Polypropylene/bis(benzoxazolyl)stilbene mechanochromic blends, an attractive feature for colorimetric strain detection

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Bis(benzoxazolyl)stilbene (BBS) incorporation into polypropylene (PP) host leads to a mechanochromic polymer composite blend whose color can change (from green to blue) under UV excitation with mechanical strain. The aim of this study is to prove the feasibility of mechanical strain control by colorimetry on such a mechanochromic blend and to understand the mechanical, chemical and radiative behaviors differences between stretched and unstretched parts. The first part, dedicated to mechanical and radiative characterizations, leads to the choice of the dye concentration of 1%wt, where mechanical properties are preserved and photoluminescence output is optimized. Then, a colorimetric measurement system is set-up and show remarkable potential for strain evaluation by marking the necking initiation and the beginning of the first plastic flow. Moreover, the change in luminescence emission is concomitant with mechanical necking and continues during the first plastic flow. Secondly, the RGB image treatment analysis developed here involves the calculation of the image ratio of the green channel over the blue one. It promises remarkable capacities to detect and localize the very beginning of mechanical break on polymeric 2D structures.

1. Introduction

Development of new materials that can give information about their environment and operating conditions has been on the rise over the last few years. In this context, numerous studies have been carried out to develop systems able to be optically responsive to mechanical stimuli [1–3]. This phenomenon is called mechanochromism.

A lot of systems can be developed to obtain mechanochromism phenomenon, such as plasmonics [4,5], photonics [6,7], or photo-elastomers [8] systems. Burel et al. created strain sensors using micrometer-size capsules [4]. These capsules are made of packed gold nanoparticules embedded in a spherical silica crust. They can be recovered into polymer film. When this film is stretched, the color change due to plasmonics effect. To make mechanochormic sensors based on plasmonic effect is difficult. For this reason, Minati et al. optimized the process to deposit gold nanoparticles on a surface [5]. Chan et al. described different photonic gels which can be used to create mechanochromic sensors [6]. Photonic gels consist of periodic dielectric structures with different refractive index. Several strategies exist to create this kind of gel, but the mechanochromic properties are not always efficient [6]. Cho et al. used the photonic properties of the inverse opal to develop polymeric mechanochronic sensors to detect 17.6–20.4 MPa strain [7]. Photosensitive elastomers can be used to develop mechanochromic sensors [8]. This kind of material has periodic refractive index variations, which change when the material is stretched or compressed. Photo-elastomers are soft and permit measurement of strain in the surface of soft tissue, such as skin [8]. Wintzheimer et al. developed a new mechanochromic system based on two different com-ponents, a luminescence-quenching core material coated with silica nanoparticles, surrounded by raspberry-like nanostructured silica par-ticles [9]. During the stretching, the contact with these two components provoked the luminescent change of the system. To use diffraction of light is possible by integrating a diffraction grid in a soft structure, as in soft opto-magnetic actuators [10]. A recent systematic literature review shows that soft crystals can have mechanochromic properties, but this kind of properties are not yet used to develop strain detection [11].

In this work, due to the future use of the developed strain detection sensor, a strain sensor was developed based on the dispersion of

chromophore dyes into the amorphous phase of a semi-crystalline polymer matrix host [12]. Effectively, due to their strong aromaticity, photoluminescent dye molecules have the capacity, above a concentration threshold, to create electronic interactions such as π-bonding among aromatic cycles [13]. π-stacking leads to the formation of metastable molecular assemblies, called excimers [14,15]. These molecular structures have a lower potential energy than dye molecules themselves [16]. Hence, under UV light excitation, excimer emission wavelengths are distinct and at a higher wavelength than the ones of dissociated molecules [14]. Under mechanical strain, a structural modification of the dye molecules architecture can occur, which induces a disaggregation process of the dye assemblies [17]. This structural modification leads to a change in the relative intensity between the excimer and isolated dye molecules absorption/emissions, from an excimer dominated absorption/emission to a dye dominated absorp-tion/emission, causing a perceptible color variation [18]. Because of the straightforward link that could be established between color changes and the strain sustained by the material, mechanochromic polymers thus holds a promising potential for the development of self-diagnostic products, for example in safety equipment such as security helmets or harnesses.

Mechanochromic behavior can be obtained from polymer composites with different kind of additives such as cyano-derivatives [19–23], bis(benzoxazolyl)stilbene [14–28], perylene and its derivatives [29,30], polymeric dyes [31–33] and also organometallic complex [34,35]. All these additives are high-aromatic fluorophore dyes which may exhibit a variation in their absorption or emission properties when molecules are aggregated into supramolecular assemblies [36]. The phenomenon of aggregation then depends on the dye's self-assembling characteristics and miscibility within the polymer host matrix [37]. Bis(benzoxazolyl) stilbene (BBS) derivative displays a significative mechanochromism shift from green to blue emission upon disaggregating. Contrary to CN-additives or highly aromatic molecules such as perylene, BBS com-plies with the REACH toxicity directives [38], which makes it a good candidate to functionalize widespread semi-crystalline polymers for end-user products and applications.

Regarding the optical detection system, the change in the optical responsiveness of mechanochromic materials requires the use of a photonic excitation and detection system, mainly in the ultraviolet or visible spectral bands. The measurement is then performed by spectrometry, either by measuring the absorption or the photoluminescence spectrum [39–43]. Once the spectrum is acquired, the wavelength which maximizes the intensity ratio of the excimer (I_E) emission divided by the monomer (I_M) emission (I_E/I_M) is computed. The selection of this wavelength determines the final sensitivity of the stress/strain mea-surement by the mechanochromic sensor. An alternative method is to compute the decay time at one wavelength [44–47], which also varies according to the disaggregation state of the excimer. To enhance the sensitivity further, Pucci et al. [48–50] proposed to study the polarized properties of the fluorescence, and to compute the dichroic ratio for each elongation of the specimen. Pucci et al. have also used fluorescence imaging with a confocal microscope to investigate the morphology of BBS aggregates in PLA-PBS blends [51]. To go further, Cellini et al. [52, 53] have coupled the visualization of stressed specimen based on TPU-BSS blends by a color camera, enabling the evaluation of the spatial range of the elongation. However, few studies mention the possibility of monitoring the strain field online, using a color camera for a quantita-tive measurement.

The aim of this article is the development of a full field optical strain detection and/or measurement system based on the mechanochromic behavior of a polypropylene/BBS blend. Polypropylene was chosen as the host material because it is a widely used polymer, easy to process, which is not fluorescent under UV excitation. The contribution of this paper is to propose both materials and methods for full field strain detection on 2D polymeric structures. To do so, the mechanical and photoluminescence characterizations conducted on a system which optimize the mechanochromic response to mechanical stimulus, while preserving mechanical properties of the host. A PP host blended to BBS at 1 wt% enables to reach this compromise. Alternatively, the colorimetric method has to spatially detect the beginning of mechanical damage and be insensitive to experimental conditions (angle, distance…). A choice has been made to exploit RGB cameras and to compute the image ratio of the green over blue channels.

Regarding the organization of the paper, the first part focuses on the characterization of physico-chemical properties of BBS dyes dispersed in a polypropylene host at several concentration, for the selection of the most appropriate concentration for mechanochromic applications. The second part deals with the instrumentation for a full-field measurement system of the strain by mechanochromy with a simple color camera.

2. Materials and methods

2.1. Materials

The material developed in this study is composed of a dispersion of bis(benzoxazolyl)stilbene (BBS) dye into a thermoplastic host matrix of polypropylene (PP). PP511A® polypropylene, specifically designed for extrusion applications, was purchased from Sabic (Riyad, Saudi Arabia). Bright 200 BBS was purchased from MPI Chemie BV (Houten, Netherlands), in the form of a pale-yellow powder. Their transformation temperatures, detailed in Table 1, were measured by Differential Scan-ning Calorimetry (Perkin Elmer, DSC 8000) with a heating rate of 20 °C per minute.

2.2. Sample preparation

The samples investigated in this study were six 200–300 μm thick PP/BBS films cut into a normalized tensile test specimen shape according to standard ISO527–1:2019 (region of interest (ROI) dimensions: 20 × 4 mm^2) at six different BBS concentrations (0.02, 0.2, 0.5, 1, 2 and 5 wt% of BBS). These concentrations were chosen according to the discussion of Pucci et al., [44] study, in which it was shown that the mechanochromic phenomena disappear if the BBS concentration is too high. A concentration of 5 wt% was selected as an upper limit, lower than in reference [44], as a good compromise between luminescence intensity output and alteration of the host matrix's mechanical properties.

PP/BBS blends were prepared in a twin-screw extruder at 210 °C. Resulting compounds were compressed into 200–300 μm thick films with a hydraulic press at 30 bars and 220 °C for 2 min, then cooled to room temperature.

2.3. Tensile testing

Tensile tests on all six specimens were carried out with an Instron 5942 (Elancourt, France) tensile test machine equipped with a 500 N load cell, at a strain rate of 5 mm/min, as per the recommendation of standard ISO527–1:2019. Engineering stress are the ratio between the load obtained by the load cell and the cross-section of the specimen (4 × 0.25 mm^2). Engineering strains are calculated by this equation:

$$\varepsilon = \frac{l - l_0}{l_0}$$

with l_0, the initial length of the region of interest (20 mm) and l, the

Table 1
Characteristics temperatures of each component of the blend.

Material	Glass transition temperature (°C)	Melting temperature (°C)	Degradation temperature (°C)
PP	-10	160	-
BBS	-	355–360	380

crosshead displacement.

2.4. Characterization of photoluminescence properties

Spectral changes induced by BBS concentration and by straining (blue-to-green and green-to-blue reciprocally), fluorescence spectra of the six films under UV excitation of a Hg-vapor lamp (350–405 nm, TL Mini Blacklight Blue, 6 Watts from Philips, Netherlands) were measured in the 400–730 nm range with a spectrometer USB2000 + (Ocean Op-tics, Netherlands), before and after straining (tensile test). A schematic view of the experiment is presented in Fig. 1. Images of the fluorescence emitting samples under UV excitation during tensile tests were also recorded using an 8-bit, 1.45 Mpx Bayer pattern type color camera (Pike, F-145 C from Allied Vision, Stadtroda, Germany) equipped with a 16 mm fixed objective (Fujinon), at an acquisition frequency of 1 Hz.

3. Results and discussion

3.1. Blend composition for a non-intrusive mechanochromic effect

The additive incorporated into the host matrix must be non-intrusive with regards to mechanical properties. This section investigates the additive concentration optimization for the maximization of both mechanochromic dynamic range (initial ratio of excimers emission vs. monomer emission) and the fluorescence intensity output, while limiting detrimental impacts on the tensile properties of PP.

3.1.1. Effect of additive concentration on tensile properties of PP

Fig. 2 shows the engineering stress and strain curves obtained from the tensile test carried out on the six specimens doped at various BBS concentrations. The maximum stress and Young's modulus extracted from the curves are detailed in Table 2. The tensile behavior of PP/BBS blends shows a typical trend. The polymer has a very little elastic linear region (strain less than 5%) compared to the elasto-plastic region. In the latter, there are three phases: (i) the stress decreases, corresponding to the necking activation, (ii) the stress reaches a plateau and (iii) the stress increases again until the rupture. The phase (iii) is not shown in Fig. 2, because this phase appeared randomly dispersed between specimens, even for the same BBS concentration. It can be noticed that contrary to specimens with a BBS concentration of 1 % or lower, the specimens doped at 2 wt% and 5 wt% exhibit a break almost immediately after the striction, i.e., do not exhibit a plastic flow plateau. This behavior is more marked at 5 wt% than at 2 wt%. This suggests that BBS additions of 2 wt % and above lead to a limitation of the plastic flowability of the polymer, and potentially to a more brittle behavior.

The relative stress is defined as the maximum stress in the necking region (phase *(i)*) divided by the maximum stress for PP without BBS. This relative stress is represented in Table 2 as a function of the BBS concentration. Maximum stress always increased between 12 % and 36 % with BBS additions, although no clear trend was noted. The highest increase is achieved with 0.2 wt% addition (+36 %), the lowest with

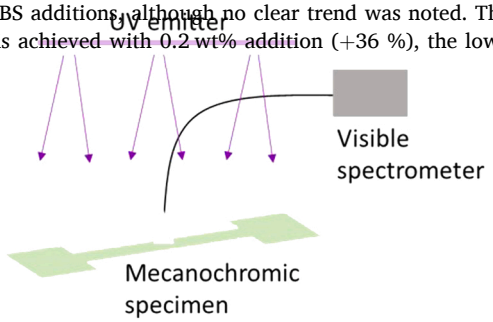

Fig. 1. Schematic view of the photoluminescence characterization system.

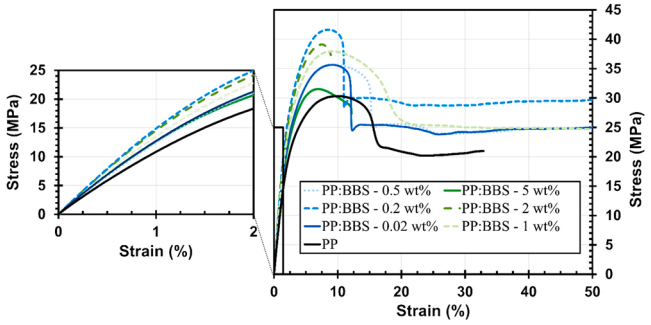

Fig. 2. Stress/strain curves for of PP/BBS films for several BBS concentration (0.02–5 wt%).

Table 2
Relative stress versus dye concentration.

BBS concentration	Ref	0.02 %	0.2 %	0.5 %	1 %	2 %	5 %
Maximum stress (MPa)	30.05	35.89	40.95	36.15	36.60	39.73	33.63
Relative maximum stress	1.00	1.19	1.36	1.20	1.22	1.32	1.12
Young's Modulus (MPa)	11.80	13.87	15.99	13.45	14.75	15.95	13.92
Relative Young's Modulus	1.00	1.18	1.36	1.14	1.25	1.35	1.18

5 wt% additions (+12 %). As for maximum stress, BBS added to PP increases the Young's modulus, although again no statistically significative trend was observed. The highest Young's modulus increase was observed for 0.2 wt% BBS addition (+36 %), the lowest for 0.5 wt% BBS addition (+14 %). This trend is verified by other studies [54,55]. Indeed, adding an additive increases the Young's modulus of the formed polymer.

To summarize, dye additions increase the maximum stress and the Young's modulus, but no significant trend is observed. However, additions of 2 wt% and higher seems to lead to a significant reduction of the ductility of the PP, with potentially more brittle behavior (limited plastic flow after the onset of striction).

3.1.2. Effect of the additive concentration on the photoluminescence properties

The mechanochromism induced by BBS is characterized by a change of emission color from yellow-green (dominated by radiative relaxation of excimers formed in excited BBS aggregates) to blue (radiative relax-ation of disaggregated BBS monomers), which is clearly perceived with the naked eye or a color camera. The photoluminescence spectra ob-tained for each concentration are detailed in Fig. 3, with a photo-luminescence image of each specimen.

At low concentration (<0.02 wt%), the typical structured blue emissions from BBS monomer are dominant (four emission bands are observed at 407, 434, 459 and 494 nm) [56]. The yellow-green unstructured emission of excimer centered around 505 nm appears at 0.2 wt%. As the concentration increases from 0.2 wt% to 5 wt%, the excimer emission becomes predominant over the monomer's ones (70 % of the total emissions at 0.2 wt% versus 91 % of the total emissions at 5 wt%). This results in a gradual perceived spectral shift from blue to green-yellow when observing the samples excited by the UV lamp, as illustrated in the right inset in Fig. 6. This image also illustrates that concentration as low as 0.02 wt% produces a bright luminescence which is clearly perceptible. Throughout the color change, the absolute total intensity emitted by the blend was increased 18 fold with BBS

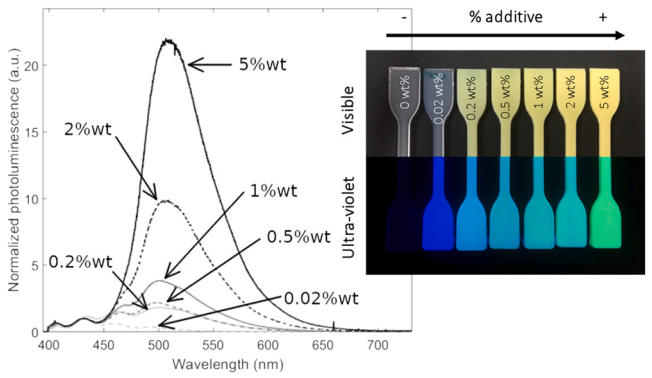

Fig. 3. Evolution of photoluminescence spectra normalized at 430 nm for PP/BBS films at several BBS concentration (0.02–5 wt%).

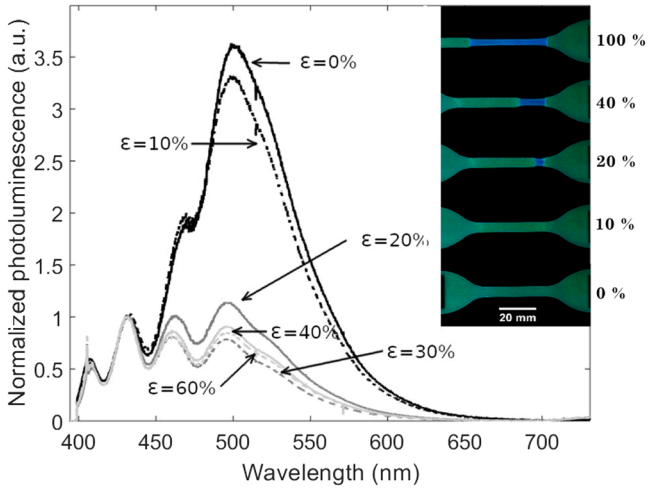

Fig. 4. Photoluminescence spectra (normalized at 430 nm) of the specimen in the stretched area for several strains and color images of the stretched specimen (1 wt% PP/BBS film).

concentration increasing from 0.02 wt% to 5 wt%, as a result of both the increase of the population of luminescent center and the strongest emission from the increasing number of excimers.

At 0.5 wt%, the color change from blue to green appears to be already quite marked. A small redshift of the excimer's emission peak is also noticed with increasing BBS concentration (from 494 nm at 0.2 wt % to 507 nm at 5 wt% for the central emission wavelength), which lead to a slightly more yellow-green color in the 5 wt% sample. This redshift supports the assumption that the new luminescence contribution has shifted from an emission of BBS isolated molecules to an emission of aggregated excimer-type arrangement [56].

As expected, the excimers formation is closely linked to an increase of the amount of BBS dyes, which promotes molecule aggregation and intermolecular interactions such as π-stacking [39,45,57,58]. At 0.02 wt %, BBS monomer density is low, hence excited molecules exist pre-dominantly as free monomers, decaying to ground state before they could interact with an unexcited monomer to form an excimer when photoexcited. At higher concentration (> 0.2 wt%), the formation of excimer under photoexcitation is promoted by the higher monomer density and their tendency to aggregate, driven mostly by the weak, non-covalent intermolecular attraction between aromatic rings coming from π-π molecular overlaps. The increase in total photoluminescence can be estimated integrating each spectrum over the wavelength. The ratio of this integral at the highest concentration over the one at the lowest concentration is equal to 20, emphasizing the wide photo-luminescence dynamics enabled by the concentration adjustment.

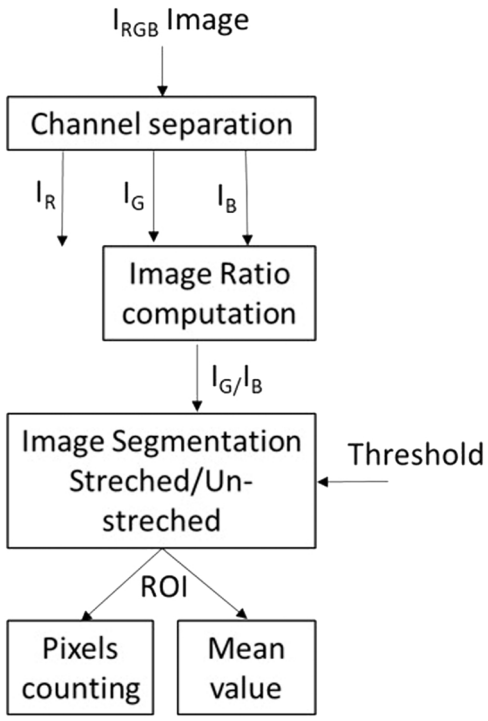

Fig. 5. Synoptic scheme of the image treatment procedure.

3.1.3. Conclusions on the effect of dye concentration on the mechanochromic behavior of PP/BBS

Results of the previous sections demonstrate that the BBS dye concentration impacts the mechanochromic behavior of PP/BBS blend. Nevertheless, there are other parameters of influence. Effectively, different studies have shown that mechanochromic effect may be influenced by three parameters: dye aggregate size, polymer host crystallinity and strain rate [59,60].

To conclude about the mechanochromic phenomena of the PP/BBS blend, the optimal wavelength for its detection is around 505 nm, and both the intensity output and the ratio between monomer and excimer emissions (potential dynamic range of the mechanochromism effect) are maximum at the highest additive concentration investigated (5 wt%) (see Fig. 3). However, tensile tests showed that high concentrations (>1 wt%) could lead to a brittle behavior. To reach a sufficient compromise, a concentration of 1 wt% was selected for the rest of the study, to have a low effect on the mechanical properties, but with an appreciable ratio between monomer and excimer emissions and a suf-ficient photoluminescent signal output.

3.2. Mechanical monitoring by colorimetric measurement

In this section, a tensile test is performed on the 1 wt% PP/BBS film, with the same UV excitation source as before. Spectrometric in-situ monitoring is performed, followed by a colorimetric measurement by color camera.

3.2.1. Effect of strain on the photoluminescence spectra

This section investigates the change in the photoluminescent spectrum during the tensile test. Fig. 4 shows the luminescent spectra in the stretched area. The corresponding luminescent images acquired by a color camera during the tensile test can be found in the inset in Fig. 4.

The mechanochromic effect is activated between 10% and 20% in strain. This strain range corresponds to the necking for 1 wt% specimen (Fig. 2), the 20 % stretched sample showing clear evidence of localized deformation. Then, two areas (stretched/unstretched) coexist, with the stretched blue-colored area propagating along the gauge length while

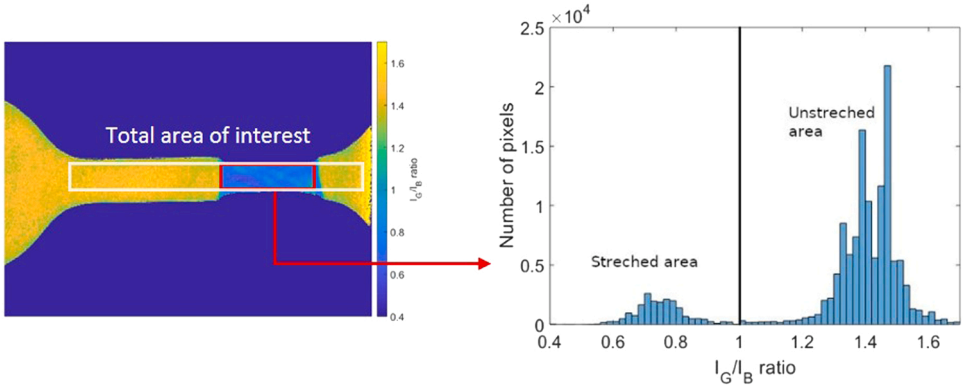

Fig. 6. a) Ratio image and b) its associated histogram at 60% strain of 1 wt% PP/BBS film.

getting thinner with the strain level, until the stretched area occupies the integrality of the image. The global strain of the specimen is then completely ruled by the necking stretched area, appearing in blue luminescence color, where BBS is organized as monomers. The "blue" region becomes more and more present in the image, even in the strain 'plateau' region. The spectra obtained corroborates the fact that only two energy states exist: the excimer one, in the unstretched area, and the quasi-monomer one, activated after necking. Indeed, the presence of a low peak at 470 nm, compared with the spectrum for very low con-centrations displayed in Fig. 6, implies that a part of the excimer has not completely moved to a monomer structure. According to previous studies [56,57] this brutal change is a crossing from a dye aggregated to a disaggregated state.

This physico-chemical behavior can be explained by the arrangement of the molecular chains which vary with the deformation. Excimer formation is a short-range interaction that requires molecular contact between BBS monomers, hence it is very sensitive to the BBS-to-BBS distance. However, it appears that this condition is no longer met at high level of plastic deformation, i.e. during necking, when the rear-rangement of PP chains in amorphous regions of the material to align with the direction of traction become significant. It is assumed that the shear forces involved in the rearrangement of PP chains become enough to break apart BBS aggregates.

Thereby, mechanochromic mechanism is triggered by plastic deformation, which is encouraging for a strain threshold detection system, but it seems difficult to build a measurement system able to monitor a continuous spectrum of deformation.

3.2.2. Colorimetric system description, channel choice and image analysis

During tensile test, the initial localization of necking is a priori unknown. The use of a field measurement system is then necessary, and a color camera appears to be an adapted technology. The originality of this work is to use a color camera as a quantitative system for the strain measurement/detection evaluation. The signal is then recorded by an 8- bit, 1.45 Mpx Bayer pattern type color camera (Pike, F-145C from Allied Vision, Stadtroda, Germany) equipped with a 16 mm fixed objective (Fujinon), at an acquisition frequency of 1 Hz. The distance between the camera and the sample was set to obtain a spatial resolution of 43 μm/ pixel in recorded images. Image analysis was carried out using the commercial software Matlab® (Mathworks, Natick, Massachusetts, USA).

The image analysis is set up to improve the colorimetric measurement, especially its sensitivity and repeatability. Indeed, the color change from green-blue to blue-green is inconspicuous regarding the potentiality of the entire colorimetric diagram. It is then essential to select the appropriate color channel (R, G; B) of the color camera for the measurement. Moreover, repeatability is important because photo-luminescence intensity depends on the geometrical set-up (angles and distances).

To comply with those requirements, the first step is to split the 3-color image into three monochrome images. Then, the dynamic range (proportional to sensitivity) can be predicted from spectrometry results, dividing the integral of the excimer PL spectrum by the integral of the monomer one:

$$\left.\frac{I_E}{I_M}\right|_{X=R,G,B} = \frac{\int_{\lambda_1}^{\lambda_2} QE_X(\lambda) PL_E(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} QE_X(\lambda) PL_M(\lambda) d\lambda}$$

with QE: quantum efficiency of each spectral band (X = R, G, B) of the camera (%); PL: photoluminescence spectra of the excimer, resp. the monomer (a.u.); I_E, I_M: integrated intensity of the excimer, resp. the monomer (a.u.). The quantum efficiency of each channel QE_x is included in the datasheet of the camera, the main characteristics and the results are detailed in Table 3.

The red-color channel is ignored for the dynamic range calculation as the monomer shows almost no-emission at this wavelength. The dy-namic range will then tend to an infinite erroneous value. The highest dynamic range (72) is obtained for the green spectral band, which is notably reduced compared to the spectral value (186). This decrease is the consequence of the spectral integration of low wavelengths, which exhibit poor variations of PL with strain.

At this step, the photoluminescent signal still depends on the geometrical settings of the experiment. Indeed, the UV flux received by the sample (source distance and angle) determines the emitted flux to

Table 3
Characteristics of the RGB Channels and ratio of the excimer emission (IE) over the monomer emission (IM).

		Chanel			Channel ratio
		B	G	R	$\left.\frac{I_E}{I_M}\right\|_G$ / $\left.\frac{I_E}{I_M}\right\|_B$
Maximum quantum efficiency	QE (%)	38	38	38	–
Wavelength t maximum QE	λ_c (nm)	470	540	610	–
Detection spectral bandwidth	$[\lambda_{min} - \lambda_{max}]$ (nm)	[400–550]	[430–630]	[560–970]	
Spectral dynamic range at λ_c	$\left.\frac{I_E}{I_M}\right\|_{\lambda_c}$	10	186	–	18.6
Color integrated dynamic range	$\left.\frac{I_E}{I_M}\right\|_{X=R,G,B}$	15	72		4.8

the detector. A classical approach used in luminescence is to compute intensity ratio from PL peaks at distinct wavelengths, which may produce a usable calibration curve when plotted against the physical variable to monitor from the change of PL. Under the assumption that the experimental conditions have the same effects on the signal at both wavelengths, this ratio of intensity should be independent from small variations of experimental conditions (illumination, angle of observations). The extrapolation of this approach to a color camera based measurement is to calculate the channel ratio I_G (Green channel) over I_B (Blue channel), for each pixel of the image. The following equation displays its expression, and the associated dynamic range:

$$I_{G/B} = \frac{I_G}{I_B} and \frac{I_E}{I_M}\Big|_{G/B} = \frac{\frac{I_E}{I_M}\Big|_G}{\frac{I_E}{I_M}\Big|_B}$$

Table 3 indicates a dynamic range of 4.8 for the intensity ratio, with a strong reduction compared to the spectral value (18.6), also linked with spectral integration.

As the projection of one pixel in the object is equal to a square of 40 * 40 μm^2, there is no need to perform spatial average over a region of interest (ROI), as homogeneity is guaranteed. To conclude about the detection of mechanochromism by color camera, the ratio I_G/I_B is selected as the signal of interest for the measurement. The decrease in dynamic range is compensated by the improvement of repeatability.

A synoptic scheme of the image analysis approach is presented hereafter, in Fig. 5. The first step of the image treatment is to separate each RGB channel into three separated channels. Then an image ratio I_G/I_B is computed for each pixel, on which segmentation can be performed to isolate the stretched and unstretched areas, based on a fixed threshold. This threshold is obvious in the PP/BBS case, where the change from blue to green is clearly marked, as seen in Fig. 4. An example of a ratio image at 60 % strain is presented hereafter (Fig. 6), with its associated histogram showing a threshold choice of 1. From the two identified ROIs (stretched area in red and unstretched area in white), the percentage of pixels belonging to the stretched area and the ones of the unstretched area is computed for each image of the tensile test. The mean spatial value (in the stretched area) of the ratio I_G/I_B is also calculated. The analysis is stopped when the stretched area over-passes the image frame.

3.2.3. *Mechanical monitoring by colorimetric measurement*

The mechanochromic potential in relation with BBS concentration in the PP host was investigated with tensile tests on 1 wt% doped films, by comparing the photoluminescent signal with the tensile behavior. Fig. 7 presents both the number of pixels belonging to the stretched and unstretched areas and the stress/strain curve. This relative number of pixels is computed thanks to the following equation:

$$N(\%) = \frac{N\left(\frac{I_G}{I_B} < Threshold\right)}{N\left(\frac{I_G}{I_B} < Threshold\right) + N\left(\frac{I_G}{I_B} > Threshold\right)} * 100$$

In the first elastic domain, the majority of pixels belong to the unstretched green colored area, corresponding to a high value of the ratio $I_{G/B}$ (excimer emission). After 12% strain, blue colored pixels appear in the stretched area and the number of pixels increase linearly all along the elongation of the specimen. At 80% strain, the number of blue pixels reach a plateau because the stretch area overpasses the image frame. The important point is that the number of blue pixels is a good signature of the beginning of necking. It marks the end of the quasi- linear domain and can be used as a maximum strain marker.

The other relevant quantity, i.e. the spatial mean value of the ratio I_G/I_B in the stretched area, is computed in Fig. 8 along with the tensile curve. Before the first flow threshold, the mean value is not consistent, as there is no stretched area. After the first flow threshold (10 % strain), the mean value of the intensity ratio starts to decrease, synchronized with necking ignition. This decrease can be surprising referring to the quasi "binary" nature of the luminescence (aggregated/disaggregated). Indeed, it supposes that the blue color of the stretched area becomes deeper and deeper with strain. At 70 % in strain, the blue color seems to stabilize around an intensity ratio of 0.7. The origins of this phenomenon (residual disaggregated excimers, material whitening by shear band formation, specimen thinning) are currently under investigation. How-ever, the variation of this intensity ratio shows a remarkable potential for stress evaluation in the range [25–35] MPa.

To sum-up, the in-situ strain control of PP/BBS mechanochromic specimen by colorimetry shows a remarkable potential. The computation of the image ratio I_G/I_B, allied with an optimized threshold of one, enables the accurate counting of pixels belonging to the unstretched area. Consequently, it marks the beginning of the necking phenomena. Alternatively, the mean value of the ratio image I_G/I_B in the stretched area, which depends on the whitening of the polymer, shows a great potential for stress estimation application and/or stress gauges in the range [25–35] MPa.

4. Conclusion

In this paper, PP/BBS mechanochromic blends were elaborated and their mechanical and photoluminescent properties were characterized. A particular attention was paid to the description of the link between photoluminescent properties, mechanical behavior and structure change in the polymer blend. Moreover, an original approach was adopted to use a color camera as a "low-cost" field measurement spectrometer.

The first part of the paper was dedicated to the selection of an appropriate optical dye concentration for mechanochromic application in PP. Under UV light, color changing emission from green to blue was

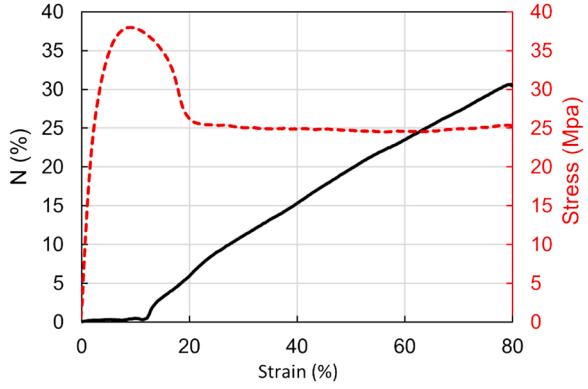

Fig. 7. Stress/strain curves and number of pixels in the streched-unstreched area of 1 wt% PP/BBS film.

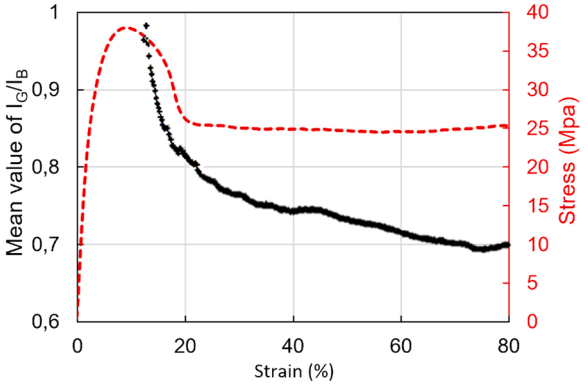

Fig. 8. Stress/strain curves and means value of IG/IB ration in the stretched area for 1 wt% PP/BBS film.

observed for moderate BBS dispersion, and 1 wt% concentration was chosen as a good compromise between a high green- to-blue emission dynamic and good tensile performance (non-brittle behavior). Then, a colorimetric monitoring method has been developed, using the RGB channels of a color camera to build a "low-cost" spectrometric field measurement. The calculation of the ratio image I_G/I_B, versus tensile test and strain measurements allowed identification of a well-defined mechanochromic transition. This color change appears simultaneously with plastic deformation and clearly marks the onset of necking. These results were confirmed by spectroscopic measurements where it was observed that the specific BBS excimer band decreased drastically between 10 % and 20 % strain. This suggests a brutal excimer disaggregation driven by the shear forces resulting from the movement of polymer chains during necking deformation.

The novelty of this work lies in the use of the ratio image method on the PP/BBS blend at 1 wt%. This method applied on this mechanochromic blend shows a sufficient sensitivity to mechanical strain and a remarkable robustness to experimental conditions (angle, distance…). Quantitative estimation of mechanical strain can even be investigated immediately after the first flow threshold. The other huge potential is the possibility to identify the very first damaged areas on 2D structures and to set up targeted repairs. Moreover, the apparatus is simple and uses a low-cost solution (RGB camera), which facilitates its use for widespread applications. Those results are very promising for applications in colorimetric detection systems as the blend color is changing in such a binary way. Further studies must be performed to characterize effects of other parameters on the mechanochromic properties of the PP/BBS blend, such as strain rate. The investigation of new material shape other than films and the search for reversible mechanochromic formulation is also ongoing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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