Preparation and Properties of Polystyrene/SiCw/SiCp Thermal Conductivity Composites

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ABSTRACT: The silicon carbide whisker (SiCw) and silicon carbide particle (SiCp) were employed to prepare polystyrene/silicon carbide whisker/silicon carbide particle (PS/SiCw/SiCp) thermal conductivity composites, and the titanate coupling reagent of NDZ-105 was introduced to functionalize the surface of fillers. The thermal conductive coefficient λ improved from 0.18 W/mK for native PS to 1.29 W/mK for the composites with 40% volume fraction of SiCw/SiCp (volume fraction, 3 : 1) hybrid fillers. Both the thermal decomposition temperature and dielectric constant of the composites increased with the addition of SiCw/SiCp hybrid fillers. At the same addition of SiCw/SiCp hybrid fillers, the surface modification of hybrid fillers by NDZ-105 could improve the thermal conductivity and the mechanical properties of the composites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 132–137, 2012

Key words: polystyrene; composites; hybrid fillers; thermal conductivity

INTRODUCTION

Polystyrene (PS) is a kind of general-purpose plastic, combining many excellent properties, such as excellent dielectric property, good dimensional stability, good chemical resistance, easy processing, and low cost, and has been widely used in the electronics industry, food packing, and kitchen appliances. In some cases, the new applications of dissipating heat and maintaining operating temperature require new composites with high thermal conductive properties.[1–6]

To the best knowledge of us, a lot of thermal conductivity composites have been prepared by different kinds of fillers (carbon fiber,[7] carbon nanotube,[8–10] AlN,[11–13] BN,[14] Si_3N_4,[15] and graphite.[16–18]) Silicon carbide (SiC) possesses a relatively high thermal conductivity, high strength, and modulus, and has been widely used in the preparation of high-performance composites.[19,20]

In our present work, the novel PS/SiCw/SiCp thermal conductivity composites were prepared. We attempted to maximize the abundance of thermal conductive chains and networks by using SiCw/SiCp hybrid fillers. In addition, the titanate coupling reagent of isopropyltrioleictitanate (NDZ-105) was introduced to functionalize the surface of SiCw/SiCp hybrid fillers, for the purpose of improving the thermal conductivity and the mechanical properties of the PS/SiCw/SiCp composites.

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EXPERIMENTAL

Main materials

PS of GPPS-PG33 was received from Qimei Chemical Co. Ltd. (Jiangsu, China). SiC whisker, with aspect ratio of more than 20; SiC particle, with grain diameter of 1.5 μm were received from Xuzhou Hongwu Nanomaterial Co. Ltd. (Jiangsu, China). Titanate coupling reagent of isopropyltrioleictitanate (NDZ-105) was supplied by Nanjing Shuguang Chemical Group Co. Ltd. (Jiangsu, China). Isopropyl alcohol and ethyl alcohol were supplied from Tianjin Ganglong Chemical Group Co. Ltd. (Tianjin, China).

Surface modification of SiC

Titanate coupling reagent of NDZ-105 was introduced to ensure the improvement of the interface action between SiC and PS matrix, and the uniform dispersion of SiC in the PS matrix.

The surface modification of SiC was carried out as follows: (i) stirring and ultrasonic dispersing SiC in ethanol, (ii) mixing SiC and NDZ-105 in ethanol by stirring and ultrasonic treatment at 80°C for 4 h, (iii) drying in vacuum to remove solvent at 100°C for 24 h.[11,19–21]

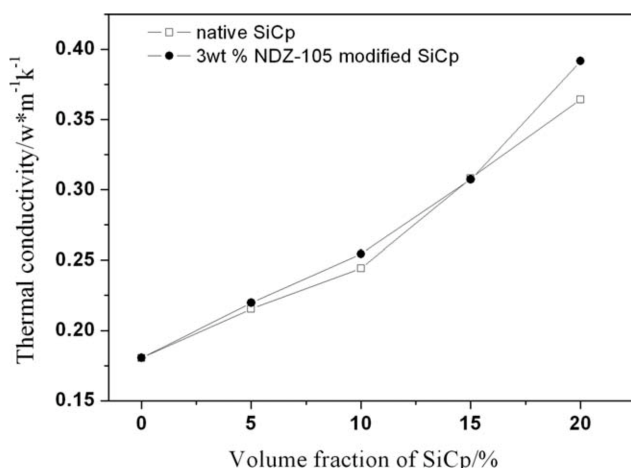

Figure 1 Effects of NDZ-105 on the thermal conductivity of the composites.

Preparation of PS thermal conductivity composites

PS and SiC were dried in vacuum at 60°C for 6 h and at 100°C for 4 h, respectively. The composites were prepared according to the following procedures: (i) mixing PS and SiC with appropriate proportion to get homogeneous blends and (ii) compression-molding (190°C, 15 MPa) to prepare PS thermal conductivity composites.

Characterization

The thermal-gravimetric analyses of samples were carried out at 10 °C/min over the whole range of temperature (50–600°C) under nitrogen atmosphere on TGA Q50. The scanning electron microscope (SEM) morphologies of the composites were observed by JEM-6700F to analyze the dispersion state of SiCw/SiCp hybrid fillers in the PS matrix. Thermal conductive coefficient λ of the composites was measured using a Hot Disk Instrument (AB, Sweden), and the corresponding dimension of specimen was 20 × 20 × 4 mm^3. The dielectric constant of composites was measured using high frequency Q instrument (QBG-3D) and dielectric-constant detector (S914) from Aiyi Electronic Equipment Co. Ltd. (Shanghai, China), and the corresponding dimension of specimen was 27 × 27 × 4 mm^3. The tensile and flexural properties were measured with Electron Omnipotence Experiment Machine SANS-CMT5105 (Shenzhen New Sansi Co., China) according to standard ISO527-1993 and ISO178-1993, respectively. The impact strength of the composites was measured with ZBC-4B impact testing machine (Shenzhen New Sansi Co., China) according to standard ISO179-1993.

RESULTS AND DISCUSSION

Thermal conductivity of the composites

Figure 1 shows the effects of NDZ-105 on the thermal conductivity of the composites. For a given SiCp loading, the surface modification of SiCp improves the thermal conductivity of the composites. It can be attributed that the interface compatibility between SiCp and PS matrix increases. The dispersion state of SiCp in PS matrix improves, decreasing the interfacial phonon scattering effectively, and the thermal conductivity of the composites increases.

The thermal conductivities of PS/SiCw and PS/SiCp composites versus SiC shape and content are shown in Figure 2. For both PS/SiCw and PS/SiCp composite systems, a nonlinear increase in the thermal conductivity is observed with an increasing volume fraction of SiC. The composites filled with SiCw displays better thermal conductivity than those filled with SiCp for varying SiC contents. This difference is more significant for the composites at higher SiC content. The thermal conductive coefficient λ is 1.18 W/mk with 40% volume fraction of SiCw.[6]

Many theoretical and empirical models have been proposed to predict the effective thermal conductivity of the composites. Agari's semiempirical model can yield better results than the theoretical ones. The logarithmic equation of Agari is shown as follows.[22,23]

$$\log\lambda_c = V_f \times C_f \times \log\lambda_f + (1 - V_f)\log(C_p\lambda_p)$$

where C_p represents the effects of the particles on the polymer structure, i.e., C_p is related to the change of thermal conductivity of the polymer, as a consequence of a change of its crystallinity; C_f represents the ability of the fillers to continuous chains, $0 < C_f < 1$.

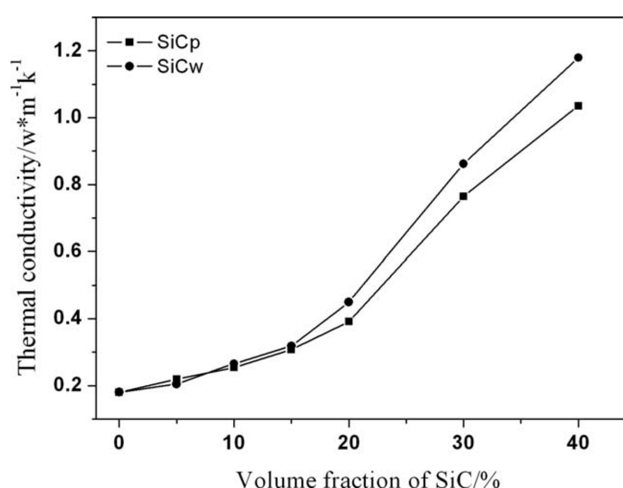

Figure 2 Effects of the content of SiC on thermal conductivity of the composites.

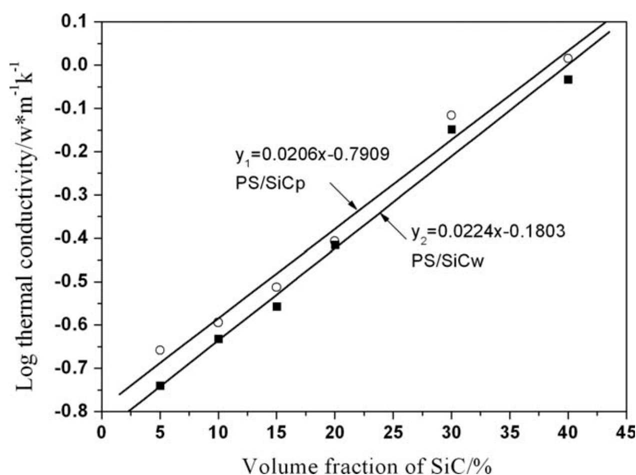

Figure 3 The thermal conductivity of the composites by Agari model fitting.

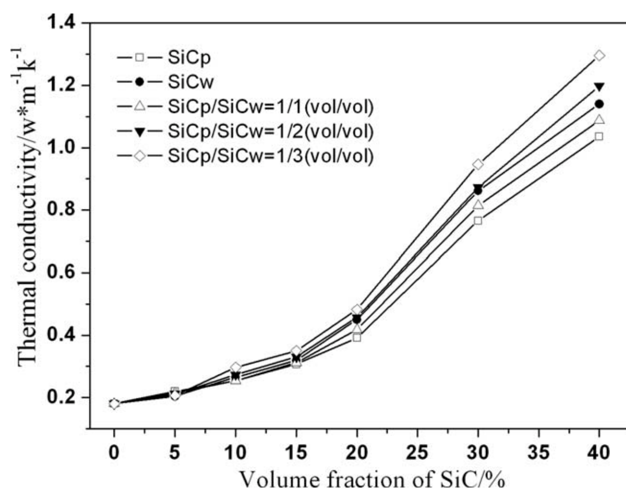

Figure 4 Effects of SiCw/SiCp hybrid fillers on the thermal conductivity of the composites.

By Agari model fitting of the composites (shown in Fig. 3), the values of C_p and C_f of the composites can be obtained as shown in Table I. The values of C_p and C_f of the composites are different when filled with SiCw and SiCp, respectively. The C_f value of PS/SiCw composite is much closer to 1. It reveals that the SiCw is much easier to form the thermal conductive chains and networks in the composites than SiCp.[6]

Figure 4 shows the effects of SiCw/SiCp hybrid fillers on the thermal conductivity of the composites. The SiCw/SiCp hybrid fillers are more favorable to improve the thermal conductivity of the composites. And the thermal conductive coefficient λ improves from 0.18 W/m K for native PS to 1.29 W/m K for the composite with 40% volume fraction of SiCw/SiCp (volume fraction, 3 : 1) hybrid fillers.

It is due to the thermal conductive chains and networks filled with SiCw/SiCp hybrid fillers being enhanced. SiCw can connect the SiCp and play the role of "thermal conductive bridge" between one SiCp and another. With the further increasing volume fraction of SiCw/SiCp hybrid fillers, the interconnected function between SiCw–SiCw and SiCw–SiCp improves obviously (shown in Fig. 5), and the probabilities of thermal conductive chains and networks increase, thus the thermal conductivity improves obviously.

Mechanical properties of the composites

Figure 6 shows the effects of SiCw/SiCp hybrid fillers and NDZ-105 on the mechanical properties of the composites. The mechanical properties of the composites decrease with the increasing volume fraction of SiCw/SiCp hybrid fillers. The results are ascribed to the decreasing PS phase. Moreover, interface defects and stress concentration points are easily introduced into the composites with excessive addition of SiCw/SiCp hybrid fillers.

At the same addition of SiCw/SiCp hybrid fillers, surface modification can improve the flexural and impact strength of the composites, but decrease the tensile strength slightly. It can be ascribed to the improving interface adhesion between PS and SiCw/SiCp hybrid fillers. However, a soft interlayer between PS and SiCw/SiCp hybrid fillers can yield plastic deformation of the composites near

TABLE I
C_p and C_f of Agari Model for the Composites

Composites	C_p	C_f
PS/SiCp	0.899	0.596
PS/SiCw	0.875	0.701

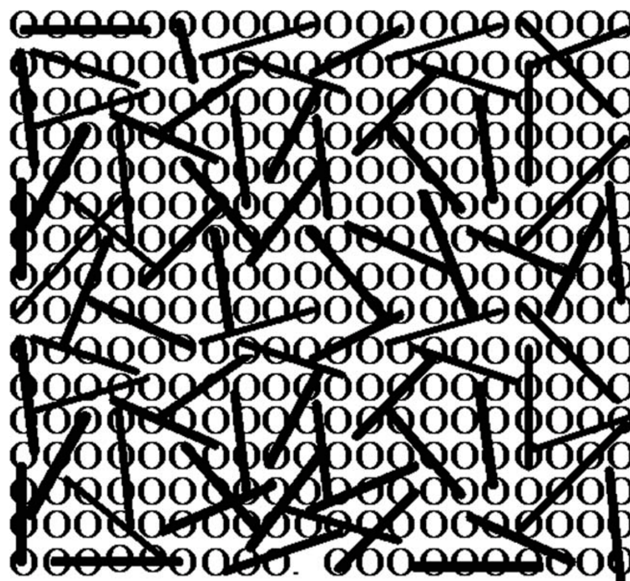

Figure 5 The interconnected function between SiCw–SiCw and SiCw–SiCp.

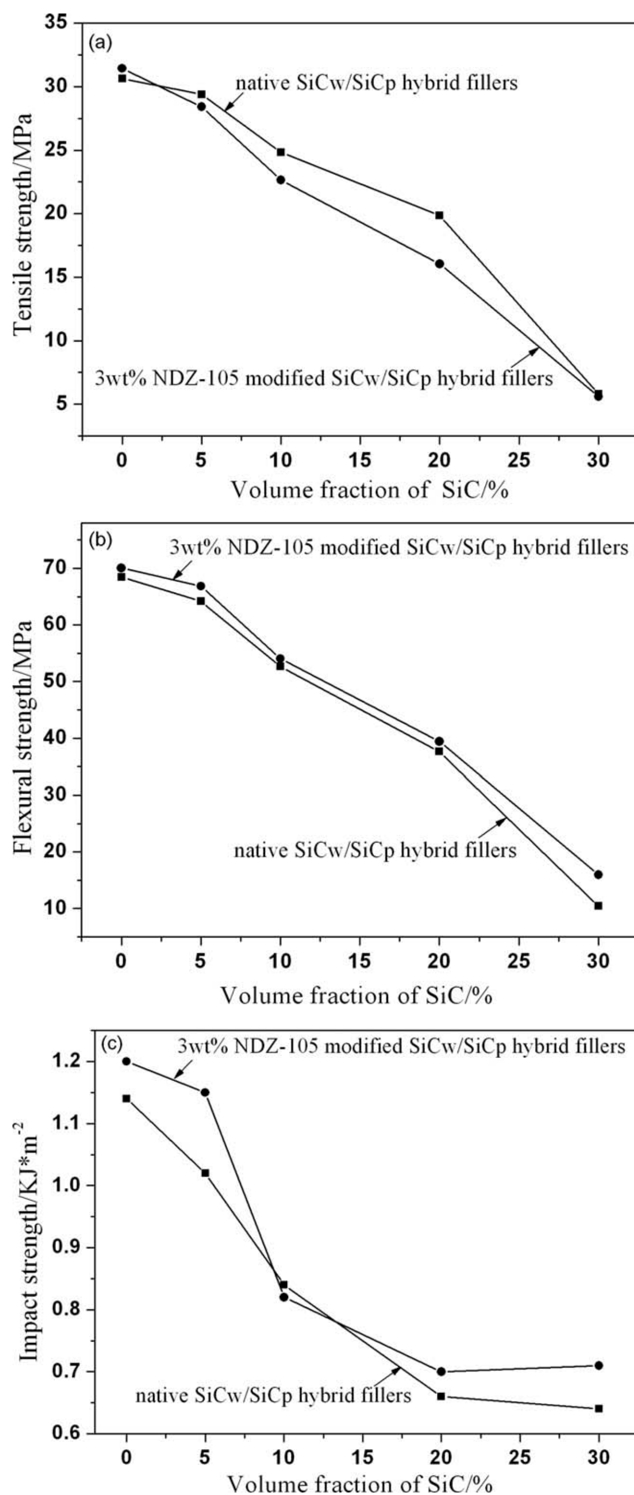

Figure 6 Effects of SiCw/SiCp hybrid fillers and NDZ-105 on the mechanical properties of the composites.

SiCw/SiCp hybrid fillers, thus decreases the tensile strength of the composites.

Thermal property of PS/SiCw/SiCp composites

TGA curves of native PS and PS/SiCw/SiCp composites are presented in Figure 7. It can be seen that the weight loss of the native PS is 1% at the beginning of the experiment (0–275°C), the moment is mostly due to the loss of absorbed water and other volatilization vaporizing. The weight loss of the native PS reaches 100% over the range of 275–450°C, the moment can be contributed that the PS begins to fuse, char, and further decompose, until all organic compounds volatilize.

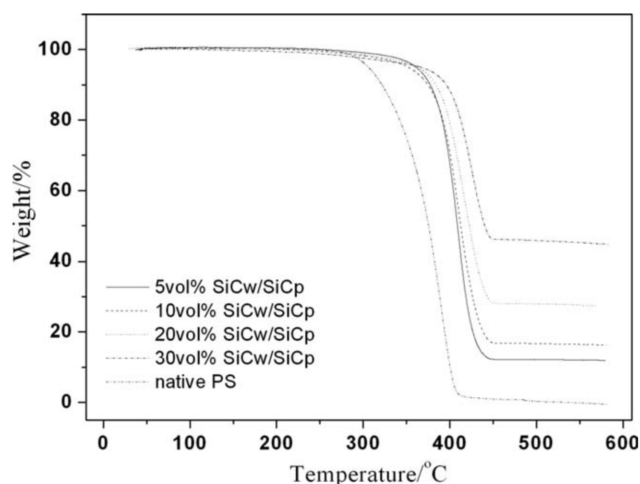

Figure 7 TGA curves of native PS and PS/SiCw/SiCp composites.

From Figure 7, it is also shown that the thermal decomposition temperature increases with the addition of SiCw/SiCp hybrid fillers. It is mainly due to the efficient combination between PS and SiCw/SiCp hybrid fillers. Moreover, SiCw/SiCp hybrid fillers have a relatively higher heat capacity and thermal conductivity. Therefore, SiCw/SiCp hybrid fillers are preferable to absorb the thermal energy, and make the main chain of PS decompose at higher temperature.

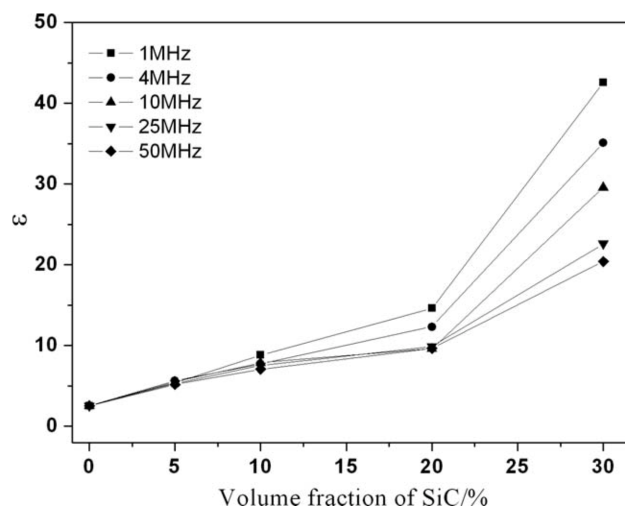

Figure 8 Effects of SiCw/SiCp hybrid fillers on the dielectric constant of the composites.

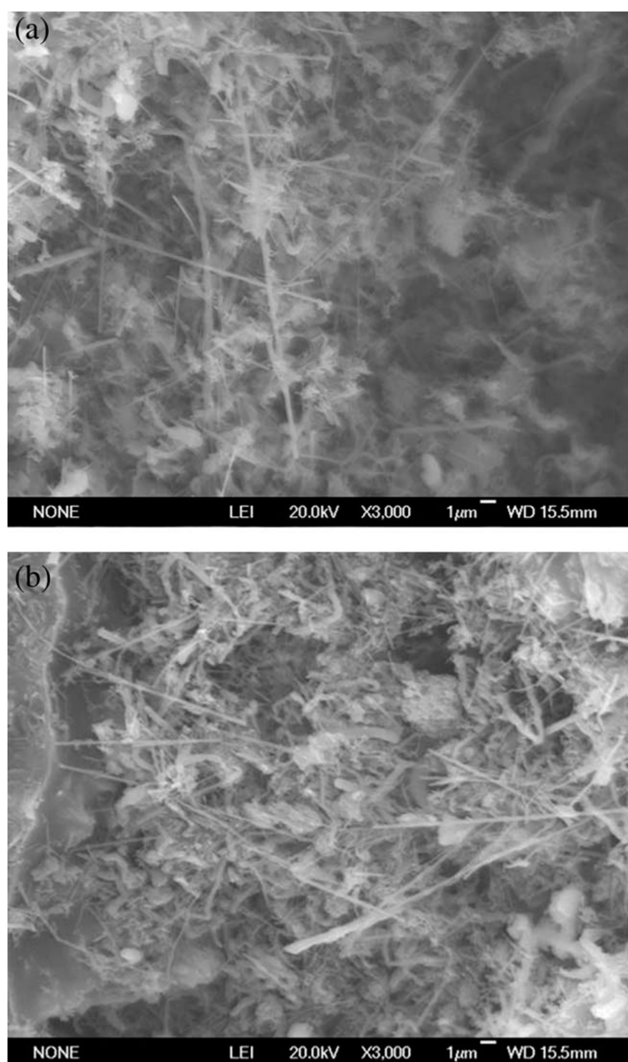

Figure 9 SEM morphologies of PS/SiCw/SiCp composites (3000×) (a) 10 vol % SiCw/SiCp; (b) 30 vol % SiCw/SiCp.

Dielectric properties of PS/SiCw/SiCp composites

Figure 8 shows the effects of SiCw/SiCp hybrid fillers on the dielectric constant of the composites. The dielectric constant of the composites increases with the increasing volume fraction of SiCw/SiCp hybrid fillers. It is attributed to a relatively higher dielectric constant of SiCw/SiCp hybrid fillers. The polarization performance of the composites improves, and the dielectric constant increases.

The low volume fraction of SiCw/SiCp hybrid fillers disperses randomly in PS matrix and has weak interaction between each other to present a little increase of dielectric constant. With the further increasing volume fraction of SiCw/SiCp hybrid fillers ($\geq$20 vol %), the concentration reaches at the region to contact with each other, and the continuous channel can be formed by tunneling effect or electron transition. And the dielectric constant enhances obviously.

SEM morphologies of PS/SiCw/SiCp composites

The SEM morphologies of PS/SiCw/SiCp composites are shown in Figure 9. There is a certain connectivity of SiCw/SiCp hybrid fillers in small region, and the clusters occur at higher volume fraction of SiCw/SiCp hybrid fillers, as well as the formation of percolation paths of SiCw/SiCp hybrid fillers in the PS matrix. However, interface defects and stress concentration points are easily introduced with the more clusters formation of hybrid fillers.

CONCLUSIONS

The SiCw/SiCp hybrid fillers are more favorable to improve the thermal conductivity of the composites. The thermal conductive coefficient λ of the composites is 1.29 W/m K with 40 vol % SiCw/SiCp hybrid fillers, about seven times higher than that of native PS. The mechanical properties of the composites decrease with the increasing volume fraction of SiCw/SiCp hybrid fillers. Both the thermal decomposition temperature and the dielectric constant of the composites increase with the addition of SiCw/SiCp hybrid fillers. At the same addition of SiC, surface modification results in the composites improving the thermal conductivity by minimizing the interfacial phonon scattering, and enhancing the mechanical properties by improving the wettability and uniform dispersion of SiC in the PS matrix.

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