

Miscibility Characterization of SMA/SAN and SMA/PMMA Blends by Differential Scanning Calorimetry and Fluorescence Techniques

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ABSTRACT: In this study, styrene-maleic anhydride (SMA) copolymer was modified by monoesterification method with 9-(hydroxymethyl)anthracene fluorophore to prepare a fluorescent anthracene labeled SMA (SMA-An) material. The latter was then characterized by attenuated total reflection (ATR) and thermogravimetric analysis (TGA) techniques. In the second step of this work, SMA-An was added to SMA/[Styrene-Acrylonitrile Copolymer (SAN)] and SMA/[Poly(methyl methacrylate) (PMMA)]

blends to investigate the miscibility of these blends at the molecular level. The miscibility of SMA/PMMA blends was characterized using fluorescence quenching of anthracene by the succinic anhydride and succinic acid functions on SMA macromolecule itself. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2955–2962, 2007

Key words: blend miscibility; anthracene fluorophore; fluorescence; DSC

INTRODUCTION

Polymer blending is an efficient way to produce new materials, exhibiting improved application properties at a lower cost, than synthesizing new polymer formulations. Generated morphologies and final blend properties depend not only on the individual properties of blend components, but also on their degree of miscibility. However, most polymer systems are immiscible and only limited polymer pairs are partially miscible under specific temperature range and component concentrations.

Many characterization techniques, such as differential scanning calorimetry (DSC), light scattering, pulsed nuclear magnetic resonance (NMR), and electron microscopy, have been used to characterize the miscibility of polymer blends.¹ All these techniques have their particular criteria and technical limits. For example, it is largely accepted that blends having a single glass transition temperature (T_g) are miscible. However, T_g measurement is insensitive when the weight fraction of the dispersed phase is less than 10 wt % and cannot be

used for miscibility characterization if the difference between components' T_g is less than 20°C. Light scattering technique can also be used to characterize blend miscibility if the difference between the refractive indexes of the blend components is greater than 0.01. Microscopy techniques, such as optical microscopy and transmission electron microscopy (TEM), are respectively, limited by the degree of magnification and the difficulty of sample preparation.

On the other hand, fluorescence spectroscopy, which uses excimer fluorescence^{2–9} or nonradiative energy transfer,^{10–13} has been proven to be sensitive to detect both small-scale phase separation and miscibility of polymer blends. The phenomenon of excimer fluorescence, discovered by Förster¹⁴ in concentrated solutions of pyrene, was found to be common for many other aromatic molecules, such as styrene,^{2–4} naphthalene,^{5,6} and carbazole^{7–9} molecules. An excimer consists of a short-life molecule formed between two identical aromatic molecules lying parallel to each other in which one of them is in an electronic excited state.¹⁵ Changes in excimer and monomer fluorescent intensity in polymer blends depend on the degree of polymer aggregation and interchain penetration. In miscible polymer blends, polymer chains can interpenetrate each other, leading to the dilution of fluorophore concentration and a decrease in the probability of excimer formation. Since excimer formation requires that the distance between two fluorophores approaching each other must be

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around 3–4 Å, the decrease of the excimer fluorescence is then a signal of blend miscibility at the molecular level.

Amrani et al.¹⁰ used, for the first time, the nonradiative energy transfer (NRET) technique to study the miscibility of polymer blends. For two fluorophores existing in the same polymer system, when the emission spectrum of the donor fluorophore (which is excited by light of a specific wavelength) overlaps the absorption spectrum of the acceptor one, the donor can transfer the energy surplus to the ground state acceptor over a considerable distance. The energy transfer efficiency, E , can be calculated according to the following equation:¹⁰

$$E = R_0^6 / (R_0^6 + r^6) \quad (1)$$

where r is the distance between the donor and the acceptor and R_0 is the characteristic distance at which half of the excitation energy is transferred from the donor to the acceptor. With a suitable selection of donor/acceptor pairs, a value of R_0 situated between 2 and 3 nm can be obtained. For example, $R_0 = 2.1$ and 2.8 nm for naphthalene/anthracene and carbazole/anthracene pairs, respectively.^{10,13} Therefore, the efficiency of the energy transfer, experimentally given by the ratio of the donor fluorophore emission intensity (I_D) to that of the acceptor (I_A), can be related to the magnitude of chain miscibility of the polymers at a molecular scale of about 2–3 nm.

The fluorescence quenching phenomenon was initially used by Halarý et al.¹⁶ to study the phase separation in polystyrene/poly(vinylmethylether) (PS/PVME) blends. PS was first labeled with anthracene in the middle chain. In miscible PS/PVME blends, the ether group of PVME quenches the anthracene attached to PS. As phase separation takes place above the lower critical solution temperature (LCST), anthracene quenching decreases because of the decrease in the probability of interaction between PVME and anthracene in the heterogeneous state. Fluorescence quenching technique was also successfully used to study the effect of shearing on phase separation of PS/PVME blends.^{17,18} For approximately identical weight contents of styrene, it was reported that SMA and SAN are miscible.^{19–23} SMA/SAN systems show the LCST behavior, which is determined by the characteristic single glass transition temperature (T_g) on the DSC curve. It was also reported that SMA and PMMA blends are miscible when the weight fraction of maleic anhydride in SMA is in the range of 8–33 wt %.³ As in the case of SMA/SAN systems, SMA/PMMA systems also show the LCST behavior.

The monoesterification reaction of maleic anhydride in SMA with aliphatic alcohols was investigated by Hu and Lindt²⁴ and Martínez et al.²⁵ in

both organic solution and batch mixer. An increasing reaction rate was observed with increasing the alcohol chain length. The main objective of the present experimental study is to investigate the miscibility of SMA/SAN and SMA/PMMA blends at the molecular level using the fluorescence technique. To do this, SMA is firstly labeled by esterification with an aromatic alcohol (9-(hydroxymethyl)anthracene), although anthracene function has high steric hindrance compared with aliphatic alcohols used in literature. SMA-An is then used as a component of the studied blends to probe their miscibility at the molecular level. The experimental results obtained using the fluorescence technique are compared with those obtained by DSC, which is one of the main techniques commonly used to study blend miscibility.

EXPERIMENTAL

Materials

The poly(styrene-*co*-maleic anhydride) (SMA) used in this study has 14 wt % of maleic anhydride. The styrene-acrylonitrile copolymers (SAN-17 and SAN-29) have 17 and 29 wt % of acrylonitrile, respectively. The polymethyl methacrylate (PMMA) is a commercial grade graciously supplied by Atohaas Americas, USA. Polymer characteristics are summarized in Table I. 9-(Hydroxymethyl)anthracene fluorophore (97%) and 1,2-dichloroethane (HPLC grade) are purchased from Sigma-Aldrich. Hexane, tetrahydrofuran, and chloroform solvents are GR grades from EMD chemicals. All materials were used as received.

SMA labeling with anthracene fluorophore (SMA-An)

A mixture of SMA (10 g), 9-(hydroxymethyl)anthracene (5 g), and pyridine (1.1 g), used as catalyst, were dissolved in 125 mL of xylene. The mixture was stirred and kept at 100°C in an oil bath for 24 h. Purification of the modified polymer was achieved by precipitation in hexane followed by filtration. The solid product was then dissolved in THF and re-precipitated in hexane for two additional times. The purified solid sample was dried under vacuum at 40°C for 7 days then compressed at 180°C to form a film of around 200 μm.

Preparation of SMA/SAN and SMA/PMMA blends

SMA/SAN and SMA/PMMA blends of varied composition were prepared using the solution-cast film technique. Blend mixtures (1 g) were first dissolved in 20 mL of chloroform or 1,2-dichloroethane sol-

TABLE I
Characteristics of the Different Polymers Used in this Study

Polymer designation	Composition	M_w (g/mol)	M_n (g/mol)	Supplier
SMA	14 wt % of maleic anhydride	185,000	90,000	Arco Chemical
SAN-17	17 wt % acrylonitrile	178,100	64,900	Bayer Corporation
SAN-29	29 wt % of acrylonitrile	109,700	69,400	Bayer Corporation
PMMA	—	131,700	101,300	Atohaas Americas

vents to obtain an homogenous solution, which was then casted on a Teflon film. The solvent was then evaporated overnight at room temperature and the obtained film was dried at 40°C under vacuum for 1 week.

Blend characterization

ATR and TGA techniques were used to characterize the synthesized SMA-An. ATR spectra were collected using a Specac FTLA 2000 instrument. TGA was conducted under nitrogen [from 10 to 500°C at a heating rate of 10°C min⁻¹ using a TGA Q500 analyser (TA Instruments)]. ¹H-NMR spectra were recorded (with a nuclear magnetic resonance spectrometer, INOVA400) in a deuterated chloroform solution using tetramethylsilane as an internal standard.

The miscibility of SMA/SAN and SMA/PMMA blends was characterized by both DSC and fluorescence techniques. DSC was carried out under nitrogen using a DSC Q100 system (TA Instruments) at a heating rate of 10°C min⁻¹. To ensure reproducible DSC thermograms free of prior thermal history effect, a second scan was done and the T_g was taken from this second scan. Fluorescence measurements were carried out at room temperature using a Cary Eclipse spectrofluorometer (from Varian) equipped with a xenon flash lamp. Excitation wave length was 365 nm, which corresponds to the anthracene highest UV absorption peak. Film samples were fixed on a solid sample holder and the fluorescence intensity was measured at four different positions. Average fluorescence intensity was then calculated from these measured values.

EXPERIMENTAL RESULTS AND ANALYSIS

ATR spectra of SMA and SMA-An

ATR spectra of pure SMA and SMA-An are presented in Figure 1. The figure shows the characteristic peaks of carbonyl absorption of the anhydride groups in five-membered rings at 1779 and 1857 cm⁻¹. It also shows C=C vinyl stretching of styrene at 1602 cm⁻¹. For SMA-An, the two new signals appeared at 1707 and 1732 cm⁻¹ can be respectively,

assigned to the vibration of the carbonyl of carboxylic acid and the vibration of the ester carbonyl. The peak at 1602 cm⁻¹, which was not modified by the reaction, was used to calculate the conversion of the reaction using the following equation:²⁵

$$P = (1 - A_t/A_0) \times 100\% \quad (2)$$

where A_0 and A_t are respectively, the ratios between the absorbance at 1779 cm⁻¹ and that at 1602 cm⁻¹ before and after modification with anthracene. According to Figure 1, the reaction conversion is 47%.

¹H-NMR spectra of SMA and SMA-An

Figure 2(a,b) show respectively, the ¹H-NMR spectra of pure SMA and SMA-An in DCCl₃ solution. The peaks at 6.0–7.4 ppm are assigned to the aromatic protons. For the spectrum of SMA-An, multiple peaks appear in the 7.7–8.5 ppm region. This is due to the protons on anthracene,²⁶ which confirms that anthracene is labeled on SMA chain.

TGA characterization of SMA and SMA-An

The TGA and TGA derivative curves of SMA and SMA-An are presented in Figure 3(a,b), respec-

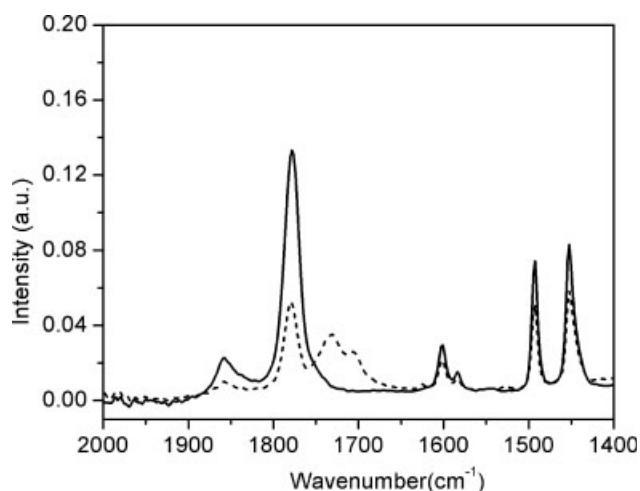


Figure 1 ATR spectra of SMA (—) and SMA-An (- - -).

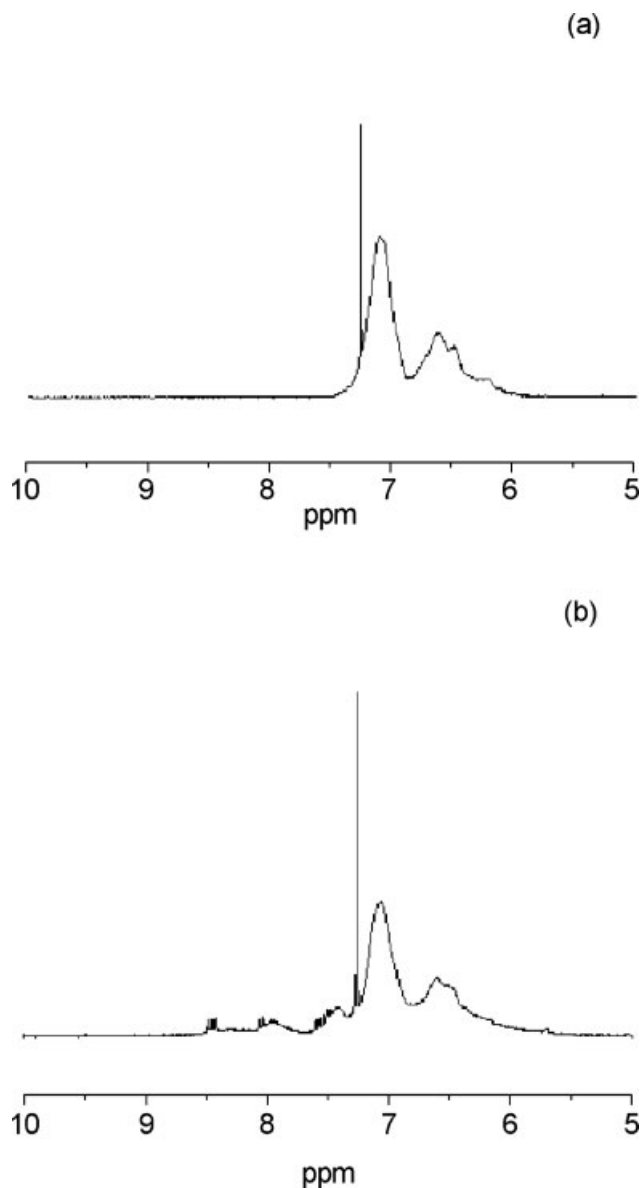


Figure 2 $^1\text{H-NMR}$ spectra: (a) pure SMA (b) SMA-An.

tively. Figure 3(a) shows that pure SMA presents a single decomposition temperature at 400°C . However, as shown in Figure 3(b), SMA-An exhibits three decomposition processes. The first decomposition (3.5% of weight loss), detected at 233°C , is attributed to the residual 9-(hydroxymethyl)anthracene monomer and some traces of the solvent used in blend preparation. The second decomposition (20% of weight loss), detected at 349°C , is attributed to the deesterification of SMA-An.²⁷ The third and main decomposition occurred at 402°C , which is slightly higher than the original decomposition temperature of SMA. Because of its high thermal stability at 200°C , of SMA-An can be adequately used to monitor the miscibility behavior of SMA/SAN and SMA/PMMA blends at processing tem-

peratures, such as those used in batch mixers and twin screw extruders.

Miscibility characterization of SMA/SAN and SMA/PMMA blends by DSC technique

The miscibility of three blends (SMA/SAN-17, SMA/SAN-29, and SMA/PMMA) with different SMA weight concentrations has been studied. The corresponding DSC curves are presented in Figure 4(a–c). Figure 4(a,c) clearly show that SMA/SAN-17 and SMA/PMMA blends present a single glass transition for all SMA weight concentrations studied. This behavior is a characteristic of miscible blends. For SMA/SAN blends, literature results^{19–23} show that these blends are miscible when SMA and SAN contain approximately identical weight percentage of styrene, which is the case in this study. The used

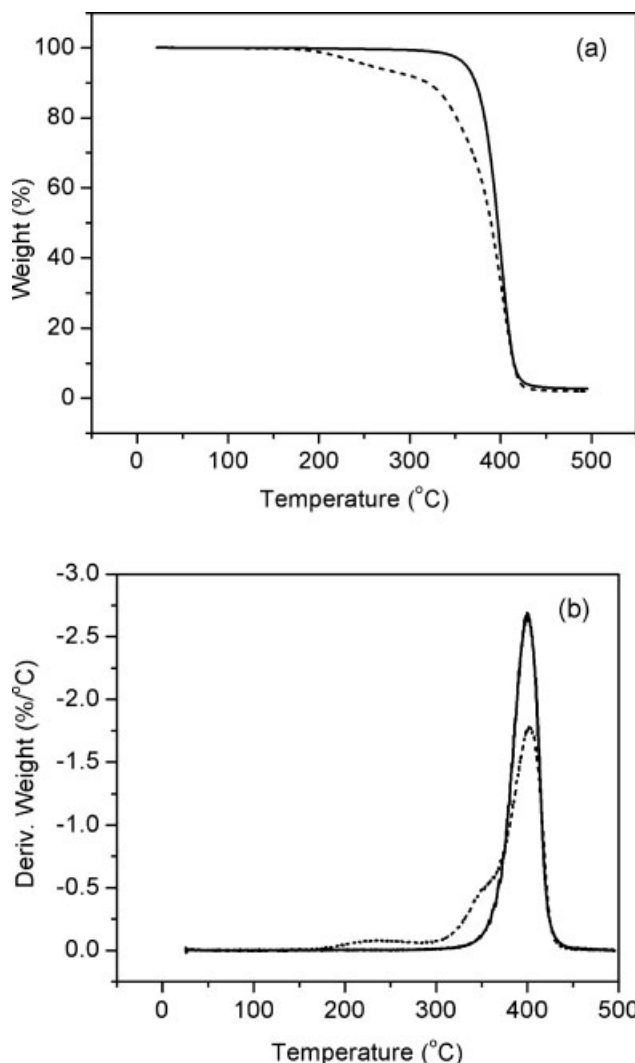


Figure 3 (a) TGA curves of SMA (—) and SMA-An (---). (b) First order derivative of TGA curves of SMA (—) and SMA-An (---).

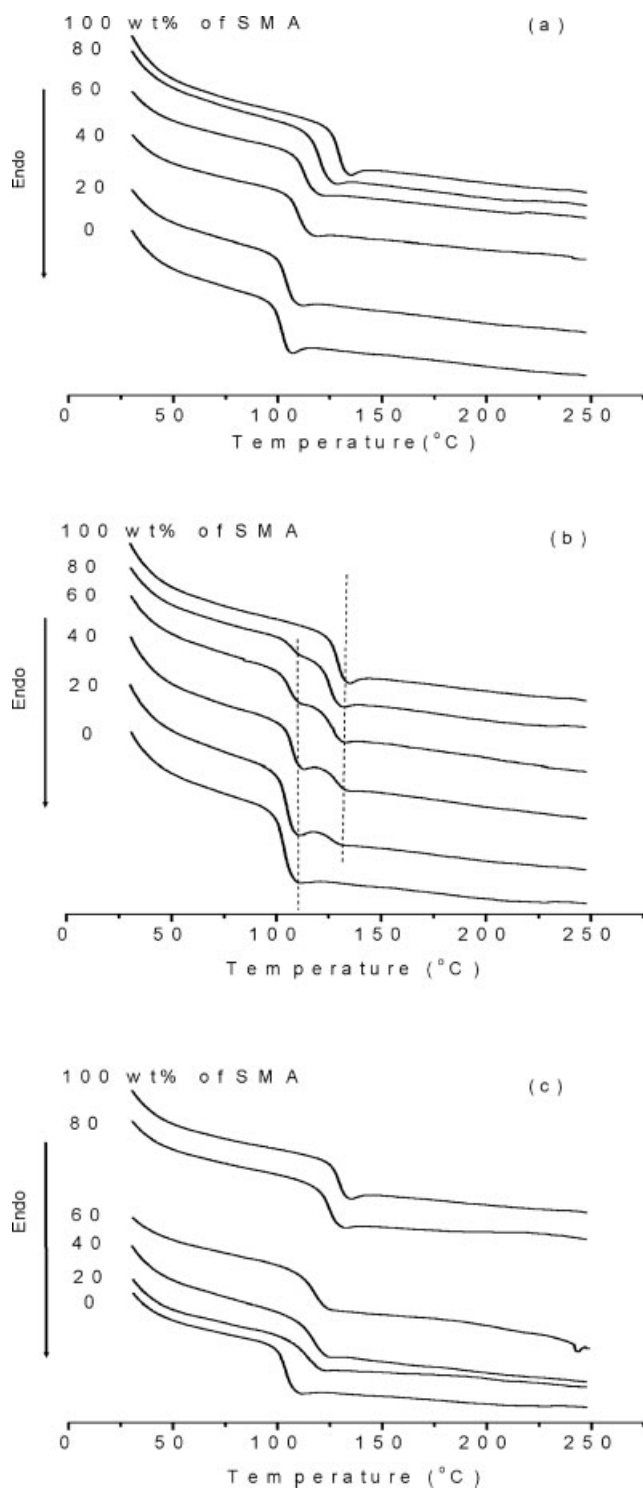


Figure 4 Blends DSC characterization curves for different SMA concentrations: (a) SMA/SAN-17. (b) SMA/SAN-29. (c) SMA/PMMA.

SMA and SAN-17 contain respectively, 86 and 83 wt % of styrene. However, as shown in Figure 4(b), SMA/SAN-29 blends present double glass transitions for the different SMA concentrations studied. This behavior is a characteristic of immiscible blends. The main difference between the miscibility

behavior of SMA/SAN-17 (miscible) and SMA/SAN-29 (immiscible) blends is that the weight percentage of styrene in SAN-29 phase (71 wt %) is lower than that in the SMA phase (86 wt %).

Figure 5 presents the evolution of the T_g of SMA/SAN-17 and SMA/PMMA blends as a function of SMA weight concentration. For both blends, which are miscible, the blend T_g data obey to the Gordon-Taylor equation:²⁸

$$T_g = (w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2) \quad (3)$$

where T_{gi} and w_i ($i = 1, 2$) are respectively, the T_g and the weight fractions of the blend components. K is an adjustable (fitting) parameter. After curve fitting optimization, the following values, $K = 0.5$ and 1.0 , were obtained for SMA/SAN-17 and SMA/PMMA, respectively.

Fluorescence emission of anthracene in SMA and SAN-17 films

Figure 6 shows the fluorescence intensity of anthracene in SMA and SAN-17 films (presented in closed and open symbols, respectively) as a function of anthracene molar concentration. The solid and dashed fitting curves will be discussed later in this section. For SMA-An films, fluorescence intensity increases with increasing anthracene concentration up to around 0.035 mol/L. Further increase of anthracene concentration results in fluorescence intensity decrease. This behavior means that the fluorescence emission of anthracene labeled on SMA chains can easily be quenched by the succinic anhydride and

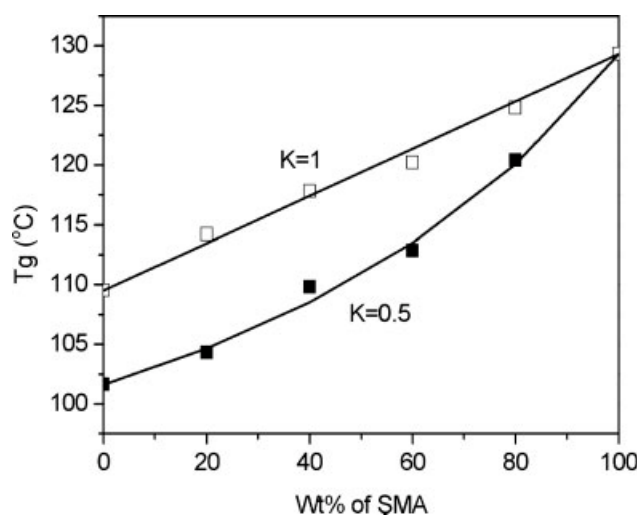


Figure 5 Glass transition temperatures of SMA/SAN-17 (■) and SMA/PMMA (□) blends as a function of SMA weight concentration.

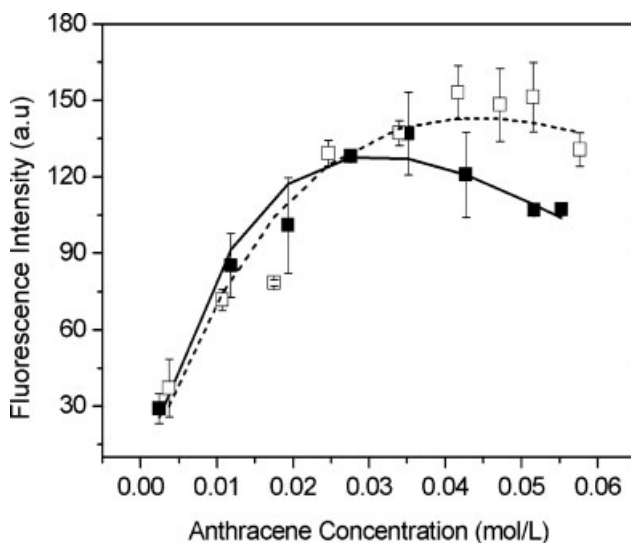


Figure 6 Fluorescence intensity (au: arbitray unit) as a function of anthracene tracer concentration in SMA (■) and SAN-17 (□) films. Continuous and dashed curves correspond respectively, to SMA and SAN-17 fluorescence fitting curves according to eq. (7a).

succinic acid functions at intramolecular and intermolecular levels, which is in concordance with literature.²⁹ Figure 6 also shows that anthracene fluorescence intensity in (SAN-17)-An films increases with increasing anthracene concentration up to around 0.045 mol/L and decreases for higher anthracene concentrations. The fluorescence emission of anthracene labeled on SAN-17 can also be quenched by acrylonitrile as reported by Selvarajan and Ramakrishnan.³⁰

For both SMA-An and (SAN-17)-An films, the fluorescence intensity is not a linear function of anthracene concentration. This nonlinear behavior can be represented by the following Perrin fluorescence quenching model equation:³¹

$$\ln f = VQ = \left(\frac{4}{3}\pi R_s^3 N\right)Q \quad (4)$$

where f is the ratio between fluorescence intensities in the absence and in the presence of a quencher. R_s is the radius of the quenching sphere. This model describes the static quenching between randomly distributed and immobile fluorophores and quenchers, which are in proximity inside a spherical volume, V . It assumes that an excited fluorophore is instantaneously quenched by the quencher if this latter is inside the same volume V . However, there is no quenching if the quencher is outside of this volume. In the present work, the succinic anhydride and succinic acid quencher concentrations in SMA are constant, but the fluorophore concentration increases progressively. So, the quenching effect is

supposed to be related to the tracer concentration and eq. (4) can be modified as follows:

$$\ln f = VC \quad (5)$$

where C is the tracer molar concentration in the polymer film. For fluorescence emission without quenching, the intensity I^0 is proportional to the tracer concentration:

$$I^0 = K_1 C \quad (6)$$

The fluorescence emission in the presence of a quencher is then derived from eqs. (5) and (6):

$$I = I^0/f = K_1 C/\exp(VC) \quad (7a)$$

$$\ln(I/C) = \ln K_1 - VC \quad (7b)$$

Figure 7 presents the experimental fluorescence emission data for SMA and SAN-17, presented in Figure 6, together with their fitting curves according to eq. (7b). The corresponding values of $\ln K_1$ and V , which correspond respectively, to the intercept and the slope of the fitting curves, are (i) for SMA: $\ln K_1 = 9.3$, $V = 33$, and (ii) for SAN-17: $\ln K_1 = 9.1$, $V = 23$. The value of $\ln K_1$ obtained for SMA is higher than that obtained for SAN-17. This means that the SMA fluorescence intensity is higher than that of SAN-17 in the absence of anthracene quencher. Also, the value of V for SMA is higher than that obtained for SAN-17, which explains the higher quenching efficiency of the succinic anhydride group (at high concentrations) compared with that of the acrylonitrile group. By using the above values of $\ln K_1$ and V , the fluorescence emission of SMA-An and (SAN-

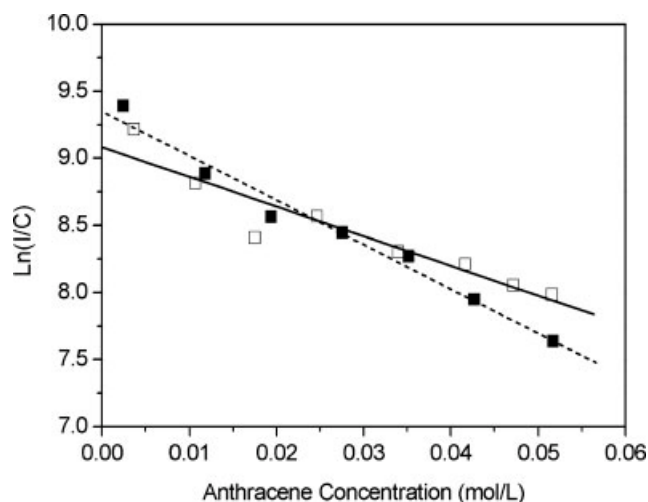


Figure 7 Fitting curves [according to eq. (6)] of fluorescence intensity data presented in Figure 5 [SMA (■), SAN-17 (□)].

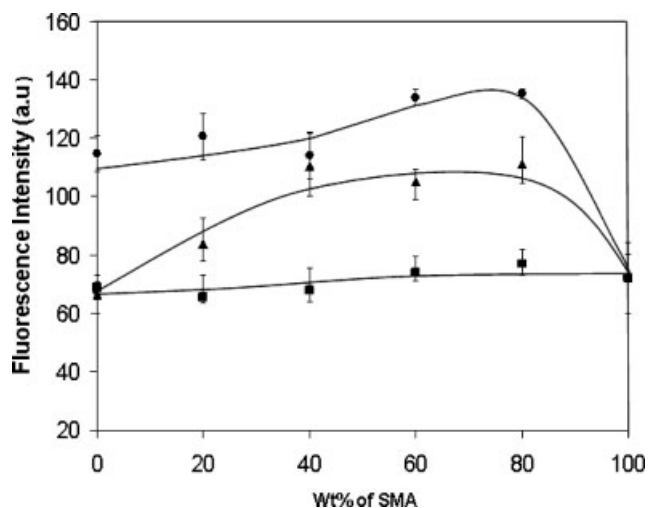


Figure 8 Fluorescence intensity in SMA/SAN-17 (■), SMA/SAN-29 (▲), and SMA/PMMA (●).

17)-An is well-described by eq. (7a), as shown in Figure 6.

Miscibility characterization of SMA/SAN and SMA/PMMA blends by fluorescence technique

Fluorescence emission of SMA-An in two SMA/SAN blends and in one SMA/PMMA blend is plotted in Figure 8 as a function of SMA weight concentration. For all blends, the weight concentration of SMA-An tracer was maintained constant at 0.5 wt %. For SMA/SAN-17 blends (lower curve), the blend fluorescence intensity varies almost linearly between the fluorescence emission intensities of pure SMA and SAN-17, which are not very different. This behavior indicates that SMA and SAN-17 molecules are completely interpenetrated and SMA-An chains are randomly dispersed in the blend. However, for all SMA concentrations, the fluorescence emission intensities of SMA/SAN-29 blends (middle curve) are higher than those of pure SMA and SAN-29 components. This behavior can be explained by the immiscibility of SMA/SAN-29 blends. This immiscibility leads to anthracene tracer accumulation in the SMA phase and consequently to an increase of the blend fluorescence intensity. For SMA/PMMA blends (top curve), it is clear that PMMA fluorescence intensity is higher than that of SMA because PMMA has much less quenching effect on anthracene emission than SMA. Consequently, PMMA chains increase the fluorescence emission by diminishing the deleterious impact from quenching effect.³² For all SMA concentrations, the fluorescence emission intensities in SMA/PMMA blends are much higher than those of the pure SMA and PMMA components and increase with increasing SMA concentration. The SMA and PMMA chains interpenetrate each other and anthra-

cene prefers to be located in PMMA phase. With decreasing PMMA concentration in the SMA/PMMA blend, the actual anthracene concentration in PMMA phase is increased, leading to higher fluorescence intensity emission.

CONCLUSIONS

In this work, SMA-An was synthesized successfully and its conversion and thermal stability were characterized by ATR and TGA techniques. Results show that about the half of the succinic anhydride was attached with the anthracene function. The dependence of fluorescence emission of SMA-An and (SAN-17)-An on anthracene tracer concentration was investigated. The nonlinear behavior between the fluorescence intensity and tracer concentration was well-described by Perrin model equation.

The miscibility of SMA/SAN-17, SMA/SAN-29, and SMA/PMMA blends was investigated by both DSC and fluorescence techniques. The miscibility of SMA/PMMA blend was determined based on the fluorescence quenching by the self-quenching of SMA. In such miscible blend, PMMA chains increase the fluorescence emission by diminishing the fluorescence quenching interaction between the anthracene and the maleic anhydride functions.

Starting from the phase separated state of the miscible SMA/PMMA, a future work will be devoted to the phase interdiffusion in SMA/PMMA systems during annealing near the T_g of SMA. We anticipate that the fluorescence intensity increases with polymer chain interdiffusion during annealing.

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