Tunable Optoelectronic Properties of Polydimethylsiloxane-Arylazopyrazole Flexible Composite

Ikemefuna Uba
Hampton University
Hampton, USA
ikemefuna.uba@hamptonu.edu

Kesete Ghebreyessus
Hampton University
Hampton, USA
kesete.ghebreyessus@hamptonu.edu

Demetris Geddis
Hampton University
Hampton, USA
demetris.geddis@hamptonu.edu

Uwe Hommerich
Hampton University
Hampton, USA
uwe.hommerich@hamptonu.edu

Abstract*— Growing interest in flexible electronic platforms spurs introduction of guest structures into polymeric materials to achieve composites with novel optical and electronic properties. In this work, optoelectronic composites were realized by incorporation of novel derivative of arylazopyrazole (AAP) in polydimethylsiloxane matrix. The composites were investigated before and after irradiation with 365 nm UV source through optical spectroscopy. The responses at UV – Vis region, revealed significant regulation of properties by the presence and photo-isomerization of embedded AAP, as well as a strong dependence on concentration. The refractive indices ranged from 1.83 – 2.38 in pristine state and 1.59 – 1.71 upon UV irradiation; and associated dielectric constants were 3.5 – 5.5 and 3.0 – 4.0, respectively. The impact of concentration manifested in increasing magnitude of properties as AAP concentration increased. In pristine state, composites absorbance spectra showed maxima centered at 340 nm that was typical of $\pi \rightarrow \pi^*$ transition in the AAP. After exposure to UV, the maxima shifted to ~310 nm with secondary peak occurring at 450 nm due to $n \rightarrow \pi^*$ transition because of conformal change of the AAP to cis structure. Analyses of absorbance spectra showed that the secondary $n \rightarrow \pi^*$ transition was indirect and assisted by phonons due to rotation of AAP molecules during photo-isomerization, while primary $\pi \rightarrow \pi^*$ excitation was direct with gap values 3.1 – 3.5 eV.

Keywords—composite, arylazopyrazole, polydimethylsiloxane, optical property

I. INTRODUCTION

Interest in optoelectronics applications and flexible devices has enhanced the need for materials whose optical and electronic properties would be amenable to external stimuli. In this niche, polymeric materials are very much in focus, where controlled optical characteristics is a major study. A widely used approach to modify optical properties like refractive index of polymeric materials involves the incorporation of organic and inorganic functional groups with high refractive index into the polymer structure [1 – 3]. The Resultant hybrid materials adopted optical and electronic traits of both host and guest. For instance, polyimide-polydimethylsiloxane (PDMS) composite featured $\pi \rightarrow \pi*$ electronic transitions due to double bond in polyimide, while amount of PDMS in the matrix regulated refractive index and dielectric constant [1]. Alternatively, light-induced index change in materials could be obtained through simple photochromic compounds. To achieve photo-controlled optics, it is essential to use a photo-responsive building material that can respond quickly to an applied light along with a flexible polymeric system. Given its chemical inertness and thermal stability, PDMS is a good candidate for polymer-photoswitch hybrid material.

Unlike polyimides, PDMS is devoid of double bond and cannot exhibit electronic transition [4]. Therefore, in PDMS-photoswitch composite, while PDMS dominates the thermo-mechanical properties, the photo-switch as well as its conformal change would have significant impact on the optoelectronic characteristics. This is because a material's dielectric constant (permittivity) has atomic, dipole and electronic contributions where the latter is linked to charge transport. Moderating these contributions via conformal change can regulate optical and electronic properties of the composite

Among all the classes of photoswitchable compounds studied, azobenzenes are the most widely explored owing to their reversible trans-to-cis isomerization and remarkable cyclability [5]. However, application of azobenzenes have been hampered by two major performance issues: low switching efficiency and thermal instability of the metastable cis-isomer, which causes thermally induced reversal to the more stable trans-isomer. To circumvent these shortcomings, Weston et al [6] recently introduced arylazopyrazoles (AAPs) as improved light-responsive molecular switches. These novel photo-switches exhibit near quantitative and better light-triggered reversible trans-to-cis isomerization compared to the commonly

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used azobenzene counterpart. The near quantitative photo-isomerization of the AAP moiety is expected to facilitate better light responsive systems compared to the typical azobenzene. They also possess very high thermal stabilities of the cis isomer (slow cis-to-trans thermal isomerization; $t_{1/2}$ up to 1000 days) [6] at room temperature in solution. The photo-isomerization process induces a large structural change in the shapes of these molecules and forms the basis for their photo-switching ability. These novel yet, largely unexplored photochromic compounds are readily produced and can be easily derivatized. With these unique properties of the AAP molecular photoswitches in mind, we sought to create hybrid soft photonic materials based on isomerization that will generate large index changes upon light irradiation. In particular, in this study, we report the development of new photo-switchable polydimethylsiloxane (PDMS) flexible polymeric composite films that incorporated AAP molecular switches and exhibit light-induced index changes. The light-responsiveness property could be tuned by varying the concentration of the embedded azo compound. Absorbance, refractive index, and dielectric constant are discussed to buttress the optoelectronic characteristics of the composite.

In general, the structure of the AAP photoswitch encourages existence of permanent dipole moment (D). Since trans-to-cis conformational change results from interaction with photon, then from electrodynamics consideration we see that, given disparity in electron cloud density at either sides of the molecule, electric field **E** of the light causes net force **F** such that torque about a pivot atom or bond in the molecule,

$$\tau = P \times \boldsymbol{E} + (\boldsymbol{F} \times r) \qquad (1)$$

Where $P \times \boldsymbol{E}$ is dipole moment at center of molecule ($P = qd$, q is net charge, d distance between net charge) and $\boldsymbol{F} \times r$, the moment about a pivot atom or bond at distance r. For the AAP molecular switches, the trans-isomer absorbs UV light polarized parallel to its molecular axis, generating the cis- structure mainly by rotation of the chromophores about a nitrogen atom in the N=N bond [6], thus r is associated with the atomic chain attached to one of the nitrogen atoms. $\boldsymbol{F}$ is effective electrostatic force, existing when molecule is irradiated and is responsible for rotating the molecule. The implications are (i) dielectric and refractive index of a polymer-AAP composite are tunable and (ii) AAP switching efficiency is controllable by either length of atomic chain or incorporation of elements that would enhance disparity in electron density. Recent analyses of our in-house AAP derivatives validated (ii) in agreement with "large volume change" switches in literature [5]. We found that the switching efficiency ranged from 68% - 100% in accordance with the length of chromophore chain [7]. In this work, we utilized one of the AAPs with efficiency of 100% shown in Fig. 1. Its electron cloud and permanent dipole moment in trans state optimized with Avogadro [8] are shown in Fig. 2. Regions of high electron density are marked in red, and the permanent dipole moment is directed out of plane. One easily notices the disparity in electron density at either side of the nitrogen – nitrogen double bond.

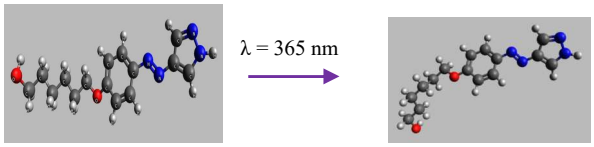


Fig. 1. Structure of Arylazopyrazole used in this work. (a) trans isomer. (b) cis isomer. The structure was optimized using Avogadro software [8].

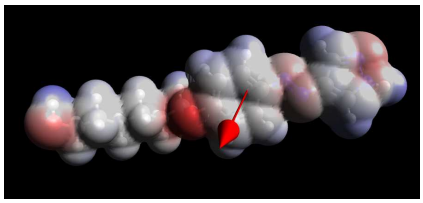


Fig. 2. Electron density distribution of the Arylazopyrazole assessed with Avogadro software [8]. Red regions indicate more negative charge density. Permanent dipole points out of the plane.

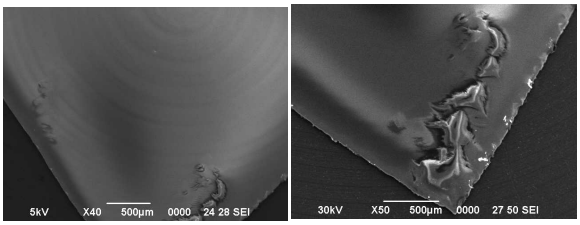
II. EXPERIMENT

A. Material

Commercial Sylgard 184 PDMS kit from Dow Corning Inc was mixed in the standard 10:1 ratio using 1.0 ± 0.04g elastomer and 0.1 ± 0.02g curing agent. Appropriate amounts of the AAP were dissolved in acetone to make 0.015M, 0.02M, 0.05M and 0.1M solutions. 50µL of each molar solution were added to dedicated PDMS mixtures, stirred manually with glass rod and then deposited on previously cleaned glass substrates via spin-coating at 1000 rpm. The high spin speed eliminated the need to degas the blend prior to coating. The coated substrates were then cured at 150°C for 20 minutes. The resulting PDMS-AAP photocomposites were transparent and could peel off the substrates. The samples, ~25µm thick, were labeled composite 1, composite 2, composite 3 and composite 4 respectively for composites containing 0.015M, 0.02M, 0.05M and 0.1M AAP.

B. Surface characterization

Surface morphology of the composites was investigated with JEOL 6390 Scanning electron microscope for structuring or clusters that would indicate phase segregation. A snippet of each composite was cut and peeled off for the imaging done at (i) 5kV/40x magnification and (ii) 30kV/50x magnification. An instance of the images is as in Fig. 3, where the absence of segregation and localized spots indicate seamless integration of photo molecules with polymer chains.



(a) (b)

Fig. 3. SEM images of composite 1. (a) 5 kV, 40x imagnification. (b) 30 kV, 50x magnification. Raised features are imprint of tweezer used to peel film off glass substrate.

C. Optical characterization

Optical properties of the composites were determined via absorbance spectra recorded with Shimazu 3600 spectrophotometer in UV – Vis range and compared to that of plain PDMS film of same thickness. A free space baseline was set in 270 – 800 nm wavelength range to eliminate stray interference and ensure that only absorbance of composites and PDMS films were recorded. A snippet of each sample was peeled off and mounted on sample holder for measurements. First, absorbance spectrum of the plain PDMS was acquired as a reference to be used to assess deviations in the composites because of the integrated photoswitch. Measurement on the composites was in two stages: (i) before UV irradiation, when embedded molecules were in trans state and (ii) after 5minutes UV (λ = 365 nm) irradiation when molecules were in cis state. We tagged these stages pristine and UV respectively. The 5 minutes exposure time was informed by prior observation that our AAPs achieve photo-stationary state (maximum trans-cis conformation) at this duration [7]. Other optical parameters of the plain PDMS and the composites were then determined from their absorbance spectra. Refractive indices, n, derive from,

$$R = [(n - 1) /(n + 2)]^2, \quad (2)$$

Where reflectance, $R = 1 - A - T$ with A and T being absorbance and transmittance. n, is associated with optical real dielectric constant of material by,

$$\varepsilon_r = n^2 - k^2 \quad (3)$$

which describes the response of a material to polarizing electric field. The extinction coefficient, k quantifies the level of attenuation of external field in the material and is given by,

$$k = (2.303A/d)(\lambda/4\pi), \quad (4)$$

with d, A as film thickness and absorbance respectively, and λ, the wavelength. The value of the extinction coefficient is a qualitative indicator of the level of energy lost by photon of particular wavelength. Therefore, through careful analysis of real dielectric constant, understanding of some of the transport phenomena in a material can be achieved. Further, when examined as is or as absorption coefficient, the slope at the onset of maximum absorbance underscores the type of charge excitation in a material. That is, abrupt or gentle rise in absorption indicates a direct or an indirect excitation and the associated band gap may be determined with Tauc expression,

$$\alpha h\nu = \beta(h\nu - E_g)^m. \quad (5)$$

Where α is absorption coefficient, ν is frequency and $h\nu$ photon energy. E_g is the bandgap and β, is a constant. m = 1⁄2, 3⁄2 is index for direct and indirect excitation, respectively.

III. Results and Discussion

SEM imaging (Fig. 3) ascertained that the photoswitching molecules engrafted homogenously into the polymer chains without localized clusters that would have resulted from phase differences. As such, any response of the composites to external stimulus would be a hybridized contribution from both the matrix and the AAP molecular switch. With respect to optical stimulus, the composites' transparency to ambient light is typical of PDMS, whereas the absorbance spectra show band excitations due to the N = N double bond of the AAP and are moderated by photoisomerization upon irradiation with 365 nm UV. As representative examples, comparative absorption spectra of pure PDMS and composites 1 and 2 are given in Fig. 4. As evidenced in Fig. 4a, the PDMS film exhibited a spike in absorbance at 270 – 300 nm. It has been observed in 170µm PDMS film that, after irradiation with laser of this wavelength range, elevated absorbance occurred at upper ultraviolet region because of photochemical surface degradation [9]. Further, absence of double bond in PDMS negates every probability of electronic excitation even at 300 – 800 nm, the range at which optoelectronic properties of materials resolve. Therefore, we consider that small thickness (25µm) made the PDMS susceptible to similar degradation from the spectrophotometer source which caused the elevated absorbance. In order to gain information about the optical nature of the PDMS-AAP composite films, UV-visible absorption spectra were recorded (Fig. 4b-c). As shown in Fig. 4b-c, absorbance spectra of composites 1 and 2 exhibit characteristics typical of trans-to-cis isomerization upon irradiation with appropriate wavelength of light at ambient temperature. This is due to isomerization of the embedded AAP molecules. Significant decrease of the UV-Vis absorption band around 340 nm was observed when slices of the films were irradiated with 365 nm light for 5 min. This observation shows both relatively fast trans-to-cis isomerization of embedded molecules and tunability of optical properties of the composites. Major absorption edges manifested at 400 nm and 350 nm respectively, for pristine and UV responses and each was underscored by a sharp rise in absorption, which indicated direct transition between energy levels. This transition occurred due to the $\pi \rightarrow \pi^*$ excitation in the embedded AAP. Thus, the primary bandgaps of the composites were evaluated with (6) for m = 0.5 to yield 3.10 eV and 3.3 – 3.5 eV for pristine and UV-exposed, respectively. Fig. 5 is a representative plot, showing absorption coefficient of composite1 with indications of the bandgaps from the extrapolation of linear region of the spectra to the energy axis. On the other hand, secondary absorbance peak at visible region after UV irradiation is associated with n $\rightarrow \pi^*$ excitation. Its gentle gradient is characteristic of indirect transition that requires contributions from other effects like phonons, defects etc. In the present case, since a photo molecule interacts with its surrounding atomic environment, it contends

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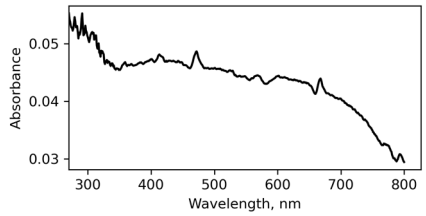
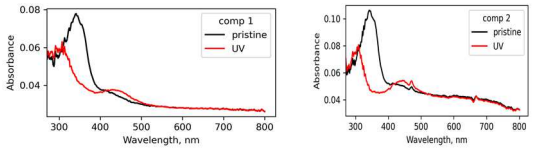
with nanoscale friction during conformal change which would increase atomic vibration that contributes to n→π* transition.



(a)



(b) (c)

Fig. 4. Absorbance of (a) 25μm PDMS ffilm, (b) – (c) 25μm composites 1 and 2 in pristine and after λ = 365 nm UV irradiation.

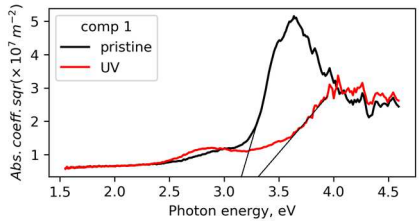
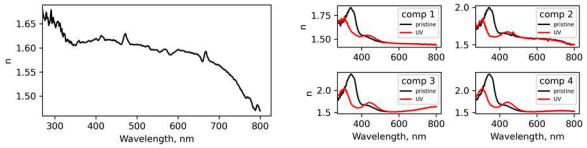


Fig. 5. Absorption coefficient of composite 1. The π→π* transition bandgaps before and after UV exposure are 3.1 and 3.3 eV respectively.

Refractive indices in UV-Vis range of PDMS and composites in Fig. 6, show significant impact of photo molecules and their concentrations. The values for PDMS range from 1.65 – 1.45 with a mean of 1.60 which is also the value at 340 nm. For a given wavelength, the indices of the composites relied on the structural state of the embedded molecular photoswitches. The results show that, at 340 nm, the indices of the pristine state range from 1.83 – 2.38 and 1.59 – 1.71 after exposure to UV (Table I). Comparing these to 1.60 of PDMS at 340 nm, gives 12.5% - 50% increase for pristine state and 6.8% after UV irradiation. This demonstrates remarkable regulation of refractive index in the composite because of the presence and the trans-to-cis isomerization of AAP molecules.



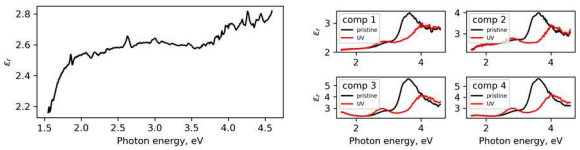
(a) (b)

Fig. 6. Refractive indices of 25μm: (a) PDMS film and (b) PDMS-AAP composites before and after 365 nm UV irradiation. The magnitude for composites is dependent on AAP concentration and photo-isomerization.

TABLE I.
REFRACTIVE INDICES
OF COMPOSITES AT 340 NM

	Refractive Index	
	Pristine*	***UV-irradiated***
Composite 1	1.83	1.59
Composite 2	1.99	1.64
Composite 3	2.36	1.70
Composite 4	2.38	1.71
PDMS	1.60	
*Maximum value		

Dielectric responses of the samples were determined with (3) over 270 – 800 nm wavelength. As function of photon energy, the real dielectric constant (ε_r) of the PDMS thin film shown in Fig. 7a varied from 2.1 – 2.8 in agreement with 2.3 – 2.8 in literation [1] and may be interpreted as first order variation typical of linear dielectrics where atomic charge displacement dominates polarization. Atomic contribution to polarization tends to decrease as frequency increases unless the polarizing external field is strong enough to ionize the atom, which would register as higher order in dielectric response and in absorbance spectrum. As no enhanced value exists in ε_r and absorbance of the PDMS, the high frequency increase in ε_r may be caused by Si-O bond, known to be flexible [1] and surface degradation mentioned above. Incorporating AAP guaranteed significant control of ε_r of the composites in pristine state and after UV irradiation as can be seen in Fig. 7b. The higher order contributions are evident and exhibited blueshift after exposure to UV. The peak values of ε_r range from 3.5 – 5.5 in pristine state at 3.5 eV and 3.0 – 4.0 at 4.0 eV after UV exposure due to π →π* and n→π* charge excitations. The attendant consequence is that charge traps are created during these transitions and can be leveraged for opto-regulated electric conductivity by further functionalizing the composites with donor fillers. Recent reports have demonstrated effective fabrication of conducting PDMS film using graphene and metal nanoparticles [10, 11]. So, incorporating AAP in such conducting PDMS is a promising approach to flexible electronics. In addition, the dielectric behavior described here makes the composites good candidates for optical waveguide applications.



(a) (b)

Fig. 7. Real dielectric constants of 25μm (a) PDMS and (b) PDMS-AAP composites before and after 365 nm UV irradiation.

IV. Conclusion

We have successfully incorporated novel arylazopyrazole based molecular switches into Polydimethylsiloxane matrix. These molecules modified the optical properties of the host material before and after exposure to 365 nm UV radiation, thereby demonstrating low-cost method for opto-regulation of material properties. In pristine state, at which embedded AAP molecules are in trans configuration, the composites real dielectric constant maxima, as function of AAP concentration range from 3.5 – 5.5 with attendant $\pi \rightarrow \pi^*$ transition at 340 nm. Upon irradiation with 365 nm UV light that induced cis configuration of the AAP, the range shifted to 3.0 – 4.0 at 310 nm with secondary significant range of 2.0 – 3.0 at 450 nm. Thus, potential application of the composites in waveguides for optofluidic systems is apparent, where tunability is attainable by photoisomerization. Further, if conductive fillers functionalize the composites, electric conductivity may be regulated in pristine state by 340 nm wavelength and in cis state by 310 and 450 nm wavelengths since transitions in the composites associated with these wavelengths tend to create charge traps. Therefore, the novel PDMS-AAP composite presented here, is a potential candidate for flexible electronics applications.

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