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Mills, A., Hawthorne, D., Burns, L., & Hazafy, D. (2017). Novel temperature-activated, humidity-sensitive optical sensor. *SENSORS AND ACTUATORS B-CHEMICAL*, 1009-1015. https://doi.org/10.1016/j.snb.2016.08.182

Published in: SENSORS AND ACTUATORS B-CHEMICAL

Document Version: Peer reviewed version

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Novel Temperature-activated humidity-sensitive optical sensor

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Abstract

A novel, colorimetric, temperature-activated humidity indicator is presented, with a colour change based on the semi-reversible aggregation of thiazine dyes (esp. methylene blue, MB) encapsulated within the polymer, hydroxypropyl cellulose (HPC). The initially purple MB/HPC film is activated by heat treatment at 370°C for 4 s, at which point the film (with a colour associated with a highly aggregated form of MB; $\lambda_{max} = 530$ nm) becomes blue (indicating the presence of monomeric and dimeric MB; i.e. with λ_{max} = 665; 605 nm respectively). The blue, heat-treated MB/HPC films respond to an ambient environment with a relative humidity (RH) exceeding 70% at 21°C within seconds, returning to their initial purple colour. This colour change is irreversible until the film is heat-treated once more. When exposed to a lower RH of up to ca. 47%, the film is stable in its blue form. In contrast, a MB/HPC film treated only at 220°C for 15 s also turns a blue colour and responds in the same way to a RH value of ca. 70%, but it is unstable at moderate RH 37-50% values, so that it gradually returns to its purple form over a period of approximately 6 hours. The possible use of the high heat-treated MB/HPC humidity indicator in the packaging of goods that cannot tolerate high RH, such as dry foods and electronics, is discussed.

1.0 Introduction

Sensors for the monitoring of humidity are routinely used in industrial manufacturing, in environmental monitoring and, indeed, any of the myriad environments in which the presence of moisture is likely to effect a change on a given process or product [1-8]. The manufacture, packaging and storage of foods and electronic goods are perhaps amongst the most obvious examples of where humidity monitoring and regulation are essential [9-11]. For example, too low an humidity and electronic components become brittle [9], and wet foods (fresh fruits and vegetables, for example) dry out and become susceptible to oxidative degradation [10]. On the other hand, too high an humidity and electronic goods run the risk of corrosion of their metallic components [11], and dry foods (grains and cereals, for example) lose their desirable texture and become ideal hosts for infection by microorganisms [10].

Typically, humidity monitoring and regulation are achieved using electronic hygrometers, in which humidity is measured via the calibrated resistance or conductivity value exhibited by a ceramic or polymer film. Of course, the cost and bulk of the sensor, and its need for electronic power, make these devices unsuitable for widespread use in the monitoring of the humidity of individually-packaged goods. As a result, colour-changing optical humidity indicator cards (HICs), developed in the late 1940s by P.B. Davis [12-15], have become an established popular, simple, alternative. HICs are based on the colour changes due to the hydration of transition metal salts bound to silica gel, and the most successful and widely-adopted of these is the cobalt(II) chloride indicator [15], which changes colour from a sky blue to a pink, as the relative humidity surpasses a threshold level (see Table 1). This threshold value is adjusted through the process of pre-activation of the silica gel, to which the transition metal salt is bound, so that activation at different temperatures gives humidity indicators with different sensitivities or threshold values [12-15]. These indicators are irreversible in their response, and so, once 'tripped'/changed, will retain their pink colouration until baked in an oven at >100°C to remove the bound water, at which point they can be re-used. Figure 1 illustrates a typical, commercial HIC, with some of its spots 'tripped', by the ambient humid atmosphere.

Unfortunately, these indicators are largely incompatible for working with foods due to their use of the heavy metal, and classified carcinogen, cobalt [16]. In addition, some regulatory bodies recommend that components containing halides, as in the case of most HICs, should not be used with electronic goods [17]. Alternative, less problematic HICs have been developed in recent years [18-19], but appear less popular, possibly due to cost and poor colour change issues.



Figure 1: The CoCl₂ HIC system, which is a blue colour when dry, and a pink colour when exposed to an ambient RH greater than the threshold indicated for each spot. This photograph was mid-way through the indicator's response to exposure to an RH \approx 40%; hence, the 10 and 20% spots are 'tripped', the 30% spot is partially tripped, and the 40% spot has not yet tripped.

An alternative approach to humidity indicating has been presented by Matushima *et al.* in a series of reports on reversible humidity-sensitive indicator films, formed from a combination of a dye with a sugar-based hydrogel (such as agarose or κ -carrageenan), which undergo a reversible colour change due to the formation of an aggregated form of the dye at high humidities, and its subsequent breakdown at low humidities [20-22]. In these RH indicators, the colour change is attributed to the humidity-promoted aggregation of the dye, as outlined in reaction (1),

where D is the monomer and D(agg) the aggregated form of the dye, and where D and D(agg) are both differently coloured – i.e. colours A and B respectively. When the dye employed is thionine (TH), in carrageenan, for example, the colours A and B are purple and red respectively, whereas if the thiazine dye is methylene blue (MB), in the same encapsulating medium, the colours are blue and purple, respectively [21-22].

The observed colour changes exhibited by above the thiazine dye humidity indicators with a change in ambient humidity, are consistent with the spectral changes expected for an aggregation process as summarised in reaction (1). For

example, in the case of the MB indicator, the absorbance λ_{max} in aqueous solution of MB is *ca.* 665 nm (and characteristic of the monomer form of the dye), so that the dye appears blue in colour [23]. But, this value of λ_{max} (absorption) decreases as the dye becomes increasingly aggregated, with the dimer and trimer exhibiting λ_{max} values of 605 nm and 578 nm respectively [23], so any solution containing these species adopts a more purple colouration.

Spectroscopic details for a number of these different 'dye-in-hydrogel' type humidity indicators, as reported by Matsushima *et al.* [20-22] and others [24-26], are given in **Table 1.** The hydrogel type humidity indicators are not suitable for commercialisation, since the colour changes are not particularly striking, i.e. the change in absorbance λ_{max} , $\Delta_{\lambda max}$, is \leq 50 nm. In addition, the nature of the sugar gel systems makes them difficult to produce and store.

In 2009, our group published details of a humidity indicator based on the thiazine dye, MB, encapsulated in a film of hydroxyethyl cellulose (HEC) containing urea [24]. In this system, the urea was present in a quantity that was roughly 20 times that of the dye. Under both dry (i.e. relative humidity, RH, = 0%) and ambient conditions (RH \cong 60%, at 23°C), the film was a bright purple, but turned a deep blue after exposure to an ambient atmosphere with RH ≥85%. As a consequence, the latter colour change could be easily effected simply by breathing on the film (RH *ca.* 100%), and the striking colour change could then be reversed upon exposure to a gas stream with RH <85%. Interestingly, this observed reversible wavelength shift (bathochromic, i.e. $\Delta\lambda_{max} = -ve$, as opposed to hypsochromic, i.e. $\Delta\lambda_{max} = +ve$) is much larger than, and opposite to that observed, by Matsushima *et al.*, using the thiazine dyes MB and TH in carrageenan gels, as is indicated by the colour and wavelength changes listed in **Table 1** [15,20-26].

From the colour changes observed in the MB/urea/HEC system, it appears that the dye is in a highly aggregated form (and so purple coloured) when largely dry (and in a crystalline environment of urea), and disperses into the film in a largely monomeric form (and so becomes blue coloured) when the ambient atmosphere is rendered humid, which causes the urea crystals in the indicator film to dissolve [24]. The concomitant reversible loss in the crystallinity of the urea in an indicator film, when it is exposed to a humid (RH \geq 85%) atmosphere was confirmed using XRD [24], and established the significant role that the crystallinity of the encapsulation medium

played in the overall humidity-driven, colour changing process for this indicator.

Table 1: A summary of the colour, and λ_{max} changes, for the wet and dry forms for some of the major dye-based humidity indicators in the literature, and work described here.

System	Colour	λ_{max} (dry) /	Colour	λ_{max} (wet)	Δλ _{max}	
	(dry)	nm	(wet)	/ nm	/ nm ª	
CoCl ₂ / SiO ₂	Sky	665	Purple	550	+ 115	[15]
	blue					[:0]
7-diethylamino-4'-						
dimethylaminoflavyliu	Purple	550	Red	520	+ 30	[20-22]
m perchlorate / κ-						
carrageenan						
Thionine / κ-	Purple	570/600	Red	520	+ 80	[21]
carrageenan						
5-dimethylamino-1-						
naphthalenesulfonic	Yellow	360	Yellow	330	+ 30 ^b [[25-26]
acid/hydroxypropyl						
cellulose (HPC)						
5-dimethylamino-1-						
naphthalenesulfonam	Yellow	366	Yellow	330	+ 36 ^b	[25-26]
ide / HPC						
Methylene blue /						
urea / hydroxyethyl	Purple	550	Blue	600 / 660	+ 110	[24]
cellulose						
Methylene blue /	Durola	406	Durala	505	0	
HPC	Fulple	490	Purple	505	- 9	

^a $\Delta\lambda_{max} = \lambda_{max} (dry) - \lambda_{max} (wet)$

^b These values are $\Delta \lambda_{max}$ for fluorescence; all other values are $\Delta \lambda_{max}$ for absorption

The polymer encapsulation medium that is used here, hydroxypropyl cellulose (HPC), has been investigated previously, in the context of an optical humidity sensor, when used in thin film form with fluorophoric dyes, including 5-dimethylamino-1-naphthalenesulfonic acid (DNSA) and 5-dimethylamino-1-naphthalenesulfonamide

(DNSM) [25-26] embedded in it. In the DNSA/HPC and DNSM/HPC studies, it was found that as the RH was increased from 0 to 88%, the fluorescence λ_{max} values exhibited by the dyes in the film shifted by ca. 30 nm for each dye (see Table 1). These less-than-striking changes in λ_{max} (emission) are similar to the absorbance spectra shifts $\Delta \lambda_{max}$ seen in Matsushima's work for thiazine and flavylium dyes in hydrogels (see Table 1), and suggest that such dyes in HPC are unlikely to give striking (i.e. $\Delta \lambda_{max} \geq 50$ nm) optical responses to changes in humidity. However, despite this lack of apparent promise, it is interesting to note that HPC is guite an unusual polymer, in that it exhibits a cholesteric crystalline phase when cooled from a melt, and its glass transition temperature is in the region of 200°C [27-28]. This feature, coupled with the fact that the aggregation of MB can be, as noted earlier, dramatically affected by the degree of crystallinity exhibited by the encapsulating medium [24], suggests that the combination of MB encapsulated in HPC, after an initial heat treatment above 190°C, might lead to a significant change in dve aggregation, and therefore a change in the film colour. If the degree of crystallinity exhibited by the HPC is also humidity-sensitive, as in the case of urea, then it might be expected that such a heat-treated MB/HPC film will then exhibit a striking sensitivity towards ambient humidity levels. This idea is tested here and this paper describes the results of a humidity sensitivity study on films formed of MB, and other thiazine dyes, encapsulated in HPC.

2.0 Experimental

2.1 Reagents and materials

All chemicals used were of the highest purity grade available and used as received from Sigma Aldrich, unless stated otherwise. All solutions were made up using doubly-deionised water and freshly prepared prior to each experiment, with agitation provided by a magnetic stirrer bar for a minimum of 120 minutes to ensure full dissolution and dispersion of the different components that were used to formulate the various inks under test.

2.2 Preparation of a typical ink and humidity sensor film

A typical humidity-sensitive ink, in this case using MB as the dye, D, in reaction (1), was prepared by adding 40 mg of the dye along with 0.8 g of HPC (average $M_w = 80,000$ g mol⁻¹) to 8 g of ethanol (Fluka), and stirring vigorously for 2 hours. The resulting ink was dark blue in colour.

In the preparation of a humidity-sensitive thin film from the ink, a spin-coating technique was used, in which 3 drops of the ink were placed onto the centre of a 24 mm diameter, 0.1 mm thick borosilicate microscope cover slide (VWR), placed on a spin coater, and subsequently spun at 800 rpm for 30 s. The films were allowed to dry further in air for 30 min. The films formed were purple in colour (see **Table 2**), and were *ca*.0.9 µm thick as measured by scanning electron microscopy.

2.3 Relative humidity (RH)

For experiments in which the individual RH sensitivities of the films were determined, the RH (at 21°C for all experiments conducted, unless otherwise stated) was adjusted using dry air, split through a T-connector, so as to direct one stream through a series of Dreschel bottles filled with water. The then-dry (0% RH) and wet (100% RH), separate air streams were then blended using a gas blender (Cole-Parmer), where the ratio of dry to humid air could be adjusted to give an airflow with the desired RH. The humid air flow was then directed to a gas flow cell, usually placed in the sample compartment of a UV/vis spectrophotometer, and containing the humidity sensing film formed from the thiazine dye under test (usually MB) encapsulated in HPC. In all cases, the value of the RH of the air stream was confirmed separately, using an electronic hygrometer (Tecpel; DTM-550), and the overall flow rate for each experiment (unless otherwise stated) regulated at 120 mL min⁻¹.

For longer term stability studies, in which the humidity remained constant at constant temperature, a climate control oven (Votsch; VCL 4010) was used. Thus, the humidity-sensing films were placed inside the oven, the RH and temperature were computer-regulated as defined, and UV-vis spectra of the indicator film recorded at

regular intervals.



Table 2: A summary of the results when alternative dyes to MB were encapsulated in HPC as thin films for use as humidity sensors.

^a Δ indicates heating to 370°C for 4 s, and δ indicates exposure to an atmosphere of 100% RH.

2.4 Methods

All UV-visible spectrophotometric measurements were made using a Cary 60 series UV-visible spectrophotometer (Agilent). All digital photographic images were recorded using a model EOS 7D DSLR camera (Canon).

3.0 Results & Discussion

3.1 Initial experiments

A freshly-spun MB/HPC humidity indicator film is purple-coloured with, initially, some evidence of unevenness in colour at its centre. When exposed to a high relative humidity (RH = 100%), the film colour changes very little (λ_{max} shifts from 496 to 505 nm; see **Table 1**), and although the process is fully reversible, the colour change is indistinct and so the non-heated, as-prepared, MB/HPC film is, like the DNSA/HPC film, a poor visual indicator of RH and even significant changes in RH [25-26].

The colour of this film does not change when it is placed in a desiccator for any length of time, or an oven at 70°C, for 24 h. Thus, simply drying out the film does not effect any significant change in dye aggregation. In contrast, when the same MB/HPC film is placed in an oven at temperatures exceeding the T_g of HPC (*ca.* 190°C [27-28]), *ca.* 220°C, for 20 s, the film develops a new, striking, homogeneous blue colour (i.e. the initial unevenness in film colour, noted earlier, disappears). This heat-treated, blue-coloured MB/HPC film then reverts back to its original, bright purple coloured form upon exposure to highly humid air (e.g. from human breath). The heat-treated blue, MB/HPC indicator is indefinitely stable when stored under conditions of 0% RH (i.e. in a desiccator). When the purple form of the indicator is stored under ambient conditions, its colour remains unchanged. However, the purple form of the indicator film can be readily reactivated to its blue form upon heat treatment at T>T_g(HPC).

UV/visible absorption spectra taken of the film in: its heat-treated (220°C dry for 20 s) form (blue): (i) under RH = 0%, i.e. dry conditions, and (ii) after subsequent exposure to 100% RH (purple) forms, are displayed in **Fig. 2**, and reveal that the dry, blue film appears to comprise a mixture of the monomeric and dimeric forms of MB (i.e. λ_{max} = 665 nm and 605 nm, respectively), whereas the humid form (i.e. the form generated upon exposure of the heat-treated film to a high, >80%, RH) is dominated by a peak at 530 nm, which suggests that the dye is in an extended aggregated form, *vide infra*.



Figure 2: Absorption spectra of a freshly spun MB/HPC film (solid trace) after heat treatment in an oven at 220°C for 20 s, and after subsequent exposure to saturated humid air (dashed trace)

Although the blue (heat-activated: 220°C for 20 s) form of the indicator was stable indefinitely when stored under dry (RH = 0%) conditions, it was not particularly stable when stored under ambient conditions of 40-50% RH. Thus, the initially blue, heat-treated film returned to an intermediate blue/purple colour within 30 minutes under conditions of 50% RH, and to its original, bright purple after a further 5.5 hours. Subsequent work showed that the same colour changes (and associated poor ambient storage stability) could be effected using a heat gun (used for stripping paint) set at *ca.* 220°C for a period of 15 s, as well as with an oven, as used previously. Further work, carried out using the heat gun method, then showed that when the purple form was exposed to more rapid (4 s) heating at a much higher temperature, 370° C (the maximum temperature attainable using the heat gun), then the same, blue-coloured film is produced, but with a much greater stability when stored under ambient RH conditions.



Figure 3: The absorbance (at 665 nm) variation of a 370°C (4 s) and a 220°C (15 s) treated MB/HPC film (open and filled circles, respectively) as a function of time, when held at to RH = 40% (T = 23°C).

As a demonstration of this difference in stability, when stored at a moderate RH, the variation in the absorbance value, at 665 nm, of a typical MB/HPC film, heat-treated at either (i) 370°C for 4 s or (ii) 220°C for 15 s, respectively, were recorded as a function of time after heat-treatment and subsequent storage under conditions of moderate humidity and temperature (i.e. 23°C and 40% RH). The results are illustrated in **Fig. 3**, and demonstrate that the (370°C, 4 s) MB/HPC film is much more stable when stored under moderate humidity conditions, compared to the (220°C, 15 s) film. Note also that both of these films responded instantaneously, changing from blue to purple, when exposed to a much more humid atmosphere (i.e. > 80% RH) at ambient temperatures (23 °C).

Results obtained from experiments carried out using a quartz crystal microbalance (QCM) to measure the uptake of water by films of both HPC with no dye, and the MB/HPC films, showed that in both cases the films' rate of adsorption of water was independent of its heat treatment history. As such, it appears that the rapid heat-treatment (4 s, 370°C), when compared to a less-rapidly (220°C, 15 s) heated film, does not affect the ability of the film to absorb water under ambient conditions. As a consequence, it is not clear why the rapidly heated, high temperature-treated MB/HPC film (370°C for 4 s) has a much greater stability towards moderate RH

levels than that of a lower temperature-treated (220°C for 15 s) film.

Further work showed that the response of a 370° C, 4 s heat-treated MB/HPC film is repeatable, and shows little sign of deterioration, when subjected to a continuous cycle of heating (370° C for 4 s) followed by exposure to a saturated, humid (RH = 100%) air stream, as illustrated by the results in **Fig. 4**. From the results of this work, typical 90% response and recovery times of 3 s and 45 s, respectively, were measured.



Figure 4: Absorption at the monomer peak (665 nm) over repeated heating cycles (Δ) and exposure to 100%RH (\blacklozenge), demonstrating that the films are repeatable with little depreciation of response.

In a study of the RH sensitivity of the high heat-treated, 370°C 4 s, MB/HPC film, the absorbance, at 605 nm, of the film was measured as a function of ambient RH, starting from 0%, and increasing in increments of 5%, to 70%, with each incremental level maintained for one hour to allow the film to equilibrate. The results of this work are displayed in **Fig. 5**, a plot of film absorbance at 605 nm against %RH. As can be seen from these results, a typical MB/HPC film only begins to respond to ambient RH at a level of *ca.* 40%, and does not appear to reach its final, full purple colouration until the RH surpasses *ca.* 65%. Between 65% and 100% RH, the films'

spectrum and colour (purple) remained unchanged, and as illustrated by the data in **Fig. 5**.



Figure 5: The absorbance at 605 nm of a MB/HPC film initially treated at 370°C for 4 s, and exposed to a humid air stream with RH varying from 0 to 100%. Photographs of the film at each measurement point are displayed above the plot.

3.2 Other thiazine / HPC humidity indicator films

A number of other humidity-sensitive films, with the same formulation as the MB/HPC film, but with alternative thiazine dyes, were prepared and almost all showed spectral characteristics similar to those exhibited by a MB/HPC film, both in terms of approximate colour change (blue to purple) and RH sensitivity, and the results of this work are summarised in **Table 2**.

The one exception was thionine, TH, since the TH/HPC film was found to be red (not blue) in its dry, heat-treated, form, and purple/blue in its humidified form, i.e., once thermally activated, it exhibited a significant bathochromic shift in spectrum when

exposed to a high humidity, whereas all the other thiazine dyes exhibit a hypsochromic shift. It is not initially obvious why TH should exhibit such a different behaviour when heat-treated, followed by exposure to high humidity. However, the absorption spectrum of the red-coloured, dry TH film ($\lambda_{max} = 510$ nm) is very typical of that of the organo-soluble, water-insoluble, monomeric freebase form of TH ($\lambda_{max} = 487$ nm in toluene [29]); and TH is the only thiazine dye in **Table 2** to form such a species. Thus, heat treatment appears to promote the formation of the latter, red, monomeric freebase form ($\lambda_{max} = 510$ nm), of the thiazine dye, TH, rather than the usual cationic, monomeric/dimeric blue-purple form ($\lambda_{max} = 602$ nm [29]), and exposure to high humidity (>100 %) promotes the conversion of the red TH to its cationic form ($\lambda_{max} = 610$ nm), which subsequently forms an extended aggregated species like all the other thiazine dyes tested.

3.3 Dye aggregation

As noted earlier, a brief inspection of the spectra illustrated in Fig. 2, and the subsequent comparison of the measured and literature values for λ_{max} , reported for aggregated forms of MB in aqueous solutions, suggest that the blue form of the MB/HPC film is formed from a combination of monomeric and dimeric MB with λ_{max} values of 665 nm and 605 nm, respectively [23]. However, the unusually low λ_{max} value (530 nm), observed (see Fig. 2) for the humid form of the MB/HPC film indicates that the MB is in an unusually extensively aggregated or 'polymeric' form. This high degree of aggregation is not readily observed in aqueous solutions of MB, even at high concentrations (>10 mM) [23, 30], and thus the mechanism responsible for formation of this species for MB, and all the other thiazine dyes (except TH), must be due to RH-related, significant changes in the encapsulated dye's microenvironment [25].

Interestingly, spectrally similar, purple, 'polymeric' (i.e. highly aggregated) forms of MB, with $\lambda_{max} = 550$ nm, have been reported previously in several papers by Shirai *et al.*, [31-32], in which the polyanion poly(potassium vinyl sulfonate) (PVS) was added to a dilute (10 ⁻⁴ mol L⁻¹) aqueous solution of MB. In this work, as the molar ratio, PVS/MB, was increased from 0 to 20, the λ_{max} value shifted significantly from 665 nm

to 550 nm [32-33]. Shirai *et al.* concluded that the polymer, PVS, stabilised the highly-aggregated, 'polymeric MB' species through ion-pairing of the MB cation to the sulfonate anion moieties along the polymer chain, effectively 'holding' the MB molecules at a set, regular intermolecular distance, so as to allow significant overlap of the π -systems, and promote the creation of a supramolecular 'polymeric' form of MB [32]. The spectrum of the MB/PVS MB aggregate ($\lambda_{max} = 550$ nm), reported by these researchers, is very similar to that observed in this work ($\lambda_{max} = 530$ nm; see **Fig. 2**) for the humid form of the MB/HPC indicator, and, assuming the same cause, a schematic illustration of the key process involved in the MB/HPC RH indicator's response to changes in humidity is given in **Fig. 6**.



Figure 6: Representation of the aggregate species of MB seen in the dry and humid forms of the HPC film. The stacked aggregates are stabilised in the presence of water and HPC, and broken up by heating to T > HPC's T_g .

It is well-known that, on heating a polymeric material, such as the HPC film, above its T_g, more flexible, less crystalline regions are created within the polymer [27]. This high temperature treatment will also promote the disaggregation of the polymeric (purple) form of MB, and the increased number of amorphous regions produced at high temperature will then aid the subsequent distribution of the dye in its monomeric and dimeric forms throughout the heat-treated film, causing the originally purple indicator film to turn blue. However, upon exposure to a high level of ambient humidity, water is absorbed into the bulk of the HPC film [33], which, as usually happens, promotes the dye aggregation process. It is unclear why the water promotes such a high degree of dye aggregation (so that $\Delta\lambda_{max}$ is *ca.* 135 nm), when compared with other water-induced dye aggregation-based RH indicators, such as thiazine or flavylium dyes in carrageenan, where $\Delta\lambda_{max}$ typically \cong 30 nm; see **Table** **1**. Nor is it clear why the (370°C, 4 s) MB/HPC film is unaffected by prolonged exposure to a relatively high (*ca.* 40%) RH, while the (190°C, 15 s) heat-treated film is unstable (and turns purple eventually) under these conditions. However, it is clear that this resistance to aggregation exhibited by the MB/HPC film, heat-treated at 370°C for 4 s, renders it more attractive in terms of storage and utilisation as a humidity indicator.

4.0 Conclusions

A film formed from the thiazine dye, MB, and the polymer HPC, is purple when freshly made, under most conditions of humidity, but changes to a striking blue upon exposure to temperatures exceeding the T_g of HPC. This blue form of the MB/HPC is humidity-sensitive, yielding a colour change from blue to purple when the ambient RH exceeds 60%. This colour change is attributed to the self-aggregation of MB, as promoted by the film's microenvironment which is influenced by the unusual liquid crystal properties of HPC. The film's response (to humidity and re-generation with heat-treatment) is rapid and repeatable. Its stability (as the blue, dry film) under moderate ambient RH has been shown to differ depending on whether the film is heat-treated at 220°C (i.e. only just exceeding HPC's T_g), where it will revert to purple within hours, or 370°C (i.e. vastly exceeding HPC's T_g), where it will remain blue indefinitely until exposed to RH >60%.

Such a film is suitable for use as an indicator in the packaging of goods which cannot tolerate highly humid environments. Thus, the MB/HPC (370°C for 4 s) humidity-sensing film, with its ability to change colour dramatically (blue to purple) at RH \geq 70% (at *ca.* 23°C), but remain unchanged indefinitely under low (<40% RH) humidity conditions, may find application for use in packaged foods which need to be stored at an RH << 70%. For example, the indicator might be used as a humidity indicator in the packaging of: (i) table salt (which deliquesces at 75% RH and undergoes caking if not packaged in a dry environment [34], (ii) onions and garlic (which quickly begin to rot if stored above 70% RH) [34], and (iii) confectionary items such as Turkish delight, marzipan, and marshmallows (all of which have optimum storage conditions at between 60-73% RH) [34]. Foods which are enjoyed dry, but

not brittle, such as beef jerky, also have optimum storage conditions of between 65-75% RH [35]. The MB/HPC humidity sensor would also make an appropriate indicator for the storage of wooden instruments or artwork, which deteriorate if exposed to RH in excess of 70% for any appreciable time [36].

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