Preparation and characterization of lignocellulosic material filled eco-composites

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Abstract

The interest in lignocellulosic material filled eco-composites is growing rapidly due to their's high performance in terms of mechanical properties, significant processing advantages, excellent chemical resistance, low cost and low density. The focus in this work has been put on the preparation and characterization of lignocelllosic material filled eco-composites. The materials have been kenaf fibers (KF) and rice straw (RS) as reinforcements and polypropylene (PP) and poly(lactic acid) (PLA) as matrices. Rice hulls from rice processing plants and natural lignocellulosic kenaf fibers from the bast of the plant Hibiscus Cannabinus represent renewable sources that could be utilized for composites. Maleic anhydride grafted PP (MAPP) and maleic anhydride grafted PLA (MAPLA) were used as coupling agents (CA) to improve the compatibility and adhesion between fibers and matrix. The composites containing 30 wt % reinforcement were manufactured by compression molding and their mechanical and thermal properties were obtained. It was found that the PP-based composites are less sensitive to processing cycles with respect to PLA-based composites. The experimental results suggest that the compression molding are promising technique for processing of eco-composites. Moreover, the PP-based composites and PLA- based composites are appropriate for processing by compression molding. Both composites are suitable for applications as construction materials.

Keywords: eco-composites, polypropylene, poly(lactic acid), rice hulls, kenaf fibers, compression molding

Introduction

Public attention is now being placed on the environmentally gentle composite materials using natural lignocellulosic fibres and thermoplastics. The development of eco composite materials has accelerated rapidly, primarily due to improvements in process technology and economic factors [1, 2].

Natural fibers (NF) reinforced materials offer many environmental advantages such as reduced dependence on non-renewable energy/material sources, lower pollution and greenhouse emission. Natural lignocellulosic fibers (flax, jute, hemp, etc.) represent an environmentally friendly alternative to conventional reinforcing fibers (glass, carbon). Advantages of natural fibers over traditional ones are their low cost, high toughness, low density, good specific strength properties, reduced tool wear (nonabrasive to processing equipment), enhanced energy recovery, CO_2-neutral when burned, biodegradability. Due to their hollow and cellular nature, natural fibers perform as acoustic and thermal insulators, and exhibit reduced bulk density. Depending of their performance, when they are embedded in the polymer matrix, lignocellulosic fibers can be classified into three categories: (1) wood flour particulates, which increase the tensile and flexural modulus of the composites, (2) fibers of higher length/diameter ratio that improves the composites modulus and strength when appropriate additives are used to regulate the stress transfer between the matrix and the fibers, and (3) long natural fibers with the highest efficiency

amongst the lignocellulosic reinforcements. The most efficient natural fibers have been considered those that have a high cellulose content coupled with a low microfibril angle, resulting in high filament mechanical properties [3, 4].

There are many different polymers of renewable sources: for example polylactic acid (PLA), cellulose esters, poly(hydroxyl butyrates), starch and lignin based polymer materials. Among these, PLA has the potential for use in electronic and construction applications because it can be fabricated with desired physical properties, such as heat resistance, mechanical response coupled with moldability, and recyclability. PLA is a degradable thermoplastic polymer with excellent mechanical properties and it is produced on a large scale by fermentation of corn starch to lactic acid and subsequent chemical polymerization. This polymer is characterized by its transparency, humidity and oil resistance. Pure PLA can degrade to carbon dioxide, water and methane in the environment over a period of several months to 2 years, compared to other petroleum plastics needing very longer periods [5, 6, 7]. The mechanical properties of PLA have been extensively studied as a biomaterial in the medicine, but only recently it has been used as a polymer matrix in eco-composites [8]. Its applications and use in eco-composites is still limited by its high price when compared with other biodegradable polymers. Xia et al. [9] investigated the use of PLA resin reinforced with kenaf fibers for the interior parts of its Prins hybrid car. In 2002 Cargill-Dow LLC started up a commercial polylactide plant, with the aim of production of PLA fibers for textiles and nonwovens, PLA film packaging applications, and rigid thermoformed PLA containers [10].

Amongst eco-compatible polymer composites, special attention has been given to polypropylene composites [11]. PP could not be classified as a biodegradable polymer, but PP takes an important place in eco-composite materials. For example, Mohanty et al. have demonstrated that the NF reinforced PP composites have potential to replace glass-PP composites [12]. It has also been reported that PP can be effectively modified by maleic anhydride, providing polar interactions and covalent bonds between the matrix and the hydroxyl groups of cellulose fibers [13]. Visteon and Technilin developed flax/PP materials, R-Flax® based on low cost fibers. Tech-Wood International from the Netherlands announced Tech-Wood® eco-composite, suitable for construction elements [14]. Tech-Wood® eco-composite material contains 70% pine-wood fibers and 30% compatibilized PP.

The purpose of this study was to preparation of lignocelllosic material filled eco-composites with compression molding technique (which is usually applied for the production of conventional composites), with respect to their resulting properties. The fillers/fibers were compounded with the matrix and the coupling agent by reactive blending, and the compounds were compression molded. The influence of the processing technique on the properties of composites was evaluated through the mechanical and thermal characterization of the composites.

This work is a follow up of the successfully finished ECO-PCCM project [15], in which eco-composites based on PLA, PHBV and PP were prepared by molding techniques and investigated in order to obtain new eco-compatible construction panels and elements for eco-houses [15,16].

Experimental

Isostatic PP, Moplen X30S, kindly supplied by Basell Polyolefins (Ferrara, Italy), and PLA, produced by Biomer, Krailling - Germany, were used as matrices. Rice hulls from agricultural waste were kindly supplied by Rice Institute from Kocani, Macedonia. Kenaf fibers, average length of 5.1mm and average diameter of 21μm, were kindly supplied by Kenaf Eco Fibers Italia S.p.A. (Guastall-Italy). Before mixing, kenaf fibers (K) and rice hulls (RH) were vacuum-dried for 24h to adjust their moisture content to 1-2 wt%. Maleic anhydride-grafted PP (MAPP), KA 805 (Basell Polyolefins Ferrara, Italy), and maleic anhydride-grafted PLA (MAPLA) were used as coupling agents (CA) and they have been added to PP and PLA during the reactive blending.

The preparation of the composite compounds has been preformed by melt mixing, in a Haake Rheocord 9000 batch mixer (New Jersey, USA). First, the polymer and coupling agent were mixed for 3 min at 185 ^{O}C and 175 ^{O}C, respectively for PP and PLA based composites; then 30 wt% of fillers/fibers were added and the mixing proceeded for further 10 min at the same temperature. The mixing speed was progressively increased during mixing, up to 64 rpm (3 min with a mixing speed of 8 rpm, then 4 min at 38 rpm and finally 3 min at 64 rpm). Then the obtained composites were cut into granules suitable for molding. The codes of the samples obtained are shown in Table 1.

Table 1. Codes of composite samples

Codes	Matrix (wt%)		Fiber/Filler		Coupling agent (CA)	
	Type	Content (wt%)	Type	Content (wt%)	Type	Content (wt%)
PP/K/CA	PP	65	Kenaf fibers	30	MAPP	5
PP/RH/CA			Rice Hulls			
PLA/K/CA	PLA	65	Kenaf fibers	30	MAPLA	5
PLA/RH/CA			Rice Hulls			

The samples for mechanical testing were fabricated by compression molding.
The pellets obtained after melt mixing of starting materials, were put in molding frame with desired dimensions and compression molded at T= 185 ^{O}C for PP based composites and T= 175 ^{O}C for PLA based composites, both for 10 minutes, with progressively increasing pressure from 50 to 150 bar. Finally, the press was cooled using a cold water flow. Sheets with a thickness of about 5 mm were obtained.

Mechanical and thermal properties of the moldings such as impact resistance (Charpy impact test according ASTM D 256), compression strength (ASTM D 695), flexural strength and the modulus (ASTM D 790) were determined. For all mechanical tests, the universal testing machines (Schenk and Frank, Germany) were used.

The thermal stability of compression molded composite samples were measured using a Perkin Elmer Pyris Diamond Thermogravimetrical Analyzer (TGA). About 10 mg of each sample was heated from 50°C to 600°C at heating rate of 20°C/min under nitrogen flow (25mL/min).

Results and discussion

PP and PLA based composites were prepared by a proper *in situ* reactive compatibilization. This preparation strategy consists into the addition of low amount of MAPP and MAPLA (reactive coupling agents), to the composite components. These coupling agents are constituted from PP and PLA segments (the same as the polymer matrices) and by MA groups grafted onto PP and PLA segments, which become reactive with respect to hydroxyl groups present on the reinforcement surface. In this way, physical and/or chemical interactions between hydroxyl and maleic anhydride groups, generated during the mixing, are responsible for *in situ* formed grafted species that can act as effective compatibilizer for the PP and PLA/natural reinforcements composites [17, 18].

The physical and mechanical properties of compression molded composites are summarized in Table 3. It should be mentioned, that, prior to this investigation, the optimization of compression molding processes was already done, as reported in our earlier work [19,20]. As can be seen from the results, the composites reinforced with kenaf fibers show higher modulus and strength with respect to composites reinforced with rice hulls.

Table 3. The physical and mechanical properties of the composites produced by compression molding

Characteristics	Unit	Composite: PP/K/CA	Composite: PP/RH/CA	Composite: PLA/K/CA	Composite: PLA/RH/CA
Flexural strength	MPa	51.3 ± 4.84	42.6 ± 3.45	46.7± 3.83	28.8 ± 3.14
Flexural modulus	GPa	2.11 ± 0.07	1.94 ± 0.08	2.05 ± 0.11	1,63 ± 0.09
Impact strength	kJ/m^2	71.4 ± 4.67	69,2 ± 3.83	54.3 ± 3.49	48,7 ± 4.16
Compression strength	MPa	47.2 ± 2.93	36.3 ± 2.39	34,5 ± 3.11	21,6 ± 2.67
Compression modulus	GPa	1.86 ± 0.12	1,58 ± 0.09	1,74 ± 0.11	1,46 ± 0.07
Tensile strength	MPa	29.6 ± 3.84	22.7 ± 4.82	28.3 ± 6,54	26.7 ± 1,49
Tensile modulus	GPa	1.65 ±0,025	1.78 ± 0,014	2.87 ± 0.23	2.76± 0.11

Sanadi et al. [21] have studied the possibility of using highly filled agro-based fiber thermoplastic composites for furniture, automotive and building applications. They have shown that the performances of thermoplastic based composites are better than most of wood particle, low and medium density fiberboards. For our systems, a comparison of flexural properties of commercially available formaldehyde-based wood composites [22] and 30% filled PP/kenaf and PP/rice hulls compressed composites is given in Table 4. The investigated compressed composites show flexural properties comparable to conventional formaldehyde-based fiberboards.

Table 4. Comparison of flexural properties of commercially available formaldehyde-based wood composites [22] and compatibilized PP/Kenaf, PP/Rice hulls, PLA/Kenaf and PLA/Rice hulls composites produced by compression molding

Sample	Flexural strength range (MPa)		Flexural modulus range (GPa)	
	low	high	low	high
High-density fiberboards [22] (commercial)	38	69	4.48	7.58
Medium-density fiberboards [22] (commercial)	13.1	41.4	2.24	4.83
PP/Rice hulls/CA [b]	42.6 (3.4) [a]		1.94 (0,08) [a]	
PP/Kenaf/CA [b]	51.3 (4.8) [a]		2.11 (0.07) [a]	
PLA/Rice hulls/CA [b]	28.8 (3.1) [a]		1.63 (0.09) [a]	
PLA/Kenaf/CA [b]	46.7 (3.8) [a]		2.05 (0.11) [a]	

[a] Standard deviations are in brackets for the PP/kenaf, PP/rice hull, PLA/kenaf and PLA/rice hull composites
[b] CA: coupling agent

Thermogravimetric (TGA) curves and derivate thermograms (DTG) for PP/RH/CA and PP/K/CA composites are shown in fig.1, whereas TGA results are summarized in Table 5.
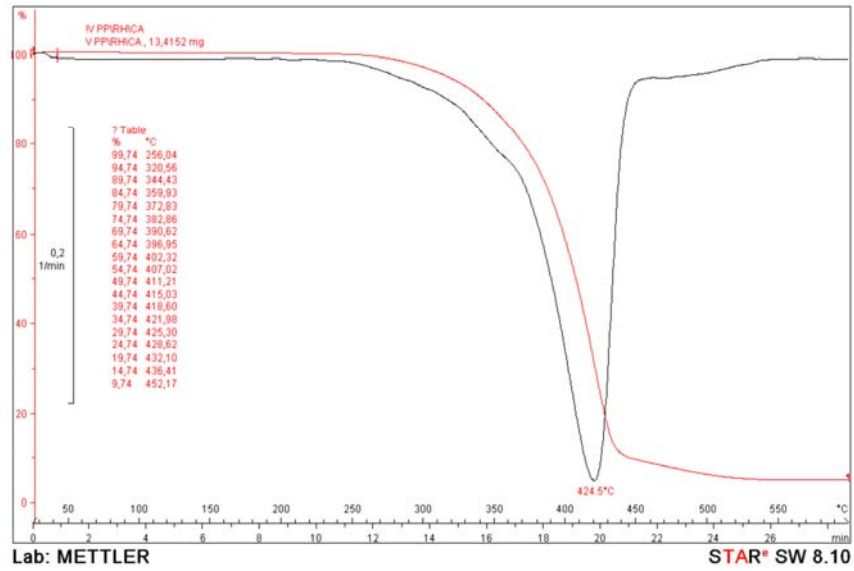
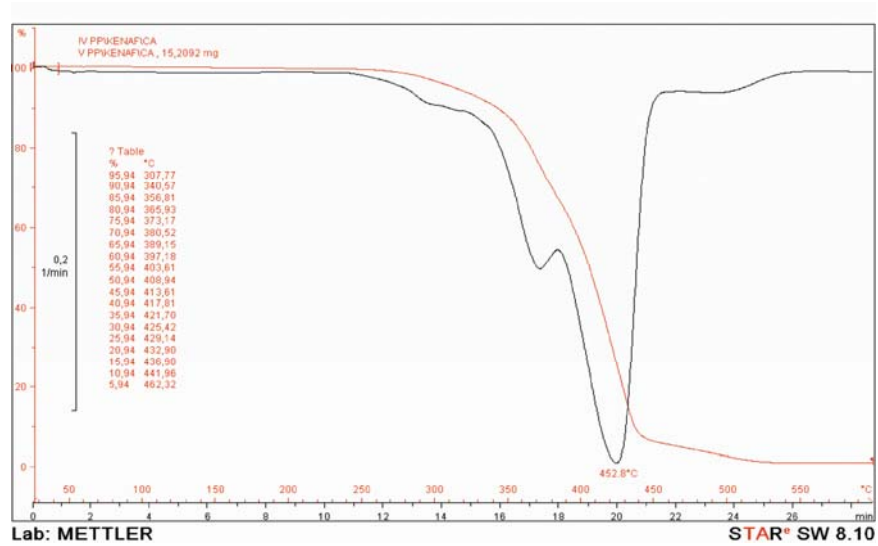*Figure 1a. Weight loss and weight loss rate curves of PP/RH/CA*

Figure 1b. Weight loss and weight loss rate curves of PP/K/CA

Table 5. Degradation temperature of composites determined by TGA at residual weight 90% (Td_{90}), 50% (Td_{50}), and 10% (Td_{10})

Sample	Td_{90} (°C)	Td_{50} (°C)	Td_{10} (°C)
PP/RH/CA	344.4	411.2	452.2
PP/K/CA	340.6	408.9	442.0

As it can be observed, thermal degradation of PP/RH/CA composite shows single stage process; maximum weight loss rates were observed at 424.5°C for PP/RH/CA. A small shoulder can be noticed at approximately 350°C corresponding to the beginning of the thermal degradation of rice hulls. Notwithstanding the degradation process occurs in a single step, it can be considered the overlapping of the degradation phenomena associated to the different composite components. Lignocellulosic materials decompose thermochemically between 150°C and 500°C: hemicellulose, mainly between 150 and 350°C, cellulose between 275 and 350°C, and lignin between 250 and 500°C as reported by Kim et al. [23]. The residue at about 550°C corresponds to the amount of silica (approximately 10 wt %) in the rice hulls, as determined in our earlier work, by TGA [24]. Ash in the rice hulls is mainly constituted by silica (~96 wt %), and the amount and distribution of silica in the rice hulls is likely to be an important factor in determining the properties of the composite products [23].

In the case of PP/Kenaf composites a two-stage weight loss process was observed.. The first stage, occurring in the temperature range from 350°C to 400°C, is correlated to the degradation of low molecular weight components, such as hemicelluloses and cellulose, corresponding to thermal degradation of kenaf [23].

Results from the thermogravimetric analyse of PLA, rice hulls and their composite PLA/RH/CA (65/30/5wt. %) are presented in figure 8 (a) and table 7. PLA gradually losses 10% of its weight till 350 °C, and afterward suffers almost complete weight loss in a temperature interval from 350 °C till 400 °C. PLA based composite PLA/RH/CA (65/30/5wt.%) lose 10% of its weight till 300 °C, followed by ongoing 75% weight loss till 360-365 °C, after that, weight loss continues with slower degradation rate. It should be noted that at temperature of 600 °C rice hulls exhibit high residual weight of 39.7%. These findings are in accordance with the finding of Lee et al. [25] that thermal stability of PLA/bamboo fibre composites is lower than thermal stability of neat PLA matrix.
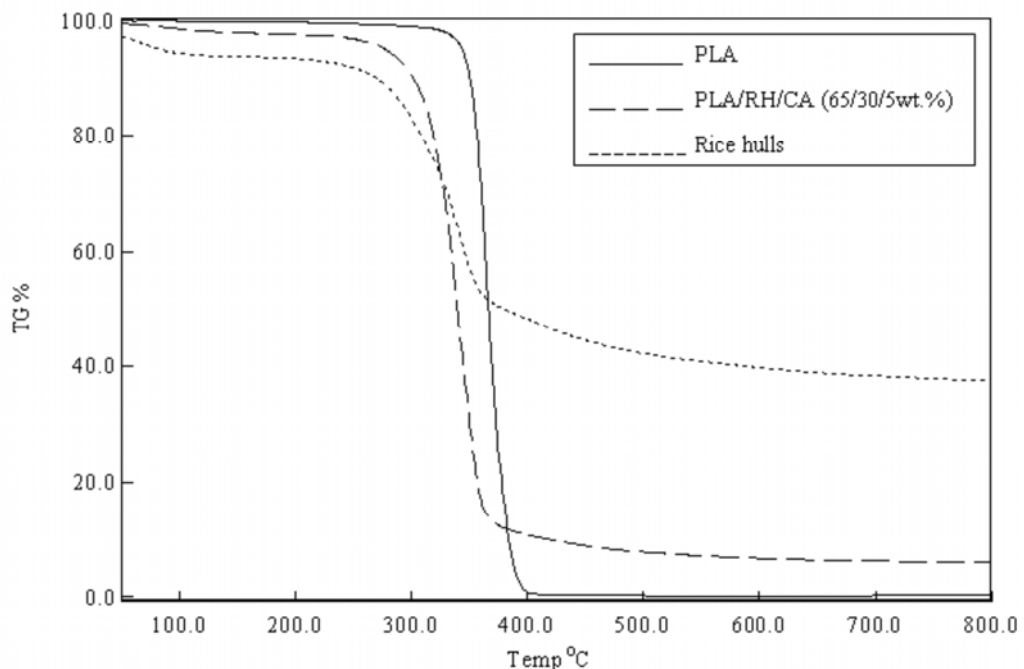

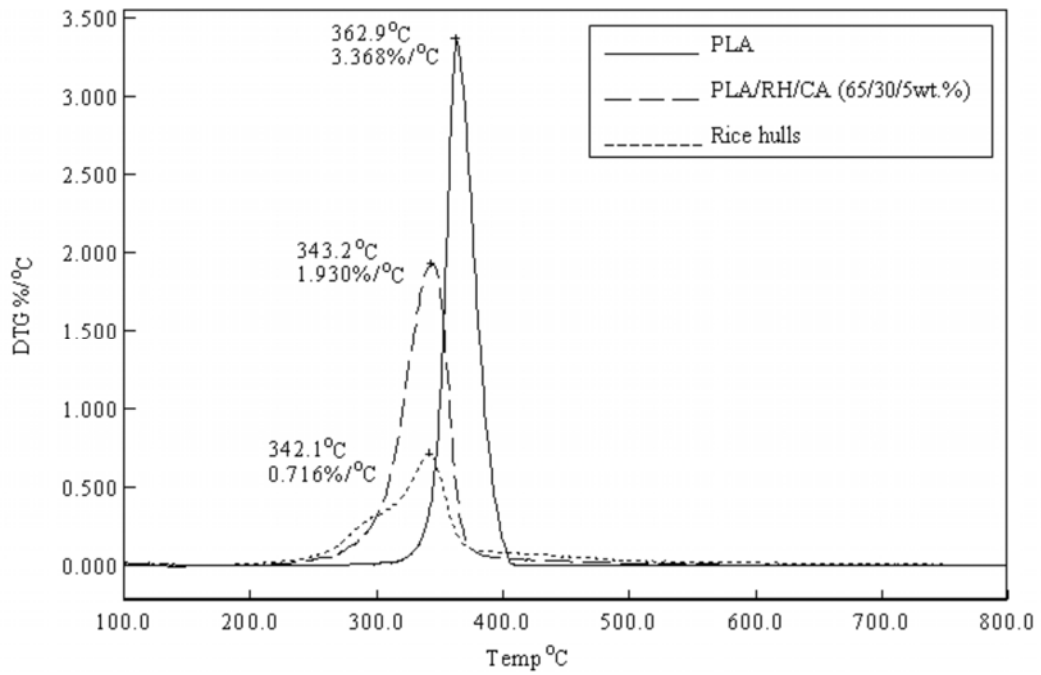Figure 2a. Thermogravimetric curves, weight loss (TG) versus temperature

Figure 2b. Derivative thermogravimetric curves, derivative weight loss (DTG) versus temperature

Table 6. Thermal stability of PLA, rice hulls and composite PLA/RH/CA (65/30/5wt. %)

T (^{o}C)	Weight loss (%)		
	Rise hulls	PLA/RH/CA	Neat PLA
50	2.7	0.5	0
100	5.6	1.4	0
250	8	3.2	0.5
290	14	6.9	0.9
310	20.6	13.7	1.2
330	29.7	33.5	2.1
350	43	69.8	9.5
370	49.1	86.9	61.3
390	51	88.7	95.7
410	52.6	89.7	99.6
600	60.3	93.3	100

Derivative thermogravimetric curves for neat PLA, rice hulls and their composite PLA/RH/CA are presented in figure 8 (b). Maximum weight loss rate for PLA (3.37 %/^{o}C) is reached at 362.9 ^{o}C, and for rice hulls weight loss rate is uppermost (0.72 %/^{o}C) at 342.1 ^{o}C. Composite PLA/RH/CA exhibits maximum weight loss rate of 1.93 %/^{o}C at 343.2 ^{o}C, a temperature almost 20 ^{o}C lower than the corresponding one for neat PLA, proving again the previous finding of composites lower thermal stability.

In table 7 the degradation temperature values (*Td*) calculated as the maximum of the degradation rate, and the residual weight at 500 ^{O}C are reported.

Table 7. Degradation temperature (Td) and residual weight at 500ºC of neat PLA and PLA based composite

Codes	Td (ºC)	Residual weight at 500 ºC (%)
Neat PLA	365	0,9
Kenaf fibers	348	17,2
PLA/K/CA (65/30/5wt. %)	351	7,2

The thermal degradation for PLA/K/CA composite occurs in a single step; maximum rate for this overall degradation process is centered at about 352 ºC. It can be noted that kenaf fibers show very high residual weight at 500ºC, about 17 %, which is in agreement with data reported in reference [19].

CONCLUSION

Based on the obtained results of the effect of applied technique for manufacture of eco-composites on their mechanical properties, the following conclusions can be drawn. Mechanical properties of composites containing 30wt% of kenaf fibers and 5 wt% of coupling agent obtained by compression molding have shown better mechanical properties with respect to composites reinforced with rice hulls. Moreover, PP/kenaf and PLA/kenaf composites seem to be less sensitive to processing technique with respect to PP/RH and PLA/RH composites. Thermal stability of the PP-based composites is slightly higher as compared to the PLA ones. For all composites complete weight loss were observed at temperature interval from 400 ºC to 460ºC. Both, the PP- and PLA-based composites, especially those reinforced with kenaf fibers, represent a good potential for processing by conventional molding technique. Moreover, the obtained results for mechanical properties of composite samples, processed by compression molding, are comparable to those of conventional formaldehyde wood medium density fiberboards used as construction elements for indoor applications.

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