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Poly(methyl methacrylate) embedded with spiropyran as photochromic material and lemongrass oil as insect repellent for smart window application

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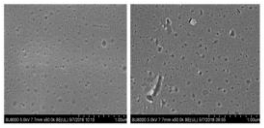
GRAPHICAL ABSTRACT



Morphology image for clear surface of PMMA-spiropyran- lemongrass oil using FESEM at 50k magnification

ABSTRACT

Spiropyran (SP) is one of the most widely used photochromic species that have attracted much attention in the field of optical data storage and smart windows due to their unique properties which can reversibly switch from closed form spiropyran (SP) into opened form zwitterionic merocyanine (MC) under irradiation of ultraviolet (UV) light. Essential oils are well-known for its wide range of application such as in pesticide control. However, SP itself tends to have lower photostability which can limit its application thus by incorporating SP into polymeric matrices, their photostability can be increase. This study reports on preparation of polymer embedded with SP and lemongrass oil to investigate its photochromic behaviour. Lemongrass essential oil was extracted from lemongrass leaves by solvent extraction and steam distillation. Poly(methyl methacrylate), PMMA was prepared through soap free emulsion polymerization by using potassium persulphate as initiator while spiropyran, 2H-1-benzopyran-2, 2’-(8’-hydroxy-1’,3’,3’-trimethylindoline) was prepared by condensation reaction of precursor Fisher’s base, methylene indoline derivative with 2,3-dihydroxybenzaldehyde in 1:1 mole ratio. The synthesized compounds were mixed together in dichloromethane to give a thin film of PMMA embedded with SP and lemongrass oil. The obtained products were structurally characterized by ATR, FTIR, and NMR spectroscopic technique. GC-MS analysis was used to confirm the presence of chemical composition in the essential oil. Photochromic behaviour of SP and PMMA thin film was studied by UV- VIS spectroscopy. SP showed a maximum absorption wavelength at 400 nm while SP coated onto PMMA film showed a maximum absorption wavelength at 500 nm. The presence of polymeric matrices has shifted the absorption band of closed form SP to the longer wavelength in the visible band which indicating the formation of open form MC. This study suggested that by incorporating SP in polymer matrices, its photostability can be increased thus be able to be used in smart window application.

Keywords: spiropyran, poly(metyl methacyalate), polymerization, photochromic

1. INTRODUCTION

Photochromism is a reversible conversion of chemical species induced by electromagnetic radiation between two states of species having different absorption spectra. Colour changes in photochromic compound is due to the changes in its molecule or conformation [1]. A photochromic material is one that changes from transparent to a colour when it is exposed to light and reverts the transparency when the light is dimmed or blocked. Nowadays, spiropyran (SP) type compounds are one of the most widely use photochromic species. Spiropyran (SP) contains typical photo-isomerization group which can be converted from closed form hydrophobic spiropyran into opened form hydrophilic zwitterionic merocyanine (MC) under irradiation of light and revert back to SP form upon exposure to visible light [2,3].

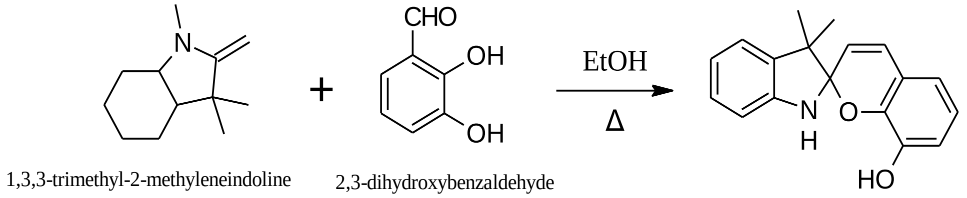
Due to photochromic properties in spiropyran, the research has grown significantly with high potentials in optical data storage, sensors as well as smart windows application. Smart window is a new technology to replace glass window which can provide much more advance features [4]. In addition, usage of natural base product for example essential oil has grown rapidly as it is safe to be used by human being as compared to synthetic chemical base product [5]. Spiropyran is capable to absorb and block the UV rays from the sunlight while essential oil like lemongrass oil had been investigated to have an ability to be used as insect repellents which can repel mosquitoes that can spread mosquito-borne diseases especially dengue hemorrhagic fever [6,7]

A common problem arises with spiropyran based smart materials is the loss of reversibility induced by photodegradation, photobleaching. This photofatigue occurs when the photoswitching cycle is repeated several times. Therefore, this problem can be minimized by immobilization of spiropyran to a polymer matrix. This combination has possibility to enhance the photochromic effect of spiropyran thus improving its characteristics which is photostability, expanded operative wavelength range, and increased darkening intensity [8].

This research will emphasize on extraction of lemongrass essential oil, synthesis and characterization of poly (methyl methacrylate), PMMA and spiropyran. In this case, lemongrass oil was extracted with solvent extraction and steam distillation [9] by which the oil compositions were identified by GC-MS and FTIR. The synthesis of PMMA was carried out by soap free emulsion polymerization [10] while spiropyran was synthesised through condensation reaction of precursor base and aldehyde [11]. PMMA embedded with spiropyran and lemongrass oil was prepared by solution casting and their physico-chemical properties were studied. Resulting spiropyran and PMMA thin film showed a shift in electronic absorption wavelength while the morphology of thin film showed a clear smooth distribution of spiropyran and lemongrass oil.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage focused on extraction of the lemongrass oil. Lemongrass stem was cut from the root and subjected to solvent extraction and steam distillation using hexane and water as the solvent and later was extracted with dichloromethane (DCM) using the separating funnel. Structure and chemical compositions in lemongrass oil were analysed by FTIR and GC-MS. Secondly, PMMA was prepared by free radical polymerization by dissolving monomer MMA and initiator, potassium persulphate in aqueous methanol media with medium content methanol/water (40/60). The reaction started by purging the reaction medium over inert nitrogen gas for 1 hr and reaction was left to complete the polymerization for 24 hrs. The presence of functional groups of PMMA were analysed by using ^{1}H-NMR, FTIR and ATR. The third stage was to synthesize spiropyran. Spiropyran was synthesized by condensation reaction (Scheme 1) of precursor Fisher's base 1,3,3-trimethyl-2-methyleneindoline (0.87 g, 5 mmol) with 2,3-dihydroxybenzaldehyde (0.7 g, 5 mmol) by dissolving into anhydrous ethanol and refluxed for 5 hrs and checked by TLC to confirm the formation of product. The resulting solution was subjected to flash column chromatography for further purification. Flash column chromatography was packed with silica gel as stationary phase. Petroleum ether-ethyl acetate with the ratio (4:1) was used as the eluent. Spiropyran was structurally characterized using ^{1}H-NMR and ATR. Lastly, PMMA thin film embedded with spiropyran and lemongrass oil were prepared by solution casting using DCM as the solvent. Spiropyran and lemongrass oil were mixed together in DCM and poured into a petri dish for complete evaporation of solvent before baked in an oven at 60°C for 20 min. Both spiropyran and thin film were characterized by UV-Vis spectroscopy to study their photochromic properties and the thin film's morphology was analysed using FESEM.



Scheme 1 Synthesis Spirobenzopyran.

3. RESULTS AND DISCUSSION

3.1. Extraction and Characterization of Lemongrass Oil

The lemongrass essential oil obtained appeared as slightly dark yellow with fresh and lemony odor. The percentage yield of lemongrass oil obtained through solvent extraction and steam distillation were 0.45% (0.67 g) and 0.21% (0.32 g). Solvent extraction technique gave higher yield of oil as compared to steam distillation since highly non-polar solvent hexane was used to extract non-polar lemongrass oil. Non-polar solvent was known to dissolve other non-polar chemical compounds. In contrast, steam distillation was carried out for 6 hrs by heating a lemongrass in water and caused thermal degradation of some constituents in lemongrass causing the loss of highly volatile compound therefore gave the lower yield of oils.

GC-MS analysis of the lemongrass oils revealed the presence of 18 compounds representing 71.88% of the total oil (Table 1). The major components were geranial (32.27%), neral (24.42%), isogeranial (2.95%) and β-myrcene (0.53%). The quality of the lemongrass oil is generally determined by its citral content. Citral (3,7-dimethyl-2,6-octadienal) consists of the *cis*-isomer, geranial and the *trans*-isomer, neral. These two aldehyde compounds present in lemongrass essential oil in 61.57% of the total oils.

FTIR spectrum of lemongrass oils obtained using steam distillation (Figure 1(a)) showed a strong absorption band at 3469 cm^{-1} which indicated the presence of OH functional groups. Absorption bands observed at 2968, 2918, and 2857 cm^{-1} were attributed to the sp^3 C–H stretching. A sharp and strong absorption band at 1675 cm^{-1} showed the presence of conjugated C=O group while absorption bands at 1632 and 1611 cm^{-1} implied the presence of C=C stretching. Figure 1(b) showed the FTIR spectrum of lemongrass oils obtained by solvent extraction technique. The spectrum showed strong and broad absorption band at 3368 cm^{-1} that indicated the presence of OH functional group while absorption bands at 2975, 2916 and 2848 cm^{-1} showed the sp^3 C–H stretching. The presence of conjugated C=O group were shown by a weak absorption band at 1654 cm^{-1} while C-O absorption band was observed at 1031 cm^{-1}. Absorption bands for OH, C=O and C=C functional groups in the FTIR spectra supported the GC-MS analysis which showed the presence of geranial, neral, linalool, and citronellol.

Table 1 Chemical Compositions of Lemongrass Essential Oils Determined by GC-MS

No.	Compound Name	Retention Time (Min)	Area (%)
1	6-methyl-5-hepten-2-one	10.031	0.80
2	β-myrcene	10.272	0.53
3	linalool	22.637	0.67
4	isoneral	34.785	1.93
5	isogeranial	37.057	2.95
6	nerol	41.262	0.35
7	citronellol	41.566	0.76
8	neral	42.256	24.42
9	geranyl formate	46.570	0.18
10	geraniol	43.486	2.51
11	geranial	44.552	32.27
12	geranic acid	50.478	2.14
13	geranyl acetate	51.131	0.54
14	germacrene D	53.963	0.09
15	δ-selinene	55.874	0.16
16	α-muurolene	56.289	0.14
17	citral	76.719	0.18
18	neric acid	78.734	1.26
	Total		71.88

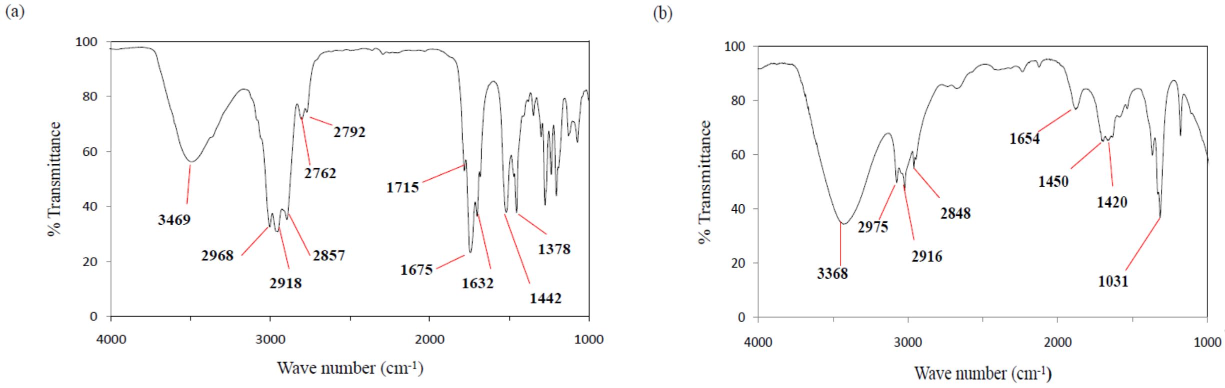


Figure 1 FTIR spectra of lemongrass oil extracted using (a) steam distillation and (b) solvent extraction.

3.2. Synthesis and Characterization of PMMA

Polymerization of PMMA was prepared from monomer MMA and initiator KPS as shown in proposed mechanism in Figure 2. The formation of white solid precipitate was obtained in the solution indicating the formation of PMMA due to hydrophobic properties of PMMA and thus will repel the water in solution and form dispersion precipitate. Yield of white solid PMMA obtained was 73% (4.4 g).

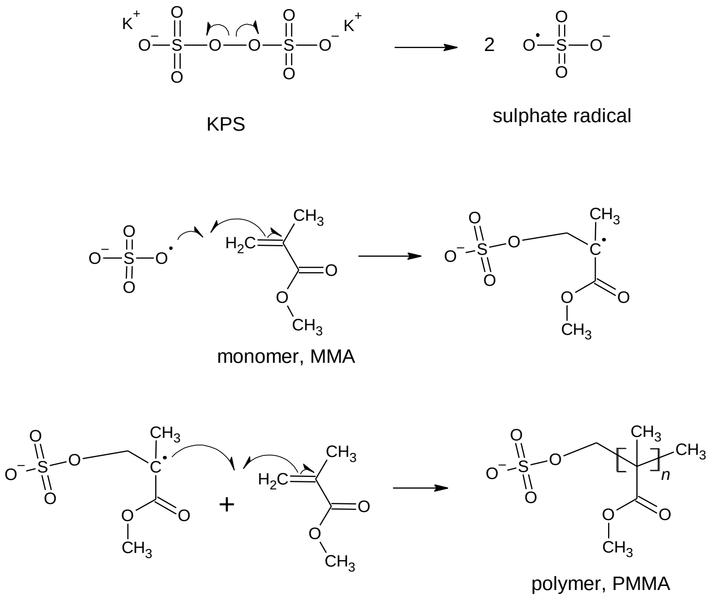


Figure 2 Proposed mechanism of PMMA.

Both liquid MMA monomer and solid PMMA were structurally characterized by ATR, FTIR and ^{1}H-NMR. Figure 3(a) and (b) of FTIR clearly shows the absorption band for C=O ester group present in MMA and PMMA at absorption band 1716 and 1727 cm^{-1} respectively. It can be seen that there was a strong and sharp absorption band at 1162 and 1148 cm^{-1} in both MMA and PMMA which can be attributed to the C–O–C stretching. Another stretching band at 2955 and 2931 cm^{-1} in MMA and 2951 and 2843 cm^{-1} in PMMA implied the presence of C–H (sp^3) in both structures. However, the peak intensity in MMA was medium strength as compared to PMMA due to the presence of only one C–H (sp^3) before polymerization. The absorption band ranging from 1387-1448 cm^{-1} can be attributed to the bending vibration of the C–H bonds of the –CH_3 group in both structures. Furthermore, there was one medium absorption bands at 3433 cm^{-1} in MMA which can be attributed to the –OH stretching due to residual inhibitor present in purified liquid MMA. Absence of absorption band at 1637 cm^{-1} in MMA which was attributed to C=C stretching mode of vinyl group significantly supports the formation of PMMA polymer.

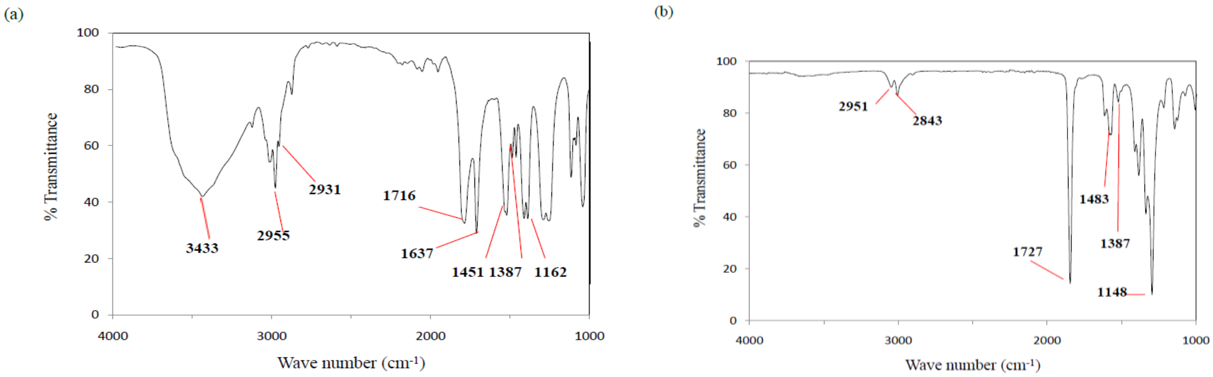


Figure 3 FTIR spectra for (a) MMA and ATR spectrum for (b) PMMA.

The ^{1}H-NMR spectra of MMA (Figure 4a) showed two signals at δ 6.06 ppm and δ 5.53 ppm attributable to two vinyl protons (H-1). These signals were absence in the ^{1}H-NMR spectrum of PMMA. Figure 4(b) showed a chemical shift at δ 1.82 ppm (2H) which corresponded to H-2 that present in the polymer. Signal for the methoxy protons, H-4 of MMA was observed at δ 3.71 ppm (Figure 4(a)). These signals became more shielded and thus shifted upfield to δ 3.61 ppm in PMMA (Figure 4(b)) due to the increase in electron density because of the polymer formation. Chemical shift of methyl protons, H-3 at δ 1.90 ppm in MMA was shifted upfield to δ 1.03 ppm. It can be concluded that the synthesised polymer was indeed a macromolecular PMMA.

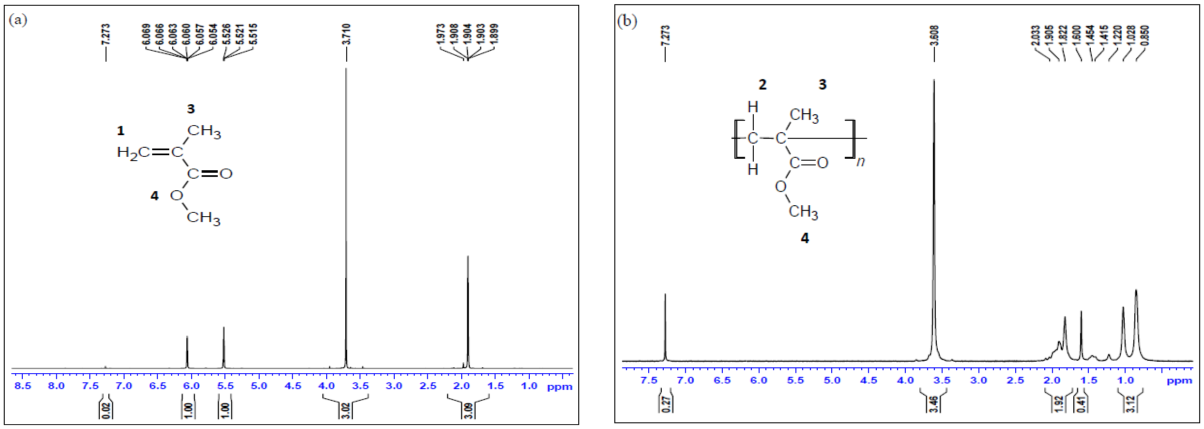


Figure 4 ^{1}H-NMR spectra for (a) MMA and (b) PMMA in $CDCl_3$.

3.3. Synthesis and Characterization of Spiropyran

2*H*-1-Benzopyran-2, 2'-(8'-hydroxy-1', 3', 3'-trimethylindoline) which can be referred as spiropyran was prepared by reaction of precursor Fisher base 1,3,3-trimethyl-2- methyleneindoline with 2,3-dihydroxybenzaldehyde in 1:1 mole ratio through a condensation reaction by which the final product was attained as greenish brown powder with percentage yield 62% (0.98 g). The ATR spectrum of spiropyran (Figure 5) showed an absorption band at 3309 cm^{-1} for the OH group which formed an intermolecular bonding with salicyldehyde. Strong absorption bands at 1605 and 1463 cm^{-1} were belongs to the aromatic C=C. The weak absorption bands at 2962 and 2866 cm^{-1} were corresponded to sp^3 C–H stretching. Absorption bands of C–O stretching was observed at 1248 and 1075 cm^{-1} with sharp and medium intensity. Furthermore, C_{spiro}–O absorption band was observed at 934 cm^{-1} that signifies the indolinobenzospiropyran compound.

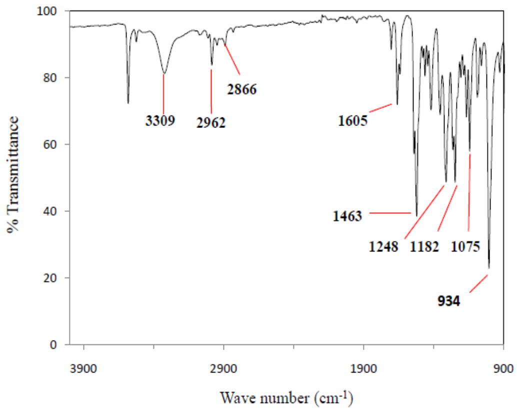


Figure 5 ATR spectrum of spiropyran.

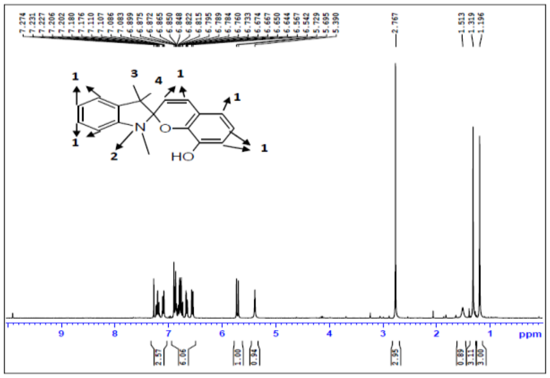


Figure 6 ^{1}H NMR spectrum of spiropyran in $CDCl_3$.

The ^{1}H-NMR spectrum of spiropyran (Figure 6) showed signals in the range of δ 7.19-5.39 ppm which belong to the aromatic protons of spiropyran molecule. Signals of two germinal methyl protons, H-3 and H-4 were observed at δ 1.19 ppm and δ 1.31 ppm. Signal for N-methyl (H-2) was seen at δ 2.76 ppm due to ring closed form consisting of orthogonal nature of both indoline and benzopyran.

In addition, photochromic study of spiropyran to merocyanine upon irradiation with electromagnetic radiation (UV) was monitored with UV-Vis spectroscopy. The greenish brown of spiropyran was dissolved in DCM in concentration of 10 µm. The UV- Vis spectra were recorded until no change in absorbance observed. From the UV- Vis spectra in Figure 7, it shows that the absorption maximum of spiropyran was located between wavelength 400 and 410 nm. The formation of open zwitterrionic coloured form (merocyanine) has strong absorption in the visible region (400-600 nm). The merocyanine form has a fully delocalized π-electron system which shows a red shift (shifted to longer wavelength) in the absorption spectrum accompanying the ring opening of spiropyran. In addition, increase in absorbance from 0 to 0.35 within 10 min of irradiation under UV light indicating the formation of spiropyran to merocyanine form.

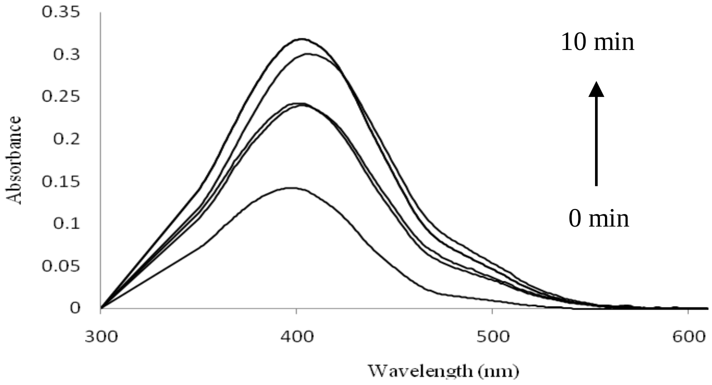


Figure 7 UV spectra of spiropyran in dichloromethane at concentration 10 µM

3.4. Preparation and Characterization of PMMA Embedded with Spiropyran and Lemongrass Essential Oil

PMMA embedded with spiropyran and lemongrass essential oil was prepared by dissolving PMMA, spiropyran and oil in dichloromethane and the film obtained was subjected to UV-VIS-NIR spectrophotometer for photochromic study. Based on electronic absorption spectrum in Figure 8, it showed one maximum absorption wavelength (λ_{max}) at 500 nm in the visible region. This absorption band was bathocromically shifted from shorted wavelength as shown in Figure 7 to longer wavelength with respect to the free merocyanine absorption. The presence of polymeric matrices has shifted the maximum absorption band of closed form spiropyran at 330 nm to the longer wavelength between 500-600 nm in the visible band. Upon irradiation with UV light, the formation of open zwitterrionic colored form (merocyanine) shows strong absorption in the visible region (500 nm). The merocyanine form has a fully delocalized π-electron system which shows a red shift in the absorption spectrum accompanying the ring opening of spiropyran. Therefore, by incorporating spiropyran in the polymeric matrices, the absorption wavelength shifted to longer wavelength in the visible region

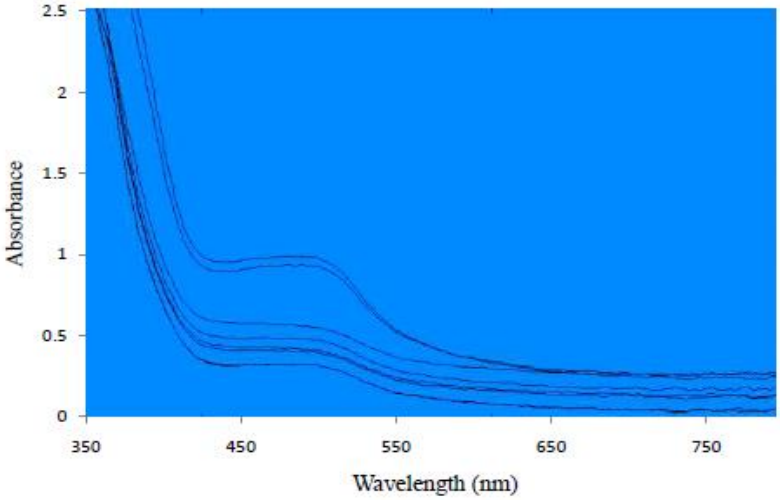


Figure 8 UV-Vis spectra spectrum of PMMA embedded with spiropyran and lemongrass oil.

Morphologies of PMMA embedded with spiropyran and lemongrass essential oil were characterized by using Field Emission Scanning Electron Microscopy (FESEM) to know the surface morphologies of the compound. As shown in Figure 9(a) at magnification 10kX, the morphology of PMMA film gave a rough unhomogenous dispersion of spiropyran and lemongrass oil. At magnification 50kX to 150kX as shown in Figure 9(b), (c), (d) and (e) a clearer image of the thin film was displayed. It was seen that, the spiropyran and lemongrass oil aggregates on the surface of PMMA film. This happen due to the unwell distributed of the spiropyran and lemongrass oil during the preparation stage. In contrast, a morphology of PMMA film at magnification 50kX taken at different point as shown in Figure 10(a) and (b) showed a clear smooth surface indicating the fully dispersion of spiropyran and lemongrass oil on the PMMA film. The difference in dispersion of spiropyran and lemongrass oil on the PMMA film could affect the ability of the thin film to absorb the UV light and repel insect when it was further developed as a coating material to be used in smart window application. Overall, thin film of PMMA embedded with spiropyran and lemongrass oil has fascinating features to be used in smart window application as it provides both abilities to absorb UV rays and insect repellent.

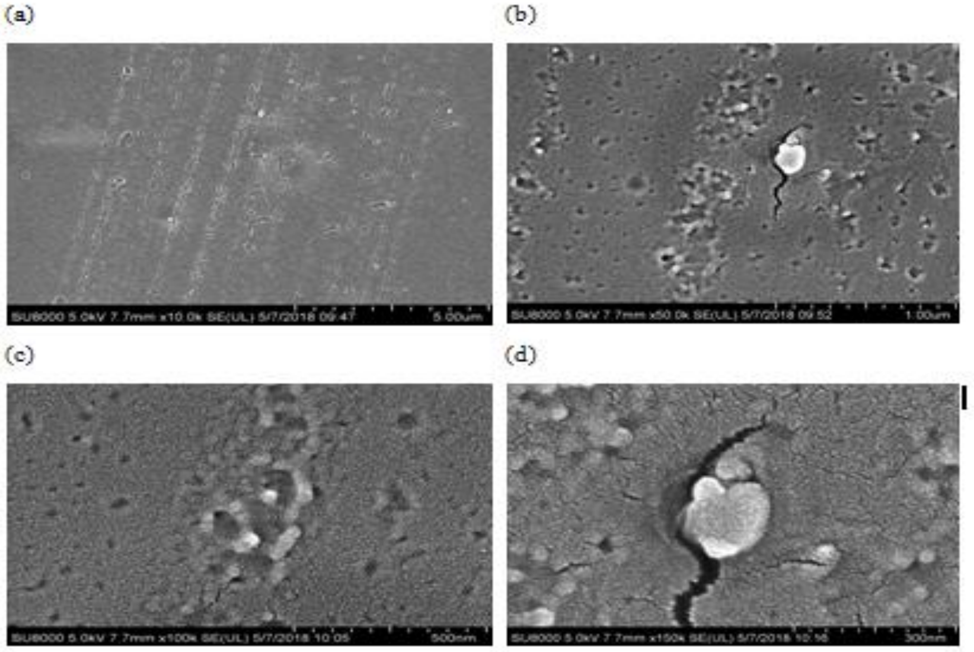


Figure 9 Morphology image for rough surface PMMA-spiropyran- lemongrass oil using FESEM at (a) 10K magnification, (b) 50K magnification, (c) 100K magnification, (d) 150K magnification.

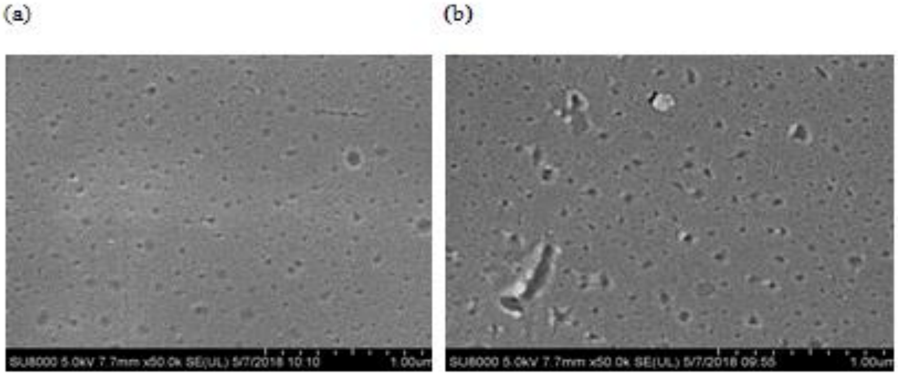


Figure 10 Morphology image for clear surface of PMMA-spiropyran- lemongrass oil using FESEM at (a) and (b) 50k magnification.

4. CONCLUSION

Poly(methyl methacrylate), PMMA embedded with spiropyran and lemongrass essential oil has been successfully prepared as brick red thin film by using solution casting system with solvent dichloromethane. Lemongrass essential oil appeared as slightly dark yellow colour with fresh and lemony odour was successfully extracted by solvent extraction and steam distillation techniques which yielded 0.45% and 0.23% oils respectively. Besides, polymer PMMA was successfully synthesis through soap free emulsion polymerization with the aid of metyl methacylate, MMA monomer and potassium persulphate, KPS as initiator giving a percentage yield of polymerization of 73% (4.4 g). Then 2H-1-benzopyran-2, 2'-(8'-hydroxy-1',3',3'-trimethylindoline) was successfully obtained as greenish brown powder in 62% (0.98 g) via condensation reaction of Fisher's base,1,3,3-trimethyl-2- methyleneindoline with 2,3-dihydroxybenzaldehyde. Structural confirmation of chemical compositions of lemongrass oil was determined by GCMS while structural characterization of PMMA and spiropyran were done using ATR, FTIR and ^{1}H-NMR. The photochromic properties and morphologies of single spiropyran and spiopyran coated onto PMMA film together with lemongrass oil showed that the maximum absorption wavelength (λ_{max}) in single spiropyran dissolved in DCM was 400 nm while spiropyran coated onto PMMA film was 500 nm. Difference in maximum absorption wavelength indicating that the presence of polymer matrices can increase photostability of spiropyran as single spiropyran less stable on its own. The Field Emission Scanning Electron Microscopy (FESEM) image of PMMA thin film showed a rough unhomogenous dispersion and clear smooth surface of spiropyran and lemongrass oil at different magnification point on the PMMA thin film. Unwell distribution of spiropyran and lemongrass oil on PMMA could be replaced by improving the method preparation by using fibre electrospinning method. As a conclusion, by utilising spiropyran and lemongrass oil on PMMA thin film, it could provides both ability to absorb UV rays and act as insect repellent which were a fascinating features to be used in smart window application.

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