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Original article

Isosorbide, pyrogallol, and limonene-containing thiol-ene photocured bio-based organogels for the cleaning of artworks

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ABSTRACT

The development of bio-based gels for the cleaning of historical artworks is an attractive area of research. In this work, we designed thiol-ene photocured organogels by combining five different thiol or allyl functionalized bio-based monomers. Isosorbide, pyrogallol, and limonene were used as the bio-based building blocks for derivatization. The chemical structures of the synthesized monomers were characterized by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform infrared (FTIR) spectroscopy. The organogel structures were examined by FTIR analysis. Thermal and thermomechanical properties of the gels were determined by thermogravimetric analyses (TGA) and dynamic mechanical analysis (DMA), respectively. The swelling behavior of the organogels in various solvents was also investigated. Gels swelled most in dimethyl carbonate (DMC). The confinement of the solvents in the gels decreased their evaporation rate. The organogels displayed a two-stage degradation profile and were found to be thermally stable up to ~200°C. The gels were evaluated for the cleaning of dammar-based varnish from historical artwork. DMC swollen gels were found to be effective in removing the varnish from the surface of the artwork. None of the prepared gels adhered to the surface layer of the paintings. Scanning electron microscope (SEM) images proved that the surfaces were cleaned without leaving any gel residue.

1. Introduction

The cleaning process of historical artworks for conservation and restoration purposes includes the removal of dirt, grime, stains, and soil as well as the removal of degraded layers such as aged, yellowed varnishes, and coatings [1,2]. Even though it has been performed since antiquity, modern, systematic and scientific approaches began to appear towards the end of the 20th century [2,3].

The traditional method is to clean the surface of paintings by using pure solvents or solvent mixtures and applying them directly on the coating layers or paintings with the aid of cotton swabs or brushes [4]. This traditional approach suffers from several drawbacks. First, the toxic and flammable organic solvents are dangerous both for the environment and the health of the restorer. Moreover, non-confined solvents penetrate beneath the surface layer which leads to unwanted swelling that damages the painting. The swelling of the top layers creates mechanical stress over the lower layers which in turn leads to softened layers and embrittlement. The solvent could also transfer the surface dirt or dissolved organic materials to the layers underneath [3,5-7].

To overcome these disadvantages of this traditional method, gel-based systems have been proposed. Gels are physically or chemically cross-linked semisolid systems that exhibit no flow when in the steady-state [8]. In gels, a liquid phase is entrapped and continuously dispersed within a 3-dimensional network. Depending on the type of the liquid phase, gels can be simply classified into two groups: 1) hydrogels in which the liquid phase is water and 2) organogels in which the liquid phase generally consists of organic solvents or oils.

Compared to organogels, hydrogels have been studied more widely for the cleaning of paintings [9–14]. The use of water in hydrogels is advantageous in terms of toxicity when compared to the common organic solvents in organogels. However, the use of water brings several drawbacks as well. When using hydrogels, you are limited to only one solvent; water. Water is highly polar and organic binders, pigments, oil residues, and degraded organic dirt on the paintings have low solubility in water due to their relatively nonpolar nature. Enzymes, surfactants, co-solvents can be added to enhance cleaning power but it's hard to adjust polarity and solubil-

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ity, and thus cleaning with hydrogels is generally limited to the removal of water-soluble matter [15]. To overcome these limitations of hydrogels, oil-in-water microemulsions (complex fluids) [16] or oil-in-water nanostructured fluids [17] were also proposed in the literature. On the other hand, organogels which can be used in personal care products, food processing, drug delivery, pharmaceuticals, biotechnology, cosmetics, and food technology, are promising materials for the cleaning of paintings [18]. Organogels offer a wide range of solvents in contrast to hydrogels, leading to organogels with highly tunable properties. Modulation of the solvents in the hydrogels allows controlling the freezing and boiling point of the liquid phase in the organogel, which in turn expands the temperature-operating window of the organogels [19].

One of the first organogels suggested for the cleaning of artifacts was consisted of methyl methacrylate (MMA, main monomer), ethylene glycol dimethacrylate (EGDMA, crosslinker) and solvent (2-butanone (MEK), ethyl acetate (EA), cyclohexanone or butyl acetate) [20]. These organogels were found to be successful for the removal of unwanted varnishes from canvas painting samples and the authors stated that by changing the solvent used in the gel, different types of resins such as terpenes or acrylic ones could be selectively removed. Later, researchers started to look for more sustainable and green organogel alternatives derived from bio-based polymers [21–23]. Samori et al., prepared organogels from polyhydroxy butyrate (PHB), γ-valerolactone (GVL, as organic solvent), and triethyl citrate (TEC, as plasticizer) [22]. These gels removed the protective varnishes on oil paintings without leaving residues. Later these PHB-based gels were also successfully applied on water-sensitive varnished egg tempera paintings [15]. In another work, Prati et al., utilized a biodegradable solvent; DMC which has low toxicity for the cleaning of oil paintings [23]. PHB and DMC were mixed for about an hour at 90°C and then cooled to room temperature to form organogels. The gels were applied on new and aged natural terpenic varnishes and they displayed excellent cleaning properties.

2. Research aims

In this work, we aimed to prepare fully bio-based organogels by using thiol-ene photopolymerization (TEP) from three different bio-based building blocks; isosorbide, pyrogallol, and limonene. TEP is an environmentally friendly, green, and economic method with low energy consumption [24–26]. In TEP, upon light irradiation, multifunctional thiols generate thiyl radicals (RS·) which rapidly react with double bond containing monomers via a radical-induced step-growth mechanism to form crosslinked homogeneous networks [25,26]. TEP technique has been successfully used for the preparation of flame retardant and hydrophobic coatings [27–29], biomolecule conjugation [30], biobased coatings [31], heavy metal removal from aqueous solutions [32], antibacterial networks [33], etc. To our best knowledge, TEP was not previously used for artwork cleaning, thus with this work, we intend to extend the application area of TEP. Yet the originality of this work not only stems from the use of TEP for the first time for the removal of dirt on paintings, but also from the rationale behind the choice of these bio-based monomers and the diversity in the design of the organogels therefrom. We deliberately chose limonene and isosorbide for they resemble natural resins like dammar, mastic, terpenes, etc. Pyrogallol was chosen to introduce aromatic units that could be beneficial for aiding the removal of aromatic groups bearing degraded organic pigments and organic residues. Generally, these types of bio-based building blocks are considered to be non-toxic and indeed isosorbide [34] and limonene [35] are safe alternatives. However, we must note that pyrogallol is relatively toxic and affect vital organs [36]. This toxic effect of pyrogallol stems from its ability to generate free radicals.

We synthesized 5 different monomers: isosorbide diallyl ether (IDA), isosorbide bis-(3-mercapto)propionate (ISTMP), pyrogallol triallyl ether (PGTA), pyrogallol trithiol (PGTT), and a limonene adduct (LA). They were characterized by FTIR and ^{1}H NMR techniques. Next, organogels with various compositions were prepared by using these monomers via thiol-ene photopolymerization. The prepared organogels were utilized for the cleaning of a painting which was coated with a dammar-based varnish.

3. Experimental

3.1. Materials

The full materials list is given in the Supplementary File.

3.2. Characterization Methods

Characterization methods and procedures are given in the Supplementary File.

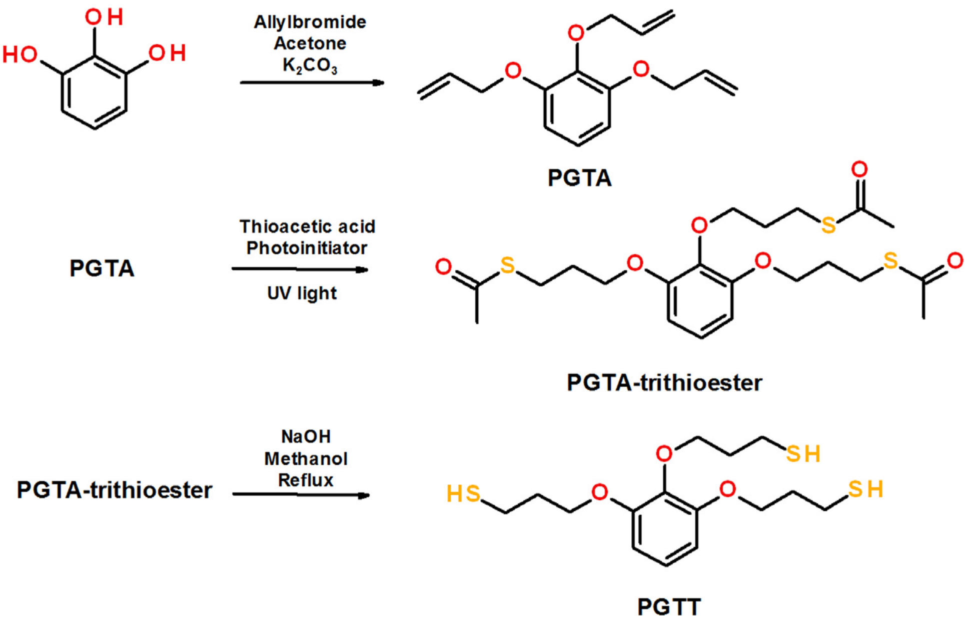
3.3. Synthesis of pyrogallol triallyl (PGTA)

PGTA was synthesized similar to previous publications [37,38]. 12.61 grams of pyrogallol (0.1 moles) and 49.75 grams of K_2CO_3 (0.36 moles, 1.2 eq.) were dissolved in 300 mL of acetone in a 500 mL three-neck round bottom flask equipped with N_2 inlet, dropping funnel, and condenser. The flask was placed in an ice bath and 40.0 grams of allyl bromide (0.33 moles, 1.1 eq.) was added dropwise into the flask within 2 hours. After that, the mixture was refluxed for 24 hours. After that acetone was removed via rotary evaporator. 100 mL of CH_2Cl_2 was added to the crude product, filtrated to remove undissolved salts and the organic phase was washed with saturated NaCl solution (20 mL x3 times). Finally, the organic phase was dried with $MgSO_4$, filtrated, and organic solvent and volatile unreacted monomers were removed by rotary evaporator. PGTA was obtained as a yellowish liquid (Yield = 18.5 g, 75%).

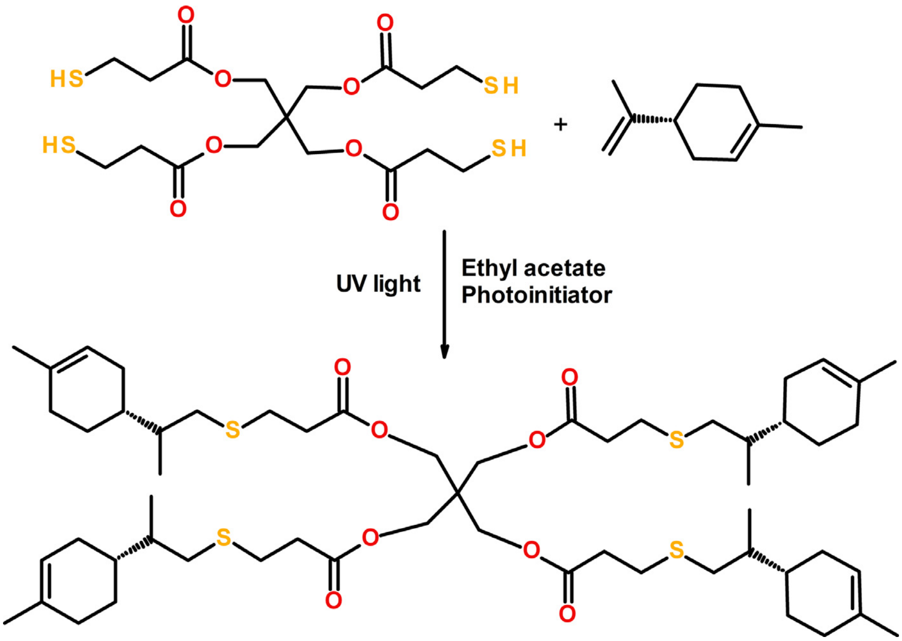
3.4. Pyrogallol trithiol (PGTT)

The synthetic procedure for PGTT was adapted from literature [39]. PGTT was synthesized in two steps. In the first step, a thiol-ene click reaction was employed. First, 3.69 grams of PGTA (0.015 moles) was mixed with thioacetic acid (6.85 g, 0.09 moles, 2 eq) and 0.25 grams of Darocur 1173 (photoinitiator) in a one-neck round bottom flask. The flask was purged with nitrogen gas and then irradiated with UV light in a photoreactor (Luzchem) under stirring for 1 hour. After that ethyl acetate (50 mL) was added to the mixture and it was washed several times with $NaHCO_3$ solution (5%) until no more gas evolved. The ethyl acetate phase was washed with saturated NaCl solution, separated, and dried over anhydrous $MgSO_4$. Finally, after filtration, the organic solvent and remaining volatiles were removed under vacuum to obtain pyrogallol trithioester (Yield = 4.6 g, 65%).

In the second step, the obtained thioester product was hydrolyzed with methanolic NaOH solution. 2.37 grams (5mmol) of the thioester synthesized in the first step was mixed with 10mL of methanol and 0.60 grams of NaOH in a two-neck round bottom flask. A condenser was attached to the flask and the mixture was refluxed for 16 hours under nitrogen atmosphere. The flask was allowed to reach to room temperature. After that acidified (HCl) aqueous solution was added to neutralize NaOH and the obtained mixture was extracted with CH_2Cl_2 (20 mL x3 times). The organic phase was then washed with saturated NaCl solution (40 mL x2 times), dried over $MgSO_4$, filtered, and evaporated under vacuum.



Scheme 1. Synthesis of PGTA and PGTT.



Scheme 2. Synthesis of LA. The idealized structure is shown here where all thiols are added to the endocyclic ene of limonene. The addition of thiols to the exocyclic enes also occurs as well as oligomeric products.

PGTT was obtained as a yellow viscous liquid with a characteristic thiol odor (Yield= 1.26g, 72%). The synthetic route to PGTA and PGTT are shown in Scheme 1.

3.5. Limonene adduct

Limonene adduct was synthesized similar to a previous publication with slight modifications [40]. A 1:4 molar ratio of 4SH to limonene was employed. Required amounts of limonene and 4SH were taken into a round bottom flask. Ethyl acetate was added to make a 40% solution and finally, 2% Darocur 1173 (with respect to the total weight of the monomers) was added. The obtained mixture was purged with nitrogen gas and reacted under UV illumination in a photoreactor while vigorously stirring for 8 hours at room temperature. Finally, ethyl acetate was evaporated under vacuum and limonene adduct of 4SH (LA) was obtained as a clear highly viscous liquid. The synthetic procedure for LA is illustrated in Scheme 2.

3.6. Preparation of photocured organogels

After several trials of different compositions, we chose three different thiol-ene photocured networks which displayed relatively better film quality, curing profiles, and good solvent uptake. The recipe of the photocurable formulations is presented in Table 1. A 1:1 thiol to ene ratio was maintained for the formulations F0

Table 1
Recipe for the preparation of thiol-ene photocured organogels[*].

	PGTT (g)	IDA (g)	ISTMP (g)	PGTA (g)	LA (g)
F0	0.2088	0.3395	0.1932	-	-
F1	0.2088	0.1450	0.1932	0.1230	-
F2	0.2088	0.2267	0.1932	-	0.4132

[*] Equal amounts of photoinitiators (TPO and Darocur 1173) were added at a 5% weight ratio with respect to the total weight of the monomers. 2 mL of ethyl acetate was also added to each formulation. LA's molecular weight was calculated based on its theoretical structure without considering the formation of oligomers.

Table 2
Thermal and thermomechanical properties of the gels.

	T_1[a] (°C)	T_2[a]	Char (%)	Tanδ[b] (°C)	Tg[c] (°C)	$E'_{(20°C)}$[b] (MPa)
F0	187	379	5.4	-7.3	-12.65	2.6
F1	184	394	8.1	3.4	-7.54	7.4
F2	192	388	5.2	1.7	-8.63	3.3

[a] T_1 and T_2 are the maximum weight loss temperatures, which were determined from the maximum of the corresponding derivative curves.
[b] Determined by DMA measurements. [c]Determined by DSC.

and F1 while for the formulation F3, the ene ratio was taken 1.2 times higher than the thiol groups. All monomers, photoinitiators, and 2 mL of ethyl acetate were weighed into a clean, aluminum foil-wrapped beaker and stirred for 20 minutes until transparent homogeneous mixtures were obtained. The liquid mixtures were poured into glass molds and each side of the mold was irradiated with UV light (OSRAM, 300W) (for 10 minutes for each side). After curing gels were washed several times with ethyl acetate to remove unreacted monomers and photoinitiator residues. The structure of all monomers used in this work and the photocured organogels are illustrated in Scheme 3.

4. Results and discussion

4.1. Characterization of the synthesized organogel precursor monomers

Details for the characterization of the precursor monomers are given in the Supplementary File.

4.2. Structural characterization of the organogels

In this work, we tried to prepare bio-based organogels that can be used for the cleaning of artworks. We deliberately chose limonene and isosorbide for their structural similarity to terpene-based resins and some components used in varnishes and coatings such as rosin esters. We used difunctional isosorbide-based monomers (IDA and ISTMP) on purpose to form linear growth chains and anticipated obtaining crosslinked organogels with the aid of crosslinker monomers like PGTA, PGTT, and LA. We tried several different compositions. However, in most cases, different combinations of these monomers displayed poor curing profiles. Some of these compositions did not even produce gels while others were found to be highly tacky due to a low degree of curing. We must note that we also tried to use neat limonene (not its adduct; LA) in the formulations but almost in all cases we could not be able to get satisfactory results and could not obtain gels with good mechanical properties. We also could not be able to obtain soft gels without tacky surfaces. When the amount of the crosslinker monomers was below a certain ratio, the gels became tacky and when left in a solvent they were degraded.

Nevertheless, some of the formulations as described in Table 1 worked well, and thus, we were able to prepare rigid organogels. Here, it must be stated that to overcome the low polymerization tendency of the selected monomers we used two different photoinitiators at a relatively high ratio, and also the amount of the crosslinker monomers was relatively higher as opposed to the general approach where lightly crosslinked gels are preferred for high swelling ratios. Therefore, the prepared gels were rigid. In F0 and F1 encoded formulations we employed a 1:1 thiol to -ene ratio while in the third formulation (F2) we utilized from the Off-stoichiometry thiol-ene (OSTE) route and took excess allyl functionality (thiol to ally ratio was 1:1.2). The digital images of the prepared organogels are presented in Figure S6.

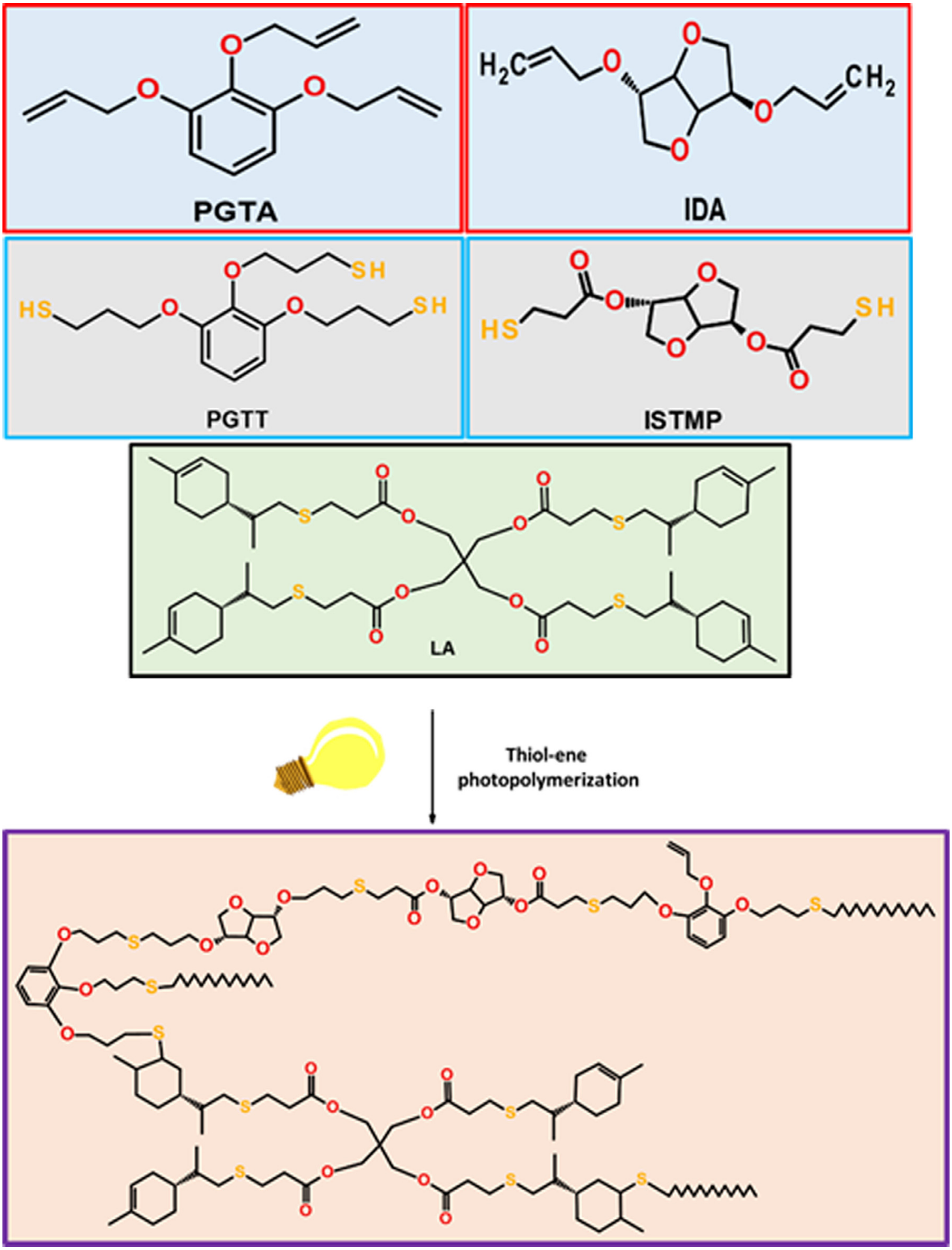
The structural characterization of the organogels was performed by FTIR spectroscopy. The FTIR spectra of the liquid precursors of the organogels prepared in this work as well as the cured gels are presented in Figure S7. In the FTIR spectra of the liquid precursors, a weak band seen at 1647 cm^{-1} is due to allylic double bonds of IDA and PGTA while the band at 1735 cm^{-1} is due to the carbonyl stretching vibrations of ethyl acetate and ISTMP. The very weak thiol bands of ISTMP and PGTT at around 2557 cm^{-1} are also present in these spectra. The band at 1676 cm^{-1} is ascribed to the photoinitiator (Darocur 1173). After curing the allyl and the thiol bands were completely disappeared as is evident from the spectra of the cured organogels in Figure S6. It must be noted that the carbonyl band of the photoinitiator (Darocur 1173) is also present in these spectra. After washing the gels with ethyl acetate to remove unreacted monomers and photoinitiator residues these carbonyl bands were disappeared in their FTIR spectra (results are not shown). Thus, we can conclude that the gels were successfully prepared.

In terms of structural characterization, we also determined the thermal and thermomechanical properties of the resulting gels. TGA, DSC, and DMA plots of the gels are presented in the supplementary file (Figure S8-S10) and the key results are listed in Table 2.

According to the TGA results, all photocured gels prepared in this work displayed a two-stage degradation profile. The first maximum weight loss temperatures (T_1) were found to be at around 188±4°C. This weight loss in the organogels was attributed to the residual solvent, photoinitiator, and unreacted monomers. The second maximum weight loss temperature (T_2) of the F0 encoded gels was found as 379°C. The addition of the aromatic crosslinker; PGTA in F1 formulation led to an increase in this T_2 temperature which can be attributed to the additional crosslinking and the thermal stability of the aromatic groups. When PGTA was replaced by LA (F2), the T_2 was also found to be higher than the first formulation (F0) but it was lower than F1. This situation was again attributed to the additional thermal stability brought by the increased crosslinking density due to the tetra-functional LA. The effects of the aromatic moieties and the crosslinking density are also reflected in the obtained char yields. The char yield of F0 was improved 50% by the addition of PGTA and raised to 8.1% from 5.4%. On the other hand, the addition of LA did not make any difference in terms of char yields and F2 exhibited a comparable char yield to F0.

Due to the use of di-functional monomers and the flexible nature of the thioether bonds in the photocured gels, they displayed low Tg values. Both the addition of PGTA and LA separately led to an increase in Tg with respect to the F0 gel. The increase in Tg was found to be much more when PGTA was used. It can be said that the additional crosslinking introduced by PGTA and LA is responsible for this increment in Tg values.

The *E'* value of F0 was determined as 2.6 MPa. When PGTA or LA was incorporated into this F0 formulation, storage modulus increased significantly which can be ascribed to the increased crosslinking density. PGTA was found to be much more effective in enhancing the storage modulus of the gels. A similar trend to the Tg values was observed for tanδ temperatures. When the tanδ tem-



Scheme 3. Preparation of the photocured bio-based organogels. The zig-zag patterns represent polymer chains. One of the double bonds of PGTA is shown without altering to distinguish it from PGTT in the figure. Some of the double bonds of the LA were also shown to illustrate the OSTE route.

peratures of the gels were compared, it can be seen that the gels composed of only PGTT, IDA, and ISTMP (F0) displayed the lowest temperature among other studied compositions. PGTA and LA additions led to almost 147% and 123% increase in this temperature, respectively. Thus, these results show that the relatively softer base organogel (F0) becomes rigid to some extent with the increased crosslinking.

4.3. Swelling and solvent evaporation properties

The swelling capacity of the organogels was investigated in different organic solvents. The gels were kept in contact with the solvents for 24 hours and after this period their swelling percentages were calculated. The results of the swelling tests are plotted in Fig. 1. When considered in general, the gels displayed much

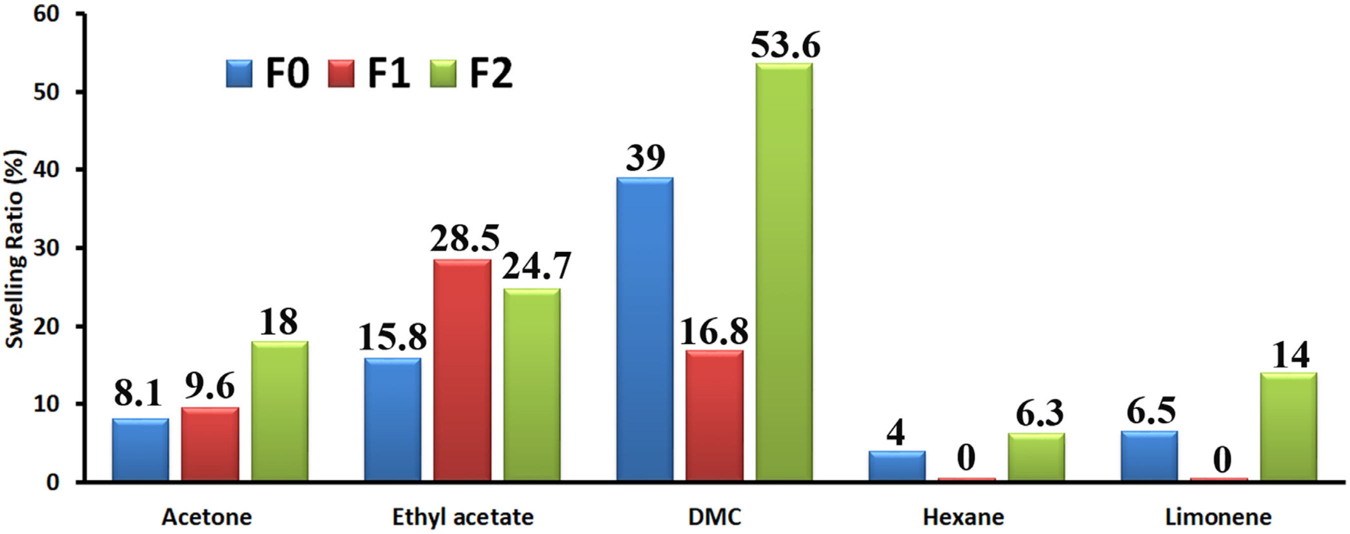


Fig. 1. Swelling percentages of the organogels in different solvents. The error bars represent a standard deviation obtained from at least three different measurement.

more absorption tendency towards the relatively polar solvents (EA, DMC, acetone) than to the non-polar ones (limonene and hexane). Since the gels are relatively highly crosslinked compared to their analogs synthesized in literature, they also exhibited rather lower swelling percentages. Nevertheless, lower swelling results for organogels were also reported in the literature, for instance, Doll et al., prepared organogel polymers by using 10-undecenoic acid and poly(vinyl acetate), measured the swelling ratios of the gels in different solvents and the gels reached a maximum swelling of ~30% [41].

Among all gels in this work, F2 encoded formulation displayed the highest swelling capacity in all studied solvents except for EA where F1 had the most swelling percentage value. The solvent which swelled the gels the most was found to be DMC. When the behavior of the gels toward the absorption of limonene is considered, we can see how LA dramatically affects the swelling. While F0 encoded gel displayed only 6.5% swelling in limonene, the swelling percentage of OSTE photocured organogel containing LA (F2) was found as 14%. This result demonstrates that the structural similarity is effective in absorption.

The evaporation rate of the confined solvent from the gels is an important parameter in terms of application and also for the health of the conservators [20]. Since the gels did not swell too much in hexane and limonene, this test was only conducted with EA, DMC, and acetone. The evaporation percentage versus time plots of the gels in different solvents are presented in Figure S11. When the evaporation rate of EA is considered, it can be seen from this figure that the gels display good performance in confining EA. F2 and F0 gels displayed almost a similar behavior for EA. For instance, F2 gel which absorbs approximately 24.7% EA, retains more than 5% of this solvent even after 1 hour at room temperature whereas F2 and F1 gels gradually lose almost all the solvent confined in their structure. In the case of DMC, gels displayed a similar behavior and the absorbed DMC gradually evaporated from the gel matrix whereas the neat DMC evaporated at a higher rate. It is clear from these results that the rate of evaporation is slowed down when confined within the gel matrix. Similar results were also obtained in the literature [20,23,42].

4.4. Cleaning test results

The cleaning procedure is detailed in the supporting information file. Several preliminary trials were conducted by using the synthesized gels on different parts of the painting. Organogel F0 did not give satisfactory results during our preliminary cleaning trials and therefore only the results of F1 and F2 gels are given here. Since the gels swelled much more in DMC and since it is a green solvent we chose it as the main solvent for the cleaning tests. F1 and F2 encoded films were separately kept in DMC for 1 hour. This period as well as the 20-minute treatment time were selected after several optimization trials. The swelled gels were applied onto a varnish-coated painting. The digital photograph of the artwork is given in Fig. 2.

Fig. 2. The easel painting by Nalan Afet Kuşlu.

Digital images of a dirty area on the painting before and after cleaning with the DMC swollen F2 film are shown in Fig. 3. As it can be clearly seen from these photographs the varnish is almost completely removed from the surface after cleaning. The blue color of the original sample appeared after the removal of the dirty greenish top layer. We further investigated the surface by SEM. From the SEM micrographs, it is clear that the degraded varnish and organic residues which were present before cleaning were almost all removed after the gel treatment. Furthermore, no gel residue was observed on the cleaned surfaces as is evident from the SEM images. To verify these findings, we also recorded the FTIR spectra of the surfaces before and after the gel treatment. Before cleaning the FTIR spectrum of the painting surface displays the characteristic bands for dammar/linseed oil-based varnish. The bands at around 2932 cm^{-1} are due to –CH vibrations while the characteristic carbonyl stretching band of the ester groups was detected as 1730 cm^{-1}. Moreover, in this spectrum, the band seen at 1647 cm^{-1} was attributed to the double bond vibrations of the dammar resin and the linseed oil. After cleaning, the intensities of–CH, -C=O, and the –C=C- bond vibration bands decreased significantly.

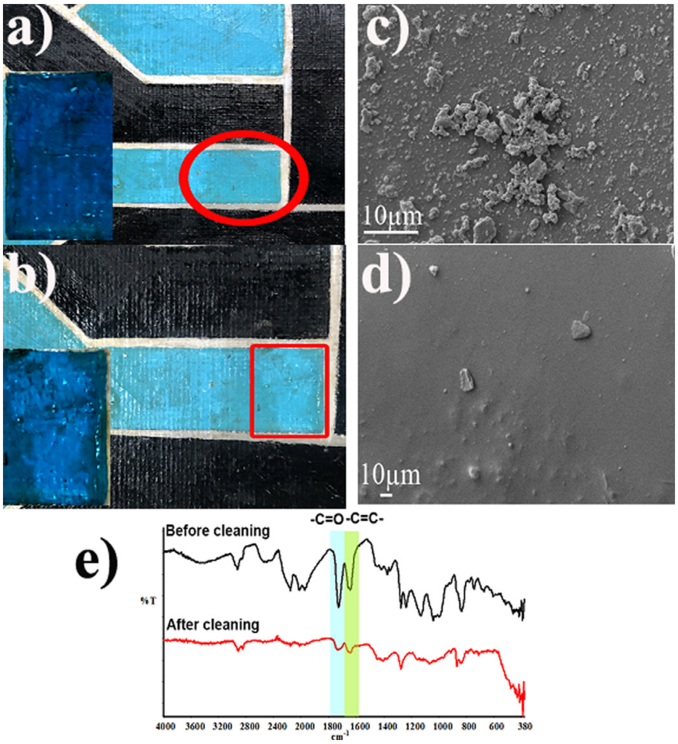


Fig. 3. Removal of dammar/linseed varnish from the painting by using the organogel F2/DMC system. (a) and (b) are the digital photographs of the surface before and after cleaning. For better visualization, contrasted images are given as inlay images. (c) and (d) are the SEM micrographs of the surface and (e) is the FTIR spectra of the surface before and after cleaning.

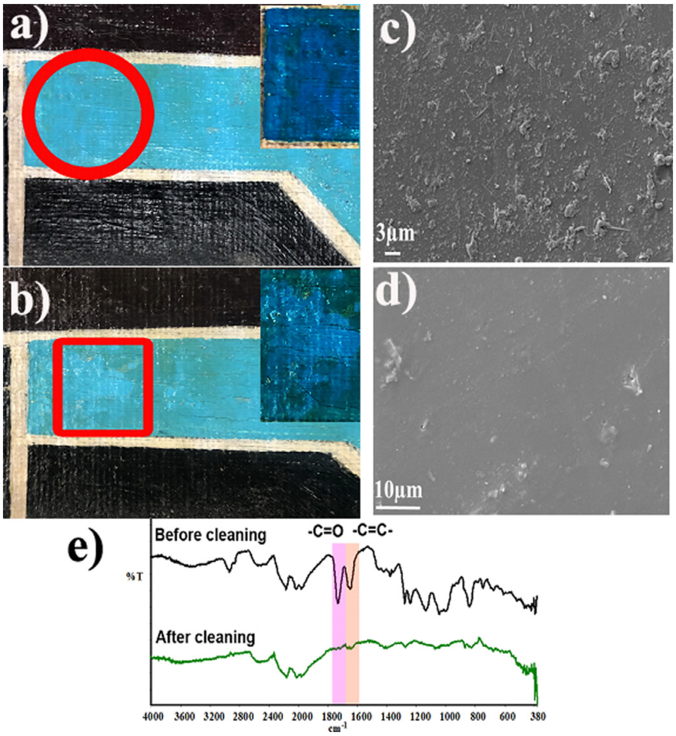


Fig. 4. Removal of dammar/linseed varnish from the painting by using the organogel F1/EA system. (a) and (b) are the digital photographs of the surface before and after cleaning. For better visualization, contrasted images are given as inlay images. (c) and (d) are the SEM micrographs of the surface and (e) is the FTIR spectra of the surface before and after cleaning.

Similarly, the F1/DMC system was also studied and similar results were obtained (Figure S12). However, since F1 encoded photocured gels displayed the highest swelling in EA, we also studied the cleaning performance of the F1/EA system. As it can be seen from the digital photographs and the SEM images given in Fig. 4, this system was found to be highly efficient for dammar/linseed oil removal. As it is evident from the FTIR spectra in Fig. 4, all the peaks related to the varnish are completely disappeared. Thus, it can be concluded that the use of EA was superior to DMC in terms of cleaning efficiency. Nevertheless, the low toxicity of DMC makes it a much safer choice as a solvent. Besides the absorption of the solvent by the layers underneath the top varnish can lead to swelling. Even though we did not observe swelling in our trials visually, owing to the confinement of the solvent within the gel matrix which relatively declined the aggressive penetration of the solvent compared to free solvent. Therefore, in the case of EA, shorter application times could be beneficial to prevent this adverse effect.

Recently, Jia et al., developed a novel composite material by sandwiching an organogel (poly(3-hydroxybutyrate) + γ-valerolactone) between two layers of electrospun membranes (either poly(vinyl alcohol) or polyamide 6,6) [43]. Similar to the F1/EA system in this work, the characteristic FTIR bands of dammar resin were completely vanished after cleaning.

Finally, we must note here that the original binder of the painting is not known and its analysis is rather difficult (due to the presence of the varnish). Even though the smooth, spotless surfaces of the cleaned sections (as evident from SEM images) indicate that the painting layer underneath the varnish was not damaged, the gels developed in this work could be too aggressive and could have removed the original binder of the painting. In future studies, we intend to expand our studies by testing our gels on aged samples with known binders.

5. Conclusions

In this work, we showed that thiol-ene photocured organogels which were prepared by using bio-based monomers are suitable materials for cleaning of artworks. To increase the greenness of the gels and to decrease toxicity we also used a green solvent; DMC. The thiol-ene photocured organogels were prepared by using thiolated or allyl derivatives of isosorbide, pyrogallol, and limonene. In one of the compositions, the OSTE route was also employed. The confinement of the solvents within the gel matrix slowed down the evaporation rate of the solvent concerning the evaporation rate of the neat solvent. None of the prepared gels adhered to the surface layer of the paintings which is a preferred feature for handling and removing the prepared films after application. DMC and EA swollen gels were found to be effective in removing the varnish from the surface of the artwork where EA outperformed. Scanning electron microscope (SEM) images proved that the surfaces were cleaned without leaving any gel residue.

The method offered here is tunable, green, energy-efficient, and low toxicity. Thus, there is a great potential in photocured thiol-ene organogels for the conservation of cultural heritage. We believe more bio-based organogels will be developed in the future with elegant designs and innovative chemical routes to be used for the cleaning of historical artworks.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2022.04.013.

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