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EFFECT OF ALKALINE SOLUTIONS ON THE TENSILE PROPERTIES OF GLASS-POLYESTER PIPES

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Construction materials, traditionally used in process equipment, are today successfully replaced by composite materials. Hence, many pipes are made of these materials. The subject of this study was the influence of liquids on the state of stresses and tensile strengths in the longitudinal and circumferential direction of glass-polyester pipes of a definite structure and known fabrication process. These analyses are of great importance for the use of glass-polyester pipes in the chemical industry.

The tensile properties (the ultimate tensile strength and the modulus of elasticity) were tested and determined for specimens cut out of the pipes; flat specimens for the tensile properties in the longitudinal direction and ring specimens for the tensile properties in the circumferential direction. First, the tension test was performed on virgin samples (without the influence of any liquid), to obtain knowledge about the original tensile properties of the material composite studied. Subsequently, the specimens were soaked in alkaline solutions: sodium hydroxide (strong alkali) and ammonium hydroxide (weak alkali). These solutions were selected because of their considerable difference in pH values. The specimens and rings were left for 3, 10, 30 and 60 days in each liquid at room temperature. Then, the samples were tested on tension by the standard testing procedure. A comparison of the obtained results was made based on the pH values of the aggressive media in which the examined material had been soaked, as well as based on the original tensile properties and the number of days of treatment. Micromechanical analyses of sample breakage helped in the elucidation of the influence of the liquids on the structure of the composite pipe and enabled models and mechanisms that produced the change of strength to be proposed.

KEY WORDS: glass-polyester composite pipe, tension test, ring test, influence of liquids on the tensile mechanical properties, micromechanical analysis

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INTRODUCTION

The intensive development of polymer engineering, as well as the capabilities of polymers in combination with other materials to form new synthetic structures of improved mechanical properties, has led to a real expansion in the application of composite materials, which was followed by a continuous improvement of the technology of their manufacture. Composite materials have a wide range of applications thanks to their good properties under loading conditions, specific mechanisms of crack initiation and growth and capabilities for the accumulation of energy, and represent the greatest competitors to classical construction materials. Their advantages lie in their relatively small mass, good strength/mass and stiffness/mass balances, good static and dynamic properties, good resistance to corrosion and simplified fabrication and short mounting time.

All the stated advantages led to composite pipes being very much used today in the chemical industry, building, infrastructure and war techniques. An important application of pipes made of composites glass fibres - polyester resin is in the chemical industry. Pipes made for this use are in exploitation under the influence of static and dynamic loads. Considering the conditions of possible exploitation in the chemical industry, the objective of this study was to predict the useful life of such pipes and the determination of the influence of the fluids transported through glass-polyester composite pipes on the tensile properties of pipes in the longitudinal and circumferential directions.

The different structures of composite pipes result in different distributions of stresses and strains, and with it the development of failure after the initiation of the first cracks. In the last few decades, many researchers have considered these points. Special attention was always paid to the determination of the stress conditions in the longitudinal and circumferential directions. The best results for pipes were obtained by the radial cut method and the ring test. The radial-cut method is a simple, inexpensive, and approximate method for determining the residual stress state in a cylindrical part. In this method, the ring is cut in the radial direction to release the residual stress. Measurements of the subsequent deformation of the ring in the circumferential and radial directions givean indication of the magnitude of the stresses present prior to the cut. Aleong and Munro (1) used this method to determine the residual stresses in radially-thick, filament-wound composite rings. In their experiments, the rings were cut along the radius, and the radial and circumferential strains in the rings were measured using resistive gauges. The authors performed the radial cut method on eight E/XA-S Grafil carbon and three S2-glass fibre epoxy matrix composite rings with outside to inside diameter ratios of approximately 1.22 to 1.30. The aim of another study (2) was to characterise the influence of the structure on the mechanical performance of cylindrical structures under various loadings. The specimens studied were glass/epoxy tubes with a $[\pm 55°]_6$ lay-up. All manufacturing parameters were kept constant except for the winding pattern. The quality of the fabrication was assessed by strict monitoring of the geometry and the microstructure of the tubes. The tests performed on the specimens consisted in progressively repeated loadings, aimed at characterising the damage behaviour under various loading conditions. Micro-structural analyses, mechanical behaviour and damage mechanisms of composite tubes under pure tensile loading were presented by Bai et al. (3). The test materials were ±55° filament-wound glass-fibre/epoxy-resin tubes.

In another study (4), the effects of hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acids (H_3PO_4) on the physical and mechanical properties of glass fibre-polyester composite pipes internally lined with C glass were investigated. Specimens cut from the pipes were immersed for various periods, *i.e.*, 30, 60, and 90 days, in 20 % acid solutions at room temperature and 100 °C. Furthermore, the effects of conc. sulphuric acid and the sequential lay-up of glass fibre reinforcements on the diffusion behaviour of glass fibre - epoxy composite laminates were studied in (5). Experimental results for the direct effect of an acidic stress environment on the stress intensity factor of woven E-glass fibre-reinforced bisphenol–vinylester resin, woven E-glass fibre-reinforced bisphenol–epoxy resin and woven C-glass fibre-reinforced bisphenol–vinylester resin composites were presented in (6). The influence of different conditions on the mechanical properties of coir fibre reinforced polymer composites as well as glass fibre-reinforced polymer composites were analyzed and compared in (7). Degradation studies were performed in different solutions, such as 10 % NaOH, 1M HCl, and 10 % NaCl, and also in water. The effects of these liquids on the mechanical properties of the composites were studied in detail. The deterioration of the mechanical properties of the composites by environmental weathering was also studied.

The subject of this study was the influence of liquids on the state of stresses and tensile strengths in the longitudinal and circumferential direction of glass-polyester pipes of a definite structure and known fabrication process. These analyses are of great importance for the use of glass-polyester pipes in the chemical industry.

EXPERIMENTAL

Composite pipes were fabricated under laboratory conditions. The properties of the components of the investigated glass-polyester pipes were given in the official certificates from the producers. The producers of the glass fibres, A.D. “OHIS” and “Vidoe Smilevski-Bato” from Gostivar (FYR Macedonia), certified “E” glass with 1 % of alkali (Tables 1 and 2). Thermo-reactive polyester resin produced by “Color” (Medvode, Slovenia) was used as the matrix. A certificate was given for “COLPOLY 7510” for the type: UP/SOM, a highly reactive, low-viscosity polyester based on orthophthalic acid in standard glycol (Table 3).

Table 1. Structural components of "E"- glass

Structural component	**Percentage (%)**
Silicon(IV) oxide	52 – 56
Aluminium(III) oxide	12 – 16
Boron(III) oxide	5 – 10
Sodium(I) oxide, Potassium(I) oxide	0 – 2
Magnesium(II) oxide	0 – 5
Calcium(II) oxide	16 – 25
Titanium(IV) oxide	0 – 1.5
Iron(III) oxide	0 – 0.8
Iron	0 – 1

Table 2. Physical properties of "E"-glass fibres

Properties		
Specific weight	g/cm^3	2.54
Ultimate tensile strength	MPa	2400
Modulus of elasticity	GPa	73
Extension	%	3.3
Thermal expansion	$10^{-6}\ K^{-1}$	5
Thermal conductivity	W/mK	1
Dielectrical constant	ξ	6.7
Specific electrical resistance	Ωcm	10^{14}
Moisture absorption at 20 °C	%	0.1

Table 3. Catalogue properties of the polyester resin

Properties		**Specification**
Appearance		Viscous yellow liquid
Density	g/cm^3	1.11–1.12
Viscosity at 25 ºC	mPas	220 – 320
Specific weight	g/cm^3	1.19–1.21
Ultimate tensile strength	MPa	75 – 85
Modulus of elasticity	GPa	3.6
Extension	%	2 – 3
Impact toughness /Charpy/	10 – 15	KJ/m^2

The pipes were made by the "Filament Winding" method, with the angle of the glass fibres reinforcement being $[90°]_2[\pm 55°]_4[90°]_4$. Specimens for the tests (flat specimens and rings) were cut from the samples of pipes according to the standard dimensions; the flat specimens 250 x 25 (20g age area) x 3.5 mm and the rings ∅70 x 35 x 3.5 mm (average values of all the tested samples). The cut was realised on a machine type NC-2010 (Nr 95110, Ar 001), with diamond-tip tools and a moving speed chosen to reduce the heat in the sample.

Testing on the flat test specimens was performed on a servo-hydraulic testing machine SCHENCK TREBEL RM 100, and the ring test specimens on a servo-hydraulic testing machine INSTRON 1332, using an INSTRON FAST TRACK 80800 controller and hydraulic jaws. The testing was defined by the standard ASTM D 3039 (8). Loading was registered with a measuring cell of capacity 100 kN. Displacements were measured using a double extensometer HOTTINGER DD1.

The tensile properties (the ultimate tensile strength and the modulus of elasticity) were first determined for specimens cut out of the pipes that were not placed in any liquid (six flat specimens, marked F-WS and six rings, marked R-WS), and subsequently for specimens that were placed into an aggressive medium for the required number of days (three flat specimens and rings for each test). The samples were exposed to the liquids on the inner side of the pipes (pipes were filled with liquids). The solutions were selected

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because of their considerable difference in pH value; hence, the results obtained for the tensile properties could be compared related to the pH value of the medium in which the examined specimens were previously placed. The selected solutions were 25% alkaline solutions of sodium hydroxide (strong alkali, pH=14), ammonium hydroxide (weak alkali, pH=12). The pH values of the applied solutions were measured using a pH-meter, type TESTO 206-pH1 (TESTO, USA).

The specimens and rings were kept in each liquid at room temperature for 3, 10, 30 and 60 days. Afterwards, they were washed with clean water, dried at room temperature for 2 hours, and their tensile properties were measured.

The obtained tension test results were compared based on the pH value of the aggressive medium the examined materials were soaked in, and based on the number of days they were kept in the specified liquids.

RESULTS AND DISCUSSION

Stress-strain (σ-ε) diagrams were plotted for all tests. As an example, the stress-strain (σ-ε) diagrams for virgin samples (without soaking), obtained from tension tests in the longitudinal direction (flat samples F-WS) and in the circumferential direction (ring samples R-WS), are presented in Fig. 1.

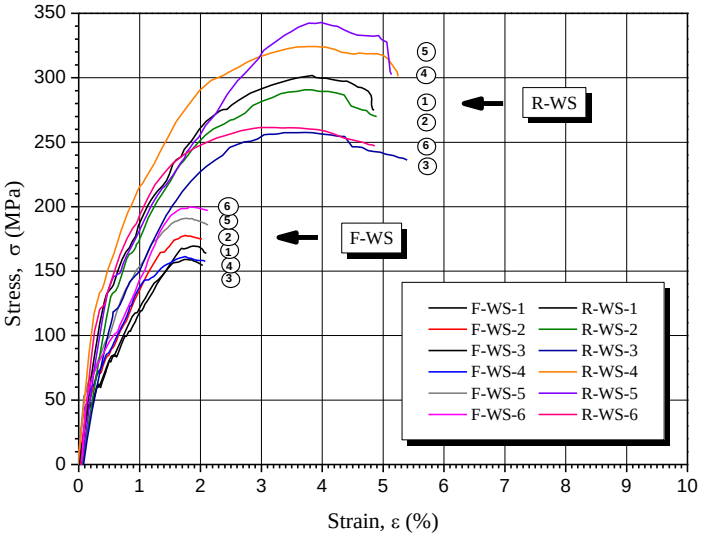

Figure 1. Comparison of the stress-strain (σ–ε) curves for the two tests of the virgin samples

The ultimate tensile strength was calculated for the flat test specimens (longitudinal direction) and for the rings (circumferential direction) according to Equations [1] and [2], respectively.

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$$R_{\mathrm{m,l}} = \frac{P_{\max}}{b_{\mathrm{l}} \cdot d} \quad [1]$$

$$R_{\mathrm{m,c}} = \frac{P_{\max}}{2 \cdot b_{\mathrm{c}} \cdot d} \quad [2]$$

where: $R_{\mathrm{m,l}}$(MPa), is the ultimate tensile strength in the longitudinal direction; $R_{\mathrm{m,c}}$(MPa), is the ultimate tensile strength in the circumferential direction (MPa); $P_{\max}$(kN), is the maximal applied load force; b_{l}(mm), is the width of the flat test specimen; b_{c}(mm), is the width of the ring test specimen and d(mm), is the thickness of test specimen (flat specimens or rings) - subscripts l and c stand for longitudinal and circumferential direction in the remainder of the text.

The modulus of elasticity, $E_{\mathrm{l,c}}$ (GPa), was calculated by linear regression of the rectilinear parts of the force – elongation ($\Delta P / \Delta l$) curves, obtained directly from the testing machine.

All the tension test results for the flat and ring samples are given in Tables 4 and 5 (for virgin samples and samples exposed to liquids for a certain number of days), and the deviations of the ultimate tensile strength and the modulus of elasticity after soaking from the values for the virgin samples are shown in Figs. 2 and 3, respectively.

Table 4. Average values of the tension test results for the flat samples (longitudinal direction)

Sample	pH	Number of days	Ultimate tensile strength $R_{\mathrm{m,l,av}}$ (MPa)	Deviation (%)	Modulus of elasticity $E_{\mathrm{l,av}}$ (GPa)	Deviation (%)
Without liquid	–	–	176.4	–	20.73	–
F-NaOH	14	3	167.9	4.82	20.33	1.93
		10	156.3	11.40	19.64	5.26
		30	132.4	24.94	19.03	8.20
		60	128.8	26.98	18.94	8.63
F-NH_4OH	12	3	170.4	3.40	20.48	1.21
		10	157.3	10.83	19.93	3.86
		30	135.5	23.18	19.58	5.55
		60	130.7	25.91	19.54	5.74

Table5. Average values of the tension test results for the ring samples (circumferential direction)

Sample	pH	Number of days	Ultimate tensile strength $R_{m,c,av}$ (MPa)	Deviation (%)	Modulus of elasticity $E_{c,av}$ (GPa)	Deviation (%)
Without liquid		–	296.4		31.20	
R-NaOH	14	3	289.8	2.22	30.94	0.58
		10	278.4	6.07	30.31	2.60
		30	266.7	10.02	29.16	6.30
		60	265.4	10.45	28.98	6.87
R-NH_4OH	12	3	290.9	1.85	31.02	0.32
		10	281.4	5.06	30.63	1.57
		30	273.5	7.72	29.57	4.98
		60	267.2	9.85	29.52	5.14

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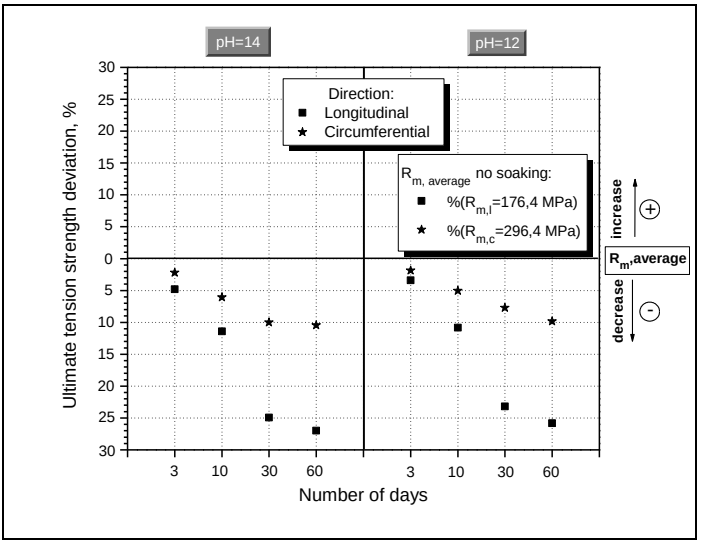

Figure 2. Ultimate tensile strength deviation for the samples exposed to the liquids for a certain numbers of days

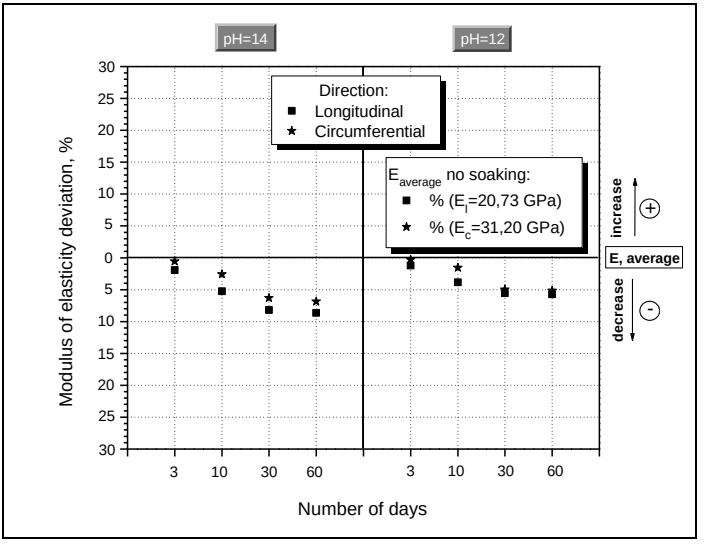

Figure 3. Modulus of elasticity deviation for the samples exposed to the liquids for a certain numbers of days

The treatment of the samples with alkaline solutions led to a decrease in the parameters of their tensile properties (ultimate tensile strength and modulus of elasticity),

which in both cases were higher in the longitudinal direction. It can be seen that with increase in the pH value of the alkaline solution, their influence on the ultimate tensile strength increased, hence, the deviations from the average values measured for the untreated samples were higher.

Based on this analysis, it can be concluded that the changes in the strength parameters in alkaline solutions are proportional to the treatment duration (number of days in the liquid). Besides, it is obvious that in the period of 30 to 60 days, the values of the ultimate tensile strength and modulus of elasticity changed so little that it can be concluded that after 60 days no further changes in the values of these properties are to be expected.

Also, it should be emphasised that the deviations of the modulus of elasticity are much smaller than those of the ultimate tensile strength of the samples.

All these conclusions can be related to the fact that the matrix is ageing due to the action of the liquids on it. In this way, *i.e.*, with a decrease in the quantity of the resin, there was an increase in the number of micro-cracks in the pipes and a decrease of fibre-matrix debonding where the micro-cracks were initiated and a large strain concentration area was formed. The loss of resin went from the inner surface of the pipe, because that side was exposed to the liquids. It is assumed that the fibres, considering their nature, were not drastically damaged. Their specific properties lead to different models of the initiation and propagation of crack. This is very important because of the pipe structure, $[90°]_2[\pm 55°]_4[90°]_4$, which produced a different distribution of strains in the layers, and hence the fibres were not loaded to the same extent.

Fibres that broke earlier (Fig. 4) caused a disturbance in the crack zone, that is, local shear stresses appeared with the broken fibres.

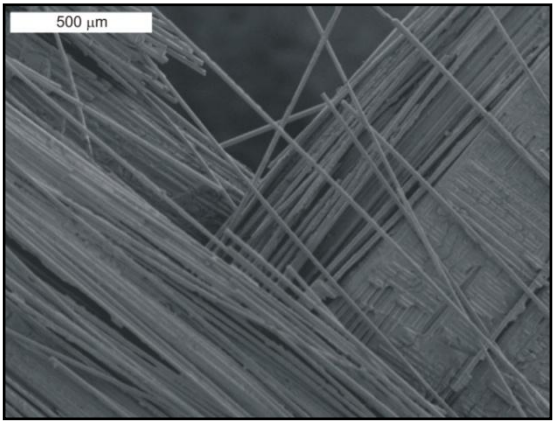

Figure 4. SEM micrograph of the initially broken fibres

Information concerning the important contribution of the shear components of strain could be obtained from the stress-strain (σ-ε) curves, which, unlike those of most composites, were not linear. With increasing load, cracking in the fibre-matrix debonding occur-

red, and the cracks made by breaking of the fibres grew along the neighbouring fibres and caused macro-cracks. The result was local cracking of the fibres and whole layers (Fig. 5), but the composite still carried the outer load. With increasing loading, the local failures spread and the final crack appeared with a strong acoustic effect, because ofthe simultaneous cracking of a large number of fibres. The fibres did not crack according to exactly specified levels, but chaotically in all directions.

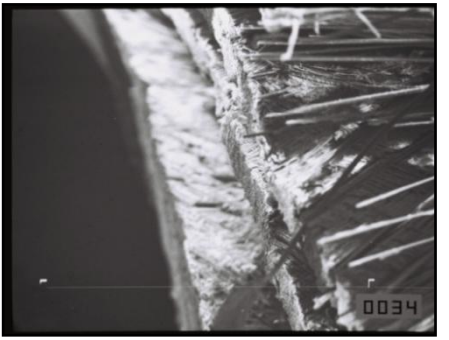

Figure 5. SEM micrograph of a macro-crack in a flat specimen

CONCLUSIONS

The aim of this study was the determination of the strength and stiffness of glass-polyester pipes and, because of their possible application in the chemical industry, the influence of alkaline solutions on the changes of these values. These properties were determined on flat test specimens and rings cut out from the pipes. The tests were first conducted on specimens cut out of the pipes that were not placed in any liquid, and also after subjecting the pipes to the influence of 25% solutions of sodium hydroxide (strong alkali, pH=14) and ammonium hydroxide (weak alkali, pH=12). Tensile properties of untreated and treated samples after 3, 10, 30 and 60 days of exposure were determined.

Considering the alkaline solutions, the obtained results can lead to the conclusion that they caused a decrease of the tensile properties. Besides, their influence was higher with increasing alkalinity. This is completely in accordance with the known fact that alkaline solutions (sodium hydroxide and ammonium hydroxide) are highly corrosive. During the treatment of samples, they coated the inner surfaces and went deeper into the samples through the micro-cracks and other surface damages which existed after fabrication and shrinkage of the material. The greatest influence was on the fibre matrix connection, and this influence spread and directly weakened the carrying capacity of the material.

All the mentioned conclusions are very important considering the possible time of transport of these fluids and life time prediction of composite pipes. However, bearing in mind that the strength and stiffness attained certain, almost constant, values after 60 days and that there were no cracks on the outer surface, it may be assumed that these values can be taken as relevant for the calculation, and in that case, the pipelines can be exploited for longer periods.

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УТИЦАЈ БАЗНИХ РАСТВОРА НА ЗАТЕЗНЕ КАРАКТЕРИСТИКЕ СТАКЛО-ПОЛИЕСТЕР КОМПОЗИТНИХ ЦЕВИ

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Конструкциони материјали традиционално коришћени у процесној опреми су данас успешно замењени композитним материјалима, тако да су и многе цеви израђене од ових материјала. Утицај базних течности на стање напона и затезне чврстоће у уздужном и обимном правцу стакло-полиестер композитних цеви је тема овог рада. Цеви су дефинисане структуре и познатог процеса производње. Ове анализе су од великог значаја за коришћење стакло-полиестер цеви у хемијској индустрији.

Затезне особине (затезна чврстоћа и модул еластичности) су експериментално испитиване на исеченим узорцима; равни узорци у удужном правцу, а узорци у

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облику прстена у обимном правцу. Испитивање је прво извођено на узорцима који нису били изложени утицају раствора база да би се дошло до сазнања о првобитним затезним својствима испитиваних композитних материјала. Након тога, узорци су стављени у растворе база натријум-хидроксида (јака база, pH=14) и амонијум хидроксида (слаба база, pH=12) 3, 10, 30 и 60 дана на собној температури. Након тога су испитивани на затезање према стандардној процедури. Поређење добијених резултата је изведено на основу pH вредности раствора и броја дана излагања растворима база, а на основу оригиналних затезних особина. Микромеханичка анализа се изводила у односу на фотографије са скенинг елоктронског микроскопа са преломних површина чиме се дошло до података о утицају раствора база на структуру композитних цеви и моделе и механизме који су доводили до промене затезних својстава.

Кључне речи: стакло-полиестер композитне цеви, затезне особине, утицај база на затезне особине, микромеханичка анализа

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