Synthesis and Characterization of PSSA-Polyaniline Composite with an Enhanced Processability in Thin Films

Abstract: This paper reports the synthesis and investigation of a polymer composite based on poly(4-styrenesulfonic acid) (PSSA) and polyaniline (PANI) directly obtained in an aqueous PSSA medium, with improved conductivity and solubility in polar solvents. The oxidative polymerization reaction of aniline takes place in-situ with PSSA as protonating agent. The synthesis was tested at three PSSA/PANI molar ratios, an intense green colored aqueous composite solution being obtained in each case. For comparison purposes, commercially available polyaniline and PSSA were also investigated. PSSA-PANI composites, PANI and PSSA were investigated through thermal analysis, Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy. Thin films of PSSA/PANI complex were spin coated on glass substrates which were further investigated through Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Also, thin films of PSSA-PANI were deposited on interdigitated electrodes for dielectric measurements.

Keywords: polyaniline, poly(4-styrenesulfonic acid), oxidative polymerization, polymer composites, thin films

1 Introduction

Conjugated polymers with conductive and semiconductive properties suitable for applications in electronics and various related fields have received a significant amount of interest in the last decade [1]. Polyaniline (PANI) represents one of the best candidates for electronic applications. The special attention given to PANI is mainly due to its electric conductivity and remarkable capacity to modify reversibly the color and oxidation potential as a function of certain parameters, such as the pH of medium and/or presence of oxidants and reductants [2].

Most of the PANI synthesis methods result in powders, which are difficult to process and solubilize. Obtaining a polymer soluble in water and/or in polar solvents is strongly related to the dopant employed in the synthesis process.

In recent years many attempts have been made to improve the processability of PANI. The introduction of alkyl substituents in the polymer chains significantly improved the solubility of doped and undoped PANI in organic solvents and even in water [3-5]. Adding aromatic substituents in PANI has improved its solubility and processability. However, the presence of these substituents also results in a decrease in electrical conductivity [6].

One method to improve the processability of polyaniline is to dope it with functionalized proton acids. Cao et al. synthesized polyaniline (soluble in water) doped with dodecylbenzenesulfonic acid (DBSA), the latter acting both as agent and doping surfactant for PANI [7]. Another way to get processable PANI is to prepare it in colloidal form. Numerous attempts have been undertaken to prepare PANI using colloidal polymer surfactants [8,9]. Other dopants such as 4,4-bis(4-hydroxy phenyl)-valeric acid, 1,2-benzene dicarboxylic acid, 4-sulfo-, 1,2-bis(2-ethylhexyl) ester (DEHEPSA) with dichloroacetate acid (DCAA) or difluorochloroacetic acid (DFCAA) as solvent dibutylphthalene sulfonic acid (DBNSA) have
been successfully used in the preparation of a soluble polyaniline [10-12]. Morphological modification of polyaniline in aqueous solutions of poly(vinylsulfonic acid), poly(acrylic acid) and poly(styrenesulfonic acid) used as electrolytes, was previously tested in electrochemical polymerization of aniline [13], while chemical polymerization of aniline in a polymeric proton acid medium was reported to enhance the solubilization of conductive PANI in common organic solvents as dimethylformamide or dimethylsulfoxide [14].

Other approaches involved the polyaniline doping by mixing with functionalized acid and using a suitable solvent. Kim et al. prepared polyaniline-Na⁺ montmorillonite nanocomposite using an emulsion intercalation method in order to employ this material as dispersing material for electro-rheological fluids (ER) [15]. Choi et al. conducted oxidative polymerization of aniline using poly (vinyl alcohol) (PVA) in the presence of multi-wall carbon nanotubes (MWCNT), in order to synthesize PANI/MWCNT nanocomposites for electrorheological applications [16].

Sulfonate-doped polyaniline was obtained from the polyaniline prepared according to Epstein method [17]. Ultrafine layers of polyaniline/polystyrene sulfonic acid (PSSA) were prepared through a “self-assembling” process by first immersing the substrate in a solution of PANI dissolved in N-methyl-2-pyrrolidone (NMP) and then in a solution of PSSA. The obtained films were uniform and strongly adherent to the substrate [18]. Nanofiber polyaniline/poly (styrene sulfonate) complex was also prepared through the interfacial method [19].

PANI may have potential applications in various fields. Its commercial uses are due to the advantage of reducing manufacturing costs of conducting polymers. The increasing interest in the study of these materials is argued by the numerous reported applications, such as chemical sensors, light-emitting devices and other.

The aim of this study is the preparation and investigation of water soluble PSSA-PANI composites obtained through oxidative polymerization of aniline in PSSA medium, as protonating agent, at three SO₃H-ANI molar ratios. Bulk prepared composites were investigated through thermal analysis, FT-IR and Raman spectroscopy. The reported PSSA-PANI composites are easily processable from their aqueous solutions, thin films deposited on glass substrates being obtained through spin coating, their morphology and dielectric properties being also investigated.

2 Experimental

2.1 Materials

Aniline (99.5%), poly (4-styrenesulfonic acid) (PSSA) (Mw 75,000, 18 wt. % in water), ammonium persulfate (APS) (98.0%) and Emeraldine base polyaniline (PANI-EB) (Mw ~20,000) were purchased from Sigma Aldrich. Acetone and high purity Milli-Q water were used for preparation and washing operations.

2.2 Preparation of PSSA-PANI composite

PSSA-PANI composite was obtained by oxidative polymerization of aniline in aqueous PSSA medium using ammonium persulfate (NH₄)₂S₂O₈ as initiator. The polymerization was performed at ambient temperature for 10 hours in the presence of polystyrene sulfonic acid as protonation agent (18% in water) at three different molar ratios [SO₃H]/[ANI] (1:1, 2:1, and 3:1, respectively). In less than 15 minutes after ammonium persulfate was added, a gradual change of original solution color to dark green was observed. This is another indication of the formation of polyaniline. A noteworthy observation is that the reaction medium is homogeneous throughout the polymerization reaction. The processes which are performed within the aqueous PSSA medium leading to PSSA-PANI composite are summarized in Scheme 1.

In a typical synthesis procedure for 1:1 molar ratio, 10 ml PSSA (wt. % water) was diluted with 3 mL MilliQ water, after which 0.9 mL aniline was added dropwise under continuous, moderate agitation. Separately, the initiator solution was prepared by dissolving 0.22 g (NH₄)₂S₂O₈ in 2 mL high purity water. The initiator solution was also added dropwise in the PSSA-aniline mixture and stirred for about 15 min. After adding the initiator, the solution gradually changed its color into intense green. For the completion of the polymerization reaction, the recipient was kept without stirring, in ambient temperature conditions for about 8 h. For the PSSA/PANI molar ratios of 1:2 and 1:3 the synthesis was conducted under the same conditions with the change of the reactants ratios accordingly. Fig. 1 shows the aspect of dried complex in bulk, deposited in thin films on glass substrate and prepared for dielectric measurements.

For purification, the product was obtained in the form of thick layers on glass substrates. After drying, the prepared composites are removed from the glass substrate and subjected to repeated washing operations.
in acetone. Then, the composites were dried in an oven at a temperature of approx. 60°C for 3-4 h. For morphology and dielectric properties investigations, the composites were re-dissolved in water and deposited in thin layers on glass substrates using spin coating technique, at a speed of 2200 RPM. Carefully cleaned microscope slides were used for depositing the layers on glass. The cleaning step consisted of washing with isopropyl alcohol followed by sonication (for 15 min). The resultant films were uniform and had good adhesion to the substrate. Also, deposition on metal electrodes (Interdigit electrodes) was performed in order to characterize the composites in terms of dielectric characteristics.

2.3 Characterization

IR spectra were recorded in the range of 400-4000 cm⁻¹ using a Digilab FTS-2000 FT-IR spectrometer, according to KBr pellet method. Thermal behavior was studied on a Mettler Toledo TGA-SDTA851e, under N₂ atmosphere with an airflow rate of 20 mL min⁻¹. The heating rate was adjusted to 10°C min⁻¹ in the 25-900°C range. The variation of electrolytic conductivities during the polymerization process performed in aqueous medium was monitored with a CONSORT C863 laboratory conductometer. The film deposition of compounds in solution on solid supports was carried out by means of Laurell WS-400-6NPP Spin Coater.

Raman spectra from a minimum of three areas were acquired for each sample in the range of 100-3200 cm⁻¹ with a Renishaw inVia Raman Microscope integrated with a NTEGRA Probe NanoLaboratory AFM. The Raman laser excitation beam was operated at 785 nm in single scan measurement mode. SEM micrographs were recorded with a Hitachi TM-3000 equipment, working at 15 kV accelerating voltage. Further morphologic properties of the prepared thin complexes films were investigated through AFM, with a Solver PRO-M, NTMDT equipment, provided with a NSG10/Au, NTMDT tip.

The dielectric measurements were performed by means of a Novocontrol Broadband Dielectric Spectrometer (Alpha-A High Performance Frequency Analyzer, frequency...
domain 0.001Hz to 3GHz). The polymeric films were deposited on interdigitated electrodes which consisted of two overlapping comb-type structures allowing the generation of a gradient of electric field with variable magnitude and frequency. The interdigitated electrodes of 20 mm diameter were placed in the Novocontrol Alpha active sample cell. The measurements were performed at ambient temperature; the frequency domain was spanned between 0.01 Hz up to 1 MHz while the applied AC voltage was set to 1 V.

3 Results and Discussion

3.1 FT-IR analysis

Fig. 2 presents the FT-IR spectra recorded for the prepared PSSA-PANI composites at three PSSA-ANI molar ratios (Figs. 2c,d,e). For comparison and investigation purposes, commercially PANI-EB and PSSA were also investigated (Figs. 2a,b). Oscillatory vibrations of C-H bond in benzene rings 1,4 and 1,2-disubstituted in PSSA are located at 833 and 774 cm⁻¹, respectively [20,21]. The wide absorption at 3436 cm⁻¹ is assigned to water absorbed in the sample (sulfonic acid groups are strongly hydrophilic). From the recorded spectrum of PANI-EB (Fig. 2b) one can observe the characteristic peak at 1593 cm⁻¹, which is due to the C=C stretching in the quinoid ring, the 1378 cm⁻¹ peak typical for C-N stretching [22-24].

In the spectra recorded for PSSA-PANI composites (Fig. 2c-e) almost all peaks characteristic to PSSA and PANI are clearly visible, excepting those masked by the wider or larger intensity peaks as in case of –N–H stretching vibration (3391 cm⁻¹), which is present in case of PANI-EB but it is masked by the wide peak located at 3440 cm⁻¹ due to the presence of water in the investigated sample. In Table 1 there are details of some significant peaks of PSSA, PANI-EB and their presence in the PSSA-PANI complex.

A series of characteristic peaks of PSSA and PANI-EB are displaced in case of PSSA-PANI composites which is most probable due to the interactions occurred during the polymerization of aniline in aqueous PSSA medium. The C-N stretching vibrations at 1297 and 1378 cm⁻¹ in PANI-EB appear displaced (1304 and 1407 cm⁻¹, respectively) due the vicinity of SO₂H groups. Also C=C stretching in the quinoid ring (1593 → 1599 cm⁻¹) and aromatic ring in plane deformation (1006 → 997 cm⁻¹) appeared displaced as their positioning was different in prepared PSSA-PANI. The situation was similar for all the prepared PSSA-PANI composites at any ratio. The presence of groups at ~1562 cm⁻¹ and 1493 cm⁻¹ characteristic to N-benzenoid and quinoid ring respectively emphasizes the conductive form of the polymer. The peak at 1496 cm⁻¹ could denote a π-electron delocalization degree due the protonation of PANI [25]. IR spectra of the polyaniline synthesized in the presence of PSSA at three molar ratios confirm the presence of Emeraldine salt – conducting polyaniline.

Figure 2: Recorded FT-IR spectra of (a) PSSA, (b) PANI-EB, (c) PSSA-PANI 1:1, (d) PSSA-PANI 2:1, (d) PSSA-PANI 3:1 complexes.
3.2 Raman spectroscopy

Fig. 3 shows the spectra recorded for PSSA-PANI composites prepared at above mentioned three molar ratios (Figs. 3b-d) and for comparison purposes PANI-EB (Fig. 3a) was also investigated. As could be noted, the spectrum recorded for PSSA-PANI 1:1 is close resembling with the one recorded for PANI-EB with slight shifts of the peaks, most probable due to the interactions occurred with the PSSA matrix. The stretching vibrations of C–N bond located at 1357 cm⁻¹ are slightly displaced at 1343 cm⁻¹, while the C–H bending located at 1011 cm⁻¹ was found at 986 cm⁻¹ in the PSSA-PANI 1:1. The antisymmetric stretch at 1343 cm⁻¹ of the –SO₂ group in PSSA becomes noticeable, increasingly higher intensities being observed at higher PSSA-PANI molar ratios.

Higher PSSA-PANI molar ratios (Figs. 3c,d) lead to a changed shape of the recorded spectra due the increasing presence of specific vibrations of PSSA. In 1650-1520 cm⁻¹ spectral region a series of peaks corresponding to C–C ring stretching vibrations are located, while in the 1520-1210 cm⁻¹region various stretching modes of C–N bonds are present. Also peaks corresponding to various deformations of the C–H bonds are located in the 1210-1100 cm⁻¹ region [26]. Assigned to the deformation of benzene ring in the chain of polyaniline salt, the peaks located at 597 and 600 cm⁻¹, respectively (Figs. 3c,d) suggest interactions that occurred between the groups specific to PSSA and PANI [27 -29]. Vibrational bands characteristic to polyaniline were observed in all cases, yet with some certain differences. The band at 1357 cm⁻¹ in case of PANI-EB, which is characteristic to delocalized polaron states, is slightly shifted thus indicating a modification of molecular geometry in the mixture.

3.3 Thermal Analysis

Fig. 4 presents the thermogravimetric (TG) derivatograms recorded for PANI-EB, PSSA and PSSA-PANI (at three molar ratios). Also, thermal stability of PSSA-PANI at different molar ratios was analyzed and compared to those of PSSA and PANI-EB.

By analyzing the data in derivatograms recorded for PSSA, it was distinguished three ranges of mass loss. The first mass loss which occurred from 50 to 130°C, is

<table>
<thead>
<tr>
<th>Functional group/assignment</th>
<th>PANI-EB (cm⁻¹)</th>
<th>PSSA</th>
<th>PSSA-PANI composite</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>C-H oop wagging</td>
<td>501</td>
<td>-</td>
<td>504</td>
<td>[23]</td>
</tr>
<tr>
<td>oop ring bending</td>
<td>695</td>
<td>-</td>
<td>-</td>
<td>masked by the wide 669 cm⁻¹ peak in the PSSA-PANI</td>
</tr>
<tr>
<td>C–H oop deformation</td>
<td>829</td>
<td>-</td>
<td>825</td>
<td>[22]</td>
</tr>
<tr>
<td>C-H def. in N=Q=N sequence</td>
<td>1165</td>
<td>-</td>
<td>1161</td>
<td>[22,23]</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1297</td>
<td>-</td>
<td>1304</td>
<td>see text</td>
</tr>
<tr>
<td>C–N stretching in QBQ units</td>
<td>1378</td>
<td>-</td>
<td>1407</td>
<td>vibration in the neighborhood of a quinoid ring (typical for PANI base) [22]</td>
</tr>
<tr>
<td>C=C stretching of the Quinoid ring</td>
<td>1593</td>
<td>-</td>
<td>1599</td>
<td>see text</td>
</tr>
<tr>
<td>aromatic C-H stretching</td>
<td>3031</td>
<td>-</td>
<td>-</td>
<td>in the PSSA-PANI complex is masked by the large 3440 cm⁻¹ peak due the presence of water</td>
</tr>
<tr>
<td>–NH– stretching</td>
<td>3391</td>
<td>-</td>
<td>-</td>
<td>masked by the large 3440 cm⁻¹ peak due the presence of water</td>
</tr>
<tr>
<td>C-H out of plane bending</td>
<td>-</td>
<td>672</td>
<td>669</td>
<td>-</td>
</tr>
<tr>
<td>C-H wagging</td>
<td>-</td>
<td>774</td>
<td>771</td>
<td>in 1,4- and 1,2-substituted benzene rings of PSSA [20]</td>
</tr>
<tr>
<td>aromatic ring in-plane def.</td>
<td>-</td>
<td>1006</td>
<td>997</td>
<td>see text</td>
</tr>
<tr>
<td>S=O symmetrical stretching</td>
<td>-</td>
<td>1035</td>
<td>1033</td>
<td>[26]</td>
</tr>
<tr>
<td>Aromatic ring in-plane skeleton def.</td>
<td>-</td>
<td>1128</td>
<td>1123</td>
<td>-</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>2927</td>
<td>-</td>
<td>2925</td>
<td>CH₃ groups in the side chain</td>
</tr>
<tr>
<td>water in the sample</td>
<td>-</td>
<td>3436</td>
<td>3440</td>
<td>due highly hydrophilic sulfonic acid groups</td>
</tr>
<tr>
<td>Quinoid ring deformation</td>
<td>833</td>
<td>-</td>
<td>825</td>
<td>see text</td>
</tr>
</tbody>
</table>
attributed to water loss; the second range, 299-350°C, corresponds to the decomposition of sulfonil groups; while the third one, 390-450°C, is due to the decomposition of the main chain in polymer. For PANI-EB, a significant mass loss (43.5%) begins around the value of 470°C and continues up to 581°C due to the degradation processes of polymeric chain.

Data recorded in case of PSSA-PANI at all three molar ratios indicate an important mass loss since the first degradation stage. This might be explained by the presence of water due to PSSA hygroscopicity. Thus, from 50 to 160°C the following mass losses occur: 3.27% (1:1), 8.79% (2:1), 13.21% (3:1). Significant discrepancies are noticed in the following two stages of degradation. For the range 289–330°C the recorded mass losses of about 28% for the ratios 1:1 and 2:1, and 15% for 3:1 ratio. At temperature range between 343 and 425°C, mass loss values are 22% (1:1), 15% (2:1), and 25% (3:1) respectively, and peak degradation temperature ($T_{\text{peak}}$): 1:1 (379°C) < 2:1 (409°C) < 3:1 (425°C). Higher values of decomposition temperature were recorded for sample synthesized using higher concentration of sulfonate groups in polystyrene [30]. For all of the investigated products, the degradation process is not complete. In each case there is a residue varying between 35.89%, for 1:1 PSSA-PANI, and 39.59%, for 3:1 PSSA-PANI. Comparison of the data obtained for the three mixtures with those of the native polymers showed a sufficiently high thermal stability. The property is improved with reducing the amount of PSSA in the initial mixture.

3.4 Electron Microscopy

Fig. 5 presents the images recorded by scanning electron microscopy (SEM) of PSSA and PANI-EB, as well as those of PSSA-PANI at the three mentioned molar ratios. These images indicate completely different morphologies, rough for PANI (Fig. 5a), and very smooth in case of PSSA (Fig. 5b). A different aspect of the two polymers is determined by the fact that PSSA is an amorphous polymer while PANI is a highly crystalline one. The morphology of the three films obtained with PSSA-PANI is modified as a function of the molar ratio (Figs. 5c-e). It can be noticed that with the increase of molar ratio in favor of PSSA, the surface aspect changes from unregulated, which is specific to PANI, towards a smooth one, which is common to PSSA.
Figure 4: Recorded TG (a) and DTG (b) pattern for (a) PANI-EB, (b) PSSA and PSSA-PANI at (c) 1:1, (d) 2:1, (e) 3:1 molar ratios.

Figure 5: Recorded SEM micrographs for (a) PANI-EB, (b) PSSA, PSSA-PANI (c) 1:1, (d) 2:1, (e) 3:1.
3.5 Atomic Force Microscopy

The morphology of PSSA-PANI films at the three molar ratios was analyzed by atomic force microscopy (AFM). Fig. 6 shows three-dimensional images (3D-AFM) of the surfaces of thin layers deposited by spin coating. The recorded images pinpoint successful, relatively smooth films of PSSA-PANI and confirm the conclusion obtained by means of SEM analysis. Likewise, it can be observed that as the PSSA percent increases, the surface irregularities of the obtained films diminish. They practically reduce from 210 nm in case of PSSA-PANI 1:1 to 62 nm for PSSA-PANI 3:1.

3.6 Specific conductance

The influence of the PSSA quantity over the conductivity of the aqueous solutions containing 0.6 M aniline, 0.06 M ammonium persulfate and SO$_3$/ANI ratio of 1:1 during the polymerization process is shown in Fig. 7. As can be noticed that the conductivity of electrolyte solutions increases with the PSSA/ANI ratio due to the increase of the concentration of electrolyte (PSSA). The conductivity of each solution before the ammonium persulfate was added was 15.05, 66.7 and 135.8 mS cm$^{-1}$ for the molar ratios 1:1, 2:1 and 3:1, respectively. After adding the initiator, the conductivity increased to 35.9 and 67.6 for 1:1 and 2:1 solutions respectively. In case of 3:1 solution initially a slight decrease was observed, followed by an increase up to a maximum, which was then followed by a plateau.

3.7 Dielectric measurements

The dielectric properties of the samples were evaluated on the basis of dielectric constant ($\varepsilon'$). It was decreasing with increasing the frequency and dielectric losses (tan delta), which may have exhibited one or more peaks on the frequency characteristic. The dielectric constant characterizes the ability of a material to store energy while the dielectric loss is related its capacity of dissipating energy. In Fig. 8a the dielectric constant is plotted against the frequency, while in Fig. 8b, the dielectric losses dependency on frequency is presented.

With regards to the dielectric constant of PANI-EB and PSSA-PANI 1:1, no variation with respect to quantitative values is observed. However, as the frequency increases, the classical behavior of PANI was observed. In case of PSSA-PANI 2:1 and PSSA-PANI 3:1 one can notice an increase of the dielectric constant at low frequencies. This phenomenon can be assumed to be characteristic to interfacial polarization caused by the displacement of charges in the bulk of the material towards the interfaces which are forming imaginary dipoles.

For the dielectric losses, the highest values are observed in the case of PANI-EB. While varying the PSSA-PANI ratio, a decrease of the tan delta from PANI-EB to PSSA-PANI 1:1 occurs. Simultaneously, on the PSSA-PANI 1:1 spectra two dielectric relaxations occur around 1 kHz and 1 MHz. While modifying the ratio PSSA-PANI to 2:1 and 3:1, respectively the tan delta is decreasing. In spite of the closer values for tan delta, on the PSSA-PANI 2:1 spectrum three dielectric relaxations can be observed, while in case of PSSA-PANI 3:1 there are only two. Dielectric relaxations displayed in case of PSSA-PANI 2:1 move towards higher frequencies on the PSSA-PANI 3:1 spectrum, and are less visible. PSSA is less conductive than PANI, which leads to a decrease of the values of tan delta. This explains the less visible dielectric relaxations in the of PSSA-PANI 3:1 in comparison to PSSA-PANI 2:1. The electric dipoles appearing in the case of PSSA-PANI 3:1 are smaller than those which are forming for PSSA-PANI 2:1. This explains the shift of dielectric losses towards higher frequencies.
4 Conclusions

A straightforward synthesis method for preparing PSSA-PANI composites, suitable for obtaining qualitative thin films deposited on various substrates, was presented in this paper.

IR spectra of synthesized compounds in the presence of poly(4-styrenesulfonic acid) at three different values of molar ratio confirm the existence of a conductive Emeraldine salt polyaniline. Raman spectra pinpoint a shift of the 1353 cm⁻¹ band (characteristic to the delocalized polaron states), which indicates a modification of the molecular geometry of synthesized compounds. Both analysis methods suggest interactions between the macromolecular chains of PSSA and PANI. Thermal analysis comparative study of PSSA-PANI at three different molar ratios and native polymers indicate a thermal stability sufficiently high due to the intermolecular interactions between SO₃⁻ and anilinium ion, this property getting improved with lowering the amount of PSSA in the initial mixture.

The morphology of the three PSSA-PANI films varies as a function of the molar ratio. By increasing the ratio in favor of PSSA, the surface aspect changes from rough which is specific to PANI towards the smooth aspect specific to PSSA.

Dielectric relaxations are less visible in case of PSSA-PANI 3:1 in comparison to PSSA-PANI 2:1. The electric dipoles appearing in the case of PSSA-PANI 3:1 are smaller than those which are forming in the case of PSSA-PANI 2:1.
a fact which explains the shift of dielectric losses towards higher frequencies.

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