Macromol. Symp. ***194***, *13–26 (2003)*

Polymerization-Filled Composites and Nanocomposites by Coordination Catalysis

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Summary: Polyolefinic microcomposites and layered silicate nanocomposites were prepared by the in-situ polymerization of ethylene (and α-olefin) via the so-called polymerization-filling technique. Various fillers with either basic, acidic, metallic or carbonaceous surface, as well as non-modified clays such as montmorillonite and hectorite, were first treated by trimethylaluminum-depleted methylaluminoxane before being contacted by a titanium or zirconium-based metallocene catalyst. The (nano)composite was formed by addition and polymerization of ethylene (and α-olefin). This technique makes possible the complete encapsulation of every filler particle within the (co)polyolefinic matrix ranging from thermoplastics to elastomers. The so-obtained (nano)composites, often coined as "homogeneous" (nano)composites, exhibit improved mechanical properties, as compared to more conventional melt blends for a same filler content.

Introduction

Combination of organic polymers with inorganic fillers is an effective and flexible method to tune up the range of properties of these polymers. Actually, most composites that consist of a thermoplastic matrix and particulate filler are commonly prepared by mechanical blending of the constituents above the melting temperature of the polymer. Mechanical kneading is however unable to promote fine and homogeneous dispersion of the filler, particularly at high filler content. Above ca. 60 wt % filler, the particle aggregation results in extremely brittle materials.[1] As a typical example, melt blending of thermoplastic polyolefins with hydrophilic fillers usually leads to materials with poor mechanical

CCC 1022-1360/00/$ 17,50+.50/0

properties, as result of the weak interfacial adhesion between the hydrophobic matrix and the hydrophilic surface of the filler.[2] In order to alleviate this problem, fillers have been modified by surface active agents and coupling agents.[3-6] The encapsulation of the filler by a polymeric matrix[7,8] is another technique, which allows a zone of intermediate modulus between the filler and the matrix to be built up, so reducing local stress concentration responsible for the filler-matrix debonding and the crack propagation, and improving accordingly the mechanical and impact properties. However, this technique requires to use functional polymers in order to crosslink the encapsulation layer, which increases the cost of the final material.

Besides the straightforward melt blending technique, exists another method that has proved very efficient in improving the degree of dispersion and deagglomeration of inorganic fillers, particularly in polyolefinic matrices. This method, known as the Polymerization-Filling Technique (PFT),[2,9-11] consists in polymerizing an olefinic monomer like ethylene directly onto the surface of the filler by anchoring on the latter a Ziegler-Natta organometallic complex able to catalyze the polymerization reaction. The obtained composites exhibit improved mechanical properties, as compared to classical melt blends for a same filler content.[12-14] This method leads to so-called "homogeneous" composites,[4,5] as result of deagglomeration and stabilization of the filler particles when treated by the constitutive components of the polymerization catalyst. Since polymer chains are formed from the filler surface (including pores open to the surface), they are physisorbed onto the particles. These characteristic features explain that, in contrast to conventional mechanical melt blending, PFT leads to composites with a much more uniform filler distribution, a considerably enhanced interfacial adhesion, even at high filler content (>90wt%).[3] Formation of ultra high molecular weight polyethylene (UHMWPE) is one characteristic feature of PFT, with the undesirable consequence that the material cannot be processed by the commonly used techniques (injection molding, extrusion). Recent works[14,15] reported on the combination of hydrogen and a new Ti/Mg/Al-based Ziegler-Natta catalyst in order to control the molecular weight of the PE matrix, failing however in producing valuable filled-polyolefins. Kaminsky et al.[16,17] have been the first to treat filler surface by metallocene-based catalysts for the production of filled-polyolefins. The interesting point is that this family of catalysts is well known for its ability to copolymerize ethylene with α-

olefins.[18]

This paper aims at reporting on the use of metallocene catalysts in the polymerization-filling technique for the production of composites based on polyethylene and ethylene/linear olefin copolymers. Attention will also be paid to the potential of hydrogen to act as transfer agent, so decreasing the molecular mass. The versatility of the investigated method will be illustrated by producing (co)polyolefin-based composites from particulate fillers of deeply different characteristics, including composition (inorganic, organic or metallic), morphology and surface property (acidic or basic). This study will also show that nanocomposites consisting of polyethylene and non-modified layered silicates (Li^+ hectorite, Na^+ montmorillonite) can be prepared by the polymerization-filling technique catalyzed by metallocene/methylaluminoxane (MAO) complexes.

Experimental

Materials

The catalysts investigated in the present work were (tert-butylamido) dimethyl (tetramethyl-η^5-cyclopentadienyl) silane titanium dimethyl (CGC) and bis(n-butylcyclopentadienyl) zirconium dichloride provided respectively by DOW Benelux N.V. and Witco GmbH and were used as received. Methylaluminoxane (MAO, 10wt% solution in toluene) was purchased from Witco GmbH and used as received. Ethylene (Air Liquide, 99.95%) was dried by passing through a 4A molecular sieve column. Hydrogen (Air Liquide, 99.999%) was used as received. 1-octene (Aldrich) was passed through alumina, dried over calcium hydride, and then distilled over Na/K alloy prior to use. 1,9-decadiene (DOW Terneuzen) was dried over Na/K before use. Kaolin (Satintone W/W, average particle size : 1.4 μm, Engelhardt), silica (FK 160, average particle size : 7 μm, Degussa), glass beads (CP7000, 90% beads size being in the 2.4 μm and 4.5 μm range, Potters-Ballotini), wollastonite (Vansil 30, average particle size : 10 μm, Vanderbilt), magnesium hydroxide (Hydrofy N 1.5, particle size between 1 and 50 μm, Nuova Sima), nickel powder (110, average particle size : 1.2μm, INCO) and graphite (EP1002, average particle size : 2μm, Contimet N.V.) were kindly provided by the producers/suppliers. Two layered silicates were studied as well : natural montmorillonite (Swy-1 from the University of Missouri, Crook County, Wyoming, USA) and synthetic hectorite (Laponite RD from Southern Clay Products, USA). The two clays were prepared as follows, prior to MAO treatment : dispersion in water, elimination of non-swollen particles by decantation and isolation of the purified layered silicate by freeze-drying. Heptane and toluene were refluxed over sodium and CaH_2, respectively, and distilled off just prior to use.

Filler treatment

Activation of filler surface by MAO has been conducted as follows. 20 g of filler (previously dried for 16 hours under reduced pressure (10^{-2} mm Hg) at 105°C) were suspended in 250 ml of dried n-heptane. Before addition to the filler slurry, the MAO solution was let to evaporate under reduced pressure in order to eliminate residual trimethylaluminum (TMA), and then solubilized in 20 ml of freshly dried toluene. The TMA-depleted MAO solution was immediately added to the filler suspension, and the mixture was allowed to react at room temperature for one hour. Solvents were evaporated and the dry filler was treated at 150°C under reduced pressure for two hours. The filler was then washed twice with dried toluene (2 x 100 ml) at 80°C, and it was finally suspended in 250 ml of dried n-heptane. The catalyst solution was added to the filler and allowed to react with it at 80°C for 1 hour, before being transferred into the reactor.

Polymerization

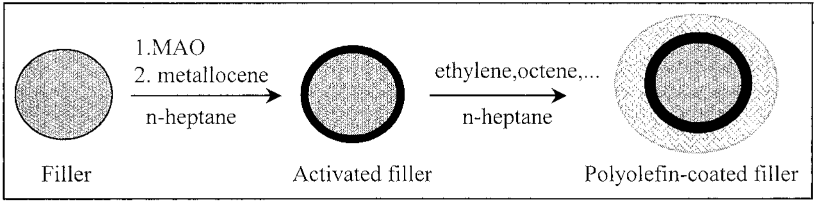
Batch-mode polymerization was carried out in a 2L stainless steel Zipperclave® reactor (Autoclave Engineers). The dried and oxygen-free reactor was heated up to 70°C and sequentially filled with 1100 ml of dried n-heptane, dried 1-octene and 1,9-decadiene when needed, and the treated filler suspension. When required, the reactor was saturated by hydrogen at a given partial pressure. The reactor was then flushed in with dried ethylene (from 9 to 20 bars) at 70°C. Ethylene consumption was monitored by a mass flowmeter. When the desired amount of ethylene was consumed, the polymerization was stopped by the simultaneous release of the ethylene pressure and the cooling down of the reactor. The final product was filtered out when possible, otherwise the solvent was let to evaporate or the composite was recovered by "precipitation" from acetone added with a few drops of aqueous HCl. It was then dried under vacuum at 70°C for at least 6 hours.

Measurements

Thermogravimetric analysis (TGA) was performed under a dry air flow with a DuPont 51 thermogravimetric analyzer at a heating rate of 20°C/min. The filler content was calculated from the constant mass observed at 600°C. The melting behavior of the composites was analyzed with a DuPont 910 differential scanning calorimeter. Measurements were carried out from -150°C to 200°C, under nitrogen, at a heating rate of 10°C/min, data of the second run being recorded. The melting temperature (T_m) was ascribed to the temperature at the maximum of the melting endotherm. Scanning Electron Microscopy (SEM) was carried out with a JEOL6100 microscope. Mechanical properties were measured with an Instron universal tensile tester (model DY24) in accordance with the D6385 ASTM norm. U-notched specimens were tested with a Charpy Ceast 6546 apparatus, according to the ASTM D1238 norm.

Polymerization-filled microcomposites via metallocene catalysis

The usual way to handle Ziegler-Natta catalyst in the polymerization-filling technique consists in anchoring the catalyst directly onto the filler surface followed by its activation (if necessary) with a cocatalyst[14] before starting up the olefin polymerization. In case of metallocene catalysts, whose the active species might be very sensitive towards the filler surface, the reverse sequence for the filler surface treatment has been followed (Scheme 1). Therefore the cocatalyst (MAO) has been first reacted with the filler surface. The Me-Al bonds of MAO can indeed react with the hydroxyl groups available on the surface of acidic fillers leading to Al-O covalent bonding. In the case of more basic fillers, the Lewis acid sites of MAO are reactive towards the surface. Therefore, MAO has the power of being attached to a large variety of surfaces (kaolin, wollastonite, silica, glass, $Mg(OH)_2$, metallic nickel, graphite,...).[19,20] In the second step, a metallocene such as bis(n-butylcyclopentadienyl) zirconium dichloride or (tert-butylamido) dimethyl (tetramethyl-η^5-cyclopentadienyl) silane titanium dimethyl (so-called constrained geometry catalyst; CGC), is reacted with the activated surface with formation of the active polymerization species. It is worth noting that the use of trimethylaluminum-free MAO solution at high temperature, e.g. at 150°C, leads to a significant increase of the amount of MAO fixed onto the filler surface.



⇨ **PFT on a wide range of fillers :**

- ☞ acidic surface (kaolin, silica, glass beads,…)
- ☞ basic surface (magnesium hydroxide,...)
- ☞ organic fillers (graphite, carbon black,...)
- ☞ metallic fillers (nickel,…)

Scheme 1

Ethylene polymerization

Whatever the properties of the filler surface previously activated as aforementioned, ethylene is polymerized with good to very good catalyst efficiency, which is a substantial improvement compared to the Ziegler-Natta type (or other) catalysts that can only be anchored to acidic surfaces and promote the ethylene polymerization from this type of filler.[2] Each filler particle is homogeneously coated by a layer of polyethylene. This encapsulation of the particles is commonly observed whatever the filler used in this study. It leads to a more homogeneous distribution of the filler throughout the polyolefinic matrix when melted. This characteristic feature, previously observed for Ziegler-Natta activated fillers is one of the reasons for the improvement of the mechanical properties of the composites.[15] Typical examples of such an improvement are displayed in Table 1. Compared to more conventional mechanical blends achieved with HDPE and either kaolin or silica particles, this data show how much the tensile and impact properties can be enhanced by the PFT technique (while keeping the filler content at about the same level).

Although the catalyst is fixed onto the filler particles, hydrogen keeps on behaving as a transfer agent, as testified by the strong reduction of the molecular weight of polyethylene.

so making the composite much more easily processable.[19] For instance, in the absence of hydrogen, the ethylene polymerization catalyzed by CGC ([Al]/[Ti] = 600) deposited on kaolin particles (ethylene pressure fixed at 10 bars) yields UHMWPE chains insoluble in usual SEC solvents and unable to flow at 190°C. The addition of hydrogen (initial partial pressure = 1.2 bar) triggers a significant drop of the polyethylene molecular weight with Mn values in the range of 10,000 g/mol. Furthermore it is worth noting that the catalyst activity is substantially enhanced by the presence of the transfer agent. Indeed, the catalyst efficiency has been increased from 91 to 169 kgPE/gTi.h as a result of the addition of molecular hydrogen.

Table 1 : Mechanical properties of PFC based on HDPE matrices for 2 different model fillers. Comparison with equivalent melt blends prepared by roll milling at 190°C.

Filler and composite type		Content of filler (wt%)	Ultimate tensile stress (Mpa)	Elongation at break (%)	Impact energy[a] (kJ/m^2)
kaolin	melt blend[b]	24.5	27.2	14	6.1
kaolin	PFC	22.7	27.1	302	67.3
silica	melt blend[c]	20	26.1	600	53.4
silica	PFC	22.4	20.6	80	576.4

a) Charpy impact testing; b) polyethylene of 0.8g/10 min melt flow index under 2.16kg; c) polyethylene of 10.2g/10 min melt flow index under 2.16kg

Ethylene and α-olefin copolymerization

Ti-based constrained geometry catalyst (CGC) has also been used in order to prepared composites based on ethylene/1-octene copolymers and ethylene/1-octene/1,9-decadiene terpolymers.[19,21] This catalyst is indeed known for its ability to incorporate easily α-olefins in polyethylene chains. The ethylene/1-octene/1,9-decadiene polymerization has been carried out from the surface of glass beads, kaolin, wollastonite and magnesium hydroxide. For each type of investigated fillers, the decrease in the melting temperature of polyethylene is the signature for the incorporation of 1-octene (see Table 2, in case of kaolin as selected filler). Similarly to the ethylene homopolymerization, hydrogen allows for some control of the molecular weight and it enhances further the catalyst activity. Expectedly, the content of 1-octene comonomer in the feed has a strong influence on the thermal behavior of the final polymer, and on the mechanical (tensile) properties of the related polymerization-filled composites.[19]

Table 2 : Kaolin-filled polyolefins by PFT. Effect of comonomer(s) on the melting behavior of the resulting composites. Conditions : polymerization in heptane at 70°C starting with 20g kaolin particles.

Comonomer at start			P $_{\text{hydrogen}}$ (bar)	Filler content[a)] (wt%)	Melting temperature (°C)
Ethylene (bar)	1-Octene (mmol)	1,9-decadiene (mmol)			
9	-	-	1.1	14.2	137
20	191	-	0	25.3	116
20	191	-	3	17.5	116
20	636	-	3	16.6	94
10	318	5.4	1.1	19.0	94
a) filler content determined by TGA					

Homogeneous coating of filler particles by PFT

When the polymerization reaction is stopped at the very early stage, the filler particles can be completely covered by a thin polymer layer. As typical examples, glass beads have been fully encapsulated by polyethylene and ethylene/1-octene copolymer via the polymerization-filling technique using CGC catalyst activated by surface-anchored MAO.[21] Ca. 10 wt% of (co)polymer proved to be enough to coat fully and homogeneously the glass bead surface as confirmed by SEM (Figure 1). The surface-modified glass beads have been mechanically blended within melted high density polyethylene (HDPE) (Table 3). The polyethylene precoating improves by more than ten times the impact resistance of the HDPE composite filled by 20 wt% of uncoated glass beads. The ultimate tensile strain and the elongation at break are also slightly improved. As far as the glass beads precoated by the ethylene/1-octene copolymer are concerned, both the tensile properties and the impact resistance of HDPE filled by 20 wt% glass beads are improved by the low modulus polyolefinic precoating of the filler (Table 3). The improvement is however less pronounced in this case, as result of a lack of miscibility between the polyethylene matrix and the copolymer coating.[22]

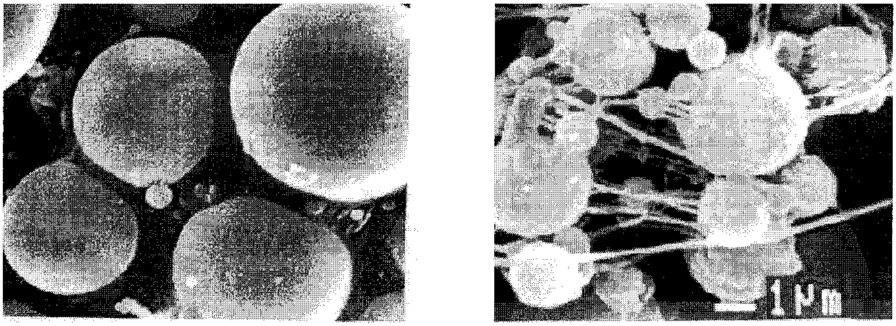


Figure 1 : SEM micrographs of (a) pristine glass beads, and (b) glass beads coated with 7 wt% of ethylene/1-octene copolymer.

Table 3 : Effect of the precoating of glass beads by either polyethylene (HDPE) or ethylene/1-octene copolymer (LLDPE) on Young's modulus (E), stress at break (σ_r), elongation at break (ε_r) and impact energy (I.E.) of composites filled with 20 wt% glass beads.

Composite		E (Gpa)	ε_r (%)	σ_r (MPa)	I.E. (kJ/m^2)
HDPE Matrix	Filler coating (wt %)				
1[a)]	-	1.7	636	24.7	12.0
1[a)]	HDPE (14.5)	1.3	659	28.5	150.5
10[b)]	-	1.4	4.2	26.4	14.5
10[b)]	LLDPE (7.0)	1.5	6.9	28.9	41.0
a) Melt flow index under 2.16 kg load MI_2 = 1g/10min.; b) MI_2 = 10g/10min.					

Polymerization-filled nanocomposites via metallocene catalysis

Nanocomposites consisting of polyethylene and non-modified layered silicates (Li^+ hectorite, Na^+ montmorillonite) have been also prepared by the polymerization-filling technique catalyzed by a metallocene/MAO complex. Non-modified clays are first treated by trimethylaluminum-depleted methylaluminoxane before being contacted by CGC catalyst.[23] The nanocomposite is formed by addition and polymerization of ethylene. The MAO has to be reacted with the filler in a non solvent for MAO (e.g. heptane), because in a good solvent, such as toluene, the filler surface is passivated and most of the alumoxane is lost during washings as result of molecular rearrangement.

In the absence of hydrogen, ultra high molecular weight polyethylene (UHMWPE) is formed and dictates the mechanical properties of the composites (Table 4). Addition of hydrogen expectedly decreases the molecular weight of PE and leads to composites with improved tensile properties, i.e. a marked increase in the Young's modulus and an improved strain behavior. At constant nanofiller loading, the origin for these improvements has to be found in the fine dispersion and exfoliation of the silicate sheets (average thickness ~ 1nm) as attested by XRD and TEM analyses.

Table 4 : molecular weight, thermal and tensile properties of polyethylene-based (hectorite or montmorillonite) nanocomposites prepared by PFT and compression-molded at 190°C.

Filler		Mn	Melting Temp. (°C)	Crystallinity (%)	Strain at break (%)	Stress at break (MPa)	Young's modulus (Gpa)
Type	Loading (wt%)						
-	-	UHMWPE[a)]	142	37	244	25.2	0.69
Hectorite	3.8	UHMWPE[a)]	143	39	205	34.8	0.64
Mont.	3.9	UHMWPE[a)]	145	39	145	29.8	0.66
Hectorite[b)]	3.4	77,000	149	52	467	27.9	1.28
Hectorite[b,c)]	3.4	77,000	n.d.	n.d.	458	29.7	0.89

a) insoluble in 1,2,5-trichlorobenzene for SEC analysis; b) synthesized in the presence of hydrogen; c) premelting at 190°C with the two-roll mill (5 min.)

The compression-molded nanocomposites have been analyzed by DSC. Crystallinity has been quantitatively measured by subtracting the filler mass contribution. As a rule, nanocomposites prepared in the presence of hydrogen display much higher degree of crystallinity and higher melting temperature. The prohibitively high viscosity of the samples prepared in absence of hydrogen may account for a lower crystallinity. Interestingly it has been observed that the melting temperature of HDPE nanocomposites (thus prepared in the presence of hydrogen) decreases as consequence of a decreased heating rate in DSC analysis (from 20 down to 5°C/min.). These data show that the higher melting temperature in the compressed-molded samples results from a slow heat transfer through the composite. This observation suggests that the nanofiller and the way it is dispersed within the polymer can modify the heat transfer properties. A preferential orientation of the filler, parallel to the pressing plane could result in the building up of a heat barrier. For samples prepared in absence of hydrogen, the matrix is too much viscous for the filler to get a preferential orientation, and the melting temperature remains close to the value observed for the powdery HDPE/hectorite nanocomposite as recovered from the reactor, thus before compression-molding (melting temperature : 144°C).

Moreover, the method used for the sample preparation has a direct influence on the mechanical properties, particularly on the Young's modulus, known to be highly dependent upon the existence of a nanocomposite structure. For instance, the HDPE/hectorite nanocomposite has been shaped for testing according to two different methods, i.e., compression-molding of the as-recovered powder (entry 3, Table 4) and compression-molding of the pre-melted composite collected after 5-min kneading at 190°C with a 2-roll mill (entry 4, Table 4). The roll-milled sample shows a Young's modulus (0.89 GPa) lower than the compression-molded sample (modulus at 1.28 GPa). In order to account for this difference, the two processed samples as well as the original powdery nanocomposite have been analyzed by XRD (not shown here). Whereas the powdery sample shows no diffraction peak (which is representative of an exfoliated nanocomposite), the two compression-molded samples (with and without pre-melting) display a very broad diffraction peak between 4 and 8°, evidence for the formation of repetitive structures with a broad distribution of interlayer spacings. The apparition of these broad peaks may arise from a partial collapse of the exfoliated structure upon matrix melting. The broad peak, more intense in case of the melt-kneaded composite, possibly results from a more important collapse of the exfoliated structure as more time and energy has been brought to the system to reach a more thermodynamically stable state. Indeed, theoretical studies have shown that dispersions of relatively polar nanoscopic platelets within a non-polar matrix like PE, are unstable for thermodynamic reasons and cannot be preserved in the melt.[24,25] Separation of the silicate layers by PE chains is therefore thermodynamically unfavorable and the layers tend to collapse as soon as the composite is melted and sufficiently fluid.

The resulting new hybrid structure gives rise to extremely elongated structures as long as 10 μm. This new morphology is characterized by a decrease in stiffness as depicted by the drop in Young's modulus (see last entry of Table 4). On a structural basis, one can note that the collapse of the exfoliated structure may be prevented by increasing the viscosity of the matrix. This is demonstrated in the case of nanocomposites based on UHMWPE. In this case, the molecular weight of the matrix is such high that it prevents collapse from occurring during compression molding.

It is worth noting that Heinemann et al. recently prepared nanocomposites of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) as result of the polymerization of ethylene and long chain α-olefins by various catalytic systems, included metallocene/MAO complexes, in the presence of previously ammonium-exhanged silicates, i.e. organo-modified clays.[26] Intercalation and exfoliation were assessed by X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM).

Conclusion

This study has emphasized that new types of micro- and nanocomposites can be prepared by the polymerization-filling technique (PFT) when metallocenes are used as catalysts. This alternative route requires the filler to be activated by methylaluminoxane (MAO), ideally trimethylaluminum-depleted MAO, before the metallocene is added. Compared to traditional Ziegler-Natta catalysts that can only be attached to acidic fillers, this new system makes possible the encapsulation of a large variety of filler particles by (co)polyolefinic matrices ranging from thermoplastics to elastomers. Furthermore, the molecular weight of the polymer can be tuned by addition of hydrogen such that the matrix melt viscosity can be easily suited to the requirements of the extrusion processes. PFT also allows for the full precoating of filler surface by a thin layer of either ethylene or ethylene /1-octene copolymer (ca. 10wt%). This homogeneous coating has proved beneficial to the tensile and impact properties of composites prepared by kneading this modified filler with melted HDPE, at least compared with the same composites containing the unmodified particles.

Acknowledgements

Authors are grateful to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" for general support in the frame of the "Pôles d'Attraction Interuniversitaires : Polymères et Catalyse". This work was partially supported by the *Région Wallonne* and the *Fonds Social Européen* in the frame of Objectif 1 - Hainaut : Materia Nova. M.A. thanks Dow Benelux for financial and scientific support.

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