DSC and DMA Studies on Silane-Grafted and Water-Crosslinked LDPE/LLDPE Blends

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ABSTRACT: Effects of silane grafting and water crosslinking reactions on crystallizations, melting behaviors, and dynamic mechanical properties of the LDPE/LLDPE blends are investigated using DSC and DMA. From DSC data, cocrystallization of LDPE and LLDPE does not occur, but cocrosslinking of these two polymers is evidenced at the experimental temperature of 100°C, a temperature lower than melting temperatures of both polymers. The water crosslinking reactions of the LLDPE-rich blends enable development of a new phase having a melting endotherm in between that of LDPE and LLDPE. From the thermal fractionation data, interaction between LDPE and LLDPE is observed, and compatibilization of the blends can be achieved by the crosslinking reactions. From DMA data, the storage moduli of the blends are not found to be consistent with their degrees of crosslinking. The storage moduli of the blends are not simply determined by the degree of crosslinking but determined by very complicated but unclear factors. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1808–1816, 2001

Key words: LDPE; LLDPE; grafting reactions; crosslinking reactions; thermal fractionation; dynamic mechanical properties

INTRODUCTION

Silane grafting and water crosslinking reactions of LDPE and relevant changes in thermal properties and physical properties of the polymer due to these reactions have been reported.¹⁻¹⁰ Recently in our laboratories¹¹ silane grafting and water crosslinking reactions of LDPE/LLDPE blends were studied as functions of temperature and time. Degrees of crosslinking of the blends are quantitatively compared and discussed in detail in terms of crosslinking capability, composition, phase separation, molecular weight, and

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morphology of the constituents in blends and in pure state. The silane-grafted LLDPE is found to exhibit a higher crosslinking capability than the silane-grafted LDPE. Degrees of crosslinking of the silane-grafted LDPE/LLDPE blends are found to be not linearly but are zigzagly related to the compositions of the blends, with the silanegrafted LDPE/LLDPE = 50/50 blend giving a relatively high degree of crosslinking compared with the silane-grafted LDPE/LLDPE = 75/25 and 25/75 blends.

LDPE and LLDPE are heterogeneous in the molecular structure, and so are the blends of the two polymers. The extent of heterogeneity of the blends should depend on compatibility of the two constituents. There have been a few methods developed to characterize the molecular heterogeneity including solvent-gradient elution fractionation (SGEF) and temperature-rising elution

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fractionation (TREF).¹²⁻¹⁸ The TREF method is based on crystallizability of the sample by slow cooling from its dilute solution followed by continuous elution with a simultaneous and fairly rapid rate of temperature rise. The SGEF method is based on molecular weight of the sample and carried out by using solvent and nonsolvent mixtures with a variety of compositions. The drawback of these fractionation techniques is that they are time consuming and costly. Differential scanning calorimetry (DSC) has been, thus, used as an alternative technique for thermal fractionation of polymers with heterogeneous molecular structure.^{19–21} The DSC method is based on the same principle of separation as TREF, but it does not physically separate the fractions. With this DSC method, the sample is first melted, then annealed at various decreasing temperatures, starting from the melt to the totally crystallized solid. The melting behavior of the heat-treated sample is then analyzed by DSC. Using the DSC fractionation method, Adisson and coworkers¹⁹ and Keating and coworkers²⁰ evaluated the comonomer distribution of linear low-density polyethylene and ethylene copolymers. Wolf and coworkers²¹ used the DSC fractionation method to identify and distinguish between different types of LDPE.

The silane-grafted water-crosslinked LDPE is also heterogeneous in the molecular structure, and has been demonstrated by multiple endothermic DSC thermograms in our previous articles.^{8,22} Compared with pure LDPE, the introduction of irregularities to the structure of LDPE by the silane grafting and the subsequent network formation have led to a more complicated multiple endothermic DSC thermogram.²² As can be expected, the molecular structures of the LDPE/ LLDPE blends and these blends after silane grafting reactions and/or water crosslinking reactions should be much more heterogeneous than those of the constituents of the blends. After thermal fractionation, the multiple endothermic behavior of the blends should be affected by compatibility or interaction between the two constituents of the blends.

In this article, the DSC thermal fractionation, in combination with heating and cooling scans, is used to characterize the heterogeneous molecular structures of the LDPE/LLDPE blends of both before and after silane grafting and/or water crosslinking reactions. The multiple endothermic behaviors of these blends are examined in terms of compatibility and interaction between LDPE and LLDPE. The effects of silane grafting and/or water crosslinking reactions on the compatibility and interaction between LDPE and LLDPE in the blends are emphatically investigated by using the thermal fractionation analyses and dynamic mechanical property measurements.

EXPERIMENTAL

Materials

All materials were used as received. LDPE (LE4074) was received from Borealis Corporation in Portugal, with a melt index of 2.8 g/10 min and a density of 0.917 g/cm³. LLDPE (AL3108ZD) was received from Exxon Corporation with 3.5 mol % of 1-hexene comonomer in the copolymer, a melt index of 0.8 g/10 min, and a density of 0.921 g/cm³. Melt indices were determined according to the ASTM D1238 at 190°C and 2.16 kg of loading for the two polymers. Dicumyl peroxide was used as an initiator for grafting reactions and supplied by Aldrich Chemical Company (Milwaukee, WI). Vinyl trimethoxysilane was received from Tokyo Kasei Kogyo Co (Tokyo, Japan).

Silane Grafting Reactions

Silane-grafted LDPE and LLDPE were individually prepared by a melt extrusion of the polymer with 0.05 phr (part of reagent per hundred parts of the polymer) of dicumyl peroxide and 5 phr of vinyl trimethoxysilane. A single-screw extruder was used for the silane grafting reactions, and was operated at a speed of 10 rpm and at temperatures ranging from 180°C at the feeding zone to 200°C at the compression zone to 160°C at the metering zone of the extruder (30 mm in diameter, L/D, 19, compression ratio, 3.5).

Preparation of LDPE/LLDPE Blends

The LDPE/LLDPE blends were prepared by melt blending of LDPE and LLDPE in the single-screw extruder. The extruder was operated at 150°C at the feeding zone, 160°C at the compression zone, and 150°C at the metering zone. The constituents of the blends include both before and after silane grafting reactions. Thus, LDPE/LLDPE = 50/50 was the blend of a mixture of 50 parts by weight of LDPE and 50 parts by weight of LLDPE, and S-LDPE/S-LLDPE = 75/25 was the blend of a mixture of 75 parts by weight of silane-grafted LDPE and 25 parts by weight of silane-grafted LLDPE, to give two examples. The obtained

Blend Compositions	Descriptions
LDPE/LLDPE = 100/0	Pure LDPE
LDPE/LLDPE = m/n	The blend of a mixture of m parts by weight of LDPE and n parts by weight of LLDPE
LDPE/LLDPE = 0/100	Pure LLDPE
S-LDPE/S-LLDPE = 100/0	Pure silane-grafted LDPE
S-LDPE/S-LLDPE = m/n	The blend of a mixture of m parts by weight of silane-grafted LDPE (S- LDPE) and n parts by weight of silane-grafted LLDPE (S-LLDPE)
S-LDPE/S-LLDPE = 0/100	Pure silane-grafted LLDPE
X-LDPE/X-LLDPE = 100/0	The water-crosslinked S-LDPE
X-LDPE/X-LLDPE = m/n	The water-crosslinked S-LDPE/S-LLDPE = m/n blend
X-LDPE/X-LLDPE = 0/100	The water-crosslinked S-LLDPE
E-LDPE/E-LLDPE = 100/0	The remainder after decalin extraction of X-LDPE
E-LDPE/E-LLDPE = m/n	The blend remainder after decalin extraction of the X-LDPE/X-LLDPE = m/n blend
E-LDPE/E-LLDPE = 0/100	The remainder after decalin extraction of X-LLDPE

 Table I
 Descriptions for Representative Compositions of Blends Containing LDPE and LLDPE

 before and after Silane Grafting Reactions, Water Crosslinking Reactions, and Decalin Extractions

LDPE/LLDPE and S-LDPE/S-LLDPE blends were then compressed in a hot press at 150°C for 30 s to make film samples for water crosslinking reactions and measurements of dynamic mechanical properties.

Water Crosslinking Reactions

The silane-grafted film samples were immersed into water at 100°C for 24 h to conduct crosslink-ing reactions.

Degrees of crosslinking of the water-crosslinked samples were measured by determining their gel contents after extraction of the soluble component from the samples in decalin refluxing for 6 h. X-LDPE/X-LLDPE = 25/75 denotes the watercrosslinked product from the S-LDPE/S-LLDPE = 25/75 blend. E-LDPE/E-LLDPE = 50/50 denotes the remainder after decalin extraction of the X-LDPE/X-LLDPE = 50/50 blend. Table I lists descriptions for representative compositions of blends containing LDPE and LLDPE before and after silane grafting reactions (with a prefix S for the polymer), water crosslinking reactions (with a prefix X for the polymer), and decalin extractions (with a prefix E for the polymer). After crosslinking reactions in water at 100°C for 24 h, degrees of crosslinking for X-LDPE/X-LLDPE = 100/0, 75/25, 50/50, 25/75, and 0/100 blends were 34.2, 13.5, 34.2, 17.9, and 58.5%, respectively.

Normal DSC Analyses

Samples were heated in DSC (DSC 2010, TA Instruments, New Castle, DE) under nitrogen at a

rate of 10°C/min from 30 to 150°C holding 3 min, followed by cooling at 2°C/min to 30°C, and then heating again at 2°C/min to 150°C to obtain the first cooling exotherms and the second heating endotherms.

Thermal Fractionation

The samples were heated under nitrogen in DSC from 30 to 150° C at 10° C/min, maintained at this temperature for 3 min, and then successively cooled by 10° C at a rate of 10° C/min. The specimens were maintained at each temperature for 30 min. Thus, the specimens were kept at each of the following temperatures: 140, 130, 120, 110, 100, 90, 80, and 70^{\circ}C for 30 min and then cooled to 30° C at 10° C/min. The samples were then heated again to 150° C at 10° C/min to obtain the second endotherms, during which several peaks were obtained for each sample.

DMA Measurements

Dynamic mechanical analyzer (DMA 2980, TA Instruments) was used to analyze storage modulus, loss modulus, and tan δ of film specimens in dimensions of 25 m*M* long, 6 m*M* wide, and 0.33 m*M* thick. DMA was measured in the tensile mode at a constant frequency of 50 Hz and a heating rate of 3°C per minute from -150 to 100°C.

RESULTS AND DISCUSSION

Normal DSC Analyses

Figures 1 and 2 show DSC exothermic thermograms of first cooling scans for LDPE and LLDPE,



Figure 1 DSC thermograms of the first cooling scans for LDPE, S-LDPE, X-LDPE, and E-LDPE.

respectively, including both before and after silane grafting reactions, water crosslinking reactions, and decalin extractions. As can be seen in Figures 1 and 2, LDPE and LLDPE exhibit crystallization temperatures at around 98 and 115°C, respectively. For S-LDPE (or S-LLDPE) and X-LDPE (or X-LLDPE), the exothermic peaks begin at higher temperatures, resulting from a decreased chain mobility due to the grafting and/or crosslinking compared with LDPE (or LLDPE). For E-LDPE (or E-LLDPE), the exothermic peaks shift to lower temperatures due to extractions of those molecules having no or low degree of crosslinking. The widths of the exothermic peaks in Figures 1 and 2 are, apparently, in the order of E-LDPE (or E-LLDPE) > X-LDPE (or X-LLDPE) > S-LDPE (or S-LLDPE) > LDPE (or LLDPE) for both polymers. In other words, the heterogeneity of molecular structure of these polymers is increased by the silane grafting and water crosslinking reactions.



Figure 2 DSC thermograms of the first cooling scans for LLDPE, S-LLDPE, X-LLDPE, and E-LLDPE.



Figure 3 DSC thermograms of the second heating scans for LDPE, S-LDPE, X-LDPE, and E-LDPE.

Figures 3-7 show DSC endothermic thermograms of second heating scans for LDPE/LLDPE = 100/0, 75/25, 50/50, 25/75, and 0/100 blends, respectively, including both before and after silane grafting reactions, water crosslinking reactions, and decalin extractions. As can be seen in Figures 3 and 7, pure LDPE and pure LLDPE exhibit melting temperatures at around 107.5 and 124.5°C, respectively. For both polymers, the melting temperatures shift to lower temperatures after silane grafting reactions, to still lower temperatures after water crosslinking reactions, and to much still lower temperatures after decalin extractions. Similar to findings from Figures 1 and 2, the widths of the endothermic peaks are also in the order of E-LDPE (or E-LLDPE) > X-LDPE (or X-LLDPE) > S-LDPE (or S-LLDPE) > LDPE (or LLDPE) for both polymers.

From Figures 4-6 for LDPE/LLDPE = 75/25, 50/50, and 25/75 blends, respectively, two endother-



Figure 4 DSC thermograms of the second heating scans for LDPE/LLDPE = 75/25, S-LDPE/S-LLDPE = 75/25, X-LDPE/X-LLDPE = 75/25, and E-LDPE/E-LLDPE = 75/25 blends.



Figure 5 DSC thermograms of the second heating scans for LDPE/LLDPE = 50/50, S-LDPE/S-LLDPE = 50/50, X-LDPE/X-LLDPE = 50/50, and E-LDPE/E-LLDPE = 50/50 blends.

mic peaks including a peak at a lower temperature for the LDPE constituent and the other peak at a higher temperature for the LDPE constituent are observed, an indication that cocrystallization of LDPE and LLDPE during cooling from melt blending does not occur. In other words, LDPE and LLDPE phases are separated from each other. After silane grafting and water crosslinking reactions, two peaks remain to be seen, indicating that these reactions do not enable the development of a single phase from these blends. These two peaks, however, are closer to each other, with the peak for the LLDPE constituent shifting to a temperature much lower than the peak for the LDPE constituent after reactions. This suggests that the silane grafting and water crosslinking reactions enable compatibilization between LDPE and LLDPE phases. From Figures 5 and 6, an endothermic peak appears at near



Figure 6 DSC thermograms of the second heating scans for LDPE/LLDPE = 25/75, S-LDPE/S-LLDPE = 25/75, X-LDPE/X-LLDPE = 25/75, and E-LDPE/E-LLDPE = 25/75 blends.



Figure 7 DSC thermograms of the second heating scans for LLDPE, S-LLDPE, X-LLDPE, and E-LLDPE.

115.5 and 117.5°C for X-LDPE/X-LLDPE = 50/50 and 25/75 blends, respectively. This indicates that a new phase develops during the crosslinking reactions in these LLDPE-rich blends. After extraction, the E-LDPE/E-LLDPE = 25/75 blend exhibits only an endothermic peak, suggesting that the network from crosslinking reactions have only one phase. The peak at around 115°C in Figure 6 for the E-LDPE/E-LLDPE = 25/75 blend is found to be different from that at around 117.5°C in Figure 7 for the E-LDPE/E-LLDPE = 0/100 blend, indicating that LDPE is capable of crosslinking with LLDPE to form a networked phase, despite the fact that the LDPE constituent is phase separated from the LLDPE constituent.

Thermal Fractionation Analyses

Figure 8 shows DSC thermograms of multiple melting endotherms for the LDPE/LLDPE blends



Figure 8 DSC thermograms of heating scans for LDPE/LLDPE = 100/0, 75/25, 50/50, 25/75, and 0/100 blends that have been thermally fractionated.



Figure 9 DSC thermograms of heating scans for LDPE, S-LDPE, X-LDPE, and E-LDPE that have been thermally fractionated.

that have not been grafted with the silane but have been thermally fractionated by DSC. As can be seen in Figure 8, both pure LDPE and pure LLDPE give multiple melting temperatures, an indication that both polymers are heterogeneous in their molecular structures. These multiple melting endotherms involve the strongest peak at the extremely right at near 109 and 128°C for LDPE and LLDPE, respectively, along with several weak peaks at the left (at low temperatures) on the DSC thermograms. The strongest peak apparently corresponds to the melting of crystals from the most regular segments of the polymer molecules. For LDPE/LLDPE = 75/25, 50/50, and 25/75 blends, the two strongest peaks corresponding to the LDPE and LLDPE constituents shift to lower temperatures resulting from interference of each other constituent to their respective crystallizations in the binary blends. This suggests that LDPE and LLDPE are melt miscible, and a favorable interaction is present between two polymers. The strongest peak at near 109°C increases in its intensity with increasing LDPE content in the blends, while the peak at near 128°C increases in its intensity with increasing LLDPE content in the blends, indicating that cocrystallization of LDPE and LLDPE does indeed not occur.

Figures 9–13 show DSC thermograms of multiple melting endotherms for LDPE/LLDPE (together with S-LDPE/S-LLDPE, X-LDPE/X-LLDPE, and E-LDPE/E-LLDPE) = 100/0, 75/25, 50/50, 25/75, and 0/100 blends, respectively, that have been thermally fractionated by DSC. As can be seen in Figure 9 for S-LDPE/S-LLDPE = 100/0, the silane grafting reactions cause the shifting of the strongest peak to a lower temperature by introducing irregularity into LDPE molecules. For X-LDPE/X-LLDPE



Figure 10 DSC thermograms of heating scans for LDPE/LLDPE = 75/25, S-LDPE/S-LLDPE = 75/25, X-LDPE/X-LLDPE = 75/25, and E-LDPE/E-LLDPE = 75/25 that have been thermally fractionated.

= 100/0, the crosslinking reactions, however, cause the shifting of the strongest peak back to a higher temperature because the molecules having no or a low degree of crosslinking are excluded to outside the network during crosslinking reactions leading to enhancement of crystallization of these molecules. E-LDPE exhibits a low melting temperature for its strongest peak due to the extraction of the soluble component having no or a low degree of crosslinking. For LLDPE in Figure 13, the temperature shifting is similar to that in Figure 9 for LDPE. From Figure 13, the peaks at near 120°C for S-LDPE/S-LLDPE = 0/100 and X-LDPE/X-LLDPE= 0/100 are relatively strong compared with LDPE/ LLDPE = 0/100, suggesting that the silane grafting and water crosslinking reactions are capable of developing a fraction of molecular structure exhibiting



Figure 11 DSC thermograms of heating scans for LDPE/LLDPE = 50/50, S-LDPE/S-LLDPE = 50/50, X-LDPE/X-LLDPE = 50/50, and E-LDPE/E-LLDPE = 50/50 that have been thermally fractionated.



Figure 12 DSC thermograms of heating scans for LDPE/LLDPE = 25/75, S-LDPE/S-LLDPE = 25/75, X-LDPE/X-LLDPE = 25/75, and E-LDPE/E-LLDPE = 25/75 that have been thermally fractionated.

a melting temperature corresponding to the peak at near 120°C during thermal fractionation. The LDPE/LLDPE = 0/100 blend gives the strongest peak at near 128°C after thermal fractionation. This strongest peak completely disappears for E-LDPE/E-LLDPE = 0/100 due to complete extraction of the component (with no or a low degree of crosslinking) corresponding to the strongest peak.

As can be seen in Figure 10 for the LDPE/ LLDPE = 75/25 blend, peaks in the range of 100-130 °C exhibit significant changes after grafting reactions, crosslinking reactions, and decalin extractions. The strongest peak in the range of 100-110 °C, corresponding to the melting of crystals from the LDPE constituent, is not found to be affected by grafting and crosslinking reactions in the same way as is found for single LDPE system



Figure 13 DSC thermograms of heating scans for LLDPE, S-LLDPE, X-LLDPE, and E-LLDPE that have been thermally fractionated.



Figure 14 Storage modulus curves of DMA for LDPE/LLDPE = 100/0, S-LDPE/S-LLDPE = 100/0, and X-LDPE/X-LLDPE = 100/0 blends.

(Fig. 9). For example, the strongest peak of the S-LDPE/S-LLDPE = 75/25 blend is relatively broad, and does not shift to a lower temperature compared with S-LDPE/S-LLDPE = 100/0 (Fig. 9). For the peaks in the range of 110-130°C (Fig. 10), which correspond to the melting of crystals from the LLDPE constituent, the peak temperatures of a sample are all at relatively low values compared with single LLDPE system (Fig. 13). Crystallization of LLDPE is indeed interfered by the presence of LDPE.

Similar effects of silane grafting reactions and water crosslinking reactions on the multiple endotherms of the LDPE/LLDPE blends can be additionally seen in Figures 11 and 12. The strongest peaks for E-LDPE/E-LLDPE = 50/50 and 25/75 are both at near 116°C (Figs. 11 and 12), which is lower than 120°C for the strongest peak of E-LDPE/E-LLDPE = 0/100 (Fig. 13), indicating that LDPE can crosslink with LLDPE at the experimental temperature, namely, 100°C (a temperature lower than the melting temperature of LLDPE). In other words compared with E-LDPE/ E-LLDPE = 0/100, the strongest peaks for E-LDPE/E-LLDPE = 50/50 and 25/75 shifting to a relatively low temperature suggests the crosslinking reactions between LDPE and LLDPE constituents.

Dynamic Mechanical Properties

Figures 14–16 show effects of silane grafting reactions and water crosslinking reactions on storage modulus in the temperature range of –150 to 100°C for LDPE/LLDPE (together with S-LDPE/ S-LLDPE and X-LDPE/X-LLDPE) = 100/0, 50/50,



Figure 15 Storage modulus curves of DMA for LDPE/LLDPE = 50/50, S-LDPE/S-LLDPE = 50/50, and X-LDPE/X-LLDPE = 50/50 blends.

and 0/100 blends, respectively. As can be seen in Figures 14 and 15, effects of silane grafting reactions on storage modulus of LDPE/LLDPE = 100/0 and 50/50 blends are insignificant in the temperature range studied. The storage modulus of LDPE/LLDPE = 0/100 (Fig. 16), however, is slightly increased in the low temperature range but is slightly decreased in the high temperature range by silane grafting reactions. Water crosslinking reactions can expectedly lead to the increase in storage modulus for LDPE/LLDPE = 100/0 and 50/50 blends (Figs. 14 and 15), whereas the reactions can cause the decrease in storage modulus, with an unclear reason, for LDPE/LLDPE = 0/100 (Fig. 16) in the temperature range studied. Figure 17 compares storage moduli of X-LDPE/X-LLDPE = 100/0, 75/25, 50/50, 25/75, and 0/100 blends in the temperature range of -150 to 100°C. As can be seen in Figure



Figure 16 Storage modulus curves of DMA for LDPE/LLDPE = 0/100, S-LDPE/S-LLDPE = 0/100, and X-LDPE/X-LLDPE = 0/100 blends.



Figure 17 Storage modulus curves of DMA for X-LDPE/X-LLDPE = 100/0, 75/25, 50/50, 25/75, and 0/100 blends.

17, X-LDPE/X-LLDPE = 100/0 blend gives a higher storage modulus than X-LDPE/X-LLDPE = 0/100 blend despite the experimental data that the X-LDPE/X-LLDPE = 100/0 blend (having 34.2% gel content) has a lower degree of crosslinking than the X-LDPE/X-LLDPE = 0/100 blend (having 58.5% gel content). The possible reason for such a discrepancy is that the water crosslinking reactions of the silane-grafted LLDPE proceed on mostly one or two methoxy groups of the silyl trimethoxy grafts on LLDPE, whereas the crosslinking reactions of the silane-grafted LDPE proceed on mostly two or three methoxy groups of the silyl trimethoxy grafts on LDPE. In other words, the network structure formed from the crosslinking reactions is more three-dimensional for X-LDPE than for X-LLDPE. Thus, although X-LDPE has a poorer crosslinking ability, it has a higher storage modulus than X-LLDPE.

As can be seen in Figure 17, the storage modulus of the X-LDPE/X-LLDPE = 50/50 blend is higher than the X-LDPE/X-LLDPE = 100/0blend. This finding contradicts the hypothesis of the network formation as proposed above. The possible reason for the X-LDPE/X-LLDPE = 50/50 blend to give the highest storage modulus is attributed to the contribution of the higher melting temperature from the LLDPE constituent in addition to the considerably high degree of crosslinking (34.2%) for the blend. The X-LDPE/ X-LLDPE = 75/25 and 25/75 blends give roughly the same storage moduli, which are between moduli of X-LDPE/X-LLDPE = 100/0 and 0/100 blends. This may be simply attributed to the low degrees of crosslinking. Thus, from Figure 17 the storage moduli of the blends are found not to be

consistent with their degrees of crosslinking. In other words, the storage moduli of the blends are not simply determined by the degree of crosslinking but determined by very complicated but now unclear factors.

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