Analysis of the influence of tensile loading rate and artificial aging on the mechanical properties of Vinnol-based polymeric membranes

L. Kun[1], A.C. Murariu[1], L. Macarie[2], N. Pleşu[2]

[1]National R&D Institute for Welding and Material Testing – ISIM Timisoara, Romania
[2]Romanian Academy, Institute of Chemistry Timisoara, Romania
E-mail: lkun@isim.ro

Keywords

Polymeric membrane, SPE, Vinnol, tensile testing, artificial aging, UV, mechanical properties.

1. Introduction

During the last decades there has been a growing interest in synthesis and characterization of solid polymeric electrolyte (SPE) membranes [1-4]. These materials are very important from a scientific and technological point of view because of the numerous fields of application: various types of chemical separations, biochemistry, food technologies, waste water treatment, medical technologies, electrolyte polymer membranes in fuel cells, metal filtering, ion exchange chromatography, etc. As a result, extensive research is being done in order to obtain different functional polymers with application-tailored chemical and physical properties. Due to the presence of functional groups in their structure, these special polymers possess specific reactivity, physical and chemical behavior and advanced optical or electrical properties. Some further advantages of functional polymers are: attractive mechanical properties, easy processing and low to medium production costs [5-6].

SPEs have drawn the attention of many researchers as they find applications in lithium batteries and also in other electrochemical devices. Unlike the liquid electrolytes, these solid polymer electrolytes have a number of advantages like high-energy density, no leakage of electrolytes and absence of non-combustible reaction products at the electrode surfaces [7].

The mechanical properties of the SPE used in batteries are important to the performance and affect durability and cell longevity, preventing membrane failure from stresses induced by changing temperature and water content during operational cycling. Also, it is important to design the SPE by combining the electrochemical and mechanical properties [8-10].

Vinnol H 40/50 is a copolymer of approx. 60 wt.% vinyl chloride and approx. 40 wt.% of vinyl acetate. Its main use is for surface coating. The films show good toughness, permanent flexibility, abrasion resistance, low swelling in the presence of common solvents. The solid polymer electrolyte membranes based on Vinnol H 40/50 and Lithium bis(oxalate)borate (LiBOB) were obtained in order to be used as solid electrolyte in lithium batteries.

The preliminary experimental program presented in this paper has the objective of highlighting the influence of loading rate and grade of artificial aging on the tensile properties of Vinnol and LiBOB based polymeric membranes, used in the manufacturing of lithium-polymeric batteries.

2. Experimental plan, equipment and materials

The experimental program has been developed in order to highlight the influence of operating conditions on the most important mechanical properties of polymeric membranes. The stages of the experimental program are the following:

1. Tensile testing of non-aged specimens, using different loading rates;
2. Selection of a loading rate at which the following tensile tests will be carried out;
3. Tensile testing of non-aged specimens using constant loading rate (determined at step 2) and recording of the obtained mechanical properties;
4. Artificial aging of a new set of specimens, identical with the ones used at step 3, over a controlled period of time;
5. Tensile testing of the artificially aged specimens using constant loading rate (determined at step 2) and recording of the obtained mechanical properties;
6. Comparison of the obtained results in case of non-aged and aged specimens with the analysis of the parameters' influence on the mechanical properties.

The tensile tests were carried out according to the SR EN ISO 527 standard, parts 1 and 3 (films and sheets) [11-12].

The equipment used for the tensile tests consisted of the universal tensile testing machine Zwick/Roell Z005, with a maximum load of 500 N. The machine was equipped with special grips, designed and executed at ISIM Timisoara for this purpose, as shown in Figure 1. The equipment was controlled through a laptop by the dedicated software testXpert II v3.5.

The fixed loading rates used for the tensile testing were: 10 mm/min, 25 mm/min, 50 mm/min, 100 mm/min, 300 mm/min and 500 mm/min.

The artificial aging of the specimens was carried out using an experimental UV radiation equipment, designed and manufactured at ISIM Timisoara (Figure 2).

The artificial aging equipment is fitted with 6 Cleo HPA 400/30 SD UNP 400W high performance UV lamps respectively the corresponding BHA 400 L33 HD2-151 electromagnetic ballasts and HID SND 58 igniters. Thus the overall installed power of the lamps is 2.4 kW.

During the design of the equipment it became obvious that the intensity of the UV radiation needs to be uniformly distributed at the surface of the specimens and it also needs to be adjustable. As a result, the constructed aging equipment allows the use in pairs of 2, 4 or 6 UV lamps. Furthermore, the geometry of the 6 lamps and the structure is adjustable, the operator being able to choose different relative distances between the two rows of lamps and different distances (height) between the lamps and the specimens, as highlighted in the cross-section represented in Figure 3.

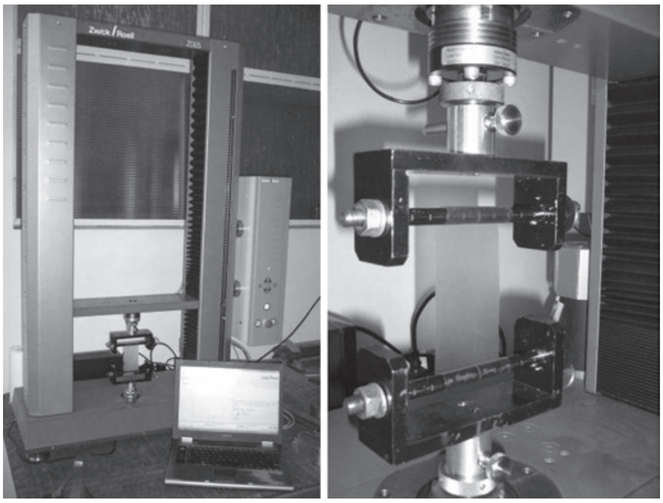

Figure 1. Experimental equipment for tensile testing of polymeric membranes.

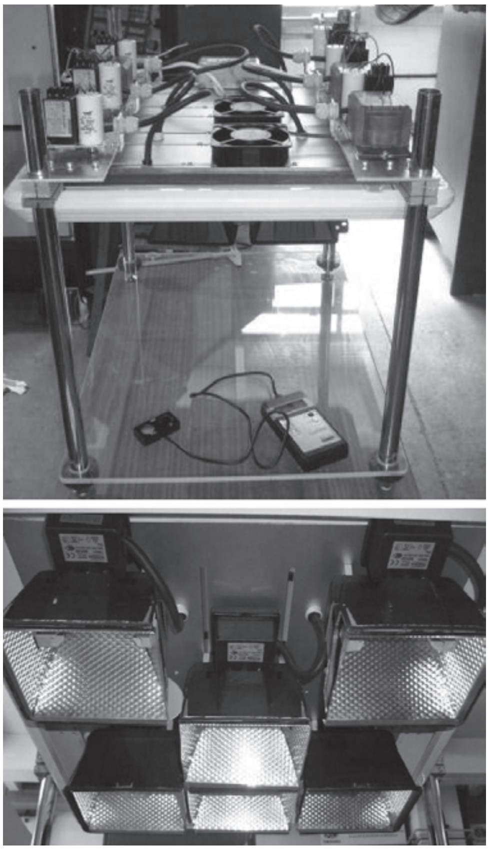

Figure 2. Equipment for artificial aging using UV emission lamps.

The actual parameters chosen for aging the specimens were the following:

1. Number of UV lamps: 2 (cumulated power: 800 W);
2. Height of lamps from specimens: 400 mm (max);
3. Relative distance between UV lamps: 90 mm;
4. Temperature measured at specimens: 40°C;
5. Time of UV exposure: 4h.

The experimental program was applied for two different types of specimens, realized from polymeric membranes used mainly in the manufacturing of lithium-based batteries. The two materials carry the code names: V15P 20%Li (material 1) and V15P 30%Li (material 2).

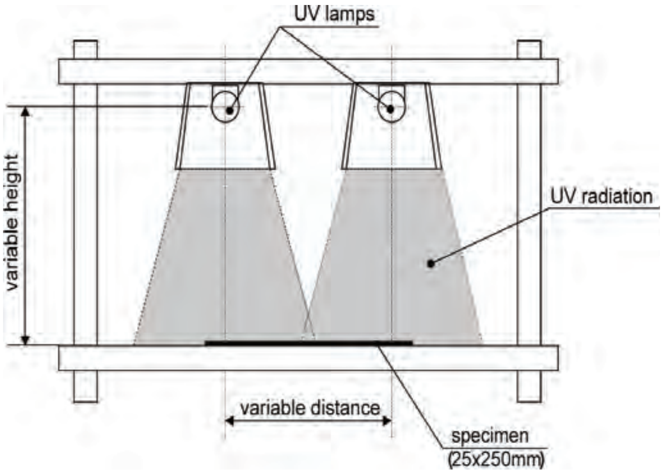

Figure 3. Cross-section of the artificial aging equipment, showing the variable relative distance between the two rows of UV lamps and the variable height of the lamps relative to the specimens.

The membranes were obtained by casting the mixture containing Vinnol H 40/50, LiBOB, plastifiant tris (2-chloropropyl) phosphate and methylethylketone on a glass plate using a film applicator.

Constant width sheet-type specimens were extracted from both materials, according to the SR EN ISO 527-1 and SR EN ISO 527-3 standards, with the dimensions: 250x25 mm. The specimen thickness is given in Table 1.

Table 1. Thickness of the tested specimens

Material	Thickness [mm]
Material 1 – V15P 20%Li	0.040
Material 2 – V15P 30%Li	0.055

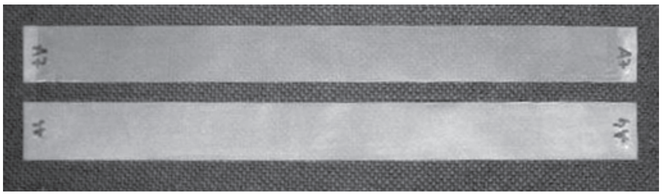

Figure 4. Image of an aged (upper) and a non-aged (lower) specimen, both extracted from material 1.

Two specimens are presented in Figure 4, one non-aged and one after a 4 hour exposure to UV radiation in the artificial aging equipment. The aged specimen can clearly be distinguished by its darker color, which is a side-effect of the UV exposure.

3. Results and discussion

The specimens were subjected to tensile testing in order to determine their mechanical properties and to analyze the influence of the loading rate on the results. The tests were carried out in controlled laboratory conditions, with constant ambient temperature of 23°C.

In the first phase of the experimental program, 6 non-aged specimens from material 1 were subjected to tensile testing with different loading rates: 10 mm/min, 25 mm/min, 50 mm/min, 100 mm/min, 300 mm/min, respectively 500 mm/min. The obtained stress-strain curves are given in Figure 5.

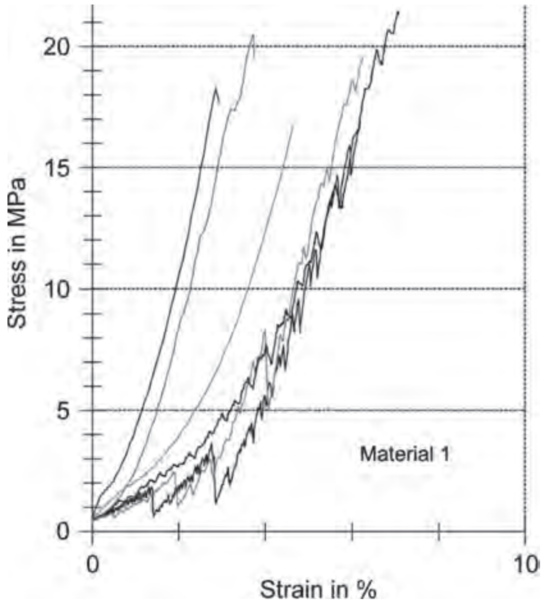

Figure 5. Stress-strain curves of 6 specimens extracted from material 1, with loading rates between 10-500 mm/min.

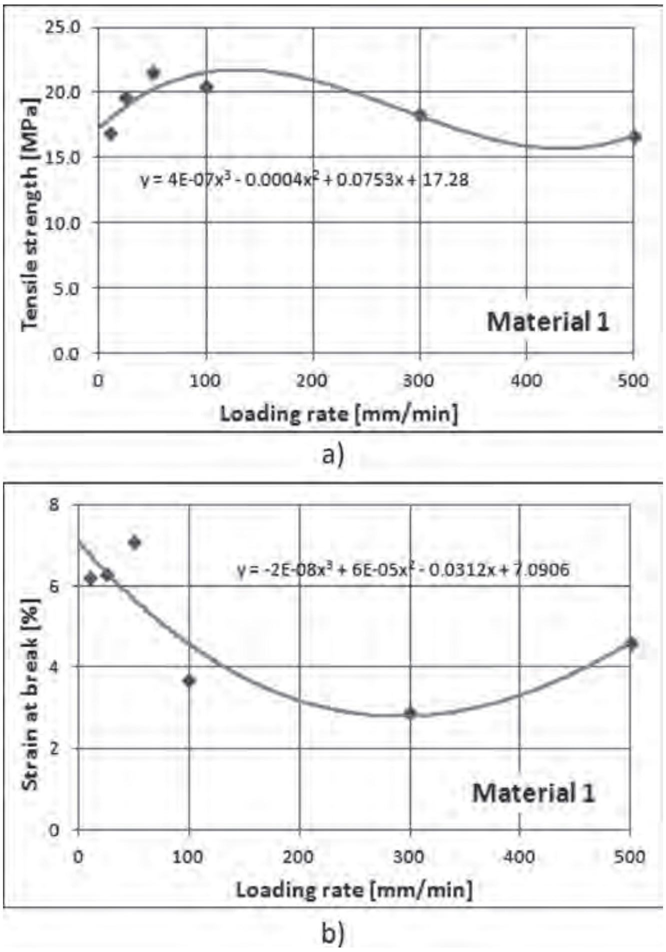

Figure 6. Variation of tensile strength (a) and strain at break (b) as functions of loading rate, in case of material 1.

The main mechanical properties were extracted from the stress-strain curves and they are given in Table 2, while the variation of the tensile strength and the strain at break as functions of the loading rate are plotted in Figure 6.

Based on these results, the loading rate of 100 mm/min has been selected as reference for the tensile tests of the aged specimen. Figure 7 presents the stress-strain curves of 2 specimens extracted from material 1, one in initial non-aged state, while the other one having previously suffered a 4 hour exposure UV aging.

Table 2. Obtained mechanical properties for material 1, as functions of the tensile loading rate,

Loading rate v [mm/min]	Tensile strength σ_M [MPa]	Young modulus E_t [MPa]	Strain at break ε_b [%]
10	16.9	86.9	6.2
25	19.6	74.2	6.3
50	21.5	89.6	7.1
100	20.5	117.0	3.7
300	18.3	-	2.9
500	16.7	101.0	4.6

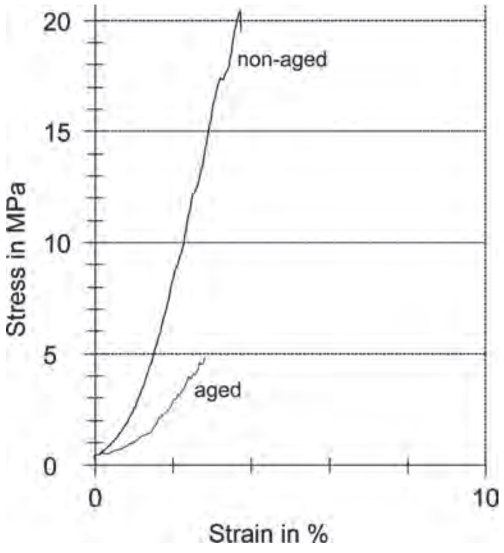

Figure 7. Stress-strain curves of one non-aged and one aged specimen, extracted from material 1, tensile tested at 100 mm/min.

The effect of the artificial aging on the mechanical properties can be clearly seen in Figure 7. The reduction of the tensile strength and the reduction of the strain at break both indicate the embrittlement of the material relative to the initial state.

The influence of the loading rate was also analyzed in case of material 2.

Three different loading rates were applied (50 mm/min, 100 mm/min, 300 mm/min) and the obtained stress-strain curves are plotted in Figure 8.

The values of the most important mechanical characteristics were extracted from the stress-strain curves and they are given in Table 3.

The variation of the tensile strength and the strain at break as functions of the loading rate is presented in Figure 9.

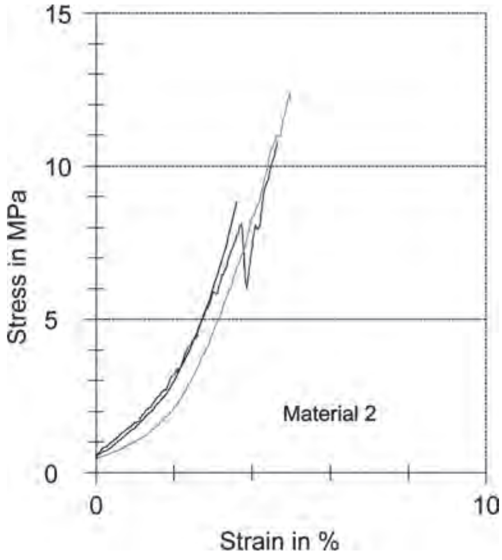

Figure 8. Stress-strain curves obtained at different speeds for three specimens extracted from material 2.

Table 3. Obtained mechanical properties for material 2, as functions of the tensile loading rate.

Loading rate v [mm/min]	Tensile strength σ_M [MPa]	Young modulus E_t [MPa]	Strain at break ε_b [%]
50	10.8	136	4.7
100	12.4	46.6	5.0
300	8.8	74.7	3.6

The variation curves of the tensile strength and strain at break are different for material 1 (Figure 6) and material 2 (Figure 9). The tensile strength during the tensile tests is higher in case of material 1 than in case of material 2, but both curves tend to have a maximum value between 100 and 200 mm/min loading rate. In case of the strain at break, the variation curves of the two materials are completely different: the strain at break of material 1 has a minimum around 300 mm/min while the strain at break of material 2 has a maximum around 150 mm/min.

As previously mentioned, these results are preliminary and need to be backed up by further tests in case of both materials. Albeit the above, the general conclusion can be drawn that the two materials have different tensile behavior which needs to be further analyzed.

4. Conclusions

A preliminary experimental program was realized in this paper in order to determine the influence of tensile loading rate and artificial aging with controlled UV radiation on the mechanical properties of Vinnol-based polymeric membranes used in manufacturing batteries.

Two different materials were tested and it is concluded that their mechanical properties show different variations depending on the tensile loading rate. Furthermore, a significant decrease in the mechanical properties was registered when the artificially aged material was subjected to tensile testing, proving the material's high reactivity to UV radiation.

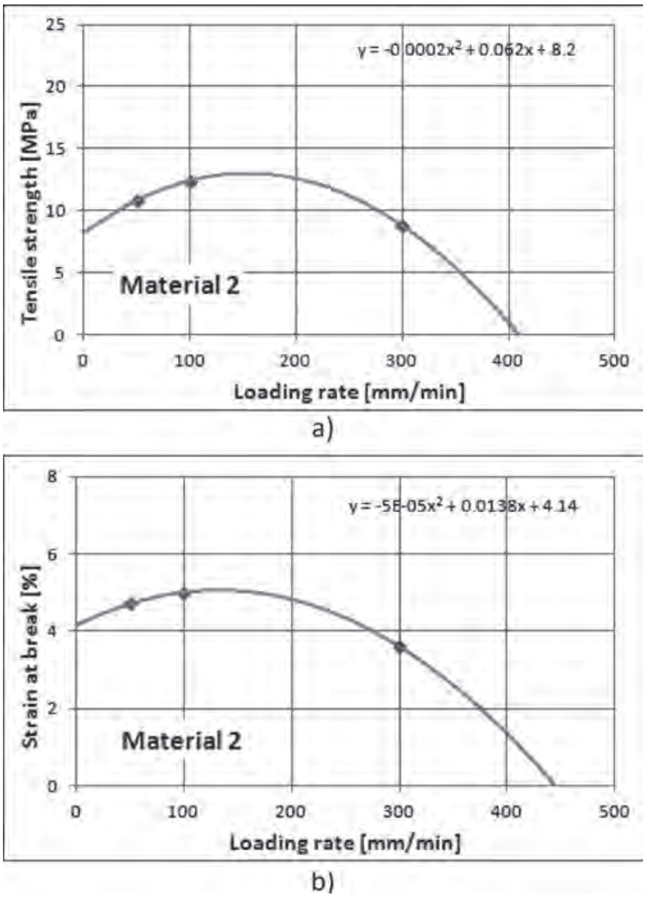

Figure 9. Variation of tensile strength (a) and strain at break (b) as functions of loading rate, in case of material 2.

The obtained preliminary results justify, on one hand the continuous development of the presented tensile testing and artificial aging equipment, and on the other hand the continuation of the experimental efforts to ensure a better mechanical characterization of polymeric membranes used in special applications.

Acknowledgement

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OVER 50 YEARS DEDICATED TO THE ROMANIAN RESEARCH

Professor Dr. Eng. VOICU SAFTA at reaching the age of 80 years.

Prof. Dr. Eng. VOICU SAFTA was born in Cluj, on April the 6th, 1933. In 1952 he has graduated with honors from the „Frații Buzești" high school in Craiova, and in 1957 with highest honors from the Polytechnic Institute of Timişoara, Mechanical Engineering Faculty, Hydraulic Machines specialization. In 1970 he has been awarded the title of doctor in engineering by defending the thesis "Behavior of low carbon steels subjected to tri-axial inhomogeneous tensile loadings" under the guidance of Acad. Şt. Nădăşan.

Between 1957 and 1959 he worked at the "Electromotor" company in Timișoara, and during 1960-1970 at the Romanian Academy's Timișoara Base for Scientific Research, as senior scientific researcher under the supervision of Acad. Şt. Nădăşan.

Together with Traian Sălăjan, Mircea Rațiu and Mircea Hrelescu, he is the co-founder of today's National R&D Institute for Welding and Material Testing – ISIM Timișoara, which took form in 1970 after the disbandment of the Romanian Academy's Institute. In the period between 1970 and 1982, as chief of laboratory, he was in charge of the Material Testing Department at ISIM Timișoara.

Starting with 1980 he has been full professor and head of department (1980-2000) at the "Politehnica" University of Timișoara.

During the period between 1997 and 2004 he returns to the Timișoara branch of the Romanian Academy with the title of chief of laboratory, while from 2006 to 2010 he is working as scientific counselor at ISIM Timișoara.

In 1999 he has been elected as corresponding member of the Romanian Academy of Technical Sciences, and from 2004 he serves as full member. In the same year he has been elected as member of the European Academy of Sciences and Arts from Salzburg.

The rich technical-industrial activity of Prof. dr. eng. Voicu Safta is concentrated in 78 research contracts at which he participated wholeheartedly, serving as director, coordinator or as member of the research team.

While acting as chief of the research laboratory of ISIM Timișoara, he has personally coordinated the creation and installment of the biggest and most competitive material testing laboratory in Romania. This laboratory successfully carries out static and dynamic material testing, fatigue, creep and non-destructive defectoscopy up to present day.

Prof. dr. eng Voicu Safta's scientific activity has been channeled mainly in the field of material sciences. His lifetime work is impressive, containing more than 320 scientific items, from which 12 monographies, 210 published papers and 78 reports (technical memoirs) presenting results of research contracts. It is worth mentioning that he has published over 40 papers in different journals and in the volumes of international conferences, under the print of publishers such as: Pergamon Press, Elsevier, VDEh-Verlag, etc.

The preferred scientific topics of Prof. dr. eng. Voicu Safta are from the domain of material sciences and are comprised of non-destructive defectoscopy, strength of materials and material testing, in some of which he is considered to be a pioneer.

One of his most notable work in this field is entitled "Technological and strength testing of welded or soldered joints", published at Editura Sudura in 2006, covering over 360 pages. The tests for evaluating the welded joints' susceptibility to embrittlement using criteria from elastic and elasto-plastic fracture mechanics and the theory of crack growth inhibition are described for the first time in the Romanian technical literature.

From the many distinctions that were awarded in time to Prof. dr. eng. Voicu Safta, we mention:

- the "Aurel Vlaicu" prize of the Romanian Academy in 1986;
- Honorary Professor of the "Transilvania" University of Brașov in 2004;
- selection in the „Top 100 Scientists" by the University of Cambridge in 2011;
- introduction in the „World Hall of Fame" by the American Biographical Institute in 2012.

The team of ISIM Timişoara deeply appreciates the activity of Prof. dr. eng. Voicu Safta and wished him long lasting health and happiness.

On the anniversary of this venerable age, in the name of the colleagues at ISIM, we wish Professor Safta new successes in life and the traditional

"La mulți ani!"

Associate Professor Dr. Eng. Doru Romulus Pascu,
Corresponding member of the Romanian Academy
of Technical Sciences

Dr. Eng. Alin Constantin Murariu
General Manager of ISIM Timişoara