

Thermal degradation of mixtures of polycaprolactone with cellulose derivatives

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Abstract

Thermal degradation processes for a series of mixtures based on polycaprolactone (PCL), with microcrystalline cellulose (MC) and sisal fiber (SF) powder, were investigated by thermogravimetric analysis (TGA), in order to predict the thermal behaviour of biodegradable matrixes reinforced with cellulose derivatives. The maximum degradation temperature of each component in the mixture was higher than those of the individual components; thus an increase in thermal stability was expected. Apparent activation energies were obtained from Friedman isoconversional plots. Mixtures were considered as multistage processes. Predicted apparent activation energies agreed well with the increment in thermal stability due to the presence of the co-components. This effect was associated with either, solid–solid or solid–gas interactions between cellulose derivatives and PCL during thermal degradation.

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1. Introduction

Biodegradable polymers have recently attracted much public and industrial interest because of the increasing waste disposal problem [1]. Besides solutions such as incineration, recycling or re-use, biodegradable polymers can be entirely converted by microbial activity in a biologically active environment to biomass and biological by-products.

Nowadays, the use of biodegradable polymers as replacement of commodities for large scale applications is quite small, as their cost is still not competitive [2,3]. One economically and ecologically attractive approach to overcome these limitations is to incorporate natural fibers into biodegradable polymers to obtain environmentally friendly composite materials called *bio-composites*, which are quite similar to the already known synthetic fibre-reinforced plastics with the advantage of being completely biodegradable.

Thermal degradation of cellulosic materials was recently studied [4–9]. Cellulose degradation proceeds by two competing reactions: dehydration and depolymerisation. The first reaction progresses by forming char, CO₂, CO, H₂O and other volatiles (i.e. aldehydes) with intra-ring scission of the glucose unit in cellulose chains [10]. The second reaction is initiated by depolymerisation at high temperature producing CO₂, CO, liquid products and char. These products may influence the degradation of the co-component in a cellulose–polymer mixture.

Several articles in the literature were devoted to the study of the thermal decomposition of biomass derived materials [8], and mixtures of vinyl polymers and lignocellulosic materials [5,6,11,12]. Jakab et al. [4,10] analysed the effect of cellulose derivatives on polypropylene (PP), polystyrene (PS) and polyethylene (PE) thermal degradation. The presence of cellulose materials produced a slight increase on the degradation temperature associated with a change in the degradation mechanism of PP. The yield of monomer and trimer from thermal decomposition of PS was reduced in the presence of cellulose derivatives, indicating that the radical chain reactions are hindered by the presence of

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lignocellulosic char. On the other hand, the effect of PP on thermal decomposition of cellulose derivatives was negligible. However, in some cases, the polymeric matrix can influence the thermal degradation of cellulosic materials. Matsuzawa et al. [11] reported that poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC) may affect the thermal degradation of cellulose. HCl evolved in the dehydrochlorination reaction of vinyl chlorides seems to act as acid catalyst to promote the dehydration reaction much more than the depolymerisation in cellulose pyrolysis. In summary, a mutual interaction of the two degradation processes should be expected. However, and in spite of the above-mentioned studies, there is a lack of information about the influence of cellulosic materials on the thermal degradation of biodegradable polymers. The analysis of the thermal behaviour of mixtures of lignocellulosic materials and biodegradable polymers is important not only from the recycling but also from the processing point of view. During processing, cellulose components produce a significant amount of char as the result of thermal degradation, which may affect the pyrolysis of the biodegradable polymer as in the case of polyolefins [4].

Among all the biodegradable synthetic polymers which are nowadays on the market, polycaprolactone (PCL), polylactic acid (PLA) and polyhydroxybutyrate (PHB) are the most attractive, since they combine biodegradability, compostability and compatibility with different forms of waste disposal and remarkable physico-mechanical performances [13]. The understanding of their thermal stability and degradation has importance in processing and recycling. Thermal degradation of PCL under dynamic conditions was recently studied [14–16]. Persenaire et al. proposed a two-step degradation mechanism, based on the results obtained from high-resolution thermogravimetric analysis (TGA) coupled to mass spectrometry (MS) and Fourier transform infrared spectrometry (FTIR) [14]. Derivative TGA (DTG) showed two well resolved degradation peaks and, based on the gases evolved, they concluded that PCL degradation proceeds via a first step, involving *cis*-elimination which produces CO₂, CO and 5-hexenoic acid, and a second step, via unzipping depolymerisation, to form ϵ -caprolactone. Aoyagi et al studied PCL, PHB and PLA thermal degradation under dynamic and isothermal conditions [16]. In the case of PCL, TG/DTG curves suggested only one single step. The constant apparent activation energy (E_a) during all the degradation process also suggested a simple degradation mechanism, however this last result did not exclude the possibility of a two-step mechanism.

Interactions between biodegradable polymers and biomass are not well known. The main goal of this paper is to evaluate the interaction between PCL and cellulose derivatives, such as microcrystalline cellulose

(MC) and sisal fibre (SF) during pyrolysis. Thermal analysis of the mixtures and pure components was performed by TG/DTG under dynamic conditions. The calculation of apparent activation energies was based on the application of the classic kinetic model proposed by Friedman [17]. The influence of the co-components on the thermal degradation was also evaluated

2. Materials and methods

Polycaprolactone (PCL) ($M_w = 80000$) was supplied by Aldrich (Steinheim, Germany) and microcrystalline cellulose (MC) was purchased from Merck (Darmstadt, Germany). Sisal fibre (SF) was purchased from Brascorda (Brazil).

Dynamic degradation measurements were carried out by using a Mettler-Toledo 851e-TGA-SDTA system (Schwarzenbach, Switzerland) with STAR-E software. Temperature programs for dynamic tests were run from 30 to 600 °C at different heating rates, between 5 and 30 °C/min. TGA tests were performed in alumina crucibles where samples were placed without any previous treatment and experiments were run immediately. TGA tests were carried out in nitrogen environment using a flow rate 20 ml/min in order to avoid thermoxidative degradation.

Kinetic parameters of the degradation process were calculated by using the classical Friedman method [17]. This approach was successfully used for many polymers [18–20].

In order to analyse the effect of each co-component on the thermal degradation, PCL, MC and SF mixtures were prepared manually in different mass proportions, varying between 5 and 20% in weight.

3. Results and discussion

3.1. Thermal degradation of pure components

Fig. 1 shows dynamic TG/DTG curves for PCL at different heating rates. The maximum degradation temperatures (T_{max}) obtained from DTG curves are summarised in Table 1. The shape of the PCL weight loss curves does not change with variations in heating rate, but temperature for the maximum mass loss shows a slight increase at higher heating rates. This is an indication of the activated character of the degradation process, as was reported in recent papers [20].

Fig. 2 shows the TG/DTG thermograms for MC and SF obtained at 30 °C/min. The weight loss pattern for MC shows that degradation is a one-step process as can be concluded by the presence of only one peak in DTG at 345 °C. SF thermal decomposition seems to be a gradual process with no clear steps in the TG curve.

However, two overlapping peaks can be observed in DTG curves, the first one corresponding to hemi-cellulose (299 °C) and the second to the main component, cellulose (359 °C). The lignin peak is completely overlapped by the other two because it shows a wide range of degradation temperatures (up to 800 °C). The maximum degradation rate is also shifted to higher temperatures as the heating rate increases. Therefore, as in the case of PCL, an activated degradation process should be expected. Maximum degradation temperatures for MC and SF are summarised in Table 1.

3.2. Thermal degradation of mixtures

Fig. 3 shows the weight loss curve for a PCL:MC mixture (2:1, w:w) obtained at 30 °C/min. For comparison purposes, MC and PCL curves are also presented. For the mixture, two peaks are clearly observed in the DTG curve, corresponding to both components, with T_{\max} 376 °C for MC and 432 °C for PCL. Some differences in such temperatures are observed when compared to those of pure materials. MC significantly increases its maximum temperature (365 °C for the pure component), while the variations for PCL are less pronounced

(1–3 °C), but both materials increase their thermal stability. As can be seen in Fig. 3, the decomposition curves of both components are partially overlapped, therefore some kind of solid–solid or solid–gas interaction must be considered.

Since MC thermal degradation occurs at lower temperature than PCL, two main interactions can be assumed: in the solid state, between the char produced during cellulose degradation and PCL; and solid–gas, between PCL and the gaseous products evolved from cellulose degradation. In the solid state, hydrogen type interactions may occur between the hydroxyl group of cellulose and PCL carbonyl groups. Those interactions delay the MC dehydration reaction, which takes place at lower temperatures than depolymerisation. As degradation proceeds, the effect of hydrogen interactions decreases, but char and gases evolved from cellulose degradation (mainly CO₂, CO and aldehydes) may interact with solid PCL. On the other hand, char formed during cellulose degradation may act as a

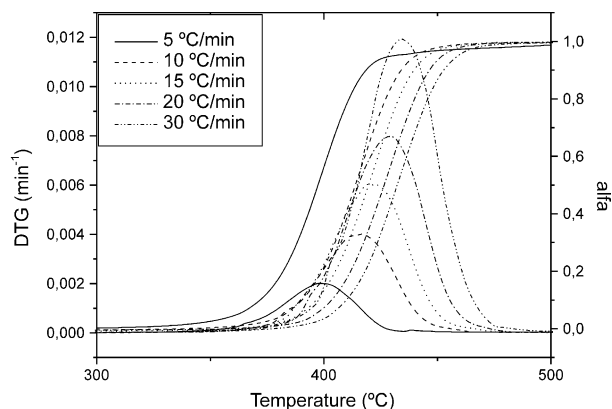


Fig. 1. TG/DTG thermograms for polycaprolactone (PCL) at different heating rates.

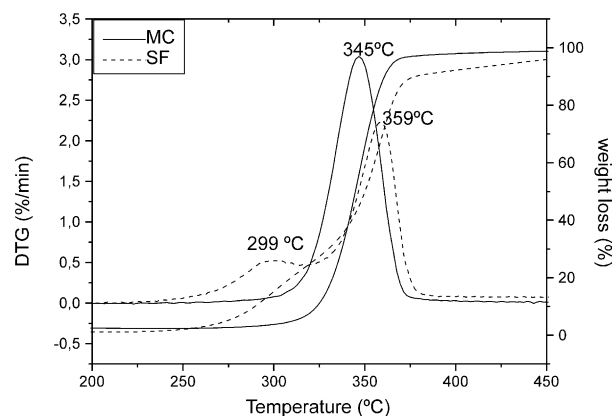


Fig. 2. TG/DTG thermograms obtained for microcrystalline cellulose (MC) and sisal fibre (SF) at 10 °C/min.

Table 1
Maximum degradation temperatures (T_{\max}) obtained for the pure components and the mixtures, at different heating rates (°C)

Sample	10 °C/min	15 °C/min	20 °C/min	30 °C/min
PCL	415	418	430	433
MC	347	355	361	365
SF ^a				
SF ₁	300	306	313	316
SF ₂	359	370	377	382
PCL:MC 2:1				
MC	362	370	375	376
PCL	412	423	426	433
PCL:SF 2:1				
SF ₁	299	305	309	315
SF ₂	365	377	349	382
PCL	407	419	422	428

^a SF₁ = first peak, SF₂ = second peak.

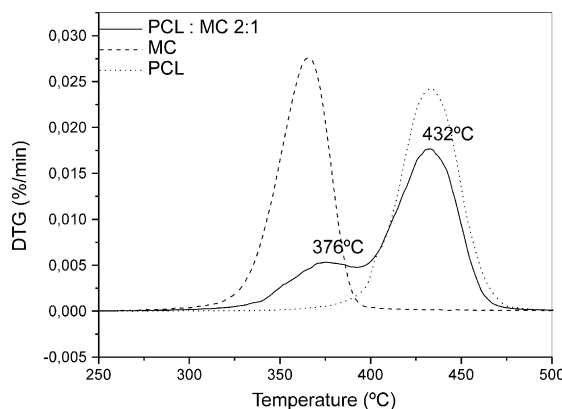


Fig. 3. DTG for a mixture 2:1 (w:w) of PCL:MC performed at 30 °C/min.

thermal stabiliser for PCL. Thus, the increment in MC thermal stability may be a consequence of the presence of strong interactions (such as hydrogen bonds) between both co-components in the solid state. The formation of char as a decomposition product of cellulose may be the main cause of the changes in PCL degradation processes.

On the other hand, mixtures of PCL and sisal fiber (PCL:SF), were also analysed. Fig. 4 shows the DTG curve for PCL:SF (2:1, w:w), obtained at 30 °C/min. This is a multi-stage process. The maximum degradation rate for each step is summarised in Table 1. The analysis of the results reported in Table 1 reveals that the presence of sisal fiber shifts the T_{max} of PCL to lower temperatures. Indeed, sisal fibres have an unfavourable effect on the thermal stability of PCL.

This last result has very important practical implications. Processing a composite material based on PCL and sisal fiber (as well as other lignocellulosic fibres) will require lower temperatures than those actually used for processing PCL in order to avoid thermal degradation. On the other hand, mixing PCL with lignocellulosic materials may be economically favourable for recycling

because of the lower energy required to produce the complete pyrolysis.

3.3. Determination of kinetic parameters

Kinetic parameters, mainly apparent activation energies (E_a), were evaluated in order to analyse more deeply the above-mentioned observations. Dynamic TG/DTG permits the analysis of the relationship between kinetic parameters and conversion (α) from mass loss curves obtained at different heating rates. Isoconversional Friedman plots obtained at different heating rates (q) for the PCL degradation process are shown in Fig. 5. The average E_a for $0.3 < \alpha < 0.9$ was 203 kJ/mol. E_a values do not change significantly with conversion (as can be concluded from the slopes in Fig. 5). This result indicates that pyrolysis of PCL seems to proceed through the cleavage of linkages with similar bond energies. In order to explain such behaviour, two different approaches were found in the literature. Draye et al. proposed a two-stage mechanism with a *cis*-elimination followed by a depolymerisation with production of the monomer and other oligomers [15]. On the other hand, Aoyagi et al., studied the thermal degradation and degree of polymerisation of several biopolymers in isothermal conditions [16]. They proposed the evolution of volatile products from PCL via an unzipping mechanism. They also claimed the formation of a stable intermediate for the decomposition with no change in the mechanism for the whole process. The E_a calculated by using Ozawa method was 74 kJ/mol, notably lower than the values obtained in the present work. The proposal of a unique unzipping mechanism for the thermal degradation of PCL agrees with our results. Reaction order was also calculated from the intercepts in Fig. 5 resulting in a value of 1.2.

A similar study was carried out for the cellulose derivatives, MC and SF. Fig. 6 shows the isoconversional Friedman plots for MC. From the slopes, average E_a

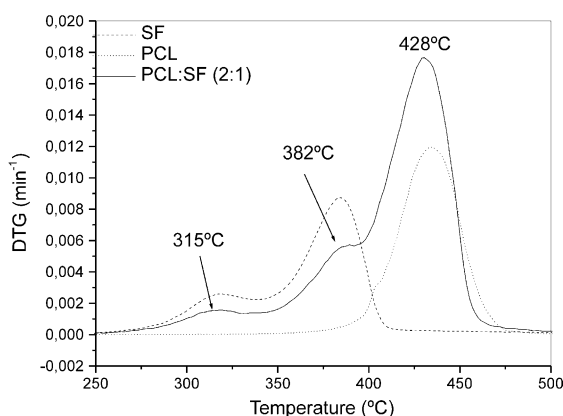


Fig. 4. DTG for a mixture 2:1 (w:w) of PCL:SF performed at 30 °C/min.

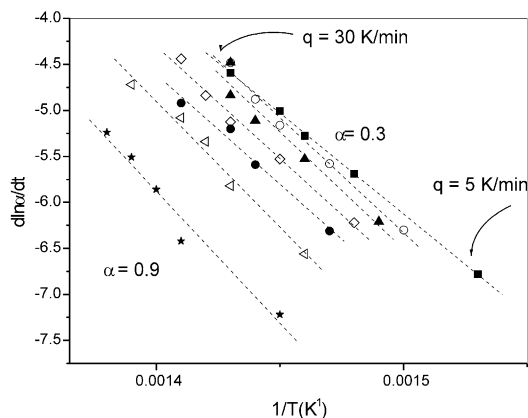


Fig. 5. Isoconversional Friedman plots obtained for PCL. Conversions (α): 0.3 (■), 0.4 (○), 0.5 (▲), 0.6 (□), 0.7 (●), 0.8 (△), 0.9 (★). Heating rates 5, 10, 15, 20, 30 °C/min.

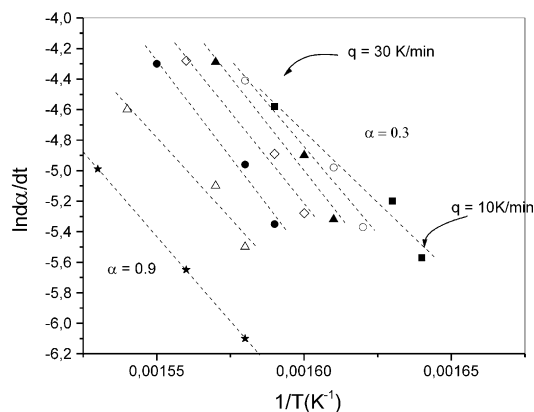


Fig. 6. Isoconversional Friedman method plots for MC. Conversions (α): 0.3 (■), 0.4 (○), 0.5 (▲), 0.6 (□), 0.7 (●), 0.8 (△). Heating rates 10, 15, 20, 30 °C/min.

can be calculated (187 kJ/mol), lower than those reported in the literature ranging from 240 to 250 kJ/mol [21,22]. As observed in Fig. 6, slopes, and thus E_a , are dependent on the degree of conversion. This result indicates the existence of at least two stages for the thermal degradation of cellulose, i.e. dehydration and depolymerisation, as was previously indicated [5,23].

Isoconversional plots obtained for SF are shown in Fig. 7, where two regions can be clearly identified. It is assumed that the first process ($\alpha < 0.3$) corresponds to the hemicellulose degradation, while the second one ($\alpha > 0.4$) corresponds to the cellulose degradation. As the lignin degradation process is observed for a wide range of α , it is not considered in the E_a calculation as well as those values in the transition region ($0.3 < \alpha < 0.4$). The average E_a calculated in such way for the first region was 166 kJ/mol, while E_a for the second region was 119 kJ/mol. These results seem to confirm the existence of two different processes in the SF thermal degradation. García Pérez et al. analysed the thermal degradation of sugarcane bagasse, a lignocellulosic derivative [8]. The global pyrolysis of

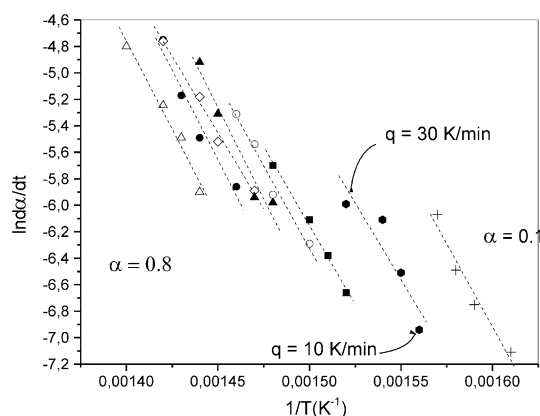


Fig. 7. Isoconversional Friedman plots for SF. Conversions (α): 0.1 (+), 0.2 (buq), 0.3 (■), 0.4 (○), 0.5 (▲), 0.6 (□), 0.7 (●), 0.8 (△). Heating rates 10, 15, 20, 30 °C/min.

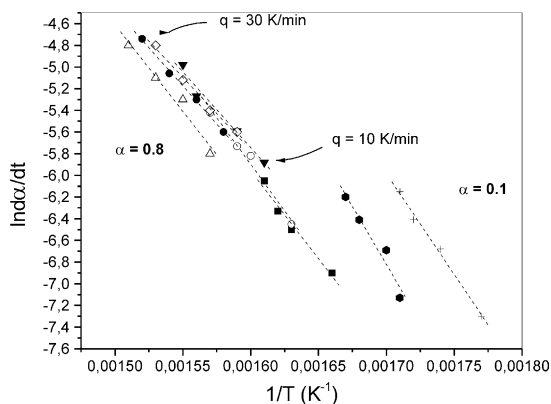


Fig. 8. Isoconversional Friedman plots for PCL:MC (2:1). Conversions (α): 0.1 (+), 0.2 (buq), 0.3 (■), 0.4 (○), 0.5 (▲), 0.6 (□), 0.7 (●), 0.8 (△). Heating rates 10, 15, 20, 30 °C/min.

sugarcane bagasse was assumed to be the sum of the contribution of each component (hemicellulose, cellulose and lignin), and they used an algorithm to predict the kinetic parameters as the best fitting to the proposed equation. E_a values found by them were 105 kJ/mol and 235 kJ/mol for hemicellulose and cellulose respectively.

Friedman method was also applied to the study of thermal degradation of the PCL:MC 2:1 mixture. The isoconversional Friedman plots are shown in Fig. 8. It is possible to take two different regions corresponding to both degradation processes, with a transition area for $0.3 < \alpha < 0.4$. E_a calculated with this method was 200 kJ/mol for the first region, 202 kJ/mol for the transition area and 271 kJ/mol for the second process. When comparing these results with those of the thermal decomposition of the pure materials, it is noteworthy that the presence of MC leads to an increase in the thermal stability of PCL, as was previously observed from the values of T_{max} in TG/DTG experiments (Table 1). Therefore, cellulose derivatives can be used as thermal stabilisers of biopolymers. This stabilisation caused by cellulose derivatives can be attributed to a PCL–MC interaction, either in the solid state or between PCL and gases evolved from the cellulose degradation. The formation of char as a decomposition product of cellulose is another factor to be taken into account in the changes in PCL degradation processes. This behaviour was also noted for blends of biomass derivatives with other common polymers, such as polystyrene (PS), with changes in the mechanism of thermal degradation [4,10].

Another factor to be considered is the influence of PCL in the thermal degradation of cellulose derivatives. Apparent activation energies for MC in blends are slightly higher than those of the pure material. As mentioned above, one possible explanation of this fact can be the formation of some hydrogen bonds between terminal groups of PCL and MC in the solid state. As the bond energy is slightly higher, degradation processes

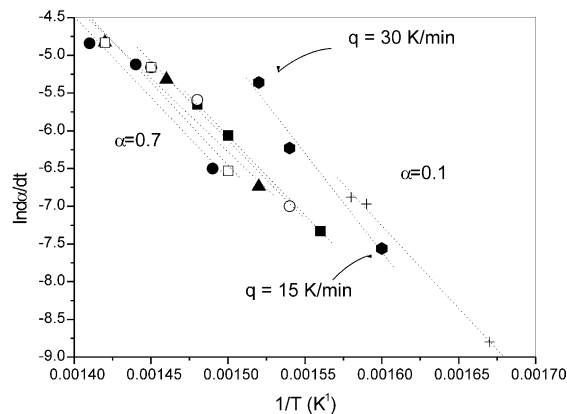


Fig. 9. Isoconversional plots for PCL:SF (2:1). Conversions (α): 0.1 (+), 0.2 (buq), 0.3 (■), 0.4 (○), 0.5 (▲), 0.6 (□), 0.7 (●), 0.8 (△). Heating rates: 15, 20, 30 °C/min.

should need higher energies to proceed. Therefore, the overall effect of the addition of cellulose derivatives to PCL is a stabilisation of the biocomposite.

The same method was applied to PCL:SF (2:1) mixtures and isoconversional plots are shown in Fig. 9. As expected, two regions can be clearly identified. The calculated E_a value for the first zone ($0.1 < \alpha < 0.2$) was 200 kJ/mol and 164 kJ/mol for the second. By comparing with the value obtained for pure PCL, it is easy to conclude that the presence of sisal fiber produces a decrease in the thermal stability of PCL.

4. Conclusions

The effect of the formulation of biocomposites based on PCL and cellulose derivatives in the thermal degradation of both co-components was evaluated. Thus, MC shows a stabilising effect on PCL thermal degradation and can be considered a promising thermal stabiliser of biodegradable polymers. The use of lignocellulosic materials, such as sisal fibres, shows an unfavourable effect on PCL thermal stability. In consequence, processing of composites derived from lignocellulosic fibres and PCL have to be carried out at lower temperatures than in the case of pure PCL in order to prevent PCL degradation. On the other hand, thermal recycling of PCL and sisal fiber mixtures requires lower energy and should be considered as an economic eco-compatible strategy for energy recovery.

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