Effects of Polyphenylene Oxide Content on Morphology, Thermal, and Mechanical Properties of Polyphenylene Oxide/Polyamide 6 Blends

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ABSTRACT: A series of composites of PPO/PA 6 with improved toughness were synthesized by using ε-caprolactam as a reactive solvent. Inserting minor PPO macromolecules (1–3 wt %) into PA 6 matrix obviously reduced the crystallinity of PA6. Two crystallization temperatures were found when 6 wt % PPO was added. SEM revealed that the phase morphology of the composites could be manipulated by varying the content of PPO in PA 6. As a consequence, the impact strength and the elongation of PPO/PA6 were improved with maintenance of tensile strength when quite small content of PPO (1–3 wt %) was incorporated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2076–2081, 2006

Key words: crystallization; polyamide 6; polyphenylene oxide; reaction-induced phase separation; toughness

INTRODUCTION

Polyamide 6 (PA 6) is one of the important engineering plastics with excellent solvent resistance and good processability. However, most polyamides have a number of deficiencies, including low-heat distortion temperature, poor dimensional stability, and low impact strength. On the other hand, polyphenylene oxide (PPO) has maintained a key position within engineering plastics since its inception in the late. It exhibits high-dimensional and good thermal properties, but deficiencies such as poor solvent resistance and difficulty to process prohibit it from a broad usage. The combination of PPO and PA 6 has a chance to give mutually complementary properties. Polymer blends of PA 6 and PPO have attracted great interest from both industries and academia.[1]

However, PA 6 and PPO are immiscible. Simple melt blending of the two polymers generally results in poor mechanical properties because of ill dispersion and the lack of adequate interfacial adhesion.[2]

The mechanical properties of blends are dominated by its microstructure, especially by the morphological structure, which is strongly influenced by processing conditions.[3] Besides the thermodynamic factor, the final phase morphology can also be controlled by the phase separation kinetic factors, such as temperature, concentration, viscosity change, etc.[4]

Phase separation often occurs upon polymerization of the reactive solvent in solution of polymer/reactive solvent with respect to the incompatibility of most polymers. Studies of chemically induced phase separation create possibilities for controlling the final morphology of polymer blends and enable preparation of special morphologies impossible to obtain them via conventional method by mixing.

Conventionally, much attention has been given to the toughening of epoxies by applying a neat epoxy resin as reactive solvent for PC, PEI, PPE, PSF, rubbers, etc.[5] Lactams, such as ε-caprolactam, are another special group of reactive solvents, whose polarity can favor solubility of various polymers. For example, less polar lauryllactam is a better solvent for PE, while more polar ε-caprolactam easily solve PEI, PPE, PSF, rubbers with functional groups, etc.[6] Furthermore, ε-caprolactam can be polymerized via anionic ring opening polymerization, which generally proceeds faster than the step growth polymerization of epoxy or the radical polymerization of styrene, MMA, etc.

Recently, anionic polymerization of ε-caprolactam in the presence of PPO has already been reported.[6,7] However, to our knowledge, systemic study of mechanical, thermal, and morphological properties has not been made.

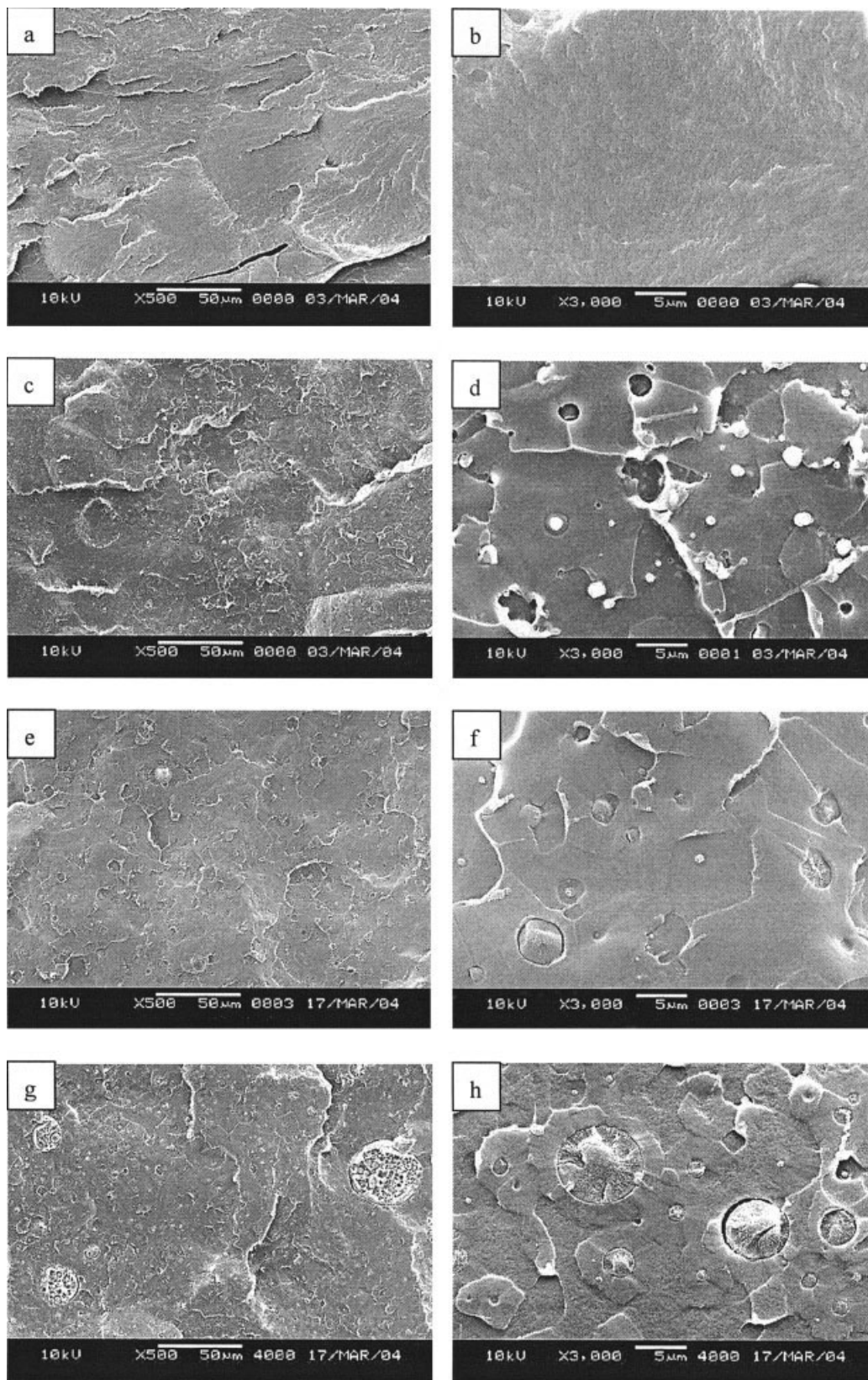*Correspondence to:* G. S. Yang (ygs@Geniuscn.com).

Figure 1 SEM micrographs of fractured surfaces of PPO/PA 6 containing (a, b) 0 wt % PPO; (c, d) 1 wt % PPO; (e, f) 3 wt % PPO; (g, h) 4 wt % PPO; (i, j) 5 wt % PPO; and (k, l) 6 wt % PPO.
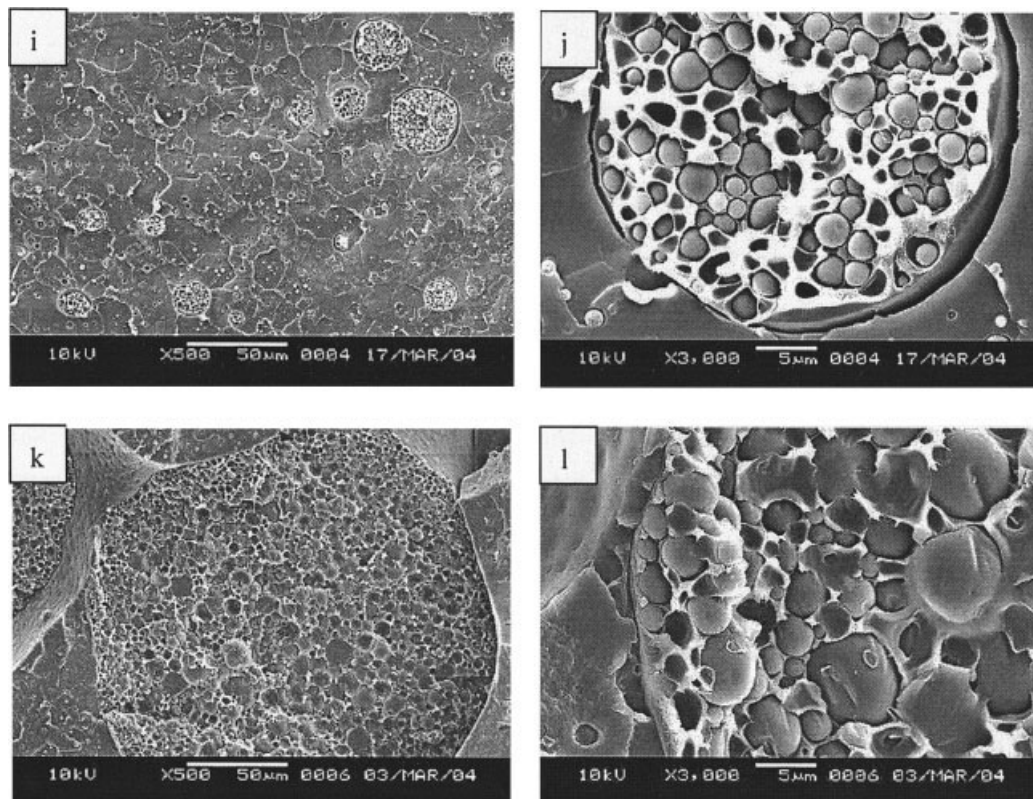
Figure 1 (*Continued from the previous page***)**

Our previous paper indicated that impact resistance of PA 6 was improved markedly by incorporating a small content of PA 66, at molecular level, into PA 6 matrix. It was found that hydrogen bonding between PA 66 and PA 6 had a significant role in the improvement of PA 6 toughness.[8]

The purpose of this contribution is to investigate that whether an amorphous polymer polyphenylene oxide (PPO), which does not form strong hydrogen bonding with PA6, can enhance impact resistance of PA 6. Still, composites of PPO/PA 6 with improved toughness were synthesized by using ε-caprolactam as a reactive solvent. The effect of the PPO modifier content on the mechanical properties was studied. The corresponding morphology and crystallization behavior of the final composites were characterized by means of DSC and SEM.

EXPERIMENTAL

Materials

PPO was obtained from General Electrics (commercial grade; BHPP 820) and ε-caprolactam was bought from Nanjing Oriental Chemical Company, (commercial grade; Jiangsu province, P. R. China). Sodium hydrate (NaOH) and toluene diisocyanate (TDI) were purchased from Shanghai Chemical Reagents Company

TABLE I
Crystallization Behavior of PURE PA 6 and PPO/PA 6 by DSC

PPO content (%)	T_{g_1} (°C)	T_{g2} (°C)	T_{m1} (°C)	ΔH_{f1} (J/g)	T_c (°C)	ΔH_c (J/g)
0	72.9	52.3	213.2	63.99	173.2	55.0
1	74.3	50.2	212.3	54.58	172.7	56.5
2	81.0	50.9	214.8	47.19	172.6	54.6
3	81.3	51.6	212.1	55.27	169.1	52.9
4	86.0	52.6	213.9	58.8	171.0	54.8
5	87.3	54.0	213.8	48.19	171.8	53.1
6	82.9	53.6	213.8	51.71	170.1 + 144.2	40.9 + 3.1

Subscript "1" indicates first scanning and subscript "2" indicates second scanning.
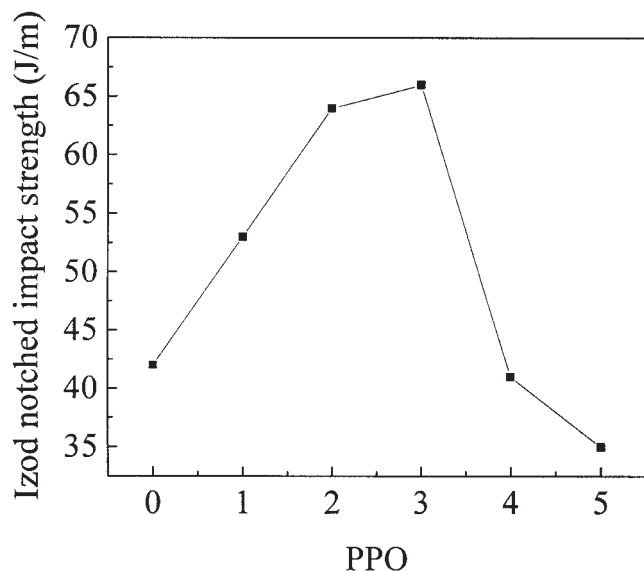
Figure 2 Izod notched impact strength versus PPO content for blends.

(analysis grade; P. R. China) and used without further purification.

Preparation of PPO/PA 6 composites

PPO was dissolved in melted ε-caprolactam monomer at 180°C under nitrogen, and a homogeneous transparent polymer–monomer solution was observed. It was vacuumed at 170°C for about 20 min to remove water. Then, 0.2 wt % NaOH was added under stirring and continuously vacuumed for another 10 min. After this, 0.4 wt % TDI was added with stirring. The mixture was then immediately poured into a mold pre-heated to 180°C and polymerized in oven at 180°C for 20 min. After polymerization, the products were cooled to room temperature and extracted with boiling water to eliminate the residual monomer for 10 h. As a result, the PPO/PA 6 composites with different PPO contents were obtained, which were designated as "PPO/PA 6" below for short.

Measurements

The tensile testing was performed on a universal testing machine (SANS; Shenzhen, P. R. China) according to ASTM D638, with cross-head speed of 50 mm/min. The Izod notched impact strength was measured with an impact testing machine (XJU-22; Chengde, P. R. China), according to ASTM D256. The samples were dried under vacuum for 10 h with 80°C before testing.

The impact-fractured surfaces of specimen images were observed on scanning electron microscope (SEM; JEOL, Tokyo, Japan). Surfaces of fracture specimens were gold-sputtered before observation.

DSC was carried out on a differential scanning calorimeter (DSC; Perkin–Elmer Pyris-1, USA) calibrated with indium. All the DSC measurements were performed from room temperature to 260°C at a heating rate of 20°C/min under nitrogen atmosphere and left there for 10 min to eliminate residual crystals.

RESULTS AND DISCUSSION

Development of the morphology with composition of PPO

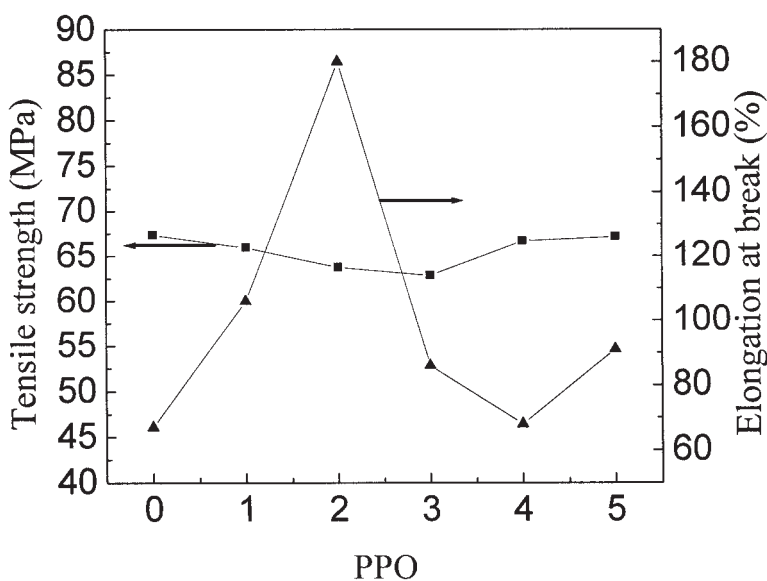Thermodynamics, kinetics, and polymerization rates are competing factors that control the phase separa-

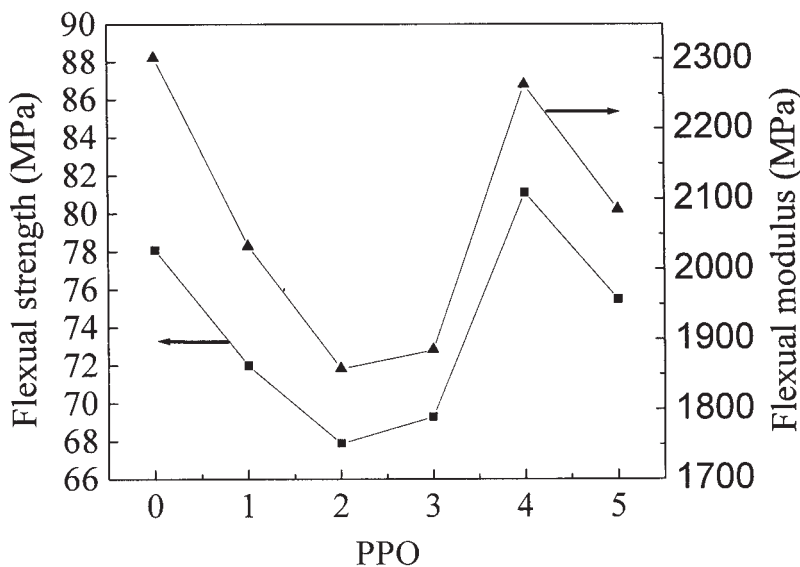**Figure 3** Tensile and elongation versus PPO content for blends.

Figure 4 Flexual strength and flexual modulus versus PPO content for blends.

tion of in situ polymerization system during the process of polymerization of reactive solvent.[9]

It is easier for thermoplastic/ε-caprolactam systems via in situ polymerization to manipulate morphological structure than common thermoplastic/thermosetting system, due to its faster reaction rate of the former than that of the latter.[7]

To characterize the morphology of the composites, SEM measurements of the impact-fractured surfaces were performed (Fig. 1). The SEM micrographs indicated that for PPO/PA 6 containing 1–3 wt % PPO, the PPO phase as the minor phase was dispersed as small droplets in a continuous matrix of PA 6. The size of the droplets obviously increased with increasing amounts of PPO. For PPO/PA 6 with >3 wt % PPO, besides the appearance of particles with larger size, morphologies of dispersed PPO-rich particles with the spherical inclusions of PA 6 were found.

Secondary phase separation may take place in reaction-induced phase separation, which results in dispersed particles with inclusion of the continuous phase matrix.[10] The secondary phase-separation process occurs when the blend first passed into the metastable region and then into the unstable region such that some nucleation and growth precedes spinodal decomposition, or the composition of the coexisting phases changes due to continuous polymerization of the reactive monomers such that they themselves become unstable.[11]

PPO has a poor miscibility with PA 6, and its phase separated in the early stage of curing. At that time, the PPO-rich phase formed due to the relatively low viscosity of the composites at the early stage. Then, the further phase separation occurred just in the separated phases. Because of quite high glass transition of PPO,

and the relatively low polymerization temperature and quick polymerization rate of ε-caprolactam, the diffusion between PA 6-rich phase and PPO-rich phase would be hindered by the increase of viscosity of the system. As a consequence, the individual PPO-rich phase appeared with the introduction of >3 wt % PPO, and the phase separation became more obvious with increasing PPO content in the composites.

Thermal properties

Compared with pure PA 6, both T_c and ΔH_{f1} of the PPO/PA 6 decreased with the addition of PPO into PA 6 (shown in Table I). With increasing PPO, T_{g1} of PA 6 in PPO/PA 6 gradually increased, which may be attributed to the glass transition of PA 6 in the gradient interphase between PPO and PA 6 and/or in the PPO-rich phase.

T_{g2} of PA 6 was less than the corresponding T_{g1} of PA 6 in the first scanning. Owing to the rapid reaction rate, PPO could be finely dispersed of PPO into PA 6 in the in situ polymerization process. The well-dispersed PPO with quite high T_g restricted the chain motion of PA 6 to leading to increasing T_g of PA 6 in PPO/PA 6 with the increase of PPO. Postmelting and corresponding crystallization completed phase separation process of PPO and PA 6 due to their poor miscibility. This led to decreasing glass transition of PA 6 in the second run compared with those in the in situ composites.

It is interesting that two T_c appeared when 6 wt % PPO was added. The lower T_c may be ascribed to the crystallization of PA 6 in PPO-rich phase. In the PPO-rich phase, PA 6 phase was isolated from PPO matrix

and crystallized individually, and so the crystallization of PA 6 was markedly hindered by PPO matrix.

Mechanical properties

The mechanical properties were measured with tensile and impact tests. From the mechanical data, it can be seen that the impact resistance and elongation of PPO/PA 6 were greatly improved compared with those of pure PA 6, while the tensile strength still maintained.

Figure 2 indicates that the Izod notched impact strength of PPO/PA 6 improved as a small amount of PPO, around 3 wt %, was incorporated. The impact strength may increase 1.5 times as compared with pure PA 6.

Figure 3 shows that the elongation of PPO/PA 6 increased three times with increasing PPO contents until 2 wt % compared with that of pure PA 6. Then, no such an increase of elongation could be observed in PPO/PA 6. PPO/PA 6 still kept good tensile strength until 5 wt % of PPO were added.

From Figure 4, it can be seen that flexual strength and flexual modulus of PPO/PA 6 decreased until 2 wt % PPO added. Then, the flexual strength and flexual modulus increased with the addition of PPO in the range of 2–4 wt %. With more than 4 wt % of PPO added, the corresponding flexual strength and flexual modulus decreased again.

Changes in mechanical properties as a function of PPO content may be primarily attributed to change in the portion of amorphous phase of the composites and the resulting morphological structure. The fine dispersion of PPO resulting from rapid in situ polymerization led to decrease of crystallinity, which made the composites easier to deform to dissipate the impact energy. From Figure 4, it can be seen that the trend of the flexual strength and flexual modulus of the composites was similar to that of ΔH_{f1} of the composites. On the other hand, the morphological structure was the same importance for the mechanical properties. Because of the quite large phase of PPO/PA 6 with >3

wt % PPO added, the mechanical properties, especially the notched impact strength, again decreased.

CONCLUSIONS

A series of composites of PPO/PA 6 with improved toughness were synthesized by using ε-caprolactam as a reactive solvent. Inserting minor PPO macromolecules (1–3 wt %) into PA 6 matrix obviously reduced the crystallinity of PA6. Two crystallization temperatures were found when 6 wt % PPO was added. SEM revealed that the phase morphology of the composites could be manipulated by varying the content of PPO in PA 6. Because of quite high glass transition of PPO, the relatively low polymerization temperature and quick polymerization rate of ε-caprolactam, PA 6-rich phase, and PPO-rich phase were in situ formed by the hindrance of the interdiffusion between them due to the rapid increase of viscosity of the system with >2 wt % PPO added. Because of the comprehensive effects of decreasing crystallinity and changing morphology of the blends, the impact strength and the elongation of PPO/PA6 were improved with maintenance of tensile strength when quite small content of PPO (1–3 wt %) was incorporated.

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