

Study of Miscibility of Poly(vinyl acetate) and Poly(vinyl alcohol) Blends by Fluorescence Spectroscopy

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SYNOPSIS

Secondary relaxations of poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc), and their blends in different proportions (9 : 1, 1 : 1, and 1 : 9) were studied by photoluminescence of anthracene, fluorescein, and both probes dissolved in the polymer blends. The temperature of the glass transition in the homopolymers was determined by the radiationless deactivation of anthracene as $T_g(\text{PVAc}) \cong 304$ K and the photobleaching of fluorescein as $T_g(\text{PVA}) \cong 350$ K. The relaxation processes of the different phases of the polymer blends occur at temperatures close to the homopolymers, which may be explained by the localization of each molecular probe within the matrix. These deactivation curves, however, are not similar to those of the individual homopolymers, suggesting a partial miscibility between these polymers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Studies of polymer miscibility are relevant from both the fundamental and technological points of view because the applications of these materials depend on their morphology. An important property of the polymer blends, which defines the field of their applications, is the mechanical one, controlled by the relaxation processes of the material at different temperatures. Secondary relaxation of polymers forms a set of processes that include either the rotation of small segments of the chains or the glass transition process. These processes can be studied by various methods.¹⁻⁵

One of the methods that can be utilized to study both properties of the polymer blends (miscibility and relaxation processes) is fluorescence spectroscopy. Two spectroscopic methods have been developed to study polymer miscibility: The first one determines the ratio of the fluorescence intensity from the monomer and excimer groups bonded to the polymer chains, and the second utilizes the energy-transfer process between a donor (a molecule in the

electronically excited singlet state) and an acceptor (a molecule in the electronic ground state) bonded to the components of the polymer blends.⁶⁻⁹ On the other hand, since the luminescence is a characteristic of a molecular system strongly dependent on the medium, this kind of spectroscopy has also been used to determine relaxation processes in polymers.^{3-6,10-16}

We have already determined relaxation processes in polymers and polymer blends using luminescence spectroscopy of molecular probes dissolved in the polymer systems. These studies allowed us to determine secondary relaxation and glass transition temperatures of polymers and polymer blends, as well to estimate the dimension of the macromolecular segments involved in the relaxation processes.¹²⁻¹⁵ In a recent work, we combined fluorescence spectroscopy to determine relaxation temperatures of polymer blends with fluorescence optical microscopy in order to define the domains where the fluorescent probes are mainly localized.^{14,16}

Poly(vinyl alcohol) (PVA) is a commercial polymer usually produced by acidic or basic hydrolysis of poly(vinyl acetate). Its properties depend on its molecular weight and degree of hydrolysis. It is a semicrystalline polymer with its crystalline index dependent on the synthetic process and physical aging. The glass transition temperature of this polymer

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is $\cong 350$ K and the polymer chains are maintained together by hydrogen bonds, even in the amorphous phase. On the other hand, poly(vinyl acetate) (PVAc) is an amorphous polymer, with $T_g \cong 305$ K, depending on the molecular weight and physical aging. Blends of these polymers should be immiscible since the solubility parameters are $\delta(\text{PVA}) = 12.6 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ and $\delta(\text{PVAc}) = 9.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$.¹⁷ However, if one chooses partially hydrolyzed PVA samples, instead of a 100% hydrolyzed sample, one should expect a partial miscibility of these polymers.

In this work, we present studies for determining the relaxation temperatures in PVA/PVAc blends of different compositions (9 : 1, 1 : 1, and 1 : 9 w/w) using fluorescence spectroscopy of anthracene and fluorescein dissolved in the samples. These fluorescent molecules were chosen due to the possibility of different specific interactions with the homopolymers and, consequently, allow us to study the total relaxation processes of the different domains of the matrices that undergo a solid-phase separation.

EXPERIMENTAL

Anthracene (AN) (Carlo Erba) was used as received. Fluorescein (FL) (Merck) was purified by a process known as lactonization.¹⁸

Poly(vinyl alcohol) (PVA) (Aldrich Chemical Co., average molecular weight $\bar{M}_w = 124,000$ – $186,000$, 87–89% hydrolyzed) was used as received. Fluorescein is incorporated into the PVA film by casting an aqueous solution containing both the homopolymer and the dye on a glass plate. The final concentration of the dye dissolved in PVA is estimated to be $10^{-5} M$ since the fluorescence spectrum, centered at $\lambda \cong 520$ nm, corresponds to the monomeric form of the dye. Because of the low solubility of AN in PVA, this molecule is dissolved only in the PVAc homopolymer and in the polymer blends.

Poly(vinyl acetate) (PVAc) (Aldrich Chemical Co.; high molecular weight, $\bar{M}_w = 237,000$) was used as received. Anthracene is incorporated into the film by casting an acetone solution of the homopolymer containing the dye over a glass plate. The final concentration of the AN is estimated to be $10^{-5} M$ by fluorescence spectroscopy.

Blends of PVA and PVAc in different proportions by mass (w/w) (9 : 1, 1 : 1, and 1 : 9), containing fluorescein or both molecular probes (AN and FL), were prepared in the form of films, by casting appropriate solutions containing both the homopolymers and the probes over a polystyrene plate covered by a polyethylene film. All the films prepared in this

work were dried at room temperature and normal pressure and maintained in a desiccator under vacuum until the measurements.

Electronic absorption spectra were recorded at room temperature with an Intralab DMS-100 spectrometer using a home-made support for the polymer films (thickness in the range from 30 to 100 μm). Fluorescence spectra were recorded using a Jarrell-Ash 0.5 m spectrometer with an 1800 g mm^{-1} holographic grating and an EMI 62568 photomultiplier tube; the excitation source was a high-pressure short-arc, 200W Oriel mercury lamp. The 310–330 nm lines were isolated using a previously described filter set.¹⁵ The photomultiplier signal was collected by a lock-in amplifier (Stanford Research Systems Model SR-530) and the data were stored in a PC-type computer.

The fluorescence spectra at many different temperatures were obtained with the samples placed in an FMX-1E optical vacuum shroud assembly of a Displex model DE-204S cryosystem, pumped by a closed-cycle system low-pressure helium gas compressor (module APD Cryogenics Model HC-4 MK1). The temperature range of the samples was changed from 10 to 400 K by a digital temperature controller (Scientific Instruments Model 9650). The optical sample holder in the cryosystem was positioned in order to get a 90° angle between the incident light and the emission beams, which were focused by a cylindrical lens on the entrance slit of the spectrometer. X-ray diffraction scattering was recorded from a Shimadzu Model XD-3A diffractometer, operating with $\text{CuK}\alpha$ radiation over the range $5^\circ < 2\theta < 45^\circ$, current 20 mA and voltage 30 kV.

RESULTS AND DISCUSSION

Characterization of Samples

The X-ray scattering patterns of the PVA samples are composed of one crystalline peak centered at $\cong 18.5^\circ$, assigned to the reflection of index 10 $\bar{1}$, and one wide scattering band. A similar profile was determined for PVA by many authors.¹⁹ Moreover, it is known that both the amorphous and the interphase amorphous-crystalline domains of PVA exhibit a very complex morphology with supermolecular structures produced by hydrogen-interaction.^{1,19} The glass transition temperature of this polymer has been determined by DSC and by near-infrared spectroscopy as $T_g \cong 360$ K,²⁰ following the dependence of the intensity of the bands around $\bar{\nu} = 5,200 \text{ cm}^{-1}$

(combination band of $\nu_{\text{OH}} + \delta_{\text{OH}}$) on the temperature. We did not observe by X-ray diffraction any distortion of the crystalline structure of PVA samples containing AN or FL, indicating that these molecules were not located within the crystalline phase of the polymer.

Otherwise, PVAc is an amorphous polymer, with a $T_g \cong 305$ K, as determined by DSC and by thermal isomerization of different azo-compounds.²¹ However, amorphous domains of a polymer are not homogeneous media. There are many spectroscopic data showing that amorphous domains of polymers exhibit a free-volume distribution.^{6,8,22-24}

From these results, we could consider that each polymer blend studied in this work is composed of at least four complex phases: The crystalline phase has been assumed to be constituted purely of crystallizable PVA macromolecules; there is an interphase between the homopolymers of PVA and PVAc, whose composition is not easily determined, but probably presents a gradient of concentration between the two amorphous domains of the homopolymers; and there are two amorphous phases that should be formed by both the pure noncrystallizable homopolymer PVA and PVAc macromolecules, localized in the interfibrillar space.

Aromatic condensed hydrocarbon molecules (like AN) dissolved in semicrystalline polymers may be preferentially located both in the amorphous phase and on the surface of the crystallites.^{12-14,25-27} Similar results have been obtained for azo-compounds in amorphous domains of some polymers, indicating that there is a heterogeneous distribution of the dyes within the matrix, which will only occupy regions of appropriate free volume. From this information, we are assuming that FL may also be localized in similar domains inside the polymer matrices. Using the results for the morphology of the blends prepared in this work and the most probable distribution of the molecules in semicrystalline polymers, we are suggesting that while FL and AN may be localized in the amorphous phases of PVA and PVAc, respectively, both molecules may also be localized in the interphase amorphous regions.

We have also shown,¹⁶ using fluorescence optical microscopy and fluorescence spectroscopy, that the PVA/PVAc blends present a solid-phase separation and that FL has been a useful molecule to identify the PVA domains, whereas AN has been useful to identify the PVAc domains. The diffusion of these molecules toward different homopolymers has been controlled by specific dye-polymer interactions, such as hydrogen bonding between FL-PVA and dispersive forces between AN-PVAc systems. In this

sense, the relaxation process in PVA, PVAc, and PVA/PVAc blends may be monitored by different molecular probes that would be localized in different microenvironments dependent on the specific dye-polymer interactions. Moreover, since FL may be present in different molecular forms, due to a very complex dissociation equilibrium, depending on the medium, as demonstrated earlier, the specific interactions involving FL have also been defining the ionization form of this dye present in the system.^{18,28} These different dye-polymer interactions may also significantly change the photophysical processes of the dye in the electronically excited singlet state.

PVA/PVAc polymer blends exhibit a solid-phase separation producing, on the optical microscopic scale, two kinds of domains whose proportions and dimensions are dependent on the composition. In the cases of the 1 : 9 and 1 : 1 PVA/PVAc blends, we observed two different regions: The first one is rougher and thicker and is formed in the first stage of the phase separation process during the solvent evaporation [Fig. 1(c) and (e)]. The second one is thinner and forms a continuous film [Fig. 1(d) and (f)]. These domains have been named 1 and 2, respectively, and each one may be analyzed separately. In the case of the 9 : 1 PVA/PVAc blend, these two domains have also been obtained. However, since region 1 [dark region in Fig. 1(a)] is dispersed in region 2 [Fig. 1(b)], it cannot be separated. However, during the excitation process of the samples by the mercury lamp, we selected regions richer in one type of this domain, since the diameter of the excitation beam is, in general, smaller than is the size of the domains.

Relaxation Processes of PVA/FL and PVAc/AN Systems

To study the relaxation processes in the PVA and PVAc homopolymers, FL and AN molecules have been used as a molecular probes. In the case of FL dissolved in PVA, of AN dissolved in PVAc, and both molecules dissolved in the blends, the relative integrated intensity of the fluorescence bands (I_T/I_0) is plotted vs. temperature. I_0 and I_T were considered the integrated intensities of the fluorescence bands at 15 K and the temperature T, respectively.

The fluorescence emission of FL dissolved in PVA is shown in Figure 2(a). These spectra, centered at $\lambda \cong 520$ nm, are characteristic of an isolated molecule. The relative fluorescence intensity (I_T/I_0) of FL vs. temperature is shown in Figure 2(b) and it is composed of two segments with different slopes, with an inflection at $T \cong 350$ K. This temperature

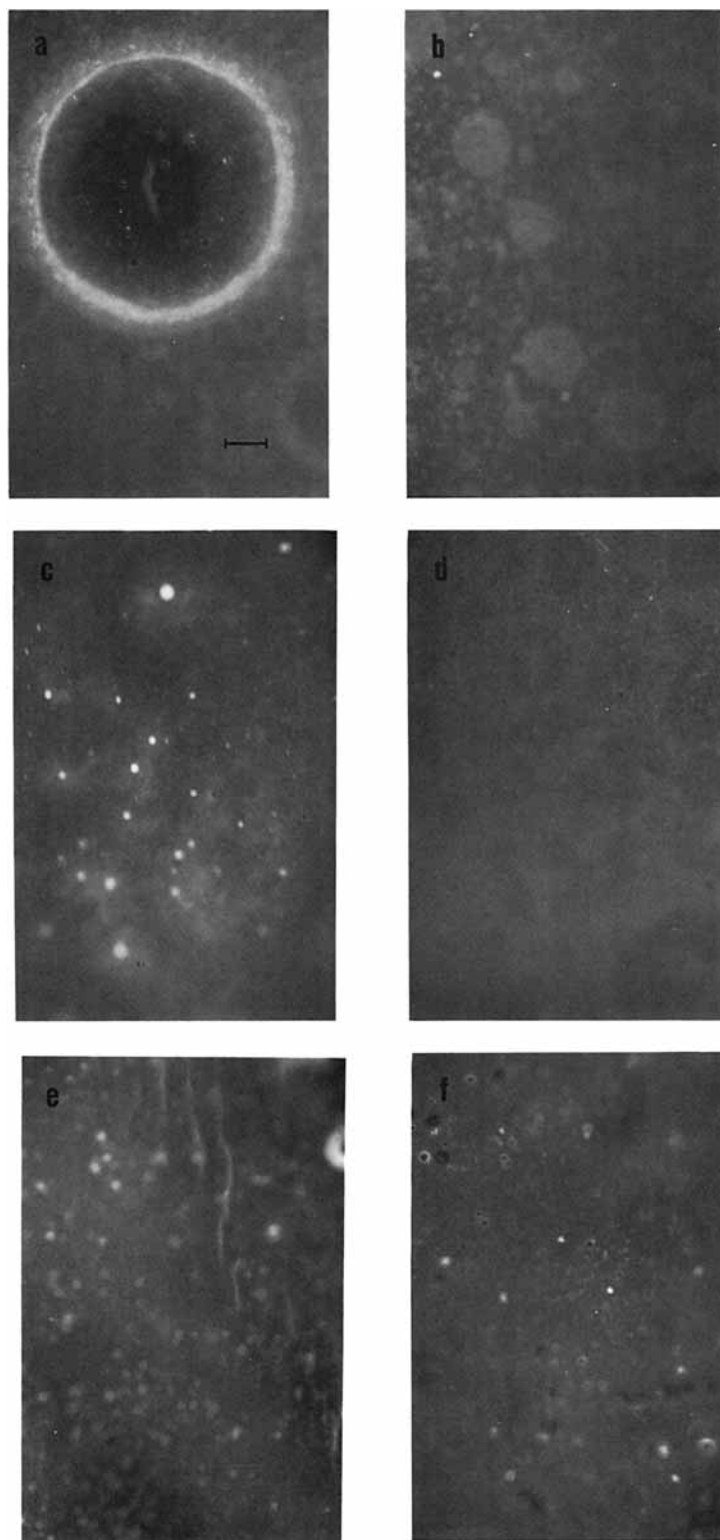


Figure 1 Optical photomicrographs of two regions of PVA/PVAc blends in different proportions: (a, b) 9 : 1; (c, d) 1 : 1; (e, f) 1 : 9. (scale 100 μm). (a, c, e) represent region 1; (b, d, f) represent region 2, described in the text.

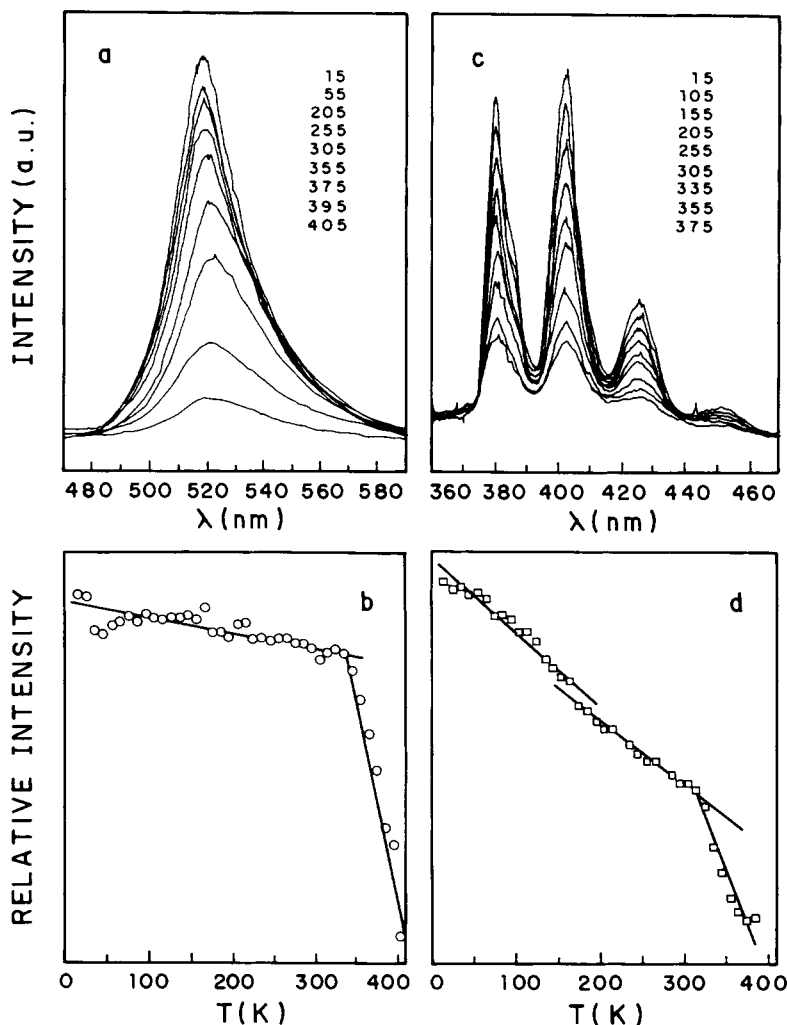


Figure 2 Fluorescence spectra and relative integrated intensity vs. temperature for (a, b) FL in PVA and (c, d) AN in PVAc. I_0 is the intensity at 15 K.

is coincident with the glass transition temperature of PVA obtained with other techniques such as DSC²⁹; infrared spectroscopy³⁰; and dynamic mechanical analysis.³¹ The slope of the first segment (from 15 to 350 K) is lower than the slope of the second segment (for $T > 350$ K), suggesting that the rate constants for the radiationless deactivation processes of FL in this temperature range are smaller than those for $T > 350$ K. Although the fluorescence intensity of FL is almost constant in the temperature range from 15 to 350 K and the deactivation processes are controlled by photophysical pathways, there is a pronounced decrease of the fluorescence at temperatures higher than 350 K that is explained by a photobleaching process of the dye, an irreversible process.²⁰ From this result, we can conclude that this molecule is very efficient for following this re-

laxation process in PVA, which is occurring in the amorphous phase of this homopolymer.

The fluorescence emissions of AN dissolved in PVAc at many different temperatures are shown in Figure 2(c). These spectra are composed of a vibronic progression and may be assigned to the AN in the isolated form. The relative intensities of the vibronic bands allow us to obtain some information concerning the photophysical mechanisms leading to the radiationless deactivation of AN molecules in the electronic excited singlet state induced by the relaxation processes of the polymer.¹²⁻¹⁴ The intensity of the vibronic bands of the AN molecules centered at $\lambda = 380$ nm is higher than that centered at $\lambda = 402$ nm, indicating that these spectra are characteristic of an isolated molecule and that the self-quenching process is negligible.³²

The relative integrated intensity of the AN fluorescence emission (I_T/I_0) vs. temperature is shown in Figure 2(d). This curve exhibits two inflections at the following temperatures: 180 and 304 K. There are many reports of relaxation processes in PVAc, using different techniques: Dielectric relaxation and thermally stimulated current depolarization studies indicated that the glass transition occurs at 304 K, with an apparent activation energy of 138 kcal/mol. This activation energy is composed of two barriers: one for conformational changes of the macromolecules and other for frictional resistance to the macromolecular motions.³³⁻³⁷ The other relaxation, revealed by dynamic mechanical measurements, is termed the β process and is believed to be characteristic of amorphous packing and may involve small amplitude rotatory motions of one or two monomeric units. The apparent activation energy lies around 20 kcal/mol.³⁸ This relaxation process is believed to occur at $T_\beta \cong 180$ K ($\cong -100^\circ\text{C}$) and it was also observed by photoluminescence using a phosphorescent molecular probe¹⁵ and by dynamic mechanical spectroscopy.³⁸

As pointed out by Kauzmann,² while the volume [$V = (\partial G/\partial P)_T$] is unchanged at the temperature of the relaxation process, the coefficient of thermal expansion $\alpha_V = (1/\bar{V}) (\partial^2 G/\partial P \partial T)$ does undergo a rather sudden change. The magnitude of this expansion is dependent on the size of the macromolecular segment involved with the polymer relaxation, and as a consequence, as the polymer chain displays a relaxation process, there is an expansion of the material and, consequently, the distance between two molecules dissolved in the medium increases. The increase of the distance reduces the probability of the radiationless migration energy and the intensity of the fluorescence emission increases. However, if there is an increase in the available free volume, the probability of the deactivation process by internal conversion mechanisms is higher and the intensity of fluorescence should be reduced. Therefore, the final fluorescence intensity is a result of these two types of opposite effects.

Furthermore, during a relaxation process, there is a fluctuation of the thermal expansion coefficients that induces a fluctuation of the density, which modifies the probability of light scattering inside the material.³⁹ Modification of the light-scattering probability inside the material changes its refractive index and, consequently, changes the probability of energy migration by the trivial radiative process. If the relaxation process reduces the light-scattering probability, the pathway that the fluorescence photon must travel inside the material is lower because

one reduces the probability of multiple reflections. In this case, the apparent quantum yield is closest to the real quantum yield, at one specific temperature. The magnitude of this effect is also dependent on the size of the macromolecular segments involved with the polymer relaxation process. Therefore, it should be possible to observe an increase of the fluorescence intensity with the increase of the temperature if the light-scattering probability is reduced.

The magnitude of the radiationless deactivation of AN in the electronically excited singlet state, represented by the slopes of the curves in Figure 2(d), depends on the temperature range. For example, the deactivation of this molecule produced by the glass transition is higher than that produced by the secondary β -relaxation process. This result is in agreement with the amplitude of the macromolecular motion involved in the relaxation process of the polymer as shown earlier.¹²⁻¹⁴ From these results, we can conclude that AN is a convenient molecule to follow both relaxation processes in PVAc as $T_\beta(\text{PVAc}) \cong 180$ K and $T_g(\text{PVAc}) \cong 304$ K.

Relaxation Processes of PVA/PVAc/FL Blends

Figure 3 shows fluorescence spectra at different temperatures of FL dissolved in two different parts of 9 : 1, 1 : 1, and 1 : 9 PVA/PVAc blends, as those shown in Figure 1. All these spectra may be assigned to FL in the isolated form and localized in a protic media like PVA.¹⁹ Nevertheless, the intensity of the fluorescence decreases with the increase of the PVAc concentration (from the top to the bottom in the figure) in the blends and is always higher in the PVA richer phase [Fig. 3(b), (d), and (f)]. The relative integrated intensities vs. temperature for all samples are shown in Figure 4. From this figure, we can observe that each curve may be divided into three segments with different slopes:

1. *Temperature range from 15 to 300 K:* In this temperature range, we are observing a continuous decrease of the fluorescence intensity as the temperature increases. Both homopolymers are, in this temperature range, in the glassy state. In this situation, the medium imposes restraints to the FL molecules, maintains the phenyl group sterically hindered perpendicular to the xanthene group, and reduces the amplitude of other vibrational motions. These restraints reduce the efficiency of the radiationless deactivation of this dye by an internal conversion pathways. Therefore, in this case, the mechanisms of

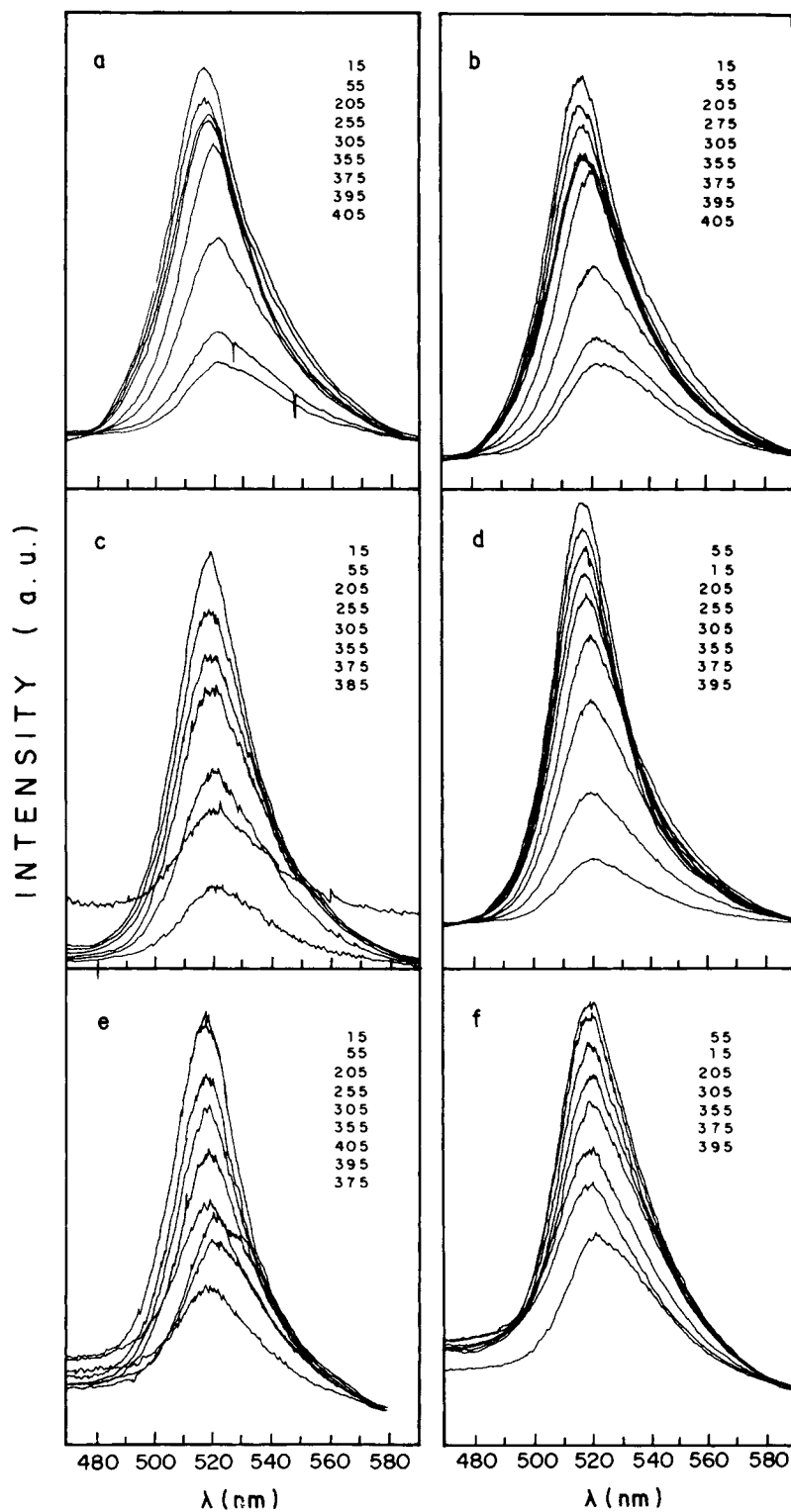


Figure 3 Fluorescence spectra of FL dissolved in samples of the two domains of PVA/PVAc blends at many temperatures, for varying proportions (w/w): (a, b) 9/1; (c, d) 1/1; (e, f) 1/9. (a, c, e) represent region 1; (b, d) represent region 2; (f) represents a mixture of the two domains.

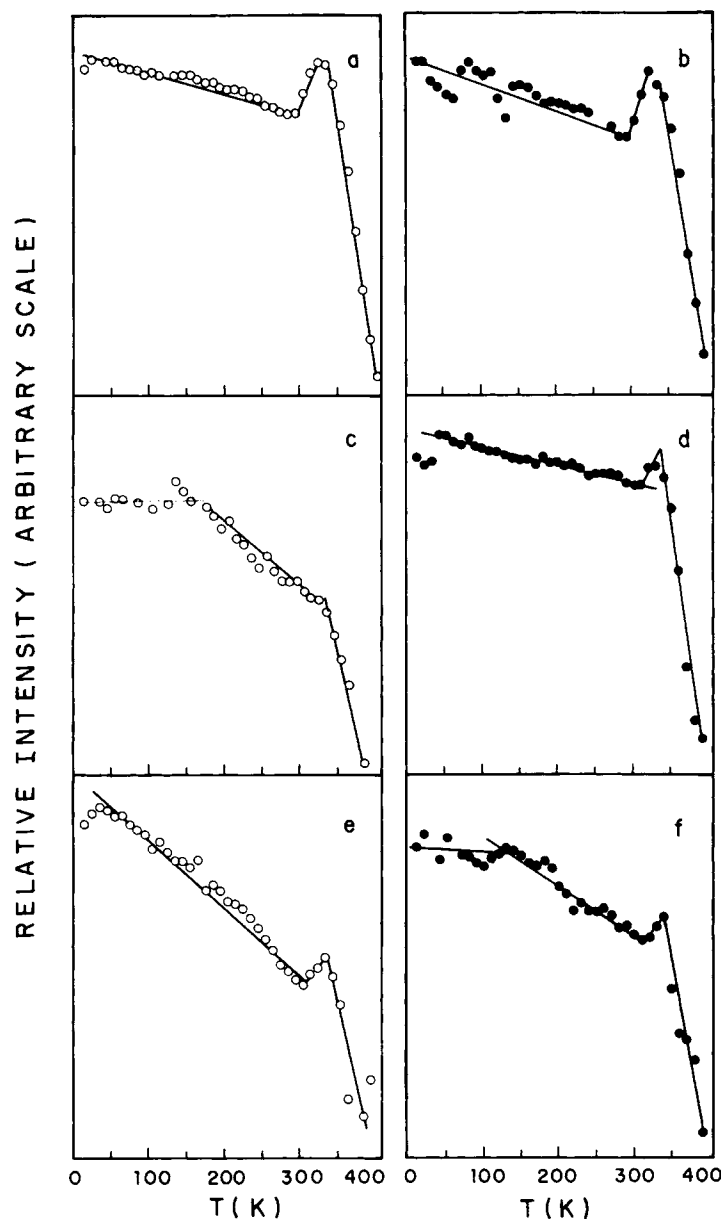


Figure 4 Relative integrated intensity of fluorescence of FL in the domains described by the spectra of Figure 2. Open circles represent region 1 of similar morphology, and solid circles represent region 2. The sequence of figures is the same as in Figure 3.

FL radiationless deactivation may involve energy transfer between neighborhood molecules at a distance closer than r_0 , which is not important since the concentration of the system is very low. For the blends containing higher proportions, the concentration of the system is very low. For the blends containing higher proportions of PVAc, one observes a higher slope of the curves that can be explained by an increase of the efficiency of ra-

diationless deactivation by the internal conversion process. In this case, we should consider that this molecule is localized in a free-volume domain that allows both the partial rotation of the phenyl group bonded to the xanthene group and other vibrational motions of higher amplitude creating new channels for the radiationless process of FL. These processes may only be occurring if the medium is composed preferentially by PVAc,

since the polymer chains containing acetate groups are more flexible than those containing the hydroxyl groups of PVA, whose macromolecules are bonded together by hydrogen bonds.

2. *Temperature range from 300 to 350 K:* In this range, the emission reaches a maximum value for all samples excluding region 1 of the 1 : 1 PVA/PVAc blend [Fig. 4(c)] and they are significantly different from the PVA/FL system [Fig. 2(b)]. The glass transition of PVAc at $T \cong 305$ K produces a significant expansion of the system, as indicated earlier. This expansion induces a diffusion of the FL molecules and increases the distance between two neighborhood molecules, reducing the nonradiative energy migration process and, consequently, the fluorescence intensity increases. Moreover, the relaxation process also produces change in the trivial radiative process, which increases the apparent quantum yield fluorescence of the system. Nevertheless, if the temperature increases until it reaches the glass transition temperature of PVA, a new process take place, i.e., the photobleaching of the dye, an irreversible process, which has also been observed for FL dissolved in PVA [Fig. 2(b)]. Therefore, the maximum of the fluorescence intensity at 350 K may be explained by the relationship between the decrease of the efficiency of the photophysical deactivation process of the FL, produced by the glass transition of PVAc, and the increase of the efficiency of the photochemical process, produced by the glass transition of PVA. In the absence of PVAc, as in the case of the system PVA/FL, we cannot observe the increase of the fluorescence intensity.

These results suggest that

1. There are significant differences in the radiationless deactivation processes for FL dissolved in the PVA/PVAc polymer blends, demonstrated by the slopes of the deactivation curves, which depend on both region and the composition of the blend.
2. Different regions of the 1 : 1 PVA/PVAc blend also contain a significant mixture of both polymers, as revealed by the modification of the deactivation processes of FL, which in the cases present photobleaching at $T > 350$ K. In the case of region 1, there is no increase in the intensity of the fluorescence band at $T > 300$ K; however, the slope of the curve in the temperature range from 15 to 304 K suggests a significant deactivation process for FL. These observations indicated that FL molecules are localized in the PVA domains, but those domains are much more flexible than is the homopolymer. In the case of region 2, although there is an increase of the intensity at $T > 304$ K, indicating a presence of PVAc, the deactivation rate constant is low from 15 to 304 K and very similar to the PVA homopolymer, a result only possible in a PVA-rich medium. In both cases, the photobleaching process is important at $T > 350$ K.
3. For all compositions of the blends, different deactivation processes for FL may be used to probe both the glass transition processes of PVA ($T_g \cong 350$ K) and PVAc ($T_g \cong 304$ K). However, from these data, one cannot obtain information about the qualitative homopolymer compositions and distribution in each phase of the blends. To get this qualitative information for each phase, we carried out relaxation studies of these blends containing a mixture of the two molecular probes: AN and FL.

Relaxation Processes in PVA/PVAc/FL/AN Blends

In the case of PVA/PVAc blends containing both FL and AN molecules dissolved in the matrices, we observed that, in general, the region richer in PVAc exhibits a higher relative AN fluorescence intensity than that richer in PVA. Figure 5 shows the fluorescence spectra at some temperatures of AN and FL dissolved in PVA/PVAc blends with the same proportions in mass as indicated earlier. From these spectra, much qualitative information can be obtained:

1. The relative intensity of the fluorescence of FL, compared with AN, is higher in region 2 (richer in PVA) than in region 1 (richer in PVAc), if samples for each composition are compared to themselves [e.g., Fig. 5(a) and (b)]. Therefore, one can conclude that region 2 [Fig. 5(b) and (d)] is richer in PVA than is region 1 [Fig. 5(a) and (c)]. Nevertheless, the FL emission in the 1/9 PVA/PVAc blend is not easily observed, although the initial concentration of this dye is similar in all samples. This result can be explained by two

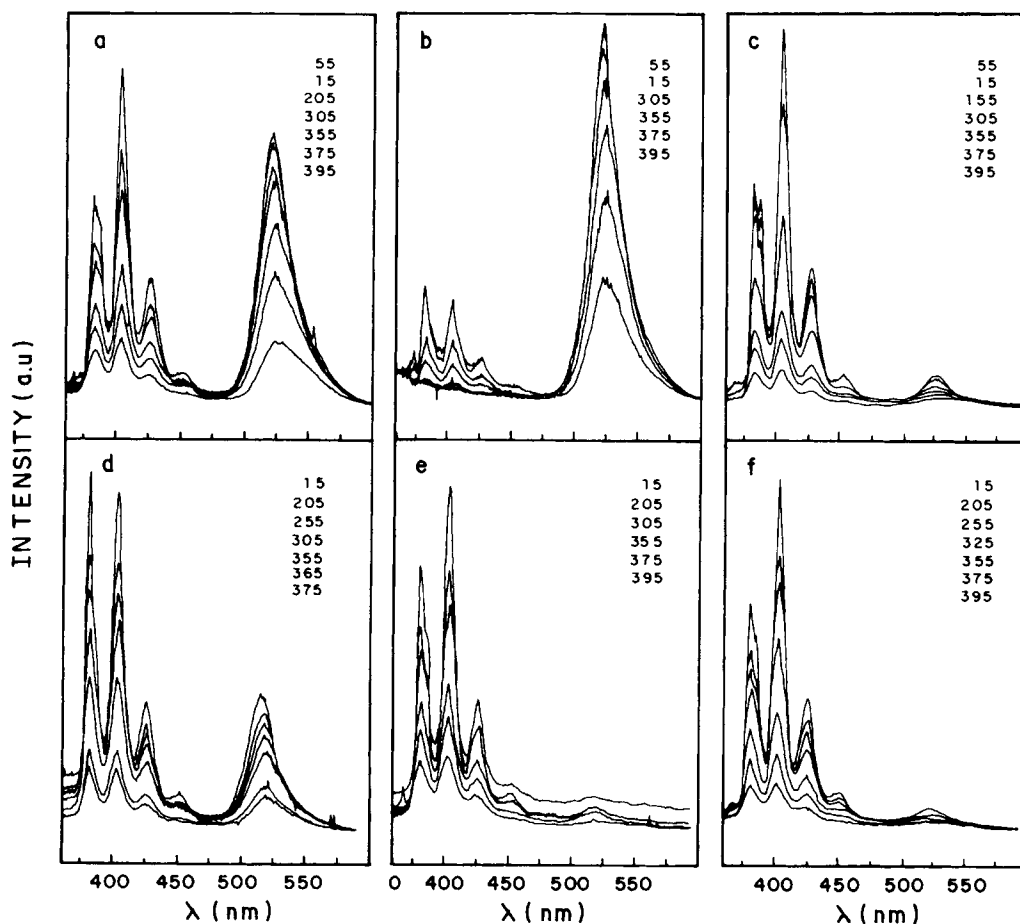


Figure 5 Fluorescence spectra of FL and AN dissolved in different domains of PVA/PVAc blends at many temperatures, for varying proportions (w/w): (a, b) 9/1; (c, d) 1/1; (e, f) 1/9.

reasons: The lower solubility of FL in PVAc, resulting in crystallization of the dye, produces a nonfluorescent solid, and the shift of the chemical equilibrium of the dissociation of the dye produced by a nonprotic medium, like PVAc, results in a specimen exhibiting a low fluorescence quantum yield.

- As pointed out earlier, the fluorescence band of AN is composed of a vibronic progression. The relative intensity of the components centered at $\lambda \cong 380$ nm (I_I) and at $\lambda \cong 402$ nm (I_{II}) is informative about the mechanisms of the migration energy of this molecule in the electronically excited singlet state and, consequently, about the concentration of this molecule in each region of the different blends. In general, if one obtains $I_I \gg I_{II}$, there is an efficient energy-transfer process between two AN molecules. This process de-

pends on the distance between the AN molecule and, consequently, on the concentration. From Figure 5(a), (c), and (e), we can observe that if region 1 of the blends exhibits lower relative I_I/I_{II} values than does region 2 [Fig. 5(b), (d), and (f)], then it contains a higher concentration of AN than does region 2, confirming that the solubility of AN is higher in the homopolymer PVAc than in PVA, as shown earlier.

- It is noteworthy that the band at $\lambda \cong 380$ nm always exhibits a shoulder at the highest wavelength for the samples richer in PVAc. This result may be explained by the presence of two types of domains in a solid polymer containing AN.^{25,26} In this case, there are more rigid sites, which produce a quasi-linear fluorescence spectrum of AN, and more flexible sites, which produce a diffuse and broad

fluorescence emission. These domains are contained in region 1, producing the spectra presented in Figure 5(a), (c), (e), and (f).

The temperature of the relaxation processes of these blends were determined by plotting, in a separate way, the relative integrated intensities of the fluorescence of AN (squares) and FL (circles) vs. temperature, similar to what has been done for the

homopolymers, or even for the blends containing FL. These curves are shown in Figure 6, for the relative integrated intensity, and follow the same scheme for the different domains as shown in Figure 4. In Figure 6, the open points represent region 1, and the dark points, region 2.

The relative integrated intensity vs. temperature curves for AN in each region of the blends (Fig. 6, squares) can be compared with that obtained for

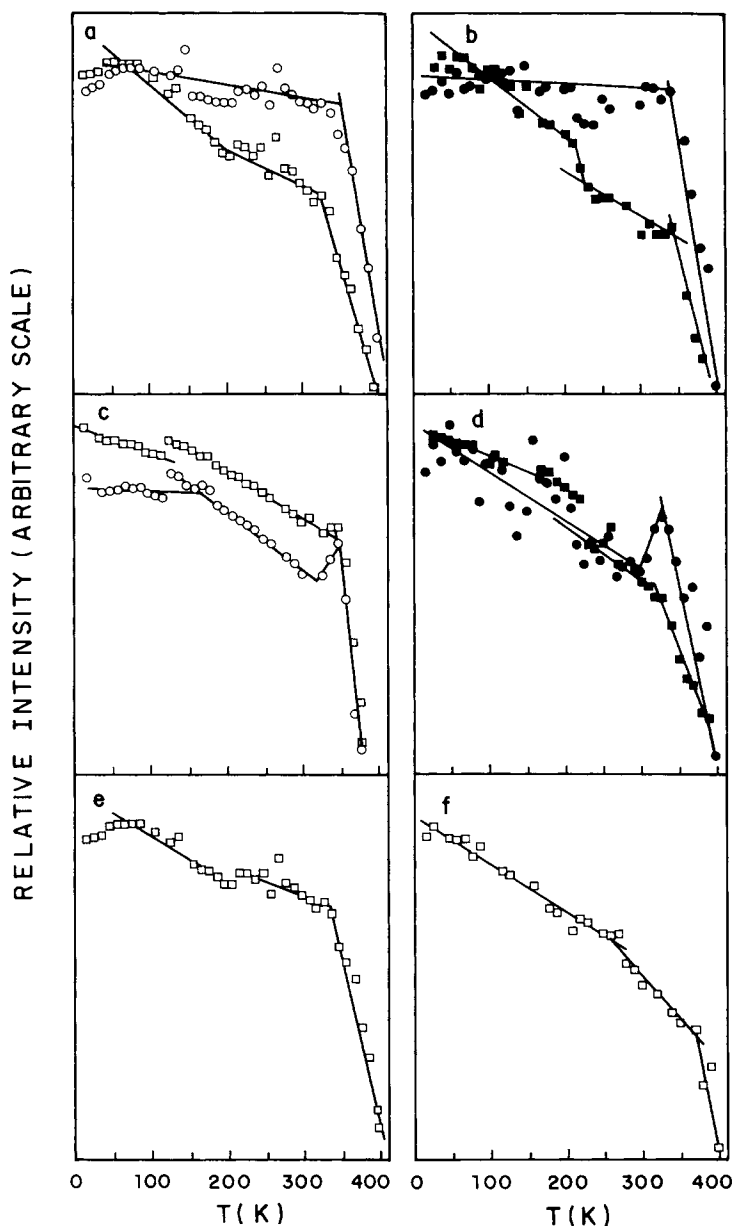


Figure 6 Integrated relative intensity of fluorescence of FL (circle) and AN (squares) in the domains described by the spectra of Figure 5. Open circles and squares represent the domains of similar morphologies (a, c, e), and solid circles and squares represent the other region (b, d, f).

AN dissolved in PVAc [Fig. 2(d)]. The curves in these figures present a higher slope for all the samples and domains of the blends than that obtained for the PVAc homopolymer, indicating a more efficient deactivation process of the AN in the electronic excited singlet state. The slopes observed in Figure 6(a), (b), and (d) change in a very clear way at two different temperatures ranges: There is a small change at $T > 200$ K and a more significant change at $T > 304$ K. These results are similar to those obtained for PVAc homopolymer, although the deactivation processes are more efficient in the polymer blends.

An interesting behavior has been observed in the analysis of the curves representing the two domains of the blend for each composition, in the temperature range close to each homopolymer glass transition. From the curves of Figure 6(a), (c) and (e) (square points, region 1 of each blend), we can clearly determine a relaxation temperature at $T \cong 304$ K, which has been assigned to the T_g of PVAc. As pointed out earlier, region 1 is richer in PVAc, and from the apparent independence of the T_g value with the PVA composition, we are suggesting two possible explanations:

1. The AN molecules are only localized close to PVAc macromolecules.
2. The region separation is complete, resulting in a pure region composed of the PVAc homopolymer.

Considering that the slopes of these curves are different from those for the PVAc homopolymer [Fig. 2(d)], we are suggesting that the first possibility is more probable, i.e., the polymer blend contains higher free volumes where the AN molecules are localized and these domains are richer in PVAc macromolecules. The glass temperature of PVAc resulting in a polymer in the rubbery state also raises the internal conversion of the AN molecules, decreasing the fluorescence intensity. Although the T_g values for PVAc in the blends are very well defined, the β -relaxation processes of this homopolymer at $T \cong 200$ K is less well defined for the 9 : 1 and 1 : 9 polymer blends and it is undefined for the 1 : 1 blend. This result indicates that the nature of the domains where the AN molecules are localized presents a different mobility compared with the PVAc homopolymer and that the motions of these domains probably involve some weaker restraints.

From the curves of Figure 6(b), (d), and (f) (square points), representing the relaxation pro-

cesses of region 2 of the polymer blends, we can see that the glass transition of both homopolymers and the relaxation processes at $T \cong 200$ K are less well defined, and there is a higher dispersion of the points. Although the concentration of AN in these domains are lower, all those observations indicate that the motions of the macromolecules or their segments in region 2 suffer fewer restraints and may induce an easier diffusion of AN molecules, producing efficient radiationless processes. As pointed out before, this region is richer in PVA homopolymers and these results suggest a certain miscibility of the homopolymers. The presence of the PVAc homopolymer in region 2 in all blends has also been observed in the blends containing FL, as shown in Figure 4(b), (d) and (f).

We show in Figure 6, (circle points) the curves for the dependence of the FL intensity on the temperature for the 9 : 1 and 1 : 1 PVA/PVAc blends. The FL fluorescence emission in the 1 : 9 PVA/PVAc blend is too low to be considered within the range of experimental error. Figure 6(a) and (b) show the curves for domains 1 and 2, of the 9 : 1 PVA/PVAc blend, respectively. We can see, in this case, that the profiles of the curves are very similar to those obtained for FL in the PVA homopolymer [Fig. 2(b)], but they are very different from the 9 : 1 PVA/PVAc/FL blend [Fig. 4(a) and (b)]. For example, we cannot see a significant increase in the fluorescence intensity induced by the glass transition process of the PVAc homopolymer. From these data, we can conclude that FL is localized only in the PVA domains and this segregation has been induced by the presence of AN molecules.

The curves for the 1 : 1 PVA/PVAc blend [Fig. 6(c) and (d), circle points] present a higher slope in the temperature range from 16 to 300 K than observed in Figures 4(c) and (d) and 2(b), indicating that the FL quenching processes by photophysical pathways are more efficient than in the case of the 9 : 1 polymer blend and PVA homopolymer. Nevertheless, in this case, we are observing the PVAc relaxation processes, represented by the increase of the fluorescence intensity in the temperature range from 300 to 350 K, in both domains, reflecting the relationship between the photophysical and photochemical mechanisms for this dye deactivation, produced by the homopolymer relaxation processes as described earlier. This behavior, for region 1 [Fig. 6(c), open circles] is different from that of the 1 : 1 PVA/PVAc/FL blend [Fig. 4(c)], which did not show the intensity increase at $T \cong 350$ K. Moreover, the curve for region 2 [Fig. 6(d)]

exhibits a high dispersion of the points, indicating a much more complex region than the correspondent region of the blend containing only FL [Fig. 4(d), solid circles]. From all these results, one can conclude that AN molecules produce a disturbance of the polymer blend formation that, in this way, induces a higher efficiency of the FL quenching processes by photophysical mechanisms in the temperature range from 15 to 350 K.

The similarities of the curves for the two domains for one specific composition of the blends also suggest that FL molecules are probing domains in the polymer blends of same kind as dye-polymer interactions. However, the quenching processes have a higher efficiency, which indicates that these domains have higher free volume and that the fluorescence of the molecules may decrease by an internal conversion mechanism.

CONCLUSIONS

From the data obtained in this work, we can conclude that

1. Fluorescent molecules appear to be localized in domains determined by both the polymer structure, like amorphous domains and interphasial regions, and by dye-polymer interactions. In this work, we determined that AN molecules are localized in domains richer in PVAc homopolymer, whereas FL molecules are localized in domains richer in PVA.
2. The concentrations of AN and FL used in this work are sufficiently low to prevent their crystallization. However, AN is almost insoluble in PVA, and FL presents a very complex dissociation equilibrium depending on the medium, but despite this fact, the stable specimens are less soluble in PVAc than in PVA.
3. The β -relaxation process of the PVAc homopolymer may be determined by the radiationless processes of AN, which may involve different types of photophysical processes, such as energy migration from the electronically excited singlet state and internal conversion. The efficiencies of these processes are modified by the cooperative motions of the polymer segments.
4. The glass transition process of PVA may be determined by the photobleaching process of FL, an irreversible process.

5. Relaxation processes in the PVA/PVAc/FL blends are dependent on the region of each blend composition and involve photophysical processes of FL in the PVAc domains and photobleaching processes in the PVA domains. All these processes present higher efficiency than those observed for the PVA homopolymer, suggesting some miscibility between the two homopolymers.
6. Relaxation processes in PVA/PVAc/FL/AN blends are also dependent on the region for each composition. The same kind of deactivation processes of the probes may be considered to explain the decrease of the fluorescence emissions. However, the efficiency of the processes are different from those observed for the homopolymers and for the PVA/PVAc/FL blends, suggesting that AN molecules modify the solid region separation of the blends.

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