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REVIEW

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Polymer/dye blends: Preparation and optical performance: A short review

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Abstract

This review focuses on the optimization of the optical performance of polymer/dye blends in which dyes are physically dispersed in polymer matrices. The optimization of the optical performance of polymer/dye blends is discussed in terms of: (i) the preparation procedure of polymer/dye blends (melt processing is considered particularly effective for producing polymer/dye blends with optimal dye distribution); (ii) mechanical and thermal solicitations after polymer/dye blend preparation; (iii) the polymer matrix, whose affinity for the dye and crystallinity affects the optical performance the polymer/dye blend; and (iv) the dye, whose chemical structure and concentration are significant determinants of the optical properties of polymer/dye blends.

KEYWORDS

dye, dye aggregates, dye dispersion, optical performances, photostability, polymer matrix, preparation process

1 | INTRODUCTION

Natural and synthetic dyes have been studied for decades and play fundamental roles in everyday applications. They are used in a wide variety of technical and industrial applications, including serving as laser dyes and dyes for organic light-emitting diodes, liquid-crystal displays, optical data storage, and fluorescent labelling. The need to improve the efficiency[1] or photochemical and photophysical properties of dyes,[2,3] develop procedures based on green chemistry,[4,5] reduce dye toxicity, and decrease production costs has led to intense research in this field.[6,7] A promising strategy for realizing these goals is the combination of dyes with polymeric materials. Indeed, dye-containing polymers are today widely applied in medicine, paint technology, and optical sensors.[8] Some of these applications often require plastic materials to obtain the desired properties of the final dye-containing polymers.

Two approaches to preparing dye-containing polymers that demonstrate both typical polymer properties (viscoelasticity) and optical responses to visible light have been reported (Figure 1). In the first approach, dye units are covalently attached to the macromolecular chains of a polymer, forming a material with a color and color intensity resulting, respectively, from the selected dye and dye concentration (Figure 1a). The associated synthetic procedure involves the copolymerization of a colorless monomer and a dye-functionalized monomer, with a random or block distribution. However, this synthetic approach is often limited by the availability and reactivity

In memoriam P. Gravisse and M. Schiffmann.

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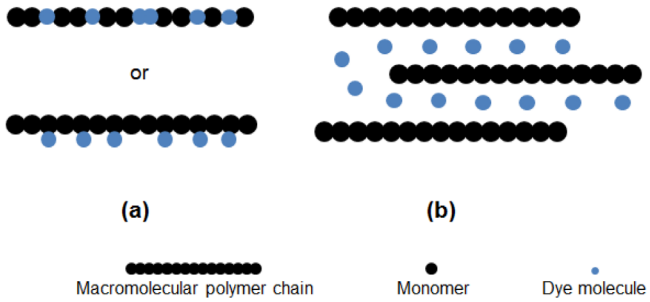


FIGURE 1 The two possible approaches to preparing dye-containing polymers. (a) First approach: The covalent attachment of dye molecules to polymer chains. (b) Second approach: The dispersion of dye molecules in a polymer matrix. [Color figure can be viewed at wileyonlinelibrary.com]

of dye-functionalized monomers. To overcome this limitation, the direct grafting of a dye onto preformed macromolecular chains has been explored.[9–12]

In the second approach, dye is directly dispersed into a polymer matrix (Figure 1b), leaving the macromolecules structurally unaltered and generally producing a biphasic system, unless the dye is fully soluble in the polymer. Procedures to disperse dyes into polymers, mainly virgin plastic, have been used to prepare pigmented materials since the early days of the plastic age.[13] However, dyes can impart properties besides color for aesthetic purposes. Specific interactions between self-organizing macromolecules and dye molecules tune the optical behavior of the system.[9] Unlike the optical responses of dye-functionalized polymers, the optical responses of dyes dispersed in polymer matrices to mechanical stimuli can be modulated in terms of intensity and selectivity by controlling the interphase interactions of the systems and their supramolecular conformations.[14] This approach, even though it produces materials with less structural stability than the former, is considered more viable, in terms of material development, as it enables the use of dyes already on the market.[15]

Dye-containing polymers, prepared by dispersing dyes in polymer matrices (the second approach described above), have been of great interest since the 1980s. Indeed, this dispersion approach enables the combination of different polymers and dyes to obtain materials that differ in terms of their preparation processes, response to mechanical and thermal solicitations, polymer matrix properties (chemical structure, crystallinity, and oxygen permeability), and dye characteristics (chemical structure and concentration). The main objective of this review is to discuss the optimization of the optical performance of polymer/dye blends in terms of these parameters. Since the optical performance of a polymer/dye blend depends on the photostability of the dye in the polymer matrix, the photostability of the polymer/dye blend is discussed first. Table 1 presents the structures of the dyes featuring in our discussions.

2 | PHOTOSTABILITY OF POLYMER/DYE BLENDS

Long-term photostability under various environmental conditions (with regard to factors such as such as light, temperature, and humidity) is an important requirement of polymer/dye blends, considering that these blends are expected to maintain their high optical performance for at least several years. Some polymers demonstrate excellent environmental stability; in fact, one supplier of poly (methyl methacrylate) (PMMA)–based materials (Figure 2) recently offered a stability guarantee of 30 years. In general, poor long-term photostability in polymer/dye blends is mainly ascribed to the associated luminescent dyes.[16] This is because ultraviolet (UV) light and oxygen exposure adversely affect the optical performances of dyes and, thus, impact the long-term photostability of polymer/dye materials.

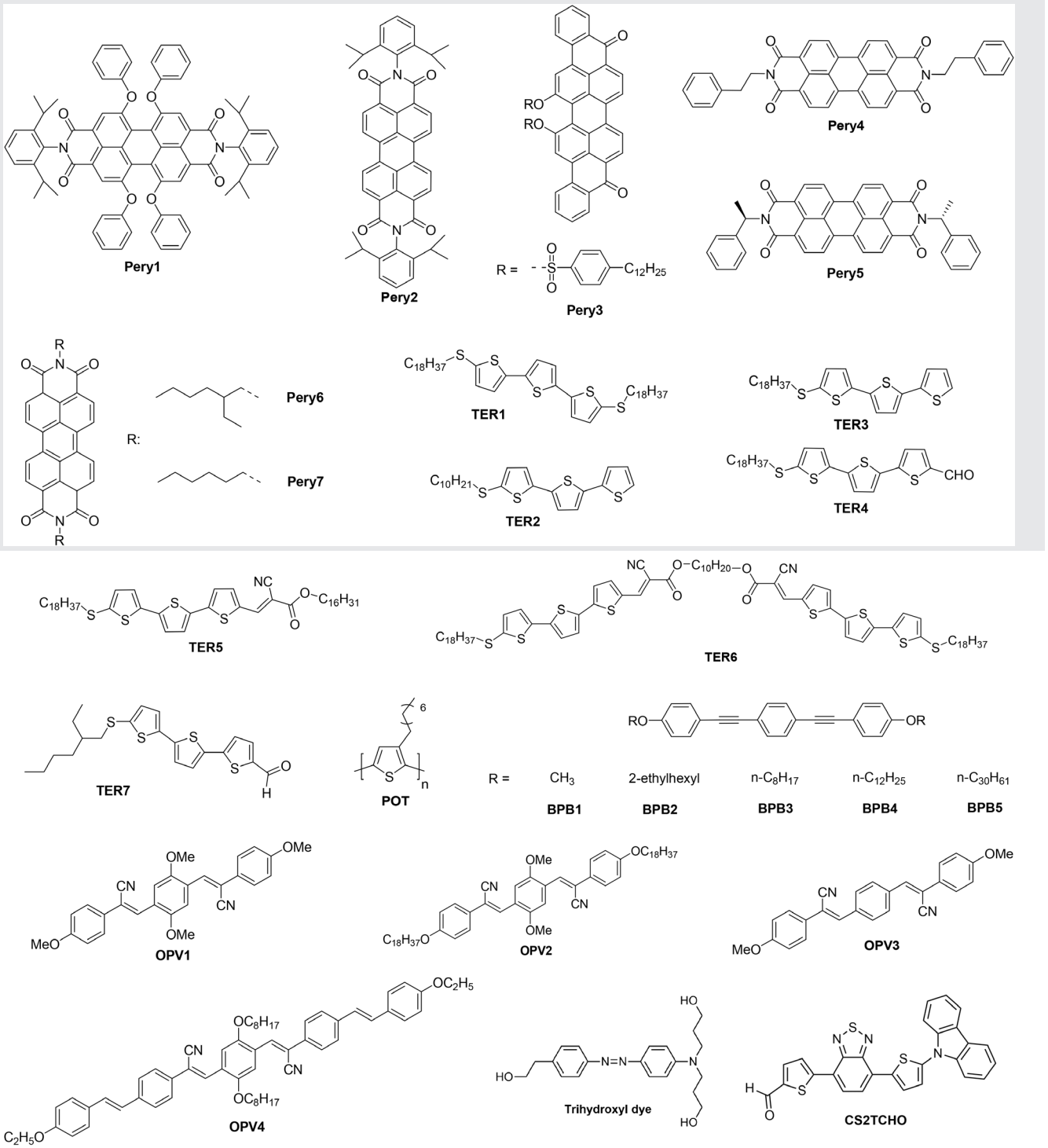
Griffini et al.[17] studied the effect of UV light exposure on the photostability of red perylene (Pery1) and PMMA solid-state blends. The absorption spectra (Figure 3a) of PMMA/Pery1 blends subjected to different periods of UV light exposure show two absorption peaks. The shorter-wavelength absorption peak centered at 445 nm is attributed to the absorption of light by the lateral substituents of Pery1, whereas the longer-wavelength absorption peak ($\lambda_{max} = 576$ nm) is associated with the absorption of light by the perylene core of Pery1. The corresponding fluorescence spectra (Figure 3b) are characterized by single, sharp emission peaks centered at 612 nm, attributed to the fluorescence of the perylene core of Pery1. Griffini et al.[17] found that the absorbance and fluorescence emission of PMMA/Pery1 solid-state blends decrease with increasing duration of UV light exposure, and are significantly reduced after 5 h of UV light exposure.

A similar investigation of orange perylene (Pery2) in a PMMA matrix showed that prolonged exposure to UV light causes not only a reduction in the absorbance of the dye at $\lambda_{max} = 526$ nm but also an increase in its absorbance at longer wavelengths (560–720 nm), owing to the formation of aggregates or radical groups resulting from photodegradation.[18] The exposure of the dye to light from which the of UV light—up to 345 nm—has been filtered out, does not cause significant decomposition of the dye or an increase in its absorbance at longer wavelengths; thus, the photostability of the PMMA/Pery2 system is substantially improved. In the same study,[18] the absorbance ($\lambda_{max} = 526$ nm) of PMMA/Pery2 blends under oxygen and nitrogen atmospheres was investigated. The increase observed in the

absorbance of the system at longer wavelengths (560–720 nm) is more pronounced under a nitrogen atmosphere than under an oxygen atmosphere. Nevertheless, the overall decomposition of Pery2 is more severe under an oxygen atmosphere than under a nitrogen atmosphere (that is, the decrease in its absorbance at 526 nm is greater under an oxygen atmosphere than under a nitrogen atmosphere).

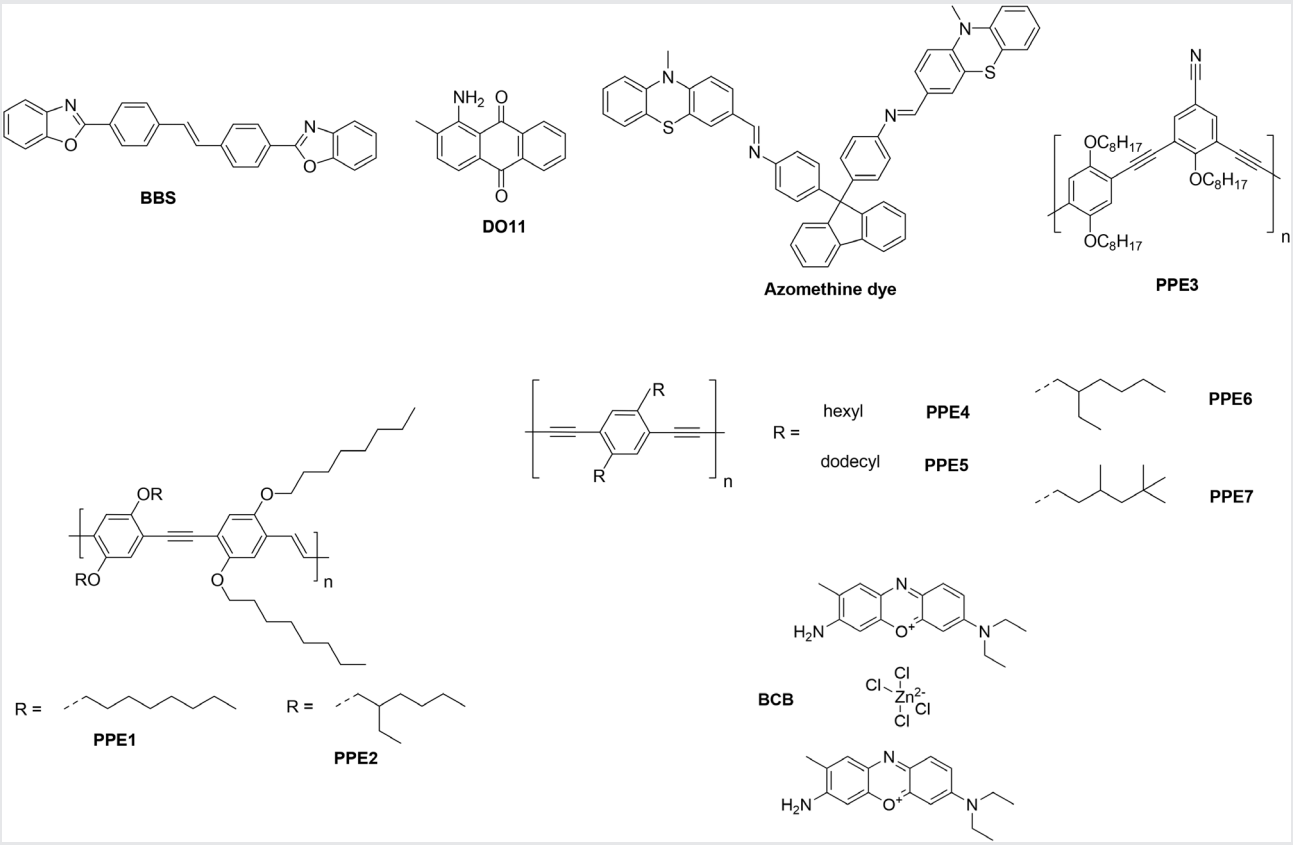
Evidently, UV light and oxygen exposure are partly responsible for the chemical degradation of dyes in polymer/dye blends. Griffini et al.[17] proposed a mechanism

TABLE 1 Structures of dyes commonly used in polymer/dye blends.



(Continues)

TABLE 1 (Continued)



for the photodegradation of Pery1. In the first phase (Figure 4), lateral phenyl ring substituents of the dye are abstracted from its perylene cores via the homolytic scission of oxygen–phenyl bonds, thus generating phenyl radicals that are converted to benzene. This abstraction also leads to the formation of phenoxy radicals that are converted to phenyl alcohols by hydrogen abstraction. In the second phase (Figure 5), diisopropylphenyl substituents of the dye are abstracted via the homolytic scission of nitrogen–phenyl bonds. This leads to the formation of diisopropylphenyl radicals. Subsequent successive alkyl radical abstraction can lead to the formation of *m*-xylene, ethyl benzene, styrene, and toluene. The perylene core, in turn, may be oxidized if oxygen is present or participate in crosslinking reactions with other radical species formed during photodegradation to produce cross-linked species.

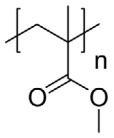
Although the dyes in polymer/dye blends are inevitably degraded by UV light and oxygen exposure, this degradation can be limited by filtering part of the UV light[18] or by reducing the oxygen permeability of the materials (vide infra).

In addition to dye degradation resulting from UV light and oxygen exposure, factors that affect the dispersion of a dye within a polymer matrix or its tendency to form aggregates must be considered to optimize the optical performance of polymer/dye blends.[19] Such factors include the preparation process of the polymer/dye blend, the polymer matrix, and the nature and concentration of the dye.

3 | EFFECT OF THE PREPARATION PROCESS ON THE OPTICAL PERFORMANCE OF POLYMER/DYE BLENDS

The processes used to prepare polymer/dye blends play an important role in determining their optical performance as the dispersion of dyes in polymer matrices varies according to the mixing process used. Dyes can be dispersed in polymer matrices in solution or in molten polymers (using compounding devices) depending on the physicochemical characteristics of the components of the polymer/dye blends.

In the case of polymer matrices such as PMMA (Figure 2), poly(ethylene terephthalate) (PET, Figure 6), and polystyrene (PS, Figure 6), which consist of repeating units that are highly compatible with various dyes (in terms of their chemical structures and/or polarity), homogeneous polymer/dye films can be obtained by film casting.[9]



PMMA

FIGURE 2 Chemical structure of poly(methyl methacrylate) (PMMA).

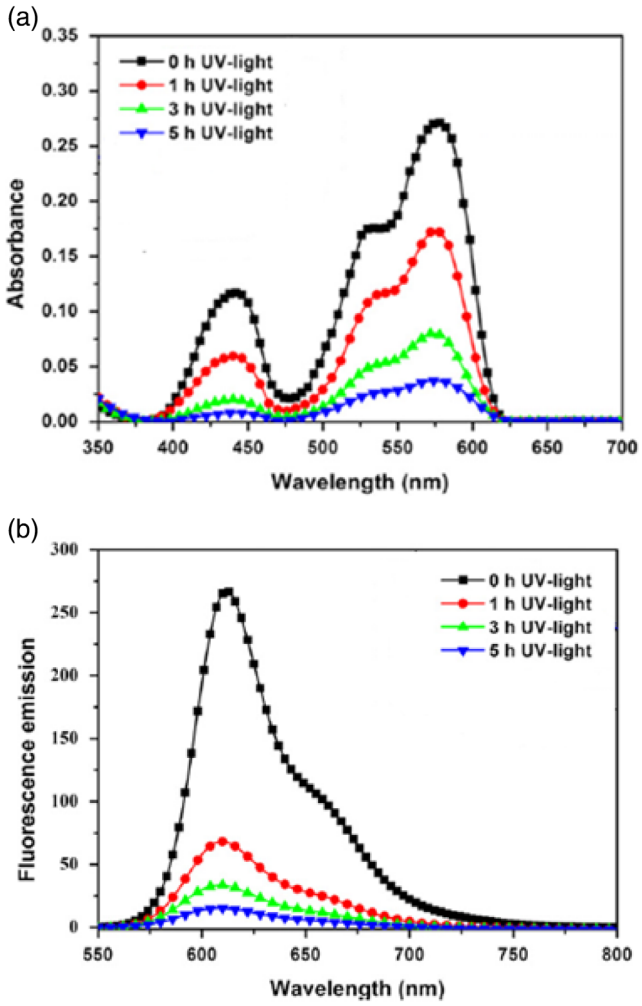


FIGURE 3 Absorption (a) and fluorescence (b) spectra of PMMA/Pery1 blends after 1, 3, and 5 h of UV light exposure. Reproduced with permission.[17] Copyright 2013, Elsevier [Color figure can be viewed at wileyonlinelibrary.com]

Film casting involves the dissolution of polymer granules or powder along with a desirable amount of dye in an appropriate solvent. The solution is then poured into a mold, and a film is obtained after solvent evaporation at room or elevated temperatures (Figure 7).

However, this preparation process does not always yield polymer/dye films with optimal optical performance. Indeed, Pucci et al.[20] found that solvent-cast films based on ultra-high-molecular-weight PE (UHMWPE) and 5,5″-bis-thiooctadecyl-2,2′:5′,2″-terthiophene (TER1) are characterized by poorly dispersed dye molecules in a polymer matrix, resulting in inferior optical performance. The homogeneity of a polymer/dye film is typically inferior when the polymer matrix is incompatible with the dye in terms of their chemical structures and/or polarity. This is the case with polyolefin/dye blends based on polyethylene (PE) or polypropylene (PP) (Figure 8), which typically undergo phase separation during casting and drying, producing inhomogeneous blend films containing dye aggregates.

In these cases, the preparation of polymer/dye blends requires special techniques, such as melt extrusion (Figure 9), to avoid phase separation. Homogeneous polymer/dye blends can be realized using continuous mechanical mixers, which are able to completely disperse dyes in polymers. The shearing forces associated with the melt-blending process tend to break up any dye aggregates to optimize dye distribution and concomitant optical performance.[9]

Unlike the casting of dilute solutions of incompatible dyes and polymers, melt blending leads to multicomponent materials with comparatively good phase distribution.[21] Indeed, Pucci et al.[20] showed that blends obtained by mixing TER1 with processable PE (linear low-density polyethylene (LLDPE) and high density polyethylene (HDPE)) are characterized by well-distributed dye and good optical performance.

In summary, the selection of the process used to prepare a polymer/dye blend is important for achieving optimal blend morphology in terms of the distribution of the dye within the polymer matrix. Among the processes used to prepare polymer/dye blends, melt blending appears most effective at optimizing the morphology of a polymer/dye blend and, concomitantly, its optical performance.

4 | EFFECT OF MECHANICAL AND THERMAL SOLICITATIONS ON THE OPTICAL PERFORMANCE OF POLYMER/DYE BLENDS

Mechanical and thermal solicitations performed on prepared polymer/dye blends can induce changes in the absorption and emission properties of the dye and, thus, be used to modulate the optical performance of polymer/dye blends.

4.1 | Effect of mechanical solicitations

The mechanical solicitation of prepared polymer/dye blends can alter their optical performance. For instance,

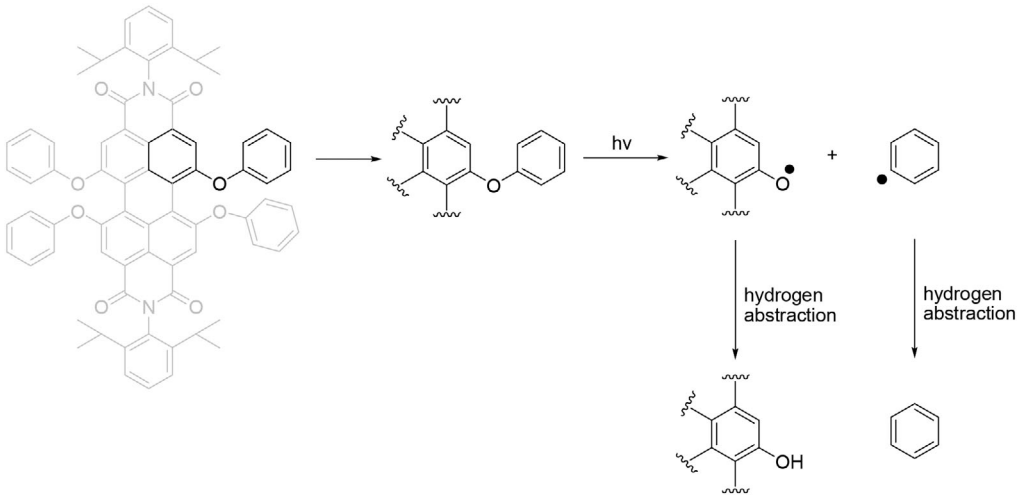


FIGURE 4 First phase of the photodegradation mechanism of Pery1 in polymer/dye blends. Reproduced with permission.[17] Copyright 2013, Elsevier

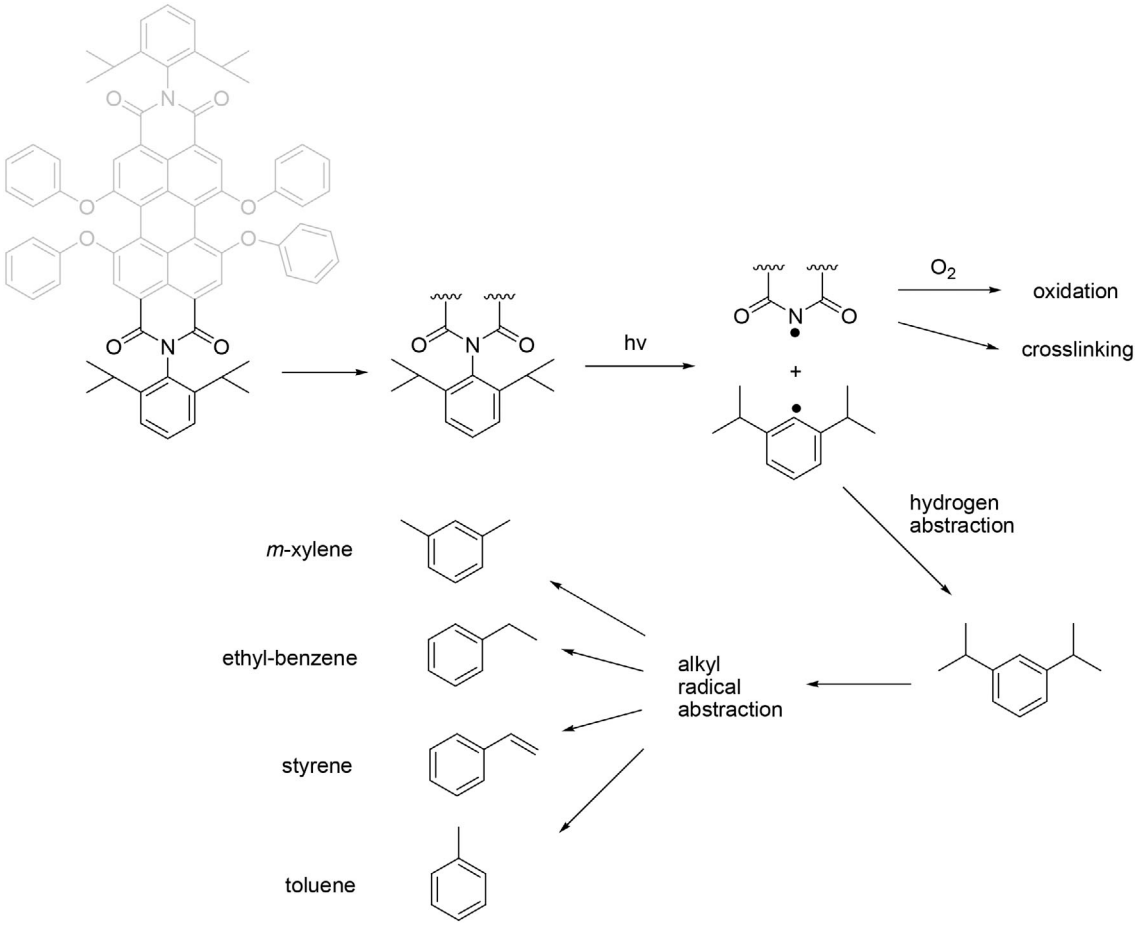


FIGURE 5 Second phase of the photodegradation mechanism of Pery1 in polymer/dye blends. Reproduced with permission.[17] Copyright 2013, Elsevier

tensile deformation affects the optical performance of polymer/dye blends. It has been demonstrated that the optical performance of blends based on PE and excimer-forming cyano-oligo(p-phenylene vinylene) (OPV) dyes (1,4-bis(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (OPV1) and 1,4-bis(α-cyano-4-octadecyloxy-styryl)-2,5-

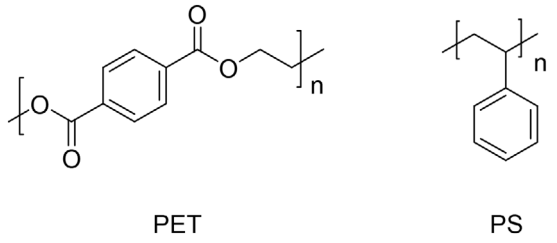


FIGURE 6 Chemical structures of poly(ethylene terephthalate) (PET) and polystyrene (PS).

dimethoxybenzene (OPV2)) is altered by strain.[22] The fluorescence spectra of these blends obtained in the absence of strain ($\varepsilon = 0$) show two peaks at 495 and 537 nm, attributed to the molecular dyes, and a peak at 650 nm attributed to excimers formed due to aggregation of the dyes. The fluorescence spectra (Figure 10) of unstretched films comprising OPV1 and OPV2 ($\varepsilon = 0\%$) show similar features and are dominated by excimer emission ($\lambda_{max} = 650$ nm). However, tensile deformation has a pronounced effect on the fluorescence emission spectra of both polymer/dye systems. At a strain of 0%, films of both compositions emit orange light; however, at a strain of 500%, they emit green light. This transformation is demonstrated by the fluorescence spectra (Figure 10) of the films obtained at strains of 0% and 500%, which show a significant change in the relative intensities of the emission attributed to the molecular dyes ($\lambda_{max} = 495$ and 537 nm) and their excimers ($\lambda_{max} = 650$ nm). The emission of the stretched blend films is mainly molecular dye emission because the tensile deformation associated with the strain leads to the breaking up of dye J-aggregates (excimers) and dye redistribution in the PE matrices. Thus, tensile deformation reduces excimer emission and increases molecular dye emission.

In an effort to modulate the optical performance of polymer/dye blends, Löwe and Weder[23] showed that the emission characteristics of blends of LLDPE and different OPV derivatives (OPV1 and 1,4-bis(α-cyano-4-methoxystyryl)benzene (OPV3)) are substantially altered by tensile deformation. The rapid quenching of homogeneous melts of these blends produces phase-separated morphologies in which the OPV derivatives form small aggregates; consequently, the mechanical deformation of these materials leads to a pronounced change in their emission characteristics.[24]

The melt processing and subsequent tensile deformation of blends based on different macromolecular dyes (such as poly(2,5-dialkoxy-*p*-phenyleneethynylene) derivatives (PPE1 and PPE2)) and PE (more specifically, LLDPE) can optimize the orientation of the conjugated macromolecular dyes. Experiments suggest that dye orientation and optical anisotropy are optimized by the introduction of an appropriate amount of dye with superior optical properties and the limitation of phase separation between the dye and the polymer matrix during film preparation.[25,26] These oriented blend films were found to be extremely stable; they could be stored under ambient conditions (exposed to air and light) for months without any noticeable change in their properties.[26]

4.2 | Effect of thermal solicitations

Thermal solicitation can also affect the optical performance of polymer/dye blends. Crenshaw et al.[27] showed that an increase in temperature above the glass transition temperature (T_g) of a blend based on OPV3 and PMMA (Figure 2) or poly(bisphenol A carbonate) (PC, Figure 11) leads to phase separation and the crystallization of the dye in the polymer matrix due to its aggregation by self-assembly. This behavior, determined by optical characterization, is revealed by some permanent and significant changes in the emission and absorption characteristics of the blend[27,28]; namely, shifts in the peaks in the emission or absorption spectra of the blends to longer wavelengths.

Furthermore, homogeneous blends based on LLDPE or PET (Figure 6) and OPV1 or OPV2 can be produced by conventional melt processing followed by quenching to below the T_g.[28] Indeed pristine quenched films (e.g., PETG/OPV1 films) display a yellow color characteristic of well-dispersed dye molecules. Subsequent thermal solicitations (e.g., annealing) at temperatures above the T_g (78°C) irreversibly change the color of the film to orange, indicating the aggregation of the dye (Figure 12). The rate of this color change increases with increasing annealing temperature. For instance, the self-assembly of the dye takes hours at 90°C (i.e., at a temperature just above the T_g) but only minutes at 120°C.

Donati et al.[29] also studied the effect of thermal solicitations on a blend based on 4,4′-bis(2-benzoxazolyl) stilbene (BBS) and poly(ethylene-*co*-norbornene) (P[E-*co*-NB], Figure 13) characterized by a copolymer T_g of approximately 64°C. Optical characterization showed that thermal solicitations at temperatures exceeding 64°C promote the aggregation of BBS molecules, leading to the formation of sub-micron, phase-separated chromophoric aggregates and to a permanent change in the optical properties (UV–Vis absorption and emission) of the blend film.[29]

Another study investigated a blend based on poly(1,-4-butylene succinate) (PBS, Figure 14) and BBS.[30] PBS has a T_g of approximately −34°C and a melting

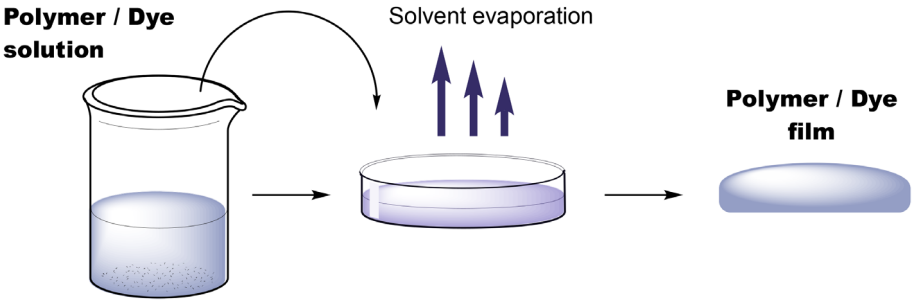


FIGURE 7 Polymer/dye blend preparation by film casting in an open mold. [Color figure can be viewed at wileyonlinelibrary.com]

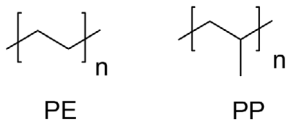


FIGURE 8 Chemical structures of polyethylene (PE) and polypropylene (PP).

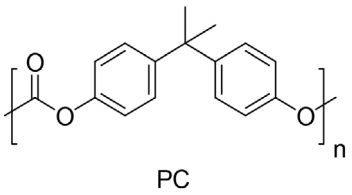


FIGURE 11 Chemical structure of poly(bisphenol A carbonate) (PC).

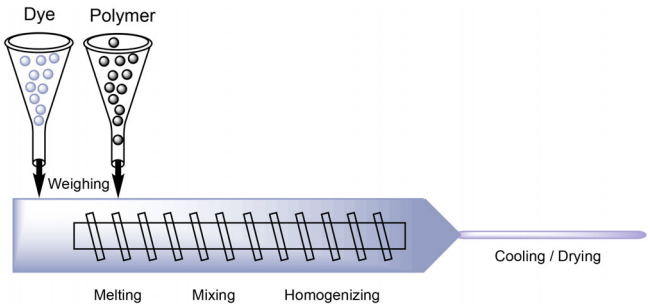


FIGURE 9 Polymer/dye blend preparation using a melt-extrusion process. [Color figure can be viewed at wileyonlinelibrary.com]

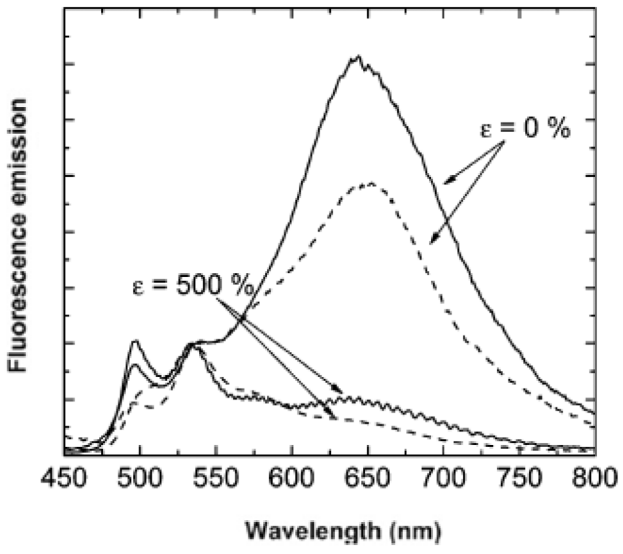


FIGURE 10 Fluorescence spectra of PE films containing OPV1 (solid lines) or OPV2 (dashed lines) at 0% and 500% strain. Reproduced with permission.[22] Copyright 2007, American Chemical Society

temperature of approximately 113°C; moreover, it is as processable as PE by film blowing, extrusion coating, and foaming for packaging applications. In addition, PBS is one of the most promising biodegradable polyester materials and, thus, potentially less environmentally hazardous than conventional plastic waste. Pucci et al.[30] showed that the luminescence behavior of PBS/BBS films can be controlled by thermally modifying BBS aggregation, and that the emission color of the polymer/dye blend changes with increasing annealing temperature (from 50 to 80°C).

The thermochromic properties of polymer films based on a perylene diimide dye and LLDPE have also been investigated.[31] Perylene dye (Pery4) was selected due to its well-known tendency to aggregate in a PE matrix, while semi-crystalline LLDPE was selected owing to its wide melting point range. The fluorescence intensity of the LLDPE/Pery4 films was studied at temperatures ranging from 30 to 70°C, revealing that a variation in the fluorescence intensity attributed to dye aggregates and molecules gives rise to an effective color change from red-violet at 30°C to yellow-green at 70°C. Moreover, once heating is suspended, the film rapidly recovers its original optical properties, those demonstrated at 30°C, suggesting that the phenomenon is completely reversible. These findings support the hypothesis that during heating at temperatures much higher than the T_g of the polymer (i.e., during polymer fusion), the high solubility of Pery4 in the polymer and the increased mobility of the macromolecules of LLDPE in its amorphous phase keep the low concentration of dye molecules apart to prevent their interaction. The observed thermochromic behavior of the blend is mostly ascribed to the ability of the dye to

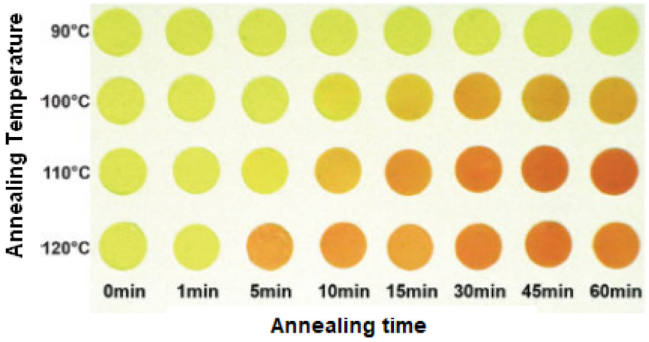
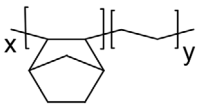


FIGURE 12 Images of quenched PET/OPV1 blends subjected to annealing at different temperatures. Reproduced with permission.[28] Copyright 2006, Wiley-VCH [Color figure can be viewed at wileyonlinelibrary.com]



P(E-*co*-NB)

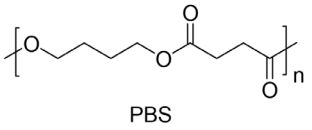
FIGURE 13 Chemical structure of poly(ethylene-*co*-norbornene) (P[E-*co*-NB]).

diffuse within the bulk polymer at high temperature (well above the T_g of the polymer).[31]

Another study investigated blends based on OPV2 and PMMA (Figure 2), poly(butyl methacrylate) (PBMA, Figure 15), or copolymers of methyl methacrylate (MMA) and butyl methacrylate (BMA) with a T_g ranging from 13 to 108°C (denoted as PAMx, where x is the T_g of the polymer/dye blend).[32]

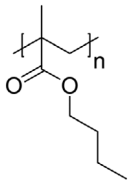
Annealing the blends at temperatures exceeding their T_gs result in dye aggregation, as manifested by their orange fluorescence characteristic of the emission of excimers, which form due to phase separation. As shown in Figure 16, all the films display green fluorescence at 0°C, characteristic of the emission of dye molecules, indicating that no aggregation has occurred. Heating the films to 30°C results in the emission of PAM23 changing color, the color of the emission of the other blends is unchanged. The subsequent sequential heating of the films to 60, 85, and 115°C reveals that their emission only changes color above a certain threshold temperature, which correlates with the T_g of each polymer blend.

Figure 16 shows another interesting feature of the PAM23 system. If annealed at temperatures significantly exceeding its T_g, the color of its emission reverts to that of the emission of the molecular dye. This phenomenon is attributed to two effects. First, the degree of aggregation of the dye is expected to be somewhat lower at elevated annealing temperatures due to its concomitant heightened solubility. Second, optical microscopy reveals that the return of the green fluorescence is accompanied by the development of large dye aggregates and that an associated self-quenching effect accounts for the development of the green color.



PBS

FIGURE 14 Chemical structure of poly(1,4-butylene succinate) (PBS).



PBMA

FIGURE 15 Chemical structure of poly(butyl methacrylate) (PBMA).

5 | EFFECT OF THE POLYMER MATRIX ON THE OPTICAL PERFORMANCE OF POLYMER/DYE BLENDS

The polymer in a polymer/dye blend also plays an important role in its optical performance. For instance, it must have an affinity for the dye to promote the dispersion of the dye molecules within the matrix. Accordingly, various studies have investigated the modification of the chemical structures of polymers to optimize dye dispersion. In addition, the crystallinity, oxygen permeability, and purity of polymers significantly impact the optical performance of polymer/dye blends.

5.1 | Effect of the polymer chemical structure

The chemical structure of a polymer affects the Stokes shift of a dye in the same way as low-molecular-weight solvents. For a given fluorescent dye molecule, the overlap of its absorption and fluorescent bands can be reduced by increasing the affinity of the polymer matrix for the dye. This can be achieved by changing the chemical structure of the polymer or by adding polar dopants.[33]

Scanning electron microscopy (SEM) images of the sections of films prepared by the compression molding of

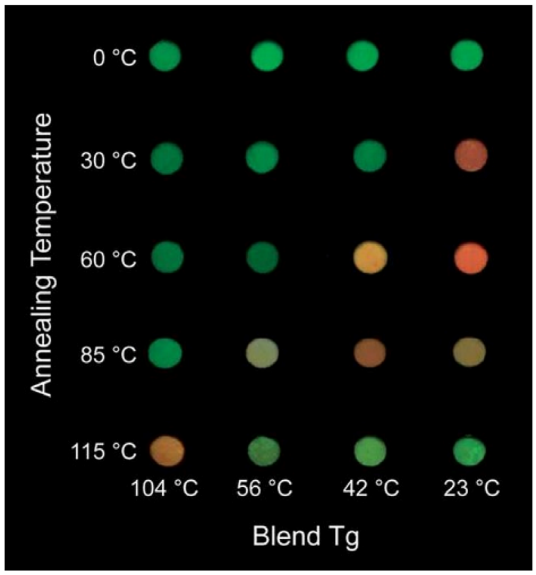


FIGURE 16 Images of quenched PAMx blends annealed for at least 15 h at various temperatures. Reproduced with permission.[32] Copyright 2007, Wiley-VCH [Color figure can be viewed at wileyonlinelibrary.com]

melt-processed blends based on PE or poly(ethylene-*co*-vinyl acetate) (PEVA, Figure 17) and TER1 reveal that the distribution of the dye within the polymer bulk, and thereby optical performance, is improved by the presence of polar groups (vinyl acetate (VA)) on the polymer.[21]

Marin et al.[34] studied the optical properties of blends of azomethine dye and PMMA (Figure 2), polysulfone (PSU, Figure 18), or chitosan (Figure 18). The color of the emitted light was found to vary from yellowish green to greenish blue, depending on the polymer structure. PSU was found best able to preserve the optical properties of the azomethine dye which is attributed to the structural affinity between the PSU matrix and the azomethine dye which both feature aromatic rings.

Slark et al.[35] investigated blends based on a trihydroxyl dye and PS (Figure 6), PE (Figure 8), or poly(2-vinyl pyridine) (PVP, Figure 19) which are characterized by weak (π-cloud–hydroxyl), moderate (carboxyl–hydroxyl), and strong (amine–hydroxyl) hydrogen bonding interactions, respectively. The infrared spectrum of the weakly interacting PS/trihydroxyl dye system indicates significant dye–dye interaction (self-association) and minimal polymer–dye interaction. Additionally, the dye–dye interaction is stronger than the polymer–dye interaction as indicated by the comparatively low peak frequency associated with the IR absorption of the former. The IR spectrum of the moderately interacting PE/trihydroxyl dye system indicates that dye–dye interaction dominates but polymer–dye interaction is also evident, as evidenced by a pronounced shoulder. The dye–dye interaction is also stronger than the

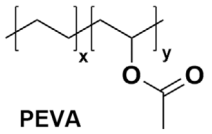


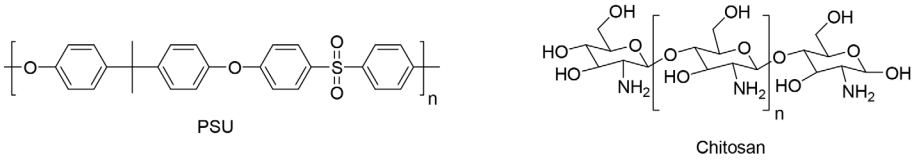
FIGURE 17 Chemical structure of poly(ethylene-*co*-vinyl acetate) (PEVA).

polymer–dye interaction, since the peak frequency associated with the IR absorption of the former is lower than that associated with the IR absorption of the latter. In contrast, the IR spectrum of the strongly interacting PVP/trihydroxyl dye system indicates that polymer–dye interaction dominates; the main peak observed is attributed to IR absorption associated with polymer–dye interaction while the observed shoulder is attributed to IR absorption associated with dye–dye interaction. The strength of the intermolecular polymer–dye interaction in the blends increases with increasing electron-donating strength of the polymer, as demonstrated by the shift in the associated IR peaks to lower frequencies. The strength of intermolecular dye–dye interaction (self-association) in the blends correspondingly decreases, as demonstrated by the shift in the associated IR peaks to higher frequencies. The effect of the environment on polymer–dye interaction is considerably greater than its effect on dye–dye interaction, with the variation in the latter being just outside the experimental error.

5.2 | Effect of polymer crystallinity

In addition to the chemical structure of a polymer, its crystallinity affects the optical performance of a corresponding polymer/dye blend. Crenshaw et al.[22] studied several blends based on OPV2 and PE with different polymer crystallinities, and showed that the rate of dye-aggregate formation increases with decreasing polymer crystallinity. This observation is consistent with the corresponding increase in amorphous polymer phase, dye mobility, and dye aggregation. In particular, a blend based on OPV2 and PE, with a degree of crystallinity of 9% (denoted as PE9), shows almost no emission characteristic of dye molecules, indicating that virtually all dye molecules are in an aggregated state. In fact, the fluorescence spectrum of PE9/OPV2 presents a single peak centered at 650 nm, characteristic of excimer emission (Figure 20). This result is consistent with the low crystallinity (high free volume) of PE9, which leads to the high mobility and aggregation of dye molecules, modifying the optical performance of the dye in the polymer/dye blend. The fluorescence emission spectra of PE/OPV2 blends with degrees of polymer crystallinity of 36%, 44%, 58%, and 66% (denoted as PE36, PE44, PE58, and PE66, respectively), show peaks, centered at 495 and 537 nm

FIGURE 18 Chemical structures of polysulfone (PSU) and chitosan.



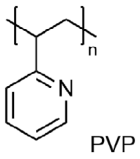


FIGURE 19 Chemical structure of poly(2-vinyl pyridine) (PVP).

(Figure 20), characteristic of the emission of dye molecules. This is consistent with the higher crystallinity (lower free volume) of these materials, which prevents the complete aggregation of dye molecules. Interestingly, the intensity ratios of the dye emission to excimer emission for the PE36/OPV2, PE44/OPV2, PE58/OPV2, and PE66/OPV2 blends are similar, suggesting that the differences in their polymer crystallinities do not significantly affect the fraction of dye molecules incorporated within their PE matrices (Figure 20).

In summary, the extent of the color change of polymer/dye blends is significantly affected by the crystallinity of the polymer matrix, thus, the optical properties of polymer/dye blends can be tuned by modifying polymer crystallinity.

5.3 | Effect of oxygen permeability

A recent study has shown that PMMA (Figure 2) is the most suitable host material for perylene dyes, Pery2 and Pery3, because it prevents the penetration of oxygen and subsequent chemical photodegradation of the dyes (as discussed in Section 2). Cerdan et al.[36] observed that perylene dyes mainly suffer from chemical photodegradation and their photostability increases with decreasing oxygen exposure. They compared the degradation of Pery2 and Pery3 in different host materials, such as PMMA (Figure 2) and four fluorinated polyimides (FPIs; Figure 21), using amplified spontaneous emission (ASE). The degradation of the dyes in the blends based on the FPIs is quite similar, whereas the degradation of the dyes in the blends based on PMMA is significantly less; this is indicated by the high ASE intensity of the blends based on PMMA relative to that of the blends based on the FPIs after optical pumping. These results indicate PMMA is less permeable by oxygen than the FPIs.

A study on poly(vinyl alcohol) (PVOH, Figure 22) has shown that it is a promising candidate material for multilayer encapsulating foils for polymer solar cells composed

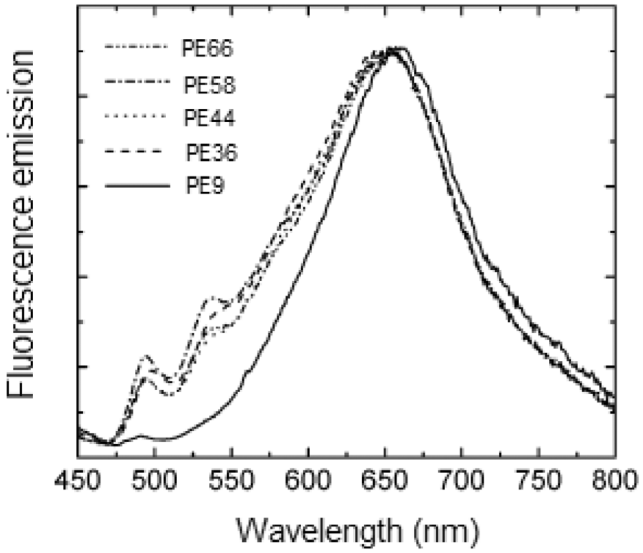
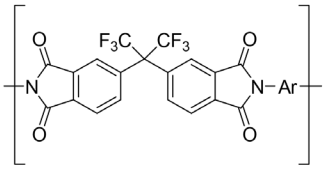


FIGURE 20 Fluorescence spectra of PE/OPV2 blends with different polymer crystallinities. Adapted figure with permission.[22] Copyright 2007, American Chemical Society

of polymer/dye blends, as it is an excellent oxygen barrier.[37] PVOH films have been subjected to photo and thermal aging cycles to thoroughly investigate their photostability, these aging cycles combine irradiation at wavelengths exceeding 300 nm and heating at 60°C. It was found that PVOH resists thermal oxidation even after 7000 h of heating; however, photooxidation causes a progressive reduction in its transmittance. The photooxidation of PVOH typically produces carboxylic acids on the polymer backbone and low-molecular-weight volatile fragments such as acetic, oxalic, and malonic acids. However, PVOH appears to be resistant to photo-induced degradation in the absence of oxygen.

5.4 | Effect of impurities in the polymer matrix

Earp et al.[38] studied yellow perylene (a Pery2 derivative) dispersed in a liquid matrix in order to introduce and evaluate the effect of impurities (ketones) on the optical performance of the dye. Liquid matrices containing MMA, methyl isobutyrate, methyl pyruvate, or acetol (Figure 23) were investigated. The liquid matrix/Pery2 blends were irradiated using a fiber-optic illuminator, and after each exposure period, their absorption was measured to determine the photo-induced change in the optical properties of



FPI

Ar:

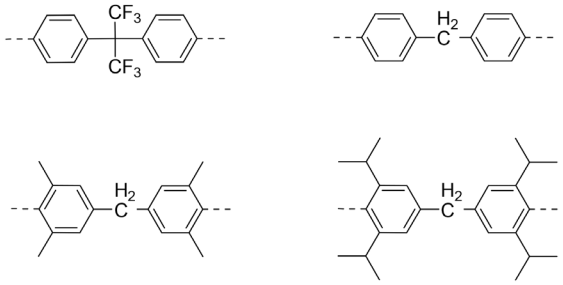
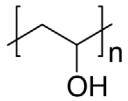


FIGURE 21 Chemical structures of fluorinated polyimides (FPIs).



PVOH

FIGURE 22 Chemical structure of poly(vinyl alcohol) (PVOH).

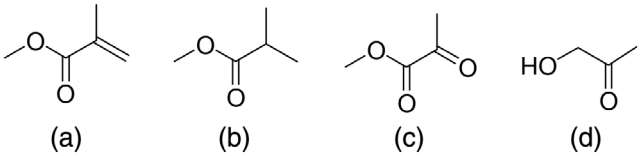


FIGURE 23 Chemical structures of (a) methyl methacrylate, (b) methyl isobutyrate, (c) methyl pyruvate, and (d) acetol.

Pery2. It is clear from the results that the presence of ketones in the liquid matrices affects the rate of dye degradation. Ketones enhance the photodegradation of perylene dyes in solution and the rate of photodegradation increases with increasing ketone concentration. Among the ketones tested, methyl pyruvate, which is an impurity found in MMA, is the greatest accelerator of photodegradation and particularly deleterious to dye photostability. However, the distillation of MMA prior to PMMA/dye blend preparation may prevent the introduction of impurities and the associated photodegradation of the dye species. An observed improvement in the photostability of the dye in a liquid matrix containing MMA is partly attributed to the removal of ketone impurities.[38]

In summary, the chemical structure of the polymer matrix must have an affinity for that of the dye to achieve optimal dye dispersion within the polymer matrix. Moreover, the polymer should ideally be highly crystalline to limit dye mobility and free of impurities to limit dye degradation. Finally, to ensure the long-term optical performance of polymer/dye blends, it is necessary to use a polymer that is a good oxygen barrier to delay dye degradation.

6 | EFFECT OF THE DYE ON THE OPTICAL PERFORMANCE OF POLYMER/DYE BLENDS

Two important parameters of polymer/dye blends, related to the dye, can affect their optical performance, namely the concentration and chemical structure of the dye.

6.1 | Effect of the concentration of the dye

Luzzati et al.[39] studied the effect of the concentration of poly(3-octylthiophene) (POT) on the optical performance of PE/POT blends. At low concentrations (<1 wt%), POT is dispersed in the PE matrix, and at high concentrations (>1 wt%), POT is aggregated, as determined by photoluminescence spectroscopy. The peaks in the photoluminescence spectra of the blends shift to lower energies with increasing POT concentration (Figure 24).

Pucci et al.[30,40] performed two studies on the effect of BBS concentration on the optical properties of PBS/BBS (Figure 14) and PP/BBS (Figure 8) blends. At BBS concentrations exceeding 0.05 and 0.2 wt%, the luminescence of PBS/BBS and PP/BBS films, respectively, changes from blue to green. This color change suggests the formation of excimers, which is promoted by π–π interaction between the conjugated planar structures of the dye. The original blue color of the films, corresponding to isolated BBS molecules, can be restored by tensile deformation, which promotes the breaking of the J-aggregates responsible for the formation of excimers and the green color.[30,40]

Two other investigations on the effect of dye concentration on the optical properties of polymer/dye blends have been carried out using perylene dye (Pery5) and PE. The tendency of the chiral Pery5 molecules to form supramolecular aggregates was revealed by dispersing the dye into a completely apolar PE matrix (LLDPE) at moderate concentrations (0.01–0.1 wt%) and investigating the obtained blends by fluorescence spectroscopy.[41] The fluorescence spectrum of a blend containing isolated Pery5 is characterized by two main peaks at 525 and 565 nm (Pery5 concentration: 0.01 wt%), while that of a blend containing Pery5 J-aggregates is characterized by a

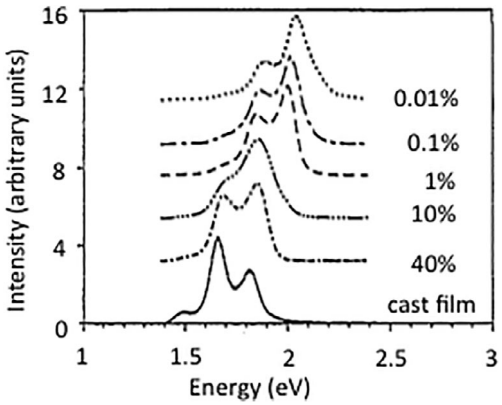


FIGURE 24 Photoluminescence spectra of PE/POT blends with different concentrations (wt%) of POT (excitation energy: 2.41 eV). Reproduced with permission.[39] Copyright 1996, Elsevier

broad and unstructured peak at 620–630 nm (Pery5 concentration: 0.1 wt%). Carlotti et al.(31) studied the same system (LLDPE/Pery5) and obtained similar results for Pery5 concentrations ranging from 0.01 to 0.5 wt%.

Donati et al.[42] studied blends based on perylene dye (Pery6) and LLDPE. They found that dye aggregation is favored at high Pery6 concentrations (≥0.05 wt%). The emission of the blend films changes from red to green with increasing Pery6 concentration. Here again, the emission spectra of the polymer/dye blends show a decrease in the intensities of the molecular emission peaks of the dye at 530 and 570 nm and an increase in the intensity of its aggregate emission peak at 620 nm.

It has also been shown that the optical properties of PE films containing a macromolecular dye (poly[(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] with cyano groups (PPE3)) can be modulated by controlling the dye concentration.[43] Indeed, LLDPE films with low PPE3 concentrations (0.02–0.05 wt%) exhibit optical properties very similar to those reported for PPE3 in solvents (THF, for example); their emission spectra reflect peaks centered at approximately 450 nm. In contrast, the emission spectra of LLDPE films containing more than 0.1 wt% PPE3 show a new peak at approximately 480 nm, the intensity of which markedly exceeds that of the peak attributed to the emission of isolated PPE3 (450 nm). The green light emitted by these films is attributed to high concentrations of dye aggregates.

Embaye et al.[44] showed that, at low concentrations, orange dye (DO11) dispersed in PMMA (Figure 2) does not aggregate; however, irreversible photodegradation does occur. This implies that the photodegradation process (as discussed in Section 2) is independent of DO11 aggregation and more pronounced at low DO11 concentrations.[44]

Another two recent studies investigated polymer/dye blends featuring PMMA (Figure 2). In the first study, El-Gamal et al.[45] prepared brilliant cresyl blue dye (BCB)–doped PMMA films with different concentrations of BCB, ranging from 0.2 to 2 wt%, by solution casting. They revealed that BCB is soluble in the PMMA matrix; however, the introduction of 2 wt% BCB reduces the crystallinity of PMMA from 32 to 11.9%. A similar decrease is observed in the transmittance of PMMA from 91.2 to 71.2%. These results show the effect of BCB concentration on the optical properties of PMMA/BCB blends. In the second study, Gao et al.[46] investigated CS2TCHO dye–doped PMMA films with different dye concentrations (0.2, 0.5, and 1.0 wt%), prepared from dichloromethane solution. The maxima in the emission spectra of the films shift to longer wavelengths with increasing dye concentration, due to re-absorption effects. The transmittance of the film with the highest dye concentration (1.0 wt%) is much lower than those of the other films. This is due to the limited solubility of the dye in the PMMA matrix, which causes the formation of aggregates.

6.2 | Effect of the chemical structure of the dye

The second important parameter of a polymer/dye blend, related to the dye, is the chemical structure of the dye. In this section, the features of the chemical structure of a dye that can be modified to tune its optical properties are discussed.

An important feature of a dye is its conjugated aromatic core structure, which is the source of its optical properties. A study investigating the effect of the length of the conjugated aromatic core of dyes (OPV2 and OPV4) dispersed in PET (Figure 6) found that dyes with longer rigid cores are slower to aggregate due to their limited mobility in the polymer matrix.[32] This limited mobility preserves the dispersion of the dyes in the polymer matrix and, concomitantly, optimizes the optical properties of the polymer/dye blends.

In addition to their conjugated aromatic cores, the covalently attached alkyl substituents of dyes can be modified to modulate the optical properties of polymer/dye blends. An investigation of terthiophenes, 5″-thiodecyl-2,2′:5′,2″-terthiophene (TER2) and 5″-thiooctadecyl-2,2′:5′,2″-terthiophene (TER3) featuring different alkyl substituents, $C_{10}H_{21}$ and $C_{18}H_{37}$, respectively, revealed that their dispersion in PE films is only partial, owing to the tendency of the polymer/dye blends to undergo phase separation (determined by thermal analysis). This behavior is attributed to the chemical structure of the substituted terthiophenes as the dispersion of terthiophenes with long alkyl substituents is not thermodynamically favorable[47]; phase separation increases with increasing length of the alkyl substituent. It is worth noting that the number of aliphatic chains does not play a significant role in the orientation of terthiophene

dyes. Indeed, the optical performance of a dye/polymer blend featuring an oligomeric terthiophene derivative, TER6, is comparable to that of polymer/dye blends featuring TER4 and TER5.[48]

Several studies have also investigated the effect of the branching of the alkyl substituents of dyes on their dispersion within a polymer matrix. One study compared the orientations of PPE1 and PPE2 with unbranched and branched side chains, respectively, in a UHMWPE matrix. The orientation of PPE2 with its branched side chains is superior to that of PPE1 due to steric effects. These results suggest linear side chains strongly interact with the PE matrix, resulting in poor dye orientation and optical performance.[26] Donati et al.[42] studied blends based on Pery6 or Pery7 and LLDPE, and found that more planar and less hindered Pery7 demonstrates a greater tendency to aggregate even at very low concentrations (0.01 wt%). Furthermore, in thin films, although the greater bulkiness of the side chains of PPE6 and PPE7, relative to that of the side chains of PPE4 and PPE5, does not prevent the formation of dye aggregates, it delays its onset.[49] The dye dispersion of a PE/TER7 blend, featuring a dye with a branched alkyl substituent, is also superior to that of a PE/TER4 blend, featuring a dye with a linear alkyl substituent. SEM micrographs of the surface and cross section of a PE/TER7 film do not show the presence of dye aggregates, unlike corresponding SEM micrographs of the surface and cross section of a PE/TER4 film.[50] Finally, owing to the branched alkoxy substituent of BPB2, LLDPE/BPB2 blends are generally optically homogeneous, unlike LLDPE/BPB1, LLDPE/BPB3, LLDPE/BPB4, and LLDPE/BPB5 blends.[51] However, in other matrices (e.g., UHMWPE), the degree of orientation of this dye is only modest.

In summary, the chemical structure of the dye of a polymer/dye blend is a significant determinant of its optical performance and must be strategically chosen. The mentioned studies demonstrate that the functionalization of a dye with branched alkyl chains and the lengthening of its aromatic core are effective strategies for improving the dispersion the dye in a polymer matrix and delaying its aggregation. Dye concentration also plays a significant role in modulating the optical performance of polymer/dye blends.

7 | CONCLUSIONS

Various polymer/dye combinations can be obtained using a procedure that enables the physical dispersion of dyes in polymer matrices. These preparation procedures partly determine the distribution of dyes in polymer matrices and can be used to modulate the optical performance of polymer/dye blends. However, the dyes in polymer/dye blends degrade regardless of the blend preparation procedure or selected dye or polymer matrix. Oxygen and UV light exposure degrade dyes and produce radical species that affect the optical performance of polymer/dye blends; however, filtering the UV light or reducing the oxygen permeability of the host matrix can limit this degradation.

Various approaches to the optimization of the optical performance and photostability of polymer/dye blends have been explored. The first approach involves the selection of an appropriate preparation procedure. Melt processing is considered more effective than film casting for producing polymer/dye blends with optimal dye distribution as the shearing forces associated with the process break up any dye aggregates than form. Moreover, prepared polymer/dye blends should not be subjected to thermal solicitations at temperatures exceeding their T_gs to preserve their optical performance. The second approach involves the selection of an appropriate polymer matrix. Dye dispersion and optical performance are optimized if the polymer matrix has a strong affinity for the dye in terms of its chemical structure. In addition, high crystallinity limits the mobility of a dye and its aggregation while low oxygen permeability limits the oxygen exposure of the dye. PMMA is a popular polymer for polymer/dye blends due to its low oxygen permeability. Note that the impurities found in some polymer matrices must also be considered as they can affect the optical performance of polymer/dye blends. Finally, the third approach involves the selection of an appropriate dye, which is the source of the optical properties of a polymer/dye blend. The chemical structure of a dye affects its dispersion in a polymer matrix. It has been shown that a long aromatic rigid core limits the mobility of a dye and its aggregation in a polymer matrix while the branching of the alkyl substituents of a dye promotes its dispersion in a polymer matrix. In addition, dye concentration is a significant determinant of the optical performance of a polymer/dye blend. Indeed, above a certain dye concentration, the optical properties of a polymer/dye blend can change completely. All these parameters should the considered in the development of dye-containing polymers that demonstrate optimal optical performance for specific applications.

AUTHOR CONTRIBUTIONS

Maud Plouzeau: Conceptualization (supporting); data curation (equal); formal analysis (equal); investigation (lead); validation (equal); writing – original draft (lead). **Sandie Piogé:** Data curation (lead); formal analysis (equal); investigation (lead); methodology (lead); supervision (equal); validation (equal); writing – review and editing (equal). **Frédéric Peilleron:** Funding acquisition (equal); investigation (supporting); methodology (supporting); project administration (supporting); resources (equal); supervision (equal); writing – review and editing (supporting). **Laurent Fontaine:** Funding acquisition

(lead); investigation (equal); methodology (lead); project administration (lead); resources (lead); supervision (lead); validation (lead); writing – review and editing (lead). **Sagrario Pascual:** Conceptualization (lead); data curation (equal); formal analysis (equal); investigation (lead); methodology (lead); project administration (supporting); supervision (lead); validation (lead); writing – review & editing (lead).

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