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Mechanical and thermal properties of boric acid and paper mill sludge reinforced polyester composites

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ABSTRACT

This study is aimed to produce polymer composite materials with low thermal conductivity coefficient and high mechanical strength. Therefore, different rates of boric acid and paper mill sludge were added to the polyester matrix and the composite materials were characterized in terms of mechanical and thermal properties. Based on the experimental results, the highest bending strength (21.83 MPa) was achieved in the presence of 5% paper mill sludge and 3% boric acid. Compared to the reference, the decomposition temperatures of composites increased with the addition of additives. Also, the densities of composites ranged from 1.141 g/cm^3 and 1.409 g/cm^3. The additives of paper mill sludge and boric acid decreased the thermal conductivity coefficient of composites and lowest coefficient of thermal conductivity was reported as 0.61 W/mK. Consequently, boric acid and paper mill sludge additions enhance the mechanical and thermal properties of polyester-based composite material.

1. Introduction

Polymeric composite materials are produced with different fibers and particles to improve the mechanical and thermal properties of polymers which have a wide usage area. In this context, there are many studies on the polymer properties by fiber and particle reinforcement in the literature [1-5]. For instance, boron nitride was added to polypropylene and boron nitride addition was found to increase the thermal conductivity of polypropylene [6]. In another study, weight loss of epoxy composites with different ratios of boric acid (H_3BO_3) was investigated [7]. Polymers have very low thermal conductivity values when compared to many other materials [8]. Improving the thermal conductivity properties of polymers may result in greater energy savings, especially in thermal insulation applications. In this study, H_3BO_3 was used to reduce the thermal conductivity coefficient of polymer material.

In paper manufacturing plants, some of the cellulose fiber and mineral additives are collected in tailings impoundments during production process and are called paper mill sludge (PMS). It is a problem both in terms of environment and factory economy. Therefore, paper manufacturers are making great efforts to solve this problem and evaluate it in different applications. Nowadays, PMS is either landfilling or disposed of by incineration treatment [9]. Researchers have focused on alternative methods due to the decrease of landfills, increasing storage costs, and because of no sustainable and eco-friendly of the incineration method [10,11].

PMS can also be used as filler in polymers because of containing kaolin, talc and calcium carbonate as well as cellulose fibers. Within the scope of material technologies, the studies on the utilization of cellulosic and inorganic materials in polymer composites are remarkable [12]. When viscose fiber and microcrystalline cellulose particles are added to the high density polyethylene, it is stated that cellulose has a clear effect on the thermal dimensional stability of polyethylene and the addition of viscose fiber and microcrystalline cellulose increases the tensile strength of polyethylene [13]. PMS and wood fibers are reinforced into polyethylene matrix in different rates. While there was no significant change in mechanical properties at low PMS rates, the bending strength and elastic modulus of the composite material decreased and impact strength increased, after PMS ratio reached a certain value [14]. The effect of particle size of PMS and extrusion temperature on the physical and mechanical properties of thermoplastic polymer composites were investigated. In the light of the experimental findings, when particle

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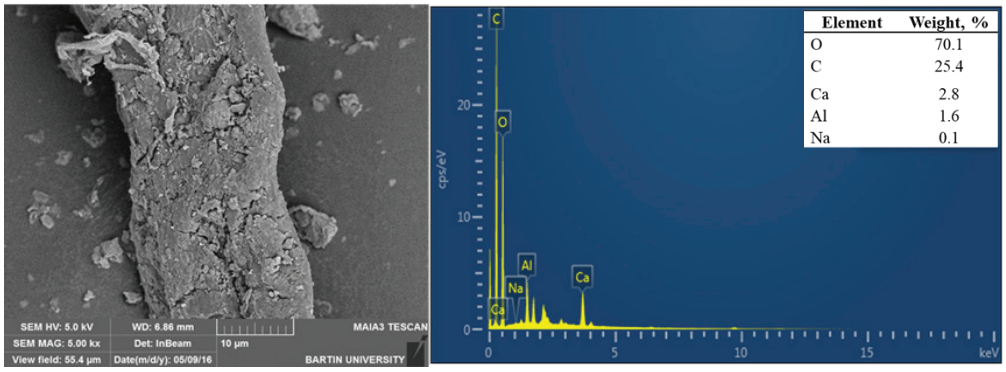

Figure 1. SEM image and EDS results of paper mill sludge.

size decreased, swelling, water absorption, tensile and bending strengths of composite material improved and increase in extrusion temperature positively affected tensile and bending properties [15].

Energy saving has become a more critical subject for economic and environmental reasons. The total energy consumed in Turkey are known for use in buildings of 32%, about half of it is lost due to insufficient insulation of buildings. Therefore, the insulation of building walls is open to new studies as it enables energy saving [16]. Although there are many studies present in literature regarding to production and characterization of polyester composite materials, no study has been issued about the use of PMS as an additive in polyester polymer. In addition, the characterization of the material in terms of thermal conductivity will make an important contribution to the literature. Therefore, in present paper, it was planned to produce polymer composites with low thermal conductivity and high mechanical strength by adding H_3BO_3 and PMS to polyester matrix. The produced composite materials were characterized in terms of bending strength and thermal degradation, thermal conductivity coefficient and surface properties.

2. Materials and methods

2.1. Material properties

PMS was provided from OYKA paper and packaging factory in Caycuma/Zonguldak. It was dried to remove moisture at 110°C for 6 h and then grinded. PMS was coated with Au-Pd mixture and then SEM-EDS analysis was performed (Tescan Maia3 Xmu). SEM image and EDS results of PMS are presented in Figure 1. It is known that PMS contains a large amount of cellulose. Also, there are also impurities in PMS such as Ca and Al arising from the paper manufacturing process. Polyester based epoxy resin used as polymer matrix and H_3BO_3 of analytical purity were purchased from a commercial company.

TG-DTG curves of PMS are presented in Figure 2. TG-DTG analysis was carried out at 10°C/min. of heating rate under nitrogen atmosphere (Hitachi, STA 7300). At the end of 800°C, the total weight loss is 69.56%. Thermal degradation of PMS took place in three stages. A weight loss of approximately 3% occurred due to the removal of physical water until 150°C. At 160-600°C, 61.35% weight loss was observed with the thermal degradation of hemicellulose and cellulose. At the last stage (>600°C), the weight loss is 69.56% due to calcination of carbonates. As shown in Table 1, functional groups of PMS were also determined by FTIR analysis.

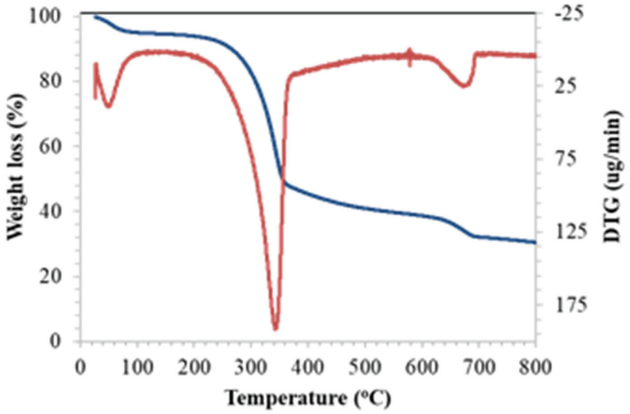

Figure 2. TG-DTG curves of paper mill sludge.

2.2. Composite material production and characterization

Composite material production was carried out using molds with dimensions of 15 cm x 4 cm x 4 cm. Samples were prepared according to the mixture ratios in Table 2. The catalyst (Butanox N60) of 1% was added to the mixtures to accelerate the chemical reaction. Lubricant (wax) was applied to the inner surfaces of the mold for easy removal of the sample. The stirring treatment was performed to ensure homogeneity of the prepared mixtures by a mechanical stirrer. Then, the prepared mixtures were molded and the samples were removed from the mold after being kept at ambient conditions for 1 h. Samples were cut on a cutting machine and brought to the appropriate dimensions for three-point flexural strength tests. All characterization experiments were carried out in triplicate.

Table 1. FTIR analysis of paper mill sludge.

Wavenumber (cm^{-1})	Functional group
3331	-OH stretching of cellulose
2918, 2850	C-H stretching of aromatic and aliphatic groups
1640	C-O (aldehyde group)
1417	calcium carbonate
1155	vibrations of C-O-C bond
1028	glucose stretching of C-O and OH
873	C-O-C bond

Table 2. Mixture ratios of prepared samples.

Sample	Polyester resin (wt. %)	PMS (wt. %)	Boric acid (wt. %)
Reference	100	-	-
A1	99	1	-
A2	97	3	-
A3	95	5	-
B1	99	-	1
B2	98	-	2
B3	97	-	3
C1	98	1	1
C2	95	3	2
C3	92	5	3

Three-point bending tests of the samples were performed using a test instrument (Universal) with a capacity of 50 kN. All tests were carried out under the test conditions of effective span of 50 mm and loading speed of 1 mm/s. The molded samples were cut to 50 mm x 20 mm x 20 mm and prepared for bending test. The samples were placed between the two supports. Then, tests were carried out until fracture occurred with the effect of an increasing force and three-point bending strength of composite materials was determined. The thermal behaviors of the composite materials were carried out using thermogravimetric analyzer (Hitachi STA 7300) at heating rate of 10°C/min under nitrogen atmosphere. Thermal conductivity values of the composite materials were measured at ambient temperature by a C-Therm TCi Thermal Conductivity Analyzer with modified transient plane source. The surface of the material was made flat and smooth for measurement. Then, the material surface was contacted with the sensor and the thermal conductivity coefficient (k) of the material is determined in W/mK units.

3. Results and discussion

3.1. Three-point bending tests

The bending test results are given in Figures 3-5. As seen in Figure 3, the bending strength of the polymer composites increased with PMS addition and the highest bending strength (11.53 MPa) was achieved in composite material containing 5% of PMS. It is possible to indicate that the presence of cellulosic fibers in PMS increases the strength of the polymer matrix. In literature, while the flexural strength of polyamide 6 based composites increased with the addition of carbon and glass fiber (from 1% to 5%), carbon fiber resulted in higher strength [17]. Another study indicates that the mechanical performance of the composite improves, as the broom grass fiber content in the polyester matrix increases. This is because the polyester matrix transmits and distributes the applied force to the fibers. Therefore, the composite material exhibits higher strength and can withstand a higher load than pure polyester [18,19].

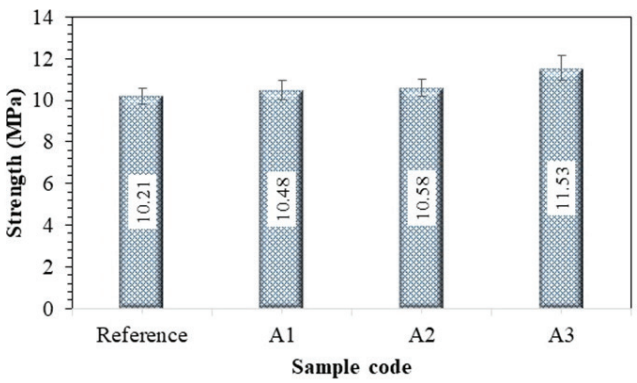

Figure 3. Effect of paper mill sludge amount on bending strength.

As shown in Figure 4, addition of H_3BO_3 up to 2% increased the bending strength, a decrease in the bending strength of the material occurred at higher concentrations. Accordingly, while the composite material containing 2% H_3BO_3 has the maximum strength of (16.64 MPa), it decreased to 14.01 MPa for the material with 3% H_3BO_3. Demirel et al. [20] added different amounts of H_3BO_3 (15%, 20% and 30%) to the polyester mixture containing 5% glass fiber. They reported that the mechanical strength of composites tended to decrease compared to pure polyester at the amount of H_3BO_3 studied. In the present article, lower amounts of H_3BO_3 were studied. And, an increase was observed up to 2%, while a partial decrease was observed in 3% H_3BO_3 addition. Similar trend in terms of mechanical strength was observed for all series of B and C.

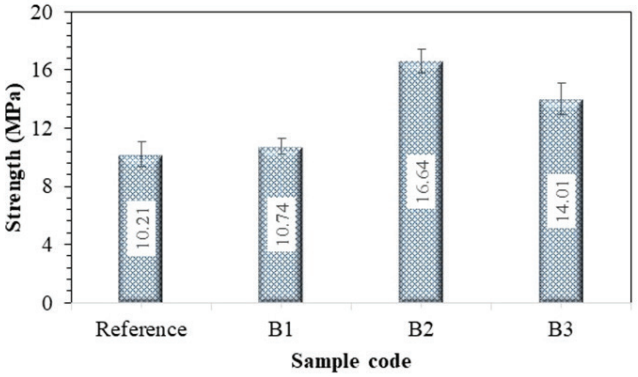

Figure 4. Effect of boric acid amount on bending strength.

According to Figure 5, the flexural strength increased to 21.83 MPa with the addition of 5% PMS and H_3BO_3 while the bending strength of the reference sample (no additive) was 10.21 MPa. However, the bending strength of the material containing 8% PMS and H_3BO_3 was reduced to 14.88 MPa. This is due to the change in the adhesion forces between the additives and the polyester. Consequently, the combined utilization of PMS and H_3BO_3 up to certain amount leads to a significant increase in bending strength. This suggests that PMS and H_3BO_3 can be evaluated to improve the mechanical properties of polyester composite materials. Another important point in bending tests is that the fracture occurs as brittle fracture. Digital images of fractured samples

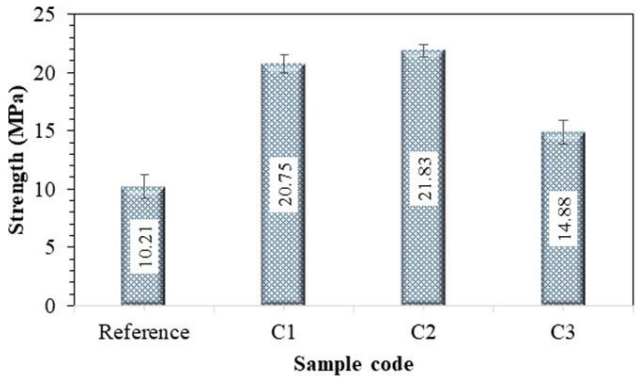

Figure 5. Effect of paper mill sludge and boric acid amount on bending strength.

are given in Figure 6.

Density of polyester material is 1.076 g/cm^3. The density of composites varies between 1.141 g/cm^3 and 1.409 g/cm^3. The densities of composites containing 1%(A1), 3%(A2) and 5%(A3) PMS were measured as 1.141, 1.158 and 1.198 g/cm^3, respectively. Also, the densities of samples with 1%(B1), 2%(B2) and 3%(B3) H_3BO_3 additives are 1.312, 1.348 and 1.392 g/cm^3, respectively. And, the samples of C1, C2 and C3 have density values of 1.341, 1.365 and 1.409 g/cm^3, respectively.

3.2. SEM analysis

SEM analyzes were performed to determine the surface morphology of the composite samples. In addition, the fracture surfaces of composite materials, the interaction between the additive and polymer matrix system and the distribution of the additives in the matrix were examined by SEM in Figure 7. The SEM image of the reference sample shows that the polyester resin is homogeneously dispersed. According to Figure 7(b), it is clearly seen that the presence of cellulosic fibers and these fibers break as a result of fracture. The lamellar occurring in different directions during the solidification and the presence of H_3BO_3 particles are shown in Figure 7(c). As seen in Figure 7(d), it is seen that the cellulose fibers are broken in the same direction as the broken polymer matrix. On the other hand, SEM images show the little polyester matrix on the surface of the broken fibers. It suggests that the adhesion between the polymer matrix and the fiber is poor [17,21].

3.3. Thermal gravimetric analysis (TGA)

Based on Figure 8, thermal degradation of the samples took place in two regions; region 1 (90°C-190°C) and region 2 (190°C-360°C). In region I, the physical water within the body is removed until 190°C temperature. The main weight loss occurred in the region II. According to DTG data, the characteristic temperatures (T_i, T_f and T_p) of DTG data for both regions are given in Table 3. Consequently, the additions of PMS and H_3BO_3 provided a relatively increased thermal resistance when compared to the reference. Similarly, the addition of H_3BO_3 (from 15% to 30%) to the polymer mixture (80% polyester and 5% glass fiber) caused an increase in the thermal decomposition temperatures of composites when compared to with pure polyester [20].

3.4. Thermal conductivity test

Based on the thermal conductivity test results in Table 4, the addition of additives caused decrease in heat conductivity coefficient. While the heat conductivity coefficient of the reference material was 0.245 W/mK, the heat conductivity coefficients of A3, B3 and C3 materials were measured as 0.212 W/mK, 0.161 W/mK and 0.209 W/mK, respectively. In literature, H_3BO_3 has been used as a reinforced material in the poly-

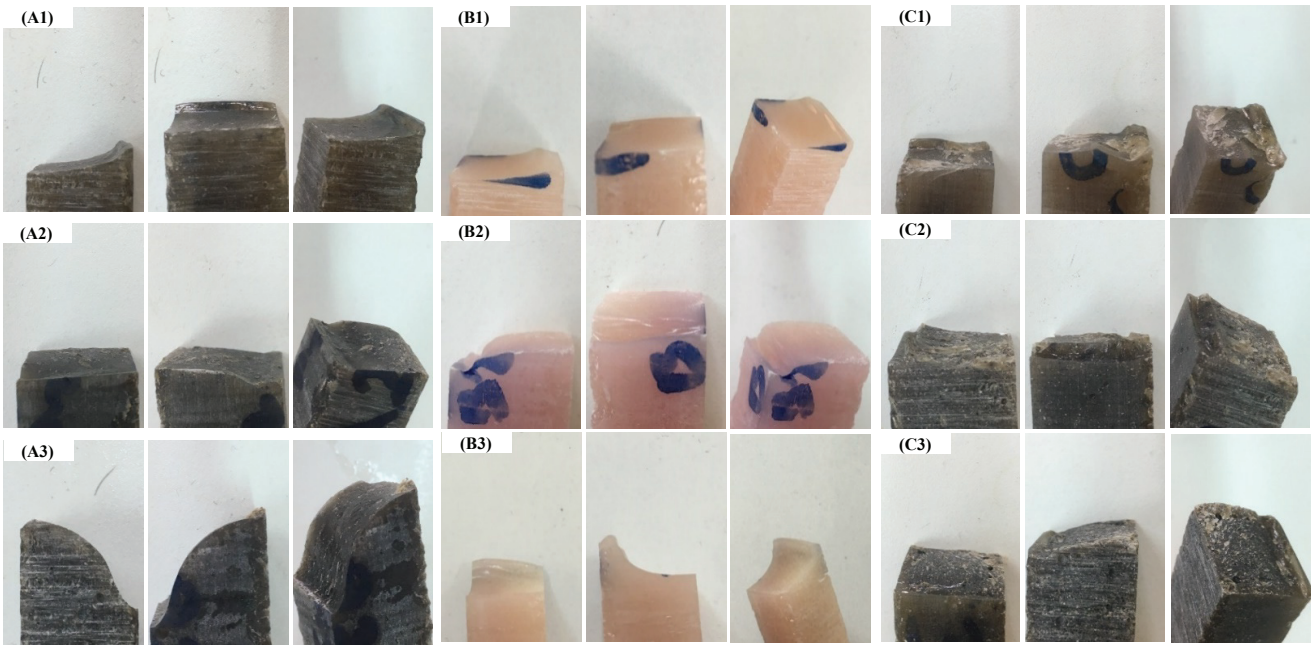

Figure 6. Digital images of the fractured surface of all samples.

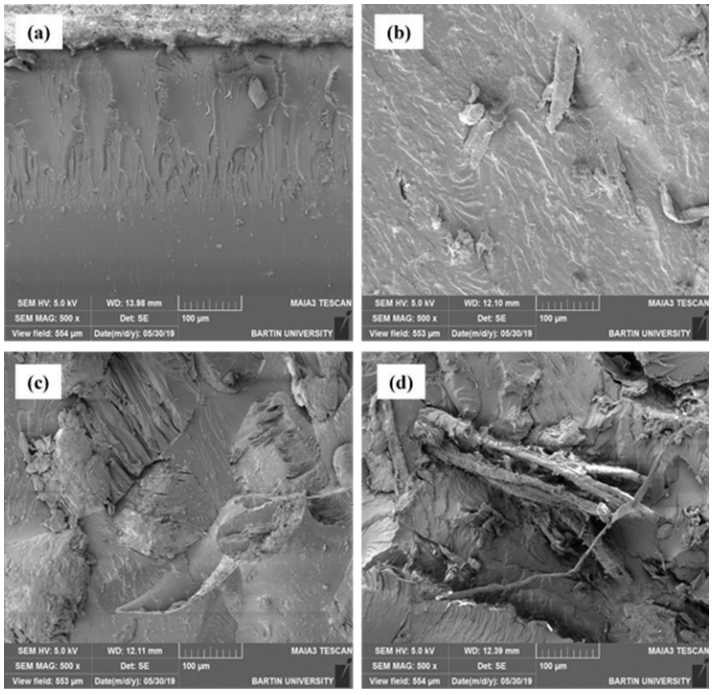

Figure 7. SEM images of fractured surfaces of samples reference (a), A3 (b), B3 (c) and C3 (d).

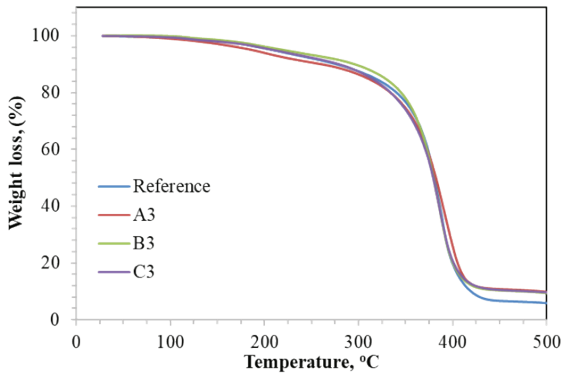

Figure 8. TGA curves of reference, A2, B3 and C3 samples.

Table 3. Characteristic peaks of thermal decomposition of reference, A3, B3 and C3.

Sample	Region I			Region II		
	T_i (°C)	T_f (°C)	T_p (°C)	T_i (°C)	T_f (°C)	T_p (°C)
Reference	80	160	125	200	295	255
A3	90	170	135	210	300	265
B3	95	175	140	215	305	270
C3	105	180	150	225	310	280

T_i = Initial temperature
T_f = Final temperature
T_p = Peak temperature

propylene matrix and improved the thermal insulation property by reducing the heat conductivity coefficient of the polymer composite material. It is attributed to the fact that the thermal conductivity of H_3BO_3 is lower than that of polypropylene [22]. In another study, thermal conductivity characteristics of polyamide 6 composites containing various fibers were investigated. The presence of carbon fiber increased the thermal conductivity of composites, however it slightly decreased with the addition of glass fiber [17]. This result shows the importance of fiber type on the thermal conductivity of composites. Also, the addition of carbon nanofillers to the epoxy polymer matrix resulted in a significant increase in thermal conductivity [23].

Table 4. Thermal conductivity coefficients of samples.

Sample	Thermal conductivity coefficient (W/mK)	Sample	Thermal conductivity coefficient (W/mK)
Reference	0.245 ± 0.008	**B2**	0.176 ± 0.024
A1	0.232 ± 0.01	**B3**	0.161 ± 0.013
A2	0.217 ± 0.021	**C1**	0.223 ± 0.013
A3	0.212 ± 0.006	**C2**	0.215 ± 0.02
B1	0.197 ± 0.017	**C3**	0.209 ± 0.018

4. Conclusions

In this study, PMS and H_3BO_3 were used as additive in polymer based composite material production and materials were characterized in terms of mechanical and thermal properties.

Based on the experimental results, the highest bending strength (21.83 MPa) was achieved in the presence of 5% PMS and 3% H_3BO_3. Compared to the reference, decomposition temperatures of composites increased with the addition of additives. Also, the densities of composites ranged from 1.141 g/cm^3 and 1.409 g/cm^3. The additives of PMS and H_3BO_3 decreased the thermal conductivity coefficient of composites and lowest coefficient of thermal conductivity was reported as 0.61 W/mK. Consequently, H_3BO_3 and PMS additions enhance the mechanical and thermal properties of polyester-based composite material.

The experimental results demonstrate the effectiveness of both H_3BO_3 and PMS in composite material production. In the following studies, we planned to use the compatibilizing agent between the polymer matrix and the additives, surface modification of PMS and the utilization of different boron compounds to achieve higher mechanical properties and further improve thermal insulation properties of the polymer composite materials.

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