

Thermal and Optical Properties of Predesigned Azobenzene-cholesteryl Based Eutectic Gels

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ABSTRACT

The thermal and optical properties of three different pre-designed eutectic gels were investigated. The gels were obtained by gelation of azobenzene-cholesteryl derivatives by varying substitutions at the terminal position of the azobenzene unit [H/unsubstituted (Azo-1), pyridine (Azo-2) and ester (Azo-3)]. Gelation ability was studied in a deep eutectic solvent of Choline Chloride: Urea (Ch: Urea). The viscosity of the gels was greater than 400 mPa·s and viscosity was found to decrease as temperature increased, due to the weakening of the attractive forces between the molecules. The thermal stability of the eutectic gels, in decreasing order, was Azo-1 > Azo-2 > Azo-3. Among the gels, Azo-1 and Azo-2 underwent a single-step degradation at 242 and 265 °C, respectively. However, Azo-3 gel underwent a two-stage degradation; the first at 160 °C due to cleavage of the ester attached to the terminal position of the azobenzene, and the second at 245 °C which corresponds to the breaking of the carbonate link [O-C(=O)-O-]. The photolysis of all the gels exhibited obvious absorption maxima at 369 nm, corresponding to the π - π^* transition band of the trans-isomers of the azobenzene units. However, the gels did not undergo photo-isomerization under irradiation. It is suspected that this was due to the high viscosity of the eutectic solvent which arrested the transformation of the *trans*-to-*cis* isomers. Reflectance spectra results showed that all the gels had a reflectance greater than 30% under visible light (> 400 nm) as well as in the near IR region (> 700 nm).

Keywords: Deep eutectic solvent; eutectic gel; azobenzene derivatives; thermal properties; viscosity; optical properties.

1. INTRODUCTION

Since their discovery, low molecular weight organogelators (LMGWs) have become an increasingly important experimental material. Over the past two decades, research on LMGWs has grown to include uses in the fields of environmental remediation of organic liquid spills, such as crude oils, refined petroleum products (engine oil, diesel etc.) on bodies of open water, drug delivery, smart materials and stimuli-responsive materials (Aykent *et al.* 2019; Hirst *et al.* 2008; Skilling *et al.* 2014; Valls *et al.* 2020; Vibhute *et al.* 2016). Depending on the molecular structure, the gels can be classified as ALS or A(LS)₂ organogelators; in which A, L and S refer to the aromatic, linker and steroidal units, respectively. The LMWG structures are successfully regulated by changing the composition of L, S or A, and the resulting gelators are able to gel in a wide variety of solvents (Rizkiana *et al.* 2015; Sangeetha and Maitra 2005). For example, selection of photochromic units, such as azobenzene for component "A", in the one gelator type creates gels that can be tuned using light. Given this phenomena, a number of azobenzene based multi-stimuli organogelators have been developed and their real world application have already been reported in studies (Bai *et al.* 2016; Balamurugan *et al.* 2014; Kuo *et al.* 2017; Yang *et al.* 2014).

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However, from an environmental point of view, these organic liquids also have many intrinsic drawbacks, such as accumulation in the atmosphere due to their low boiling points, flammability, high toxicity and non-biodegradability (Alonso *et al.* 2016). The solution to this has been to replace them with designer solvents known as deep eutectic solvents (DESs) which also comply with green chemistry principles (van Osch *et al.* 2019). DESs consist of two or more components that liquefy upon contact. Frequently this liquefaction is caused by the entropy of mixing, and the various interactions via hydrogen bonding and van der Waals forces (Francisco *et al.* 2013; Smith *et al.* 2014). DESs also share some of the well-known characteristics of ionic liquids, namely low volatility, high conductivity, wide liquid temperature range, and high solvation ability, for a large number of compounds. These benefits are in addition to their high biodegradability, ease of preparation, and their renewable nature (Abbott *et al.* 2011; Dai *et al.* 2013; Farias *et al.* 2018; Ge *et al.* 2020; Ge *et al.* 2019; Longo Jr and Craveiro 2018; Pavaglio *et al.* 2021; Rogošić *et al.* 2019; Smith *et al.* 2014; Wang *et al.* 2020). These benefits are contributing to the growing interest in DES gel development. This laboratory recently published a study on azobenzene-cholesteryl based eutectic gels, their morphology and mechanisms of gel formation (Rathinam 2021). In that paper, four different eutectic solvents were prepared including, Zinc Chloride: Ethylene Glycol (Zn: EG); Choline Chloride: EG (Ch: EG); Choline Chloride: Urea (Ch: Urea); and Choline Chloride: Glycine (Ch: Gly). The gelation ability of five different pre-designed azobenzene-cholesteryl derivatives, Azo-1 through Azo-5, and their aggregation behaviors were studied by morphological analysis using scanning electron microscopy (SEM). In a continuation of that work, this report selects three of the previously mentioned eutectic gels,

focusing on the gels formed Choline Chloride: Urea (Ch: Urea). This paper tests and documents their viscosity, thermal and optical properties by using rheometric analysis, thermogravimetric analysis and absorption spectroscopy, respectively.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were purchased from Aldrich Chemicals and used without further purification. All solvents were purified before use. Aniline, *p*-anisidine, ethyl-4-aminobenzoate, (–)-cholesteryl chloroformate and 4-(dimethylamino)pyridine were purchased from Sigma Aldrich and used as received, without further purification. Trimethylamine and *N,N*-dicyclohexyl carbodiimide (Aldrich) were used as received. The chemicals for the preparation of the deep eutectic solvent, such as choline chloride and urea were purchased from Sigma Aldrich, and used as received. Dichloromethane was distilled over calcium hydride under argon immediately before use, and all solvents were purified and dried by standard procedures before use. All the pre-designed azobenzene-cholesteryl compounds were synthesized according to the procedure described in the earlier publications (Balamurugan *et al.* 2014; Rathinam 2019, 2021).

2.2 Instrumentation

Fourier transform infrared spectra (FTIR) of the synthesized compounds were recorded using an FTIR spectrophotometer (Spectrum One, PerkinElmer). Nuclear magnetic resonance (NMR) spectra of all the precursor and eutectic gelators were obtained using a Bruker AMX-500 (Darmstadt, Germany) high-resolution NMR spectrometer, and the chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. The absorption and reflectance spectra were recorded by a Jasco-V770 spectrophotometer in Ch: Urea eutectic solvent. TGA thermograms were recorded using TA instruments TGA-2050 thermal analysis system. Viscosity of the eutectic gels were recorded using a HR-2 Discovery Hybrid Rheometer at a heating rate of 10 °C/min.

2.3 Synthesis of precursors

Reaction precursors were primarily azobenzene derivatives with different substitution (H/unsubstituted, N-substituted and ethyl ester substituted) at the terminal position of the azobenzene, and these were synthesized following the reported procedure in (Nickmans *et al.* 2018). For example, unsubstituted azobenzene (E)-4-(phenyldiazenyl)phenol was synthesized as follows: About 1 equivalent of aniline (5.12 g, 55 mmol) was dissolved in 1M hydrochloric acid and cooled to 5 °C. To this solution, aqueous sodium nitrite (3.80 g, 1 equivalent, 55 mmol; 25 ml water) was added dropwise in order to obtain diazonium salt. This mixture was added dropwise to cold phenolate solution (1 equivalent of phenol dissolved in 1 equivalent of sodium carbonate and stirred at 5 °C). The resulting mixture was then neutralized with 1M HCl to precipitate the product, which was then filtered, washed with water, and dried. The resulting crude product was purified by recrystallization in ethanol, with a yield of 79%. A similar procedure was adopted for the synthesis of the other compounds, in which respective amines were used instead of aniline.

2.4 Synthesis of gelators

The procedure for the synthesis and spectral characterization of the gelator molecules followed that described in (Rathinam 2019). For

example, compound Azo-1 was synthesized as follows: The synthesized precursor, (E)-4-(phenyldiazenyl)phenol (1.98 g, 10 mmol) and triethylamine (3.036 g, 30 mmol) were placed in double-neck round-bottom flasks with nitrogen inlets and dissolved in dry chloroform. Next, a small amount of 4-(dimethylamino)pyridine (DMAP) dissolved in chloroform was slowly added to these solutions, with constant stirring under a nitrogen atmosphere. Then, cholesteryl chloroformate (4.491 g, 10 mmol) that was dissolved in chloroform was added dropwise to the solution through a funnel. After this addition, the reaction mixture was stirred at room temperature for 48 h. The contents of the flasks were extracted with excess chloroform and washed with aqueous sodium bicarbonate, a brine solution, and water. This procedure was used to obtain the organic phase, which was dried over anhydrous magnesium sulfate and then concentrated. The resulting crude product was recrystallized from ethanol to obtain a pure final compound (yield 79%). A similar procedure was adopted for the synthesis of compounds Azo-2 and Azo-3.

2.5 Preparation of Deep Eutectic Solvents (DES) and eutectic gel

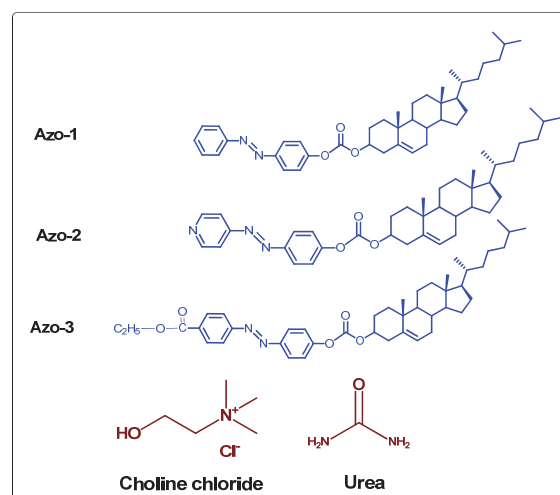
Detailed information for the preparation of DESs can be found in (Rathinam, 2021) (Ruiz-Olles *et al.* 2019). This study only used choline chloride: urea, which was prepared by mixing choline chloride and urea in a 1:2 molar ratio and heated to a temperature exceeding 80 °C. The heating continued until a homogenous liquid was obtained. The resulting DES, Ch: Urea DES, was allowed to cool to room temperature and was found to be little viscous than water.

To derive an eutectic gel, about 3 mg of gelator was taken in a small vial. To this about 100 microliters of the above prepared DES was added. The resulting mixture was heated until the solution was homogeneous, and then allowed to cool, producing the corresponding eutectic gel.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of eutectic gelators

The synthetic route and spectral characterization including FTIR, ¹H and ¹³C-NMR for the pre-designed eutectic gelators Azo-1, Azo-2, Azo-3 have been provided in an earlier publication (Rathinam 2019, 2021). The structures of the gelators and the DES are shown in Scheme 1.



Scheme 1. Structures of eutectic gelators and DES

The eutectic gelsators, Azo-1, Azo-2, Azo-3, were prepared by reaction with hydroxy azobenzene derivatives, with cholesteryl chloroformate, in the presence of triethyl amine in chloroform or dichloromethane, and had a yield of 69 ~ 79%. All the compounds were purified by recrystallization in ethanol. All the compounds were found to be soluble in DMF, CHCl_3 , CH_2Cl_2 , and acetone, but were insoluble in ethanol, methanol and toluene. The structures of all the eutectic gelators were confirmed spectroscopically.

Azo-1 (Rathinam 2019, 2021): Yield: 79%; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2868, 2947 (CH_2), 1764 ($\text{C}=\text{O}$), 1500, 1586 ($\text{C}-\text{C}$ in Ar), 1247 (COC). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, δ in ppm): 7.97 – 7.90 (m, 4H), 7.53 – 7.47 (d, 2H), 7.36 – 7.34 (m, 2H), 7.26 (t, 1H), 5.44 (d, 1H), 4.66 (m, 1H), 2.51 – 1.33 (m, 28H), 1.09 (s, 3H), 0.93 (d, 3H), 0.87 (d, 6H), 0.69 (s, 3H). ^{13}C NMR (500 MHz, CDCl_3) δ 152.91, 150.21, 139.05, 131.07, 129.07, 124.05, 123.28, 121.65, 79.13, 77.25, 56.66, 56.12, 49.97, 42.30, 39.69, 39.50, 37.92, 36.82, 36.54, 36.17, 35.78, 31.90, 31.83, 28.21, 28.00, 27.63, 24.27, 23.82, 22.81, 22.55, 21.04, 19.27, 18.71, 11.85.

Azo-2 (Rathinam 2019, 2021): Yield: 76%; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2867, 2949 (CH_2), 1763 ($\text{C}=\text{O}$), 1718 ($\text{C}=\text{O}$), 1497, 1602 ($\text{C}-\text{C}$ in Ar), 1255 (COC). ^1H NMR (500 MHz, CDCl_3) δ 8.20 – 8.19 (d, 2H), 8.18 (d, 2H), 7.99 – 7.92 (m, 4H), 7.37 – 7.36 (m, 2H), 7.26 (t, 1H), 5.43 (d, 1H), 4.43 – 4.39 (m, 1H), 2.50 – 1.33 (m, 28H), 1.17 (s, 3H), 0.99 (d, 3H), 0.87 (d, 6H), 0.68 (s, 3H). ^{13}C NMR (500 MHz, CDCl_3) δ 165.99, 154.92, 153.48, 150.10, 139.01, 132.24, 130.55, 124.38, 123.30, 122.60, 121.74, 79.21, 77.25, 61.25, 56.65, 56.12, 49.96, 42.29, 39.68, 39.49, 37.90, 36.81, 36.53, 36.16, 35.77, 31.89, 28.20, 27.99, 27.61, 24.26, 23.81, 22.80, 22.54, 21.03, 19.26, 18.70, 11.84.

Azo-3 (Rathinam 2019, 2021): Yield: 69 %; FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2874, 2947 (CH_2), 1759 ($\text{C}=\text{O}$), 1721 ($\text{C}=\text{O}$), 1490, 1606 ($\text{C}-\text{C}$ in Ar), 1251 (COC). ^1H NMR (500 MHz, CDCl_3) δ 8.36 (d, 2H), 7.94 – 8.34 (m, 4H), 7.01 – 7.26 (d, 2H), 5.39 (d, 1H), 4.04 – 4.12 (d, 2H), 2.39 – 1.85 (m, 28H), 1.11 (s, 3H), 0.97 (d, 3H), 0.87 (d, 6H), 0.66 (s, 3H). ^{13}C NMR (500 MHz, CDCl_3 , δ in ppm) 162.94, 156.06, 154.68, 148.18, 146.17, 139.40, 125.60, 124.68, 123.07, 122.88, 114.91, 77.62, 77.25, 77.00, 76.74, 68.51, 67.84, 56.67, 56.12, 49.98, 42.29, 39.50, 38.05, 36.85, 36.53, 36.16, 35.77, 31.88, 31.83, 28.20, 28.00, 27.70, 25.96, 25.70, 24.26, 23.81, 22.80, 22.54, 21.02, 19.24.

All the spectral values obtained were in accordance with the assigned structures.

3.2 Viscosity of eutectic gels

The viscosity of all the gels were measured with respect to different temperatures using a Discovery Hybrid Rheometer, and the findings are shown in Fig. 1. For measuring the viscosity of all the gels, a 0.5 M solution of each in Ch: Urea was prepared. Figure 1 shows that the highest viscosity was at room temperature (30 °C) for all the eutectic gels, where they all exceeded 400 mPa·s. Among the gels, Azo-3 eutectic gel showed lower viscosity at room temperature than the others. In all cases, gel viscosity reduced as temperature increased. Each eutectic gel attained its lowest viscosity at the highest tested temperature (85 °C), and those viscosities were 53.4, 92.4 and 149 mPa·s for Azo-1, Azo-2, Azo-3, respectively. This change is due to the increased kinetic energy through heating weakening the attractive forces between molecules (Ramirez Verduzco 2013; Yusof *et al.* 2014). Since all eutectic gels were prepared in Ch: Urea, there were no obvious individual differences found in the viscosity of the gels when the temperature was increased.

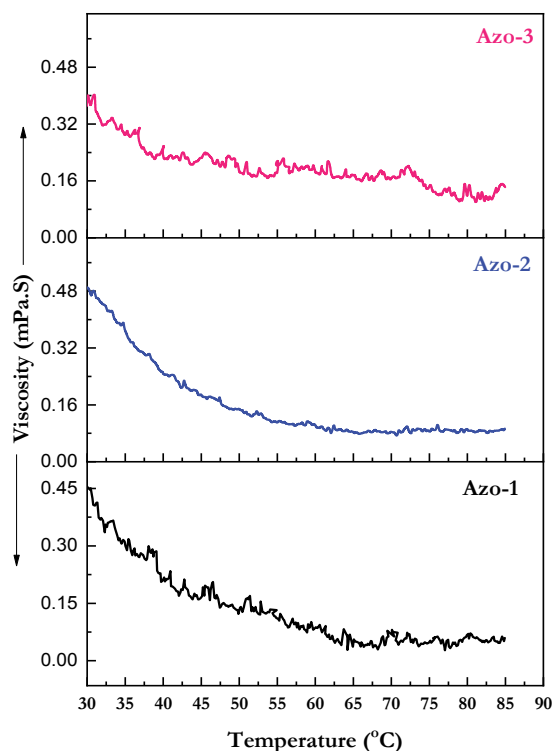


Fig. 1 Temperature dependent viscosity of the three eutectic gels in Ch:Urea.

3.3 Thermal Properties of the eutectic gels

The thermal behavior of the eutectic gels was evaluated by TGA in a nitrogen atmosphere at a heating rate of 10 °C/min; the traces of all derivatives are shown in Fig. 2, and the data is presented in Table 1. The thermal stability of all the eutectic gels were evaluated by 5 and 50% weight loss at the minimum temperature.

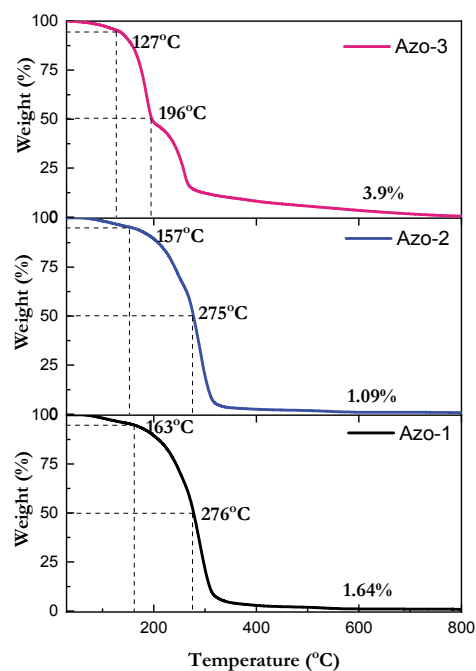


Fig. 2 TGA thermograms of the three eutectic gels in Ch: Urea.

Table 1 Thermal decomposition values of eutectic gels.

Eutectic gel	TGA			
	^a 5%	^b 50%	Degradation at	% of Residue at 600 °C
Azo-1	163	276	242	1.64
Azo-2	157	275	265	1.09
Azo-3	127	196	160&245	3.9

^aTemperature corresponding to 5 wt % loss.

^bTemperature corresponding to 50 wt % loss.

The results showed that in a nitrogen atmosphere, all the eutectic gels were stable up to 127 °C, and began to degrade above that. From the 5 and 50% weight loss measurement, the thermal stability of the derivatives was found to be in the following order: Azo-1 > Azo-2 > Azo-3. From the results it was observed that the thermal stability of Azo-2 eutectic gel was lower than that of Azo-1, which indicates that the unsubstituted azo derivative possesses a higher thermal stability than N-substituted. Similarly, pyridine substituted gel possessed a higher thermal stability than ethyl ester substituted gel. This may be due to the fact that the presence of the ester linkage at the terminal introduces greater flexibility to the azobenzene, bringing down the thermal stability below the unsubstituted and N-substituted variants, which have more rigid structures.

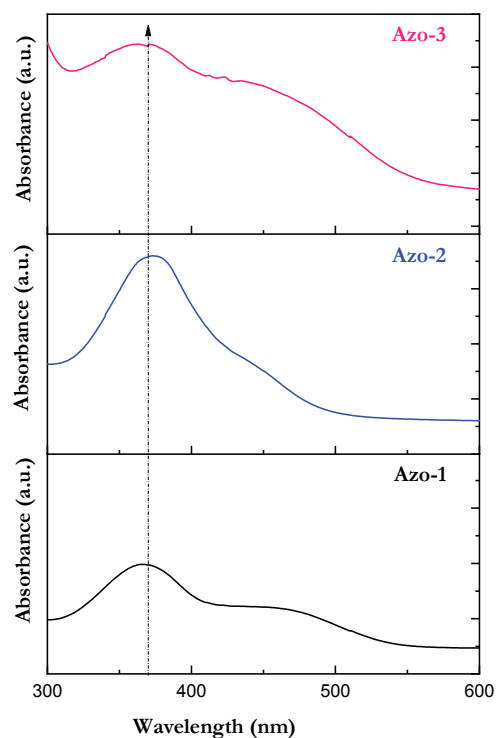
A slight weight loss was found around 65 ~ 75 °C for each gel, likely due to the loss in viscosity of the deep eutectic solvent (Ch: Urea), an effect that occurs with increase in temperature. This was shown by the temperature dependent viscosity results in Fig. 1. From the thermograms, it can be seen that compounds Azo-1 and Azo-2 underwent one stage of degradation at 242 and 265 °C, respectively; due to the breaking of the carbonate link [O-C(=O)-O-] between the azobenzene and cholesteryl units. However, Azo-3 gel underwent a two-stage degradation process. The first stage was at 160 °C, and was likely due to the cleavage of ester attached to the terminal position of the azobenzene in the Azo-3 structure (Balamurugan and Kannan 2008). The second stage was found to be at 245 °C, which can be linked to the breaking of the carbonate link [O-C(=O)-O-], in a manner similar to the Azo-1 and Azo-2 gels.

The char yield of all compounds were measured at 600 °C and the data ascribed to the Azo-3 type possessed a slightly higher char yield than the Azo-1 and Azo-2 types. This suggests that the Azo-3 compound possesses greater flame retardant properties than the others. Of the eutectic gels tested, in increasing order the char yields are described by: Azo-2 < Azo-1 < Azo-3.

3.4 Optical properties

The absorption spectra of all eutectic gels were recorded and are presented in Fig. 3. All the gels showed a similar response in their absorption spectra result. All the gels exhibited obvious absorption maxima at 369 nm, which corresponds to the π - π^* transition band of the trans-isomers of the azobenzene units.

Generally, the gel-to-sol transition is observed in the case of azobenzene based organogels (Balamurugan *et al.* 2014). However, there was no change before or after irradiation of the eutectic gels under UV light. This may be due to the viscosity of the deep eutectic solvent (Ch: Urea), which would arrest the transition of trans-to-cis.

**Fig. 3 The absorption spectra of eutectic gels in Ch: Urea.**

The reflectance spectra were also recorded for all the eutectic gels. Figure 4 shows that all the gels had a reflectance above 30% under visible light (> 400 nm), as well as in the near IR region (> 700 nm). In increasing order of reflectance the gels were ranked: Azo-1 < Azo-2 < Azo-3. These results revealed that only Azo-3 reflects about 45% (0.45) of the light at all visible wavelengths than other gels (Wang *et al.* 2019).

4. CONCLUSIONS

The thermal and optical properties of the pre-designed eutectic gels in choline chloride: urea were studied. TGA analysis thermograms revealed that all the gels underwent degradation above 240 °C due to the cleavage of carbonate link [O-C(=O)-O-] and only Azo-3 underwent one additional degradation step at 160 °C, corresponding to the cleavage of ester attached to the terminal position of the azobenzene. The photolysis of eutectic gels in ch:urea revealed that there was no photo-isomerization under irradiation. This may be due to the high viscosity of the eutectic

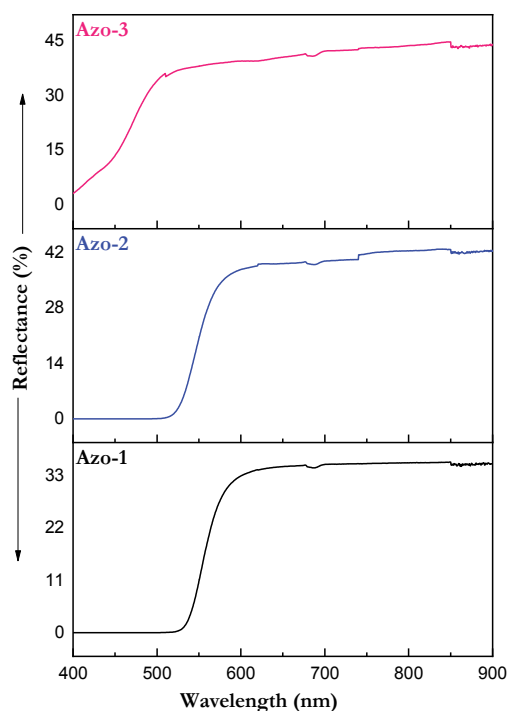


Fig. 4 Reflectance spectra of all the eutectic gels in Ch: Urea.

solvent that arrests the molecules and prevents transformation during photolysis. The reflectance spectra revealed that Azo-3 reflects about 45% (0.45) of light under all visible & near IR wavelengths, which is a greater than the individual amounts for Azo-1 and Azo-2. Temperature dependent viscosity measurements revealed that the highest viscosity at room temperature (30 °C) for all the eutectic gels were above 400 mPa·s, but reduced as temperature increased.

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