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Unraveling the surface properties of PMMA/azobenzene blends as coating films with photoreversible surface polarity†

Shameer Hisham, [ID][a] Norazilawati Muhamad Sarih, [ID] *[a] Hairul Anuar Tajuddin,[a] Zul Hazrin Zainal Abidin[b] and Zanariah Abdullah[a]

Various reports demonstrated that azobenzene derivatives are the chromophore of choice in photoresponsive surfaces showing reversible surface polarity. Hitherto the surface study of coating films based on polymer/azobenzene blends using contact angle measurements remained unexplored. To provide insight into the surface polarity of polymer/dye blend films, poly(methyl methacrylate) (PMMA) blends containing photoresponsive 4-hydroxy-4′-methylazobenzene (**AZO1**) and 4,4′-dimethylazobenzene (**AZO2**) as coating films on clear glass substrates are investigated in this work. Contact angle measurements were carried out to unravel the role of substituents in the surface polarity and the orientation of chromophores in the coating matrices before and after UV light ($\lambda_{max} = 365$ nm) irradiation. Changes in water contact angles measured on the PMMA/azobenzene coating films indicated that the surface polarity is reversible as the chromophores underwent reversible *trans–cis* isomerisation. It has been revealed that the repeated *trans–cis* isomerisation led to the random reorientation and arrangement of chromophores in PMMA/**AZO1** coating films. Then, to indicate the possibility of the disruption of interfacial interactions due to the repeated *trans–cis* isomerisation processes, as a proof of concept experiment, it is shown that the commercial acrylic-based pressure-sensitive sticker which adhered strongly to the PMMA/**AZO1**(13) coating film is peeled off from the coating surface after being subjected to a cycle of UV light irradiation for 12 hours, followed by dark conditions for another 12 hours within 14 days. The proof of concept study will lead to more development of smart photoresponsive coating films using simple polymer/dye blends.

1 Introduction

Long-lasting stickers on various surfaces indicate the successful advancement of adhesive technology. Among the commonly used adhesives are acrylic-based pressure-sensitive adhesives. Acrylic pressure-sensitive adhesives have been applied in a myriad of products including adhesive mounting tapes, labels, medical pads, and protective and decorative films, among others due to their instantaneous adhesiveness in addition to their ease of adhesive work.[1] However, those adhesives when removed may often lead to residues remaining on walls and surfaces which damage and cause hideous appearance of surfaces. The main factor to achieve strong adhesiveness is the maximum interaction between the adhesive and the surface. Therefore, it is proposed that the reversible polarity of the surface can cause gradual reduction of interactions, and hence the adhesive can peel off by itself.

Numerous reports have indicated that azobenzenes are the chromophore of choice in photoresponsive materials owing to their efficient *trans–cis* isomerisation processes as well as exceptional photostability even after prolonged irradiation.[2] Isomerisation of *trans*-azobenzene into the metastable *cis*-isomer will typically bring about a change in its molecular geometry and thus increase its molecular dipole from zero in the *trans*-isomer to about 3.0 D in the *cis*-isomer.[3] Typically, photoresponsive surfaces showing reversible wettability and polarity utilise azobenzene-functionalised molecules, side-chain polymers and even macrocycles where they are then formed into self-assembled monolayers (SAMs),[4–17] Langmuir–Blodgett films,[18,19] liquid crystalline films,[20,21] polymer thin films[22–28] and nanoparticles.[29] Detailed surface studies including contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were carried out to elucidate the photochemical effects of azobenzene chromophores on the wettability, morphology and polarity of the surfaces. However, to the best of our knowledge,

[a]Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: nmsarih@um.edu.my; Fax: +603-79674193; Tel: +603-79674240

[b]Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

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the surface study of coating films based on simple polymer/azobenzene dye blends using contact angle measurements has never been reported.

Thus, this work aimed to provide insight into the substituent effects of azobenzene chromophores on the (i) polarity of the coating blend surface, (ii) the orientation of chromophores and (iii) photochemistry of chromophores in the coating matrices before and after UV light (λ_{max} = 365 nm) irradiation using contact angle measurements. Based on a previous report,[20] the orientation of azobenzene moieties in liquid-crystalline films greatly influenced the surface polarity. Another investigation[30] demonstrated that repeated irradiation of well-ordered azobenzene-containing SAMs with UV and visible light led to the random reorientation and arrangement of azobenzene chromophores.

In this work, 4-hydroxy-4′-methylazobenzene (**AZO1**) and 4,4′-dimethylazobenzene (**AZO2**) were blended into poly(methyl methacrylate) (PMMA) and subsequently coated onto clear glass substrates. The coating film surfaces were then characterised using contact angle measurements. Since the repeated irradiation of azobenzene chromophores could trigger the rearrangement of chromophores, it is hypothesised that the interaction sites on the surface could be altered as well. Therefore, as a proof of concept, commercial acrylic-based pressure-sensitive stickers were adhered onto both PMMA and PMMA/**AZO1** coating films. Subsequently, each coating film underwent repeated irradiation with UV light for 12 hours, followed by dark conditions for another 12 hours for 14 days. If the hypothesis is true, then it is expected that the repeated changes in surface polarity could disrupt the adhesive/coating interactions, and therefore the sticker should peel off.

2 Experimental

2.1 General information

All chemicals and reagents were obtained from Merck unless otherwise stated. The melting point of **AZO1,2** was recorded on a Mel-Temp II melting point apparatus (Laboratory Devices Inc., Holliston, MA, USA). NMR spectra were obtained using Bruker Avance III (400 MHz) (Bruker BioSpin AG, Fällanden, Switzerland) NMR spectrometers with tetramethylsilane as the internal standard. All chemical shifts are reported in ppm. FTIR spectra were measured on a Perkin-Elmer ATR-400 series FTIR spectrometer (PerkinElmer, Shelton, CT, USA). Absorption spectra were measured with a Cary 60 UV-Visible spectrometer. For the preparation of coating films, PMMA (average M_w = 120 000 g mol^{-1}) and xylene (reagent grade) were obtained from Sigma-Aldrich (Darmstadt, Germany).

2.2 Synthesis

2.2.1 Synthesis of 4-hydroxy-4′-methylazobenzene (AZO1).
AZO1 was synthesised by the azo coupling reaction using a previously reported method (Scheme 1).[31] Briefly, *p*-toluidine (10 mmol) was dissolved in a solution of HCl 37% (5 mL) and distilled water (20 mL). A solution of NaNO$_2$ (12 mmol) in distilled water (5 mL) was prepared separately. The NaNO$_2$
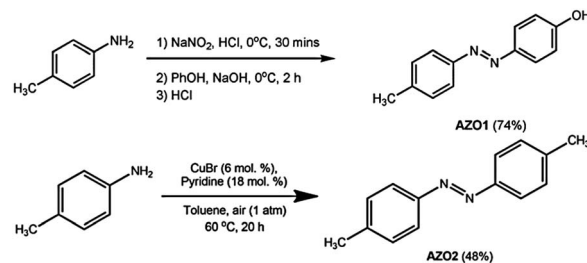
Scheme 1 Synthesis of **AZO1,2**.

solution was added dropwise to the acidic amine solution over 5 minutes at 0 °C. After stirring for 30 minutes at 0 °C, the resulting aryldiazonium salt solution was added dropwise to a solution of phenol (10 mmol), NaOH (10 mmol) and distilled water (20 mL) prepared earlier at 0 °C. The resultant coloured mixture was stirred for 2 h at 0 °C, followed by precipitation of the product by the addition of HCl solution (5%). Then, the precipitate was collected, washed with H$_2$O and dried in an oven at 60 °C for 24 h. Purification by recrystallisation from EtOH : CHCl$_3$ = 1 : 1 afforded **AZO1** as an orange crystalline solid (74%), mp 155–158 °C (Lit: 143–144 °C[31]); UV (EtOAc) λ_{max}: 348 nm, ε_{max}: 2.63 × 10^4 L mol^{-1} cm^{-1}; FTIR (ν_{max}, cm^{-1}): 3025 (br, **O–H**), 1581 (aromatic **C=C**), 1504 (**N=N**), 1274 (**C–O**); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 2.35 (s, 3H, –**CH$_3$**), 5.76 (bs, 1H, –**OH**), 6.85 (d, J = 7.56 Hz, 2H, Ar-**H**), 7.22 (d, J = 7.72 Hz, 2H, Ar-**H**), 7.71 (d, J = 7.44 Hz, 2H, Ar-**H**), 7.77 (d, J = 7.56 Hz, 2H, Ar-**H**); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 20.44, 114.76, 121.50, 123.77, 128.70, 139.93, 146.03, 149.67, 157.14.

2.2.2 Synthesis of 4,4′-dimethylazobenzene (AZO2).
AZO2 was synthesised *via* oxidative aniline coupling according to Zhang & Jiao (Scheme 1).[32] Into a suspension of CuBr (0.6 mmol) and pyridine (1.8 mmol) in toluene, *p*-toluidine (10 mmol) was added. The reaction mixture was stirred vigorously at 60 °C for 24 h. The reaction was then quenched with 5% HCl solution, and the organic layer was separated, washed with distilled water (3 × 50 mL), followed by saturated NaCl solution (1 × 50 mL), and dried over anhydrous MgSO$_4$. Removal of the solvent by vacuum distillation followed by flash chromatography over silica gel with 100% hexane as an eluent afforded **AZO2** as an orange solid (48%), mp 134–138 °C (Lit: 144–146 °C[33]), UV (EtOAc) λ_{max}: 330 nm, ε_{max}: 2.22 × 10^4 L mol^{-1} cm^{-1}; FTIR (ν_{max}, cm^{-1}): 2987 (aromatic **C–H**), 2921 (methyl **C–H**) 1598 (aromatic **C=C**). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 2.35 (s, 6H, –**CH$_3$**), 7.22 (d, J = 7.60 Hz, 4H, Ar-**H**), 7.73 (d, J = 7.80 Hz, 4H, Ar-**H**). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 21.49, 122.74, 129.72, 141.21, 150.85.

2.3 Preparation of PMMA/azobenzene blends as coating films

PMMA120K and **AZO1,2** were blended together by dissolving them in xylene at 60 °C until a homogeneous solution was formed. The compositions of the coating films are shown in Table 1. Clear glass substrates were cleaned with detergent, followed by rinsing with distilled water. Then, they were

Table 1 Composition of PMMA coating films

Coating	Binder	Dye	Dye content (wt%)	
			Binder solution	Dry film
PMMA	PMMA120K (20 wt% solution in xylene)	—	0	0
PMMA/**AZO1**(5)		**AZO1**	1	5
PMMA/**AZO1**(13)			3	13
PMMA/**AZO1**(33)			10	33
PMMA/**AZO1**(50)			20	50
PMMA/**AZO2**(5)		AZO2	1	5
PMMA/**AZO2**(13)			3	13

sonicated in distilled water for 15 minutes, and then in EtOH. Prior to the application of coating solution, the substrates were dried by purging under the flow of N_2 gas to remove residual EtOH. The coating films were prepared by the doctor blade method and dried overnight in open-air. The dry film thickness for all coating films on glass substrates was measured using a micrometer screw gauge and was found to be in the range of 30 to 40 μm.

2.4 Differential scanning calorimetry (DSC)

DSC measurements were performed using a TA Instruments DSC Q20 differential scanning calorimeter (TA Instruments, Inc., New Castle, DE, USA) at a nitrogen flow rate of 20 mL min^{-1}. The samples (5–10 mg) were first heated to 150 °C and held at that temperature for 1 minute to erase the thermal history (1st scan). Then, they were cooled to −50 °C and then reheated to 200 °C at a rate of 10 °C min^{-1} (2nd scan). Glass transition temperature, indicated as T_g, was determined from the second heating scans. T_g was defined as the inflection point of the heat flow curve.

2.5 Contact angle measurements

Static contact angle measurements were conducted using a Krüss G23 goniometer (A.Krüss Optronic, Hamburg, Germany) with deionised water (drop volume = 3 μL) as the contact liquid under ambient conditions. All data reported are the average of at least three individual measurements.

The *trans–cis* photoisomerisation kinetics of azobenzene-doped PMMA coatings were studied by first irradiating the coatings with UV-A light (365 nm, 20 W) using a Toki T8/20 W UV lamp (Toki Corporation, Tokyo, Japan). The contact angles of samples were then measured with respect to the irradiation time until a plateau of contact angles was observed, signifying that the samples reached a photostationary state (PSS). Upon reaching the PSS, the coating films were then kept under dark conditions for the thermal *cis–trans* isomerisation kinetic studies where the contact angles were recorded with respect to the relaxation time until a plateau of contact angles was noticed. For the isomerisation kinetic studies, the contact angles were measured at 10–60 minute intervals. In addition, all measurements were carried out within 60 seconds to minimise the exposure of chromophores to ambient light. The experimental

setup is shown in Fig. S7.† The relationship between contact angles and time was then correlated using the equation

$$\theta(t) = (\theta_0 - \theta_{PSS})\exp(-kt) + \theta_{PSS} \quad (1)$$

where θ_0 and θ_{PSS} are the initial contact angle and contact angle at the PSS, respectively.

2.6 Proof of concept sticker peel-off test

Commercial acrylic-based pressure-sensitive stickers were applied onto PMMA and PMMA/**AZO1**(13) coating films. Then, the backside of the coating films was irradiated first with UV-A light (365 nm, 20 W) for 12 hours, then kept in the dark for another 12 hours to simulate day and night using a Toki T8/20 W UV lamp (Toki Corporation, Tokyo, Japan). This process was repeated for 14 consecutive days. The extent of sticker peeling off was calculated by recording the area of the sticker that has peeled off from the surface. The part where the sticker remained unpeeled onto the surface appeared to be darker than other parts of the surface.

3 Results and discussion

Azobenzene derivatives **AZO1** and **AZO2** were chosen as photoresponsive chromophores for this work to study the effects of functional groups on the physical and optical properties of PMMA coating films. They were synthesised using established methods, producing moderate to good yields. **AZO1** contains one methyl group and one –OH group, whereas **AZO2** consists of only methyl groups. The –OH groups in **AZO1** molecules may improve its solubility in the PMMA matrix possibly due to the formation of intermolecular C=O⋯H hydrogen bonds. Therefore, it is expected that **AZO1** showed better homogeneity in the PMMA matrix compared to **AZO2**. It is well-known that the presence of strong electron donors such as –OH groups could also influence the speed of *trans–cis* isomerisation of azobenzene derivatives. Hence, the performance of **AZO1** and **AZO2** dyes in *trans–cis* isomerisation in PMMA can be compared.

3.1 Physical characterisation of PMMA/azobenzene blends as coating films

Fig. 1 shows the prepared coating films. Increasing the weight percentage of **AZO1** dyes beyond 33% resulted in
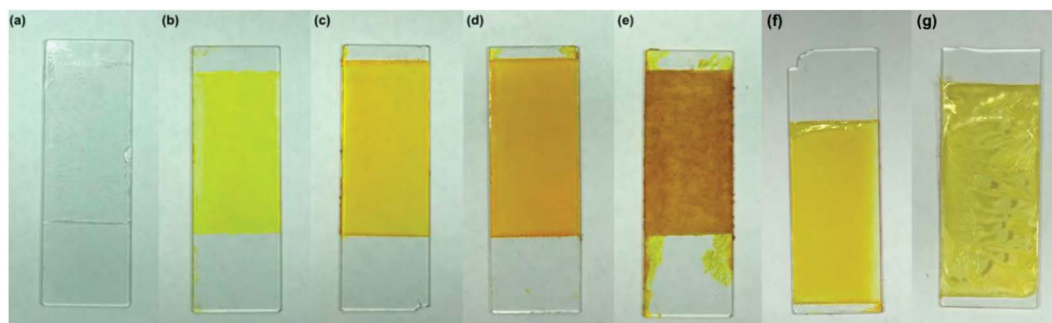
Fig. 1 (a) PMMA, (b) PMMA/**AZO1**(5), (c) PMMA/**AZO1**(13), (d) PMMA/**AZO1**(33), (e) PMMA/**AZO1**(50), (f) PMMA/**AZO2**(5) and (g) PMMA/**AZO2**(13) coating films.

inhomogeneity of the mixture, as evidenced by the significantly rough surface of the PMMA/**AZO1**(50) coating (Fig. 1(e)), in comparison to the other coating films. Consequently, this leads to the composition being inapplicable for coating systems. Hence, only coating films with 5, 13 and 33 wt% of **AZO1** dyes are further characterised.

It can be seen that increasing the content of **AZO2** dyes beyond 5 wt% triggered the crystallisation of **AZO2** in PMMA films, as shown in Fig. 1(g). This is possibly due to the poor solubility of **AZO2** dyes in PMMA matrices.[34] Therefore, only coating films with 5 wt% **AZO2** dyes are further characterised.

By changing one of the methyl groups in **AZO2** to –OH, the solubility of azobenzene dyes in PMMA matrices is enhanced, evidenced by the higher content of **AZO1** dyes able to be blended homogeneously in PMMA coating films. This is possibly due to the intermolecular C=O⋯H hydrogen bonding between PMMA and **AZO1**. Another way to circumvent the crystallisation of dyes in the polymer matrix is by synthesising azobenzene derivatives containing long alkyl chains or branches in order to increase the solubility in the polymer matrix.[34]

It can also be observed that PMMA/**AZO2** coating films have poor adhesion onto glass substrates as some parts of the film peeled off (Fig. 1(f) and (g)). In contrast, the presence of –OH groups in **AZO1** have enabled better adhesion of films onto glass substrates possibly by intermolecular hydrogen bonding interaction between the glass and coating film.

In order to investigate the role of –OH groups in increasing the homogeneity of **AZO1** in PMMA, DSC studies were carried out on PMMA/**AZO1**(5) and PMMA/**AZO2**(5) coating films for comparison study. DSC studies can provide sufficient information about the compatibility of polymer blends. From Fig. 2, the T_g of pure PMMA is 68.30 °C. The T_g of the PMMA coating film is indeed lower than that of the pure commercial grade PMMA granules used ($T_g = 105$ °C). It has been reported that the selection of solvents can influence the T_g of a polymer by altering the packing density and morphology of the polymer.[35] Moreover, it has been observed that the T_g of a polymer film can change with film thickness and the type of substrate that the film is cast on.[36] Thus, it is possible that the lower value of the observed T_g for the PMMA coating film is probably due to a combination of these reasons.

From the DSC thermograms, it is shown that only a single T_g is present in both PMMA/**AZO1**(5) and PMMA/**AZO2**(5) DSC thermograms. Typically, the DSC curve will indicate only a single T_g transition if two components are fully miscible with each other.[37] Therefore, the results suggested that the **AZO1** and **AZO2** dyes (5 wt% dry film content) were miscible in the PMMA matrices. It is expected that the addition of a low-molecular weight component would decrease the T_g of the bulk polymer, where the small amount of small-molecule additives could change the molecular arrangement and crystallinity of the bulk polymer. Thus, a careful observation indicated that the addition of **AZO1** and **AZO2** dyes into PMMA decreased the T_g of PMMA from 68.30 °C to 64.55 and 67.05 °C, respectively. The addition of **AZO1** dyes decreased the T_g further than that of **AZO2** dyes. The larger T_g deviation of the PMMA/**AZO1**(5) film in comparison to that of the PMMA/**AZO2**(5) film is a possible sign of intermolecular C=O⋯H hydrogen bonding interactions between PMMA and **AZO1**. Previous studies have also indicated that the intermolecular hydrogen bonding interactions between two components in polymer blends caused a decrease in the T_g of the bulk material.[37,38] Thus, it is probable that the presence of –OH groups in **AZO1** enhanced its solubility in the PMMA matrix due to intermolecular hydrogen bonding interactions.
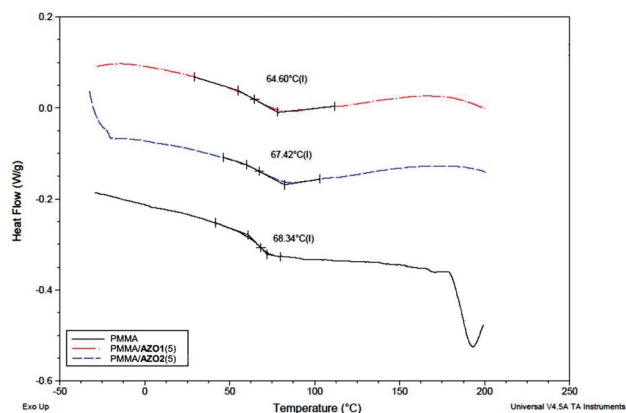

Fig. 2 DSC thermograms of PMMA (black solid line), PMMA/**AZO1**(5) (red dash dot line) and PMMA/**AZO2**(5) (blue dash line).

3.2 Contact angle measurements

3.2.1 Possible orientations of AZO1 chromophores in PMMA/AZO1 blends as coating films. Due to the extremely low M_w of azobenzene derivatives in comparison to the bulk PMMA, they tend to segregate to the surface. Segregation is thermodynamically favourable if there is a total reduction in the surface free energy of the bulk material.[39,40] Segregation of azobenzene molecules was driven by the relatively hydrophobic phenyl moieties.

Upon a closer look at the structure of **AZO1**, it can be deduced that the dye itself is asymmetric; that is, there are two different substituents at the 4- and 4′-positions, which are –OH and –CH$_3$. Therefore, **AZO1** chromophores can have a few possible arrangements on the coating surface, as illustrated in Fig. 3.

From Fig. 3(a), *trans*-**AZO1** molecules orient in a way that –CH$_3$ groups are saturated on the coating surface while in Fig. 3(b), the –OH groups are saturated on the coating surface. *trans*-**AZO1** molecules can also arrange in a random manner, as shown in Fig. 3(c). Then, when irradiated with UV-A, *cis*-**AZO1** can also have different possibilities of arrangements on the coating surface, as depicted in Fig. 3(d–f).

Well-ordered surfaces containing alkyl groups can give water contact angle values from 74 to 142° depending on surface composition, alkyl chain length and surface roughness.[41–46] However, water contact angle values of surfaces containing hydroxyl (–OH) groups could be from 22 to 44°.[45,47,48] Furthermore, surfaces containing –COOH groups can provide water contact angle values from 30° to as low as 15° depending on surface compositions.[45,47,49–51]

If *trans*-**AZO1** can have well-ordered arrangements in a way that –CH$_3$ groups saturate the coating surface (Fig. 3(a)), then it is anticipated that the static water contact angle value increases to more than 70° (hydrophobic surface). Conversely, if –OH groups saturate the coating surface (Fig. 3(b)), then it is predicted that the static water contact angle value should decrease

to below 40° (hydrophilic surface). To unravel which scenario is the best to describe the arrangement of **AZO1** in the coating surface, water contact angle measurements are taken for the blank PMMA coating as well as the dyed coatings and suitable comparisons can be made.

The water contact angle values of the PMMA/**AZO1** coating films after a few UV-A irradiation cycles are shown in Fig. 4(a). It is noted that water contact angles of the blank PMMA coating were relatively constant before and after UV-A exposure. The average contact angle value of 63° has indicated that the native PMMA surface is relatively hydrophilic (<90°). However, when
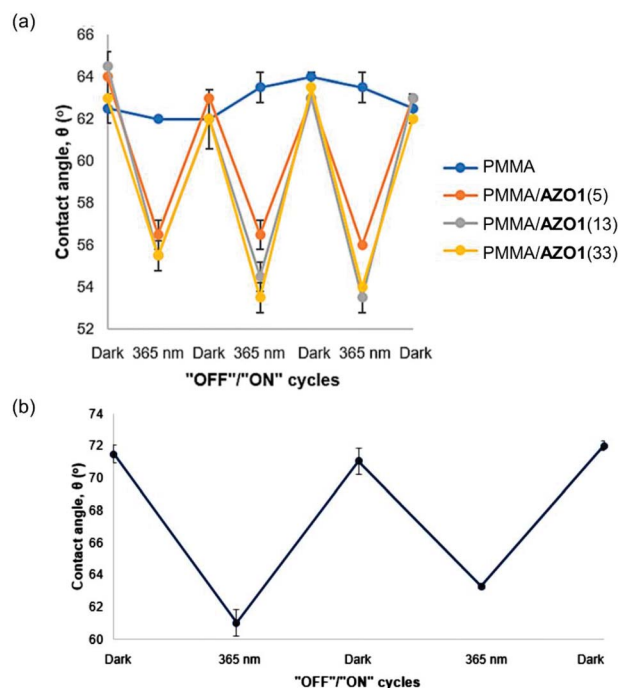

Fig. 4 Changes in contact angle values for (a) various PMMA/**AZO1** and (b) PMMA/**AZO2**(5) coating films upon UV light irradiation cycles.
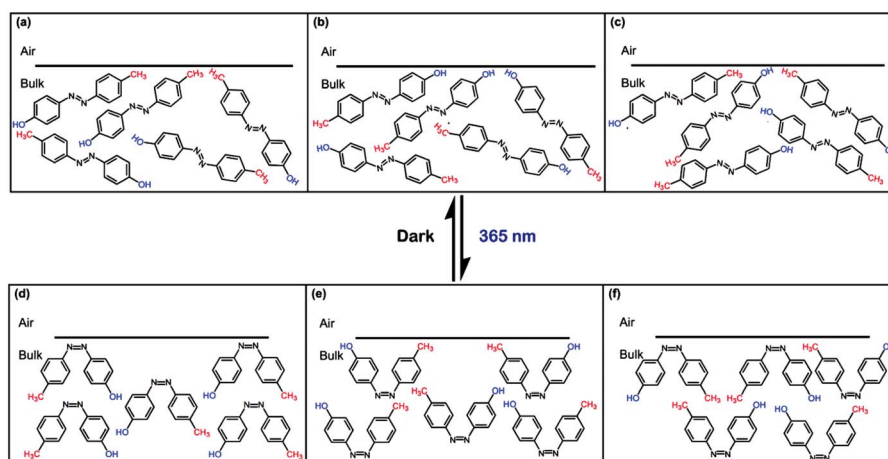

Fig. 3 Possible orientations of **AZO1** molecules in coating surfaces as *trans*-**AZO1** with (a) a –CH$_3$ (coloured red) saturated surface, (b) –OH (coloured blue) saturated surface or (c) random arrangements of –CH$_3$ and –OH. Upon UV light irradiation, *cis*-**AZO1** can have orientations with (d) functional groups facing down, (e) functional groups facing up or (f) random arrangements of –CH$_3$ and –OH.

AZO1 chromophores were added, the water contact angle values of the coating films remained nearly the same regardless of the dye concentration – indicating that the coating surfaces were neither saturated with hydrophobic –CH$_3$ groups nor hydrophilic –OH groups from the dye molecules. This can only mean that *trans*-**AZO1** molecules are suggested to have random arrangements on the coating surface (Fig. 3(c)).

After exposure to UV-A irradiation, the water contact angle of the samples dropped in the range of 55.5°–56.5°, which has clearly shown that the *trans–cis* photoisomerisation of **AZO1** has occurred in the coating films. Moreover, this indicated that the *cis*-isomer is more polar, and the changes in the dipole moment of the azo molecules contributed to an overall reduction in the contact angle values.[52] It can also be shown that increasing the content of **AZO1** chromophores in coating films from 13 wt% to 33 wt% did not give any significant decrease in the water contact angle values. This possibly showed that saturation of the surface with chromophores has occurred, most likely due to the segregation of chromophores to the coating film surface.[39] Moreover, crystallisation of chromophores due to phase separation of chromophores from the coating film may also happen at higher concentrations as indicated in Fig. 1, further signifying the segregation processes of chromophores.

It is also suggested that *cis*-**AZO1** molecules can have random arrangements on the coating surfaces as well (Fig. 3(f)). A combination of dipole moments of *cis*-**AZO1** and –OH groups on the surfaces led to a reduction in static water contact angle values. As a result, the coating films become more hydrophilic after UV-A exposure. Subsequently, when these coating films were kept in the dark, the contact angles reverted, signifying that the thermal *cis–trans* isomerisation process has occurred and this has confirmed the reversibility of **AZO1** isomerisation. The reversibility of *trans–cis* isomerisation processes is confirmed as the contact angle values changed accordingly upon UV irradiation cycles.

Since the **AZO1** chromophores were found to have random arrangements in the PMMA matrices, it is proposed that the reversible *trans–cis* isomerization processes could alter the interaction sites on the coating film surface. This is illustrated in Fig. 5. Initially, the interaction sites of PMMA/**AZO1** coating films mainly consist of hydrophilic –OH groups. Then, when *trans → cis* photoisomerization has occurred, there are new interaction sites available, in the form of dipole moments from the lone pair electrons in the azo N atoms. When *cis*-**AZO1** thermally relaxed, these additional interactions disappeared.

To prove our proposed theory, contact angle measurements on the PMMA/**AZO2**(5) coating film were conducted as well. From Fig. 4(b), it was observed that initially, the contact angle was 71.5°, which indicated that the PMMA surface became less polar. In this case, only –CH$_3$ groups are present in **AZO2** molecules, therefore eliminating the various probable arrangements of molecules as discussed previously. Thus, the presence of –CH$_3$ groups on the surface caused the surface to be more hydrophobic. By comparing the contact angle values of PMMA/**AZO1** coating films (63.0°–64.5°), it is clear that **AZO1** molecules do have random arrangements in PMMA coating
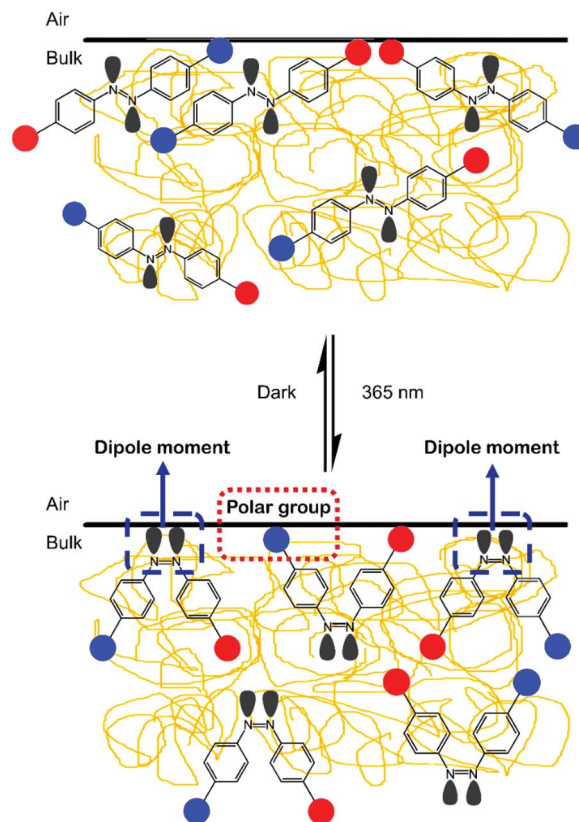

Fig. 5 The possible interaction sites of PMMA/**AZO1** blends as coating films before and after UV-A irradiation. Red circles represent –CH$_3$ groups and blue circles represent –OH groups. Nonbonding lone pair electrons are shown in grey.

films, contributing to the lower contact angle values than the PMMA/**AZO2**(5) coating film.

Upon irradiation with UV light, the PMMA/**AZO2**(5) surface became more hydrophilic as a result of the formation of *cis*-**AZO2**, in which its higher dipole moment increased the polarity of the surface. Moreover, it was shown that the change in contact angle values Δθ for the PMMA/**AZO2**(5) coating film was higher (Δθ = 10.5°) than that of PMMA/**AZO1**(5) (Δθ = 7.5°). Again, the reversibility of *trans–cis* isomerisation processes is confirmed as the contact angle values changed accordingly upon UV irradiation cycles.

3.2.2 *E–Z* (*trans → cis*) photoisomerisation kinetics of PMMA/azobenzene blends as coating films. It is expected that the *trans → cis* isomerisation kinetics would deviate from the monoexponential decay curve since the isomerisation of azobenzene derivatives in glassy polymers showed such behaviour, thereby requiring stretched exponential or multiexponential functions for accurate data fitting.[38] However, our results have indicated that the isomerisation kinetics for PMMA/**AZO1** and PMMA/**AZO2** coating films showed monoexponential decay since the data fitted well with eqn (1) with a high R^2 value (>0.98). Similar observations were made by Faupel *et al.* where the azobenzene chromophores showed monoexponential decay behaviour in PMMA matrices even at high chromophore concentrations.[34] From Fig. 6(a) and Table 2, the rates of *trans*
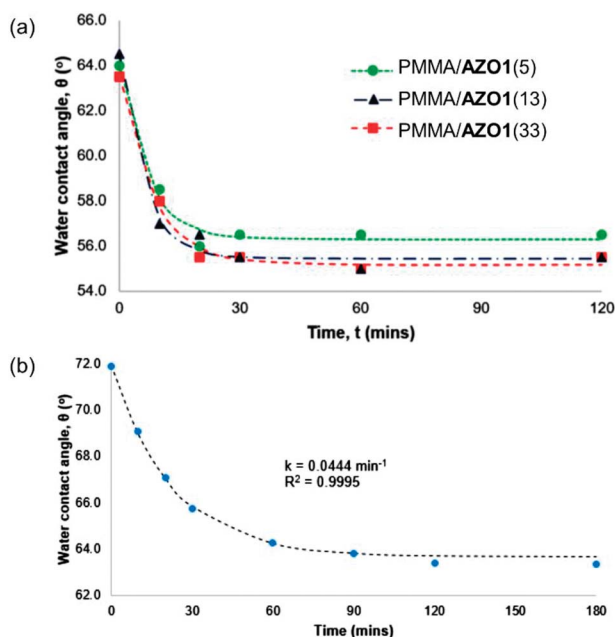
Fig. 6 *trans* → *cis* photoisomerisation of (a) various PMMA/**AZO1** and (b) PMMA/**AZO2**(5) coating films.

Table 2 *trans* → *cis* photoisomerisation kinetic parameters of PMMA/azobenzene coating films

Coating	$k_{E \to Z}$ (min^{-1})	$t_{1/2}$ (min)	R^2
PMMA/**AZO1**(5)	0.1434	4.8337	0.9838
PMMA/**AZO1**(13)	0.1603	4.3241	0.9884
PMMA/**AZO1**(33)	0.1181	5.8692	0.9921
PMMA/**AZO2**(5)	0.0444	15.6114	0.9995

→ *cis* photoisomerisation of PMMA/**AZO1**(5) and PMMA/**AZO1**(13) coating films are similar. A slight reduction in the *trans* → *cis* photoisomerisation rate for the PMMA/**AZO1**(33) coating film is possibly attributed to the matrix effect: at a certain concentration, **AZO1** chromophores have a limited free volume required to undergo photoisomerisation.[34,38] A further increase in the amount of **AZO1** chromophores would further decrease the free volume of photoisomerisation. As a result, a reduction in the photoisomerisation rate was observed.

It can also be seen that the PSS is reached for all coating films at about the 30th minute mark. In other words, 30 minutes of UV light irradiation should provide a sufficient time for the dyes to convert into the *cis*-isomers. It is also worth mentioning that the formation of a plateau or maximum contact angle when the amount of **AZO1** dyes increased beyond 13 wt% possibly implied that the chromophores are saturated on the surfaces, as discussed earlier.

The rate of isomerisation of **AZO2** in PMMA is markedly slower than that of **AZO1**, with **AZO2** reaching the PSS only after 2 hours (Fig. 6(b)). In addition, its half-life of 15.6 min is also significantly slower than that of **AZO1** (4.3 to 5.9 minutes). This

has clearly indicated that the presence of a strong electron donor on one side of the azobenzene molecule increases the photoisomerisation rate.

3.2.3 Thermal *Z–E* (*cis* → *trans*) isomerisation kinetics of PMMA/azobenzene blends as coating films. The thermal *cis* → *trans* isomerisation rates of **AZO1** and **AZO2** dyes in PMMA coating films have also shown a monoexponential increase where the data fitted well with eqn (1) with a high R^2 value (>0.98). From Fig. 7(a) and Table 3, the rates of thermal *cis* → *trans* isomerisation of PMMA/**AZO1**(5) and PMMA/**AZO1**(13) coating films are similar. Likewise with the *trans* → *cis* photoisomerisation, a slight reduction in the thermal *cis* → *trans* isomerisation rate for the PMMA/**AZO1**(33) coating film is observed. The **AZO1** chromophores fully reverted to their *trans*-configuration after about 180 minutes in the dark.

In contrast, **AZO2** chromophores showed a significantly lower thermal isomerisation rate, where the molecules fully reverted after 10 hours, with a half-life of 157.3 minutes (Fig. 7(b)). Meanwhile, the half-life of *cis*-**AZO1** in PMMA coating films ranged from 23.2 to 32.9 minutes. These indicate that the thermal *cis* → *trans* isomerisation process is fast, albeit considerably slower than pseudostilbene-type molecules (lifetimes of their *cis*-isomers are usually in the order of milliseconds/seconds).[3,53] In contrast, for the case of azobenzene-type molecules (in this respect, **AZO2**), the lifetimes of their *cis*-isomers could be in the order of hours or even days.[3,53] As a consequence, this specific property of azobenzene-type molecules may prove to be disadvantageous for the current work as it will take a significantly longer time for the *cis*-isomer to thermally revert to the more thermodynamically stable *trans*-isomer. However, rapid regeneration of the *trans*-isomer can be
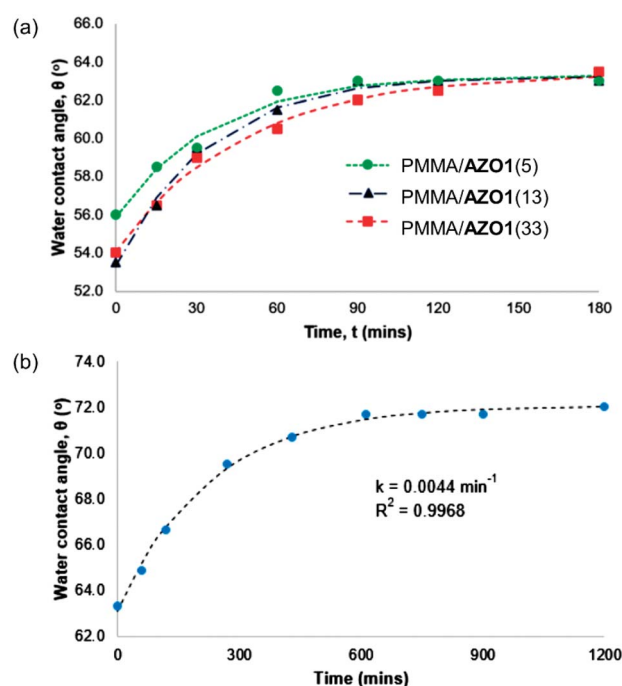

Fig. 7 Thermal *cis* → *trans* isomerisation of (a) various PMMA/**AZO1** and (b) PMMA/**AZO2**(5) coating films.

**Table 3** Thermal $cis \rightarrow trans$ isomerisation kinetic parameters of PMMA/azobenzene coating films

Coating	$k_{Z \rightarrow E}$ (min^{-1})	$t_{1/2}$ (min)	R^2
PMMA/**AZO1**(5)	0.0280	24.7553	0.9818
PMMA/**AZO1**(15)	0.0299	23.1822	0.9939
PMMA/**AZO1**(33)	0.0211	32.8506	0.9929
PMMA/**AZO2**(5)	0.0044	157.2832	0.9968

done easily and efficiently by irradiation of the *cis*-isomer with blue or white light.[34,54,55]

3.3 Proof of concept sticker peel-off test

From the results of static contact angle measurements, we showed that the polarity of surfaces can be tuned. The random orientations of **AZO1** chromophores in the coating film may bring about different interaction sites on the surface. Therefore, it is interesting to study whether interfacial interactions between the coating film surface and any adhesive can be altered when subjected to UV light irradiation. Thus, as a proof of concept, commercial acrylic-based pressure-sensitive stickers were applied on top of PMMA and PMMA/**AZO1**(13) coating films. Subsequently, both coating films were subjected to a cycle of UV light irradiation for 12 hours and then kept in the dark for another 12 hours for 14 consecutive days. The PMMA/**AZO1**(13) coating was chosen for the sticker peel-off test since it showed the best photoswitching performance, whereas the PMMA/**AZO2**(5) coating film was not chosen due to the slower isomerisation rate of **AZO2** in comparison to **AZO1**. Fig. 8 shows the conditions of the stickers on the coating films after 14 irradiation cycles.

The extent of sticker peeling off from coating film surfaces was determined by recording the area that the sticker has
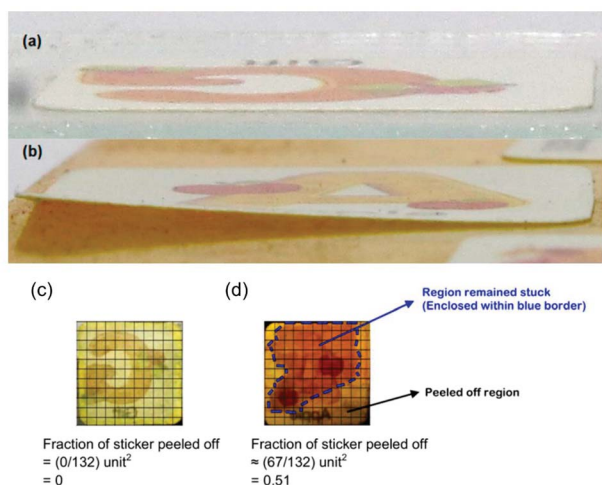
Fig. 8 The condition of acrylic-based pressure-sensitive stickers on (a) PMMA and (b) PMMA/**AZO1**(13) coating films after 14 UV-A irradiation cycles (for 14 days). (c) and (d) show the estimated area of the sticker peeled off after 14 UV-A irradiation cycles for PMMA and PMMA/**AZO1**(13) coating films, respectively.
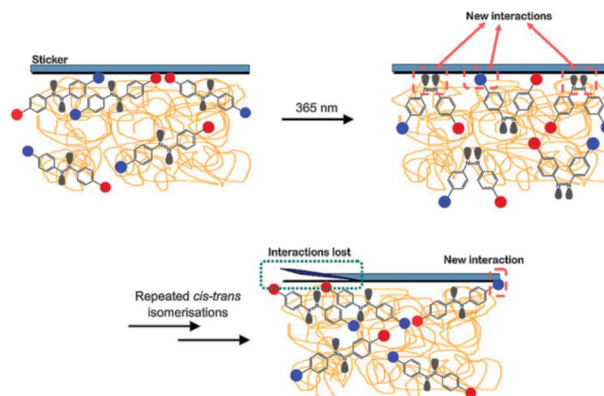
Fig. 9 Proposed sticker peeling-off mechanism. Red circles represent –CH$_3$ groups and blue circles represent –OH groups. Nonbonding lone pair electrons are shown in grey.

peeled off. Fig. 8(c) and (d) show the extent of sticker peeling off from the coating surfaces. The darker regions represent the area of the sticker still sticking onto the surface, whereas the lighter regions represent the area of the sticker already peeled off. It is clearly noticed that the sticker remained unpeeled on the PMMA coating film after 14 days. In contrast, the sticker has peeled nearly half of itself off from the PMMA/**AZO1**(13) coating film surface within 14 days.

Despite the limitations of the study, it is proposed that the repeated excitation of azobenzene chromophores in the coating film caused substantial changes in the sticker/coating interactions (Fig. 9). Initially, the sticker/coating interactions consisted of weak van der Waals forces and hydrogen bonding interactions (sticker and –OH moieties in **AZO1**). Subsequently, when the chromophores are excited upon UV light irradiation to form the *cis*-isomers, there are additional dipole–dipole interactions between the coating and sticker surfaces. However, these additional interactions are lost once the chromophores reverted to the *trans*-isomer. The repetition of *trans–cis* isomerisation has caused random reorientation and arrangements of the chromophores.[30] As a result, there is a considerable amount of alterations to sticker/coating interactions and consequently, the sticker peeled itself off slowly from the coating film surface. Furthermore, the proposed peeling-off mechanism is in agreement with the results of static contact angle measurements.

4 Conclusions

In this work, simple PMMA/azobenzene blends were applied as coating films onto clear glass substrates. We showed that both **AZO1** and **AZO2** chromophores are photoreversible in PMMA matrices upon repeated UV light irradiation, reflected by the changes in contact angles. The lower contact angles of PMMA/**AZO1** coating films in comparison to the PMMA/**AZO2** coating film indicated that the **AZO1** chromophores are oriented and distributed randomly in the coating matrix. The –OH group in **AZO1** also increased the rate of isomerisation in comparison to **AZO2**. Since the reorientation of **AZO1** chromophores brought about changes in the interaction sites on the coating film

surface, it was proved that the repetition of *trans–cis* isomerisation processes caused the commercial acrylic-based pressure-sensitive sticker that was initially adhered to the PMMA/**AZO1**(13) coating film to peel off from the coating surface possibly due to the disruption of the adhesive/coating interactions. It is expected that these findings would further catalyse the development of photoresponsive self-cleaning coating films as well as having the potential to address problems associated with illegal sticker advertisements.

Conflicts of interest

The authors declare that there is no conflict of interests.

Acknowledgements

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