Phase-Separated Polymer Blends: Complementary Studies between Scanning Electron Microscopy, Epifluorescence Microscopy, and Fluorescence Microspectroscopy

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ABSTRACT: In this work a morphological description of poly(vinyl alcohol) (PVA)/poly(vinyl acetate) (PVAc) incompatible blends was carried out combining scanning electron microscopy, epifluorescence microscopy, and fluorescence microspectroscopy, and using anthracene and fluorescein probes dissolved in the polymer blends. Because the blends were prepared by casting from a water/ethanol solution over a polyethylene surface, two topologically different faces were formed and analysed: blend/air and blend/support faces. Droplets in matrix morphologies were observed for any composition here studied and sample annealing resulted in the coalescence of domains. Fluorescence micro-spectroscopy of several parts of the material revealed that the dye distribution over the domain-matrix interface is different of the internal or external parts of each domain and it is indicative of the interpenetration of both polymers at the interface region. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci : 949–955, 2001

Key words: fluorescence microspectroscopy; fluorescence microscopy; polymer blends; poly(vinyl alcohol); poly(vinyl acetate)

INTRODUCTION

Polymer blends formed with homo- or copolymers present a great importance because they allow the optimization of certain properties compared with the isolated homopolymers. When the blends are not compatible, their properties are greatly influenced by the morphology of the segregated domains and by the nature and thickness of the polymer–polymer interface. Although the knowledge of the structure and thermodynamic state of the polymer interfaces are important features, it has not been accurately examined due to its narrow region (usually less than 10 nm).[1,2]

Direct study of polymer–polymer interfaces is, however, very difficult, and only recently theoretical models have described the interface as having an asymmetric profile.[3] Several indirect techniques are available for these studies, including: various forms of microscopy (UV fluorescence, optical microscopy with phase contrast, electron

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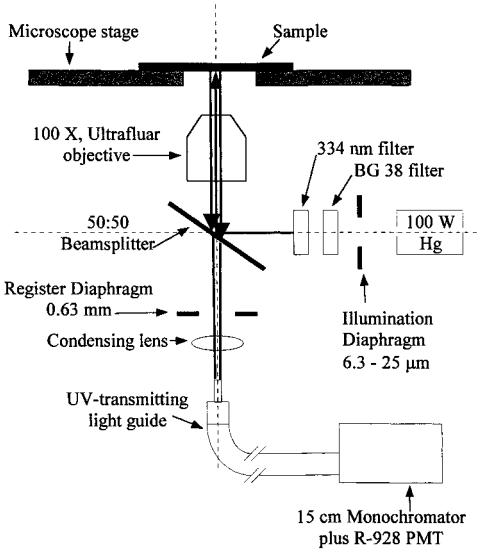
scanning, and transmission microscopy), several scattering techniques (small-angle X-ray, and neutron scattering),[4] positron annihilation,[5] electron spin resonance (e.s.r.),[6] infrared spectroscopy,[7] light spectroscopy ellipsometry,[8] X-ray microanalyses[9] and conventional methods such as mechanical, rheological, and measurements of interfacial tension.[4] It is remarkable that a similar thickness ca. 50 ± 5 Å was determined both for a blend composed by two homopolymers and a block copolymer formed by the same homopolymers.[10]

In addition, fluorescence techniques are useful in studies of polymer compatibility either by time-resolved or by steady-state methods.[11–16] Some of these methods involve comparison among the temperature dependence of the fluorescence spectra of fluorophores dissolved in the blends and in the isolated homopolymer.[17–19] Other methods are based on the measurement of the nonradiative energy transfer efficiency that depends on the distance between both fluorophores and, thus, on the interpenetration between the phases.[15,20–24]

Interesting techniques to visualize phase separation in polymer blends are based on electron or optical microscopies. In particular, epifluorescence microscopy has been very useful to identify the chemical nature of polymer domains, but it was limited by the resolution of the optical microscope. This technique requires an intrinsically fluorescent polymer or the incorporation of probes, which are able to selectively dye one phase of the polymer blends.[16,25,26] Although the resolution and/or the contrast of the image of the domain structure is worse with fluorescence than with phase contrast microscopes, epifluorescence microscopy was revealed to be quite a useful technique for analyzing the distribution of the fluorescent component of the blend. The reason is the high sensitivity of the fluorescence intensity to small composition changes undetectable by the light-scattering technique.[19]

In a previous work we showed that epifluorescence microscopy can be successfully employed to map the domains of incompatible blends formed with poly(vinyl alcohol) (PVA) and poly(vinyl acetate (PVAc) using anthracene and fluorescein as extrinsic fluorophores.[18] We have also combined epifluorescence microscopy and FTIR microspectroscopy, showing that the origin of the partial interpenetration of the two polymers in the polymer–polymer interface was the hydrogen-bonding interactions involving the VAc carbonyl and VA hydroxyl groups.[26] Simultaneously, measurements of the temperature dependence of the fluorescence emissions from anthracene and fluorescein confirmed this interpenetration.[17] Furthermore, using the ability of anthracene as an energy donor for fluorescein, we measured by time-resolved fluorescence spectroscopy, that the separation between these two fluorophores was 28 Å, considered as the average interpenetration zone between these two homopolymers.[15]



Scheme 1 Optical diagram of the microscope employed for fluorescence microspectroscopy measurements.

The present work is an attempt to obtain a better morphological description of PVA/PVAc blends combining scanning electron microscopy (SEM), epifluorescence microscopy, and fluorescence microspectroscopy techniques. Considering that both homopolymers are nonfluorescent, two fluorophores, anthracene, and fluorescein, have been employed, as in previous reports,[15,17,18] to selectively map local blend compositions rich in PVAc and PVA, respectively.

The advantage of using fluorescence microspectroscopy is the possibility of recording the fluorescence spectra of a defined area of the polymer blend, combining the aperture of the illumination and recording diaphragms (Scheme 1). Both air-blend and blend-support surfaces as well as the dye distribution have been analyzed using this technique.

EXPERIMENTAL

PVA and PVAc homopolymers were purchased from Aldrich Chemical Co., and were used as

received. Fluorescein (Merck) and anthracene (Carlo Erba) were purified and incorporated in the homopolymers or in the polymer blends using protocols established earlier.[17] Polymer blends were prepared in three compositions (PVA/PVAc 9/1, 1/1, and 1/9 w/w), and the solutions were cast over polyethylene supports and dried under air at 45°C, according to methods reported elsewhere.[17,18] Because both polymers are incompatible at the casting temperature, phase separation takes place during preparation. Samples were examined after casting and also after annealing during 1 month at 95°C at normal pressure and in a dry air atmosphere. The topology of both air-blend and polyethylene-blend surfaces was studied. Film thickness was 50 ± 10 μm in all cases.

Fluorescence microspectroscopy measurements were performed on an inverted microscope Axiovert 100 TV (Carl Zeiss Jena) coupled by an optical guide to a spectrophotometer (SpectroPro-150 Acton Research Corporation) with an imaging grating and a photomultiplier tube R-928 detector (Scheme 1). The spectrometer was controlled by a detector read-out system with data acquisition software for spectroscopy (Acton Research Corporation Spectra-card model SC-1). The microscope objective was selected for a magnification of 100×; such magnification corresponds to a focus depth of 0.72 μm. A range from a 6.3 to 40-μm aperture of the illumination diaphragm was selected, depending on the fluorescence emission intensity. The recording diaphragm of 6.3 μm was defined for all of the measurements. This diaphragm controls the light intensity focused on the optical guide tip. Samples were illuminated by a mercury arc lamp HBO-100 W, with excitation wavelength selected at 334 nm by an interference filter. This excitation wavelength was chosen to provide, preferentially, excitation of anthracene in a spectral region where the fluorescein extinction coefficient is very low. An additional filter, BG-38, was introduced to reduce the infrared irradiance over the sample surface. In general, the surface of the films was examined, but some observations were also made across the interior of the film and then, it is explicitly stated.

Optical and epifluorescence microscopy with imaging detection were measured on a Nikon Labophot microscope equipped with a CCD camera, a video-printer from Sony, and a 100-W Hg arc lamp filtered for $330 < \lambda_{ex} < 380$ nm. This broad range of excitation wavelengths allows excitation of both anthracene and fluorescein. Fluorescence was analyzed through a dichroic mirror (for $\lambda_{ex} < 400$ nm) and a barrier filter ($\lambda_{em} < 420$ nm) to record both the emission of anthracene and fluorescein simultaneously. Depth of focus for a 40× magnification is 1.2 μm.

Scanning electron micrographs, SEM, of the polymer blend films were obtained with a Phillips XL-30 microscope, at several magnifications and with an accelerating voltage of 1 kV. The surface of the polymer blends was sputtered with platinum/gold alloy prior to inspection.

RESULTS AND DISCUSSION

Domains in matrix phase-separated morphologies were observed with epifluorescence microscopy for any sample composition studied here. The color of the domains in the epifluorescence micrographs depend on their composition: PVA-rich regions are green, due to the fluorescence of fluorescein preferentially dissolved in that polymer, and PVAc-rich regions are blue, due to the fluorescence of anthracene. Films formed with blend 9/1 PVA/PVAc show blue circular PVAc domains in a PVA matrix that can be more clearly observed in blends probed only with anthracene. Films formed with blend 1/9 PVA/PVAc show green circular domains both with one or two fluorophores. Films formed with blend 1/1 PVA/PVAc show spherical domains (blue when probed only with anthracene, green when probed with fluorescein or the two fluorophores) smaller than for previous compositions (Fig. 1).

In any case, the size distribution of domains is very broad, and secondary morphologies (domain in domain) can be observed. Probably the equilibrium composition and morphology were never reached for the intermedium polymer concentrations of the different stages of solvent evaporation, due to the low diffusivities of the homopolymers in concentrated solutions. That may, in part, explain the large heterogeneity observed in samples after casting. Samples annealed for 1 month at 95°C, well above the glass transition temperature of both polymers, produced a thermal equilibrated domain size distribution with the increase of the average size (in the range of 10–20 μm for 1/1 composition, larger for the others) by coalescence of the small domains. Nevertheless, annealed samples remain heterogeneous, and thus, it must be considered characteristic of the system.

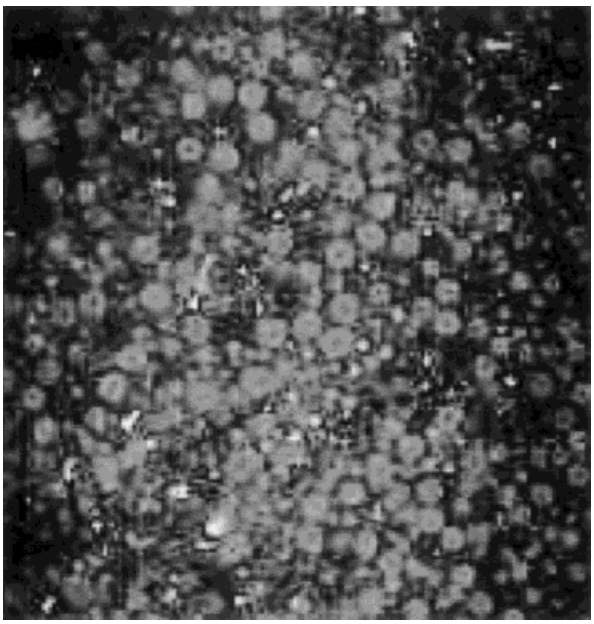


Figure 1 Epifluorescence micrograph of a 1/1 PVA/PVAc blend showing blue and green domains.

Morphological differences were also observed when comparing the two faces of any of the studied films. SEM micrographs (Fig. 2) illustrate an example of the topological differences of air-blend and support (polyethylene)-blend faces of one sample (9/1 PVA/PVAc). Usually, the polyethylene-formed face was reasonable flatter [Fig. 2(a)], while the air-formed face was corrugated [Fig. 2(b)]. Moreover, the size of domains is different in both faces.

In addition, we obtained significantly modified spectra (see, e.g., Fig. 3 for the 1/9 PVA/PVAc blend), by changing the fluorescence microscope focus position from the surface to the interior of the sample. The relative intensity of the fluorescein emission increased from the surface (air-formed face) towards the interior of the film (deep focus, complete absence of fluorescein emission). This result demonstrated the presence of a homopolymer distribution not only over the entire surface but also across the film thickness. The air-blend face was richer in PVAc (higher anthracene content), while the polyethylene-blend face was richer in PVA (higher fluorescein content).

Polymer–Polymer Interfaces

Microfluorescence spectra were recorded for 1/9 and 9/1 samples at the inner, the external and the domain–matrix interface parts of a domain. The morphology of composition 1/1 does not allow distinguishing between different regions (Fig. 1). This type of experiment was performed controlling the aperture of both the illumination and the recording diaphragms to obtain a detectable fluorescence signal of a restricted area. Although the illumination diameter is always larger than the interface thickness due to optical restrictions, the recorded spectrum is mainly representative of the interface region.

One example illustrating the possibility of recording fluorescence spectra in different microzones of a circular domain was shown in Figures 4 and 5 for a 9/1 PVA/PVAc blend. The SEM micrograph [Fig. 4(a)] illustrated the topology of this domain and allowed us to measure the size domains with higher precision than epifluorescence microscopy due to the absence of light scattering [Fig. 4(b)]. The epifluorescence microscopy

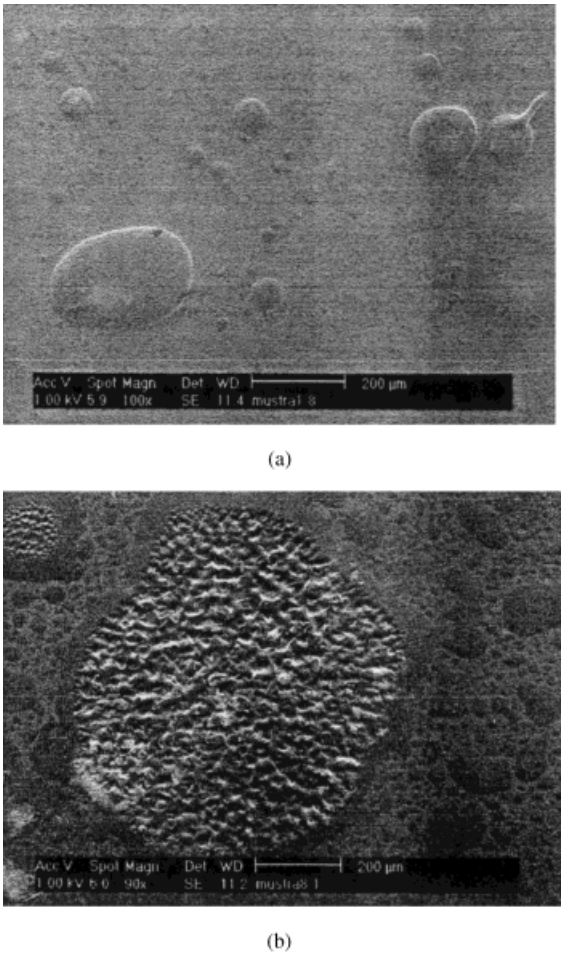


Figure 2 SEM micrographs of the two faces of 9/1 PVA/PVAc blend: (a) Polyethylene (support)-blend face, and (b) air-blend face.

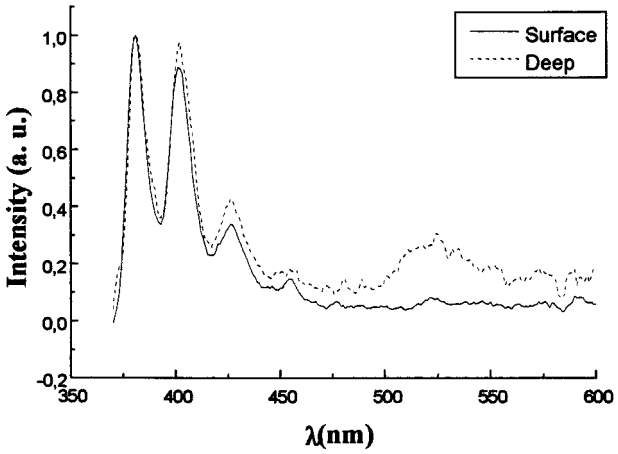


Figure 3 1/9 PVA/PVAc blend: Microfluorescence spectra for surface and deep focus.

and microfluorescence spectra revealed a heterogeneous dye distribution. Upon excitation of only anthracene, a green emission (fluorescein) is observed [Fig. 4(b)] only at the domain–matrix interface, because only there the distance between the two chromophores (and the two polymers) is in the proper range to have nonradiative energy transfer from anthracene to fluorescein.[15] Microfluorescence spectra with direct excitation of fluorescein and looking at region (a) in Figure 4(a) show a high fluorescein emission intensity [Fig. 5(a)] as expected for a PVA-rich matrix. If anthra-

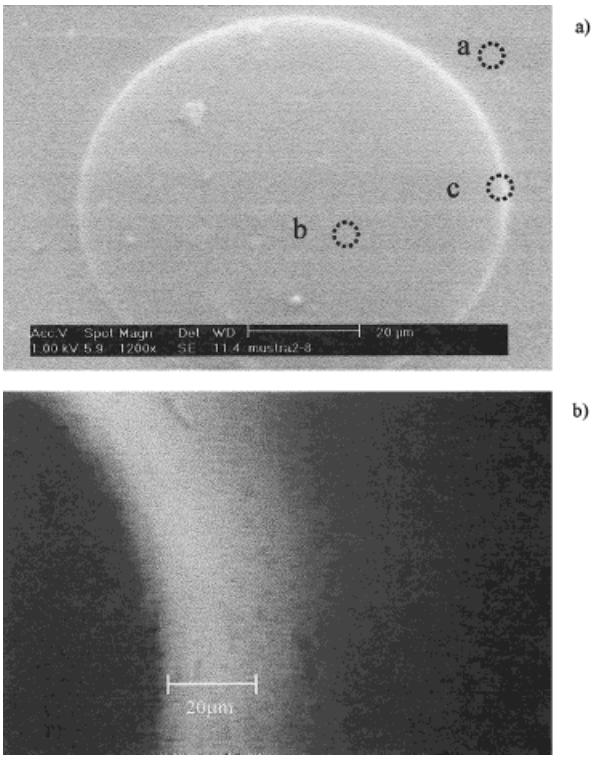


Figure 4 (a) SEM micrograph showing a circular domain in a 9/1 PVA/PVAc blend. Microfluorescence spectra from the selected regions a, b, and c are shown in Figure 5; (b) Epifluorescence micrograph of domain-matrix interfacial region. [Color figure can be viewed in the online issue, which is available at www.interscience.com.]

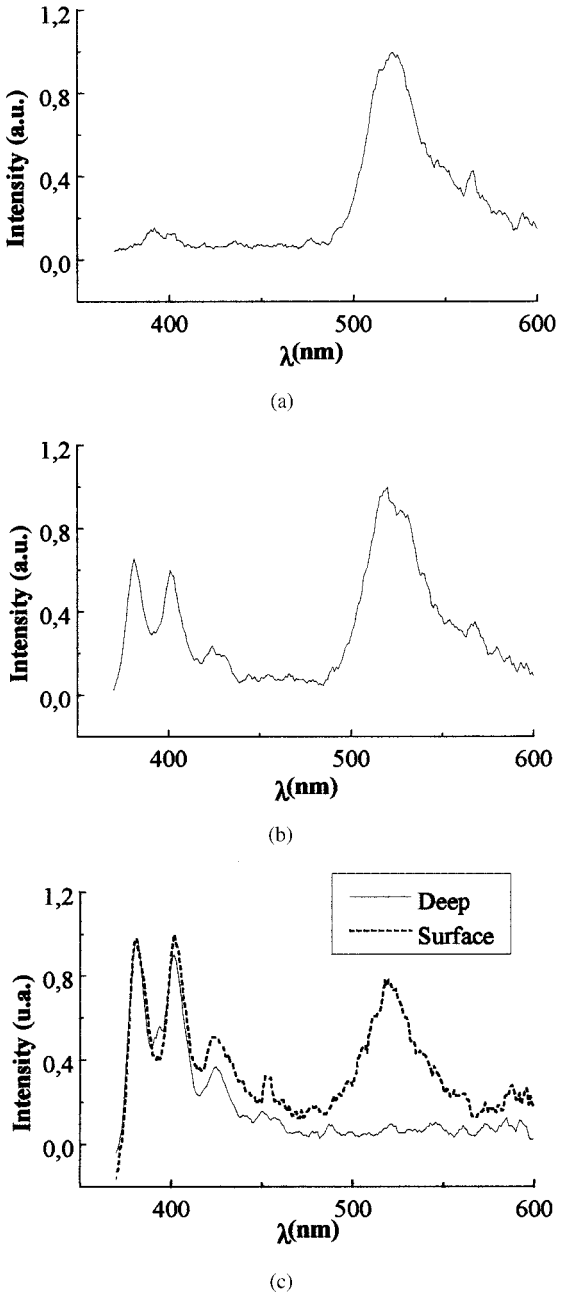


Figure 5 9/1 PVA/PVAc blend. Microfluorescence spectra of the zones marked in Figure 4(a).

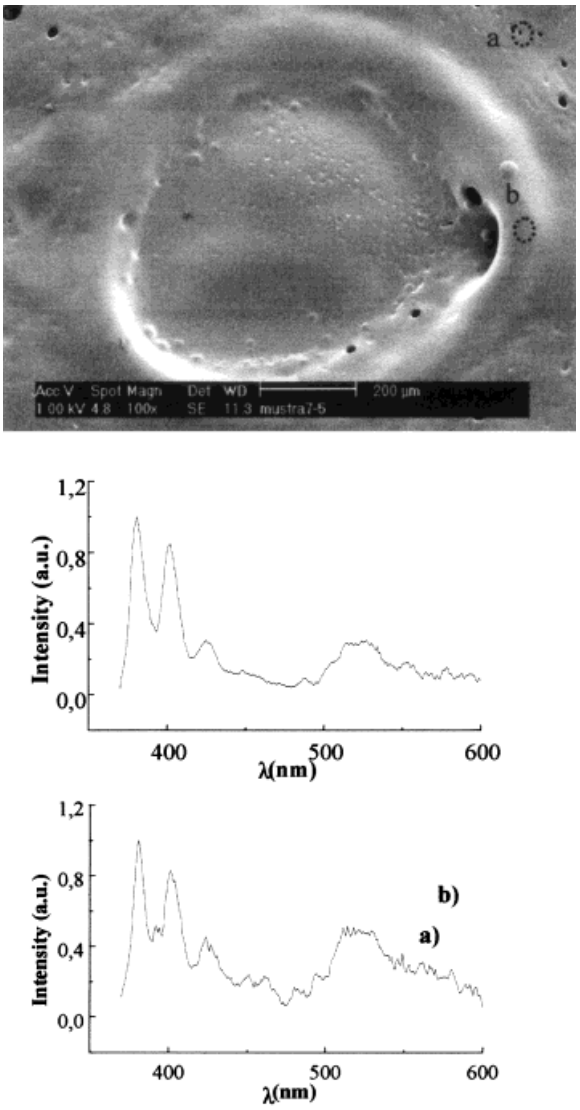


Figure 6 SEM micrograph showing a domain in a 1/9 PVA/PVAc blend. Microfluorescence spectra from selected regions a and b.

cene is excited instead, looking at regions (b) and (c) marked in Figure 4(a), a double emission of anthracene and fluorescein [Fig. 5(b) and (c)] due again to nonradiative energy transfer, is observed.

Several parts of the air-blend face of a 1/9 PVA/PVAc blend were also probed, selecting the illumination area over two types of regions: an interface, and a region external to the domain (Fig. 6). Again, the focus was illuminating a circular region, with a diameter ca. 25 μm, and, again, the recorded spectrum for the interface was contaminated by some contribution from the neighboring regions (internal and external to the interface). The relative fluorescence ratio, I_A/I_F, was calculated by integration of the spectral area for anthracene (I_A) ($380 \leq \lambda \leq 460$ nm) and fluorescein ($500 \leq \lambda \leq 580$ nm) (I_F) emissions [Fig. 6(a) and (b)]. The obtained ratio values were 1.11 and 1.77 for the interfacial (zone b in Fig. 6) and external (zone a in Fig. 6) regions, respectively, demonstrating that the interface is a PVA/fluorescein-richer region, and consequently, a region with partial interpenetration of both homopolymers.

CONCLUSION

The fluorescence spectra obtained using fluorescence microspectroscopy and epifluorescence microscopy allowed us to discriminate compositional dye/polymer gradients either across a domain–matrix interface or through the film thickness. These results demonstrated a partial interpenetration of these homopolymers involving three-dimensional domains and their adhesion on the matrix.

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