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COMPOSITES THEORY AND PRACTICE

Rafał Anyszka[1], Otmar Dobrowolski[1], Paweł Schulz[2], Ludomir Ślusarski[1*], Adam Tracz[3]

[1]Technical University of Łódź, Institute of Polymer and Dyes Technology, ul. Stefanowskiego 12/16, 90-924 Łódź, Poland
[2]Gambit – Lubawka Ltd., ul. Wojska Polskiego 16, 59-420 Lubawka, Poland
[3]Center of Molecular and Macromolecular Studies (PAN), ul. Sienkiewicza 112, 90-363 Łódź, Poland
**Corresponding author: E-mail: ludomir.slusarski@p.lodz.pl*

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SEALING PLATES: STRUCTURE, MORPHOLOGY AND CROSS-LINKING

The technology of sealing plates has been outlined, paying attention to the analogy and differences between this technology and rubber technology. The structure and micro-morphology of sealing plates were investigated by the methods of SEM, AFM and nanoindentation. An oscillatory rheometer was successfully used to examine the cross-linking course of the elastomer contained in the plate and accompanying phenomena. Significant differences were found between the courses of sulfur and peroxide vulcanizations. It has been observed that the rubber contained in the plate, after cross-linking, does not form a continuous phase but occurs in the form of isolated clusters, mostly including very thin membranes. There are also numerous visible agglomerates of fillers, especially in the middle part of the plate. It has been found that during plate formation and rubber vulcanization, a considerable temperature gradient occurs. The findings create conditions for the modification of sealing plate technology.

Keywords: sealing plates, technology, structure, micro-morphology, cross-linking

PŁYTY USZCZELNIAJĄCE, STRUKTURA, MORFOLOGIA I SIECIOWANIE

Omówiono w zarysie technologię płyt uszczelniających. Zwrócono uwagę na analogie i różnice między technologią płyt uszczelniających a technologią gumy. Zbadano strukturę i mikromorfologię płyt uszczelniających metodami SEM, AFM i nanoindentacji. Zastosowano z powodzeniem reometr oscylacyjny do badania przebiegu sieciowania elastomeru zawartego w płycie i zjawisk towarzyszących. Stwierdzono występowanie istotnych różnic między przebiegiem wulkanizacji siarkowej i nadtlenkowej. Zaobserwowano, że kauczuk zawarty w płycie, po usieciowaniu, nie tworzy fazy ciągłej, lecz występuje w postaci izolowanych skupisk, najczęściej są to błonki o bardzo małej grubości. Widoczne są również liczne aglomeraty napełniaczy, szczególnie w warstwie środkowej płyty. Ustalono, że podczas formowania płyty i wulkanizacji kauczuku w materiale występuje znaczny gradient temperatury. Wyniki badań stwarzają przesłanki modyfikacji technologii płyt uszczelniających.

Słowa kluczowe: płyty uszczelniające, technologia, struktura, mikromorfologia, sieciowanie

INTRODUCTION

Sealing plates constitute a special type of composite materials. The role of the matrix in principle is played by rubber, usually butadiene-acrylonitrile rubber (NBR), and the dispersed phase consists of dispersive and fibrous fillers and low-molecular auxiliary compounds. However, the proportions of both the component types are different than in the case of typical polymeric composite materials, the rubber content in the plates is several times lower. This has serious consequences that have not yet been examined to a satisfactory extent.

The technology of sealing plates has a long history, its beginning dates back to the end of the 19th century. It is similar to some extent to rubber technology, but there are also very essential differences between them. In both cases, the same raw materials are used, but the content of particular components, the preparation procedures of their blends and the product formation and vulcanization are fundamentally different. Rubber technology has long been a subject of versatile studies and their results are available in the form of reference works and monographic publications. The situation presents itself incomparably less favorably in the case of the technology of sealing plates. An essential source of information on this subject is the monograph by W. Tietze [1]. It is known that sealing plates production was first launched in 1896 by the Klinger Company, and the product trade name became “Klingerit”. On account of the end of this name, the products were also called “ IT plates”. For almost 100 years, asbestos was one of the basic raw materials for the production of plates. A ban on using asbestos introduced at the end of the 20th century caused significant difficulties. In Poland, asbestos-free technology was mastered in 1997 and even a bit earlier in the Gambit-Lubawka and Polonit plants in co-operation with the Institute of Polymers of the Technical University of Łódź [2, 3]. Nowadays, aramide fibers and fibers of other mineral raw materials are used as asbestos substitutes. The composition of sealing plates is only apparently similar to that of rubber blends. For instance, the content of rubber in plates amounts to 10÷15% by wt., while in rubber blends its content is 50÷60% by wt. Moreover, the procedures of blend preparation and vulcanization are different. In the case of plates, the blends are prepared in Z-mixers equipped with a chopper, i.e. a steel disk with teeth on its circumference, revolving at a rate of about 3000 rpm. Its function includes homogenization and defibering of the charge. Usually, rubber is added to the blend in the form of a granulated product together with a considerable amount of toluene (1). Furthermore, the plate formation and vulcanization of the rubber contained in the blend are carried out in a special way. A two-roll calender is used to that end. The lower roll, known as the forming roll, usually with a diameter of 1500 mm and a length of 3000 mm, is heated up to 130÷150°C. The upper roll with a considerably smaller diameter, known as the pressure roll, is cooled with water. Both rolls rotate concurrently with little friction. Calenders in a horizontal system are also used. Plates are formed with the use of previously prepared blends. Their external layers of very little thickness are called the bottom layer and top layer, respectively. They are prepared with the use of a greater concentration of toluene and owing that, their structure is more uniform. The middle layer is considerably thicker, usually from 0.3 to 5 mm. Blends of an appropriate composition are successively placed by an operator on the forming roll surface.The toluene is then evaporated and recuperated, simultaneously rubber vulcanization occurs. By selecting the appropriate components, one can influence the properties of the plates. At present, the only producer of sealing plates in Poland, Gambit-Lubawka Ltd., can offer 13 basic types of plates, including those resistant to the action of various media such as water, steam, natural gas, brake and cooling fluids, fuel oil, concentrated acids and bases. Depending on the composition, they differ in their thermal resistance within the range of 150 to 350°C. A sealing plate must fulfill rigorous requirements specified by standards. It is symptomatic that in the literature on the technology of sealing plates, there is a lack of detailed data concerning the relationships between the composition of the blends, the parameters of their processing and the properties of the final products [4- 6]. The Institute of Polymers and Dyes Technology in co-operation with Gambit-Lubawka Ltd undertook studies within the frame of Development Project No. 15003706, entitled "Improvement in the technology of sealing plates", aimed at broadening the knowledge within this scope. The properties of sealing plates that are essential from the point of view of their exploitation suitability depend on many parameters. This paper presents the results of investigating the plate structure, micro-morphology as well as the vulcanization course and the structure of the spatial network.

MATERIALS AND METHODS

Micro-morphology and structure of sealing plates

In the subject literature one can only find notes on the micro-morphology of sealing plates [1]. On the other hand, it is known that it exerts a very essential influence on the properties of rubber materials [7]. Preliminary investigations were concerned with sealing plates designed for water installations and low-parameter steam systems. Samples were observed by means of a Hitachi S-3000N scanning electron microscope with magnification within the range of 150÷3000x. The three-dimensional plate structure is visible at magnification x150, while at magnification x3000 one can observed the agglomerates of the dispersed phase (Fig. 1).

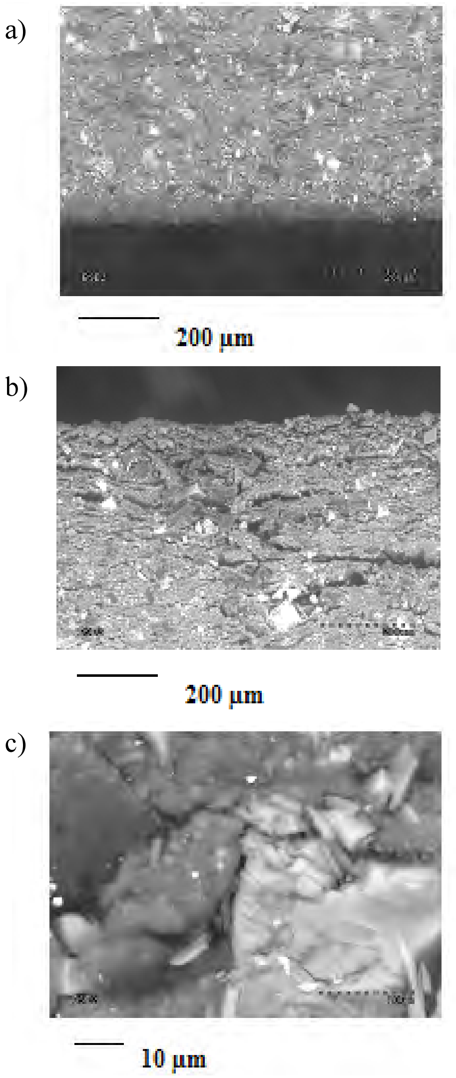

Fig. 1. Micro-morphology of plates FA 200: a, b) lower and upper layers, respectively, magn. x150, c) middle layer, magn. x3000

Rys. 1. Mikromorfologia płyt FA 200: a, b) warstwa dolna i górna, pow. 150x, c) warstwa środkowa, pow. 3000x

Unfortunately, we failed to obtain an image of the rubber phase. However, a remark arises that the micromorphology of the plates is heterogeneous and numerous agglomerates occur, which is unfavorable from the point of view of their sealing properties. We decided to assess the dispersion of the rubber phase with the use of a EDS attachment (Energy Dispersive Spectroscopy). It enables the detection and recording signals coming from elements with atomic numbers 6 – 92 including nitrogen. For further experiments, a Paro-Gambit plate was selected as it does not contain any other components containing nitrogen besides butadiene-acrylonitrile rubber. Using the SEM-EDS technique, we succeeded in obtaining information about the distribution of nitrogen in the middle part of the plate (Fig. 2).

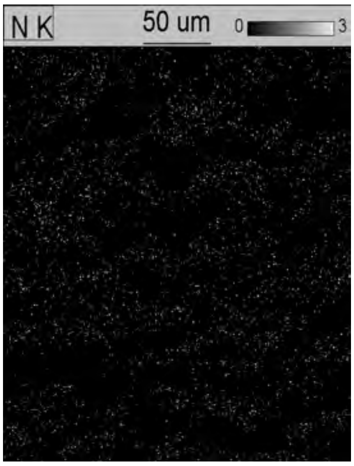

Fig. 2. Distribution of nitrogen atoms in plate middle layer

Rys. 2. Rozkład atomów azotu w warstwie środkowej płyty

A conclusion has arisen that the rubber contained in the plate does not occur in the form of a continuous phase. To make sure that this view is correct, we additionally examined the blend used to prepare the middle layer of the plate. A sample of the blend was deposited on a sheet of mica and its micro-morphology was examined by AFM methods using a Nanoscope IIIa microscope (Digital Instr.) and SEM (after applying a gold film) by means of a JSM 5500 LV-Jeol microscope at magnification x5000 (Fig. 3).

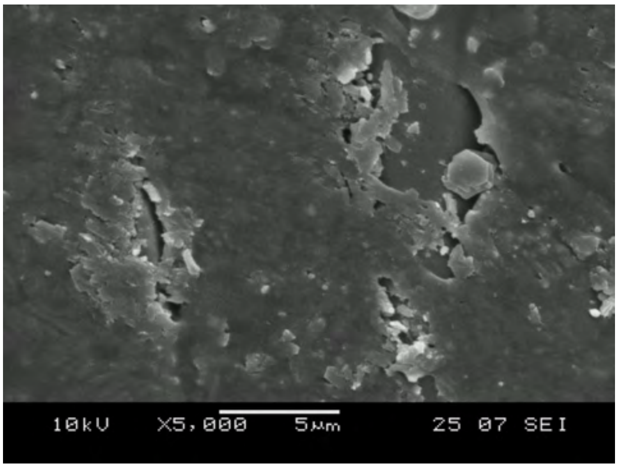

Fig. 3. Micro-morphology of plate middle layer

Rys.. 3. Mikromorfologia warstwy środkowej płyty

The rubber phase in the form of strongly defected micro-films is visible. Considering this type of structure, it becomes clear why the penetration of various media through collar gaskets cut out of plates mainly proceeds in the parallel direction and not in the transverse direction to their surface [8]. In this case, a certain role is also played by both the external layers. Moreover, a conclusion arises that improvement in the quality of gaskets could be obtained by increasing the homogeneity of the plate middle layer. The structure and properties of AF-CHEMACID plates from GAMBIT-Lubawka were examined by the method of nanoindentation under the following conditions: load increase rate 0.5 mN/s, indentation depth 3.5 μm. The lack of an upper layer is a particular feature of this plate (Fig. 4).

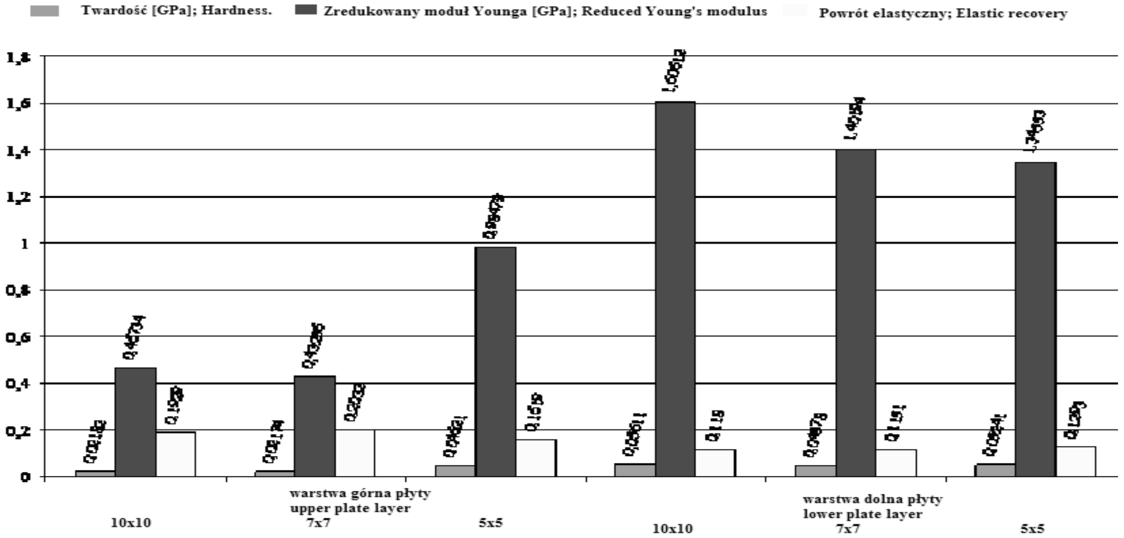

Fig. 4. Results of nanoindentation

Rys. 4. Zestawienie wyników nanoindentacji

The averaged results show that the upper layer is characterized by lower stiffness but higher elastic recovery than the bottom layer.

The temperature gradient occurring during the formation of a plate probably exerts an influence on the mentioned properties. A considerable scatter of results is observed.

CROSS-LINKING AND NETWORK STRUCTURE

In the case of sealing plates, the cross-linking process is usually carried out as in rubber products with the use of sulfur cross-linking systems. There is a lack of data concerning the course and degree of rubber cross-linking as well as the resultant spatial network structure in the subject literature. In rubber technology, the course of vulcanization is commonly examined by means of an oscillatory rheometer [9]. Admittedly, recently papers have been published on using nuclear magnetic resonance (NMR) to that end [10] but appropriate instruments are unavailable for the producers of sealing plates. Therefore, we decided to use the rheometer mentioned above. However, in comparison to rubber blends, the execution of rheometric measurements in the case of sealing plates is more complicated. From the micro-morphological examinations, it follows that rubber does not form a continuous phase in the plate but is dispersed in the form of heterogeneous films, moreover, its cross-linking proceeds simultaneously with toluene evaporation from the plate.

Initially, plates containing sulfur as a cross-linking agent with an addition of accelerators (mercaptobenzothiazole and tetramethylthiuram disulphide), zinc oxide and stearic acid as activators, were subjected to rheometric measurements. Based on preliminary tests, it has been found that the course of the cross-linking curve depends on the angle of rotor oscillation that can be 1, 3 or 5°. At an oscillation angle of 5°, one can recognize in the rheometric curve the appearance of strong disturbances. We assume that this is due to the cracking of thin rubber films visible in the photograms given in the first part of the article. Thus, the measurements were first carried out at an oscillation angle of 3°, at temperatures of 130 and 150°C. Both these temperatures can be used during plate forming and cross-linking under industrial conditions. However, some disturbances continued to appear in the initial sections of the rheometric curves. Moreover, as expected, it has turned out that temperature is of great importance. Admittedly, within the first 20 min, cross-linking at the temperature of 150°C proceeds clearly faster than at 130°C but later the situation changes. At the higher temperature, the rheometric curve runs significantly lower. This is due to the decomposition of the spatial network formed previously, the phenomenon is known as reversion (Fig. 5).

The studies of the properties of elastomers cross-linked with sulfur systems have shown that the polysulfide bonds of the network formed are decomposed particularly easily [11]. We decided to check whether a similar mechanism functions in the case of sealing plates. Using the method of thiol-amine analysis, frequently used in rubber technology [12], we examined the structure of network crosslinks in a plate formed without external layers under laboratory conditions at a temperature of 130°C. The mix composition was as follows: fillers 80, NBR 14, ZnO 1.5, stearin 0.5, accelerators (TMTD, MBT) 0.5 + 0.5, sulfur 0.7, others 2.3% by wt. The compositions of the thiol-amine reagents were as follows: "soft" reagent: 0.4 mole of isopropyl mercaptan and 0.4 mole of piperidine in the form of a toluene solution with a total volume of 1l; "hard" reagent: 1 mole of dodecil mercaptan in the form of a piperidine solution with a total volume of 1l. Samples cut out from different plate spots with a weight of about 300 mg swollen in toluene for 12 h were subjected to the action of the soft reagent for 2 h and to the action of the hard reagent for 72 h. After the removal of the thiol-amine reagents by extraction, we determined the weight and volume changes in the samples swollen in toluene, including the content of the solid phase. Based on the results obtained, we calculated the content of di- and polysulfide bonds in the cross-linked rubber. The following results were obtained (average results from three determinations) - Table 1.

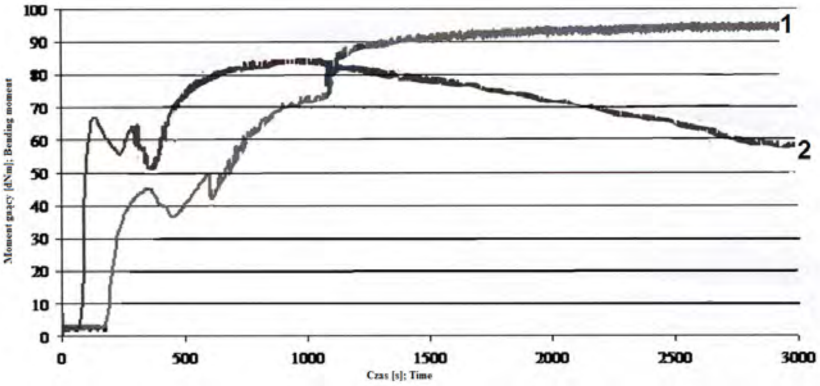

Fig. 5. Vulcanization kinetics of sealing plates cross-linked by means of sulfur system: 1 - 130°C, 2 - 150°C, oscillation angle 3°

Rys. 5. Kinetyka wulkanizacji płyt uszczelkarskich sieciowanych za pomocą zespołu siarkowego: 1 - 130°C, 2 - 150°C, kąt oscylacji 3°

TABLE 1. **Structure of spatial network**
TABELA 1. **Budowa sieci przestrzennej**

Concentration of polysulphide bonds Stężenie wiązań polisiarczkowych	$n_1 = 0.110$ mmol/g
Concentration of di- and polysulphide bonds Stężenie wiązań di- i polisiarczkowych	$n_2 = 0.152$ mmol/g

From the determination results, it follows that in the plate with the given composition, mainly polysulfide bonds are present (about 72%), while di-sulfide bonds occur in a considerably lower quantity. One cannot exclude some content of mono-sulfide bonds as the samples treated with both reagents did not dissolve. The spatial network structure is of paramount importance in practice as the thermal stability of plates is dependent on it. Hence, we attempted to cross-link the rubber contained in the plates by means of dicumyl peroxide since in such a case strong C-C crosslinks are formed [11]. However, we came across some complications; the cross-linking occurred in an effective way only when the temperature reached 150°C. Moreover, rheometric measurements of the cross-linking course were possible only at an oscillation angle of 1°. An increase in the oscillation angle to 5° and even to 3° caused a considerable reduction in the curve position (Fig. 6).

Aconjecture arises that this is a symptom of cracking of the primary spatial network. It also appeared that a considerable increase in the content of peroxide was required compared to the doses usually used in the case of elastomers, including NBR. The plate during formation and cross-linking contains a certain quantity of toluene. One may then assume that peroxide reacts not only with rubber but also with toluene as indicated by the difference in the IR spectra between the peroxide solutions before and after heating at 150°C (Fig. 7).

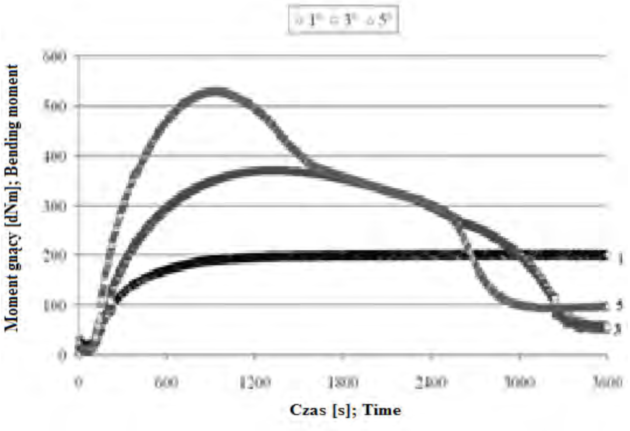

Fig. 6. Kinetics of cross-linking of sealing plates with cumyl peroxide determined at different oscillation angles of rotor: 1 - 1°, 2 - 3°, 3-5° at temperature of 150°C; NBR content 12.4% by wt., cumyl peroxide content 3.1% by wt.

Rys. 6. Kinetyki sieciowania nadtlenkiem kumylu płyt uszczelarskich oznaczana przy różnych kątach oscylacji rotora: 1 - 1°, 2 - 3°, 3-5° w temperaturze 150°C zawartość kauczuku (NBR) 12,4% wag., nadtlenku kumylu 3,1% wag.

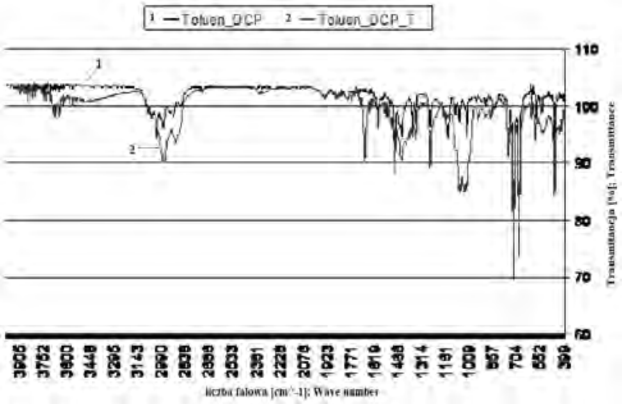

Fig. 7. Spectra of peroxide solution in toluene before (Toluene_DCP) and after heating (Toluene_DCP_T)

Rys. 7. Zestawienie widm roztworu nadtlenku w toluenie przed (Toluen_DCP) i po wygrzewaniu (Toluen_DCP_T)

As was expected on the basis of previous studies [11], the plate samples with similar degrees of cross-linking with sulfur or dicumyl peroxide were characterized by different mechanical properties (Tab. 2).

TABLE 2. **Tearing strength of plates crosslinked with various cross-linking degree systems, for 1 h at 150°C**
TABELA 2. **Wytrzymałość na rozdzieranie płyt różniących się sposobem usieciowania, w ciągu 1 godz. w temperaturze 150°C**

Cross-linking substances	Content phr.*)	Cross-linking time [min.]	Rheometric moment [d Nm]	Tearing strength [N/mm]
Sulfur	5.2	12.5	18	5.98
Accelerators	7.0			
Dicumyl peroxide	8.9	12,5	17	2.02
1,3 butyldiol dimetacrylate (coagent)	5.96			

*) parts per hundred parts of rubber, części na sto części kauczuku

From our studies, it follows that the expectations connected with the use of peroxides as cross-linking agents in the case of sealing plates are not justified.

The findings presented in this paper lead to a conclusion that the technology of sealing plates is highly complicated and its comprehensive recognition will require further studies and solutions to many complicated problems.

CONCLUSIONS

1. The micromorphology of sealing plates is not uniform; this concerns first of all their middle layer in which many agglomerates are visible.
2. The rubber used (NBR) is not distributed uniformly in the finally formed plate. It forms very thin, highly defected membranes.
3. During calendering and vulcanization of plates, a high temperature gradient is formed.

4. Plate properties depend on the vulcanized system used. In the case of sulphur vulcanization, first of all polysulphidic crosslinks are formed which to some degree diminish the thermal stability of the plate.
5. Organic peroxides e.g. dicumyl peroxide, are not effective as vulcanizing agents because they are reactive with toluene.

REFERENCES

[1] Tietze W. (Hrsg.) Handbuch Dichtungspraxis, 3 Auflage, Vulkan - Verlag, Essen 2003.

[2] Ślusarski L., Baryń W., Janczak T., Libudzisz J., Andrzejczak Z., Zielińska A., Matuszyński J., Polish Patent Nr 147805.

[3] Ślusarski L., Baryń W., Zaborski M., Libudzisz J., Technology of asbestos-free sealing materials (Gaskets), Polish Journal of Chemical Technology 1999, 1, 31-35.

[4] Braun J. Current elastomer compatibility test standards, Sealing Technology 2011, 3, 8-12.

[5] Slay B., Webber W., Stress relaxation of elastomer compounds, Sealing Technology 2011, 2, 9-12.

[6] Piringer S., Rustemeyer U., Improvement of parameters, based on fibre sealing plates, at elevated temperatures, Sealing Technology 2004, 3, 1-11.

[7] Bieliński D., Ślusarski L., Dobrowolski O., Głąb P., Dryzek E., Studies of filler agglomeration by atomic force microscopy and positron anihilation spectroscopy, Kautschuk Gummi Kunststoffe 2004, 11, 579-586.

[8] Blachura J. Wpływ struktury i właściwości sprężystych materiału uszczelnień spoczynkowych na ich szczelność, Praca doktorska, Politechnika Wrocławska, Wrocław 2005.

[9] De S.K. White J.R. (edit.), Rubber Technologists Handbook, Rapra Technology Limited, Shawbury 2001, U.K.

[10] Pazur R.J., Walker F.J., Practical state of cure measurements by magnetic resonance, Kautschuk Gummi Kunststoffe 2011, 10, 16-23.

[11] Ślusarski L. The effect of structure on properties of elastomers, Kautschuk Gummi Kunststoffe 1992, 9, 705-707.

[12] Kiroski O., Sims J., Packham D.E., Gregory A.L, The use of thiol - amine chemical probes in network Characterisation of NBR vulcanizates, Kautschuk Gummi Kunststoffe 1997, 10, 716-720.