Investigation of spectroscopic and thermo-mechanical behaviors of different phenanthroimidazole-azo dyes in solvent and polymer medium

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Abstract
The aim of this study is the investigation of the interaction between dyes and polymers which have different polarities. Dye doped polymer films have larger application areas because of the fact that dye is more stable when doped in polymer compared to solvent medium. However, dye dispersion in the polymer medium affects both the spectroscopic and mechanical properties of the polymer. The polymer-dye interaction must be high for a good dispersion. In this study, polypropylene with apolar character and polymethylmethacrylate with polar groups were chosen as a solid phase to examine polymer-dye interactions. The photophysical properties of phenanthroimidazole-azo compounds synthesized previously were examined with UV–visible and fluorescence spectroscopy techniques in tetrahydrofuran and two polymer media. Also, photostability tests of azo dyes in THF and polymer films were performed. Surface roughness characterizations of polymer films were carried out with AFM. Additionally, the viscoelastic behaviors of the polymethylmethacrylate and polypropylene films under sinusoidal vibrations at different temperatures were studied by dynamic mechanical analysis technique.

1. Introduction

Natural and synthetic dyes play an important role in every part of life. They are used in many technical and industrial applications such as textile dyeing [1, 2], laser dyeing [3], fluorescence labeling [4], organic light emitting diode (OLED) [5] and liquid crystal display (LCD) [6] technologies.

In general, dyes are classified as anthraquinone, triphenylmethane, indigo, azo, nitro and perylene, depending on their molecular structure. Azo dyes are the most important class of dyes because they make up more than 50% of all the dyes listed in the color index. Azo dyes are used in textile [7], ink-jet printers [8], leather [9], rubber dyeing [10] and food industry [11] because of having all color shades.

Among functional macromolecules, the combination of polymers and dyes has great potential in the production of high performance materials. Colored polymers are the materials that have great attention in various technical applications. Long-term use and having flexible character of dye doped polymer films under different temperatures are desired properties especially for optoelectronic applications.

Polymers containing dyes are used extensively in optic monitoring design [12], medicine [13], storage systems [14], sensors [15] and solar cells [16].

The distribution of dye in the polymer affects the photophysical properties of dye doped polymer films. Homogeneous distribution of dye in polymer is important in terms of observing the same properties throughout the polymer film. For this reason, the polymer-dye interaction must be higher than the dye-dye interaction [17].
In this study, N,N-dimethyl-4-[[4-(1H-phenanthro[9,10-d]imidazole-2-yl)phenyl]diazenyl] aniline (PA1), 4-[[4-(1H-phenanthro[9,10-d]imidazol-2-yl)phenyl]diazenyl] phenol (PA2), 1-[[4-(1H-phenanthro[9,10-d]imidazol-2-yl)phenyl]diazenyl]-2-naphthol (PA3) which synthesized previously by our group were used [18]

Figure 1. Molecular structure of PA derivatives.

The photophysical properties of phenanthroimidazole-azo dyes (PA) doped polymer films were examined. Also these characterizations were studied for PA dyes in THF. Additionally, dye behaviors in two polymer media were observed with dynamic mechanical analyses technique (DMA).

There are studies investigating the dye behaviours in polymer medium using spectroscopy techniques. In these studies, the kinetic behaviour of dye-polymer interactions and dye concentration dependences in polymer matrices were examined with UV–vis and fluorescence spectroscopy [19–21]. Also, Slark and Hadgett studied about the dye-polymer and dye-dye interactions by means of FTIR spectroscopy technique [22]. Additionally, the interaction between polymethylmethacrylate (PMMA) and dye molecules were examined by spectroscopy techniques in the literature [23, 24]. In these studies, dye-polymer and dye-solvent interactions were also compared. Although, articles about mechanical behaviours of dye doped polymer films are available [25, 26], studies on thermo mechanical analyses of these films are limited [27].

This is a novel study that examines the variations both in thermo-mechanical properties by considering dye behaviors in polymer media and compare the results obtained from spectroscopic techniques.

2. Methods

2.1. Materials and reagents

All reagents were obtained from Sigma Aldrich and Merck. THF used in spectroscopic studies were of analytical grade and used without a purification process. Sigma Aldrich brand Polypropylene (PP) and polymethyl methacrylate (PMMA) were used as a polymer medium.

2.2. Instruments

MSE™ temperature controlled press was used for film preparation. The polymer film thicknesses were measured by a micrometer with 2 digits. UV–vis spectra were obtained with a Shimadzu UV-1800 spectrophotometer. Fluorescence measurements were performed using a Perkin Elmer LS55 spectrophotometer. DMA results were obtained with TA™ Instrument Q800 analyzer. Surface roughness were also characterized with atomic force microscopy (AFM) using Nanomagnetics hpAFM.

2.3. Preparation of polymer films

PP, which is a thermoplastic polymer, is soluble in solvents with very high boiling point due to its apolar character (1,2-dichlorobenzene; 1,2,4-trichlorobenzene etc). For this purpose, hot press technique was chosen for
the preparation of polypropylene film. For PMMA films, solvent casting technique was preferred and tetrahydrofuran (THF) was used for solving of polymer and dye.

2.3.1. Preparation of dye doped PP polymer films
The films were prepared containing 0.5% wt PA derivative in PP. Granular polymer and powder dye were mixed and kept in the oven in silicone molds around their melting point temperatures. The resulting mixture was cooled and hot pressed to yield an inhomogeneous film. After the first pressing, the films were cut into pieces and re-pressed. This process was repeated for 3 times to obtain more homogeneous samples.

2.3.2. Preparation of dye doped PMMA polymer films
The films were prepared containing 0.5, 1.0 and 5.0% wt PA derivative in PMMA. Polymer film preparation was performed with solvent casting technique. In this process the polymer was dissolved in THF and PA derivative was added to that solution. This solution stirred until completing solvation process. The homogeneous solution were poured to the clean petri dish. After the solvent evaporation and drying in the oven, the films were stripped out.

3. Results and discussion
In dye-doped polymer systems, dye molecules can be linked to the polymer chains by covalent bonds or physical interactions such as Van der Waals, dipole–dipole, hydrogen-bond. The high concentration of dye enhances the dye-polymer interaction as well as the dye-dye interaction [28]. When dye concentrations in polymer media are so high, the Lambert Beer law is invalid and the luminescence quenching occurs. Because of this reason, dye concentrations were determined according to the Lambert Beer rule. All spectroscopic characterizations were studied at 0.5% wt PA in polymer medium and $1.0 \times 10^{-5}$ M PA in THF. In addition to 0.5%; also 1.0% and 5.0% wt PA in PMMA were used for DMA studies to comparing the effects of dye concentration variations. The polymer film thicknesses were approximately determined as 200 μm by a micrometer. Theoretically, if this value approaches to the mm scale, this situation leads to the self-absorption of dye molecules which corresponds to the luminescence quenching [29].

3.1. Spectroscopic studies
The photophysical properties of PA derivatives were characterized in PP and PMMA media by means of UV–vis absorption and fluorescence spectroscopy. Additionally, THF was used as a solvent medium to compare the solvent with the polymer media.

Data related with spectroscopic characterizations; maximum absorption ($\lambda_{\text{abs}}$), emission ($\lambda_{\text{em}}$) and excitation wavelengths ($\lambda_{\text{ex}}$), molar extinction coefficients (ε), singlet energy levels ($E_s$), Stokes’ shifts ($\Delta \lambda$) of PA derivatives for THF and polymer media are shown in tables 1, 2 and 3.

3.1.1. Absorption and emission studies of PA derivatives in THF and polymer media
Compared to THF, a broadening at spectral band of dye doped polymer films was occurred in figure 2.
PA derivatives exhibit two main absorption wavelengths above 300 nm. In tables 1, 2 and 3, \( \lambda_{\text{max},1} \) values belong to \( \pi-\pi^* \) and \( \lambda_{\text{max},2} \) values belong to low-energy \( n-\pi^* \) transition. Maximum absorption wavelengths are between 332–354 nm; 425–531 nm in PP and 330–349 nm; 366–486 nm in PMMA. All derivatives exhibited also two main absorption wavelengths 319–323 and 407–510 nm in THF.

When \( \lambda_{\text{max},2} \) values of all derivatives are compared in THF, these values are sorted from PA2 < PA1 < PA3 (table 1). The same order is observed in polymer media for \( \lambda_{\text{max},2} \) (tables 1, 2 and 3). From these results, it can be concluded that donor group effect and increased conjugation in these molecules caused bathochromic shift.

\( \lambda_{\text{max},1} \) and \( \lambda_{\text{ex}} \) values showed bathochromic shift in polymer medium compared to THF (tables 1, 2 and 3).

When the maximum emission wavelengths of all derivatives were examined, they showed 11–23 nm hypsochromic shift in PP as compared to THF (tables 1, 2, 3 and figure 3). PA1 and PA3 showed 23–21 nm hypsochromic shift in PMMA compared to THF whereas PA2 showed 29 nm bathochromic shift. The PA2 possessed 40 nm bathochromic shift whereas the PA1 and PA3 didn’t show any significant change in PMMA.

**Table 3.** Spectral characterization of dye doped PMMA films.

| PA Derivatives | \( \lambda_{\text{max},1} \) (nm) | \( \lambda_{\text{max},2} \) (nm) | \( \lambda_{\text{ex}} \) (nm) | \( \varepsilon_1 \) kg.mol\(^{-1}\).cm\(^{-1}\) | \( \varepsilon_2 \) kg.mol\(^{-1}\).cm\(^{-1}\) | \( \Delta \lambda \) | \( E_{\text{S1}} \) kcal/mol | \( E_{\text{S2}} \) kcal/mol |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|------------------|
| PA1           | 349             | 377             | 335             | 371             | 70485           | 73128           | 36               | 81.75            | 75.68            |
| PA2           | 335             | 366             | 394             | 433             | 81057           | 82819           | 39               | 83.16            | 77.95            |
| PA3           | 330             | 486             | 356             | 391             | 78414           | 81057           | 35               | 86.46            | 58.70            |
compared to PP. Increase of dye-polymer interaction caused the bathochromic shift of maximum emission wavelength [24, 30].

The Stokes’ shift values were between 69–80 nm in THF, 38–58 nm in PP and 35–39 nm in PMMA medium. Stokes shift values decreased in polymer medium as compared to THF.

Stokes shift values that indicates a low self-absorption of light emitted by the dye molecules can be enhanced by increasing the amount of dye in the polymer medium [31]. In this study, the films were compatibly prepared with Lambert-Beer rule. Same films were used for spectral characterization techniques. Therefore, the dye concentration of the polymer medium may not have been sufficient to promote the dye-polymer interaction. This may have been lead to lower Stokes shift values in the polymer environment as compared to the solvent medium.

3.1.2. Photostability studies
Photostability studies of PA derivatives were performed by using a steady state spectrofluorimeter in the mode of ‘Time Based Measurements’ employing a xenon arc lamp. All of the fluorophores were excited at between 330–390 nm for both THF and solid phase. The data were obtained at their maximum emission wavelengths for one hour monitoring.

The photostability results of PA3 in THF and polymer media can be seen in figure 4. The similar and stable results were achieved for all derivatives.

3.2. Dynamic mechanical analyses (DMA)
Dynamic mechanical analysis (DMA) is one of the major thermal characterization techniques that provide fundamental knowledge about the viscoelastic properties of polymer based composites as well as polymers. In this technique, a small cyclic stress or strain is applied to the samples and their corresponding responses are recorded at various temperatures. Based on DMA results, the storage modulus ($E'$) represents the elastic features while the loss modulus ($E''$) reflects the viscous properties of the materials. Their ratio ($E''/E'$) is called as damping coefficient (tanδ) and generally used to determine the glass transition temperature ($T_g$) of structures [32]. The storage modulus ($E'$) and glass transition temperature ($T_g$) values of neat polymer and dye doped polymer films were determined in dual cantilever mode at a constant vibration frequency of 1 Hz. The temperature range of the dynamic mechanical analyzer was specified between 30 °C–150 °C with a heating rate of 5 °C min$^{-1}$ in nitrogen atmosphere. In this study the DMA measurements were conducted at an extensive temperature range to describe the alterations in the molecular mobility between polymer chains and dye material. These analyses were performed to observe the interactions of azo dye doped PP films compared to PMMA environment.

The variation of storage modulus ($E'$) and damping factor (tanδ) of composite films are plotted with respect to both dye type and concentration as shown in figures 5(a)–(c). Based on these graphs it is clearly seen that the introduction of dye resulted in the increase of storage modulus as compared to neat PMMA independent of its type. This positive contribution is attributed to the strong and effective interaction between the dye and host medium as well as the restriction of polymer segment motions by the dye presence. The measured $E'$ parameters at 40 °C as and $T_g$ values are depicted in table 4. Based on this table, neat PMMA film exhibit 1874.7 MPa rigidity while the 0.5% wt PA3/PMMA composite film possessed 2482.2 MPa modulus with approximately 32.4% improvement. Among the whole dyes, the PA3 addition led to maximum storage modulus increase for each individual percentage as apparently observed in table 4. It is also concluded from these graphs that the
temperature rising promotes the mobility of polymer chains, which caused to the reduction of $E'$ [33]. The glass transition temperatures of all composite films were determined by considering the peak values of $\tan\delta$ in the graphs. There is an obvious shift toward higher temperature in terms of $T_g$ which indicates the reduced chain mobility. Due to the dye addition, many of the polymer segments are immobilized during glass transition that resulted in the enhancement of this parameter. According to table 4, whole samples exhibit significant improvements in glass transition temperatures independent of dye type. Particularly, the $T_g$ value of 0.5% wt PA2 introduced PMMA film increased to 114.5 °C, which is approximately 40.8% higher than neat PMMA. Some composites in figures such as PMMA + 1%PA1, PMMA + 5%PA1 and PMMA + 5%PA3 showed broad transition zones unlike from the other specimens. This type of character is generally observed when the
AFM was used to characterize the dye doped polymer surface roughness parameter of 5 nm. The decrease of tan δ peak points out the reinforcement efficiency, which is associated with the degradation of mobile chains during the glass transition. According to figure 5, all composite films possessed lower tan δ peak values, as expected. This state is probably due to the chemical and physical absorption of polymer molecules on the dye surface, which led to the dropping of the chain mobility. This situation can be attributed to the homogeneous distribution and low agglomeration of the dye in PMMA. Since the different polarities of the polymers change the interaction between polymer-polymer and dye-polymer molecules, it is considered that the interaction, which is stronger in PMMA environment, creates a homogenous surface.

As seen in table 6, PA3/PP film has the highest surface roughness value compared to other PP films. Because of the fact that color intensity of PA3 was very high, it is probable that cantilever of AFM didn’t measure PA3 doped PP film exactly.

Table 4. Dynamic-mechanical analysis results of PMMA based composite films.

| Sample type   | Dye content (wt%) | E’ @40 °C (MPa) | % Change of E’ over neat PMMA | Tg (°C) | % Change of Tg over neat PMMA |
|---------------|-------------------|----------------|-------------------------------|---------|-------------------------------|
| Neat PMMA     | 0                 | 1874.7         | —                             | 81.3    | —                             |
| PA1/PMMA      | 0.5               | 2039.8         | +8.8                          | 91.1    | +12                           |
| PA1/PMMA      | 1                 | 1933.2         | +3.1                          | 105.7   | +29.9                         |
| PA2/PMMA      | 0.5               | 2170.8         | +15.8                         | 108.2   | +32.9                         |
| PA3/PMMA      | 0.5               | 2240           | +19.5                         | 114.5   | +40.8                         |
| PA3/PMMA      | 1                 | 2061.7         | +9.9                          | 113.6   | +39.7                         |
| PA3/PMMA      | 5                 | 1932.1         | +4.1                          | 88.13   | +8.4                          |
| PA3/PMMA      | 0.5               | 2482.2         | +32.4                         | 90.8    | +11.6                         |
| PA3/PMMA      | 1                 | 2303.9         | +24.3                         | 110.2   | +35.5                         |
| PA3/PMMA      | 5                 | 2388.4         | +27.4                         | 97.7    | +20.1                         |

Table 5. Dynamic-mechanical analysis results of PP based composite films.

| Sample type   | Dye content (wt%) | E’ @40 °C (MPa) | % Change of E’ over neat PP | Tg (°C) | % Change of Tg over neat PP |
|---------------|-------------------|----------------|----------------------------|---------|----------------------------|
| Neat PP       | 0                 | 1055.3         | —                           | 94.5    | —                           |
| PA1/PP        | 0.5               | 1117.2         | +5.9                        | 107.3   | +13.5                       |
| PA2/PP        | 0.5               | 1274           | +20.7                       | 116.3   | +23                          |
| PA3/PP        | 0.5               | 1154.6         | +9.4                        | 108.4   | +14.7                       |

Structure exhibit heterogeneity and broader distribution of relaxation times. Based on literature the decrease of tan δ peak points out the reinforcement efficiency, which is associated with the degradation of mobile chains during the glass transition. According to figure 5, all composite films possessed lower tan δ peak values, as expected. This state is probably due to the chemical and physical absorption of polymer molecules on the dye surface, which led to the dropping of the chain mobility. There wasn’t any regular variations in E’ and Tg values due to the dye quantity in PMMA medium. These results can be attributed to the agglomeration of dye molecules at high concentrations in PMMA medium.

The dye addition to PP medium increased the storage modulus compared to neat PP (table 5). This positive change is due to the limitation of polymer segment motion in the presence of dye as in PMMA. Storage modulus values of PP medium were found lower than PMMA medium.

Based on table 5, neat PP film exhibit 1055.3 MPa rigidity while the 0.5% wt PA2/PP composite film possessed 1274 MPa modulus with approximately 20.7% improvement. Whole samples exhibit significant improvements in glass transition temperatures independent of dye type. The Tg value of PA2 introduced PP film increased to 116.3 °C, which is approximately 23% higher than neat PP.

3.3. AFM results
AFM was used to characterize the dye doped polymer films and operated in tapping mode (24 ± 2 °C) using commercial silicon microcantilever probes. The probe tip radius and probe spring constant values were in the ranges of 5–10 nm and 20–100 N/m.

In figures 6 and 7, 3-D topographical images of the neat polymers and dye doped polymer films show the surface roughness parameter of 5 μm × 5 μm and 10 μm × 10 μm respectively. Ra (average surface roughness) values were given in tables 6 and 7 for PP and PMMA polymers, respectively. As seen in these tables, the surface roughness increased with the addition of dye in both media. The results showed that the dye doped PMMA films had lower surface roughness values than PP films except for PA2. On the contrary, neat PMMA film has higher surface roughness value than neat PP film.

AFM images of PMMA had more uniform surface than PP. Dye particles could be obviously seen in PP films. This situation can be attributed to the homogeneous distribution and low agglomeration of the dye in PMMA. Since the different polarities of the polymers change the interaction between polymer-polymer and dye-polymer molecules, it is considered that the interaction, which is stronger in PMMA environment, creates a homogenous surface.

As seen in table 6, PA3/PP film has the highest surface roughness value compared to other PP films. Because of the fact that color intensity of PA3 was very high, it is probable that cantilever of AFM didn’t measure PA3 doped PP film exactly.
4. Conclusion

In this study, spectroscopic measurements of dyes with different functional groups were performed in two different polymers (PP, PMMA) and a solvent environment (THF).

The dye-polymer interactions of the PMMA polymer were investigated by both spectroscopic and DMA techniques. When the results obtained by both techniques are interpreted, it is seen that there is a good correlation between two techniques. Accordingly PA2 and PA3 derivatives, which are considered as the strongest of dye-polymer interaction, have been found to emit at higher wavelengths and exhibit higher storage modulus ($E'$) values. In addition, the storage modulus and Tg values of all dye doped polymer films are significantly increased compared to both neat polymer media. Due to the dye addition, many of the polymer segments are immobilized during glass transition that resulted in the enhancement of Tg parameter. The highest glass transition temperature value was observed for 0.5 and 1% wt PA2 dye type.

Spectroscopic studies have been carried out with only 0.5% wt PA derivatives to avoid deviations from the Lambert-Beer law. In the DMA studies, 0.5%, 1% and 5% wt PA for PMMA and 0.5% wt PA for PP were investigated.

When PA2 and PA3 were doped into polymer medium, dye-polymer interaction was observed both in spectroscopic and DMA results, but no significant differences were obtained when PA1 derivative was doped into polymer medium.

The interactions between the functional groups in polymer and dye molecules can effect thermal and spectroscopic properties.

In general, better results were obtained in PMMA compared to PP both spectroscopically and thermo mechanically.
Methyl groups bound to the N atom sterically reduce the interaction of PA1 with the polymer medium. This interaction is more definite by means of OH groups of PA2 and PA3. AFM results indicated that dye doping increased the surface roughness values of polymer films. Based on topological images, the PMMA exhibited uniform structure with low agglomeration.

Dye-polymer interactions can be examined using both spectroscopic and dynamic mechanical analysis by changing the dye or polymer structure. The weakening of the dye-polymer interaction also reduces the important thermo-mechanical properties of the polymer material. These results show that the increase in dye-polymer interaction can allow production of material suitable for long-term use with increased thermo-mechanical properties as well as longer emission wavelengths.

Table 6. Surface roughness test results for PP medium.

| Polymer medium | Neat PP | PA1/PP | PA2/PP | PA3/PP |
|----------------|---------|--------|--------|--------|
| Surface Roughness (nm) | 15.75   | 61.87  | 67.27  | 370.00 |

Table 7. Surface roughness test results for PMMA medium.

| Polymer medium | Neat PMMA | PA1/PMMA | PA2/PMMA | PA3/PMMA |
|----------------|-----------|----------|----------|----------|
| Surface Roughness (nm) | 27.57   | 46.61  | 75.42  | 119.88  |
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