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INFLUENCE OF MONTMORILLONITE NANOPARTICLES ON THERMAL AND MECHANICAL PROPERTIES OF CARBON-CARBON HYBRID COMPOSITES BASED ON PHENOLIC-FORMALDEHYDE RESIN

In this study, the effect of the addition of K-10 montmorillonite (MMT) nanoparticles on the mechanical and thermal properties of carbon-carbon composites were investigated. The composites were obtained using self-made prepregs with plain and twill 2/2, 600 g/m^2 carbon fabric and phenolic-formaldehyde resin. The composites were obtained by the hot pressing technique, followed by carbonization in an inert argon atmosphere. Modified samples of the composites contained 5 wt.% MMT, homogenously dispersed in the ceramic carbon matrix. The mechanical properties, thermal conductivity and thermal capacity of the composites were determined. Raman spectroscopy and Fourier transform infrared spectroscopy were used to investigate the carbon matrix composition and structure. The results show that the addition of MMT nanoparticles increased Young's modulus by 48%, Kirchoff's modulus by 80.2%, but did not change the interlaminar shear strength nor the bending strength. The MMT influenced the carbon microstructure, changed the I_D/I_G Raman ratios, as well as the matrix composition. The addition of MMT also increased the low temperature regime of thermal conductivity and diffusivity of the samples.

Keywords: thermal properties, mechanical properties, carbon matrix composite, montmorillonite, nanocomposite

INTRODUCTION

Interest in carbon-based materials is caused by the wide range of their properties that differ significantly between each other. Carbon fiber reinforced carbon (carbon-carbon composites) possesses extremely good mechanical properties and very high thermal conductivity [1].

Tailoring the thermal conductivity of carbons is an important issue playing a major role in the wide scope of various applications [2-6]. The high thermal conductivity of carbon materials is particularly desired in all applications which require materials capable of transferring large amounts of energy and are highly resistant to thermal stresses (i.e. electrodes for steel and aluminum smelting). Tailored thermal conductivity is also needed in various types of protective coatings, which need to have strictly matched conductivity with the protected material in order to reduce the thermal stresses [2]. Nevertheless, some applications require the thermal conductivity to be as low as possible [3]. To achieve such a goal and maintain satisfying mechanical properties, an amorphous carbon can be used as the matrix [4]. Reducing the thermal conductivity of a material plays a major role, e.g. in thermoelectric generators where its efficiency directly depends on it [5]. Further engineering of properties can be achieved by introducing additives to the material.

Nonetheless, there is still room for improvement in the field of carbon-carbon composites. One particular idea is the addition of nanoadditives to the ceramic matrix, which changes the overall mechanical, thermal, and electrical properties of the material [7]. Policandriotes and Filip showed how selected nanoadditives influence the friction and wear behavior of carbon-carbon composites dedicated for aircraft brake components [8]. They found that nanoadditives such as Si, SiC and single-walled carbon nanotubes can significantly lower oxidative and abrasive wear. An interesting approach was proposed also by Stoch et al. [9]. In their paper, they reported how multilayer ceramic coatings produced from different sols like silica, alumina and silica-alumina improved the low temperature (~ 600°C) oxidation resistance of carbon-carbon systems. Furthermore, the strong influence of an addition of SiC particles on the creep behavior of monolithic Al_2O_3 was revealed by Zhen-Yan Deng et al. [10].

Montmorillonite (MMT) is a natural, layered clay mineral belonging to the smectite group. It shows very interesting properties as nanoreinforcement and is widely used, especially in polymer matrix composites [11-13]. In this type of materials, MMT is often chemically modified, i.e. using the cation-exchange method in order to match its properties to the polymer

material [11]. Its addition can significantly reduce the ablation linear rate and change the thermal conductivity [12, 13] as well as enhance the tensile strength [12]. MMT particles are also well known for their gas and liquid adsorption properties in addition to catalytic capabilities [13].

Interest is still growing in modifying ceramic matrix composites to change their brittle behavior and fully unleash their potential, but there are still too few works describing the influence of nanoadditives on ceramic matrix composites, especially in carbon-carbon systems. In this work, we present the results of a study on how the addition of MMT influences the thermal and mechanical properties of carbon-carbon composites, which could become a starting point for more advanced research and development paths.

EXPERIMENTAL

Materials and preparation of composites

Samples of carbon-carbon composites were prepared from self-made prepregs using the hot pressing technique and subsequent carbonization of the obtained moldings. The first step was to prepare a 50% phenolic-formaldehyde resin (Nowolak© MR) solution in ethanol. Using the prepared solution, hand-cut carbon fiber fabric material (Rymatex, Poland; 600 g/m^2 and fibers 12k) was soaked in it and then left for 24 h in a dryer at 60°C, in order to evaporate the alcohol solvent. After that, prepregs were obtained. In total eight layers of prepregs were used to prepare one composite – 4 plain fabric and 4 twill 2/2 fabric arranged in turn in a stainless-steel mold (Fig. 1). Such a system was subjected to hot uniaxial pressing at 160°C. The composites obtained in that way were carbonized at 1000°C in an inert argon atmosphere (heating rate 1°C/min). The pyrolyzed samples were impregnated with the resin solution and once more subjected to the process of carbonization.

Modified samples of the composites contained 5% K-10 montmorillonite nanoparticles (Sigma-Aldrich; specific surface area of 250 m^2/g). These samples were prepared in the exactly same way, but at the stage of preparation of resin solution, the montmorillonite powder was added and dispersed in the solution using a hand sonicator tip. It allowed us to prevent agglomeration of the montmorillonite before preparing the prepregs. In this paper, the modified samples will be denoted with the abbreviation C/C5%.

Measurements of mechanical properties

Flexural strength testing was conducted using a Zwick 1435 universal testing machine. A standard three-point bending configuration was chosen with the support span set at 50 mm. The load was applied at the constant feed rate of 2.0 mm/min. Four specimens of each type of composite were evaluated. The test was performed with a respect to the ASTM D 7264 standard. Interlaminar shear strength (ILSS) tests were carried out using the same machine, but changing the support span to 20 mm. The specimens were prepared and the tests were conducted according to the ASTM D 2344 standard.

Structural characterization

Raman spectroscopy was performed using a Witec Alpha 300 M+, 488 nm excitation wavelength, 600 grooves/mm grating, 100 x objective, acquisition time of 30 s and four accumulations (point measurements). The same parameters were used to measure the depth profile of the materials up to 1.1 μm along the Z axis with a 0.1 μm step. The I_D/I_G parameter was used to estimate the structural ordering of the carbon phase. The Cançado equation was used to estimate the mean lateral sizes of the graphitic crystallites [14]

$$L_a = (2.4 \cdot 10^{-10}) \cdot \lambda_l^4 \cdot (I_D/I_G)^{-1} \qquad (1)$$

where λ_l is the wavelength of the excitation source, I_D and I_G are integral intensities of the Raman *G*- and *D*-bands.

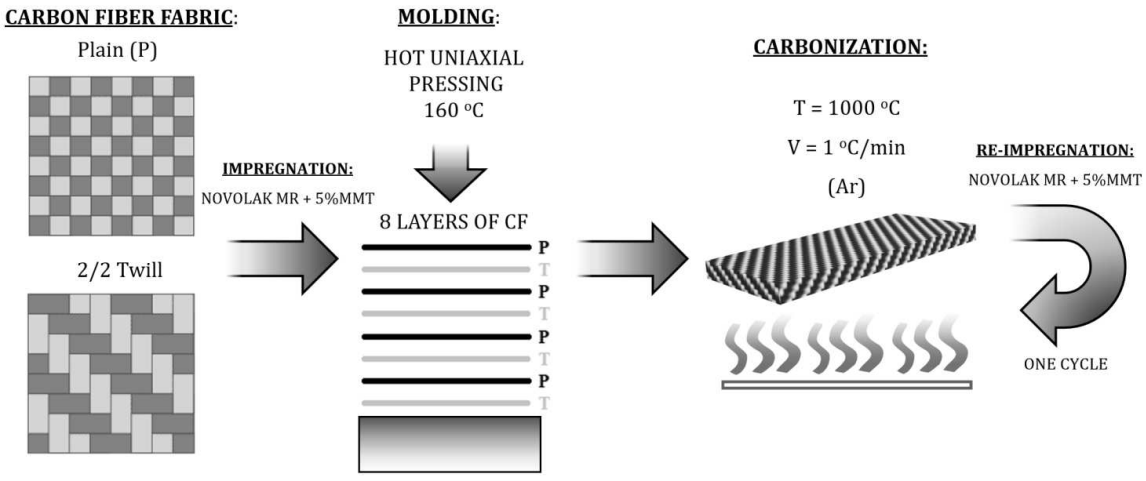

Fig. 1. Schematic diagram of composite fabrication

The chemical composition of the materials was evaluated by the Fourier transform infrared spectroscopy technique using a BioRad Excalibur FTS 3000, and DG Lab WinIR software (64 scans, resolution 4 cm^{-1}, range 4000-400 cm^{-1}, air).

Measurements of thermal properties

The thermal diffusivity and specific heat capacity of the samples were measured by the laser flash analysis (LFA) method. The specimens were in the form of thin discs (d = 13 mm, h = 2.5 mm) cut out of the original composites. Prior to measurement, the specimens were coated with a thin layer of graphite to ensure that the energy flux is not reflected from the surface. The measurement was conducted in the inert atmosphere of argon. Measuring points were registered every 50°C, ranging from 50 to 500°C. The thermal conductivity of the samples was calculated using Formula (2):

$$\lambda(T) = \alpha(T) \cdot C_p(T) \cdot \rho(T) \qquad (2)$$

where λ is thermal conductivity, α is thermal diffusivity, C_p is specific heat capacity and ρ is the density of the sample.

RESULTS AND DISCUSSION

Mechanical properties

The performed measurements show that the addition of montmorillonite caused an average 48% increase in Young's modulus and a 15% decrease in the maximum elongation as compared to the reference sample. The shear modulus was increased by 80.2%. The modification of the composites with the nanoparticles did not cause significant changes in the maximum flexural strength nor ILSS. In the case of both types of materials, the stress-strain curves have a quasi-tensile shape. All the data is summarized in Table 1.

TABLE 1. **Summarized results of mechanical testing**

Sample	Young's modulus	Strength (flexural)	Shear modulus	Strength (ILSS)
	[GPa]	[MPa]	[GPa]	[MPa]
C/C5%	26.81 ± 6.67	94.55 ± 9.45	2.09 ± 0.63	60.85 ± 8.80
Reference	18.13 ± 3.72	94.49 ± 5.52	1.16 ± 0.26	62.85 ± 1.14
Difference [%]	47.9	0.1	80.2	- 3.2

The results of the microstructural observations of the fracture of the C/C5% sample and the corresponding EDS spectra are shown in Figure 2a and 2b, respectively. One can observe an increased aluminum content (coming from the MMT) in the carbon matrix and on the pulled-out fibers, confirming the presence of well-dispersed MMT nanoparticles.

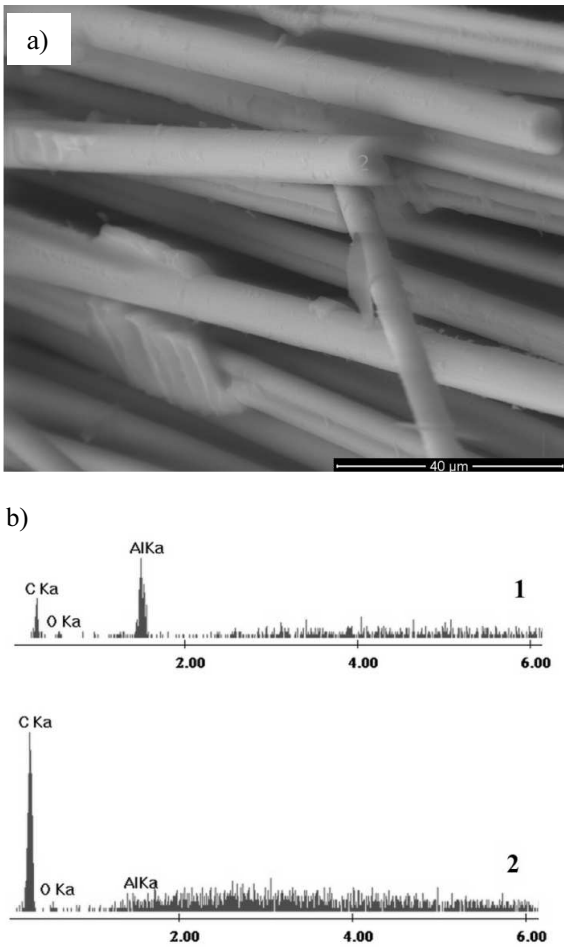

Fig. 2. SEM micrograph of fracture of composite modified with MMT (a), EDS spectra corresponding to points marked on image (b)

Nanoadditives can exert various effects on the final properties of composites – they can inhibit cracking by promoting the fiber pull-out mechanism, stress shielding or changing the strength of the bonding on the matrix-fiber interface [15, 16]. For example, Shen et al. demonstrated that carbon nanotubes electrophoretically deposited directly on carbon fibers can change the fiber-matrix interfacial strength [16]. In this work, such an accordance was not observed, which suggests that the addition of montmorillonite to the carbon-carbon system exerted rather a weak impact on the interfacial strength between the fiber and matrix. This is in opposition to the conclusion obtained for carbon nanotubes [17] and silica nanoparticles [18], where such a dependence can be observed. Nonetheless, the presence of the montmorillonite nanoplatelets in the carbon matrix influenced the elastic properties of the composites. These properties, in the case of carbon materials are dependent on the ability of cracks to propagate through the brittle matrix [18], which suggests that the addition of montmorillonite reduced this phenomenon. The reasons for the observed behavior could be as follows:

1) The montmorillonite nanoparticles probably worked as centers of nucleation for the crystallization of a turbostratic phase during carbonization, which affected the sizes of the crystallites (slightly smaller)

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and the microstructure of the matrix (more isotropic), causing modification of the elastic properties of the composites [19]. Also, the water released from the MMT during the applied heat treatment may have affected the process of forming the carbon matrix microstructure [20].

2) Assuming good dispersion and good interfacial adhesion between the montmorillonite and the carbon phase, the nanoparticles may have shielded the stresses occurring in the matrix, resulting in the observed increase in the stiffness of the composites.
3) During sonication of the montmorillonite with the resin solution, it may have partially intercalated through the MMT [21]. That, in turn may have influenced the final curing process, which changed the final microstructure of the material.

Structural characterization

Raman spectroscopy

Using the Raman spectroscopy technique, the effect of montmorillonite on the carbon matrix structure was investigated (Fig. 3). Two bands were observed: the D band and G band, which are characteristic for an sp^2 carbon material. The peak intensity decreased as the optical depth focus of the Raman microscope increased. The values of the ratios of the integral intensities of the D and G bands (I_D/I_G), carrying information about the structural ordering of carbon, and the L_a parameter describing the mean lateral graphitic crystallite sizes in the samples are shown in Table 2.

The band observed at 1353 cm^{-1} (1371 cm^{-1} in the case of the neat sample) is the so-called D band and it describes a disorder in sp^2 carbon materials. The band observed at 1585 cm^{-1} (1582 cm^{-1} in the case of the reference) is the so-called G band and it comes from the in-plane stretching of the single carbon-carbon bond in the graphitic lattice [22]. As the obtained results show, as MMT is present in the system, the structure order decreases, making the carbon matrix more amorphous and isotropic. That means a decrease in the mean sizes of the graphitic crystallites, and an increase in the fraction of carbon atoms in sp^3 hybridization [23]. The observed drop in the mean crystallite sizes confirms the effect of MMT on the isotropization of the carbon matrix microstructure in the investigated composites.

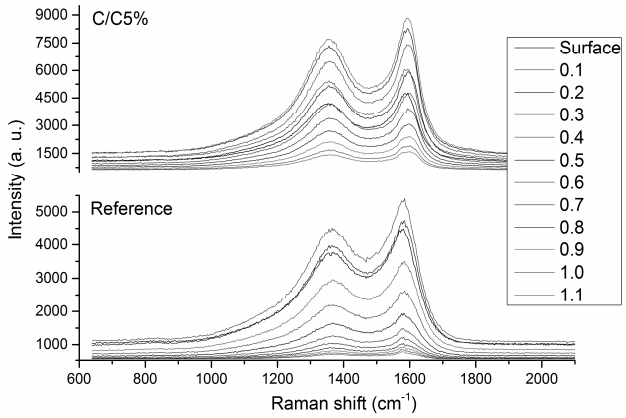

Fig. 3. Raman spectra of neat and MM-modified C-C composite samples

Fourier transform infrared spectroscopy

The FTIR spectrum of the neat sample is presented in Figure 4. and it shows a broad peak around 3450 cm^{-1} that corresponds to hydroxyl groups. Its presence originates mostly from the absorption of water from the surrounding environment by the samples. The peak at 1700 cm^{-1} comes from the C=O carbonyl groups and the peak at 1100 cm^{-1} from C–O species. These groups are related to the oxygen functionalities on the surface of the carbon, and oxygen atoms not removed during the carbonization of the phenol-formaldehyde resin. The peak at 1590 cm^{-1} is attributed to C=C bonds coming from the graphitic structure of carbon. The FTIR spectrum of the sample with the addition of MMT is very similar to the spectrum obtained for the pure composite. Although the peaks in the spectrum of the modified sample correspond to the same assignment as in the case of the pure sample, the wide, flattened peak at around 2000 cm^{-1} is not visible and there is also an additional peak at 550 cm^{-1}. The latter peak at 550 cm^{-1} is typical for montmorillonite and comes from the Si-O-Al bond [24]. All the data is summarized in Table 3.

TABLE 2. **I_D/I_G ratios for different depths of measurement**

Coefficient	Sample	Depth of measurement [μm]											
		Surf	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**
I_D/I_G [-]	Neat	1.38	1.31	1.29	1.28	1.27	1.34	1.22	1.11	1.10	1.37	1.09	1.37
	C/C5%	1.48	1.46	1.59	1.70	1.44	1.38	1.44	1.44	1.47	1.43	1.42	1.38
L_a [nm]	Neat	9.87	10.42	10.52	10.64	10.74	10.17	11.13	12.29	12.32	9.91	12.46	9.94
	C/C5%	9.19	9.34	8.54	8.02	9.45	9.89	9.48	9.48	9.27	9.54	9.57	9.87

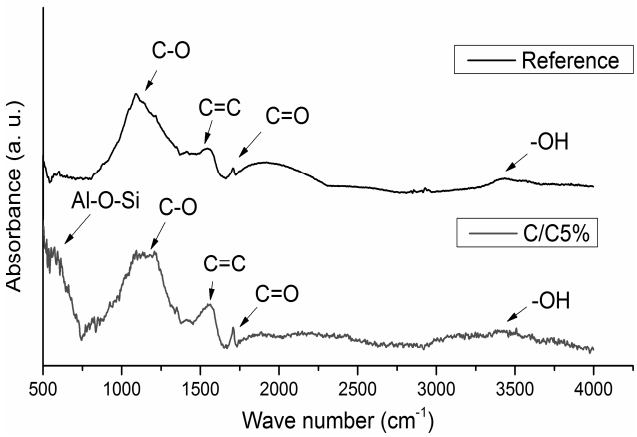

Fig. 4. FTIR spectra of obtained composites

TABLE 3. **Summarized results of FTIR spectroscopy**

Reference sample		C/C5% sample	
Wavenumber	**Bond**	**Wavenumber**	**Bond**
[cm^{-1}]	[-]	[cm^{-1}]	[-]
3250-3550	O-H	3300-3520	O-H
1700	C=O	1700	C=O
1590	C=C	1600	C=C
1100	C-O	1100-1200	C-O
		550	Al-O-Si

Thermal properties

The thermal properties of the samples were comparable to conventional carbon fiber and phenolic resin composites. The observed thermal conductivity was in the range from 0.48 to 0.70 WmK^{-1} for the pure C/C sample and from 0.67 to 0.76 WmK^{-1} for the modified sample. The results of the measurements are presented in Figure 5 (thermal diffusivity), Figure 6 (specific heat capacity) and Figure 7 (thermal conductivity).

As can be seen in Figure 5, the thermal diffusivity of both the samples decreased with temperature across the whole temperature range. The addition of MMT initially increased the thermal diffusivity of the composite and leveled off with thermal diffusivity of the pure C/C sample at around 450°C. The noted increase in thermal diffusivity most probably resulted from the increased stiffness of the modified composites, which caused enhanced phononic heat transfer through the volume of the sample. Montmorillonite also increased the specific heat capacity of the composite. As can be seen in Figure 6, the values of the specific heat capacity of the modified sample are higher than those for the pure C/C sample up to 450°C. As a result of the above, we can conclude that the introduction of MMT into the composite matrix caused an increase in thermal conductivity and changed its behavior from increasing to decreasing with temperature.

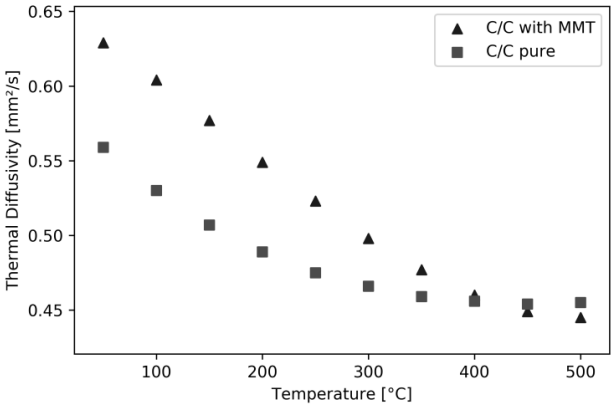

Fig. 5. Thermal diffusivity of composites

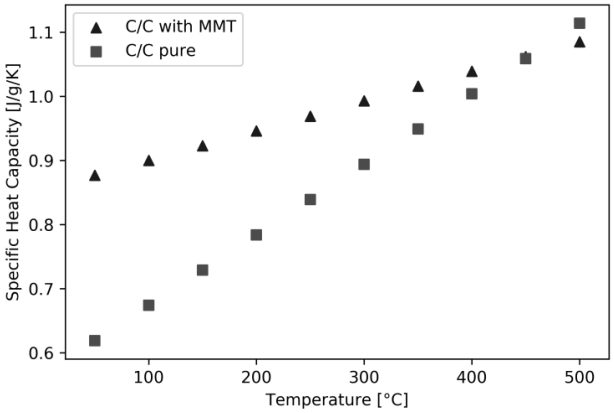

Fig. 6. Specific heat capacity of composites

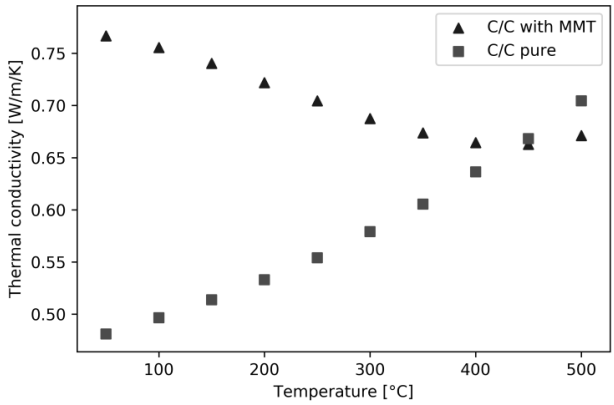

Fig. 7. Thermal conductivity of composites

CONCLUSIONS

In this work the influence of the MMT addition on the thermal and mechanical properties of carbon-carbon composites was investigated. The addition of nanoplatelets caused an increase in Young's modulus of the materials by 48%, not changing the flexural strength nor ILSS. A few potential sources of this behavior are possible, but most likely it was related to the changes in the texture and sizes of the graphitic crystallites, also noted by Raman spectroscopy.

The results indicate that C/C with MMT is a better heat conductor up to 450 C than pure C/C. The probable

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cause of this effect is the easier transmission of phonon vibrations throughout the material due to the increased Young's modulus of the ceramic matrix. Similar increases were noted in the case of thermal diffusivity and specific heat capacity, which were higher for the sample with the addition of MMT up to 450°C.

The addition of MMT shows an interesting influence on the properties of C/C materials. It shows how nanoadditives may change the basic properties of carbon-carbon composites, making them more suitable for a particular application. Nonetheless, more thorough investigation on the other properties (i.e. electrical characteristics, corrosion resistance, thermal stability etc.) of a such system are needed.

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