pH 8.1</th>
<th>pH 4.1</th>
<th>pH 8.1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-E_{\text{pc}} V</td>
<td>$i_{\text{pc}}$ cm</td>
<td>-E_{\text{pc}} V</td>
<td>$i_{\text{pc}}$ cm</td>
<td>-E_{\text{pc}} V</td>
<td>$i_{\text{pc}}$ cm</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>0.010</td>
<td>1.666</td>
<td>1.83</td>
<td>1.32</td>
<td>1.52</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>1.666</td>
<td>3.3</td>
<td>1.27</td>
<td>1.52</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>1.694</td>
<td>4.0</td>
<td>1.35</td>
<td>1.55</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>1.727</td>
<td>4.9</td>
<td>1.38</td>
<td>1.58</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>0.200</td>
<td>1.757</td>
<td>6.0</td>
<td>1.41</td>
<td>1.61</td>
<td>3.9</td>
</tr>
</tbody>
</table>

| Cu(II)         | 0.010  | 1.579  | 2.20   | 1.47   | 1.52   | 2.2    | 1.47   | 1.52   | 2.2    | 1.52   |
| Zn(II)         | 0.010  | 1.389  | 2.20   | 1.47   | 1.52   | 2.2    | 1.47   | 1.52   | 2.2    | 1.52   |
| Cd(II)         | 0.010  | 1.579  | 2.20   | 1.47   | 1.52   | 2.2    | 1.47   | 1.52   | 2.2    | 1.52   |
| Fe(II)         | 0.010  | 1.579  | 2.20   | 1.47   | 1.52   | 2.2    | 1.47   | 1.52   | 2.2    | 1.52   |
| Co(II)         | 0.010  | 1.579  | 2.20   | 1.47   | 1.52   | 2.2    | 1.47   | 1.52   | 2.2    | 1.52   |

Table 4. Kinetic and thermodynamic parameters of polargraphic reduction of M-MAH complex (1×10⁻³ M) at pH 4.1.
The shift of $E_{pc}$ value towards more negative potential [38].

**Ni(II)-MAH complex**

The results obtained are presented in Table 6. The results indicate that the complex leads to a single cathodic peak at low scan rates and two cathodic peaks along with one anodic peak at high scan rates. The electrode process was found to be diffusion controlled in nature. An inspection of the cyclic voltammograms as well as the polarograms of the complex in solutions of pH 4.1 and 8.1 indicates that the electrode process involves two electrons.

Cyclic voltammetric results showed two cathodic peaks at high scan rates. The first cathodic peak may be due to the one electron reduction of Ni(II)-MAH complex to the Ni(I)-MAH. The second peak may be due to the one electron reduction of Ni(I)-MAH complex. The peak currents increase with increase in scan rate. The peak current values were almost same for each of the two peaks indicating that the reduction involves one electron in each step. An anodic peak was noticed in reverse scan at high scan rates. The fact that the anodic peak was obtained by the application of potential below the peak potential of the second cathodic peak confirms that the anodic peak was due to the oxidation of Ni(I)-MAH to Ni(II)-MAH. The difference between the peak potentials ($\Delta E_p$) in the present investigation was found to be 60 mV. Further it was noticed that the ratio of cathodic to anodic peak currents ($i_{pc}/i_{pa}$) was almost equal to one. Hence, the electrode process may be identified as quasi reversible.

**Cu(II)-MAH complex**

The results pertaining to cyclic voltammetric behaviour of Cu(II)-MAH complex are presented in Table 6. Cyclic voltammograms obtained at pH 4.1 and 8.1 show a single cathodic peak in solutions of pH 4.1 and two cathodic peaks along and an anodic peak in reverse scan in solutions of pH 8.1 at high scan rates. In contrast only a single polarographic wave was observed at pH 4.1 and 8.1 in polarographic studies. An inspection of the cyclic voltammograms as well as the polarograms of the complex in solutions of pH 4.1 suggests that the polarographic reduction wave manifests itself as a cathodic peak in cyclic voltammetric studies. This was attributed to the reduction of Cu(II)-MAH complex to the metal.

The two cathodic peaks observed in solutions of pH 8.1 at high scan rates suggest that the reduction was taking place in two steps. The first cathodic peak was attributed to the one electron reduction of Cu(II)-MAH complex to the Cu(I)-MAH and the second cathodic peak was due to the reduction of Cu(I)-MAH to the metal. The peak current values were almost same. The reduction process involves two steps, each involving one electron. An anodic peak was noticed in the reverse scan at high...
Fe(II)-MAH was electro-inactive form. Did not undergo reduction, perhaps Fe(II) complex was out the cyclic voltammetric experiment with Fe(II)-MAH that the electrode process was quasi reversible in nature. A ratio of cathodic to anodic peak currents was due to the oxidation of Fe(II)-MAH to Fe(III)-MAH complex to Fe(II)-MAH and the anodic peak formation peak obtained was due to the reduction of Fe(III)-MAH approximately equal (difference was 10 mV) in magnitude to that of cathodic peak potential. The cathodic scan rates. This behaviour was similar to that observed in the case of Ni(II)-MAH complex at pH 8.1.

A value of 0.07 V for \( \Delta E_p \) and a value one for the ratio \( i_{pa}/i_{pc} \) suggest that the electrode process was quasi reversible.

**Fe(III)-MAH complex**

The results pertaining to Fe(III)-MAH complex are presented in Table 6.

In solutions of pH 4.1, the complex produces a single cathodic peak and an anodic peak in the reverse scan. It was observed that the anodic peak potential was approximately equal (difference was 10 mV) in magnitude to that of cathodic peak potential. The cathodic peak obtained was due to the reduction of Fe(III)-MAH complex to Fe(II)-MAH and the anodic peak formation was due to the oxidation of Fe(II)-MAH to Fe(III)-MAH complex. A ratio of cathodic to anodic peak currents i.e., \( i_{pa}/i_{pc} \) was nearly one. These arguments suggest that the electrode process was quasi reversible in nature. The fact that the Fe(II)-MAH complex formed was not undergoing further reduction was confirmed by carrying out the cyclic voltammetric experiment with Fe(II)-MAH complex. In this case, it was found that the complex did not undergo reduction, perhaps Fe(II) complex was stabilized and was in electro-inactive form.

In solutions of pH 8.1, two cathodic peaks were observed. The peak potentials in general increase with increase in scan rate. The facts that, cathode peak potentials were independent of scan rate, \( E_{pc2} - E_{pc1} \) values being greater than \( \frac{E_{pc2}}{E_{pc1}} \) mV and the peak potentials were shifted to more negative values suggest that the electrode process was irreversible. On the other hand, increase in peak current values with increase in concentration of the depolarizer and the linear plots of \( i_{pc} \) vs \( v^{1/2} \) have confirmed the diffusion controlled nature of the process. The magnitude of \( i_{pc} \) was almost twice that of \( i_{pa} \). This suggests that the first cathodic peak was due to the reduction of Fe(III)-MAH to Fe(II)-MAH and second to the reduction of Fe(II)-MAH to metal.

Based on the above mentioned facts, the reduction processes in different media are given below.

\begin{align*}
pH 4.1: & Fe(III)-MAH \xrightarrow{1e} Fe(II)-MAH \\
pH 8.1: & Step 1: Fe(III)-MAH \xrightarrow{1e} Fe(II)-MAH \\
& Step 2: Fe(II)-MAH \xrightarrow{2e} Fe(0)
\end{align*}

**Co(III)-MAH complex**

The results pertaining to Co(III)-MAH complex are presented in Table 6.

The explanation for the diffusion controlled nature of the electrode process was same as that for other complexes.

In solutions of pH 4.1, a single cathodic peak was observed at all scan rates. The peak potential and peak currents increase with the scan rate. Irreversible nature of the process was confirmed by the absence of anodic
peak in the reverse scan. Hence the reduction process in this medium is given below.

\[
\text{Co(III)-MAH} \xrightarrow{1e} \text{Co(II)-MAH}
\]

In solutions of pH 8.1, the behaviour of Co(III)-MAH complex was similar to that reported for Fe(III)-MAH complex. Hence the reduction process in this medium may be represented as follows.

Step 1: \[
\text{Co(III)-MAH} \xrightarrow{1e} \text{Co(II)-MAH}
\]

Step 2: \[
\text{Co(II)-MAH} \xrightarrow{2e} \text{Co(0)}
\]

CONCLUSIONS

The electrochemical investigations of series of metal (Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III) and Co(III)) complexes of MAH were reported. The results obtained in polarography were compared with those obtained in cyclic voltammetric studies. The effect of height of the mercury column, concentration of the complex and temperature, etc. on electrode process were explored in detail and presented. The redox properties of complexes were extensively investigated by polarography and cyclic voltammetry. Mn(II), Zn(II), Cd(II) and Co(III) complexes exhibited diffusion controlled and irreversible electrode process, where as Fe(III), Cu(II) and Ni(II) complexes have undergone diffusion controlled and quasi reversible electrode process.

REFERENCES

4. A. Bredhihhin, U.M. Groth, U. Mäeorg, Formation and use of a nitrogen dianion for selective hydrazine alkylation provides a fast and easy access to substituted hydrazines, which are widely used as drugs, pesticides, and precursors for a variety of compounds in organic synthesis, Org. Lett., 9, 2007, 1097-1099.
5. O. Tsubrik, R. Sillard, U. Mäeorg, Excellent regioselectivity is observed in the addition of diverse organometallic nucleophiles to unsymmetrical azo compounds. Primary/secondary/tertiary alkyl, aryl and heteroaryl substituents were introduced this way in high yields, Synthesis, 5, 2006, 843-846.
ABSTRACT

In this article we report the results of a study of infrared, absorption and fluorescence spectra of eight novel poly(propyleneamine) dendrimers from second generation, modified with 1,8-naphthalimide units. Special attention has been paid to the investigation of the influence of the nature of the substituents at C-4 position in the 1,8-naphthalimides and thus on the polarization of the dendrimer molecule as a whole. The influence of the dendrimer polarization on the spectral characteristics are discussed.

Keywords: poly(propyleneamine), FT-IR spectroscopy, absorbance, fluorescence, photoactive dendrimers, 1,8-naphthalimide.

INTRODUCTION

Over the last years dendrimers have been investigated intensively as a new polymer architecture [1 - 3]. They are hyperbranched, monodisperse, well defined three-dimensional macromolecules, possessing a very high concentration of different terminal functional groups in their periphery.

The studies on fluorescent dendrimers are focused generally on their synthesis and applications in different fields such as chemistry, biology, medicine and physics. Functionalizing the dendrimers with photoactive groups expands the spheres of their applications. When the periphery is modified, the dendrimer comprises a great number of closely located fluorophores which could be independent from each other or can interact. In the latter case the dendrimers acquire new properties defined as the “dendrimer effect”. These new compounds have turned out to be meeting appropriately the requirements of “high-technologies”: sensors for environment pollutants, optoelectronics, light-harvesting antenna systems for solar energy conversion, as well as those of biology and medicine [4 - 10].

The peripheral modification of PAMAM dendrimers from zero and second generation with 1,8-naphthalimide units has shown that they can be used as sensors for detection of metal ions and protons. It was found that the sensor activity depends strongly of the chemical
structure of the substituents at the C-4 position of the naphthalene nucleus (11 - 16).

Poly(propyleneamine) (PPA) dendrimers, as a new class of commercial dendrimers, have been attracting an increasing amount of interest as a result of the different application, envisaged for them [1]. These dendrimers comprise only tertiary amino groups in their core and primary amino groups in the periphery in contrast to the PAMAM dendrimers, where they have also amidic groups. The luminescent characteristics of modified PPA dendrimers can be easily customized by modifying the periphery with different types of fluorophores. Fluorescent dendrimers having 1,8-naphthalimide as fluorescent units can be interpreted as a combination of conventional dendrimers and low molecular mass fluorophores [17 - 23].

The aim of this work was to study the influence of the substituents in 1,8-naphthalimide structure on the spectral characteristics of newly synthesized PPA dendrimers by infrared, absorption and fluorescence spectroscopy. The effect that the substituents at C-4 position of the naphthalene ring have upon the main spectral characteristics has been investigated and discussed. These studies are conducted in order to better and complete characterization of the dendrimers.

EXPERIMENTAL

Materials and methods

The PPA dendrimers from the second generation, modified with 1,8-naphthalimide derivatives have the structures presented in Scheme 1. Their synthesis and main photophysical characteristic were described earlier [17, 20, 21, 13]. Infrared analysis of all 1,8-naphthalimide labeled dendrimers was carried out using an Infrared Fourier transform spectrometer (IRAffinity-1”Shimadzu”) with the diffuse-reflectance attachment (MIRacle Attenuated Total Reflectance Attachment) at a 2 cm⁻¹ resolution. UV/vis spectrophotometric investigations were performed using “Thermo Spectronic Unicam UV 500” spectrophotometer. The fluorescence spectra were taken on a “Cary Eclipse” spectrophotometer. All spectra were recorded using 1 cm path length synthetic quartz glass cells. The fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using anthracene $\Phi_a = 0.27$ and Fluorescein $\Phi_a = 0.85$ [24].

RESULTS AND DISCUSSION

1,8-Naphthalimides can be treated as a combination
of two sub-systems; viz. the naphthalene ring and a di-carboximide (-CO-NR-CO-) group in a six membered ring. Their photophysical properties depend mainly on the polarization of the 1,8-naphthalimide molecule. The polarization occurs upon irradiation, resulting from the donor-acceptor interaction between the substituents \( \text{A} \) at C-4 position, and the carbonyl groups (C=O) from the imide structure of the chromophoric system. Therefore, in the practical application of the dendrimers synthesized by us, it is important to know the effect of this substituent on their spectral characteristics. It is well known that only amino substituents in position C-4 give yellow green fluorescence. Thus, the presence of 4-aminosubstituted 1,8-naphthalimides bonded to the commercial PPA dendrimers gives them some new interesting photophysical properties.

### Table 1. Experimental infrared wave numbers of D1- D8 dendrimers in \( \text{cm}^{-1} \).  

<table>
<thead>
<tr>
<th>Demdrimer</th>
<th>( \nu_{\text{NH}} )</th>
<th>( \nu_{\text{C-H}} ) arom</th>
<th>( \nu_{\text{CH2}} ) aliph</th>
<th>( \nu^\text{AS} ) C=O</th>
<th>( \nu^\text{S} ) C=O</th>
<th>( \nu_{\text{C-C}} )</th>
<th>( \nu_{\text{CH2}} ) aliph</th>
<th>( \nu_{\text{CNC}} )</th>
<th>( \delta_{\text{C-H}} ) arom</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>3068</td>
<td>2958 2874</td>
<td>1696</td>
<td>1654</td>
<td>1624 1587</td>
<td>1437</td>
<td>1342 1232 1174</td>
<td>874 777</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>3066</td>
<td>2951 2808</td>
<td>1697</td>
<td>1655</td>
<td>1616 1570 1458</td>
<td>1435</td>
<td>1342 1231 1188</td>
<td>848 779 748</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>3078</td>
<td>2947 2808</td>
<td>1706</td>
<td>1660</td>
<td>1624 1452</td>
<td>1439</td>
<td>1330 1239 1188</td>
<td>833 783 760</td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>3356</td>
<td>3078</td>
<td>2951 2839</td>
<td>1678</td>
<td>1637</td>
<td>1614 1573 1456</td>
<td>1435 1246 1189</td>
<td>820 771 756</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>3068</td>
<td>2953 2870</td>
<td>1684</td>
<td>1643</td>
<td>1614 1576 1450</td>
<td>1425</td>
<td>1354 1242 1207</td>
<td>835 777 758</td>
<td></td>
</tr>
<tr>
<td>D6</td>
<td>3360</td>
<td>3063</td>
<td>2958 2928 2832</td>
<td>1674</td>
<td>1636</td>
<td>1612 1573 1458</td>
<td>1431 1242 1350</td>
<td>822 783 756</td>
<td></td>
</tr>
<tr>
<td>D7</td>
<td>3369</td>
<td>3076</td>
<td>2957 2932 2871</td>
<td>1679</td>
<td>1638</td>
<td>1613 1579 1460</td>
<td>1431 1191 1354</td>
<td>775 758</td>
<td></td>
</tr>
<tr>
<td>D8</td>
<td>3073</td>
<td>2955 282</td>
<td>1684</td>
<td>1640</td>
<td>1611 1578</td>
<td>1432</td>
<td>1189 1241 1397</td>
<td>785 755</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** Infrared spectra of D3 and D4 dendrimers.
**Infrared spectral characteristics**

Stretching and deformation vibrations of the main functions in the infrared region of the spectra of PPA dendrimers from second generation modified with different substituted 1,8-naphthalimides D1-D8 are summarised in Table 1.

Fig. 1 shows the infrared spectra of D3 and D4 dendrimers in the 1500 - 1750 cm\(^{-1}\) region. The C=O group of 1,8-naphthalimides gives rise to two absorption frequency bands, which are characteristic for the vibrations caused by the asymmetrical and the symmetrical carbonyl groups from the 1,8-naphthalimide chromophoric system [25]. In this case the high frequency C=O stretching vibration is assigned to the asymmetrical mode. These bands for dendrimer D3 with a substituted nitro group are at 1706 cm\(^{-1}\) and at 1660 cm\(^{-1}\). That is due to the electron-accepting nature of the nitro group. After the substitution of the nitro group with donating amino group, the characteristic bands for the 4-methylamino-1,8-naphthalimide-PPA dendrimer (D4) are shifted to the lower frequency region at 1678 cm\(^{-1}\) and 1637 cm\(^{-1}\), respectively. The difference between the symmetric and asymmetric vibrations assigned to the 1,8-naphthalimides, is 38 - 46 cm\(^{-1}\) (structures 1 and 2 in Scheme 2).

In the infrared spectra of 4-nitro-1,8-naphthalimide–PPA dendrimer D3, containing a nitro (NO\(_2\)) group, the band at 1523 cm\(^{-1}\) is characteristic for the asymmetrical vibrations of the nitro group.

The position of the absorption bands, characteristic for the C=O groups, depends on the nature of substituents at C-4 position. The spectra of the dendrimers with the donating groups (D4 - D8) have absorption bands shifted hipsocromically, if compared to those of the dendrimer with an electron accepting group.

Fig. 2 shows that for the dependence of the two C=O frequency bands of dendrimers D1 - D5 on the Hammett constants (s), a linear correlation is obtained. The analytical form of the dependence is given by Eqs. (1) and (2):

\[
\nu^S (\text{cm}^{-1}) = 1651 + 14.2 \sigma \\
\nu^AS (\text{cm}^{-1}) = 1693 + 16.9 \sigma
\]

which were derived using the least squares method with a correlation coefficient R=0.974 (1) and R=0.996 (2), SD = 1.28 -2.46, and N=5 for both C=O groups.

The aromatic naphthalene ring from the 1,8-naphthalimide units is responsible for the absorptions due to the sp\(^2\) C-H stretching vibrations at 3063 - 3078 cm\(^{-1}\).

The characteristic C-H out of plane deformation vibrations of the aromatic naphthalene rings are in the 748 - 783 cm\(^{-1}\) region. As seen from Fig. 3 D1 gives rise to a single peak at 777 cm\(^{-1}\) in the spectra of the
naphthalene rings non-substituted at C-4 position. In the other cases, dendrimers with substituents at C-4 have a doublet of peaks in the 771 - 783 cm\(^{-1}\) and in 748 - 758 cm\(^{-1}\) region, which can be explained by the different polarization of 1,8-naphthalimide molecules. Small peaks for aromatic C-H vibrations have been also obtained in the 820 - 874 cm\(^{-1}\) region.

All PPA dendrimers under study have aliphatic methylene (-CH\(_2\)-) groups in their core. The absorption in the 2808 - 2870 cm\(^{-1}\) region for the asymmetric and in the 2951 - 2958 cm\(^{-1}\) region for the symmetric stretching vibrations indicates the presence of a hydrogen atom bonded to a sp\(^3\) hybridized carbon atom. Dendrimers D4 - D8 have methyl group in their structure with absorption at 1382 cm\(^{-1}\), characteristic for a sp\(^3\) hybridized C-H bond.

Dendrimers D4, D6 and D7 with secondary amino groups at C-4 position of the 1,8-naphthalimide structure, have peaks in the 3356 - 3363 cm\(^{-1}\) and 1300 - 1303 cm\(^{-1}\) regions. Tertiary amines from the entire dendrimer core and 1,8-naphthalimide structure (D5 and D8) do not show bands in these regions.

The absorption bands in the 1330 - 1354 cm\(^{-1}\) region are characteristic for the imide (C-N-C) bonds in the 1,8-naphthalimide structure, bonded to the dendrimer molecules and to C-N from aliphatic tertiary amino groups in the dendrimer structure. In the case of dendrimers D3 these bands are overlapped with the bands characteristic for the symmetrical vibrations of the nitro group. The absorption bands are recorded as a shoulder. The infrared frequencies at 1174 - 1207 cm\(^{-1}\) are also assigned as C-N bonds.

**Spectral characteristics in dichloroethane solution**

In Table 2 are collected the basic photophysical characteristics of the dendrimers under study in a dichloroethane solution: the absorption (\(\lambda_\alpha\)) and fluorescence (\(\lambda_\beta\)) maxima, the extinction coefficient (\(\varepsilon\)), Stokes shift (\(\nu_\alpha - \nu_\beta\)), and the quantum yield of fluorescence (\(\Phi_f\)).

From the data in Table 2 it follows that the nature of the substituent at C-4 position has an important role in the dendrimer photophysical properties. When the substituent \(A\) is hydrogen, bromine atoms and nitro groups, the respective dendrimers absorb in the UV region and emit very weak fluorescence (D1 and D2). The longwave absorption band in the UV region is a charge transfer band due to electron transfer in the transition \(S_1 \rightarrow S_0\).

In dichloroethane solution dendrimers D4 - D8 exhibit yellow-green colour with absorption maxima at \(\lambda_\alpha = 402 - 430\) nm and fluorescence with maxima situated at \(\lambda_\beta = 500 - 512\) nm. The hypsochromic shift of the absorption and fluorescence maxima in the case of D4 and D5 can be explain by the steric interaction between one of the methyl groups of the 4-dimethylamino substituent at C-4 position and the hydrogen atom at the C-5 position (the peri effect) [23]. For the 4-methylamino substituent in the same position at D4, this effect is negligible. Also the absorption and fluorescence spectra of D4 and D6 are very similar which is due to approximately the same donor ability to the secondary amino groups.

The molar extinction coefficient for dendrimers D1 - D8 is approximately eight fold higher than that of the monomeric 1,8-naphthalimide derivatives with the same substituents at C-4 position [26 - 28]. This allows for the suggestion that no ground state interaction occurs between the 1,8-naphthalimide chromophoric units [29].

The Stokes shift indicates the differences in the properties and structure of the dendrimers in the ground state \(S_0\) and the first exited state \(S_1\). The Stokes shift can be calculated by the equation (3).

\[
(\nu_\alpha - \nu_\beta) = (1/\lambda_\alpha - 1/\lambda_\beta) \times 10^7 \text{ cm}^{-1}
\]  

(3)

The Stokes shift values are in the 3529-5344 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>(\lambda_\alpha) nm</th>
<th>(\varepsilon) l g(^{-1}) cm(^{-1})</th>
<th>(\lambda_\beta) nm</th>
<th>((\nu_\alpha - \nu_\beta)) cm(^{-1})</th>
<th>(\Phi_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>338</td>
<td>94200</td>
<td>385</td>
<td>3611</td>
<td>0.001</td>
</tr>
<tr>
<td>D2</td>
<td>342</td>
<td>91000</td>
<td>401</td>
<td>4302</td>
<td>0.004</td>
</tr>
<tr>
<td>D3</td>
<td>330</td>
<td>99200</td>
<td>511</td>
<td>3686</td>
<td>0.590</td>
</tr>
<tr>
<td>D4</td>
<td>430</td>
<td>99500</td>
<td>509</td>
<td>4277</td>
<td>0.146</td>
</tr>
<tr>
<td>D5</td>
<td>418</td>
<td>96000</td>
<td>500</td>
<td>3493</td>
<td>0.510</td>
</tr>
<tr>
<td>D6</td>
<td>430</td>
<td>101000</td>
<td>506</td>
<td>3529</td>
<td>0.840</td>
</tr>
<tr>
<td>D7</td>
<td>427</td>
<td>89000</td>
<td>500</td>
<td>5344</td>
<td>0.490</td>
</tr>
<tr>
<td>D8</td>
<td>400</td>
<td>83000</td>
<td>512</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Photophysical characteristics of dendrimers D1 - D8 in dichloroethane solution.
region which is in accordance with other investigations on similar 1,8-naphthalimide derivatives [26 - 28, 30]. This parameter also depends on the type of substitution in the C-4 position. Perhaps the decisive factor here is the possibility of conformational changes.

The fluorescence efficiency of the dendrimers has been estimated by measuring their quantum yield $\Phi_F$ on the basis of the absorption and fluorescence spectra by equation (4).

$$\Phi_F = \Phi_s \frac{S_u A_u n_{Du}^2}{S_{st} A_{st} n_{Dst}^2} \quad (4)$$

where the $\Phi_s$ is the emission quantum yield of the standard, $A_u$ and $A_{st}$ represent the absorbance of the standard and the sample at the excited wavelength, respectively, while $S_u$ and $S_{st}$ are the integrated emission band areas of the standard and the sample respectively, and $n_{Du}$ and $n_{Dst}$ are the solvent refractive index of the standard and sample, $u$ and $st$ refer the unknown and standard, respectively.

As seen from the data in Table 2, the dendrimers have quantum yield in the large region $\Phi_F = 0.001-0.840$. Blue emitting dendrimers (D1 and D2) have smaller $\Phi_F$ with comparison to that of the green emitting dendrimers, due to the absence of electron donating substituents at C-4 position of the 1,8-naphthalimide units. In the case of the D4 and D5 the $\Phi_F$ of D5 is lower, because of possible conformation changes of the 1,8-naphthalimide chromophoric system in the exited state. In dichloroethane, dendrimers D6 - D8 emit strong fluorescence with high $\Phi_F$ which is due to the specific nature of the substituents in the 1,8-naphthalimide structure where the photoinduced electron transfer dominates [31, 32]. Dendrimer D3 does not emit fluorescence, which is due to the electron accepting nature of the nitro group and the respective influence of this group on the polarization of the 1,8-naphthalimide structure.

**CONCLUSIONS**

Eight newly synthesized PPA dendrimers from second generation, modified with 4-substituted-1,8-naphthalimide fluorophores in the dendrimer periphery, have been studied by infrared, absorption and fluorescence spectroscopy. It has been shown that the substituents at C-4 position of the 1,8-naphthalimide have an impact upon the frequencies attributed to the carbonyl groups from the 1,8-naphthalimide fragments incorporated into the PPA dendrimer molecule, while the substituent at the imide nitrogen atom affects slightly the polarization. The electron donor or electron acceptor ability of the substituents also plays an important role in the dendrimer photophysical properties and especially - in the quantum fluorescence yield.

**REFERENCES**

1. G.R. Newkome, C.D. Shreiner, “Poly(amidoamine), polypropyleneamine and related dendrimers and dendrons possessing different 1 → 2 branching motifs: An overview of the divergent procedures” Polymer, 49, 20081-173.
11. I. Grabchev, V. Bojinov, J.-M. Chovelon, Synthesis, photophysical and photochemical properties of fluo-
rescent PAMAM dendrimers, Polymer, 44, 2003, 4421-4428.
17. I. Grabchev, P. Bosch, M. McKenna, A. Nedelcheva, Synthesis and spectral properties of new green fluorescent poly(propyleneamine) dendrimers modified with 1,8-naphthalimide as sensors for metal cations, Polymer, 48, 2007, 6755-6762.
18. I. Grabchev, S. Dumas, J-M. Chovelon, A. Nedelcheva, First generation poly(propyleneimine) dendrimers functionalised with 1,8-naphthalimide units as fluorescence sensors for metal cations and protons, Tetrahedron, 64, 2008, 2113-2119.
31. X. Poteau A.I. Brown, R.G. Brown, C. Holmes D. Matthew, Fluorescence switching in 4-amino-1,8-naphthalimides: “on–off–on” operation controlled by solvent and cations, Dyes and Pigments, 47,
SENSOR ACTIVITY AND LOGIC BEHAVIOUR OF SOME 
2-AMINOTEREPHTHALIC DERIVATIVES

Polya Miladinova, Nikolai Georgiev

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: ppolya@uctm.edu

Received 30 May 2014
Accepted 10 September 2014

ABSTRACT

Herein we report on the sensor activity of three blue-emitting triazine derivatives of 2-aminoterephthalic acid. The novel compounds are configured as a “fluorophore-receptor” system. The fluorophores designed can act as a pH-probe via an “off-on-off” fluorescence sensing mechanism due to an internal charge transfer. The sensor activity towards cations and anions in water/DMF (1:1, v/v) media is studied by monitoring the fluorescence intensity changes. The ions tested exert a high quenching effect suggesting that the compounds are sensitive to strong acid (pH<3) and strong alkaline media (pH>8). The logic function XNOR can be performed using an acid and a base as chemical inputs, while a digital comparator can be designed on the ground of pH induced changes in the spectral properties of the novel molecule.

Keywords: 2-aminoterephthalic derivatives, ICT (intramolecular charge transfer), pH molecular sensors, molecular logic gates.

INTRODUCTION

The rapid grow of nanotechnology extends the concept of a macroscopic device to a molecular level and which is why the design and synthesis of (supra-)molecular species capable of mimicking the functions of macroscopic devices are currently of great interest [1 - 3]. Molecular devices operate via electronic and/or nuclear rearrangements and just like macroscopic devices require energy, provided as chemical, electrical energy, or light for their elements’ operation and communication. The luminescence is one of the most useful techniques to monitor the operation of molecular-level devices [4 - 6]. This determines the interest towards synthesis of novel fluorescence compounds as a considerable and inseparable part of nanoscience development.

Further semiconductors miniaturization reaches its limit. Therefore, the design and construction of molecular systems capable of performing complex logic functions is of great scientific interest now [7 - 9]. The logic gates in semiconductor devices work using binary logic, where the signals are encoded as 0 and 1 (low and high current). This process is executed on a molecular level using different procedures, but the most common are based on the optical properties of the molecule switches. They encode the low and high concentrations of the input guest molecules and the output fluorescent intensities by the binary 0 and 1, respectively [10 - 12]. The first proposal to execute logic operations at a molecular level was made in 1988, but the field developed only five years later, when the analogy between molecular switches and logic gates was experimentally demonstrated by de Silva [13]. The field has recently extended from simple switches to more complex molecular systems which can perform a variety of classical logic functions [14 - 16] and act as a half-adder [16-18], a full-adder [19, 20], a keypad lock [21, 22], a half-subtractor [23, 24], a full-subtractor [19, 20], an encoder-decoder [25, 26], a digital comparator [27, 28]. The fluorescence switching development is attractive to analytical chemistry as well.
due to the increasing requirements in connection with the environment pollution and the further development of the diagnostic medicine and biology [29-31].

The fluorescence molecular sensors are designed at present using three basic approaches based on intramolecular charge transfer (ICT), photoinduced electron transfer end energy transfer [32 - 33]. The receptor in the ICT chemosensors is directly attached to the electron-donating/withdrawing unit that is conjugated to the fluorophore electron-withdrawing/electron-donating unit. During system’s excitation the fluorophore undergoes donor-acceptor intramolecular charge transfer. The subsequent change in the dipole moment results in a Stokes shift that depends on the microenvironment of the fluorophore. Changes in quantum yields and lifetimes are often observed [34, 35] in addition to these shifts.

The derivatives of 2,5-diaminoterephthalate are organic chromophores that being in solid state exhibit fluorescence of high efficiency in the visible region. They attract increasing attention in the field of functional materials and optoelectronic devices such as organic light-emitting diodes (OLEDs), light-emitting field-effect transistors, semiconductor lasers and fluorescent solid sensors [36]. 2-aminodimethylterephthalates are organic chromophores that exhibit fluorescence in the visible region too. They find application in textiles and polymers production [37 - 39], but there is no information on their possible use as chemosensors. With this in mind, the study of their sensor activity is of interest.

We have recently synthesized six blue-emitting triazine derivatives of 2-aminoterephthalic acid [38]. Herein we report on the ability of three of them (Scheme 1) to serve as pH chemosensing materials and molecular logic gates.

EXPERIMENTAL

Materials and methods

A pH meter Metrohm 704 (www.metrohm.com) coupled with a combined pH electrode was used for the pH measurements. Commercial standard buffers for pH 2, 7 and 10 (Aldrich) were used for calibration. The absorption spectra were obtained using Hewlett Packard 8452A spectrophotometer (www.geetoronto.com) against water or the buffers described above. The fluorescent spectra were recorded on a Scinco FS-2 fluorescence spectrophotometer (www.scinco.com). The excitation source was a 150 W Xenon lamp. Excitation and emission slits width was 5 nm. The fluorescence measurement was carried out in right angle sample geometry. A 1×1 cm quartz cuvette was used for the spectroscopic analysis. The quantum yields of fluorescence were calculated using 9,10-Diphenylanthracene (Φ_F = 0.95 in ethanol) [40] as a standard according to Eq. (1) [41]:

\[
\Phi_F = \Phi_{ref} \left( \frac{S_{sample}}{S_{ref}} \right) \left( \frac{A_{ref}}{A_{sample}} \right) \left( \frac{n^2_{sample}}{n^2_{ref}} \right)
\]

where A_{ref}, S_{ref}, n_{ref} and A_{sample}, S_{sample}, n_{sample} stand for the absorbance at the excitation wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

The effect of pH on the absorption and fluorescence properties of compounds 1-3 were studied by multiple addition of amounts of 0.1 M NaOH or 0.1 M HCl to 250 mL of 1x10^{-3} M of the respective compound. The solution pH as well as the absorption and the fluorescence properties were measured using the methods described above.

Scheme 1.
Fluorescence spectra were recorded following each addition of NaOH or HCl solution. The fluorescence intensity of each mixture was measured at 470 nm. The spectral data were collected using FluoroMaster Plus 1.3 and processed further by OrginPro 6.1 software.

All experiments were performed at room temperature.

RESULTS AND DISCUSSION

The basic spectral characteristics of 2-aminoterephthalic derivatives depend on the terephthalic molecule polarization due to the electron donor-acceptor interaction occurring between the amino substituent and the carbonyl groups from the chromophoric system. Thus it can be predicted that the interaction of a guest with the donor or acceptor moiety will change the photophysical properties of the fluorophore. We chose compounds 1-3 because of their remarkable structure containing both amino and amido fragments in their chromophoric system. The amide fragments are widely used functional groups in anion recognition because the acidity of the NH group can be easily tuned by adjusting the electronic properties of neighboring substituents so that it can recognize anions through hydrogen-bonding and deprotonation interactions [42, 43]. Additionally, the 2-amino moiety in the terephthalic fluorophore is a strong electron donating group and it can serve as a cation receptor fragment [44, 45]. Hence compounds 1-3 are expected to detect cations as well as anions. When a cation interacts with the terephthalic fluorophore amino group, the latter reduces its electron-donating character.

![Absorption spectra of sensor 3 in water/DMF (1:1, v/v) solution at different pH values.](image)

![Scheme 2](image)

Table 1. Quantum yields and pKa values of compounds 1, 2 and 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_F$</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 2</td>
<td>pH 7</td>
</tr>
<tr>
<td>1</td>
<td>0.006</td>
<td>0.011</td>
</tr>
<tr>
<td>2</td>
<td>0.012</td>
<td>0.021</td>
</tr>
<tr>
<td>3</td>
<td>0.032</td>
<td>0.090</td>
</tr>
</tbody>
</table>
Because of the resulting reduction in polarization, a blue shift of the absorption spectrum is expected, together with a decrease in the quantum yield of fluorescence (Scheme 2). The anion effect is similar. In case of an anion interaction with the terephthalic fluorophore amides, the carbonyl electron-accepting ability decreases due to the amides deprotonation which generates a strong electron density near the carbonyl group. This results in a decrease of the ICT efficiency in the 2-aminoterephthalic fluorophores, which in turn leads to blue shifting and lower quantum yield.

This was the reason to investigate the photophysical behaviour of compounds 1-3 in water/DMF (1:1, v/v) solution at different pH values (in presence of protons as cations and a hydroxide as anions). Compounds 1-3 show the longest-wavelength absorption band in the range of 280 nm - 430 nm in the media pointed above. It is attributed to the typical 2-aminoterephthalic ICT process. The pH effect on the absorption properties of the compounds examined is negligible in a wide pH range. This is illustrated by the absorption spectra of compound 3 at pH 2, pH 7 and pH 10 presented in Fig. 1.

The emission spectra of the compounds under study (1-3) do not show significant pH-dependent changes in the pH window of 3.5-8, since 2-aminoterephthalic fluorophore does not affect the ICT excited state. The calculated quantum yields of fluorescence are in the range between 0.011-0.09 (Table 1, pH 7). These values are very low and can be explained taking into consideration that water is an effective fluorescent quencher. Besides, the high hydrophobicity of the compounds examined results in a self-quenching effect in aqueous media due to fluorophore aggregation.

pH decrease from 3.5 to 2 results in a blue shifting ($\Delta\lambda_{\text{A}} = 4 \text{ nm}$) and a quenching effect of the fluorescence of probes 1-3 (Fig. 2A) because of protonation of 2-aminoterephthalic nitrogen, which in turn decreases the ICT efficiency. Fluorescence quenching (FQ) determined as the ratio of the maximum fluorescence intensity $I_0$ at pH 3.5 and the minimum fluorescence intensity $I$ at pH 2 is found equal to 1.52, 1.58 and 1.44 for compounds 1, 2 and 3, correspondingly.

At high pH values (pH > 8) the amido groups are deprotonated and an anion is formed. The latter decreases the electron deficiency at the adjacent carbonyl groups which in turn decreases the ICT efficiency. This is related

![Fig. 2. Fluorescence spectra of sensor 3 in water/DMF (1:1, v/v) solution at different pH values: (A) pH= 2-3.5 and (B) pH= 3.5-13.7.](image)

![Fig. 3. Fluorescence intensity of compound 3 at 510 nm in water/DMF (1:1, v/v) as a function of pH.](image)
to the lower electron accepting ability of terephthalic carboxyls. As a result, a hypsochromic shift ($\Delta \lambda = 13$ nm) and fluorescence quenching effect are observed (Fig. 2A). The values of FQ determined as the ratio of the maximum fluorescence intensity $I_o$ at pH 8 and the minimum fluorescence intensity $I$ at pH 14 are found equal to 10.88, 11.94 and 11.24 for compounds 1, 2 and 3, correspondingly.

In general, bell-shaped pH titration curves reflecting the "off-on-off" fluorescence response of compounds 1-3 are obtained (Fig. 3). The analysis of the fluorescence changes as a function of pH according to Eq. (2) [47] gives two $pK_a$ values for each compound, for the protonated and the deprotonated form, respectively.

$$\log \left( \frac{(I_{F,\max} - I_f)}{(I_f - I_{F,\min})} \right) = \text{pH} - pK_a \quad (2)$$

The significant pH effect on the emission spectra of sensors 1-3 provides to conclude that they can execute logic operation upon addition of H$^+$ and OH$^-$ as inputs. The fluorescence of sensors 1, 2 and 3 monitored at 470 nm in the presence of an acid and a hydroxide shows that a XNOR molecular logic gate (Table 2) can be constructed starting off a neutral solution. It is seen that the emission output of sensors 1, 2 and 3 is low (coded for binary 0) with the input either of an acid or a base (Fig. 4). The simultaneous input of an acid and a base annihilates each other’s effect and generates high emission (coded for binary 1) at 470 nm mimicking thus the XNOR logic function.

The XNOR logic gate is actually a comparator as the output is 1 only when both inputs are of an identical value playing thus the role of the mathematical symbol “equal”. XNOR cannot however say which input is higher than the other. An additional output value serving as the mathematical symbol “greater than” or “lower than” is required to construct a magnitude digital comparator. In fact the compounds examined are able to act as a magnitude digital comparator in a three-valued logic output mode (the output has three values “low”, “medium” and “high”) due to the different quenching effect of the cations and anions present. For example, the quantum yield of fluorescence of compound 3 in a neutral solution is 0.09 and can be coded as “high”. In presence of NaOH the quantum yield decreases to 0.021

Table 2. The truth table for the logic behaviour of compound 3.

<table>
<thead>
<tr>
<th>Input 1</th>
<th>Input 2</th>
<th>Output $F_{470}$</th>
<th>$Q_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+$</td>
<td>OH$^-$</td>
<td>0</td>
<td>0.090 (High)</td>
</tr>
<tr>
<td>$H^+$</td>
<td>&lt;OH$^-$</td>
<td>1</td>
<td>0.021 (Low)</td>
</tr>
<tr>
<td>$H^+$</td>
<td>&gt;OH$^-$</td>
<td>0</td>
<td>0.032 (Medium)</td>
</tr>
<tr>
<td>$H^+$</td>
<td>=OH$^-$</td>
<td>1</td>
<td>0.090 (High)</td>
</tr>
</tbody>
</table>

Fig. 4. Fluorescence spectra of compound 3 in presence of a chemical input of 20 $\mu$L of 0.1 mol L$^{-1}$ HCl (Input 1) and of 20 $\mu$L of 0.1 mol L$^{-1}$ NaOH (Input 2) to water/DMF (1:1, v/v).
to be referred as a “low value”, while the addition of HCl decreases the quantum yield to 0.032 corresponding to a “medium” value, i.e. a value between 0.021 (the “low value”) and 0.09 (the “high value”). When both inputs are equal (H+ = OH-), the output (Flv) is “high”. In case H+ > OH-, the output (Flv) refers to the “medium value”, while the addition of a base, i.e. when H+ < OH-, the output refers to the “low” value.

The compounds acting as molecular logic gates of chemical inputs are actually complex chemosensors. This feature is revealed in case the sample analyzed responses to a predefined standard. If the fluorescence output of novel sensors 1, 2 and 3 is 1, then the solution tested is in the pH window of 3-8. If the fluorescence output is 0, then the solution tested has a strong acid (pH < 3) or a strong alkaline (pH > 8) reaction. In other words compounds 1, 2 and 3 are sensors with neither fast response that the analyzed sample is nor strong acid and nor strong alkaline.

CONCLUSIONS

Three new fluorescent pH sensors 2-aminoterephthalic acid derivatives are presented and their photophysical behavior in water/DMF (1:1, v/v) media as a function of pH is studied. The compounds studied show low fluorescence emission intensity in alkaline and acid media. It is enhanced upon further acidification or alkalization. The system is in “on” state in pH range of 3-8. The effect is suggested to result from the amine receptor’s protonation, when pH < 3 and deprotonation, when pH > 8. The fluorescence changes indicate that sensors 1, 2 and 3 can act as an efficient “off-on-off” switch for pH determination. The sensors’ logic behavior is also examined using fluorescence as output and H+ and OH− as chemical inputs. The logic function XNOR is achieved and the logic circuit of a digital comparator is demonstrated.

Acknowledgements

The authors gratefully acknowledge the financial support from the Bulgarian National Science Fund (Project DDVU-02/97) and Science and Research Program of the University of Chemical Technology and Metallurgy, Sofia, Bulgaria.

REFERENCES

14. J. Andréasson, U. Pischel, Smart molecules at work-
17. C. Xu, W. Sun, C. Zhang, Y. Bai, C. Fang, W. Li, Y. Huang, C. Yan, Chemical approaches for mimicking logic functions within fluorescent MPT dyes, Science China, Series B, 52, 2009, 700-714.
39. P. Miladinova, On the photostability of some blue-emitting derivatives of 2-aminoterephthalic acid and
their copolymers with methyl methacrylate, Polym Degr Stab, 98, 2013, 2347-2350.


ABSTRACT

The effect of thermal ageing of neutral sulfite semi-chemical pulp derived from poplar wood is followed on the ground of the comparative investigation of bleached and unbleached samples. The brightness reversion observed in the course of the process is studied at 90 °C, 105 °C and 120 °C. The degree of brightness is determined at the 6-th, 12-th, 24-th and the 36-th hour of the process duration. The kinetic analysis carried out shows that the exponential kinetic equation valid for processes taking place on uniformly inhomogeneous surfaces describes the kinetics of the process investigated. The linear relation between the apparent pre-exponential factor and the apparent activation energy, as obtained from an Arrhenius analysis, indicates the existence of a compensation effect.

Keywords: semi chemical pulp, thermal aging, bleaching, exponential kinetic equation, compensation effect.

INTRODUCTION

The low-cost raw forest products and the processes providing the use of wood biomass could solve the problem with the scarce natural resources. The high cellulose and the relatively low lignin content make poplars well suited for all treatment methods – mechanical, semi-chemical, sulphate and sulphite. Semi-chemical pulping process is a two-stage method. It combines chemical treatment aimed at lignin partial removal and a mechanical refining step which results in defibring. The chemical treatment in case of semi-chemical pulping can be carried out using sodium sulphite, caustic soda and kraft liquor. The main advantages of the neutral sulfite semi-chemical process refer to the relatively low wood quality required, the high yields and the low consumption of chemicals [1-3]. The semi-chemical pulps produced on the ground of hardwoods have higher strength but relatively low brightness when compared to that obtained from softwoods. Because of the lignin content the unbleached samples of semi-chemical pulps age faster than the bleached one. The yellowing starts with the oxidation of the lignin phenolic hydroxyl groups, which in turn leads to the subsequent formation of quinones, quinone-methydes and cyclohexadienes [4-7]. The process rate increases with the temperature increase. The effect considered can be partially avoided with the application of a two-stage bleaching method. The latter is often used for combined bleaching. The oxidizing reagents introduced during the first stage affect strongly the chromophore groups in the lignin and the other colouring compounds present. It is worth noting that the chromophores formation is accompanied by aromatic nuclei attack and demethoxylation but it does result in lignin’s degradation. The subsequent treatment with reducing agents during the second stage provides reduction of the residual chromophores or those additionally formed in the course of the oxidation which in turn results in brightness increase. The process is limited to lignin’s transfer, mainly on the fibers’ surface, from an oxidized to a reduced form. Besides, conjugated (double or triple) bonds play an important role in organic sub-
stances coloration. Heavy metals ions form also coloured complexes with the pulp and hence decrease the bleaching effectiveness and increase the bleaching reagent consumption. Their effect is decreased or eliminated by the introduction of complex formation compounds - chelating agents like ethylenediamine tetraacetic acid (EDTA), polysulphates, etc [8-11].

The study of the kinetics of semi-chemical pulp thermal ageing is expected to provide data whose treatment may facilitate to elucidate its mechanism and hence to optimize the process taking also into consideration the advantages of the methods of treatment and storage. The problem is that ageing is a complex process which does not obey formal kinetic principles. The rate of changes in the fiber materials depends on the temperature, on the bleaching sequence, on the process duration, as well as on other factors. Some authors describe the degradation reactions brought about by ageing as first or second order reactions [12-16]. But the equations derived so far assume that the processes take place on a homogeneous surface. Other authors used the autocatalytic kinetic model to explain the biomass thermal degradation, but the temperatures used were very high and the aim was to determine the content and the mass of each component that was affected by the volatilization or the oxidation process [17].

The temperature effect on most of the catalytic processes is usually described by the temperature dependence of the rate constant k in accordance with the Arrhenius equation:

\[ k = A e^{-\frac{E}{RT}} \]  

where the apparent pre-exponential factor \( A \) and the apparent activation energy \( E \) are non-temperature dependent parameters. There are cases where they both change in the course of the process. Their variation depends on the increase of the extent of reaction, a phenomenon often referred to as the compensation effect [18-21]. The increase of \( E \) is usually attributed to energetic hindrances, while the variation of \( A \) is connected with the entropy factors effect on the rate of the process examined. In some cases, the changes in \( A \) and \( E \) display a linear dependence according to the Cremer-Constable relation [21-22].

\[ \ln A = aE + b \]  

The latter implies that values of \( \ln A \) plotted against those of \( E \) fall on a straight line with slope \( a \) and intercept \( b \). The compensation effect has been known for almost 100 years. It has been studied in a variety of cases in heterogeneous inorganic and organic catalysis [23-31], but no consensus on its nature is reached. One of the possible explanations refers to an enthalpy-entropy relationship.

This work reports experimental data obtained in a comparative kinetic investigation of the effect of the process duration, the bleaching pretreatment and the temperature increase on the thermal ageing of semi-chemical pulp derived from poplar wood. The analysis accounting of the complex influence of the samples heterogeneity is aimed at elucidating the mechanism of the process.

**EXPERIMENTAL**

The experiments were carried out with semi-chemical pulp (SCP) obtained from rapidly growing poplar wood of increased density (Populus Trichocarpa Xeuram Populus deltoides cultivar Hunneg). After bark removal the wood was chopped into chips of standard dimensions of 15 mm/ 20 mm / 3 mm.

SCP was obtained using 100 g absolutely dry chips. The hydromodule was of 1:5, the treatment temperature was 85°C, while the duration was 90 min. 7 % NaOH and 5 % Na₂SO₃·7H₂O₂ (the concentration are evaluated in respect to the mass of the absolutely dry chips used) were introduced. The same conditions were applied to 10 g of chips aiming yield determination. The chips, weighed initially, were placed in a thermostated vessel to preserve the temperature applied. Then the solutions of NaOH and Na₂SO₃ were added in the amounts pointed above. The duration of the treatment followed the technological regime. Then the solution left was removed and the chips were washed to a neutral reaction. They were subsequently fibered with the application of a disc fibering device (Spront-Valdron). The fibering extent reached was 12°SR. It was determined by Schoppet-Riegler method (Bulgarian Standard ISO 5267-1). Then the samples were washed and sorted manually using two sieves.

SCP yield was 90 %. It was determined by the weight method. The application of the latter required to soak the chips for 24 hours in distilled water, to wash them to a neutral reaction and then to dry them to a constant
weight. Non-treated samples were investigated as well to outline the bleaching effect on the kinetics of the thermal ageing of SCP.

**Bleaching of SCP**

SCP prepared under the conditions pointed above was subjected to a two-stage combined bleaching, i.e. bleaching with $\text{H}_2\text{O}_2$ (I stage) followed by bleaching using the reducing agent Rongalyt C (II stage). The first stage was applied to 10 % of SCP at 70°C within 90 min. In this case the medium $\text{pH}$ was ca 10.5, while the amount of $\text{H}_2\text{O}_2$ was 2 %. The additives used referred to 2 % NaOH, 5 % Na$_2$SiO$_3$, 0.5 % MgSO$_4$ and EDTA (Na$_2$C$_{10}$H$_{12}$O$_{8}$N$_2$·2H$_2$O) as a complexion agent. All amounts pointed so far were calculated in respect to the absolutely dry fibrous material used. The procedure applied required to place the sample in a polyethylene bag, to bring it to the temperature value envisaged and then to introduce the bleaching solution under constant stirring to provide complete homogenization. Then the sample treated was transferred to the thermostated reaction vessel where the stirring continued. Upon the first stage completion the fibrous material had to be washed until reaching a neutral reaction. Rongalyt C (NaHSO$_2$.CH$_4$O.2H$_2$O) and EDTA were introduced during the second stage of the bleaching process which was carried out for 90 min at 70°C. The concentration of SCP was 5 %, while the consumption of Rongalyt C and EDTA was 2 % and 0.5 %, correspondingly. The bleaching procedure was analogous to that applied during the first stage. The bleached fibrous material obtained was finally washed until a neutral reaction was obtained.

**Ageing of SCP**

Fiber mass casts of a diameter of about 6 cm were made. They were dried in absence of light at room temperature. Samples of unbleached and bleached SCP were subjected to thermal ageing for 36 hours at temperature of $90^\circ\text{C}$, $105^\circ\text{C}$ and $120^\circ\text{C}$. The degree of brightness was determined using ELREPHO – 2000 using a standard light source of D 65 at $\lambda = 457$ nm. The degree of brightness prior to and after the ageing was determined following ISO 2470:202. Furthermore, the degree of brightness of the bleached samples was determined at the 6th, 12th, 24th and the 36th hour of the process. This was done to follow the kinetics of the ageing process. A number of experimental series were investigated. Each value reported below is based on three identical one obtained in the course of the study.

**RESULTS AND DISCUSSION**

The effect of thermal ageing of SCP is followed using bleached and unbleached samples under the conditions pointed above. All values obtained are summarized in Table 1.

The data presented in Table 1 shows that the two-stage bleaching leads to 36 % increase of the degree of brightness. At $90^\circ\text{C}$ the brightness reversion is 3.83 % for the unbleached samples, while it is 5.11 % for the

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Brightness $W%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td></td>
<td>unbleached</td>
</tr>
<tr>
<td>0</td>
<td>31.3</td>
</tr>
<tr>
<td>6</td>
<td>30.6</td>
</tr>
<tr>
<td>12</td>
<td>30.3</td>
</tr>
<tr>
<td>24</td>
<td>30.2</td>
</tr>
<tr>
<td>36</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Table 1. Values of the degree of brightness, $W\%$, of unbleached and bleached SCP in the course of the process of ageing h at the temperature values studied.
bleached one. At 105°C it is 6.26% and 8.69%, respectively, while at 120°C the values found are 10.00% and 11.78%. These observations can be explained with the lower initial brightness of the unbleached samples.

The comparative investigation of the thermal ageing kinetics is done with the introduction of the kinetic variable, \( \alpha \):

\[
\alpha = \frac{W_0 - W}{W_0}
\]  

where \( W_0 \) is the initial brightness value in % ISO, while W in % ISO is the current value connected with the time of the treatment. The variable \( \alpha \) can be also considered as an extent of thermal ageing or as a relative decrease of the degree of brightness in the course of the process.

The kinetic curves showing the change of \( \alpha \) with time, t, h at the three temperature values studied are presented in Fig. 1.

As Fig. 1 shows \( \alpha \) increases with time and temperature for both types of samples. This increase of the kinetic variable corresponds to the increase of the extent of thermal ageing, i.e. to the corresponding brightness reversion of SCP. It is also evident that the tendency towards ageing of the unbleached samples is better outlined after the 24th hour when compared to that of the bleached one. This result is attributed to the fact that the ageing process of the bleached samples is not completed, while the stability to thermal ageing of the unbleached samples is well decreased. This effect is better outlined at 120°C.

The kinetics of thermal ageing is described by the exponential equation (Eq. 4):

\[
v = v_0 e^{-\alpha t}
\]  

where the current and the initial rate of the ageing process are designated by \( v = \frac{d\alpha}{dt} \) and \( v_0 \). It is valid for processes taking place on uniformly inhomogeneous surfaces where the active centres are distributed linearly in correspondence with their energy [30-36]. Its applicability is experimentally verified [31-33]. For a surface of this type the heterogeneous reaction rate decreases exponentially with a increase. The kinetic coefficient of inhomogeneity \( \alpha \) in Eq. (4) accounts for the energy and entropy inhomogeneity of the system.

All kinetic curves are linearized in coordinates \( \alpha \) vs. ln \( t \) in correspondence with the approximate integral form of the exponential kinetic equation:

\[
\alpha = \frac{1}{a} \ln \left( \frac{v_0}{a} \right) + \frac{1}{a} \ln t
\]  

The linear dependences obtained in correspondence with Eq. (5) are presented in Fig. 2.

As Fig. 2 shows the slope value of the lines obtained (Fig. 2) provides the determination of \( \alpha \) (Eq. 5). The values of the latter are presented in Table 2. It is seen that \( \alpha \) decreases with temperature increase. This tendency is better expressed for the unbleached SCP.

The temperature dependence of \( \alpha \) can be described
by Eq. (6) [37]:

\[ a = \frac{B}{RT} - a_0 \]  

(6)

Constant B (kJ mol\(^{-1}\)) in Eq. (8) stands for the interval of energy inhomogeneity and takes account of the active centres of different energy, while coefficient \(a_0\) stands for the interval of entropy inhomogeneity and is connected with the number of the active centres, their disposition and availability.

The specifics of the process assume in fact the presence of energy and entropy inhomogeneity of the system. The ratio of \(a_0\) and B found in the present case is a constant, i.e.

\[ \frac{a_0}{B} = \left(\frac{869}{2901}\right)_{unb} = \left(\frac{530}{1792}\right)_b = 0.3 \text{ (mol kJ}^{-1})\].

<table>
<thead>
<tr>
<th>T °C</th>
<th>Unbleached pulp</th>
<th>Bleached pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(v_0 \times 10^a)</td>
</tr>
<tr>
<td>90</td>
<td>100</td>
<td>10.78</td>
</tr>
<tr>
<td>105</td>
<td>52</td>
<td>11.33</td>
</tr>
<tr>
<td>120</td>
<td>27</td>
<td>13.43</td>
</tr>
</tbody>
</table>

It depends neither on the temperature, nor on the bleaching. This result leads to the conclusion that the inhomogeneity observed is determined only by the type of the system (i.e. it has a constant value for the particular system studied).

Combining both Eqs. (4) and (5) leads to the following expression of the current rate \(v\) of the process:

\[ v = \frac{1}{at} \]  

(7)

It is calculated at different values of \(\alpha\) leading to the conclusion that \(v\) decreases with \(\alpha\) increase for all samples studied. The dependence obtained is visualized in Fig. 4.

The logarithmic form of the exponential kinetic equation (Eq. 4) can be used as well for the determination of the initial rate, \(v_0\) (h\(^{-1}\)), of the process of thermal ageing (at \(\alpha \to 0\)), i.e.:

\[ \ln v = \ln v_0 - \alpha a \]  

(8)

The values of \(v_0\) are presented in Table 2. The initial rate of ageing of the bleached samples is relatively higher than that of the unbleached one but the latter become more stable to temperature increase and their brightness reversion proceeds more slowly with \(\alpha\) increase.

The rate-temperature dependence is used to calculate the apparent activation energy \(E\) and the pre-exponential factor \(\ln A\), according to the Arrhenius equation:

\[ v = Ae^{\frac{E}{RT}} \]  

(9)
The values obtained as a function of \( \alpha \) are summarized in Table 3. The dependence found for the bleached samples is visualized in Fig. 5. The temperature effect on the thermal aging rate of the unbleached samples shows the same tendency.

As Fig. 5 shows the linear dependences obtained have different slopes, i.e. the values of activation energy \( E \) and pre-exponential factor \( \ln A \) increase with \( \alpha \) increase. This means that the surface is energy and entropy heterogeneous.

The activation energy \( E \) (kJ mol\(^{-1}\)) of the bleached samples is higher at the beginning of the process, \( \alpha \to 0 \). But in the course of the treatment it becomes lower, most probably because of the larger number of active centres available on the surface. The ageing process is hampered with \( \alpha \) increase in case of unbleached pulp. These findings are in accord with the experimental results concerning the decrease of the current rate of the process at the bleached and the unbleached samples (Fig. 4). The rate of ageing is lower for the unbleached one and hence it can be concluded that the bleached samples are more resistant to thermal aging for a longer time and at higher temperatures. On the other hand, \( \ln A \) increases also in the course of the process. This indicates that the number of the chromophore groups responsible for brightness reversion increases. Besides, the values found at \( \alpha \to 0 \) are higher for the bleached samples but the total increase of the entropy factors in the course of the process is greater at the unbleached one.

The dependences of \( E \) and \( \ln A \) on \( \alpha \) increase is linear as required by the model of inhomogeneous surfaces [33-37]. It is described by Eq. (10) and Eq. (11), respectively:

\[
E = E_0 + B\alpha \quad (10)
\]

\[
\ln A = \ln A_0 + a_0 \alpha \quad (11)
\]

where \( E_0 \) (kJ mol\(^{-1}\)) and \( \ln A_0 \) are the apparent activation energy and the apparent pre-exponential factor at \( \alpha \to 0 \) (Table 3), respectively. The values of constant \( B \) (kJ mol\(^{-1}\)) (Eq. 10) and constant \( a_0 \) (Eq. 11) coincide with those estimated with the application of Eq. (4). It is worth noting that their ratio, i.e. the ratio between the entropy and the energy heterogeneity of the bleached and unbleached pulp coincides with that previously calculated

\[
\frac{a_0}{B} = 0.3 \text{ mol kJ}^{-1}.
\]

The dependences of \( E \) and \( \ln A \) on \( \alpha \) are presented in Figs. 6 and 7, correspondingly.

It is seen from Figs. 6 and 7 that the linear dependences presented intersect at \( \alpha \approx 0.013 \). The time required to reach this point is in the range of 1.5 h at 120 °C and 4.5 h at 90 °C. \( W_0 \) decreases with about 1.3% during this

![Fig. 5. Temperature dependence of the initial (at \( \alpha \to 0 \)) and current rate (at \( \alpha = \text{const} \)) for bleached SCP.](image)

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>Unbleached pulp</th>
<th>Bleached pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>0.0</td>
<td>0.035</td>
</tr>
<tr>
<td>( E ) (kJ mol(^{-1}))</td>
<td>18.5</td>
<td>104.59</td>
</tr>
<tr>
<td>( \ln A )</td>
<td>1.46</td>
<td>26.92</td>
</tr>
</tbody>
</table>
time interval. The effect of the energy and the entropy factors on the thermal ageing of the unbleached samples is better expressed at values greater than that pointed above. This is most probably connected with the exhaustion of the available active centers on the surface and the increase of the number of the chromophore groups responsible for brightness decrease. The bleached samples age more slowly as their lignin content is lower. The process rate is affected both by the apparent activation energy and the apparent pre-exponential factor. The simultaneous change of these counteracting factors with a increase brings about a compensation effect [23-27]. A linear dependence of \( \ln A \) on \( E \) is obtained:

\[
\ln A = n + mE
\]  

(12)

Besides, it is valid for all samples studied. The applicability of Eq. (12) is illustrated in Fig. 8. It is worth noting that the value of the slope found is given by

\[
m = \frac{a_0}{B} = 0.3 \text{ (mol kJ}^{-1})
\]

while the value of the intercept coincides with constant \( n \) described by

\[
n = \ln A_0 - \left( \frac{a_0}{B} \right) E_0
\]

The correlation obtained indicates a common mechanism of the ageing process of the treated and the non-treated samples. It suggests that the increase of the activation energy slows down the ageing process but not as much as that required to compensate the increase of the number of the chromophore groups responsible for the brightness reversion. This in turn leads to the conclusion that bleaching has a positive but limited effect on the ageing, especially at high temperatures.

CONCLUSIONS

The effect of thermal ageing of SCP is followed on the ground of the comparative investigation of bleached and unbleached samples. The kinetics of the process is described by the exponential kinetic equation valid for processes taking place on uniformly inhomogeneous surfaces. The initial rate of bleached samples ageing is relatively higher than that of the unbleached one but the
latter become more stable to temperature increase and their brightness reversion proceeds more slowly. The current rate-temperature dependence is used to calculate the apparent activation energy and the apparent pre-exponential factor of the Arrhenius equation. They are found to increase simultaneously with increase of the extent of the process. The compensation effect found is common for the samples of both types. This indicates that the mechanism of thermal ageing does not depend on the temperature, the process duration and the degree of bleaching.

REFERENCES

STUDY OF THE COMPLEX EQUILIBRIUM BETWEEN TITANIUM (IV) AND TANNIC ACID

Andriana Surleva, Petya Atanasova, Tinka Kolusheva, Latinka Costadinnova

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: asurleva@my.uctm.edu

ABSTRACT

Titanium-tannin (Ti-TA) complex is used in the modern leather technology as an alternative of chromium tannage and as an effective modification of vegetable tanning. The ratio between metal and tanning reagent is a key factor for minimizing the unused quantities of tannic acid that could reach the environment by waste waters and cause damages on aqueous ecosystems. However, a lack of reliable data about Ti-TA complexation limits the possibility for fine tuning of the composition of tanning solutions. This study is aimed at characterization of titanyl-tannin complex: its structure, stoichiometry and stability constant. The data of alpha-coefficient of titanyl-hydroxocomplexation at different pH values were also presented. The results obtained showed that in the concentration interval 5x10^-6 – 2x10^-5 M and pH 4, the main titanium IV species in titanyl/tannin/formate solutions is titanyl-hydroxo-tannin complex TiO(OH)TA. It was proved by UV-Vis and IR spectrometry that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen of tannin are involved in the coordination of titanyl ion. The stability constant of TiO(OH)TA was estimated: lgβ = 16.53. The obtained molar ratio curves and the calculated values of the equilibrium constants could be used in leather technology for selecting an appropriate composition of tanning solutions.

Keywords: tannin, titanium, titanyl, stability constant, complexation, leather tanning.

INTRODUCTION

The titanium-tannin (Ti-TA) complex is a modern tanning-coloring agent used in leather technology research in attempts to replace the synthetic dyes with natural ones and to decrease the level of allergic impact of produced leather. Moreover, the leather treated with tannic acid, is supposed to possess at a certain level the antimicrobial and antifungal properties of the used metal-tannin complexes [1, 2]. The leather treated by titanium (IV) - tannin solution is very soft, flexible and possess good thermal stability [3]. The leather technology calls for proper data about the Ti-TA complex composition and stability so that to achieve a fine tuning of the composition of tanning solutions. The ratio between metal and tanning reagent is a key factor for minimizing the unused quantities of tannic acid in wastewaters. On the one hand, high levels of tannic acid in water provoke an intensive grow of algae, on the other hand, tannin decomposition rapidly increases water COD and causes damages on aqueous ecosystems. A detailed study of the Ti (III) – tannic acid mixture in a combined tanning procedure was reported by Bo Teng et al. [3]. Tannins with different origin and different content of gallic acid were studied. The results presented showed that the quality of the treated leather depends on the structure and origin of the used tannins.

The data about Ti-TA complexes found in the literature are very scarce. Tannic acid was reported as an effective precipitating reagent for titanium determination in chloride solutions [4]. Spectrophotometric determination based on titanium complexation by tannin and thioglycolic acid was described [5], however the structure and the origin of studied tannin, as well as the
absorption spectra of the formed compound were not presented. The strong complexation of Ti (IV) by tannin was used for photosensitization of nanocrystalline TiO₂ films [6]. The force of induced photoelectricity depends on the structure and origin of the used tannin. Electrospray mass spectrometry was applied to study copper complexation by ligands derived from tannic acid [7]. Although the proposed method is important for characterization of different classes of ligands found in natural waters, quantitative data about their stability constants are not presented.

The chemistry of Ti (IV) salts tanning is reported to be dominated by the titanyl ion TiO₂⁺ [1, 9]. The complexes formed in water-sulphuric acid are described as chains of titanium ions bridged by hydroxy and sulphato ligands [10]. An advantage of tanning with titanium (IV) is the resulting white leather. However, Ti (IV) salts tend to hydrolyse and precipitate in dilute solution [1]. The hydrolysis of such titanium complexes proceeded through the coordination of hydroxo groups and formation of oxo bridges. The higher the concentration of Ti (IV) and sulphuric acid is the more extensive the degree of polymerization is [9]. It was proposed that mixtures of the metal sulphates could be stabilised against hydrolysis at pH 4 by complexing (masking) with gluconate [1].

In the research literature tannic acid (tannin, gallotannin, TA) is used to designate a large group of naturally occurring polymers with different structure and molecular mass. This fact illustrates the main difficulty of using the available in the literature data: the lack of specified information about the molecular mass and the origin or structure of studied tannins limits the application of available data and the comparability of the results. This study is focused on tannin (C₇₀H₅₄O₄₆) with molecular mass 1 701.20 g/mol and structure described in [11], often named as “Chinese tannin” as it is found in a pure form in Chinese gals (Rhus semilata) and Sumac (Rhus typhina) [12]. Our interest to Sumac is determined on the one hand, by the fact that Sumac is a plant largely available in Europe traditionally used for vegetable leather tanning [13], and on the other hand, it could be isolated in enough pure form so that comparable quantitative data to be reported.

The aim of this study is to characterize the TiO₂⁺-TA complex: its structure, stoichiometry and stability constant. The study was performed at formate buffer solution. The chosen experimental conditions are supposed to correspond more closely to the combined tanning conditions than the acetate buffer experiments often found in the literature [5]. Additionally, our recent study reported that tannic acid (Chinese tannin) is a monoprotic acid with pK = 4.2 and could be regarded as a moderately strong acid [11]. The results showed that the proton of the phenolic group in the next-to-last galloyl residue in the tannin chain is more likely to govern the protolytic reaction.

EXPERIMENTAL

Reagents

The stock solution of TiO₂⁺ (2.087 x 10⁻² M) was prepared from TiO₂ (p.a.; Merck 99.99 %) fused with K₂S₂O₈ at 780°C (p.a.; Merck). The obtained melt was dissolved in 25 mL 33 % v/v H₂SO₄ at heating, after cooling the solution was diluted up to 100.0 mL with d. H₂O. Working standard solutions were daily prepared from the stock solution by appropriate dilution. The tannin stock solution (1.000 x 10⁻⁴ M) was daily prepared from dried at 105°C for 1 h tannin reagent (p.a. Fluka, 403040) and dissolving in d.H₂O. The formate buffer (0.2 M, pH = 4.00 ± 0.02) was prepared from formic acid and potassium hydroxide (p.a.; Merck). The pH was potentiometrically controlled by Boeco (Germany) combined pH electrode. Distilled water was used throughout the experiments.

Procedures

Molar ratio method. Working solutions at different tannin/TiO₂⁺ molar ratios were prepared by mixing 25 mL formate buffer (pH 4.00) with calculated volumes of the tannin stock solution (10⁻⁴ M) and finally adding the appropriate aliquots of 1.070 x 10⁻³ M solution of TiO₂⁺. The final volume of 50.00 mL was obtained by dilution with d. H₂O. After 20 min reaction time, the absorbance was measured at 322 nm in 1 cm cuvette. A blank containing the same quantity of tannin solution in formate buffer was used as a reference. The measurements were made at 25±1°C. The spectra were acquired at Cary 100 Varian spectrophotometer (Agilent).

IR spectrometry. Titanyl-tannin (TiO₂-TA) complex was obtained by mixing TiO₂⁺ and tannin solution at molar ratio 1:2 at pH 4.00 (formate buffer). The obtained yellow solution was stable during one hour. After 24 h the precipitate was formed. The obtained precipitate was dried at room temperature. The IR spectra were registered on KBr by Alfa Aesar spectrometer.
RESULTS AND DISCUSSION

NMR study of the tannin

The NMR spectra of the studied tannin is presented on Fig. 1. As can be seen, the number of the protons from the galloylic part of the molecule is 10 times higher than the number of the protons in the glucose part. This fact proves the assumed number of galloylic residues in tannin molecule. Additionally, a large signal at 7 ppm showed that some tannin monomers combined to form oligomers. The carbon NMR spectra of the tannin couldn’t be registered due to the low solubility of tannin in denatured solvents. The structure of studied tannin is presented on the Fig. 1B [11].

Spectroscopic study of the reaction between TiO$^{2+}$ and tannin

Electronic spectra of titanyl, tannin and titanyl-tannin mixture in formate buffer at pH 4 are presented on Fig. 2. The formed complex is clearly manifested by a red shift of wave length of maximum absorption from 275 nm (tannin solution) to 300 nm (solution of TiO-TA complex) ($\Delta \lambda = 25$ nm) and by a new shoulder appearing at 400 nm. The color of the complex aqueous solution was bright yellow and the spectra profile was independent of the chemical composition of used buffers: acetate and formate. The buffer compositions at pH around 4 were chosen based on literature data [5]. However, the concentration of acetate buffer should be very high (4 M) to maintain a sufficient buffer capacity which was related to severe inconveniences in routine laboratory work. Moreover, a slight increase of the absorbance at 320 nm was noticed in formate buffer (pH 4.00) compared to the absorbance of the complex obtained in acetate buffer (pH 3.40). As regarding the application of titanyl-tannin complex in leather technology, additional advantage of formate buffer as a medium for complex study is the fact that the procedure of leather pickling is performed in HCOOH solutions. Thus the study of titanyl-tannin complex was further performed in a formate buffer. The spectra of the formed complex measured against an analytical blank containing tannin and formate buffer are presented on Fig. 3. The absorbance of pure tannin was extracted from the spectra of the titanyl-tannin complex to obtain the pure complex spectra. The differential absorbance at 270 nm due to the absorption by C=O groups in tannin molecule [14] had negative values indicating that the C=O groups did not absorb UV-light at this spectral region. The formation of titanyl-tannin complex by coordination via C=O could be supposed. The absorbance of the complex depended on the concentration of titanyl ions in the solution (Fig. 3). The maximum differential absorbance of the obtained complex was measured at 322 nm. It is worth to be
Andriana Surleva, Petya Atanasova, Tinka Kolusheva, Latinka Costadinnova

mentioned that at this wavelength the complex TiO(OH)i, formed in formate buffer solution of TiO\(^{2+}\) at pH 4.00 did not absorb photons (Fig. 2, curve 1).

The complex formation was verified by IR spectroscopy on KBr. For IR study the complex was obtained at molar ratio of TiO\(^{2+}\) to tannin equal to 1:2. The obtained solution of the complex was stable for an hour. The yellow colored complex was obtained by precipitation for 24 h. IR spectra of TiO\(_2\), tannin and the complex are presented on Fig. 4. In the region of hydrogen bonded OH groups (3500-3200 cm\(^{-1}\)) a strong wide band at 3289 -3228 cm\(^{-1}\) was observed in the tannin spectrum (Fig. 4A). The band was assigned to the stretching vibrations of hydrogen bonded phenolic hydroxyl groups (\(\nu (OH)\)) and the formation of associates between tannin molecules and also intramolecular hydrogen bonds were supposed. The corresponding band wasn’t observed in TiO\(_2\) spectrum. The moderately strong band at 3424 cm\(^{-1}\) in the IR spectra of the complex could be also assigned to O-H stretching vibration of coordinated OH groups or of lattice water molecules [15]. The reduced intensity of the band in the region 3500-3200 cm\(^{-1}\) showed the decrease in the number of H-bonded OH groups. The positive shift of the band (\(\nu (OH)= 3424 \text{ cm}^{-1}; \Delta \nu (OH) = 135 \text{ cm}^{-1}\)) suggested the coordination of tannin molecules with the metal ions via deprotonation [16]. The band due to C=O stretching vibration that appeared at 1715 cm\(^{-1}\) in the aromatic carboxylic acids (Fig. 4A) [17] was almost vanished in the complex. The decrease in the band intensity confirmed the participation of oxygen in the C=O-M bond. The changes in the spectra profile in the region 1300-1000 cm\(^{-1}\) prove that phenolic oxygen was also involved in the coordination of metal ion. The IR data suggest that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen are involved in the coordination of titanyl ion. Hence in the studied complex tannin acts as a polydentate ligand coordinating through the oxygen of C=O and OH groups. The changes of the number and the intensity of the bands in the region 1700-700 cm\(^{-1}\) might be due to chelate rings formation in the complex. The coordination of OH ions or H\(_2\)O was also supposed based on bands at 3424 cm\(^{-1}\) and 787 cm\(^{-1}\) [18]. As can be seen from Fig. 4A and 4C, the large peak at 598-533 cm\(^{-1}\) in TiO\(_2\) spectrum disappeared in the spectrum of the complex and a new peak could be found at 455 cm\(^{-1}\). The absorption band at 455 cm\(^{-1}\) was attributed to Metal---O stretching vibrations. Based on the presented data, the following composition of the complex in a solid form, obtained after precipitation and drying, could be supposed [Ti(OH)\(_2\)TA]\(^+\) [21, 22].

Fig. 3. UV-Vis spectra of titanyl-tannin complex: (A) \(C_{TiO^2}= C_{tannin} = 8 \times 10^{-4} \text{ M}\) and (B) \(C_{TiO^2}= C_{tannin} = 2 \times 10^{-4} \text{ M}\) in formate buffer (pH 4.00) acquired against analytical blank containing the same tannin concentrations.

Fig. 4. IR spectra of (A) TiO\(_2\), (B) tannin and (C) titanyl-tannin complex.
Spectrophotometric study of the titanyl-hydroxo-tannin complex

The molar ratio method was chosen for this study as the exact concentrations of metal and ligand for practically complete complex formation process could be easily obtained from the curves $A = f(C_{\text{tannin}}/C_{\text{titanyl}})$. The obtained results are presented on Fig. 5. Each curve was constructed from a large number of experiments in order to obtain reliable results; each point was obtained as a mean of six values of absorbance of two solutions at the same concentrations. The formation of a complex at 1:1 molar ratio between TiO$^{2+}$ – tannin was proved by the intercept of two linear parts of the curves. The obtained results have showed that the absorbance increased linearly with the concentration of titanyl ions at titanyl/tannin ratios more than 2 (Fig. 5B). The following equation was obtained: $A = 0.002 + 37.453C_{(\text{TiO}^{2+})}$ with correlation coefficient of 0.999 (Fig. 5B). As it was described above, the only absorbing species at 322 nm was the titanyl-tannin complex (Fig. 2, curve 3). Hence, the concentration of the formed complex TiO-TA increased linearly with the concentration of TiO$^{2+}$ and the molar absorptivity of TiO-TA complex could be calculated from the slope of the curve presented on Fig. 5B: $\varepsilon = 3.75 \times 10^4$ L mol$^{-1}$ cm$^{-1}$. The results showed also that the Beer’s law was obeyed in the studied concentration interval of the complex.

At the conditions of the present study (pH 4, formate buffer), a formation of TiO(OH)$^+$ complex could also proceed in a considerable extent. The calculated values of alpha coefficients, based on the previously reported stability constant of titanyl-hydroxo complex TiO(OH)$^+$: $\lg \beta = 13.7$ [19], are presented on Fig. 6. The logarithmic value of $\alpha_{\text{TiO(OH)}}$ at pH 4 was 3.7 or $\left[\text{TiO(OH)}^+\right]/\left[\text{TiO}^{2+}\right] = 10^{3.7}$. As it could be seen from the Fig. 2, curve 1, the species TiO(OH)$^+$ did not absorb photons at the wave length chosen for the absorbance measurement in the mole ratio method (322 nm).

Based on the above mentioned results, the formation of a mixed ligand titanyl-hydroxo-tannin TiO(OH)TA complex was supposed at the studied conditions. The coordination of OH- as a second ligand has been already reported for some Ti (IV) or titanyl complexes [21, 22]. The following mechanism of the complex formation and corresponding equilibrium constants were proposed:
The overall equilibrium constants could be described as:

\[ K_1 = \frac{[\text{TiO}(OH)]^+[\text{H}^+]}{[\text{TiO}^{2+}][\text{H}_2\text{O}]} \]

where \( K_1 \) is defined as

\[ K_1 = \frac{[\text{TiO}(OH)]^+[\text{H}^+]}{[\text{TiO}^{2+}][\text{H}_2\text{O}]} \]

and the stability constant of the mixed ligand titanyl-hydroxo-tannin complex was denoted as:

\[ \beta = \frac{[\text{TiO}(OH)TA]}{[\text{TiO}^{2+}][\text{TA}^-]} \]  

The value of \( K' \) at constant pH was experimentally determined from the molar ratio measurements. The results are presented in Table 1. The equilibrium concentrations of titanyl ion, tannin and the complex at \( 0.9<C_{\text{tannin}}/C_{\text{titanyl}}>1 \) were calculated based on the Beer’s law and the mass law equations. The obtained values of \( K' \) (eq.5) at pH 4 are presented in Table 1 and the obtained mean value was \( \lg K' = 6.53 \pm 0.05 \).

The stability constant of the formed complex \( \text{TiO(OH)TA} \) was calculated according to the theory of mixed ligand complexes [19,20]. The stability constant \( \beta \) of \( \text{TiO(OH)TA} \) was calculated based on the equation derived from eq. 4:

\[ \lg \beta = \lg K' - p\text{H} + 14 = 16.53 \]

The step stability constant \( \beta_2 \) of the process described by eq. 2 was also estimated starting from the equation of the stability constant of mixed ligand titanyl-hydroxo-tannin complex:

\[ \beta = \frac{[\text{TiO}(OH)TA]}{[\text{TiO}^{2+}][\text{TA}^-][\text{OH}^-]} \]

where \( \beta_2 = \frac{[\text{TiO}(OH)TA]}{[\text{TiO}^{2+}][\text{TA}^-][\text{OH}^-]} = 676.1 \) and \( \lg \beta_2 = 2.83 \).

**CONCLUSIONS**

The results obtained in this study warrant the conclusion that at concentrations in the interval \( 5x10^{-6} - 2x10^{-5} \) M and at pH 4 the main titanium (IV) species in titanyl tannin formate solutions is titanyl-hydroxo-tannin complex \( \text{[TiO(OH)TA]} \). It was proved by UV-Vis and IR spectrometry that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen of tannin are involved in the coordination of titanyl ion. It was supposed that in a solid form the complex composition is \( \text{[Ti(OH)_{2}TA]} \). The stability constant of \( \text{TiO(OH)TA} \) was estimated: \( \lg \beta = 16.53 \). The obtained molar ratio curves and calculated values of the derived constants could be used by leather technologists for selecting an appropriate composition of tanning solutions.

**Acknowledgements**

The financial support of the University of Chemical Technology and Metallurgy through the Science and Research program (project Nr 11156/2013) is gratefully acknowledged.

**REFERENCES**

5. S. Benerjee, Spectrophotometric determination of titanium with tannin and thyoglycollic acid and its application to titanium-treated steels and ferrous and non-ferrous alloys, Talanta, 33, 1986, 360-362.


SOLVATOCHROMISM OF HOMODIMERIC STYRYL PYRIDINIUM SALTS

Stanislava Yordanova, Ivan Petkov, Stanimir Stoyanov

ABSTRACT

The solvatochromic properties of homodimeric styryl pyridinium salts are analyzed on the ground of Lippert-Mataga correlation, solvent scales of molar electronic transition energies $E_T(30)$ values, multilinear regression with the Kamlet-Taft solvent scales and continuum McRae-Bayliss model. The protic and aprotic solvents refer to two isolated domains in the Lippert-Mataga and Reichardt plots, whereas fitting to Kamlet-Taft scales gives a linear regression valid for both types of solvents studied. Poor linearity is observed in case of McRae equation application. An intermolecular hydrogen bonding mechanism is advanced to explain the results obtained.

Keywords: cyanine dyes, styryl pyridinium tetraphenylborates, linear solvation energy relationship (LSER), solvatochromism.

INTRODUCTION

The color change of a compound induced by external influences, e.g., by solvents (solvatochromism) [1, 2], salts (halochromism) [3], and temperature (thermochromism) [4] has been intensively studied over the past decades.

Cyanine dyes which possess an electron pushing (donor) group and an electron withdrawing (acceptor) group at both ends of the molecule are characterized by an extremely large dipole moment in their ground state. They find successful application in the laser technology [5 - 7], the optical data storage [8], in the non-linear optics [9] and molecular electronics [10].

Some of the more polar examples are found to adopt an antiparallel arrangement both in a solution [14] and within a monolayer [15] formed. Several literature studies discuss the solvatochromism of such dyes. Al-Ansari and Ball [16] study four styryl pyridinium dyes and find that the absorption maximum position depends on the polarity and hydrogen bonding ability of the solvents, while hypsochromic shifts are observed with increasing solvent’s polarity or acidity. However, no solvatochromism is observed in the emission spectra. Gawinecki [17] studies eighteen styryl pyridinium cyanine dyes. He reports that there is no linear correlation between absorption energy, $E_{abh}$, and Reichardt solvent polarity parameter, $E_T(30)$, even after rejection of weakly polar solvents. He finds no correlation between $\Delta E_{abh}$ and Kamlet-Taft’s parameters for solvent polarity ($\pi^*$) and hydrogen bonding ability ($\alpha$ and $\beta$). It is evident from the literature survey there is a contradiction in the results concerning the solvent effects on the spectroscopic properties of styryl pyridinium salts. In this aspect, the current study contributes to get extra information on the
In this paper we describe the changes in the absorption and emission spectra for a series of styryl pyridinium tetraphenylborates in solvents of different polarity. The solvatochromism of these compounds were analyzed on the ground of Lippert-Mataga correlation [18 - 20], solvent scales of molar electronic transition energies, $E_i(30)$, values [21], multilinear regression with the Kamlet-Taft solvent scales [22, 23] and continuum McRae-Bayliss model [24, 25].

**EXPERIMENTAL**

The general synthetic scheme for preparation of the styryl pyridinium tetraphenylborates was previously reported [26, 27]. UV/Vis spectrophotometric investigations were performed using Thermo Spectronic “Unicam UV 500” spectrophotometer. Fluorescence spectra were recorded on a Varian “Cary Eclipse” scpetrofluorometer. All spectra were recorded using 1 cm pathlength synthetic quartz glass cells at room temperature. The fluorescence quantum yield ($\Phi_f$) was determined by the gradient method in reference to a standard Acridine yellow in ethanol ($\Phi_f = 0.47$ [28]). All solvents used in this study were of spectroscopic grade.

The structures of the homodimeric dyes under study are presented in Table 1.

**RESULTS AND DISCUSSION**

**Absorption and emission properties of the compounds studied**

The UV/Vis absorption spectra are investigated in various solvents of different dipolarity/polarizability and hydrogen-bonding ability. The dyes studied exhibit several absorption bands in the region from 250 nm to 600 nm of the electromagnetic spectrum. The energies (cm$^{-1}$) of the longest absorption band are summarized in Table 2.

The influence of the substituent’s nature can be illustrated by some representative spectra of compounds.

Table 1. Compounds studied.

<table>
<thead>
<tr>
<th>№</th>
<th>Compound</th>
<th>X</th>
<th>R</th>
<th>n</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(E)-1,1’-(butane-1,4-diy1)bis(4-(4-hydroxystyryl)-pyridinium) tetraphenylborate</td>
<td>OH</td>
<td>H</td>
<td>2</td>
<td>H4</td>
</tr>
<tr>
<td>2</td>
<td>(E)-1,1’-(pentane-1,5-diyl)bis(4-(4-hydroxystyryl)-pyridinium) tetraphenylborate</td>
<td>OH</td>
<td>H</td>
<td>3</td>
<td>H5</td>
</tr>
<tr>
<td>3</td>
<td>(E)-1,1’-(hexane-2,5-diyl)bis(4-(4-hydroxystyryl)-pyridinium) tetraphenylborate</td>
<td>OH</td>
<td>CH$_3$</td>
<td>2</td>
<td>H6</td>
</tr>
<tr>
<td>4</td>
<td>(E)-1,1’-(butane1,4-diy1)bis(4-(4-(N,N-dimethylamino)-styryl)-pyridinium) tetraphenylborate</td>
<td>N(CH$_3$)$_2$</td>
<td>H</td>
<td>2</td>
<td>D4</td>
</tr>
<tr>
<td>5</td>
<td>(E)-1,1’-(pentane-1,5-diyl)bis(4-(4-(N,N-dimethylamino)-styryl)-pyridinium) tetraphenylborate</td>
<td>N(CH$_3$)$_2$</td>
<td>H</td>
<td>3</td>
<td>D5</td>
</tr>
<tr>
<td>6</td>
<td>(E)-1,1’-(hexane-2,5-diyl)bis(4-(4-(N,N-dimethylamino)-styryl)-pyridinium) tetraphenylborate</td>
<td>N(CH$_3$)$_2$</td>
<td>CH$_3$</td>
<td>2</td>
<td>D6</td>
</tr>
<tr>
<td>7</td>
<td>(E)-1,1’-(butane1,4-diy1)bis(4-styryl-pyridinium) tetraphenylborate</td>
<td>H</td>
<td>H</td>
<td>2</td>
<td>S4</td>
</tr>
<tr>
<td>8</td>
<td>(E)-1,1’-(pentane-1,5-diyl)bis(4-styryl-pyridinium) tetraphenylborate</td>
<td>H</td>
<td>H</td>
<td>3</td>
<td>S5</td>
</tr>
<tr>
<td>9</td>
<td>(E)-1,1’-(hexane-2,5-diyl)bis(4-styryl-pyridinium) tetraphenylborate</td>
<td>H</td>
<td>CH$_3$</td>
<td>2</td>
<td>S6</td>
</tr>
</tbody>
</table>
of identical spacer in the same solvent (Fig. 1). The main absorption maximum, which appears due to a $\pi \rightarrow \pi^*$ transition in the chromophore system of the unsubstituted styryl pyridinium fragment, is ca 350 nm (see series S). As expected, the electron-donor substituents cause a bathochromic shift – to approximately 400 nm for the hydroxyl and ca 490 nm for the dimethylamino group. Moreover, a donor-π-acceptor type conjugated system is formed in the substituted compounds. The earlier work of Huang et al. [29, 30] on a large number of flexible dichromophoric compounds documents that the visible absorption spectra exhibit an intramolecular charge transfer transitions ($S_0 \rightarrow CT$) affecting the electron pairs in the donor and the cationic nitrogen atom of the pyridinium fragment. The nature of the CT-band is verified by the following indications – it is relatively broad, intense and structureless, and its position depends strongly on the solvent type (see below).

The emission spectra of the dyes studied are characterized by broad and structureless bands and large Stokes’ shifts. The latter differences in case of low and high polar solvents are ca 2000 cm$^{-1}$ which is a further indication for charge transfer transitions. It is worth adding that the large Stokes shift suggests difference between the excited state geometry and that of the ground state. The energies (cm$^{-1}$) of the fluorescence emission band are summarized in Table 3. The emission wavelength, fluorescence intensity, fluorescence quantum yields and lifetimes are strongly structure-related and solvent-dependent. The low fluorescence quantum yields may be attributed to the ultrafast internal twisting process in the excited state of the molecule. This is in good agreement with the properties of hemicyanine dyes described earlier [31, 32].

The steady-state fluorescence spectra of the dyes studied exhibit fluorescence bands in the region from
420 nm to 440 nm for unsubstituted dyes ($\lambda_{ex} = 350$ nm), between 500 nm and 530 nm for hydroxy substituted derivatives ($\lambda_{ex} = 400$ nm) and between 600 nm and 640 nm for dimethylamino substituted salts ($\lambda_{ex} = 490$ nm).

The compounds studied do not generally show intensive emission. The relaxation processes in the hemicyanines excited state have been studied for several decades and the display of twisted intramolecular charge transfer (TICT) [33] is one of its most discussed features. The TICT state is considered a non-radiative but favorable state, especially in polar solvents. Its formation is responsible for the low fluorescence quantum yield. There is no consensus concerning the torsion mode of TICT formation of hemicyanine but the most recently published works tend to consider that twisting takes place around the C-C single bond [30].

**Linear Solvation Energy Relationship**

**McRae-Bayliss equation**

We used the continuum McRae-Bayliss model of solvatochromism. The analysis carried out is based on Equation (1):

$$v_{\text{max}} = v_0 + A \frac{(n^2 - 1)}{(2n^2 - 1)} + B \left[ \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$  

where $v_{\text{max}}$ is the solute transition energy in a solution (cm$^{-1}$), $v_0$ is the solute transition energy in the gas phase, $n$ is the refractive index, while $\varepsilon$ is the dielectric constant. $A$ is the electronic polarization term describing the transient polarization induced by the solute on the solvent molecules during excitation. $B$ is the orientation polarization term describing the electrostatic forces between the solute and polar solvent molecules.

The performed multiple regression analysis of the experimental data did not show a satisfying correlation between the measured wavenumbers and the terms in the McRae-Bayliss equation illustrated by the outlined deviation (Fig. 2). This is due to the theoretical basis of the McRae model which treats the solvent as a continuum. Besides, the polarization changes are the only effects taken into account. It is evident that the Franck-Condon excited state in this type of chromophores is characterized by a dipole moment which is inverse in respect to the ground state. This is due to a charge transfer transition upon irradiation, while the first solvation cage remains intact in its timescale. The relaxation processes in such a non-equilibrium environment are of more complex nature. They include full reorientation of the solvent molecules adjacent to the excited particle and

<table>
<thead>
<tr>
<th>solvent</th>
<th>H4</th>
<th>H5</th>
<th>H6</th>
<th>D4</th>
<th>D5</th>
<th>D6</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>19.61</td>
<td>19.61</td>
<td>19.72</td>
<td>15.92</td>
<td>15.95</td>
<td>15.87</td>
<td>23.09</td>
<td>23.31</td>
<td>23.26</td>
</tr>
<tr>
<td>MeCN</td>
<td>20.00</td>
<td>20.00</td>
<td>19.96</td>
<td>16.16</td>
<td>16.21</td>
<td>16.21</td>
<td>23.09</td>
<td>22.83</td>
<td>22.88</td>
</tr>
<tr>
<td>2-PrOH</td>
<td>19.92</td>
<td>19.84</td>
<td>19.92</td>
<td>16.64</td>
<td>16.29</td>
<td>16.64</td>
<td>23.70</td>
<td>23.81</td>
<td>23.70</td>
</tr>
</tbody>
</table>
their further interaction with the outer solvation shells, which makes the McRae model inapplicable.

**Lippert-Mataga equation**

Solvent effects on the dyes photophysical properties are due to their interaction with the environment (such as the solvation cage) via dipole-dipole interaction, hydrogen bonds formation, charge transfer processes, reorientation of the dipole moments of the solvents upon excitation of the fluorophores, etc. [34]. General and specific solvents effects as well as the structural relaxation of the molecular skeleton at the excited state determine the intrinsic origin of the Stokes’ shift. The simplest consideration of the general solvents effect on the Stokes shift is based on the applicability of the Lippert-Mataga equation (2).

\[
\Delta \nu = \frac{2 \Delta f}{4 \pi \varepsilon_0 n c a^2} (\mu_g - \mu_e)^2 + C
\]

\[
\Delta \nu = \frac{2 \Delta f}{4 \pi \varepsilon_0 n c a^2} (\mu_g - \mu_e)^2 + C
\]

\[
\Delta f = \frac{s-1}{2s+1} - \frac{n^2-1}{2n^2+1}, \quad \Delta f = \frac{s-1}{2s+1} - \frac{n^2-1}{2n^2+1}
\]

where \(\Delta \nu\) stands for the Stokes’ shift, \(h\) is the Planck’s constant, \(c\) is the velocity of light in vacuum, \(a\) is the Onsager cavity radius, \(\Delta f\) is the orientation polarizability, \(\mu_e\) and \(\mu_g\) are the ground-state dipole in the ground-state and the excited dipole in the excited-state geometry, correspondingly, while \(\varepsilon_0\) is the permittivity of the vacuum.

The Lippert-Mataga correlations of the Stokes’ shifts of compounds H1 are illustrated in Fig. 3. Poor linearity is found for the overall regression for all compounds studied. The protic and the aprotic solvents are clearly divided, i.e. two isolated domains appear in the plot. Such isolation in the Lippert-Mataga plots is reported in case of polarity probes like PRODAN and its analogue [35]. Besides, the exclusive regression of the two isolated domains gives good linearity. It is worth noting that the Lippert-Mataga model cannot explain a specific solvent–fluorophore interaction because it does not consider chemical interactions. Therefore, the non-linearity of the correlations considered above should indicate a specific solvent effect, most probably intermolecular hydrogen bonding between the solute and the solvent molecules [36].

**Reichardt model**

A solvent scale accounting of the specific solvent effect contributions was used aiming a better description of solvatochromism observed. Thus the Stokes’ shifts (cm\(^{-1}\)) were correlated with the molar electronic transition energies, i.e. the \(E_{\text{r}}(30)\) values. A representative correlation for H1 is depicted in Fig. 4. Poor linearity is observed – the protic and the aprotic solvents in case of all compounds studied are again separated in two
isolated domains, each of good linearity but a different slope. This suggests that the Reichardt scale is not applicable to this type of chromophores. In fact this is a common weakness of the experimentally derived scales which can be correctly used only if the compound studied has behavior upon excitation similar to that of the probe molecule.

**Multilinear regression of the photophysical properties using the Kamlet-Taft scale**

The solvent dependency of the photophysical properties of a dye, such as $\nu_{abs}$ (absorption energies), $\nu_{em}$ (emission energies) and the Stokes shifts ($\Delta\nu_{St}$, in cm$^{-1}$) can also be described by multilinear regression with the application of Equation (3). The solvatochromic parameters $\alpha$, $\beta$, and $\pi^*$ are summarized in Table 4.

$$\nu_{max} = \nu_0 + a\alpha + b\beta + s (\pi^* + d\delta)$$  \hspace{1cm} (3)

Fig. 4. Relationship between the Stokes shift values ($\Delta\nu_{St}$, cm$^{-1}$) and $E_T(30)$ for H1 (the squares refer to the aprotic solvents, while the triangles – to the protic one): 1 - Tetrahydrofuran, 2 - Ethyl acetate, 3 - Acetone, 4 - N,N-Dimethylformamide, 5 - Dimethyl sulfoxide, 6 - Acetonitrile; 7- 2-propanol, 8 - Ethanol, 9 - Methanol, 10 - water.

where $\nu_{max}$ represents the property to be correlated, $\nu_0$ stands for the property related to a standard process, $\alpha$ is the hydrogen bond donor acidity, $\beta$ is the hydrogen bond acceptor basicity, $\pi^*$ is the dipolarity-polarizability, $\delta$ stands for the polarizability correction term while $a$, $b$, $s$ and $d$ are coefficients which are characteristic for a given compound.

The $\pi^*$ scale is based on the solvent-induced shifts of the longest wavelength ($\pi \rightarrow \pi^*$ absorption band of seven nitro aromatic indicators). This electronic transition is connected with an intramolecular charge transfer from the electron-donor part to the acceptor one through the aromatic system. The correlations provide statistically a solid base for understanding the manifold solvent effects on the solvatochromic long wavelength UV/Vis absorption band of the dyes studied. The linear solvation energy relationships (LSERs) show a high quality for a multi-linear regression with 6 degrees of freedom, as indicated by the correlation statistics - coefficients $R^2$ are higher than 0.9 (see Table 5) and F-stat is lower than 10 in all cases.

For the hydroxy-substituted derivatives the coefficients $s$ are positive. This suggests that the excited state is more polar than the ground one and positive solvatochromism is expected. It can be concluded that the term $\alpha$ plays no role since the calculated values are close to zero. It is seen that the values of $b$ are larger than those of $a$. This means that the hydrogen bond accepting (HBA) ability of the solvent affects the transition energy to a greater extent than its hydrogen bond donor (HBD) ability.

An opposite conclusion can be drawn for compounds from series D. The HBD ability of the solvents is more important than HBA as the values of $b$ are smaller than those of $a$. The negative sign of $s$ indicates that the first singlet excited state of these molecules is better stabilized when the solvents’ polarity increases. This is in good agreement with the results reported in ref. [37].

It can be further concluded that the three parameters

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\epsilon^1$</th>
<th>$n^2$</th>
<th>$E_T(30)$</th>
<th>$\pi^*$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>80</td>
<td>1.34</td>
<td>63.1</td>
<td>1.09</td>
<td>1.71</td>
<td>0.47</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.2</td>
<td>1.479</td>
<td>45.1</td>
<td>1</td>
<td>0</td>
<td>0.76</td>
</tr>
<tr>
<td>DMF</td>
<td>38.3</td>
<td>1.429</td>
<td>43.2</td>
<td>0.88</td>
<td>0</td>
<td>0.69</td>
</tr>
<tr>
<td>MeCN</td>
<td>37.5</td>
<td>1.346</td>
<td>45.6</td>
<td>0.75</td>
<td>0.19</td>
<td>0.40</td>
</tr>
<tr>
<td>MeOH</td>
<td>32.7</td>
<td>1.3284</td>
<td>55.4</td>
<td>0.60</td>
<td>0.98</td>
<td>0.66</td>
</tr>
<tr>
<td>EtOH</td>
<td>24.55</td>
<td>1.3613</td>
<td>51.9</td>
<td>0.54</td>
<td>0.86</td>
<td>0.75</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
<td>1.359</td>
<td>42.2</td>
<td>0.71</td>
<td>0.08</td>
<td>0.43</td>
</tr>
<tr>
<td>2-PrOH</td>
<td>19.92</td>
<td>1.5772</td>
<td>48.4</td>
<td>0.48</td>
<td>0.76</td>
<td>0.95</td>
</tr>
<tr>
<td>THF</td>
<td>7.50</td>
<td>1.407</td>
<td>37.4</td>
<td>0.58</td>
<td>0</td>
<td>0.55</td>
</tr>
<tr>
<td>EtOAc</td>
<td>6.02</td>
<td>1.373</td>
<td>38.1</td>
<td>0.55</td>
<td>0</td>
<td>0.45</td>
</tr>
</tbody>
</table>

1 dielectric constant; 2 refractive index
considered have no significant effect on the $\nu_{\text{max}}$ values for the compounds of series $S$.

The correlation between the absorption maxima (cm$^{-1}$) predicted by the multilinear regression and the experimental values obtained is presented in Fig. 5. A linear correlation is observed for all compounds studied.

**CONCLUSIONS**

The solvatochromic properties of homodimeric styryl pyridinium salts were analyzed with the application of various Linear Free Energy Relationship methods. McRae-Bayliss, Lippert-Mataga and Reichardt equations were found not applicable for quantitative description of the absorption and emission energies as a function of the respective solvent parameters. The Kamlet-Taft model describing hydrogen bond formation gave excellent results in terms of statistics - the correlation coefficients were found higher than 0.9 for all compounds studied. The values of the constants in the corresponding equations were obtained and the parameter of greatest importance for each series was determined.

**REFERENCES**

4. E. Lambi, D. Gegiou, E. Hadjoudis, Thermochromism and photochromism of N-salicylidenebenzylamines and N-salicylidene-2-aminomethylpyridine, J. Photo-


14. F. Würthner, S. Yao, Dipolar Dye Aggregates: A Problem for Nonlinear Optics, but a Chance for Supramolecular Chemistry This work was supported by the Deutsche Forschungsgemeinschaft (Wu 317/1), the Fonds der Chemischen Industrie and BASF AG (travel grant for S.Y.). We thank Dr. Udo Werz for 2D NMR experiments and Prof. Peter Bäuerle for his support, Angew. Chem. Int. Ed. Engl., 39, 2000, 1978-1981.


ELECTRIC-ARC-CARBOTHERMIC PROCESSING OF AGGLOMERATED WASTE DISPERSAL MATERIALS FROM FERROUS METALLURGY

Daniela Grigorova, Maxim Marinov, Rossitza Paunova

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: d.dimitrova@uctm.edu

ABSTRACT

The present paper reports results referring to the production of pig iron under laboratory conditions using a low shaft electric furnace. Wastes from ferrous metallurgy subjected to a preliminary agglomeration are used as iron containing raw materials in the sintering charge. Material and heat balance calculations are carried out. It is found that sinters of high waste powders and sludge content can be used to give pig iron of low content of sulphur, phosphorus and non ferrous metals. The chemical composition, the yield and the specific energy consumption are found close to the existing standards.

Keywords: waste materials, balance calculations, agglomeration, pig iron, a low shaft electric furnace.

INTRODUCTION

The practice of some countries verifies the economical effectiveness of pig iron production using electric arc furnace at predetermined technical and economical conditions [1 - 4]. These furnaces have less requirements referring to the chemical and mechanical indexes of the ore when compared to those used in case of blast furnace production. Under identical conditions the metal obtained in a low shaft electric furnace is of higher quality compared to that of the pig iron produced in a blast furnace [5 - 7]. Besides iron ores which are not applicable to the blast furnace process can be utilized if low shaft electric furnaces are used. Hence the latter extend the possibilities for iron ores use [8 - 10].

Most of the waste powders from the gas cleaning equipment used in the extraction metallurgy are currently a subject of landfilling. These are low price materials but have a relatively high iron content ranging from 29.89 % (blast furnace powders) to 57.02 % (waste powders from LD converters) [11, 12]. Their processing as eventual blast furnace charge is not advisable because of pollution problems [11, 12].

The aim of the present paper is to carry out material and heat balance calculations of agglomerated mixtures of waste materials coming from the extraction metallurgy and to produce pig iron in a low shaft electric furnace using the sinters obtained.

EXPERIMENTAL

Waste powders and sludge from the extractive metallurgy require agglomeration preceding their further processing. That is why those used in the present investigation were sintered. The charge materials comprised of stack mixture, limestone, coke breeze, waste mixture and sludge. The waste mixture contained 33.80 % of sinter dust from an electrostatic precipitator, 35.88 % of blast furnace powder, 28.32 % of oxygen converter (BOF) powders and 2 % of electric arc furnace (EAF)
Daniela Grigorova, Maxim Marinov, Rossitza Paunova

The mixture composition was selected on the ground of the usual annual generation of these materials under actual processing conditions. Two mixtures were prepared for the investigation carried out. The first one was a reference one as its composition was analogous to that generally used. 2 % of wastes and 10 % of sludge were added to the charge of the second one. The sinters were obtained under laboratory conditions. Their chemical composition is shown in Table 1.

A monophase electric arc furnace of 75 kVA, AC power supply and secondary voltages of 15V, 20V, 25V, 30V, 35V and 40 V was used (Fig. 1). The secondary electric circuit consisted of a vertically suspended movable graphite electrode and a bottom water cooled copper electrode. The furnace control was electrical, while the driving was of a hydraulic type [13]. The gas and the powder emissions from the furnace bath space were exhausted by two independent gas conduits.

RESULTS AND DISCUSSION

The charge used consisted of sinters, limestone and coke breeze as presented in Table 1. The composition of the two systems studied is shown in Table 2. The chemical composition of the slag obtained is outlined in Table 3. The iron content in the second system is lower by 0.35 % when compared to that of the reference one. The content of phosphorus decreases in the second system as well. The content of all other components varies in relatively narrow limits. The material balance of the process is presented in Table 4.

The output includes sinters, coke breeze, limestone and 0.6 kg electrodes per 100 kg sinter. The coke breeze is partially replaced by anthracite in the second system. Higher total input of the reducing agent is required in this case.

The heat balance of the process is shown in Table 5. Five melting operations are carried out. The first two refer to the first system, while operations from 3 to 5 refer to the second one. The latter includes 2 % of wastes, 10 % of sludge and CaO/SiO₂ to provide basicity of 1.3. In this case anthracite is used as a partial substitute of the coke breeze. The quantities of the charge materials used and those of metal and slag obtained are shown in Table 6. The furnace in the course of pig iron tapping is shown in Fig. 2.

The chemical composition of the metal obtained

Table 1. Chemical composition of the sinters obtained, %.

<table>
<thead>
<tr>
<th></th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>FeS</th>
<th>MnO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>BaO</th>
<th>P₂O₅</th>
<th>ZnO</th>
<th>PbO</th>
<th>CuO</th>
<th>SO₃</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70.39</td>
<td>10.00</td>
<td>0.01</td>
<td>3.06</td>
<td>3.48</td>
<td>1.40</td>
<td>6.97</td>
<td>2.32</td>
<td>1.52</td>
<td>0.02</td>
<td>0.02</td>
<td>0.19</td>
<td>0.04</td>
<td>0.38</td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>72.40</td>
<td>10.00</td>
<td>0.01</td>
<td>3.15</td>
<td>3.59</td>
<td>1.36</td>
<td>4.78</td>
<td>2.23</td>
<td>1.46</td>
<td>0.02</td>
<td>0.12</td>
<td>0.30</td>
<td>0.04</td>
<td>0.35</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of the pig iron obtained, %.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>Al</th>
<th>C</th>
<th>S</th>
<th>Ca</th>
<th>Mg</th>
<th>Pb</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.129</td>
<td>2.513</td>
<td>0.732</td>
<td>0.022</td>
<td>0.306</td>
<td>3.766</td>
<td>0.016</td>
<td>0.268</td>
<td>0.101</td>
<td>0.037</td>
<td>0.102</td>
</tr>
<tr>
<td>2</td>
<td>91.476</td>
<td>3.257</td>
<td>0.779</td>
<td>0.016</td>
<td>0.304</td>
<td>3.621</td>
<td>0.021</td>
<td>0.208</td>
<td>0.120</td>
<td>0.069</td>
<td>0.116</td>
</tr>
</tbody>
</table>
Table 3. Chemical composition of the slag obtained, %.

<table>
<thead>
<tr>
<th>Elements</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>MnO</th>
<th>PbO</th>
<th>BaO</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.008</td>
<td>11.711</td>
<td>37.213</td>
<td>11.650</td>
<td>1.534</td>
<td>0.155</td>
<td>6.990</td>
<td>1.738</td>
</tr>
<tr>
<td>2</td>
<td>27.213</td>
<td>12.751</td>
<td>37.213</td>
<td>13.455</td>
<td>1.951</td>
<td>0.300</td>
<td>8.227</td>
<td>1.603</td>
</tr>
</tbody>
</table>

Table 4. Material balance, kg/100 kg of sinter.

<table>
<thead>
<tr>
<th></th>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>kg.</td>
<td>%</td>
</tr>
<tr>
<td>Sinter</td>
<td>100.00</td>
<td>79.65</td>
</tr>
<tr>
<td>Coke breeze</td>
<td>23.91</td>
<td>19.04</td>
</tr>
<tr>
<td>Electodes</td>
<td>0.60</td>
<td>0.48</td>
</tr>
<tr>
<td>Limestone</td>
<td>1.034</td>
<td>0.82</td>
</tr>
<tr>
<td>Total</td>
<td>125.543</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>kg.</td>
</tr>
<tr>
<td>Pig iron</td>
<td>63.931</td>
</tr>
<tr>
<td>Slag</td>
<td>16.353</td>
</tr>
<tr>
<td>Gases</td>
<td>34.517</td>
</tr>
<tr>
<td>Calculated Losses</td>
<td>1.74</td>
</tr>
<tr>
<td>Total</td>
<td>125.54</td>
</tr>
</tbody>
</table>

Table 5. Heat balance, kg/100 kg of sinter.

<table>
<thead>
<tr>
<th></th>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>kJ</td>
<td>%</td>
</tr>
<tr>
<td>1. Q - combustion of C-CO</td>
<td>1891.3</td>
<td>0.18</td>
</tr>
<tr>
<td>2. Q - slag forming</td>
<td>2092.5</td>
<td>0.19</td>
</tr>
<tr>
<td>3. Q - silicates</td>
<td>3331.5</td>
<td>0.31</td>
</tr>
<tr>
<td>4. Q - charge materials 25°C</td>
<td>2587.6</td>
<td>0.24</td>
</tr>
<tr>
<td>5. Electric power</td>
<td>1067552.3</td>
<td>99.08</td>
</tr>
<tr>
<td>Total</td>
<td>1077455.1</td>
<td>100.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>kJ</td>
</tr>
<tr>
<td>1. Q - dissociation of the oxides</td>
<td>355271.3</td>
</tr>
<tr>
<td>2. Q - dissociation of carbonates</td>
<td>1742.1</td>
</tr>
<tr>
<td>3. Q - pig iron</td>
<td>135000.0</td>
</tr>
<tr>
<td>4. Q - slag</td>
<td>49879.8</td>
</tr>
<tr>
<td>5. Q - off gas</td>
<td>393396.1</td>
</tr>
<tr>
<td>6. Q - slagging of the S</td>
<td>1628.2</td>
</tr>
<tr>
<td>7. Heat losses</td>
<td>140537.6</td>
</tr>
<tr>
<td>Total</td>
<td>1077455.1</td>
</tr>
</tbody>
</table>

Table 6. Experimental data referring to the metal and slag.

<table>
<thead>
<tr>
<th>№</th>
<th>Sinter, kg</th>
<th>Pellets, kg</th>
<th>Coke breeze, kg</th>
<th>Anthracite, kg</th>
<th>Limestone, kg</th>
<th>Metal, kg</th>
<th>Slag, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>4</td>
<td>5</td>
<td>-</td>
<td>0.20</td>
<td>9.7</td>
<td>4.5</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>4</td>
<td>5</td>
<td>-</td>
<td>0.20</td>
<td>10.4</td>
<td>3.7</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>-</td>
<td>3</td>
<td>3</td>
<td>0.40</td>
<td>11.8</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>-</td>
<td>3</td>
<td>3</td>
<td>0.40</td>
<td>12.6</td>
<td>3.9</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>-</td>
<td>3</td>
<td>3</td>
<td>0.40</td>
<td>12.6</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Table 7. Chemical composition of the metal obtained, %.

<table>
<thead>
<tr>
<th>№</th>
<th>Elements</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>S</th>
<th>Mn</th>
<th>Al</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Metal 1</td>
<td>91.47</td>
<td>0.71</td>
<td>0.04</td>
<td>0.02</td>
<td>2.3</td>
<td>0.31</td>
<td>0.03</td>
</tr>
<tr>
<td>2.</td>
<td>Metal 2</td>
<td>91.86</td>
<td>0.68</td>
<td>0.03</td>
<td>0.02</td>
<td>2.4</td>
<td>0.28</td>
<td>0.01</td>
</tr>
<tr>
<td>3.</td>
<td>Metal 3</td>
<td>91.46</td>
<td>0.68</td>
<td>0.05</td>
<td>0.02</td>
<td>2.87</td>
<td>0.29</td>
<td>0.02</td>
</tr>
<tr>
<td>4.</td>
<td>Metal 4</td>
<td>91.34</td>
<td>0.78</td>
<td>0.09</td>
<td>0.03</td>
<td>2.26</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>5.</td>
<td>Metal 5</td>
<td>91.38</td>
<td>0.76</td>
<td>0.09</td>
<td>0.02</td>
<td>2.31</td>
<td>0.32</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Fig. 2. Laboratory 75 kVA monophase electric arc furnace in course of metal tapping.

is shown in Table 7. The figures pointed out have to be compared to those referring to high manganese pig iron in accordance with FN27-4-86 – I. The chemical composition of the latter is as follows: 0.5-1.00 % of Si, less than 3.50 % of Mn, less than 0.15 % of P and less than 0.05 % of S. The specific electric consumption in the experiments described is 9.84 kWh/kg. The comparative consideration of the values presented shows that the waste poly-dispersed materials can be used for pig iron production in a low shaft electric furnace.

**CONCLUSIONS**

The possibility to use as sintering charge waste mixtures containing 33.80 % of sinter powders, 35.88 % blast furnace powders, 28.32 % of BOF converter pow- ders, 2 % of electric arc furnace powders and landfi lling sludge is theoretically and experimentally investigated.

Melting operations for pig iron production in a low shaft electric furnace are carried out. They refer to a system using a standard sinter and another one containing waste dispersed powders, sludge and anthracite substituting some of the coke breeze usually introduced.

It is found that sinters of high waste powders and sludge content and cheaper reducing agent can be used in a low shaft electric furnace to produce pig iron of low content of sulphur, phosphorus and non ferrous metals.

The values referring to the chemical composition, the yield and the specific energy consumption are very close to the standard one.

**REFERENCES**

10. R. Durrer, Metallurgic processing of iron ore Moscow, Russia, 1960, (in Russian).
UTILIZATION OF WASTE POWDER AND SLUDGE IN IRON ORE SINTERING PROCESS

Daniela Grigorova, Tsvetan Tsanev, Maxim Marinov

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: d.dimitrova@uctm.edu

Received 07 July 2014
Accepted 15 September 2014

ABSTRACT

Extraction metallurgy is characterized by low rate waste emissions utilization. The greater part of the dust and sludge generated by the gas cleaning facilities does not return to production. Their accumulation leads to ecological problems.

The present study treats theoretically calculated and experimentally obtained series of sinters of various basicity and concentrations of sludge and waste mixture. The latter contain sinter powder, blast furnace powder, convertor dust and electric arc furnace powder of a ratio corresponding to that yearly observed under real production conditions. The main characteristics of the sintering process are established. The results reveal that the main characteristics of sintering process do not significantly change in case of using waste powders and sludge.

Keywords: sintering, simulation model, waste powders, sludge.

INTRODUCTION

Sintering of the iron ore containing materials is required to obtain a product, whose treatment allows regular and intensive stock of the blast furnaces. Iron ores concentrates and waste iron containing powders are subjected to advanced sintering [1-3]. An important and durable trend at advance preparation of the raw materials for the blast furnace process is the sintering process. It is a thermal method for agglomeration. The heat required is additionally provided or comes from fuel combustion of the charged materials. The introduction of sintered iron ore containing charges to the blast furnace results in lower coke consumption and improved pig-iron quality [4 - 6].

The gas-treatment stage of the technological processes in extraction ferrous metallurgy generates considerable amounts of waste materials (powders and slurries). The total dust quantity emitted by sintering is equal to 4.34 t/24 h, while 4.65 t/24 h come from the blast furnace process. The total dust emitted by LD-converters is evaluated to 3.67 t/24 h, while that from electric arc furnaces to 0.26 t/24 h [7].

The average Fe content of the waste powders and slurries which are deposed is up to 50%. Besides, the storage of these wastes represents an environmental problem [7, 8]. There are applications [9 - 14] that provide the waste powder and sludge utilization in the sintering process. A methodology for the latter simulation is presented [15 - 17].

The present study is aimed at the simulation of a sintering process carried out with raw materials containing extraction metallurgy wastes.

EXPERIMENTAL

A mathematical method described in [17] and developed as simulation PC program “Agprice” was used for sintering modeling. The charge materials corresponded to those used under production conditions. Eight variants were developed. The first one was a base line variant analogous to that generally used under real production conditions. In the rest of the variants secondary materials (powders and sledge) from the extraction metallurgical
processes were introduced. In case of variants from 2 to 8 the added waste mixture was 2%. It contained sinter powder (33.80%), blast furnace powder (35.88%), convertor dust (28.32%) and electric arc furnace powder (2%). The composition corresponded to that required for its complete utilization as well as the components yearly generation. Sludge was added in amounts referring to 4%, 8% and 10% in case of variants 2, 3 and 4. The basicity was equal to 2. In case of variants from 5 to 8 the basicity was 1.3, while the sludge content corresponded to 4%, 8%, 10% and 20%, respectively. All variants developed referred to wet content of 10%, FeO content of 10%, powder and mechanical losses of 2% and 35% of hot sinter for recycling. The chemical composition of the materials used is shown in Table 1.

Certain devices were used for the physical modeling of the sinter process [4]. The sinters were produced on a semi-industrial sinter installation under laboratory conditions. The raw materials were introduced using a scale of 5 g accuracy. A laboratory type mixer was used for the mixing, moistening and granulation of the raw materials. The agglomeration cup was of a square section (140mmx140 mm). The cup was placed on landing 8 where a grate was installed. The laboratory installation scheme is shown in Fig. 1.

The waste gases temperature was measured by a thermocouple. The charge prepared was placed in the agglomeration cup. The layer height was determined by the experimental conditions used. Each experiment started with the ignition of the layer over the whole surface.

Upon process finalization the vacuum pump functioned for 2 extra min to provide cooling of the sinter obtained. Then the latter was weighted and sieved.

RESULTS AND DISCUSSION

The theoretical chemical composition of the sinters obtained is shown in Table 2. The reference to the base variant shows that the chemical composition in case of added waste materials changes within narrow limits. Thus the amount of iron (III) oxide in variant 4 whose sludge content is equal to 10% decreases from 70.39% to 69.84%, while that of hematite is more than 2% higher in the variants whose basicity is 1.3. The content of ZnO and PbO increases with the increase of the waste sludge presence. In analogy with the iron content that of BaO decreases from the initial 1.52% (in case of the base variant) to 1.41% in variant 4. The coarse coefficient of the charge materials decreases with the increase of the waste material presence from 0.97 to 0.91.

The material balance in Table 3 illustrates the change in the charge materials at sintering. The input includes

---

### Table 1. Chemical composition of the materials used, %.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Total Fe-content</th>
<th>Total Mn-content</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>C</th>
<th>volatile</th>
</tr>
</thead>
<tbody>
<tr>
<td>iron ore bedding</td>
<td>54.13</td>
<td>2.25</td>
<td>2.56</td>
<td>0.99</td>
<td>3.52</td>
<td>2.16</td>
<td>0.16</td>
<td>3.59</td>
</tr>
<tr>
<td>limestone</td>
<td>0.07</td>
<td>-</td>
<td>1.99</td>
<td>0.92</td>
<td>53.39</td>
<td>0.59</td>
<td>-</td>
<td>0.79</td>
</tr>
<tr>
<td>coke breeze</td>
<td>4.30</td>
<td>0.25</td>
<td>14.50</td>
<td>6.46</td>
<td>2.14</td>
<td>0.31</td>
<td>66.30</td>
<td>2.81</td>
</tr>
<tr>
<td>hot sinter for recycling</td>
<td>58.52</td>
<td>1.99</td>
<td>3.48</td>
<td>1.20</td>
<td>6.36</td>
<td>1.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>waste mixture</td>
<td>43.52</td>
<td>2.15</td>
<td>7.85</td>
<td>4.95</td>
<td>7.54</td>
<td>1.00</td>
<td>4.50</td>
<td>4.38</td>
</tr>
<tr>
<td>sludge</td>
<td>46.80</td>
<td>1.91</td>
<td>3.95</td>
<td>0.54</td>
<td>11.14</td>
<td>0.91</td>
<td>-</td>
<td>13.53</td>
</tr>
</tbody>
</table>

---

Fig. 1. Sinter installation scheme: 1 - electric motor, 2 – connector, 3 – exhauster, 4 - cleaning outlet, 5 - dust capturing, 6 - sliding rule, 7 – cup, 8 – landing, 9 - pressure gauge, 10 - millivolt meter.
iron ore, limestone, aglofuel, air as well as waste materials additives. The output includes sinter, hot sinter for recycling and waste gases. The balance is calculated on the ground of the production of 100 kg of sinter.

In case of a constant content of the waste mixture the iron ore consumption decreases from 105.04 % to 87.90 % with the increase of the waste sludge (going from the base down to the last variant). The change in aglofuel is within narrow limits. The quantity of limestone decreases in variants 5 and 6, while it is not required in the last two variants. This is explained with the lower basicity (1.3) of the mixtures considered. The addition of waste materials affects the waste gases quantities. It is 76.17 % in variant 1 and goes down to 5.17 % in variant 8.

iron ore, limestone, aglofuel, air as well as waste materials additives. The output includes sinter, hot sinter for recycling and waste gases. The balance is calculated on the ground of the production of 100 kg of sinter.

In case of a constant content of the waste mixture the iron ore consumption decreases from 105.04 % to 87.90 % with the increase of the waste sludge (going from the base down to the last variant). The change in aglofuel is within narrow limits. The quantity of limestone decreases in variants 5 and 6, while it is not required in the last two variants. This is explained with the lower basicity (1.3) of the mixtures considered. The addition of waste materials affects the waste gases quantities. It is 76.17 % in variant 1 and goes down to 5.17 % in variant 8.
Eight sintering operations are carried out under laboratory condition aiming to evaluate the impact of the different waste materials introduced. The materials ratio in the charge follows the material balance calculations shown in Table 3. The agglomeration is carried out in presence of a constant content of hot sinter for recycling (35 %). The first charge is prepared in absence of waste materials. The sinter period is 15-16 min. Only in case of sinter 8 containing 2 % of wastes mixture and 20 % of sludge the period is 19 min. The vacuum change below the grate is shown in Fig. 2 for the different variants. It is seen that it is in the range from 520 mm to 530 mm (water column). In case of basicity of 1.3 the vacuum reaches 610 mm (water column) (see variant 8). The difference of 80 mm is probably due to the increased amount of sludge and the absence of limestone. In addition worse granulation is observed in the last case pointed above.

The changes in fume gases temperature are shown in Fig. 3. It is seen that the value is 310°C in case of the base variant. It increases to 320°C for variants 2, 3 and 7, while it goes up to 380°C for variants 5 and 6. The temperature increases to 400°C in case of variants 4 and 8 where the percentage of the waste sludge used is higher. It is worth adding that temperature changes are expected in the course of the sintering process.

The physical (macro) structure of the sinter obtained in case of variant 4 is shown in Fig. 4. Corresponding to Miller’s classification [1] it has a porous structure with irregularly distributed large pores. This result indicates that the charge is sintered with increased sintering losses. This is most probably due to the fine composition of the
initial material or the low quality of the charge preliminary pelletization.

The structure of the sinters obtained in case of variants 7 and 8 (using 10 % and 20 % of sludge) is similar. All other sinters obtained are of a spongy structure with pores of 2 - 4 mm uniformly distributed in the sinter bulk. The results considered show that the physical structure of the sinters is genetically related to the physical structure of the charge materials used.

The fraction distribution of the sinters (in %) is shown in Fig. 5.

It is seen that the fractions above 30 mm amount to 28 % with the exclusion of variant 1. Fractions of 20 - 12 mm amount to 26.4 %, while those of 5 mm and below are mainly obtained in case of the base variant. They amount to 34.75 %. This is most probably due to the sinter charge preparation. In all other variants the quantity distribution varies between 6.56 % and 16.38 %. Taking into consideration all variants studied the average fraction is under 12 mm and its amount refers to 32 %. In fact the hot sinter is that to be used for recycling.

CONCLUSIONS

The sinter composition is relatively constant and it can’t be materially distinguished from that obtained in the corresponding industrial process. The addition of sludge to the charge increases the quantity of non-ferrous metals as ZnO goes up to 0.22 %, while PbO is increased to 0.39 %. The total Fe content in the sinter is 57.06 %. going from variant 1 to 4 it decreases slowly to 56.68 %. The total Fe content decreases proportionally to the amount of the waste materials used.

The consumption of iron ore mixture decreases in case of all variants with the increase of the percentage of waste powders and sludge added. It is 105.04 kg in the base variant and goes down to 87.90 kg per 100 kg of sinter.

The experimental results obtained show that the waste materials introduction does not affect the sintering process. Its parameters remain relatively unchanged. The fraction analysis is carried out without additional breakage. The amount of the sinter obtained by fine iron ore and waste materials (using up to 10% sludge) is acceptable. Besides it can be further used as a charge for the blast furnace process. The ratio of the components of the waste material mixture is chosen to guarantee the full utilization of the latter under real production conditions.
REFERENCES

RESEARCH OF INFLUENCE EQUAL CHANNEL ANGULAR PRESSING ON THE MICROSTRUCTURE OF COPPER

Sergey Lezhnev¹, Irina Volokitina¹, Toncho Koinov²

¹ Karaganda State Industrial University, Temirtau, Kazakhstan  E-mail: sergey_legnev@mail.ru
² Department of Physical Metallurgy and Thermal Equipment University of Chemical Technology and Metallurgy 8 Kl.Ohridski, 1756, Sofia, Bulgaria  E-mail: toni309@koinov.com

ABSTRACT

The effect of equal-channel angular pressing (ECAP) in step die on the microstructure and properties of preheated copper is studied. It is found that the grain size after ECAP depends slightly on the preliminary thermal treatment, but the quenching applied decreases copper hardness values by 15%, which in turn provides to decrease the pressing force during the first pass from 620 kN to 510 kN. The minimum average grain diameter reached in case of quenching alloy M1 at 700°C, ECAP in step die at room temperature and 6 cycles of deformation is 0.6 microns.

Keywords: microstructure, properties, copper, pressing force.

INTRODUCTION

A number of methods based on severe plastic deformations (SPD) proceeding in the bulk of the corresponding body have been developed during the past decade. These processes include multi-axis forging [1], twist extrusion [2], upsetting with torsion [3], etc. However, these methods of deformation are inefficient and time-consuming, because in some cases shear deformations are accompanied by large single reductions, while in others great deformation forces are required.

The ECAP method [4] is the most successful method of severe plastic deformation used today. It has great potential of producing ultrafine-grained structure with a uniform equiaxed structure and grain boundaries of predominant high-angle disorientation. It is worth adding that the workpiece retains its original size. In fact the uniform compression scheme provided excludes the formation of micro- and macro material discontinuities in the course of deformation resulting thus in high-quality pieces.

A number of designs templates to implement equal-channel angular pressing are developed. These are the equal channel angular die [5], the equal channel step die [6], the equal channel angular die with two dimensional metal flow [7], the equal channel step die with three dimensional metal flow [8], etc.

Many scientists study the process of metal deformation by equal-channel angular pressing. This is also done in the group of Prof. A.B. Naizabekov at the Karaganda State Industrial University (Kazakhstan). Good results referring to the production of ferrous and non-ferrous metals (aluminum, copper) with ultra-fine grain structure by equal channel angular pressing in equal channel step die are already obtained (Fig. 1).

This paper investigates the effect of severe plastic deformation in pressing copper workpieces using the equal channel step die. The effects of the preliminary and post thermal treatment on the metal microstructure evolution and strengthening are studied as well. The interest is mainly determined by the metal properties.
Copper has a low coefficient of friction combined with high ductility and good resistance to corrosion in a number of aggressive media as well as good electrical conductivity. Furthermore, it is easily processed by forming in a cold resulting in more than 90% of total reduction. There is an extra point which needs to be addressed. It refers to the fact that the equal channel angular pressing does not always produce metal of ultrafine grain structure in the course of a small number of cycles, which in turn requires the introduction of preliminary and final thermal treatment. The preliminary thermal treatment is applied to avoid brittle fracture products in case of severe plastic deformation. It adapts the alloys structure prior to the process providing to escape from lattice distortions and stock of residual energy. Thus improved mechanical properties are obtained.

EXPERIMENTAL

Technical copper grade M1 was used. The samples were subjected to preliminary thermal treatment which included annealing, quenching and normalizing to the standard mode. Square section (15 mm×15 mm) samples of 70 mm length were subjected to ECAP in an equal channel step die. The channels junction angle was 125°, while the tilting of the workpiece around the longitudinal axis [9] was 90°. The friction between the tool and the workpiece was decreased by using palm oil as a lubricant. The deformation was carried out at temperatures lower than that of the material recrystallization [10] to eliminate the effect of deformational-stimulated growth of grains usually brought about by ECAP temperature increase.

The experiments were carried out in three modes: mode 1 referred to pressing temperature of 25°C; mode 2 - to pressing temperature of 90°C; mode 3 - to pressing temperature of 180°C. In all cases the number of cycles applied was equal to 6.

As pointed above heating at temperatures higher than that of recrystallization resulted in significant grain growth and sharp decrease of copper strength. That is why it was necessary to determine the recrystallization temperature. Its approximate value was estimated on the ground of formulas reported [11] and further verified by a laboratory experiment. Samples after ECAP were cut into thin plates of thickness of 5 mm and heated for 1 hour at a temperature in the range from 100°C - 270°C. The subsequent cooling of the samples was carried out in water. The samples treated were studied using an optical microscope and a transmission electron microscope. They were also tested using the torsion-tensile machine. The testing referred to the median plane of the sample aiming to avoid the effect of peripheral areas. Obtained samples were examined in two sections: the transverse and longitudinal direction.

Thin samples were prepared to carry out the metallographic analysis. A standard procedure was applied using Leica optical microscope equipped with a micro hardness tester. Aiming further analysis workpieces of thickness of 250 mm were cut using a high-precision cutting machine and subjected to fine polishing to remove the cold-worked layer and electrolytic thinning using Tenupol 5. Then they were examined by JEM2100 JEOL transmission electron microscope.

The chemical composition of the samples was determined using the multifunction device RIKOR. The mechanical properties of the alloys undergone heat treatment and subsequent ECAP were studied by the torsion-tensile machine M140KU. Standard cylindrical samples were used. The tensile speed was 0.5 mm/min corresponding to a speed of deformation of 0.56 × 10⁻³ s⁻¹.

RESULTS AND DISCUSSION

Material

The chemical composition of the samples studied is given in Table 1.

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>99.94</td>
<td>0.005</td>
<td>0.004</td>
<td>0.051</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of copper M1.
Microstructure

Copper alloys can become either softer or harder by heat treatment. However, unlike other alloys, they become harder by slow cooling in air, while softer in case of rapid cooling in water.

Fig. 2 shows optical photos of the microstructure of the original sample and that subjected to preliminary thermal treatment. It is seen that the structure of the original sample is characterized by the presence of a large number of twins (Fig. 2a), while that obtained upon deformation by annealing shows equiaxed grains with the presence of twins (Fig. 2b).

The effectiveness of ECAP can be evaluated on the ground of the comparative examination of the microstructure of the copper alloys prior to and after the deformation applied. The alloy M1 microstructure obtained after pressing at different temperature values is illustrated in Figs. 3 - 5.

The changes in copper microstructure brought about by ECAP were investigated by transmission electron microscopy. Aiming a comparison the photos were taken after the 6th ECAP cycle at various temperatures of pressing.

Most of the strongly deformed metals and alloys lack ductility which leads to significant fragility. The plastic properties of the metal can be improved by reducing the stress. This is usually achieved through annealing, seasoning, and tempering of the metal. But the desired final heat treatment depends also on the recrystallization temperature.

The structure formed during ECAP at room temperature determines the behavior of copper during the subsequent heating. Samples subjected to quenching and 6 pressing cycles at 25°C were referred to as it was found that they had the most fine-grained structure.

Mechanical properties

Fig. 8 illustrates the Vickers micro-hardness observed. Results referring to the microhardness and the average grain diameter of the copper alloy M1 after preliminary heat treatment are shown in Table 2.

The ECAP tensile test was followed by compressing and determination of the Vickers microhardness.

The strength properties of alloys are characterized by

---

Fig. 2. Optical photos of the microstructure of copper prior to and after preliminary thermal treatment, x100
a) prior to thermal treatment; b) after annealing; c) after normalization; d) after quenching.
Fig. 3. Optical photos of copper microstructure after 6 cycles of ECAP in a step die at 25°C, x1000. a) prior to treatment; b) after annealing; c) after normalization; d) after quenching.

Fig. 4. Optical photos of the microstructure of copper after 6 cycles of ECAP in step die at a temperature of 90°C, x1000. a) prior to treatment; b) after annealing; c) after normalization; d) after quenching.
Fig. 5. Optical photos of the microstructure of copper after 6 cycles of ECAP in a step die at a temperature of 180°C, x1000. a) prior to treatment; b) after annealing; c) after normalization; d) after quenching.

Fig. 6. Microstructure of copper after 6 cycles of ECAP in a step die observed by a transmission electron microscope at: a) 25°C; b) 90°C; c) 180°C.
the values of the yield strength $\sigma_t$ and tensile strength $\sigma_b$, while the plastic characteristics are characterized by the values of contraction ratio and elongation samples prior to the destruction [12]. According to the mechanical tests the tensile strength of alloy M1 depends on the passes number and the temperature (Figs. 9-11).

In case of cold deformation the alloy’s most intense hardening is observed within 2-3 passes. Then the process of hardening slows down. The temperature increase to 180°C leads to a significant decrease of the alloy’s deformation resistance. The most intensive hardening of the alloy occurs at this temperature at a relatively low degree of deformation (2 passes). Then the hardening process slows down. Dynamic loss of strength is observed on further deformation. The structure obtained is inequigranular with a large average grain diameter.

The consideration presented above leads to the conclusion that pressing at room temperature is the most
efficient. Therefore, other mechanical characteristics are given only for alloy M1 after 6 ECAP cycles at room temperature (Table 3).

DISCUSSION

Effect of ECAP in step die on copper microstructure

Metallographic analysis of copper after ECAP in step die shows that during the initial pressing stage the initial grains are oriented at an angle to the sample axis, while their substructure is badly etched. After the third cycle the sample’s structure becomes partially meshed and polygonized. Formation of the submicrocrystalline structure at ECAP is a mesh structure. It is found that the formation of nanostructures by severe plastic deformation has a pronounced phase character. In order to facilitate the description of the processes taking place with copper at ECAP the deformation process is conditionally divided into stages. The first stage refers to a small degree of deformation for equal-channel angular pressing (1-2 passes). It is characterized by the appearance of a mesh structure: a dislocation is redistributed in the bulk of the grains leading to the formation of plexus blurred walls. The dislocation density of the latter is higher than that of the surrounded regions. The average size of such cells is ca 0.5-2 microns and the wall thickness is one order smaller [14]. The increase of the degree of deformation leads to cell size changes and increase of their blurred boundaries. The formation of tangles and plexus of dislocations starts to fill the entire volume of the initial grains (Fig.12) with the further increase of the degree of deformation.

Due to excess of the same sign dislocations in the wall the adjacent cells are disoriented to angles 1-20° and direction of reversal at the boundaries between different adjacent cells are different, so at the mesh structure macroscopic changes of crystallite orientations is not obtained [13].

The second stage refers to 4-5 passes at ECAP. This is accompanied by the formation of transitional structures of mesh and nanostructures features accompanied by large misorientation. The increase of the deformation degree leads to a certain decrease of the average size of the cells and disorientation increase at the cell boundaries.

Twinning takes place during the second stage.

Table 3. Mechanical testing results for copper alloy M1 after 6 cycles of ECAP at room temperature.

<table>
<thead>
<tr>
<th>Type of heat treatment</th>
<th>Alloy of copper</th>
<th>Hardness $H_{10}$</th>
<th>Yield strength $\sigma_y$, MPa</th>
<th>Tensile strength $\sigma_t$, MPa</th>
<th>$\psi$, %</th>
<th>$\delta$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>M1</td>
<td>229.4</td>
<td>402</td>
<td>469</td>
<td>25.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Annealing</td>
<td>M1</td>
<td>215.7</td>
<td>360</td>
<td>374</td>
<td>36.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Normalizing</td>
<td>M1</td>
<td>236.8</td>
<td>402</td>
<td>502</td>
<td>22.2</td>
<td>5.7</td>
</tr>
<tr>
<td>Quenching</td>
<td>M1</td>
<td>246.1</td>
<td>460</td>
<td>560</td>
<td>26.0</td>
<td>7.2</td>
</tr>
</tbody>
</table>
This process is activated when the deformation disorientation’s fields (cells) become so small in size that the generation of lattice dislocations in them becomes impossible. The twin boundaries represent a different coherent structure and besides they are randomly distributed in the metal. Therefore specific crystallographic shifts leading to their formation do not make a significant contribution to the active deformation of the metal. In this context, twinning is a complementary mechanism of grains grinding.

A homogeneous nanostructure is formed during the third stage (after more than 6 passes). The structure of the grains experiences strong elastic distortions caused by grain boundaries long-range stresses.

The results obtained provide to advance a model of microstructure evolution in the course of severe plastic deformation. It describes the transition in the course of severe plastic deformation process from a mesh to grain structure, which is characterized by angle grain boundaries. Mesh structure is formed during the initial stage of deformation. It is then transformed during the SPD. Thus the cell walls become more narrow and streamlined. However, with the further deformation proceeding the dislocation density in the walls becomes higher than the critical one. This leads to the development of a reverse transition consisting in the annihilation of opposite sign dislocations. As a result excessive dislocation of two signs playing different roles appears in the cell walls. The increased misorientations and transformation of the grains cells are due to dislocations of Burgers vector perpendicular to the boundary.

Sliding is another type of dislocation which forms long-range stress fields. It leads to an increase of the elastic microdistortions and atomic displacement of the crystal lattice sites. This results in grain boundary sliding and relative displacement of the grains.

The model advanced is in agreement with many experimental results found by electron microscopy studies of materials subjected to severe plastic deformation, i.e. the equiaxed shape of the grains, the significant distortions of the crystal lattice and the presence of a high density of dislocations in the grain boundaries.

The microstructure analysis of alloy M1 after ECAP shows that intensive grain refinement is observed after each cycle of deformation. It is also found that after 4-5 cycles of pressing the grain structure becomes substantially uniform in all sample directions.

As pointed above annealing, normalizing, quenching and tempering have to be applied prior to ECAP aiming to avoid brittle fracture of the product, to improve the efficiency of grain refinement and to improve the mechanical properties of the material. The present study shows that all preliminary heat treatments considered resulted in grain grinding. But the final grain size after ECAP is found almost identical. Hence it is concluded that the grain size after ECAP depends little on the preliminary heat treatment. It is worth adding that increased quenching reduces copper hardness by 15%, which helps to reduce the pressing force during the first pass from 620 to 510 kN.

The increase of the pressing temperature decreases the pressing force required and the deformation resistance, but increases the unevenness of the metal flow. The same effect is observed with the increase of the temperature gradient between the workpiece and the container. This results in uneven distribution of the deformation resistance over the cross section of the workpiece. Besides, the peripheral layers cooling leads to a more rapid flow of the inner layers of the workpiece (Fig. 13).

Well outlined anisotropy of properties is observed at pressing in the range of 90°С - 180°С. It consists in increase of the strength characteristics and decrease of the plasticity along the cross direction when compared to those referring to the longitudinal one.

The minimum average grain diameter obtained by pressing alloy M1 in equal channel step die is 0.6 microns. Such grain size is obtained after quenching and ECAP at room temperature and 6 cycles of deformation.
All data presented above lead to the conclusion that pressing of copper alloy M1 at room temperature is the most efficient.

The analysis of alloy M1 microstructure after recrystallization annealing shows that annealing at temperatures in the range of 100°C - 160°C coincides with the temperature range of the reverse transition, which is characterized by a gradual decrease of the dislocation density and the concentration of excess defects as well as by redistribution of dislocations leading to a decrease in the level of microdistortions. At annealing temperature of 220°C a primary recrystallization process starts, i.e. new recrystallized grains appear from the deformed matrix at the boundaries in the transition bands (Fig. 7). The further increase of the annealing temperature to 270°C leads to rapid collective recrystallization in samples undergone ECAP. This results in agreement with the observations of S.S. Gorelik [14] for small grains (d ≤ um). The value of the driving force of collective recrystallization is of the order of magnitude of the driving forces of primary recrystallization.

**Changes in the mechanical properties of the alloy under ECAP effect**

The graph presenting the dependence of alloy M1 tensile strength on the number of passes at different pressing temperatures suggests an intensive growth of the strength characteristics within the first 2-3 press cycles. The next cycle is also connected with steady growth of strength characteristics but the latter is less intensive. The temperature increase to 180°C leads to a significant decrease of the alloy’s deformation resistance. The most intensive hardening of the alloy at this temperature is obtained at a relatively low degree of deformation (2 passes). Then the hardening process slows down, while during the subsequent deformation dynamic loss of strength starts to outline. This results in less processes structure with grains of a large average diameter.

Hence it can be concluded that pressing copper alloy M1 at room temperature the most efficient.

The maximum values of the mechanical strength characteristics of alloy M1 are obtained after quenching and pressing at room temperature. They refer to σ₁ = 460 MPa and σ₉ = 560 MPa. It is evident that the tensile strength is increased almost twice when compared to that of the initial large grain material.

The values of Vickers microhardness for all alloys demonstrate a steady almost linear increase with each new cycle of deformation. The maximum value reached is equal to 246.1 units. The mechanical tests carried out verified the value of recrystallization temperature obtained by the metallographic investigations. The temperature referring to the sharp decrease in microhardness of 49.3 units (20 %), coincides with that of the appearance of new recrystallized grains.

**CONCLUSIONS**

The present work reports data on the effect of equal channel angular pressing in step die on the microstructure and properties of the heat-treated copper at various pressing temperatures. The main conclusions refer to:

- A noticeable decrease of the grains size after each cycle of deformation (after quenching from 145 microns to 0.6 microns for 6 cycles of deformation on the route Be at room temperature);

- A significant strength increase when compared to the initial one. The tensile strength increases almost twice, while the plasticity decreases less than in other metal forming methods;

- Almost no effect of the preliminary heat treatment on the grain size. Quenching reduces the hardness of copper by 15 %, which helps to decrease the pressing of the first passes from 620 to 510 kN and to obtain more fine-grained structure;

- The increase of the pressing temperature decreases the pressing force and the deformation resistance, but the unevenness of the metal flow increases. The latter effect is also observed on increase of the temperature gradient between the workpiece and the container. The results obtained refer to an uneven distribution of the deformation resistance upon the cross section of the workpiece. The peripheral layers cooling leads to a more rapid flow of the internal layers of the workpiece. Pressing in the range of 90°C - 180°C results in strong anisotropy of the properties is observed - the strength characteristics are higher while the plasticity is lower along the cross direction when compared to those along the longitudinal direction. That is why pressing of copper alloy M1 at room temperature is to be chosen.

The recrystallization temperature is that of the microhardness sharp decrease of 49.3 units (20 %) as it coincides with the appearance of new, recrystallized grains in the alloy structure.
Acknowledgements

The financial support of the project “Getting high-quality materials by a combination of thermal treatment and severe plastic deformation” within the frameworks of “2012-2014 Research Grants” program is gratefully acknowledged.

REFERENCES

3. A.N. Levanov, Technological efficiency of upsetting with the active forces of friction, Forging and stamping production, 2, 1995, 6-8.
7. V. Michenka, K. Malanika, S. Rusz, Research of influence of extreme deformation conditions on metal sub-microstructure and development of testing methods for evaluation of their technological properties, 18-th International Conference on metallurgy and materials METAL, Ostrava, Czech Republic, 2009.
GUIDE FOR AUTHORS

Journal of Chemical Technology and Metallurgy is a specialized scientific edition presenting original research results in the field of chemical technology and metallurgy, chemical engineering, biotechnology, industrial automation, environmental protection and natural sciences. The articles published in Journal of Chemical Technology and Metallurgy refer to:

Inorganic Chemistry; Organic Chemistry; Analytical Chemistry; Physical Chemistry;
Organic Synthesis and Fuels; Polymer Engineering; Textile and Leather; Cellulose, Paper and Polygraphy; Inorganic and Electrochemical Productions;
Chemical Engineering; Industrial Automation; Information Technology; Biotechnology; Economics and Management of Chemical and Metallurgical Industry; Sustainable Development and Environmental Protection;
Physical Metallurgy; Metallurgy of Iron and Casting; Metallurgy of Non-ferrous and Semiconducting Materials; Technology of Silicates; Nanomaterials.

Journal of Chemical Technology and Metallurgy publishes full-length research papers, critical and book reviews. Research papers are expected to be complete and authoritative accounts of work that has significance and interest, presented clearly and concisely. Critical reviews are commissioned by the Editor-in-Chief. Authors intending to offer critical reviews are invited first to contact the Editor-in-Chief.

Contributions will only be considered for publication if they are relevant to the topics pointed above. Presentation and discussion should be at the level of the Journal status gained. The language can be a reason for rejection if below an acceptable level of clarity. Detailed descriptions of the equipment used should only be given if the latter is new. Papers reporting experimental data without adequate interpretation are not acceptable. Contributions will be accepted for publication only on the recommendation of referees.

Submission of Manuscripts
Manuscripts should be submitted to the Editor-in-Chief at the following address:
University of Chemical Technology and Metallurgy
8 Kliment Ohridski blvd., Sofia 1756, Bulgaria,
(for JCTM)
Manuscripts may be submitted electronically to e-mail: journal@uctm.edu

Manuscript preparation
It is important that the file be saved in the native format of the wordprocessor used. All contributions should be typed, double-spaced, 12-pt font. All pages must be numbered in sequence. Most formatting codes will be removed and replaced on processing the article. In particular, do not use the wordprocessor’s options to justify text or to hyphenate words. However, do use bold face, italics, subscripts, superscripts, etc. Do not embed graphically designed equations or tables, but prepare these using the wordprocessor’s facility. When preparing tables, if you are using a table grid, use only one grid for each individual table and not a grid for each row. If no grid is used, use tabs, not spaces, to align columns.

Essential title page information
Title. It should be concise and informative. Titles are often used in information-retrieval systems. Avoid abbreviations and formulae where possible.
Author names and affiliations. The names of the authors have to be clearly indicated. Present the authors’ affiliation addresses (where the actual work was done) below the names. Provide the full postal address of each affiliation, including the country name.
Corresponding author. Clearly indicate who will handle correspondence at all stages of refereeing and publication, also post-publication. Ensure that phone numbers (with country and area code) are provided in addition to the e-mail address and the complete postal address. Contact details must be kept up to date by the corresponding author.
Present/permanent address. If the author has moved since the work described in the article was done, or was visiting at the time, a “Present address” (or “Permanent address”) may be indicated as a footnote to that author’s name. The address at which the author actually did the work must be retained as the main, affiliation address. Superscript Arabic numerals are used for such footnotes.

Abstract
A concise and factual abstract is required. The abstract should state briefly the purpose of the research, the principal results and major conclusions. An abstract is often presented separately from the article, so it must be able to stand alone. For this reason, References should be avoided, but if essential, then cite the author(s) and year(s). Also, nonstandard or uncommon abbreviations
should be avoided, but if essential they must be defined at their first mention in the abstract itself.

**Article structure**

**Introduction**

State the objectives of the work and provide an adequate background. Avoid a detailed literature survey or a summary of the results.

**Experimental**

Provide sufficient details to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

**Results and Discussion**

Results and the discussion provided should be clear and concise.

**Conclusions**

The main conclusions of the study have to be presented in a short Conclusions section.

**Acknowledgements**

Acknowledgements are given in a separate section at the end of the article before the references.

**References** should be cited in the text by an Arabic numeral in square brackets, listed numerically and typed double-spaced on a separate sheet at the end of the paper. References should be arranged in the order in which they appear in the text. Journal titles should be abbreviated according to the latest Chemical Abstracts Service Source Index. Only articles that have been published or are in press should be included in the references. Unpublished results should be cited as such in the text. References in non-English language should be translated in English. The original language must be shown in brackets. In the reference list, the styling, punctuation and capitalization should be as follows:

**For journals:**

**For books:**

**For edited books:**

**For conference proceedings, symposia, etc.:**

When you are citing papers published in *Journal of Chemical Technology and Metallurgy* you should use the abbreviation of the title as follows:


**Formulae** should be typewritten (Equation Editor) with ample space around them. The meanings of all symbols have to be given immediately after the equation in which they are first used. Equations should be sequentially numbered (on the right side of the equation and in parentheses). Subscripts and superscripts should be clearly indicated. Greek letters and other non-Latin symbols should be typed using Times New Roman Gr or Symbols.

**Units** should be given in SI system. They should be in the form, e.g. g cm$^{-1}$ rather than g/cm.

**Figures** should be numbered consecutively with Arabic numerals. All figures should be supplied on separate sheets. All illustrations must be readable when reduced to a width of 75 mm (single column figure) or 160 mm (double column figure). Photographs, charts and diagrams are all to be referred to as “Figures(s)” and should be numbered consecutively in the order to which they are referred. They should accompany the manuscript, but should not be included within the text. All illustrations should be clearly marked with the figure number. Figure captions should be typed double-spaced on a separate sheet. Figures should not include text. Graphic files should be in TIFF or JPG with resolution not less than 300 dpi.

**Tables** should be numbered consecutively with Arabic numerals in the order of appearance in the text. Each table should be given on separate sheet with a short descriptive title directly above it, with essential footnotes below.

One copy of the manuscript in English and one in Bulgarian (for Bulgarian authors) with a set of original illustrations and a disk must be submitted. The manuscript should be written with true-type font Times New Roman size 12 with double line spacing. Manuscripts of papers submitted to the journal will not be sent back to the authors.