

Effects of Mixing Time on Phase Structure and Mechanical Properties of Poly(ethylene terephthalate)/Polycarbonate Blends

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ABSTRACT: The effects of interchange reactions on the solid-state structure and mechanical properties of a 70/30 poly(ethylene terephthalate) (PET)/bisphenol A polycarbonate (PC) blend were studied. Increasing reaction levels were obtained by means of lower screw speeds in the extruder. The progressive production of copolymers with the reaction time increased the amount of each component in the other phase. The concomitant degradation of PET led to a maximum in ductility and tensile and impact strengths whereas the modulus of elasticity and the yield stress were held constant. The maximum in properties took place at a reaction time close to 2.6 min; at longer reaction times the negative effect of degradation began to overcome the positive effect of the interchange reactions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 121–127, 2001

Key words: poly(ethylene terephthalate); polycarbonate; transesterification; degradation; compatibilization; mechanical properties

INTRODUCTION

Thermoplastic polyesters are an important family of polymers that includes materials with a wide range of properties and application fields. Poly(ethylene terephthalate) (PET) is the most used member of this family. Besides blow molded bottles, it is also used¹ as extruded films, sheets, monofilaments, and so forth. PET resins modified to increase the rate of crystallization are also used for injection molding applications.

Some of the PET applications require modification of the base polymer. For example, in blow molding an increase in the glass-transition tem-

perature (T_g) is useful in reducing the crystallization ability and increasing the melt strength. For these reasons, blends of PET with other thermoplastic polyesters have been widely studied. Among them, those with bisphenol A polycarbonate (PC) are perhaps the most important. As a consequence, they have been the subject of much research interest^{2–4}; moreover, several PET/PC blends have been commercialized.⁴

It is known^{3,5,6} that the blends of two polyesters or of a polyester and PC may undergo transesterification reactions in the melt state. This offers an excellent way to control the phase structure and solid-state characteristics and consequently the final polymer properties. This is because the copolymers produced increase the amount of each component in the other phase. In miscible blends the interchange reactions scarcely affect the final properties because the

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blends are already monophasic; but in partially miscible or immiscible blends the copolymers formed act as compatibilizing agents. This has to improve the phase dispersion and the interfacial adhesion and, at least in incompatible blends, should give rise to enhanced properties.^{7,8}

The phase structure,^{5,9–11} transesterification reactions,^{5,6,10,12–19} and mechanical properties^{9,20} of PET/PC blends have been studied. The blends are partially miscible. However, different miscibility levels are reported,^{5,9,10,18,21} probably due to different interchange reaction levels. The progressive development of interchange reactions gives rise^{3,5,18,19,22–24} to homogenization of the blends and eventually leads to single-phase materials. These reactions should affect the phase structure and mechanical properties of the already interesting and commercial PET/PC blends. However, despite this and the commercial interest of the two components and the blends, to our knowledge no work has been published on the mechanical properties of reacted PET/PC blends.

The PET/PC (70/30) blend that gave the best properties in a previous work was also prepared in this study in a twin-screw extruder. Different reaction levels were obtained by means of different screw speeds that gave different residence times (RTs). After injection molding, the phase behavior and the degree of reaction were followed by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), melt flow index (MFI) measurements, and Fourier transform IR spectroscopy (FTIR). The morphology of the blends was studied by scanning electron microscopy (SEM), and the mechanical properties were determined by means of tensile and impact tests.

EXPERIMENTAL

The polymers used in this work were commercial products. The PET was Bripet-1000 from Brilén S.A. (Huesca, Spain). It has an intrinsic viscosity of 0.82 dL/g measured in *o*-chlorophenol at 30°C. The PC was produced by Bayer AG (Makrolon 2405, supplied by Quimidroga S.A., Barcelona, Spain). It has a MFI of 17 g/10 min at 300°C with a 1.2-kg load (ASTM D 1238). Both polymers were dried at 120°C for 14 h before processing in order to avoid moisture-induced degradation reactions.

The PET and PC were mixed at a 70/30 composition using a Collin ZK25 corotating twin-screw extruder-kneader. The screws had a diam-

eter of 25 mm and a length to diameter ratio of 24. The barrel temperature was 300°C and 50, 30, and 13 rpm rotation speeds gave rise to RTs of 1.6, 2.6, and 4.0 min, respectively. These speeds were relatively low, so their possible effect on the degree of shear and reaction should be insignificant compared to that of the RT. The extrudates were pelletized and injection molded in a Battenfeld BA 230E reciprocating screw injection molding machine. The barrel temperature was 295°C and the mold temperature 13°C. The screw had a diameter of 18 mm, a length to diameter ratio of 17.8, a compression ratio of 4, and a helix angle of 17.8°. Tensile (ASTM D 638, type IV) and impact (ASTM D 256) specimens were prepared. Unmodified PET was subjected to the same processing procedures as a reference material.

A Perkin–Elmer DSC-7 calorimeter was used at a heating rate of 20°C/min in a nitrogen atmosphere to analyze the phase behavior, crystallization, and melting of PET. Heating scans were carried out from 30 to 300°C. The thermal transitions (cold crystallization temperature, T_c , and melting temperature, T_m) were determined in the usual way in the first DSC scan. The DMTA tests were carried out to determine the T_g values of the blends in a Polymer Laboratories apparatus at a frequency of 1 Hz in the flexural mode and at a heating rate of 4 °C/min from –120 to 200°C. The T_g values were determined from the peaks of the tan δ –temperature plots. The structural characterization was completed by measurements of the MFI (Ceast extrusion plastometer at 300°C with a 1.2-kg load, ASTM D 1238) and FTIR. The FTIR spectra of the neat PC and the fraction of the blends soluble in chloroform were taken using a Nicolet Magna-IR 560 spectrophotometer.

The tensile tests were carried out on an Instron 4301 tester at $23 \pm 2^\circ\text{C}$ with a crosshead speed of 10 mm/min. The Young's modulus (E), yield stress, breaking stress, and strain at break were obtained from the force–displacement curves. Notched Izod impact tests were carried out on a Ceast 6548/000 pendulum. The notches (2.54-mm depth and 0.25-mm radius) were machined after injection molding. A minimum of eight specimens were tested for each reported value in both the tensile and impact tests.

The SEM (Hitachi S-2700) was carried out after gold coating (Jeol JFC-1100 fine coat ion sputter) on cryogenically fractured surfaces at an accelerating voltage of 25 kV. Previously, the specimens were heated for 6 h at a temperature of 110°C, which is slightly above the T_g of PET, in

order to facilitate PET crystallization. The specimens were subsequently cryogenically fractured and their surfaces immersed in chloroform for 20 h to dissolve the PC; then they were cleaned with the same solvent and left to dry in air.

RESULTS AND DISCUSSION

Phase Structure

The level of transesterification reaction depends on the processing method and conditions. This level should influence the phase structure and mechanical properties of the blends. Therefore, the phase structure of the blends after the different experimental conditions of this work was studied by DMTA and DSC. Figures 1 and 2 show the DMTA and DSC plots, respectively, that were obtained for the neat PC and PET and for the PET/PC (70/30) blend after different RTs in the extruder at 300°C. Table I shows the T_g values determined by DMTA and the T_c and T_m measured by DSC. As can be seen in Figure 1, the DMTA plot for PC showed a single $\tan \delta$ peak at 151°C, which corresponded to the T_g . The plot of PET showed a main T_g peak at 82°C and a small peak at higher temperatures that also appeared in the blends. It corresponded to the PET crystallization because it led to a storage modulus (E') increase. The $\tan \delta$ -temperature plots of the blends showed a low temperature peak that corresponded to a PET-rich phase. The peaks at middle temperatures corresponded to the T_g of a PC-rich phase, because they led to a decrease in E' . As stated before, the higher temperature peaks

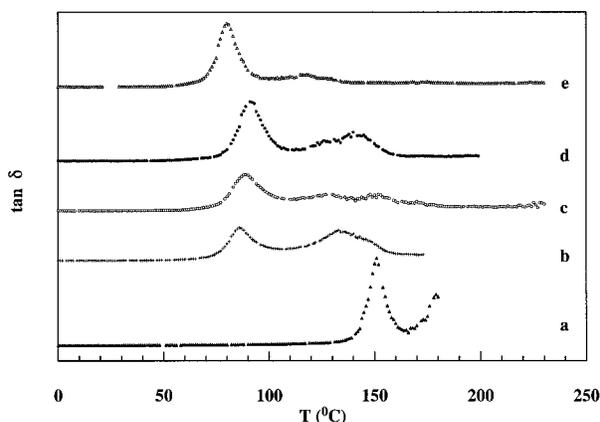


Figure 1 DMTA plots for the neat PC (plot a) and PET (plot e) and for the 70/30 blends at residence times (min) of 1.6 (plot b), 2.6 (plot c), and 4.0 (plot d).

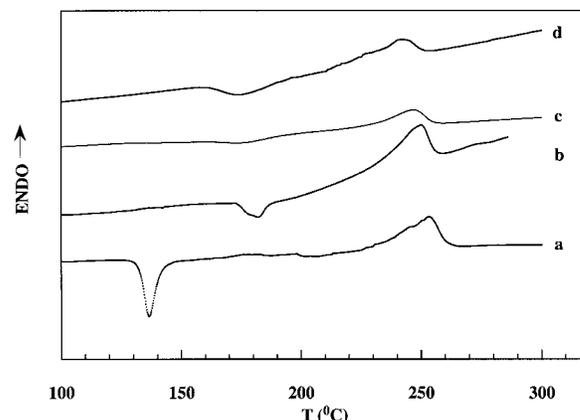


Figure 2 DSC plots for the neat PET (plot a) and for the 70/30 blends at residence times (min) of 1.6 (plot b), 2.6 (plot c), and 4.0 (plot d).

(shoulder after 1.6 min RT) were due to the PET crystallization. This behavior indicated the presence of two amorphous phases in the blends. In agreement with previous results^{10,13,18,19} and as seen in Table I, the T_g values of all the blends were intermediate between those of PET (82°C) and PC (151°C). This indicated a slight partial miscibility of PC in PET and PET in PC.

As can also be seen in Figure 1 and Table I, at increasing RTs the T_g values of the blends approached each other slightly because of the interchange reactions and the incorporation of some units of each component throughout the macromolecular chains of the other.^{3,5,6,18} This ought to enhance the mechanical compatibility of the components of the blend. The small change in both T_g values as compared to that of other works^{5,18} must have been due to the selected blend composition and the experimental conditions. The approximate composition of each amorphous phase at the different RTs, calculated from the Fox equation,²⁵

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

is shown in Table II, where the T_g is for the blend, $T_{g,1}$ and $T_{g,2}$ are the T_g values of the two pure components, and w_1 and w_2 are the weight fractions of both components.

As can also be seen in Figure 2 and Table I, the T_c of PET from the glassy state decreased very slightly with the RT. This would indicate enhanced PET crystallization. This effect, although slight, was unexpected because interchange reac-

Table I Thermal Transitions of 70/30 PET/PC Blends

Residence Time (min)	DMTA		DSC	
	T_{gPET} (°C)	T_{gPC} (°C)	T_c (°C)	T_m (°C)
1.6	86	132.5	179.1	250.4
2.6	88	127.5	175.2	244.1
4.0	90	125.5	175.2	240.8

tions should probably hinder it. This pointed to another effect taking place in addition to that of interchange reactions. A possible explanation was a molecular weight decrease of PET at high RT that is discussed later. The T_m of PET decreased with the RT, as expected, taking into account the incorporation of PC units throughout the PET chains and the consequent decrease in the crystallizable segment length of PET.^{3,5}

The melting (ΔH_m) and crystallization (ΔH_c) enthalpies are shown in Table III. The crystallinity level was calculated from the ΔH_m and ΔH_c values and a melting enthalpy of 166 J/g.²⁶ As can be seen, the crystallinity level was low and its change was too small to influence the mechanical properties that are discussed in the next section. It can also be seen that both enthalpies increased with the RT. However, the opposite was expected because the amorphous PET content in the amorphous PET-rich phase decreased with RT (Table II) and because the reactions hindered crystallization. A possible explanation, as in the T_c decrease, was a decrease in the molecular weight of PET,²⁷ which was consequence of degradation at a high RT. In order to check this possibility, the MFI of the blends were measured and are shown in Table IV. Note that the MFI increased with the RT, indicating that degradation took place.

Considering which component degrades, according to other authors^{28–30} PET suffers thermal and mechanical degradation during processing at temperatures higher than 270°C while PC is

much more stable,³¹ even at higher temperatures. Therefore, leaving out the minor hypothetical influence of the interchange reactions, the increase in MFI should be due mainly to a decrease in the molecular weight of PET. This decrease would also give rise to the observed enhanced crystallization ability. The preferential degradation of PET over that of PC was investigated further by measuring the MFI of the bulk polymers after holding each pure component in the cylinder of the MFI apparatus for additional times of 4 and 9 min at 300°C. The values obtained are reported in Table V. The MFI of PET quickly increased with time, indicating a clear degradation of PET. On the contrary, the MFI of PC slightly increased with time. These observations indicated that PET was the component responsible for degradation, which gave rise to the enhanced crystallization.

The FTIR analysis was carried out on the chloroform-soluble fraction of the blends. PC is soluble in chloroform but PET is not. The spectra in the carbonyl absorption region of the neat PC and those of the soluble fraction of the blends after RTs of 1.6, 2.6, and 4.0 min are shown and compared in Figure 3. The degradation reactions did not give rise to any noticeable change in the FTIR spectra. However, with respect to the interchange reactions, if no reaction took place, the only carbonyl absorption in the soluble fraction should be that of the soluble PC. However, in addition to the peak of the PC carbonyl at around 1770 cm⁻¹, that of the insoluble PET around 1720 cm⁻¹ also

Table II Composition of Two Amorphous Phases of Blends from Fox Equation

RT (min)	PET-Rich Phase w_{PET}/w_{PC}	PC-Rich Phase w_{PET}/w_{PC}
1.6	90/10	17/83
2.6	85/15	22/78
4.0	80/20	24/76

Table III Melting and Crystallization Heats and Crystallinity of 70/30 PET/PC Blends

RT (min)	ΔH_m (J/g)	ΔH_c (J/g)	Crystallinity (%)
1.6	17.7	14.3	2.1
2.6	24.1	18.9	3.2
4.0	27.5	24.2	3.2

Table IV Melt Flow Index (MFI) of 70/30 PET/PC Blends

RT (min)	MFI (g/10 min)
1.6	21.6 ± 0.2
2.6	25.4 ± 0.5
4.0	39 ± 2

appeared.³² Thus, interchange reactions did take place.

Therefore, the PET/PC blends of this work were composed of two amorphous phases with an initial higher presence of PET in the PC-rich phase (17%) than that of PC in the PET-rich phase (10%). The interchange reactions increased these amounts up to roughly 24 and 20%, respectively. The degradation of PET was an additional process to be taken into account. The crystallinity level of PET at the minimum RT was small (2.1%) and its barely significant variations at higher RTs were not large enough to noticeably influence the mechanical properties.

Mechanical Behavior

The Young's modulus and the yield stress of the PET/PC (70/30) blends did not change significantly with the RT in the extruder and were maintained at 2.28 ± 0.06 GPa and 56 ± 1 MPa, respectively. These values were slightly higher than those of PET (2.14 ± 0.7 GPa and 51.9 ± 0.7 MPa, respectively) and those obtained from the additive rule of mixtures (2.18 GPa and 54 MPa, respectively). Values close to the additive ones were expected because the small strain properties were scarcely sensitive to the adhesion between the phases and the compatibility level. For the same reason, the observed lack of effect of the reactions was also expected. This was in accor-

Table V Melt Flow Index (MFI) of Neat Polymers

Additional Time in MFI Cylinder (min)	MFI _{PET} (g/10 min)	MFI _{PC} (g/10 min)
0	24.6 ± 0.5	15.4 ± 0.2
4	40.1 ± 0.9	16.9 ± 0.9
9	58.2 ± 2.0	19.9 ± 1.0

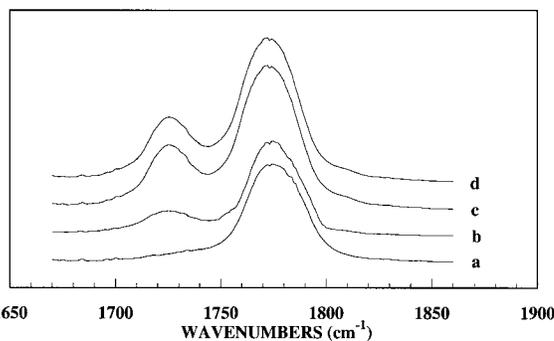


Figure 3 FTIR spectra of neat PC (plot a) and the soluble fraction of the blends at residence times (min) of 1.6 (plot b), 2.6 (plot c), and 4.0 (plot d).

dance with the behavior observed in other similar systems such as PET/polyarylate (PAr).⁸

The strain at break for the 70/30 blend was initially $218 \pm 5\%$ and then changed to 240 ± 16 and $171 \pm 4\%$ when the RT was changed to 2.6 and 4.0 min, respectively. These values were lower than that of neat PET ($357 \pm 4\%$) and the value obtained from the additive rule of mixtures (271%). The initial and slight (10% of the initial value) ductility increase from 218 to 240% with the RT was probably due to improved adhesion as a consequence of interchange reactions; but then it decreased to 171%, probably because of PET degradation. In fact, a dramatic decrease in PET ductility was observed previously as a consequence of a molecular weight decrease.^{27,29} A similar trend was observed in PET/PAr (75/25) blends at increasing RTs at high temperatures.⁸ Thus, it appeared that there was a maximum RT, close to 2.6 min, after which the positive effect of the interchange reactions was overcome by the negative effect of PET degradation.

Figure 4 shows the breaking stress and the impact strength of the blends as a function of the RT. The values corresponding to unmodified PET are plotted as a reference on the vertical axis. The breaking stress showed a trend similar to that of the strain at break, because breaking took place in the stress-hardening region after the cold-drawing zone of the tensile curves. The right side of Figure 4 shows that the poor impact strength at the minimum RT showed a maximum after a RT of roughly 2.6 min, as took place in the case of ductility. However, in the case of the impact strength, the maximum was much more important than that of the ductility. This is because the impact strength is an important property of PET and because the impact strength of the 2.6 min

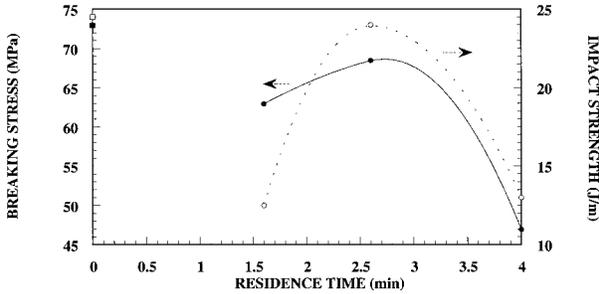


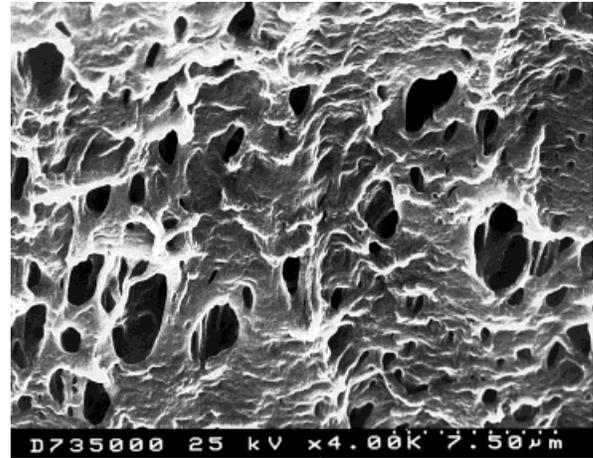
Figure 4 The (●) breaking stress and (○) notched Izod impact strength of the blends versus the residence time. (□, ■) The corresponding values of unmodified PET are shown in the vertical axis.

reacted blend in the extruder was almost 100% higher than the value of the blend with a RT of 1.6 min. As in the case of ductility, longer RTs were negative due to PET degradation. Thus, there was a maximum impact strength when the RT increased that took place at the same RT (close to 2.6 min) where the maximum ductility appeared.

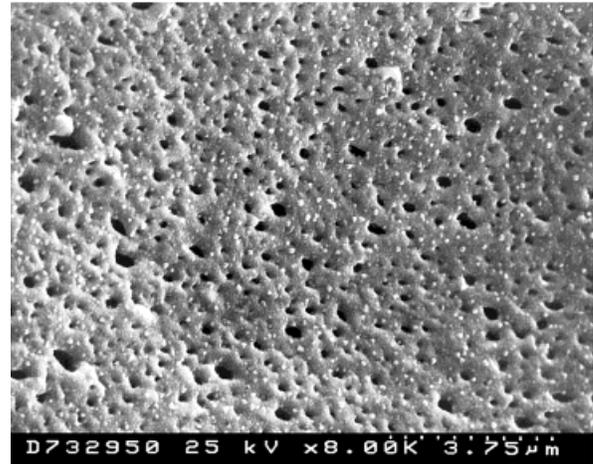
Morphology

The surfaces of cryogenically fractured tensile specimens of 70/30 PET/PC blends at different RTs in the extruder were observed by SEM. The cohesive fracture of the tensile and cryogenically fractured specimens hindered observation of the morphology. Therefore, cryogenically fractured surfaces were treated with chloroform in order to dissolve the PC without affecting the PET. The SEM micrographs corresponding to RTs of 1.6, 2.6, and 4.0 min are shown in Figure 5.

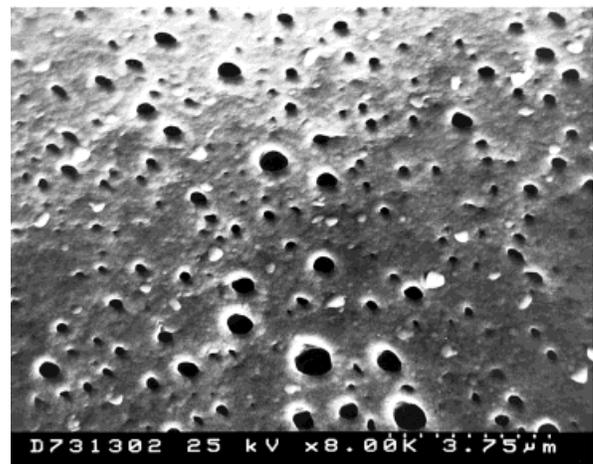
Plot a in Figure 5, which corresponds to the minimum RT of 1.6 min, showed a wide dispersed phase size distribution with some large (up to 5 μm) holes. However, the morphology of the dispersed PC phase in plot b of Figure 5 revealed much more dispersed PC particles (0.1–0.4 μm) than in plot a, showing the compatibilizing effect of interchange reactions. The PC particles coalesced after a RT of 4.0 min, giving rise to the coarser (0.1–0.8 μm) morphology in plot c of Figure 5. This was attributed to the progressive presence of PET in the PC-rich phase and mainly to a change in the viscosities of the components and a modification of the interfacial tension of the blends, a consequence of PET degradation. This coarsening was however not the reason for the deterioration of the mechanical properties at high RT. This was because the initial phase size was much larger and the ductility was large. So, leav-



(a)



(b)



(c)

Figure 5 SEM microphotographs of cryogenically fractured specimens at residence times (min) of (a) 1.6, (b) 2.6, and (c) 4.0.

ing out possible morphological reasons, the decrease in mechanical properties at RTs longer than 2.6 min must have been mainly due to the degradation of the PET matrix of the blends.

CONCLUSIONS

Two kind of reactions took place in the PET/PC (70/30) blend as the RT in the extruder increased: an interchain exchange reaction between the functional groups of both polymers and degradation reactions, mainly in PET. At the minimum RT, the presence in each phase of the other component of the blend was small (10 and 17%), but increased (20 and 24%) through the formation of copolymers, a consequence of transesterification reactions.

At an RT of roughly 4 min, the effects of the degradation reaction became more important than those of the interchange reactions, deteriorating both the ductility and the impact strength of the blends. A coalescence of the dispersed phase took place, but the decrease in properties was mainly attributed to the degradation of the PET matrix. At RTs up to 2.6 min, however, the compatibilizing effect of the transesterification reaction was more important than that of degradation and the development of interchange reactions gave rise to an improvement in both the ductility and the breaking stress while the modulus and the yield stress stayed constant.

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