SILOXANE-AZOAROMATIC POLYESTERS AS POTENTIAL COMPLEX DYE SYSTEMS

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New polyesters with siloxane-organic main chain and azobenzene side groups were used in physical mixtures with different polymers (aromatic polysulfones, polydimethylsiloxane, hydroxypropylcellulose), in order to study the intermolecular interactions. By electronic absorption spectroscopy, DSC, optical and electronic microscopy, we investigated the compatibility within the blends, as a function of siloxane length and matrix polymer's chemical structure.

INTRODUCTION

New siloxane polyesters with azoaromatic side groups have been synthesized by direct polycondensation, at room temperature, starting from Disperse Red 19 and different siloxane-organic diacids, using dicyclohexylcarbodiimide (DCC) as an activating agent and 4-(N,N-dimethylamino)pyridinium-*p*-toluenesulfonate (DPTS) as catalyst.[1]

By their complexity, these polymers can be regarded as multifunctional materials. The presence of the azoaromatic chromophore induces a specific behavior as dye polymers, confering photosensitivity and high dye capacity. On the other hand, the azoaromatic groups act as mesogenic moieties. The variations in the siloxane-organic structures of the main chain tailor the thermal and thermotropic LC properties of the polyesters. The presence of the mesophases, their type and range and the LC transition temperatures depend on the chemical structure of the main chain.

The siloxane moieties are responsible for the biphasic morphology and modified surface properties. The possibility of nanostructured morphology, as a result of thermodynamic incompatibility between the siloxane-based main chain and the lateral aromatic groups, is interesting for possible optical aplications. The polymers' surface properties may be useful in applications such as coatings or dyes. Polysiloxanes are known

to impart hydrophobicity or water repellency. The surface enrichment in Si and the formation of a silicon surface layer was widely reported for siloxane-containing block copolymers and blends.[2-7] The explanation of such behavior is the preferential orientation of the siloxane fragments towards the surface, due to their very low surface tension. This aspect, evidenced in the case of the azoaromatic siloxane polyesters,[1] may be exploited in the perspective of complex materials hydrophobization.

In this paper, we present some results of our attempt to study the behaviour of siloxane-azoaromatic polyesters as complex dye systems. The siloxane moieties improve the water repellency, while the polar functional groups may lead to intermolecular interactions (such as H-bondings, arene-arene or dipol-dipol forces) with other polymers.

Physical mixtures with polymers having various structures (aromatic polysulfones, polydimethylsiloxane, hydroxypropylcellulose) have been obtained. They have been investigated for photochemical behavior and thermal properties. By UV-VIS spectroscopy, the level of intermolecular interactions has been estimated, following the variation of the absorption maxima of azobenzene chromophore. The modifications of the polymers' glass transition temperatures, in the presence of different amounts of siloxane-azoaromatic polyesters have been investigated by DSC. The compatibility

of different polymer pairs have been thoroughly studied by optical and electron microscopy. As TEM offers informations on the supramolecular structure of multiphasic systems, it has been used in the case of these polymer-polymer-dye blends, in order to investigate the nature of the morphology, the shape and size of the domains.

RESULTS AND DISCUSSION

Three siloxane-azoaromatic polyesters were used as polymer dyes and four polymers with different chemical structure acted as polymeric matrices. Their structural units are presented in **Schemes 1** and **2**.
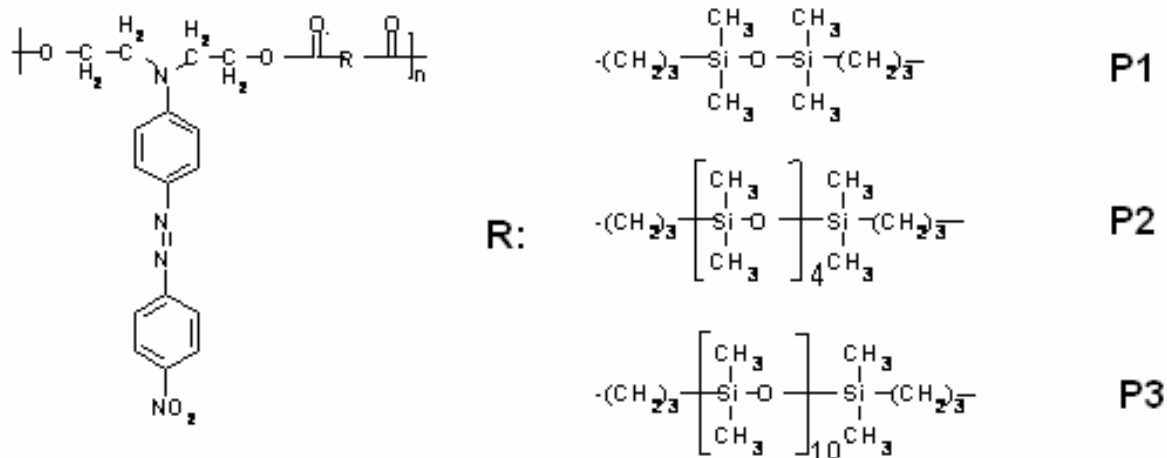
Scheme 1 – Chemical structure of the siloxane-azoaromatic polymer dyes.
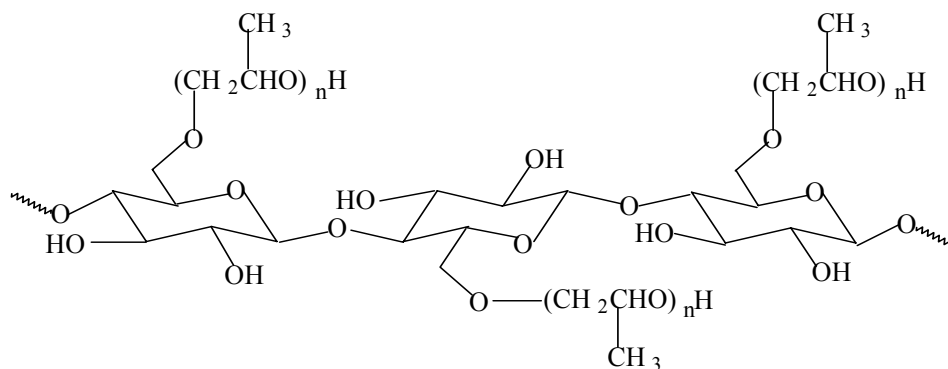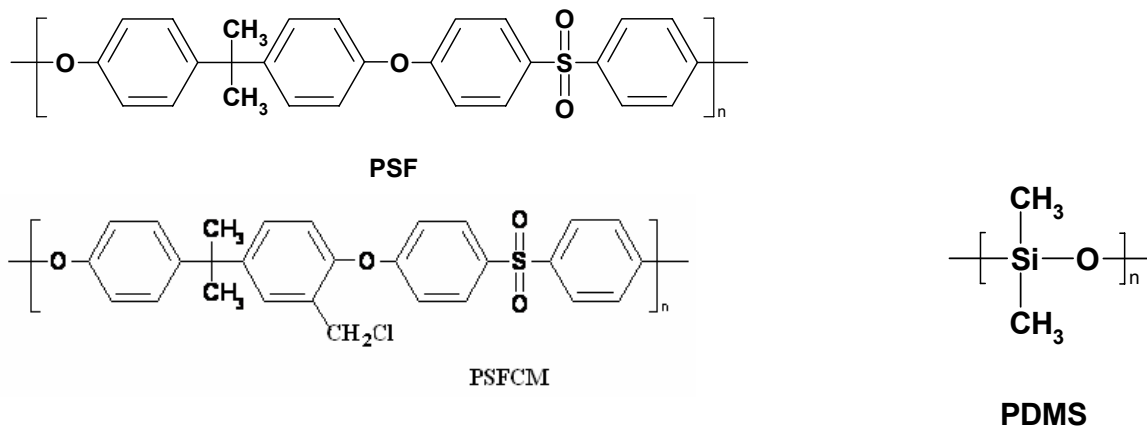
Scheme 2 – Chemical structure of the matrix polymers used in the blends.

Table 1

Composition of the blends

Matrix polymer	Dye polymer	Mixture code
PSFCM	P1	A10 A30 A50 A80
	P2	B10 B30 B50
	P3	C10 C30 C50
PSF	P1	D10 D30 D50
	P2	E10 E30 E50
	P3	F10 F30 F50
PDMS	P1	G10 G30 G50
	P2	H10 H30 H50
	P3	I10 I30 I50
HPC	P1	J10 J30 J50
	P2	K10 K30 K50
	P3	L10 L30 L50

The compositional data of the polymer blends are presented in Table 1, where the digits in the samples codes represent the dye content, in wt%.

The two-component polymer blends were investigated by different methods, in order to obtain information about the degree of mixing. The polymers were chosen as to ensure different types of potential interactions, their nature and level being the key parameters for the mixing behaviour. The dye polymers have siloxane-aliphatic chains and azo-aromatic pendant moieties, with nitro end-groups; polysulfones are aromatic polymers, with polar groups, polysiloxane is a nonpolar polymer, but may exhibit some kind of affinity for the dye chains, while hydroxypropylcellulose contains OH groups, capable of H-bonding.

The degree of interaction and hence the degree of mixing may be discussed in terms of macroscopic properties (for example Tg values or UV absorption), but also in terms of microphase segregation.

UV-VIS study

The obtained blends were studied by UV-VIS spectroscopy, both in solution and in film, following the changes that occurred in the absorption maxima corresponding to the azo-siloxane polyesters. The variation of the absorption maxima reflects the intermolecular interactions of the chromophores;[8] λ_{max} shifted towards lower values corresponds to a so-called H-type aggregation of the chromophores, while λ_{max} shifted towards higher values corresponds to a J-type aggregation.[9]

The variations of the λ_{max} values versus dye polymer concentration, in solution and in film, are presented in **Figure 1**. As PDMS is liquid at room temperature, its blends could not be investigated as films.
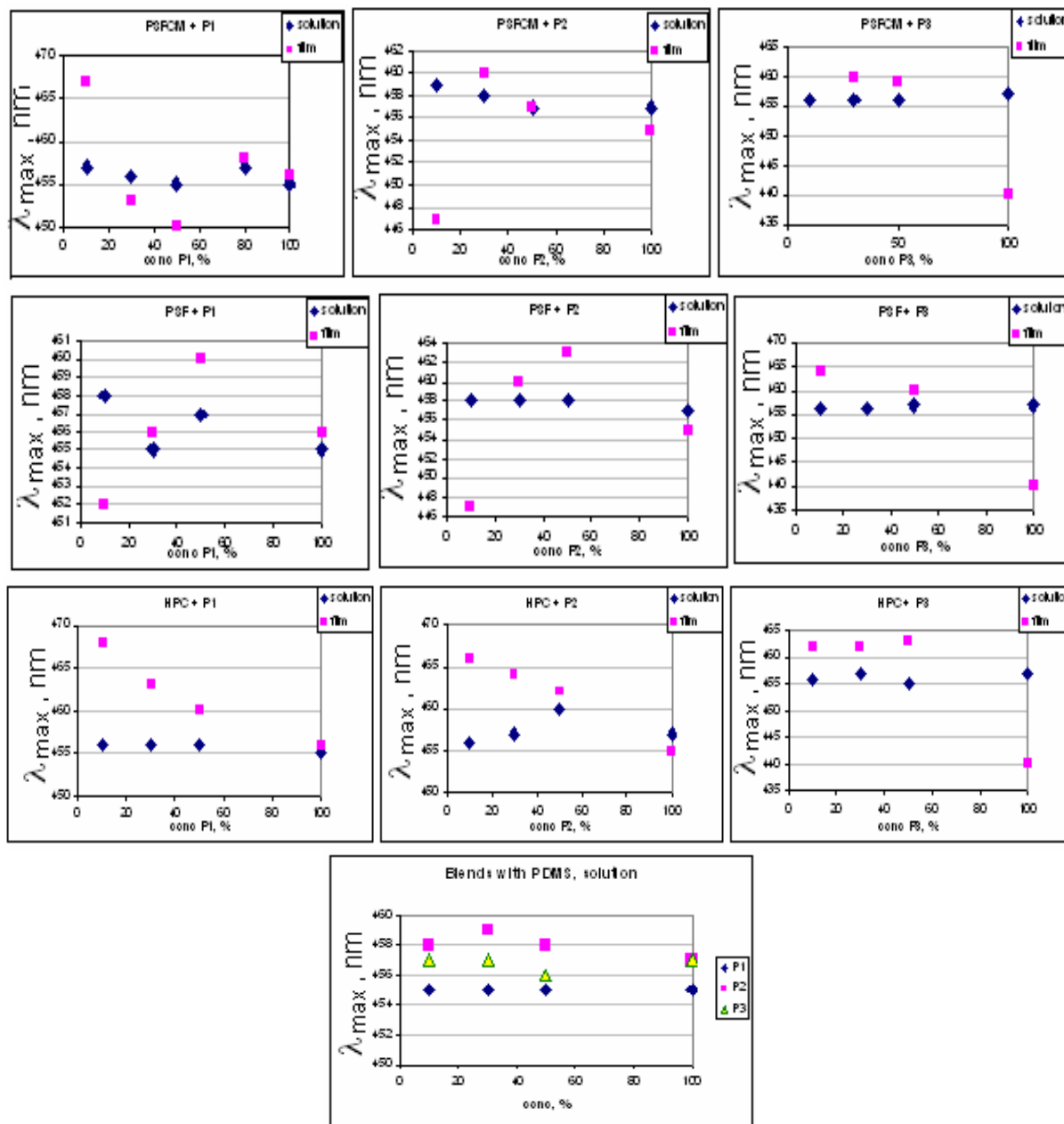
Fig. 1 – Variation of the UV absorption maximum for the studied blends, in solution and film.

As can be observed, for all blends the variation of λ_{max} in solution is insignificant. This fact is probably due to the absence of intermolecular interactions in chloroform, which means practically the same unrestricted mobility of the chromophores in the blends as in the neat dye solution. On the contrary, in films, this mobility is reduced, so that the position of the absorption maximum depends mainly on the nature of the polymers and on dye concentration.

In the case of P3 (neat dye polymer), a significant difference of the absorption maximum between the film and the solution was observed. A possible explanation could be the phase separation which may occur in the material, due to the incompatibility of polysiloxane and organic segments. Another hypothetical explanation for the different λ_{max} in solution and in film in the case of P3 could be a self-assembling in chloroform, but this is less probable, taking into account the presence of a single absorption maximum, the low concentration of the measured solution (10^{-4}-10^{-5}M) and the constancy of UV maximum in solution for all the blends. Indeed, as we shall discuss later, the TEM observations

confirmed a pronounced phase separation in the case of polyester P3. As the difference of λ_{max} between solution and film is much smaller in the blends, this could mean that the phase separation occurring in P3 chains is precluded or modified in the presence of the polymeric matrix.

Rather different UV results were obtained for the series of blends that we investigated, but for all series, the blends containing the azo polyester with the longest siloxane segment (P3) had a different behaviour than those containing shorter siloxane segments. They showed the smallest variation of the absorption maximum with concentration, in film.

The evolution of the absorption maxima position in the case of HPC-based blends was the clearest: irrespective of the dye content, a bathochromic shift reported to the dye spectrum was observed, a linear decreasing of the maximum with the dye concentration for P1 and P2, and an absorption maximum practically independent of concentration in the case of P3.

In the blends based on HPC, the presence of the OH groups favours H-bonding interactions with the N atoms (in the tertiary amine group) and with the ester groups of the dye polymer. The decrease of λ_{max} with dye concentration in the case of P1 and P2 could indicate the replacement of matrix-dye interactions with dye-dye interactions, while the constant value of λ_{max} in the case of P3 would be explained by the same type and level of matrix-dye aggregation, which would mean a good compatibility of the two components of the blend, irrespective of dye concentration. As can be observed in **Figure 1**, the longer the siloxane fragment, the smoother was the λ_{max} variation. This is in agreement with the level of matrix-dye interactions: as the siloxane segment length increases, the number of H-acceptor groups per mass unit decreases, so the level of H-bonding decreases.

For the blends obtained with polysulfones, intermolecular interactions like dipol-dipol or arene-arene are possible. In the case of PSFCM, the quaternization reaction of the tertiary amine in the azo-siloxane polyester cannot be totally excluded, although it is rather less probable in the conditions of blends preparation (mixing in a nonpolar solvent, at room temperature).

The variation of λ_{max} with dye concentration was more complicated for A – F series of blends (based on polysulfones). Mostly hypsochromic shifts at low concentration and bathochromic shifts at higher concentration were observed (with the exception of A series, were the tendency was reversed), which would mean that the type of matrix-dye interaction changes as the dye concentration increases.

Thermal properties

The thermal properties of the polymer-dye blends were investigated by DSC, following the variation of glass transition temperature, obtained in the second heating run.

The exact definition of miscibility in polymer blends is still under discussion.[10] There are different approaches, based on practical interest. From the point of view of macroscopic properties, a miscible polymer blend is defined by a single glass transition temperature. In this case miscibility means homogeneity of the blend at a scale comparable with the dimensions of the segment responsible for the major transition. For incompatible polymer blends, two glass transition temperatures are observed, while for polymer-filler systems, the decrease of Tg is indicative of plastification.[11]

In **Figure 2**, the Tg values of the blends based on polysulfones are plotted against the content of azo-siloxane polyester. The thermal behaviour of the blends obtained with polysulfones showed an important decrease of Tg of the matrix polymer (with 40 °C in the case of PSFCM and almost 80 °C in the case of PSF), even for a content of dye polymer as low as 10%. Taking into account that the Tg values of the azo-siloxane polyesters are bellow room temperature[1] and that the DSC curves showed single Tg for all samples, the found glass transitions are intermediate values, corresponding to compatible polymers blends.

Generally a minimum of Tg values corresponding to a content of about 30% of polymer dye was observed for polysulfones-based blends, which could be a critical concentration for the plastification effect. On the other hand, the effect of the siloxane segment length (which acts like a plastifier due to its flexibility) was less significant than we expected. There is rather little difference between the blends containing P1, P2 and P3 respectively, but the most pronounced plastification effect was produced by P2, which has a medium length of the siloxane segment.

For PDMS-based blends, a surprising result was obtained: all samples had the same Tg as the neat PDMS (-124°C), thus showing a complete incompatibility within the polymer pairs. As the dye polymers contain different amounts of siloxane, it would be expected that these moieties act as compatibilizing agents in the PDMS matrix.

In the case of blends based on HPC, the presence of water and internal H-bonds within the matrix and with the polymer dye molecules makes the assignment of glass transition temperature very difficult. This is the reason why it was not possible to draw an unequivocal conclusion regarding the evolution of Tg for these blends.
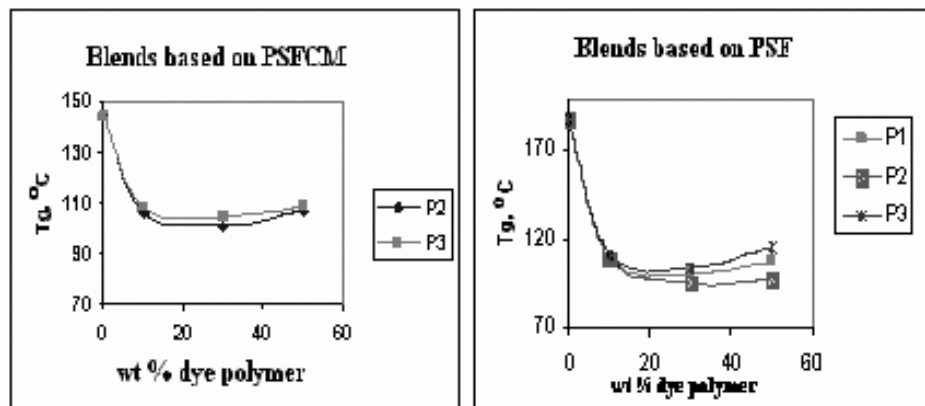
Fig. 2 – Variation of glass transition temperature (from DSC, second heating) for the blends containing
polysulfones and azo-siloxane dye polymers.

Morphology

The blends were investigated by TEM and certain aspects were correlated with optical microscopy observations (normal and polarized light). Morphological investigations were made on blends containing 30% dye polymer, and some features were always taken into account: general aspect of the film, colour uniformity, presence of separated domains, their size and shape, presence of un-mixed dye inclusions. Due to the procedure of sample preparation, some of the films were not very uniform in thickness; another problem that affects the proper assignment of the morphology is the so-called "memory of the solvent",[12] which means that the eventual self-assembling or interactions in solution may remain after the removal of the solvent. These elements may lead to misinterpretation of the microscopic images, so we tried to minimize them as much as possible.

Firstly the azo-siloxane polyesters have been analyzed, knowing that an association in a chemical structure of siloxane and aromatic moieties usually provides phase separated morphology. As can be observed in **Figure 3**, phase separation was indeed more obvious for the dye polyesters with longer siloxane segments.

Blends based on PSFCM

By optical microscopy we observed uniformly coloured films, with very small and isolated birefringent inclusions (of un-mixed dye), indicating a good compatibility at the coresponding magnification. It was interesting to notice, especially on thicker films, micelle-like formations (**Figure 4**), probably due to the above-mentioned memory of the solvent.[12]

Although on « macro-» level the samples appeared as homogeneous, by electron microscopy microphase separation was observed for the blends containing 30% dye polymers, as can be seen in **Figure 5**.

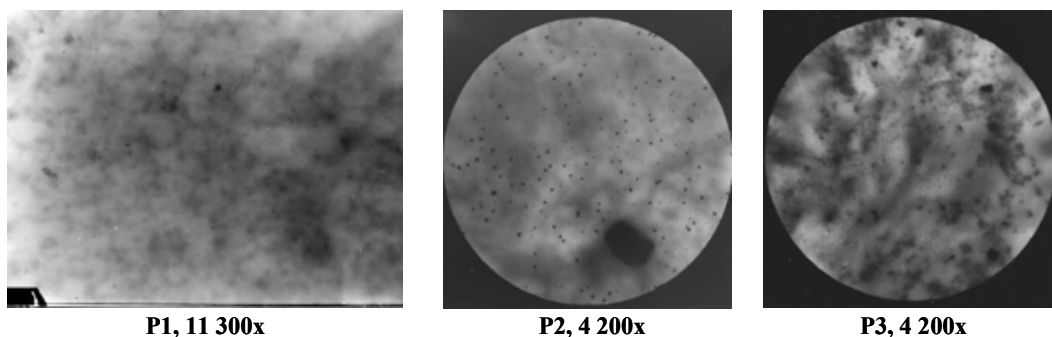**P1, 11 300x**   **P2, 4 200x**   **P3, 4 200x**

Fig. 3 – Morphology of azo-siloxane polyesters observed by TEM.
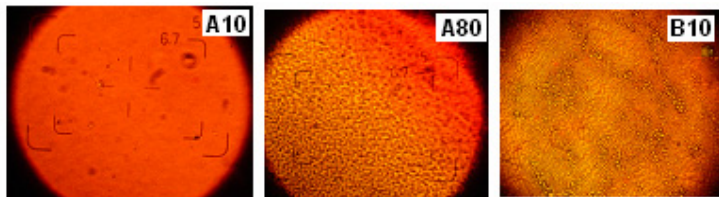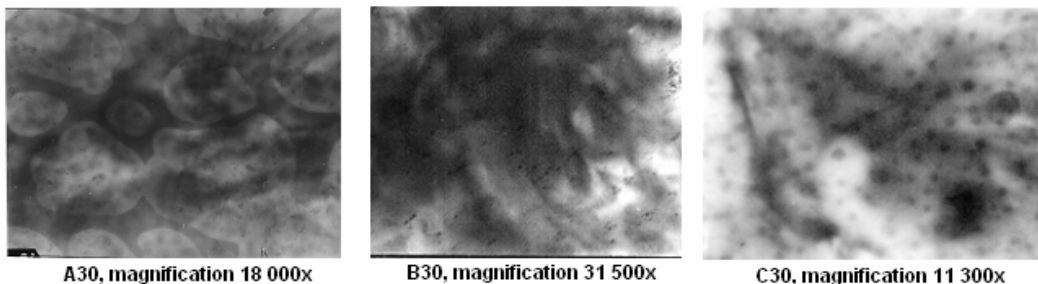
Fig. 4 – Optical microscopy of some blends having PSFCM as the matrix.

A30, magnification 18 000x   B30, magnification 31 500x   C30, magnification 11 300x

Fig. 5 – TEM microphotographs of the blends containing PSFCM and 30% azo-siloxane polymer dyes.

Blends based on PSF

Both optical and electron microscopy revealed birefringent inclusions (crystals) in the amorphous coloured film of D30, a tendency of phase segregation in the case of E30 and a better phase mixing in the case of blend F30, although very fine un-mixed particles of dye were also present (TEM observation). The representative microphotographs are shown in **Figure 6**.

Blends based on HPC

Uniformly coloured blends were obtained, with isolated and very small birefringent inclusions observed by optical microscope.

The same general observations were made by TEM; there was no clear evidence of phase separation. The films were somewhat structured, with isolated crystals (probably un-mixed dyes). Selected images are shown in **Figure 7**.
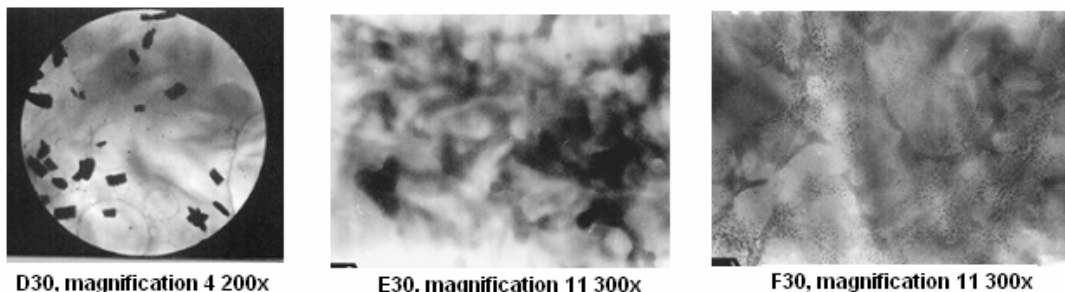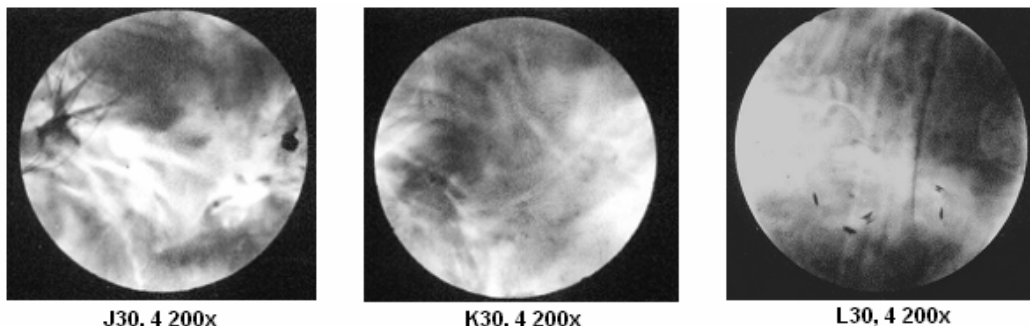

D30, magnification 4 200x   E30, magnification 11 300x   F30, magnification 11 300x

Fig. 6 – TEM microphotographs of the blends containing PSF and 30% azo-siloxane polymer dyes.

J30, 4 200x   K30, 4 200x   L30, 4 200x

Fig. 7 – TEM microphotographs of the blends containing HPC and 30% azo-siloxane polymer dyes.

Blends based on PDMS

In the case of these blends, we would expect a good compatibility, due to the chemical similarity of the main chain. Nevertheless, both optical microscopy and TEM showed phase separation, thus confirming the DSC results.

As can be observed in **Figure 8a**, by optical microscopy coloured domains dispersed into a mostly colourless matrix were observed. By TEM, the biphasic morphology of the blend G30 differed significantly from all the other samples (**Figure 9**): spherical dark domains, agglomerated into a lighter matrix were observed. In this case no birefringence

was noticed, proving that the domaines were not crystalline inclusions of un-dispersed dye, but most probably coloured polysiloxane, dispersed into the colourless matrix.

The observations for samples H30 and I30 showed a better phase mixing (**Figure 9**), with dye inclusions into a coloured matrix (birefringent domaines in polarized optical microscopy, **Figures 8b, c**). It is worth mentioning that the degree of mixing seems to increase with the length of siloxane segment in the polymer dye, probably due to the compatibilization effect of chain fragments with similar structure.
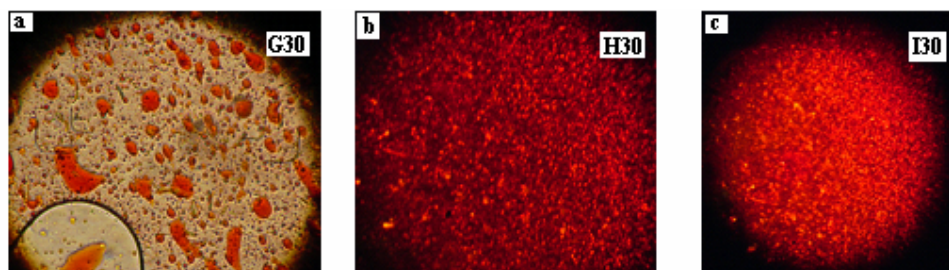

Fig. 8 – Optical microphotographs (normal light, a; polarized light, b and c) of blends containing PDMS as the matrix.

G30, magnification 11 300x

H30, magnification 4 200x

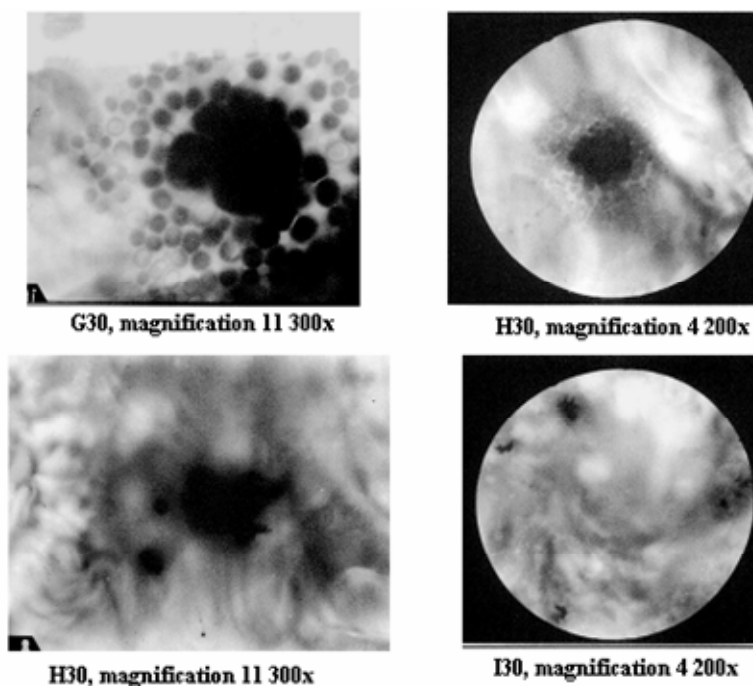H30, magnification 11 300x

I30, magnification 4 200x

Fig. 9 – TEM microphotographs of the blends containing PDMS and 30% azo-siloxane polymer dyes.

EXPERIMENTAL

Materials

Three siloxane-azoaromatic polyesters, with chemical structures shown in **Scheme 1**, have been synthesized by a previously described procedure.[1]

Three polymers with large commercial availability: UDEL polysulfone (PSF), polydimethylsiloxane (PDMS), hydroxypropylcellulose (HPC), as well as a modified polysulfone, having chloromethyl groups (8, 2% Cl) [13] were used as the polymeric matrices. Their structural units are presented in **Scheme 2**.

Polymer blends were obtained by mixing 1% w/v solutions in chloroform of dye polymers and matrix polymers, in well determined proportions, according to the compositional data presented in **Table 1** (the number stands for dye content, wt%). For dry state studies (UV, optical microscopy, DSC), the solvent was removed in vacuum, at room temperature.

Analyses

UV-VIS spectra were registered on a Specord M42 spectrophotometer, for the initial solutions mixtures, as well as for films obtained thereof on glass slides.

Polarized light optical microscopy (POM) observations were made with an Olympus BH-2 microscope (Japan), fitted with a THMS 600/HSF9I hot stage.

For TEM observations, a TESLA BS 513A transmission electron microscope was used, at an acceleration tension of 80 kV. The samples were prepared on copper grids of 200 mesh size, coated with a collodium film and carbon; microdrops of blends solutions were placed on the grids, then the solvent was removed in saturated atmosphere and the samples were vacuum dried.

The DSC analyses were performed on a Perkin Elmer scanning calorimeter; two heating scans were applied, with a heating rate of $20\,^\circ C$/min in the temperature range between -150 and 200 $^\circ C$.

CONCLUSIONS

Three siloxane-azoaromatic polyesters have been investigated as complex dye systems for different polymers: aromatic polysulfones, polydimethylsiloxane, hydroxypropylcellulose. The blends obtained have been studied for photochemical behavior and thermal properties, and their morphology has been investigated by TEM. The mixing behaviour and the miscibility of the polymer pairs were followed, in correlation with the possible intermolecular interactions.

The UV-VIS spectra displayed single absorption maxima for all the samples, with very little variation in solution, which means that no intermolecular interactions in chloroform were detected. In film, the absorption maxima were shifted from the values corresponding to the neat dye polymers, indicating the presence of intermolecular interactions.

By DSC in the second heating scan, single Tg values were detected for all the blends obtained with UDEL polysulfone and chloromethylated polysulfone respectively, showing that, on the macroscopic level compatible mixtures were obtained. We can also speculate an improvement of the polysulfones processability by adding small amounts of azo-siloxane polymers. On the contrary, the Tg of the PDMS matrix remained unchanged in all the blends, showing a total incompatibility between the polymer pairs, even though the dye polymers contain the same siloxane units.

By TEM, the specific morphology of blends containing the same amount of dye polymer was observed. Most of the samples exhibited biphasic morphology or some degree of phase mixing, depending on the length of the siloxane segment in the dye polymer and on the chemical structure of the matrix. The best compatibility was observed for HPC-containing blends, although there is no chemical similarity between the components, while the most obvious phase separation was observed for the PDMS blends. This result proves that the intermolecular interactions play a key role in blends compatibilization (HPC is capable of developing H-bonds with the dye molecules).

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