

Transparent photoactive azobenzene-functionalized poly(ϵ -caprolactone)/chitosan nanofiber composites for solid-state molecular solar thermal energy storage

Sebastián Castillo^a, Óscar Ramírez^{a,e}, Galder Kortaberria^b, Angie Carolay Forero-Giron^a, Diego Cortés-Arriagada^c, Nancy Pizarro^d, César Saldías^{a,*}, Ángel Leiva^{a,*}

^a Departamento de Química-Física, Escuela de Química, Facultad de Química y de Farmacia, Pontificia Universidad Católica de Chile, Santiago 7820436, Chile

^b Group 'Materials + Technologies' (GMT), Chemical and Environmental Engineering Department, Faculty of Engineering of Gipuzkoa, University of the Basque Country (UPV/EHU), Plaza Europa 1, 20018 Donostia-San Sebastian, Spain

^c Instituto Universitario de Investigación y Desarrollo Tecnológico, Universidad Tecnológica Metropolitana, Ignacio Valdivieso 2409, San Joaquín, Santiago, Chile

^d Universidad Andrés Bello, Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Viña del Mar, Chile

^e Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Santiago 7820436, Chile

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ABSTRACT

Transparent solid-state platforms for molecular solar thermal storage systems (MOST) are highly attractive for overcoming the intermittency of solar energy while enabling efficient light-matter interactions. Herein, we report the development of transparent photoactive polymer nanofiber composites based on azobenzene-functionalized polycaprolactone (PCL) processed via electrospinning and subsequently infiltrated with low-molecular-weight chitosan. A design of experiments (DOE) approach enabled the fabrication of uniform, bead-free nanofibers with an average diameter of 133 ± 23 nm, leading to a significant increase in surface area and wettability. Vacuum-assisted impregnation with a dilute chitosan solution effectively filled inter-fiber voids, reduced refractive index mismatches, and yielded highly transparent nanofiber composites. Importantly, the azobenzene photoactivity was preserved in the solid state, displaying reversible *Trans-Cis-Trans* photoisomerization under alternating UV and visible light irradiation and maintaining stable performance over more than 100 charge-discharge cycles. The incorporation of chitosan further modulated the thermal back-isomerization kinetics, extending the lifetime of the metastable *Cis* state. These results demonstrate a robust and transparent polymer nanofiber platform for solid-state MOST energy storage, with potential relevance for energy-related coatings and optically active materials.

1. Introduction

The use of solar energy as an alternative to traditional energy sources is one of the most widely used technologies worldwide. Nevertheless, due to the intermittent nature of this energy source, exemplified by the mismatch between peak production and demand (also known as “The duck curve”), the study and development of systems for its storage is currently a major challenge. In particular, photoactive materials capable of storing energy under light stimulation are a very promising alternative for this purpose. This has sparked a growing interest in developing technologies capable of storing excess solar energy received during the day for use when sunlight is unavailable. Efficient solar energy storage is therefore a pivotal requirement for enabling the full transition to this

renewable source. [1]

Addressing this challenge requires the development of materials capable of efficiently capturing, converting, and storing solar energy in usable forms. [2] Despite its position as the most abundant renewable energy resource, solar power currently accounts for only 5.53% of global electricity production, although rapid growth is projected in the coming decades. [3] In this context, photofunctional materials that can interact with light through absorption, conversion, or storage processes have emerged as promising solutions. These materials exhibit tailored physicochemical properties that enable efficient light harvesting and energy storage, offering viable pathways to mitigate the intermittency of solar energy. [4–6]

Among photofunctional systems, azobenzene-based compounds

* Corresponding authors.

E-mail addresses: casaldia@uc.cl (C. Saldías), aleivac@uc.cl (Á. Leiva).

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have attracted considerable attention as key components of molecular solar thermal (MOST) energy storage technologies. MOST systems store solar energy through the reversible *Trans-Cis* photoisomerization of molecular photoswitches, allowing energy to be trapped in a metastable, high-energy state and subsequently released as heat on demand. [7] In azobenzene derivatives, the stored energy is associated with the conformational change around the N=N bond, with the *Cis* isomer persisting for time scales that depend on the activation barrier for spontaneous *Cis-to-Trans* thermal back-isomerization. Upon discharge, the *Cis* isomer relaxes to the thermodynamically stable *Trans* configuration, releasing the stored energy as heat. This reversible and controllable process makes azobenzene-based MOST systems particularly attractive for addressing the temporal mismatch between solar energy supply and demand. [8]

The efficiency and kinetics of azobenzene-based energy storage processes are strongly influenced by the surrounding chemical environment, which can modulate both the amount of stored energy and the rates of photocharging and discharging. For example, solvatochromic effects in azobenzene derivatives demonstrate that molecular interactions with the surrounding medium can significantly alter photoisomerization behavior. Energy storage performance can be enhanced through intra- or intermolecular interactions that stabilize the *Trans* isomer or destabilize the *Cis* isomer. [9] Computational studies have shown that intramolecular hydrogen bonding and π - π stacking interactions present in the *Trans* state are disrupted upon *Cis* isomerization, leading to increased energy storage. In addition, even weak interactions, such as London dispersion forces, have been shown to stabilize specific isomeric states and further enhance the energy storage capacity of azobenzene compounds. [9,10] However, these effects are most commonly observed in solution, which limits practical applicability due to handling, containment, and scalability challenges. Incorporating azobenzene-based photoswitches into solid-state matrices is therefore a critical step toward improving the usability and technological relevance of MOST systems. [11]

In this regard, polymer-based photofunctional materials offer significant advantages, including mechanical flexibility, processability, and tunable chemical and physical properties, making them well-suited for solid-state MOST platforms. [12] A landmark demonstration of this concept was reported by Hu et al., who fabricated the first azo-based fabric composite for solid-state MOST applications by impregnating a flexible fabric template with a photoliquefiable azobenzene (PLAZ) derivative, achieving solvent-free charging through a photoinduced solid-to-liquid phase transition. [13] This pioneering work established the feasibility of integrating azobenzene photoswitches into flexible textile substrates for practical energy storage, laying the conceptual groundwork for subsequent fiber and nanofiber-based MOST platforms. To advance these systems, electrospun polymer nanofibers have emerged as an ideal solid-state matrix, offering significantly increased specific surface area and a highly interconnected porous morphology capable of optimizing light-matter interactions. Among candidate polymers, polycaprolactone (PCL) is a biodegradable polyester widely recognized for its flexibility, durability, biocompatibility, and excellent processability via electrospinning. [14] This fabrication technique utilizes a high-voltage electrostatic field to generate ultrafine fibrous networks. [15] Importantly, PCL can be readily functionalized through covalent attachment of azobenzene derivatives, as previously reported, enabling the integration of photoresponsive units into the polymer backbone. [16] The electrospinning process further allows fine control over nanofiber properties by adjusting parameters such as polymer concentration, feed rate, applied voltage, and tip-to-collector distance.

Despite these advantages, electrospun nanofiber mats are typically opaque, which represents a major limitation for optical and solar energy storage applications. Opacity arises from multiple factors, including intrinsic material properties, mat thickness, and refractive index mismatches at the fiber-air interfaces, which lead to significant light scattering and absorption within the nanofibrous structure. [17] As a result,

light-matter interactions required for efficient azobenzene photoisomerization are hindered, making transparency a critical yet challenging requirement for electrospun materials intended for optical applications. [18]

Two main strategies have been proposed to improve the transparency of electrospun nanofiber mats. The first involves reducing mat thickness by decreasing electrospinning time, thereby limiting fiber accumulation on the collector and reducing light scattering. [19–21] While this approach can effectively enhance optical transparency, it often compromises mechanical integrity and handling due to the reduced thickness of the resulting mats. To overcome this limitation, a complementary strategy focuses on preserving mechanical robustness while enhancing optical properties through pore filling. This approach involves infiltrating the inter-fiber voids with a secondary polymer, which smooths surface topography, reduces refractive index mismatches, and mitigates light scattering.

This pore-filling strategy has been successfully demonstrated using intrinsically opaque thermoplastic polyurethane nanofiber mats impregnated with polymethylmethacrylate or polydimethylsiloxane, achieving significant improvements in transparency while maintaining structural integrity. [21] In this context, chitosan, a natural polysaccharide obtained from the partial deacetylation of chitin, emerges as a particularly attractive candidate for nanofiber impregnation. Chitosan combines biocompatibility, biodegradability, and excellent film-forming ability with a high density of functional groups, such as amino and hydroxyl moieties, which can promote intermolecular interactions with polymer matrices. [22] These features make chitosan well-suited for pore-filling applications in electrospun nanofiber networks, offering a sustainable route to enhance transparency while preserving nanoscale architecture and mechanical stability. Herein, we report the design and characterization of azobenzene-functionalized PCL nanofibers as a transparent solid-state platform for molecular solar thermal energy storage. PCL was covalently modified with azobenzene units to introduce photoresponsive energy storage functionality and subsequently processed into nanofibers via electrospinning. A design of experiments (DOE) methodology was employed to optimize electrospinning parameters and obtain nanofibers with high surface area and controlled morphology. The initially opaque PCL-Azo nanofibers were then subjected to vacuum-assisted impregnation with a chitosan solution to enhance optical transparency, yielding transparent PCL-Azo-chitosan nanofiber composites. This work contributes to the understanding of solid-state MOST systems and demonstrates a transparent photoactive polymer platform with potential relevance for energy storage, optically active coatings, flexible electronics, smart materials, and sensing applications. [23–29]

2. Experimental section

2.1. Materials

All reagents were of analytical grade and used as received unless otherwise stated. Polycaprolactone (PCL, Mw = 80,000) and chitosan samples of low (degree of acetylation, DA $\approx$ 25%), medium (DA $\approx$ 30%), and high molecular weight (DA $\approx$ 25%) were obtained from Sigma-Aldrich. Dichloromethane (DCM), chloroform (CHL), dimethylformamide (DMF), methanol, acetic acid, and deuterated chloroform (CDCl₃) were purchased from Merck S.A. 4-Phenylazobenzoyl chloride (98.0%) was obtained from TCI America via SAGU Ltda. Dichloromethane was dried by distillation over calcium hydride (CaH₂) and stored over molecular sieves prior to use. All aqueous solutions were prepared using Milli-Q water with a resistivity of 18.2 M Ω -cm.

2.2. Synthesis of PCL-Azo

Azobenzene-functionalized polycaprolactone (PCL-Azo) was obtained via esterification of the terminal hydroxyl groups of PCL

following a previously reported procedure, with minor modifications. [16] Briefly, 5.0 g of polycaprolactone were dissolved in 50 mL of dry dichloromethane (DCM). In parallel, 2.5 mg of 4-phenylazobenzoyl chloride (0.05 wt% relative to PCL) were dissolved in 10 mL of DCM, using a slight excess of the azobenzene derivative to promote complete functionalization of the terminal hydroxyl groups. The azobenzene solution was then added dropwise to the PCL solution, and the reaction mixture was stirred at room temperature for 24 h. The resulting PCL-Azo was precipitated in cold methanol to remove unreacted azobenzene derivative, collected by filtration, and dried under vacuum. The isolated yield of PCL-Azo was 88%.

2.3. Electrospinning

PCL-Azo nanofibers were prepared by adapting previously reported electrospinning methodologies [30] and optimizing the processing parameters through a design of experiments (DOE) approach using pristine PCL. The optimized electrospinning conditions obtained for PCL were subsequently applied to the fabrication of PCL-Azo nanofibers. PCL was dissolved in a solvent mixture of chloroform (CHL) and dimethylformamide (DMF) at a volume ratio of 60:40. The polymer solutions were prepared at an overall concentration of 8 wt% and magnetically stirred overnight to ensure complete dissolution and homogeneity. Electrospinning was performed using a single-needle electrospinning setup (Linari Engineering s.r.l.) in a controlled chamber maintained at a temperature of 24 ± 5 °C and a relative humidity of 40 ± 5 %. The polymer solution was loaded into a syringe equipped with a 25G blunt-tip metal needle prior to electrospinning. A design of experiments (DOE) methodology was employed to identify the combination of processing parameters that yielded homogeneous, bead-free electrospun PCL nanofibers with minimal average diameter. The selected processing variables were tip-to-collector distance (cm), applied voltage (kV), and solution flow rate (mL h⁻¹). Each parameter was evaluated at three levels, as summarized in Table 1. The polymer concentration and the working ranges of the electrospinning parameters were selected based on previously reported studies. [31–33]

Based on the selected parameters, a total of 16 experiments were conducted using the DOE methodology, as detailed in the Supporting Information (SI). The experiments were performed in randomized order to minimize systematic errors. The response variables evaluated were the average fiber diameter (nm) and its standard deviation. Fiber diameters were determined from field-emission scanning electron microscopy (FESEM) images. Statistical analysis of the experimental design and data was performed using Minitab 21 software (version 21.4.2). The optimal electrospinning conditions identified for the preparation of PCL-Azo nanofibers were a solution flow rate of 1.0 mL h⁻¹, an applied voltage of 20 kV, and a tip-to-collector distance of 15.6 cm. To obtain wrinkle-free nanofiber mats, the electrospun fibers were mounted and stretched using a custom 3D-printed PLA frame (Fig. S1).

2.4. Preparation of transparent PCL and PCL-Azo nanofibers composites

Electrospun nanofiber mats were rendered transparent through an impregnation process using chitosan solutions. To maintain the nanofiber mats under tension during impregnation, 3D-printed PLA frames were employed (Fig. S1). The stretched nanofiber mats mounted on the rectangular frames were placed face-down in plastic Petri dishes and treated with aqueous chitosan solutions of low, medium, and high

molecular weight. For the impregnation process, 1 mL of chitosan solution at concentrations of 0.25%, 0.50%, 0.75%, 1.00%, 1.25%, or 1.50% (w/v), prepared in 1% (v/v) aqueous acetic acid, was dispensed onto the nanofiber mats. The samples were subsequently placed in a vacuum oven at 25 °C for 24 h to promote infiltration of the solution into the inter-fiber voids and allow gradual solvent evaporation, resulting in the formation of transparent nanofiber composites. Following impregnation, the resulting films were removed from the Petri dishes and immersed in 100 mL of 1 M aqueous NaOH under gentle orbital stirring for 1 h to neutralize residual acetic acid. The composites (denoted PCL-Azo-Chi) were then thoroughly washed with 100 mL of distilled water and dried overnight between two glass plates in a forced-convection oven at 45 °C for 24 h.

2.5. Photoisomerization and cycling performances

The photoisomerization behavior of azobenzene units within the PCL-Azo-Chi composites was monitored by UV-visible spectroscopy by tracking the absorption band at 330 nm, which corresponds to the *Trans* isomer of azobenzene. Upon UV light irradiation, the intensity of this band decreased because of the *Trans*-to-*Cis* photoisomerization process. The reverse *Cis*-to-*Trans* isomerization was induced either photochemically under blue light irradiation or thermally in the dark, in both cases leading to a recovery of the absorption band at 330 nm. The cycling stability of the reversible *Trans*-*Cis*-*Trans* isomerization in PCL-Azo-Chi composites was evaluated by alternating irradiation at 365 nm (UV, 9 mW/cm²) for 1 min and 475 nm (blue light, 3 mW/cm²) for 10 min over 100 consecutive cycles, all irradiation cycles were conducted with a distance of 3 cm between the material and the light source. Preliminary kinetic tracking at 10-s intervals confirmed that 1 min of UV exposure is sufficient to reach the *Trans*-to-*Cis* photostationary state. While the reverse *Cis*-to-*Trans* isomerization is also largely complete within 1 min of blue-light exposure, a conservative 10 min discharge period was employed during cycling to ensure full recovery of the *Trans* isomer and prevent cumulative baseline shifts over 100 cycles. Light intensity was measured using Newport Model 1815-C optical power meter.

2.6. Characterization

2.6.1. Proton nuclear magnetic resonance (¹H NMR)

¹H-NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer operating at 400 MHz. Approximately 10 mg of each sample were dissolved in 500 µL of deuterated chloroform (CDCl₃) to obtain clear solutions, which were transferred to NMR tubes and analyzed using 64 scans.

2.7. Field emission scanning electron microscopy analysis (FESEM)

The morphology of the electrospun nanofibers (NFs) was examined using a FEI QUANTA FEG 250 field-emission scanning electron microscope (FESEM). Prior to imaging, the samples were sputter-coated with a 10 nm gold layer to enhance surface conductivity. Fiber diameter distributions were determined by measuring approximately 400 fibers from the FESEM images using Image-J software.

2.7.1. Water Contact angle

Water contact angle measurements were performed using an optical contact angle goniometer (Data Physics OCA20 system) equipped with a high-resolution CCD camera. Data acquisition and analysis were carried out using SCA 20 software (Data Physics Instruments). Water and glycerol contact angles were measured by depositing droplets of 10.0 ± 0.2 µL onto the sample surface. Both the sample stage and the dispensing syringe were maintained at 25.0 °C during the measurements. Each sample was measured in triplicate, and the reported values correspond to the average of the three measurements.

Table 1

DOE parameters for optimization of nanofibers diameters.

Parameter	-1	0	1
Distance (cm)	10	15	20
Voltage (kV)	20	23	25
Pump Flow (mL h ⁻¹)	0.5	0.8	1.0

2.7.2. BET surface area determination

The specific surface area and cumulative pore volume of the nanofibers were determined from nitrogen adsorption–desorption isotherms using a Micromeritics 3Flex instrument. Prior to analysis, the samples were degassed at room temperature for 12 h using a Micromeritics SmartVacPrep system. Nitrogen adsorption–desorption measurements were performed at 77 K over a relative pressure (P/P_0) range of 0.00 to 1.00. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) multipoint method, while the cumulative pore volume was determined using the Barrett–Joyner–Halenda (BJH) model.

2.7.3. Determination of light transmittance and emission spectra

UV–visible absorption spectra were recorded using a Cary 60 UV–Vis spectrophotometer over the wavelength range of 250–800 nm at 25 °C. The optical transparency of nanofiber mats, before and after chitosan impregnation, was evaluated by measuring UV–visible transmittance spectra within the same wavelength range and at the same temperature. All samples were measured as free-standing films mounted directly into the spectrophotometer holder, without the use of supporting glass or quartz substrates. A fully blocked light beam was used as the 0% transmittance reference, while air was used as the 100% transmittance reference. To assess sample homogeneity, transmittance measurements were collected from three different regions of each material. Emission spectra were recorded using a Horiba Jobin–Yvon FluoroMax-4 spectrofluorometer equipped with a Quanta-φ integrating sphere.

2.7.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a PerkinElmer STA 6000 simultaneous thermal analyzer. Measurements were carried out over a temperature range from 25 to 900 °C at a heating rate of 10 °C min^{−1} under a nitrogen flow of 20 mL min^{−1} to ensure an inert atmosphere. Data were processed using Pyris Thermal Analysis software (PerkinElmer, version 13.4.0.0036).

2.7.5. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were carried out using a Mettler–Toledo DSC 821e instrument. The thermal protocol consisted of five consecutive steps: (1) heating from 25 to 130 °C at a rate of 10 °C min^{−1}; (2) isothermal hold at 130 °C for 5 min; (3) cooling from 130 to −80 °C at a rate of −10 °C min^{−1}; (4) isothermal hold at −80 °C for 5 min; and (5) heating from −80 to 10 °C at a rate of 2 °C min^{−1}.

2.7.6. Computational studies methods

The molecular structures of azobenzene-modified poly(caprolactone) nanofibers (PCL-Azo) and chitosan (Chi) were investigated using density functional theory (DFT) calculations. To balance chemical representativeness and computational cost, model systems consisting of one caprolactone monomer functionalized with an azobenzene unit and two glucosamine monomers were employed to represent PCL-Azo and Chi, respectively. Geometry optimizations were performed in the gas phase at the B3LYP-D3BJ/6-311G(d,p) level of theory, [34–36] as implemented in the Gaussian 16 software package. [37] The B3LYP

functional combined with Grimme's D3 dispersion correction, has been widely used to investigate the structural, energetic, and interaction properties of azobenzene-based compounds [38,39] and their interactions with polymeric systems. [40] Thermochemical data, including reaction enthalpies and Gibbs free energies, were obtained from vibrational frequency calculations. The *Trans*–*Cis* isomerization reaction energy of the PCL-Azo model was calculated as the energy difference between the optimized *Trans* and *Cis* conformations, which differ in the C–N=N–C dihedral angle (Fig. 1). This isomerization process was evaluated for three different systems: azobenzene alone (R1), PCL-Azo in the absence of chitosan (R2), and PCL-Azo in the presence of chitosan (R3). In addition, the interaction energy between PCL-Azo and Chi was calculated as:

$$\Delta E_{\text{int}} = E_{\text{PCL-Azo+Chi}} - (E_{\text{PCL-Azo}} + E_{\text{Chi}}) \quad (1)$$

where $E_{\text{PCL-Azo+Chi}}$, $E_{\text{PCL-Azo}}$ and E_{Chi} corresponds to the total electronic energies of the interacting PCL-Azo/Chi system, isolated PCL-Azo, and isolated Chi, respectively. Noncovalent interactions between PCL-Azo and Chi were analyzed and visualized using the NCIPLOT software. [41]

2.7.7. Atomic force microscopy (AFM)

Atomic force microscopy (AFM; JPK NanoWizard 3, Bruker Nano GmbH, Berlin, Germany) was used to obtain both topographical and local elastic modulus maps. Measurements were performed in Quantitative Imaging (QI™) mode in air, with a setpoint force of 1.2–1.7 nN. Force–distance curves were acquired at each with a resolution of 256 × 256 pixels. PPP-CONTSAuD-50 cantilevers (NANOSensors, Neuchâtel, Switzerland) were employed, with nominal dimensions of 225 μm length, 48 μm width, and 1 μm thickness, a resonance frequency of ~57 kHz, and a nominal spring constant within 0.01–1.87 N/m. Young's modulus values were extracted by fitting the approach portion of each force–distance curve using the Hertz contact model. A triangular pyramidal indenter geometry with a half-angle to face of 20° was assumed, together with a Poisson's ratio of 0.5. Data processing and mechanical fitting were carried out using JPK Data Processing software (Bruker Nano GmbH).

3. Results and discussion

3.1. Synthesis of PCL-Azo

Commercially available PCL was functionalized with an azobenzene derivative through esterification of the terminal hydroxyl group using 4-(phenylazo) benzoyl chloride in dry dichloromethane, affording the photoactive polymer PCL-Azo (Fig. 1).

The amount of azobenzene employed for PCL functionalization was calculated based on the number of terminal hydroxyl groups per mole of polymer, resulting in a theoretical loading of 0.0425 wt% relative to PCL. To maximize the degree of esterification, a slight excess of azobenzene derivative (0.05 wt%) was used during the reaction. Successful chemical modification of PCL was confirmed by ¹H NMR spectroscopy (Fig. 2A). The characteristic resonances of the PCL backbone are observed at 1.38–1.65 ppm (m, 4H, −CH₂−), 2.31 ppm (t, 2H, −COOCH₂−), and 4.03 ppm (t, 2H, −COCH₂−). In addition, new signals

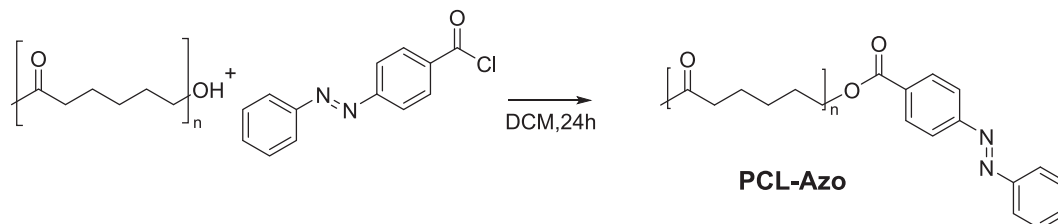


Fig. 1. Schematic representation of the synthesis of azobenzene-functionalized polycaprolactone (PCL-Azo).

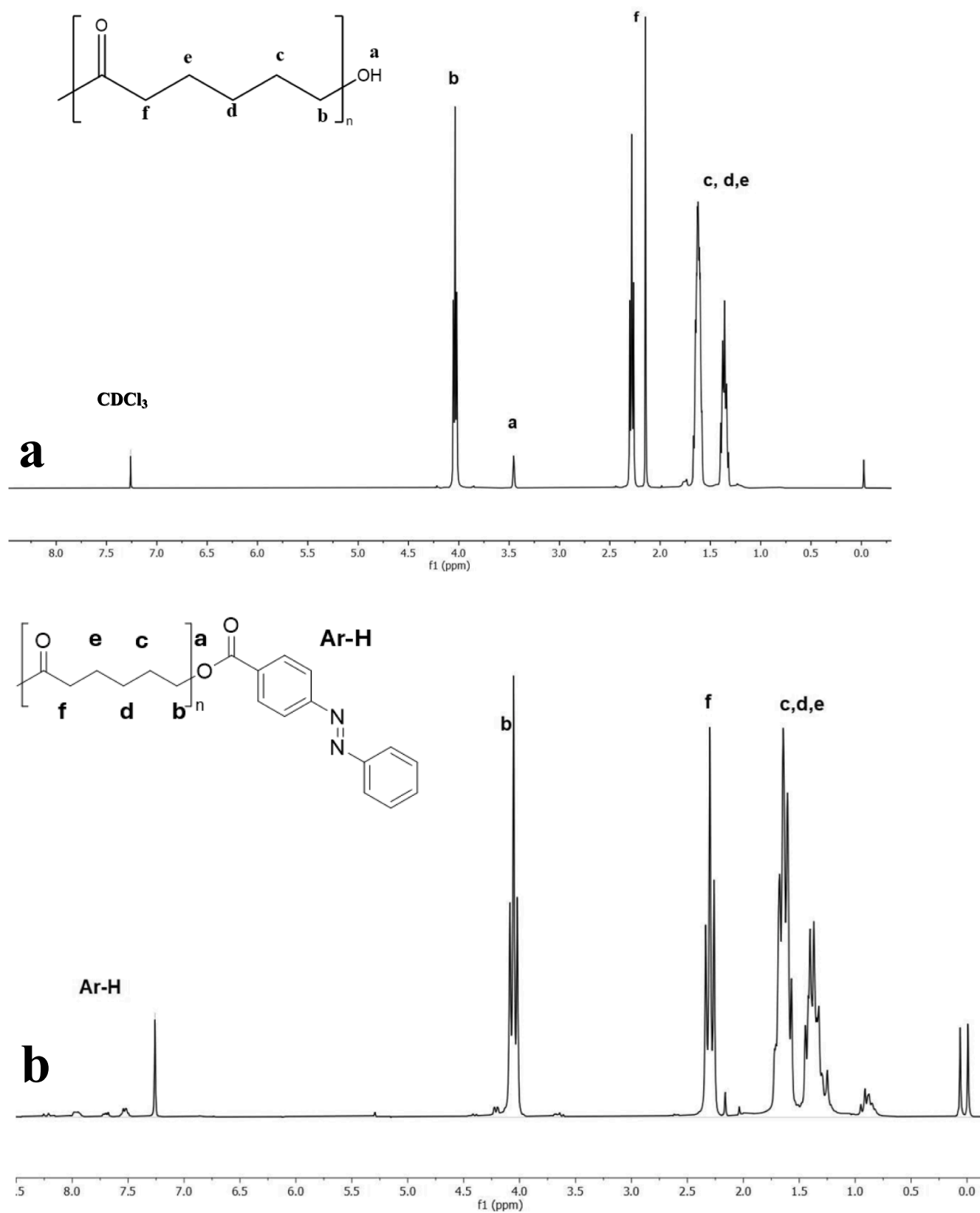


Fig. 2. ^1H NMR spectra a) pristine polycaprolactone (PCL) and b) azobenzene-functionalized polycaprolactone (PCL-Azo).

corresponding to the aromatic protons of the azobenzene moiety appear in the range of 7.40–8.40 ppm (Ar–H), confirming the incorporation of the photoactive unit. Notably, the signal associated with the terminal hydroxyl group of PCL at 3.45 ppm is significantly reduced after functionalization, providing further evidence of successful esterification and formation of the PCL-Azo structure.

3.2. Electrospinning of PCL-Azo

Nanofibers with larger diameters are known to scatter a higher amount of light due to their increased ability to act as physical obstacles, resulting in reduced transparency in electrospun materials. [18] Accordingly, the electrospinning parameters were adjusted to minimize the average nanofiber diameter, thereby increasing the specific surface area and facilitating a more uniform polymer impregnation. Improved infiltration reduces refractive index mismatches and minimizes interfacial voids within the nanofiber network, both of which are major contributors to light scattering. Consequently, reducing nanofiber diameter not only enhances surface area but also improves optical homogeneity, promoting greater transparency and more efficient light interaction with photoactive components such as azobenzene. To achieve this, a design of experiments (DOE) approach was applied using pristine PCL to identify the optimal electrospinning conditions prior to processing PCL-Azo. Three variables were considered: (1) the tip-to-collector distance, (2) the applied voltage, and (3) the solution flow rate. The average nanofiber diameter was selected as the response parameter to be minimized. This optimization strategy aimed to produce nanofibers with the smallest possible diameter while avoiding morphological defects such as bead formation, thereby facilitating subsequent impregnation and the fabrication of transparent nanofiber composites. Representative FESEM images of the PCL nanofibers obtained under the different experimental conditions are shown in Fig. S2. All samples exhibited uniform, bead-free nanofibers, indicating that the electrospinning process was well controlled across the explored parameter space. The average nanofiber diameters ranged from approximately 130 to 180 nm, with narrow diameter distributions observed in all cases. A summary of the diameter measurements extracted from the FESEM analysis for each experimental condition is provided in Table 2.

Based on the results summarized in Table 2, the optimal operating conditions for minimizing nanofiber diameter were identified and are reported in Table 3. These conditions were subsequently applied to the electrospinning of the PCL-Azo system. As shown in Fig. 3, the resulting PCL-Azo nanofibers exhibited a uniform, bead-free morphology with an average diameter of 133.25 nm. Notably, the experimentally measured

Table 2
Average diameters with standard deviation for DOE methodology study.

Experiment Number	Flow rate (mL h ⁻¹)	Voltage (kV)	Distance (cm)	Average Diameter (nm)	Standard deviation (nm)
1	0.8	25	15	130	24.4
2	0.5	23	15	137	24.8
3	1.0	20	10	153	37.6
4	0.8	23	10	164	88.1
5	0.5	20	10	180	31.8
6	0.8	23	15	140	30.4
7	1.0	23	15	148	28.1
8	0.5	25	10	180	36.1
9	0.5	20	20	172	36.6
10	1.0	25	20	155	84.1
11	1.0	25	10	165	30.1
12	0.8	20	15	147	39.6
13	0.8	23	20	157	28.9
14	0.8	23	15	135	28.4
15	1.0	20	20	138	33.9
16	0.5	25	20	165	85.1

Table 3

DOE-optimized conditions with theoretical diameter compared to that obtained experimentally for the PCL-Azo system.

Parameter	Optimized parameters	Theoretical optimized response by DOE (Diameter of fibers)	Experimental measured response (Fiber diameter)	Error (%)
Flow rate (mL h ⁻¹)	0.99			
Voltage (kV)	20.07	129.89 nm	133.25 ± 22.78	2.59
Distance (cm)	16.29			

fiber diameter (Table 3) closely matched the value predicted by the DOE model, with a deviation of only 2.59%, as determined by SEM analysis (Fig. 3). This close agreement confirms the reliability of the DOE approach and its applicability to the PCL-Azo system. Since the developed methodology enables the reliable fabrication of homogeneous, bead-free nanofibers with reduced diameters, the optimized electrospinning parameters were subsequently applied to prepare samples for the immersion treatments aimed at enhancing optical transparency.

3.3. Water contact angle and BET analysis

Water contact angle measurements were performed to evaluate the time-dependent wettability of electrospun PCL nanofiber mats. A comparative analysis was conducted between mats composed of optimized small-diameter nanofibers and those fabricated with larger fiber diameters. The results are summarized in Table 4, which correlates contact angle values with the corresponding surface area and pore volume of the nanofiber mats. At the initial measurement (0 min), nanofiber mats with the largest average diameter exhibited a high contact angle of 137.86°, reflecting the intrinsically hydrophobic nature of PCL. [42] In contrast, mats composed of optimized low-diameter nanofibers showed a lower initial contact angle, which progressively decreased over time, indicating infiltration of the liquid droplet into the nanofibrous structure. This behavior demonstrates that reduced fiber diameter enhances the penetration of polar liquids into the mat. Such time-dependent wetting behavior was not observed for nanofiber mats with larger diameters, where the contact angle remained essentially constant. These results indicate that decreasing fiber diameter promotes solvent impregnation within the nanofiber network, likely due to an increase in specific surface area and the generation of a surface energy gradient that favors wettability. [43] This enhanced wetting behavior is a critical factor for achieving efficient polymer infiltration and, ultimately, improved optical transparency.

Nitrogen adsorption–desorption isotherms (Fig. S4–S5) were used to analyze the textural evolution of electrospun PCL nanofiber of the two diameters. Both samples exhibited type IV isotherms with H3-type hysteresis loops, characteristic of mesoporous materials with slit-shaped pores arising from the random packing of fibers. This behavior indicates that the porosity of the mats is predominantly governed by inter-fiber voids rather than internal porosity within individual fibers. Quantitatively, the specific surface area increased from 4.77 to 20.80 m²/g following optimization (Table 4), consistent with the reduction in average fiber diameter from 532 ± 151 nm to 133 ± 23 nm. This increase reflects the larger external surface exposed by thinner fibers. In parallel, the total pore volume increased from 0.013 to 0.056 cm³/g, indicating a more open fibrous architecture. BJH pore size distribution analysis revealed a dominant pore diameter in the range of 15–30 nm for both samples, confirming the presence of a mesoporous domain. The essentially unchanged pore size distribution, combined with the increased surface area and pore volume, suggests that the optimization process primarily enhanced pore density and external surface

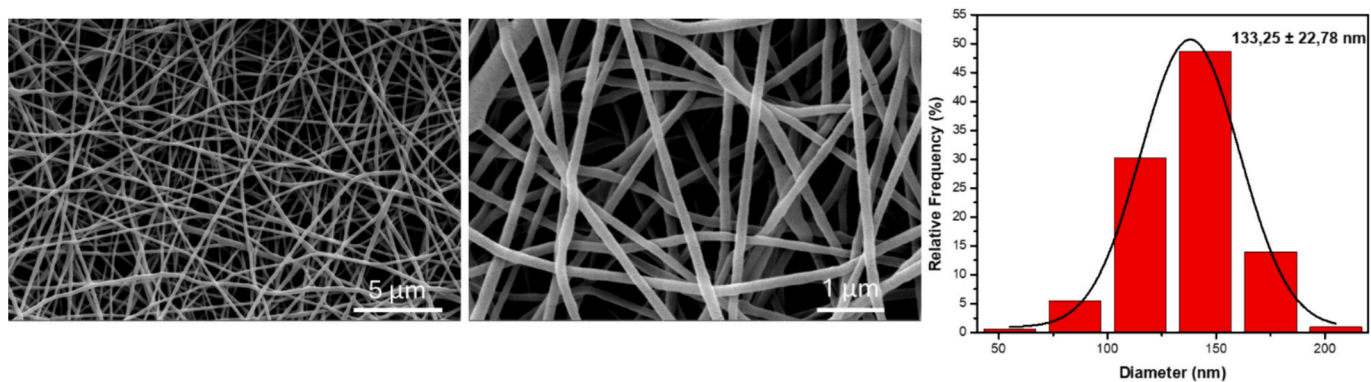


Fig. 3. FESEM micrographs of PCL-Azo nanofibers obtained under optimized electrospinning conditions, showing the average fiber diameter and diameter distribution.

Table 4
Initial (0 min) and 10 min contact angles, surface area, and pore volume parameters for mats with different fiber diameters.

Nanofiber diameter PCL (nm)	Contact angle (°) 0 min	Contact angle (°) 10 min	BET Surface Area (m ² /g)	Pore Volumen (cm ³ /g)
532.28 ± 151.28	137.86 ± 0.06	137.83 ± 0.05	4.7671	0.013231
133.25 ± 22.78	81.43 ± 0.30	40.3 ± 1.19	20.7978	0.055864

contribution rather than altering the intrinsic pore geometry of individual fibers.

These results further corroborate the enhanced wettability of the optimized nanofiber mats discussed above, demonstrating that modifications in the textural properties of the material enable effective impregnation with polar solvents. As summarized in Table 4, a substantial increase in specific surface area is observed as the average fiber diameter decreases, accompanied by a simultaneous increase in total pore volume. Both effects are expected to favor the subsequent transparency treatment by facilitating solvent infiltration throughout the nanofiber network. In general, an increase in surface area has been associated with enhanced wettability in porous materials, as surface characteristics such as roughness, surface energy, porosity, and structural organization play a critical role in wetting behavior. Higher surface area is often correlated with increased roughness and porosity, which can promote liquid penetration and spreading. The trends observed here are consistent with these reports, confirming that the optimized nanofiber architecture promotes improved wettability and infiltration, in agreement with the experimental results discussed above. [44]

To further corroborate the observed changes in wettability, the surface energy of the nanofiber mats was evaluated based on contact angle (θ) measurements. The contact angle is determined by the equilibrium shape of a liquid droplet on a solid surface and depends on the balance between the liquid–vapor surface tension (γ_{lv}), the solid–vapor surface free energy (γ_{sv}), and the solid–liquid interfacial energy (γ_{sl}). The relationship among these interfacial energies is described by Young's equation. [44]

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos(\theta) \quad (2)$$

Glycerol contact angle measurements provide an effective criterion to assess the hydrophobic or hydrophilic character of the nanofiber surfaces. Contact angle values higher than 90° indicate nonwetable, hydrophobic surfaces, as observed for PCL nanofiber mats with larger fiber diameters. In contrast, surfaces exhibiting contact angles below 90° are considered wettable and hydrophilic. [44]

Contact angle measurements were used to estimate the surface en-

ergy of the nanofiber mats using glycerol as the probe liquid. Glycerol has a surface tension of 64 mN m⁻¹ at 20 °C. [45] Surface energy values were calculated by applying the Kwok–Neumann model: [46].

$$\cos(\theta) = -1 + 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \quad (3)$$

where, β is a constant with a value of 0.001247. [46]

Table 5 summarizes the contact angle and surface energy values of PCL nanofibers with different average diameters, as calculated using the Kwok–Neumann model. The data reveals a clear increase in surface energy as fiber diameter decreases, confirming that PCL nanofibers with smaller diameters exhibit higher wettability compared to those with larger diameters. As shown in Fig. S6 and Table 5, the systematic reduction in contact angle, along with the corresponding increase in surface energy, demonstrates the enhanced hydrophilicity of the optimized nanofiber mats. Importantly, nanofibers with reduced and optimized diameters facilitate the infiltration of polar solvents into the fibrous network, which is a key requirement for achieving optical transparency through the proposed impregnation strategy.

3.4. Obtaining transparent nanofiber composites by immersion treatment in polymer solution

Given the intrinsic opacity of electrospun nanofiber mats, optical transparency was achieved by reducing light reflection through an impregnation strategy based on the replacement of air pockets within the fibrous network. This approach involves immersing the nanofiber mats in a polymer solution, allowing the polymer to infiltrate the inter-fiber voids and thereby reduce refractive index mismatches within the material. White PCL nanofiber mats were immersed in a 1% (v/v) chitosan/acetic acid aqueous solution containing different chitosan concentrations (0.25, 0.50, 0.75, 1.00, 1.25, and 1.50% w/v) and molecular weights (low, medium, and high). Vacuum was applied during the impregnation process to remove trapped air from the nanofiber network, promoting effective infiltration of the polymer solution into the pores and inter-fiber spaces. The impregnated mats were subsequently dried at 25 °C for 24 h. Representative images of the nanofiber mats after immersion, vacuum treatment, and drying using low-, medium-, and high-molecular-weight chitosan are shown in Fig. 4. Samples treated with low-molecular-weight chitosan exhibited significantly higher transparency compared to those impregnated with medium- and high-

Table 5
Contact angle and surface energy of PCL nanofibers with different diameters.

Nanofiber Diameter (nm)	Contact Angle (°)	Surface Energy (mJ/m ²)
532.28 ± 151.28	133.3 ± 2.86	3.88
133.25 ± 22.78	35.92 ± 2.02	53.79

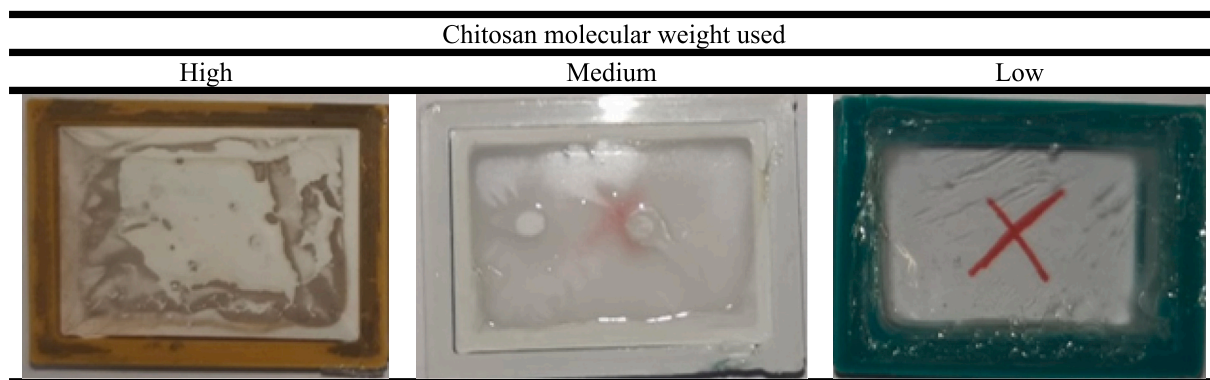


Fig. 4. Images of nanofiber mats after treatment with chitosan solutions of different molecular weights: high (yellow), medium (white), and low (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

molecular-weight chitosan solutions. This behavior suggests that low-molecular-weight chitosan solutions possess a greater ability to infiltrate the pores and air pockets within the nanofiber mats, whereas higher-molecular-weight solutions are less effective. The observed dependence on molecular weight can be attributed to the increase in solution viscosity with increasing chitosan molecular weight at a fixed polymer concentration. [22] Accordingly, low-molecular-weight chitosan was selected for all subsequent experiments.

UV-Vis transmittance spectra of nanofiber composites obtained after immersion treatments using chitosan solutions with concentrations ranging from 0.25 to 1.50% w/v, together with the corresponding transmittance values at 600 nm as a function of chitosan concentration, are presented in Fig. 5. Fig. 5a shows the optical transmittance of pristine PCL nanofiber mats and mats treated with chitosan solutions over the wavelength range from 200 to 800 nm. Untreated nanofiber mats exhibit very low light transmittance across the visible region, reflecting their intrinsically opaque nature. After impregnation with chitosan solutions, a pronounced increase in transparency is observed throughout the visible spectrum. Increasing the chitosan concentration in the impregnating solution leads to a progressive enhancement in transmittance, reaching a maximum value of approximately 87% at 600 nm for a chitosan concentration of 1.00% w/v. Further increases in chitosan concentration result in a slight decrease in transparency, with transmittance values of 84% and 82% obtained for 1.25% and 1.50% w/v solutions, respectively. At low chitosan concentrations, the amount of

polymer infiltrated into the nanofiber network is likely insufficient to fully occupy the inter-fiber voids, resulting in incomplete refractive index matching. As the chitosan concentration increases, a greater number of polymer chains penetrate the available pores, effectively reducing light scattering and increasing transparency. This effect reaches an optimum at intermediate concentrations. At higher concentrations, the slight decrease in transmittance can be attributed to the increased viscosity of the chitosan solutions, which hinders efficient infiltration into the nanofiber mat. It has been reported that chitosan solutions exhibit an exponential increase in apparent viscosity, yield stress, and storage modulus with increasing polymer concentration, particularly in acidic media, due to enhanced intermolecular interactions and chain entanglements. [47,48] Based on these results, immersion treatments of PCL-Azo nanofiber mats were performed using 1 mL of a 1.00% w/v chitosan solution. Photographs of the nanofiber mats before and after impregnation (Fig. 6) clearly illustrate the transition from an opaque to a transparent material upon treatment.

The thermal properties of the nanofiber mats, chitosan films, and the resulting composites were analyzed by thermogravimetric analysis/differential thermal analysis (TGA/DTA) and differential scanning calorimetry (DSC), as shown in Fig. 7a and Fig. 7b, respectively. The thermal degradation profile of chitosan exhibits two main weight-loss stages. The first stage, occurring around 100 °C, is attributed to the evaporation of physically absorbed water, consistent with the hygroscopic nature of the chitosan polymer chains. [49] The second

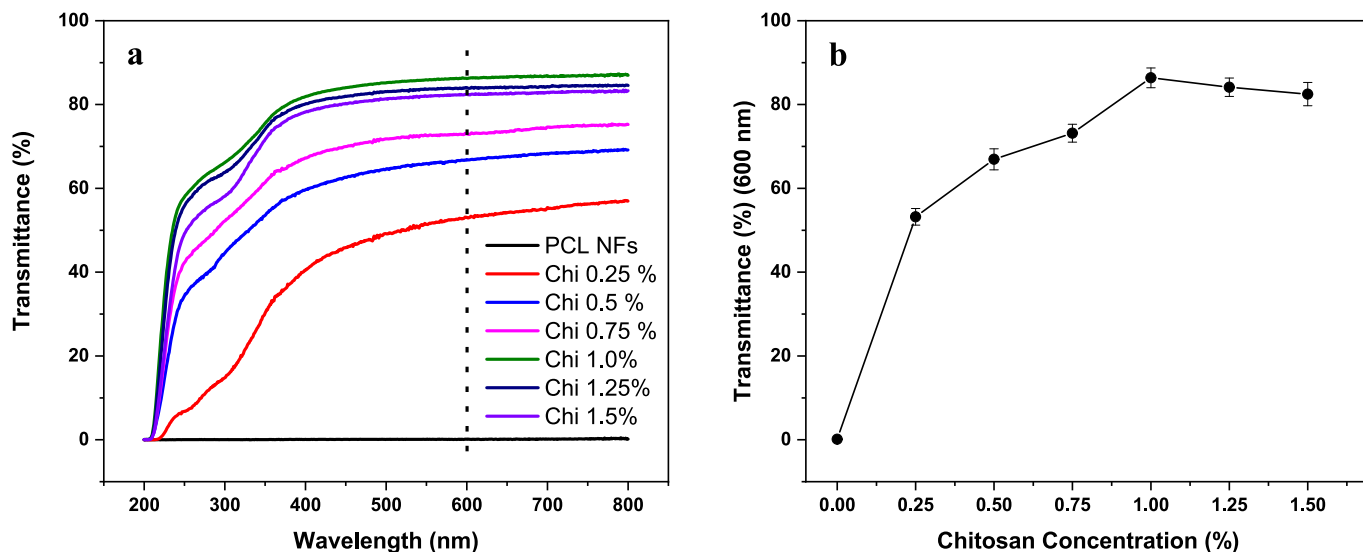


Fig. 5. a) UV-Vis transmittance spectra of pristine nanofiber mats and composites obtained after immersion treatments with chitosan solutions at different concentrations (0.25–1.50% w/v). b) Evolution of the optical transmittance at 600 nm as a function of chitosan concentration in the impregnation solution.



Fig. 6. Photographs of PCL-Azo nanofiber mats a) before and b) after chitosan impregnation. Pictures of the composite after recharging are present in the Supplementary information (Fig. S10).

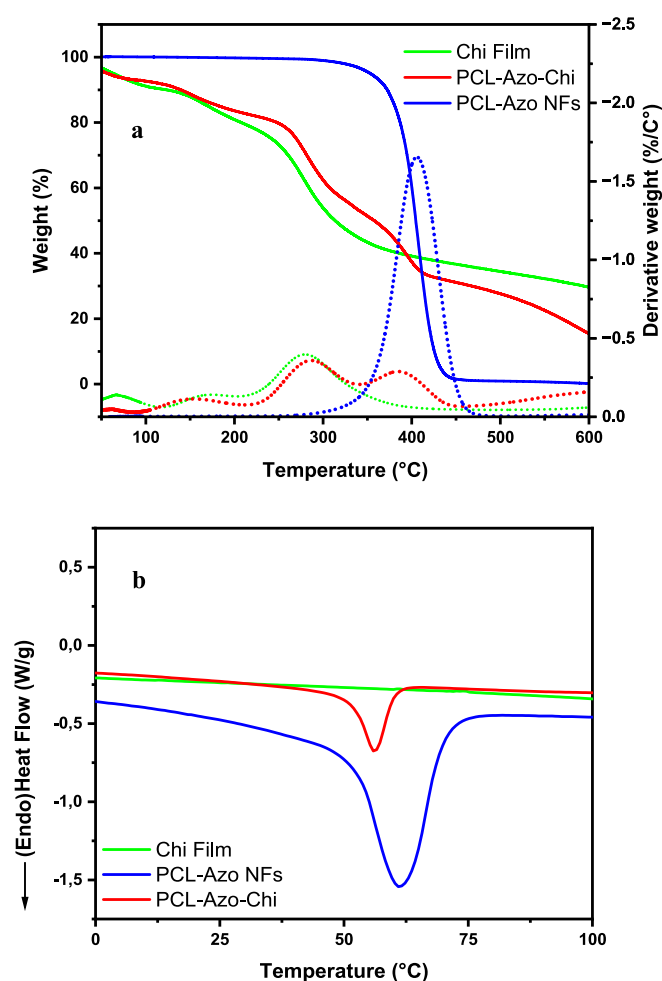


Fig. 7. a) TGA/DTA profiles of chitosan films, PCL-Azo nanofibers and PCL-Azo-Chi composite and the corresponding derivative curves. b) DSC thermograms of chitosan film, PCL-Azo nanofibers and PCL-Azo-Chi composite.

degradation step, observed near 300 °C, corresponds to the thermal decomposition of the chitosan backbone into volatile products. In contrast, the PCL-Azo nanofiber mat displays a single major weight-loss event centered around 400 °C, which is associated with the thermal degradation of the polycaprolactone main chain. [31] Notably, the PCL-Azo-Chi composite exhibits both degradation events characteristic of chitosan and PCL-Azo. This behavior is more clearly resolved in the DTA

curves, which show distinct thermal transitions corresponding to each component. The presence of both degradation processes in the composite confirms the successful incorporation of chitosan within the PCL-Azo nanofiber matrix, resulting in a hybrid material that retains the thermal signatures of its individual constituents.

In the DSC thermograms, the chitosan film does not exhibit any thermal transitions within the 0–100 °C temperature range. In contrast, both the PCL-Azo nanofiber mat and the PCL-Azo-Chi composite display endothermic melting transitions associated with the crystalline domains of PCL, with melting temperatures (T_m) of approximately 55 °C and 60 °C, respectively. [16] The presence of this melting transition in the composite further confirms the incorporation of PCL within the PCL-Azo-Chi system, in agreement with the FTIR analysis (Fig. S7). Subsequently, the impregnated samples were analyzed by FESEM to gain further insight into the nanostructural modifications induced by the impregnation process and to verify the retention of PCL-Azo nanofibers within the composite structure. To this end, the transparent PCL-Azo-Chi composite was treated with 30 mL of a 1% (v/v) acetic acid aqueous solution for 24 h to selectively dissolve the chitosan phase, thereby isolating the nanofiber component. As shown in Fig. 8, the resulting structure clearly reveals the presence of PCL-Azo nanofibers after chitosan removal, confirming that the fibrous network is preserved within the composite. Slight morphological changes were observed, including an increase in the average fiber diameter, which can be attributed to partial swelling during the treatment and/or the presence of residual chitosan still associated with the PCL-Azo nanofibers. The existence of residual chitosan was further confirmed by FTIR analysis (Fig. S8).

In parallel, a second PCL-Azo-Chi composite sample was cryogenically fractured by immersion in liquid nitrogen to expose the cross section and examine the internal morphology after the chitosan-based transparency treatment. Representative SEM micrographs of the fractured sample (Fig. 9), reveal the lateral cross-sectional view of the transparent composite. The images show an asymmetric thickness across the cross-section, with regions of higher thickness (green arrow) and lower thickness (red arrow). This thickness gradient is attributed to the impregnation process, likely arising from the dropwise application of the chitosan solution onto the upper surface of the nanofiber mat during treatment, which results in a nonuniform distribution of the impregnating polymer through the thickness of the composite.

3.5. Surface morphology and nanomechanical analysis by AFM

To gain deeper insights into how the vacuum-assisted infiltration of chitosan modifies both the surface features and the mechanical properties of the mats at the nanoscale, Atomic Force Microscopy (AFM) was conducted in Quantitative Imaging (QI™) mode. This methodology allows for the simultaneous collection of high-resolution topographical

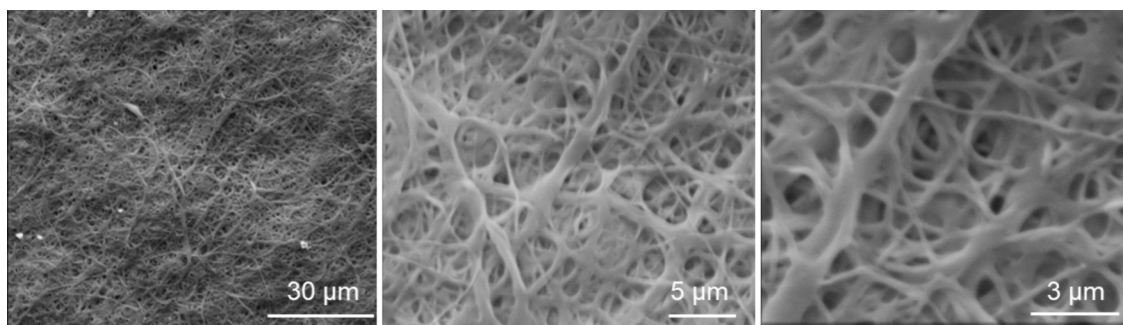


Fig. 8. SEM micrographs of PCL-Azo nanofibers after selective removal of chitosan by redissolution.

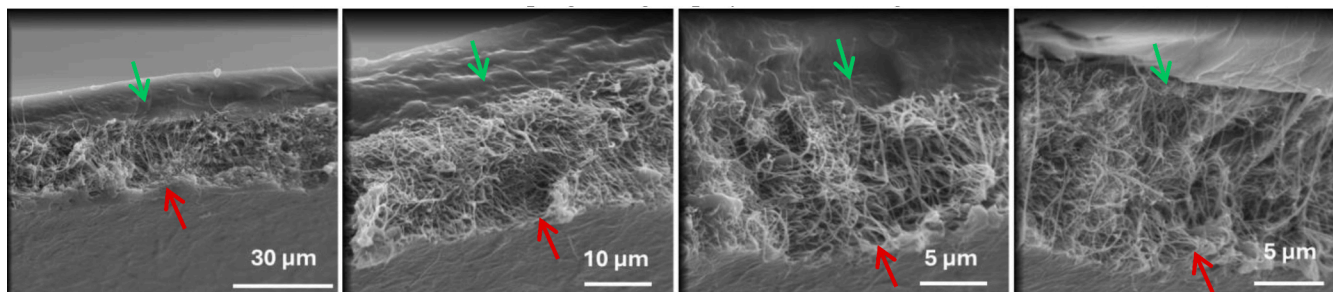


Fig. 9. SEM micrographs of the cross-section of the PCL-Azo-Chi composite.

maps and local elastic responses by recording discrete force–distance curves at every pixel coordinate. The quantitative values extracted for the pure chitosan matrix, the untreated photoactive mat, and the filled composite are summarized in Table 6.

When comparing the PCL-Azo, Chi, and PCL-Azo-Chi samples, distinct variations are observed in both their local mechanical behavior and surface profiles. (Fig. 10). The pure Chi samples exhibit an average Young's modulus of 32.27 ± 1.90 MPa, alongside remarkably low average roughness (R_a) and RMS roughness (R_q) values of 3.81 ± 0.07 nm and 8.10 ± 3.16 nm, respectively. This demonstrates that the cast chitosan reference forms a highly homogeneous, flat, and continuous surface layer, resulting in a narrow distribution of the elastic modulus due to highly uniform and stable contact interface between the AFM tip and the polymer surface.

In contrast, the untreated electrospun PCL-Azo nanofiber mat exhibits the lowest local stiffness, yielding an average Young's modulus of 8.07 ± 4.43 MPa. This lower modulus is typical for open, non-compacted electrospun networks where individual fibers can slide or deflect under localized indentation tip forces. Although the surface topography of PCL-Azo is highly irregular characterized by an elevated R_a of 181.00 ± 5.66 nm and a R_q of 314.30 ± 4.67 nm, the standard deviations across separate image frames remain small. This confirms that while the fiber-mesh surface is intrinsically rough, its overall morphologic distribution is highly reproducible across the sample layout. The noticeable standard deviation in the local Young's modulus of PCL-Azo (4.43 MPa) stems from regional variations in fiber

orientation, suspended inter-fiber voids, and geometry changes as the sharp AFM tip encounters the curved cylindrical profiles of individual nanofibers.

Interestingly, the impregnated PCL-Azo-Chi composite sample exhibits the highest average Young's modulus among all three systems, reaching a value of 50.31 ± 18.28 MPa. This pronounced increment in stiffness provides direct quantitative evidence that filling the inter-fiber macro-pores with a secondary chitosan phase successfully reinforces the electrospun architecture, restricting individual fiber displacements and establishing compact interfacial networks. Concurrently, the composite records intermediate roughness parameters ($R_a = 92.97 \pm 34.72$ nm and $R_q = 175.07 \pm 48.77$ nm), demonstrating that the pore-filling polymer effectively smooths out the deep valleys of the original nanofiber network.

The higher standard deviations observed for both the mechanical and morphologic values of the PCL-Azo-Chi composite reflect a more structurally heterogeneous surface landscape. In this composite material, the AFM tip scans across a complex layout consisting of exposed rigid fiber junctions, highly compact fully impregnated regions, and shallow polymer depressions. This localized heterogeneity changes the contact area, effective indentation depths, and tip-sample interactions across different regions, yielding a broader but representative distribution of the local elastic modulus measurements.

3.6. Study of properties and photoactivity of chitosan-treated PCL-Azo-Chi composites

Fig. 11 presents the UV–Vis transmittance spectra of four different materials: a chitosan film, a chitosan-treated PCL nanofiber composite (PCL NFs–Chi), a chitosan-treated PCL-Azo nanofiber composite (PCL-Azo–Chi), and an untreated PCL nanofiber mat. This comparison allows the individual contributions of each component to the optical response of the system to be evaluated. All samples except the untreated PCL nanofiber mat exhibit high optical transmittance in the visible region between 800 and 400 nm. Below 400 nm, a progressive decrease in transmittance is observed for all chitosan-containing materials. This behavior can be attributed to the optical properties of chitosan, as

Table 6

Nanomechanical properties and surface roughness parameters obtained via AFM for Chi, PCL-Azo, and PCL-Azo-Chi samples.

Sample	Young's Modulus (MPa)	Average Roughness (R_a , nm)	RMS Roughness (R_q , nm)
PCL-Azo	8.07 ± 4.43	181.00 ± 5.66	314.30 ± 4.67
Chi	32.27 ± 1.90	3.81 ± 0.07	8.10 ± 3.16
PCL-Azo-Chi	50.31 ± 18.28	92.97 ± 34.72	175.07 ± 48.77

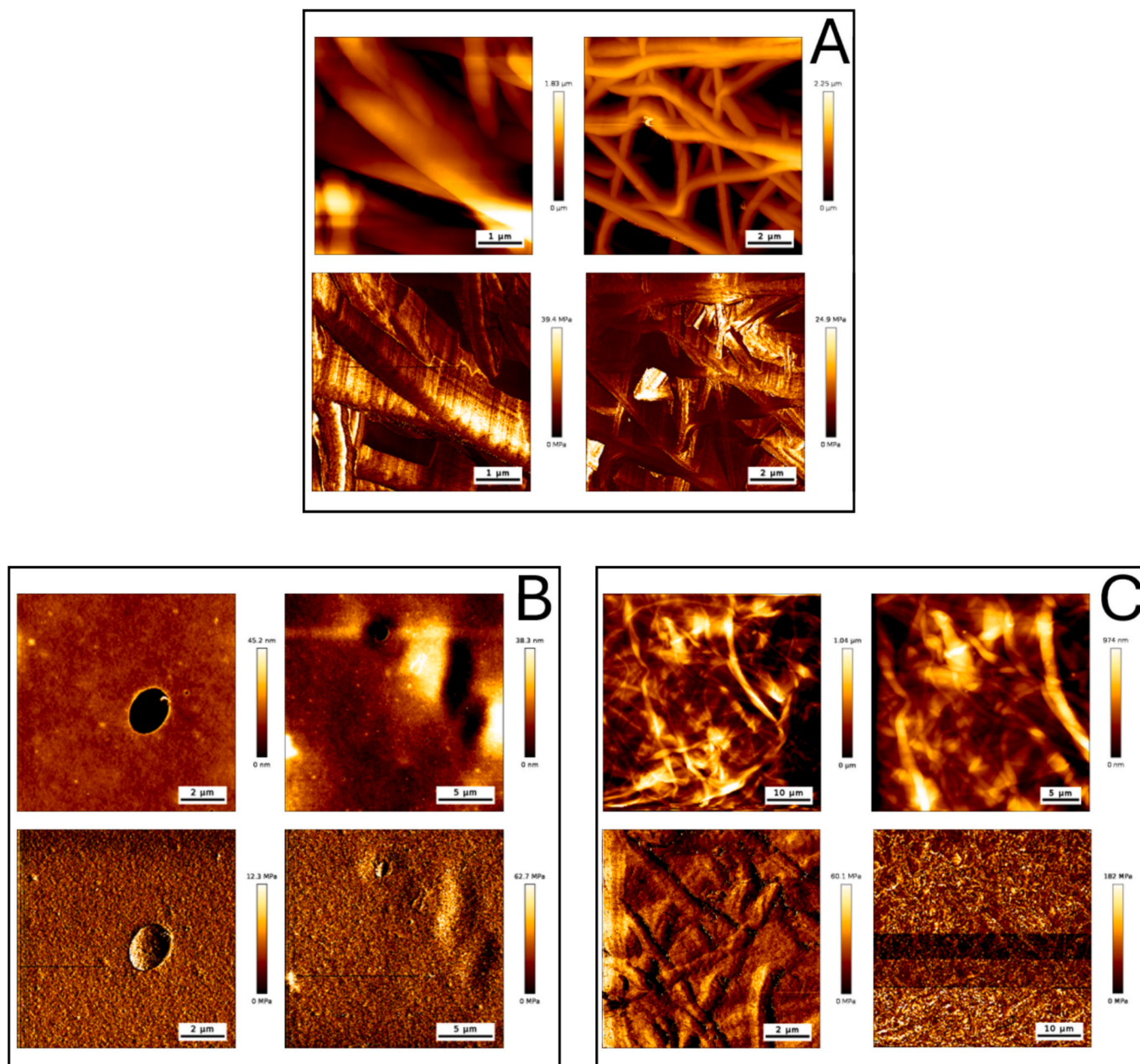


Fig. 10. surface morphology and nanomechanical mapping obtained in QITM mode: (A) Topography and Young's modulus map of untreated PCL-Azo nanofiber mats; (B) Topography and Young's modulus map of pure Chi; (C) Topography and Young's modulus map of the infiltrated PCL-Azo-Chi composite mat.

confirmed by the spectrum of the pure chitosan film, which shows a marked reduction in transmittance in the 400–300 nm region, followed by nearly complete absorption below 220 nm. This response is a characteristic feature of chitosan-based films and is consistent with previous reports. [50].

Fig. 12 shows the UV–Vis absorption spectra in the 250–400 nm range for the azobenzene derivative dissolved in acetone, the chitosan-treated PCL nanofiber composite, a chitosan film, and the PCL-Azo-Chi composite. The azobenzene derivative exhibits an absorption maximum at 325 nm, which is also observed in the PCL-Azo-Chi composite, although with a slight bathochromic shift to 330 nm. This shift is attributed to the different molecular environment experienced by the azobenzene unit when covalently bound to the polymer matrix. Importantly, this absorption band is absent in both the chitosan film and the chitosan-treated PCL nanofiber composite, confirming that the spectral feature originates exclusively from the azobenzene

chromophore.

The photoisomerization capability of the azobenzene units within the composite material was evaluated by monitoring UV–Vis absorption spectra during alternating light irradiation. Fig. 13 presents the spectra of the PCL-Azo-Chi composite before irradiation, after UV charging and after blue-light LED discharging. Initially, the composite exhibits a strong absorption band at approximately 330 nm, characteristic of the allowed $\pi \rightarrow \pi^*$ transition of the thermodynamically stable *Trans* isomer. Upon exposure to UV Light (365 nm) for 1 min, this 330 nm band undergoes a pronounced decrease. Concurrently, a broader, lower-intensity absorption band emerges in the visible region centered near 450 nm. This new feature corresponds to the dipole forbidden $n \rightarrow \pi^*$ transition of the *Cis* isomer, confirming the efficient isomerization from the *Trans* to the *Cis* state. Subsequent irradiation with blue light (475 nm) for 10 min reverses these spectral changes. The absorption band centered at approximately 330 nm reappear, confirming the occurrence

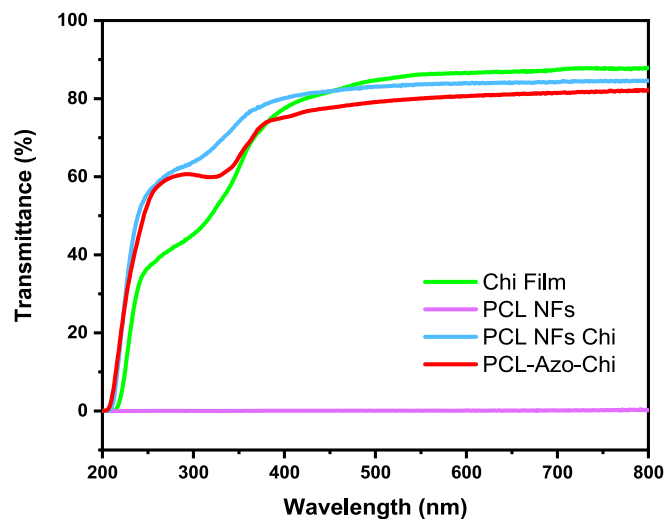


Fig. 11. UV Vis transmittance spectra of chitosan film, PCL nanofibers, treated PCL and PCL-Azo composites.

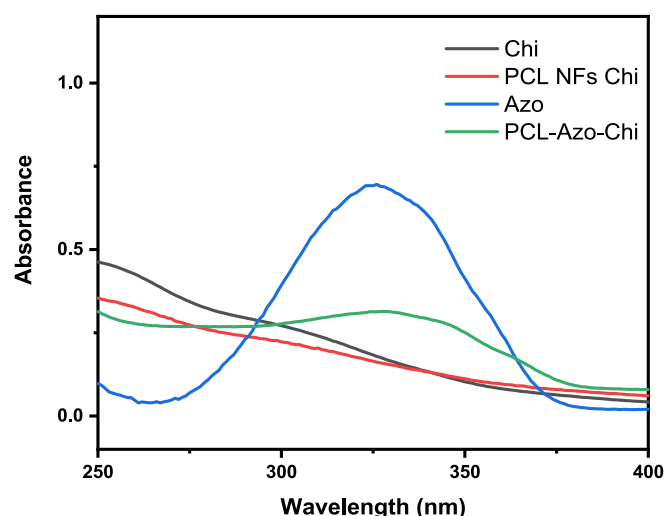


Fig. 12. UV-Vis absorption spectra of a chitosan film, azobenzene in acetone solution, and chitosan-treated PCL and PCL-Azo nanofiber composites.

of the reverse *Cis*-to-*Trans* isomerization process. [51]

Notably, the absorbance intensity before and after the irradiation cycle remains essentially unchanged, indicating that the photoisomerization process induced by alternating UV and blue light is highly reversible and does not lead to detectable photodegradation. To further evaluate the photostability of the composite, the disappearance and reappearance of the absorption band at 330 nm, corresponding to the *Trans* isomer, were monitored over 100 consecutive irradiation cycles. The samples were alternately exposed to UV light at 365 nm for 1 min and blue light at 475 nm for 10 min, allowing assessment of the long-term stability of the azobenzene units within the composite matrix. The results of the cycling experiment are shown in Fig. 14, which presents the evolution of the absorbance intensity at 330 nm as a function of the number of irradiation cycles. The material exhibits a stable and reproducible absorbance response throughout 100 cycles, with no significant loss in the absorbance difference between the charged (*Cis*) and discharged (*Trans*) states. This behavior demonstrates that both the *Trans*-to-*Cis* and *Cis*-to-*Trans* photoisomerization processes remain highly reversible and stable under repeated cycling, confirming the excellent photostability and robustness of the PCL-Azo-Chi composite. To evaluate performance under competitive illumination, preliminary

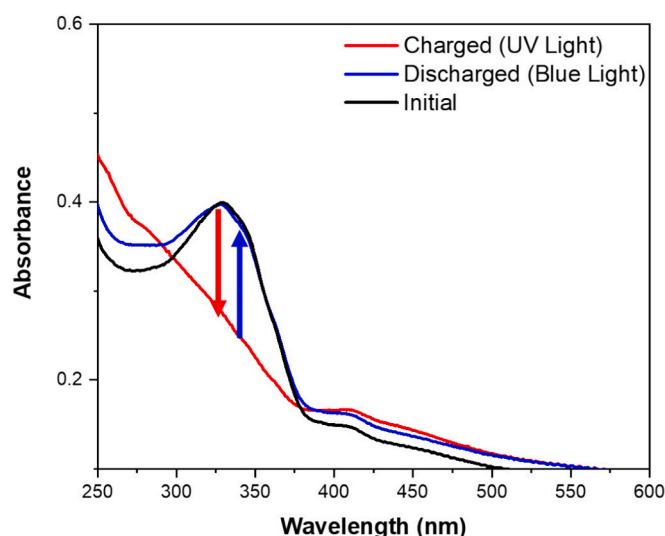


Fig. 13. UV-Vis absorption spectra of the PCL-Azo-Chi composite recorded under UV irradiation (365 nm) and after subsequent blue light irradiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

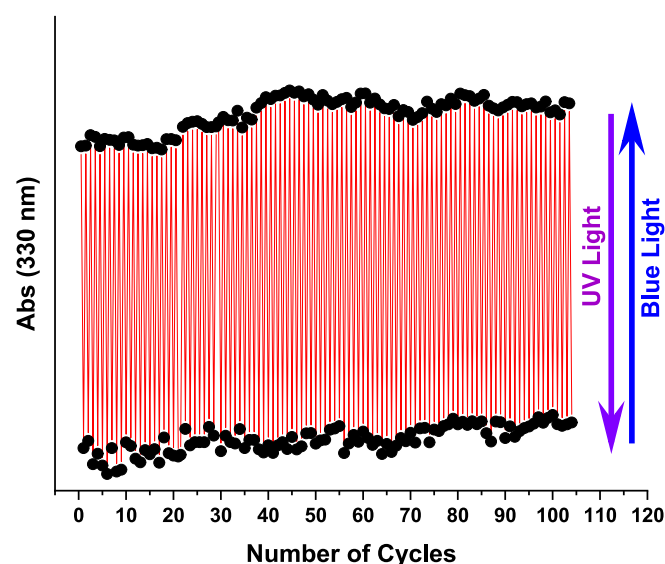


Fig. 14. *Trans*-*cis*-*trans* photoisomerization cycles of the PCL-Azo-Chi composite under alternating irradiation at 365 nm (UV, 1 min) and 475 nm (blue light, 10 min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tests were conducted using broad-spectrum White LED sources. (Fig. S11) Exposure resulted in a rapid photostationary state favoring the *Trans* isomer. This is driven by the high sensitivity of the *Cis*-to-*Trans* back-reaction, which we observed can be efficiently triggered by low-energy blue LED irradiation at an irradiance of just 3 W/m². Under broad-spectrum light, this highly efficient visible-light-induced discharge readily outcompetes the UV-driven *Trans*-to-*Cis* conversion. Consequently, while the developed composite provides a stable matrix, future implementation under natural sunlight (AM 1.5G) will require integrating core-modified azobenzenes—such as ortho-functionalized derivatives [11] designed to decouple the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions to mitigate this low-energy discharge. [4,8]

In addition to the photoinduced switching behavior, the thermal *Cis*-to-*Trans* back-isomerization of the azobenzene-containing materials was systematically investigated in the absence of irradiation. To generate the

metastable *Cis*-rich state, both samples were initially irradiated with UV light at 365 nm for 1 min and subsequently stored in the dark, with the recovery of the *Trans* isomer monitored over time by the increase in absorbance at 330 nm. The study was performed on both the PCL-Azo-Chi nanofiber composite and the PCL-Azo film containing the same azobenzene content in order to evaluate the effect of nanofiber morphology and chitosan incorporation on the thermal relaxation process.

As shown in Fig. 15A, both systems exhibited a progressive increase in normalized absorbance at 330 nm, confirming spontaneous thermal *Cis*-to-*Trans* isomerization in the dark. Nevertheless, clear differences in the relaxation kinetics were observed between the two materials. The PCL-Azo film displayed a faster recovery of the *Trans* state, reaching approximately 70% of its initial absorbance within 5 days, whereas the PCL-Azo-Chi composite recovered only about 45% during the same period, indicating a significantly slower thermal relaxation process in the nanofibrous composite. Furthermore, the PCL-Azo film approached its maximum absorbance after approximately one week, while the PCL-Azo-Chi composite required nearly two weeks to reach equilibrium.

To quantitatively analyze the thermal relaxation behavior, the experimental data were fitted using a pseudo-first-order kinetic model (Fig. 15B–D), and the extracted kinetic parameters are summarized in Table 7. This model accurately reflects the physical mechanism of the system, as the thermal *Cis*-to-*Trans* back-isomerization is fundamentally a unimolecular process driven by the spontaneous conformational relaxation of individual azobenzene units, meaning the reaction rate is

Table 7

Pseudo-first-order kinetic constants, global rate constants, and half-life values associated with the thermal *Cis*-to-*Trans* back-isomerization of PCL-Azo film and PCL-Azo-Chi composite in dark conditions.

Material	A_{∞}	Rate constant first 4 h (h^{-1})	Rate constant after 4 h (h^{-1})	Global Rate constant (h^{-1})	Half-life ($t_{1/2}$) h
PCL-Azo-Chi	0.504	0.01554	0.00678	0.00519	133.55
PCL-Azo Film	0.477	0.01513	0.01199	0.00853	81.26

dependent solely on the population of the metastable *Cis* state. [51,52] The global rate constants obtained from the full kinetic profiles were 0.00853 h^{-1} for the PCL-Azo film and 0.00519 h^{-1} for the PCL-Azo-Chi composite, corresponding to calculated half-lives ($t_{1/2}$) of 81.26 h and 133.55 h, respectively. These results demonstrate that the incorporation of chitosan and the formation of the nanofibrous architecture substantially retard the thermal back-isomerization process.

Interestingly, kinetic analysis revealed a two-step thermal relaxation behavior for both materials (Fig. 15C–D). During the initial 4 h, the apparent rate constants were higher compared to the overall process and remarkably similar between the two systems (0.01513 h^{-1} for the PCL-Azo film and 0.01554 h^{-1} for the PCL-Azo-Chi composite). This comparable early-stage recovery indicates that the intrinsic *Cis*-to-*Trans*

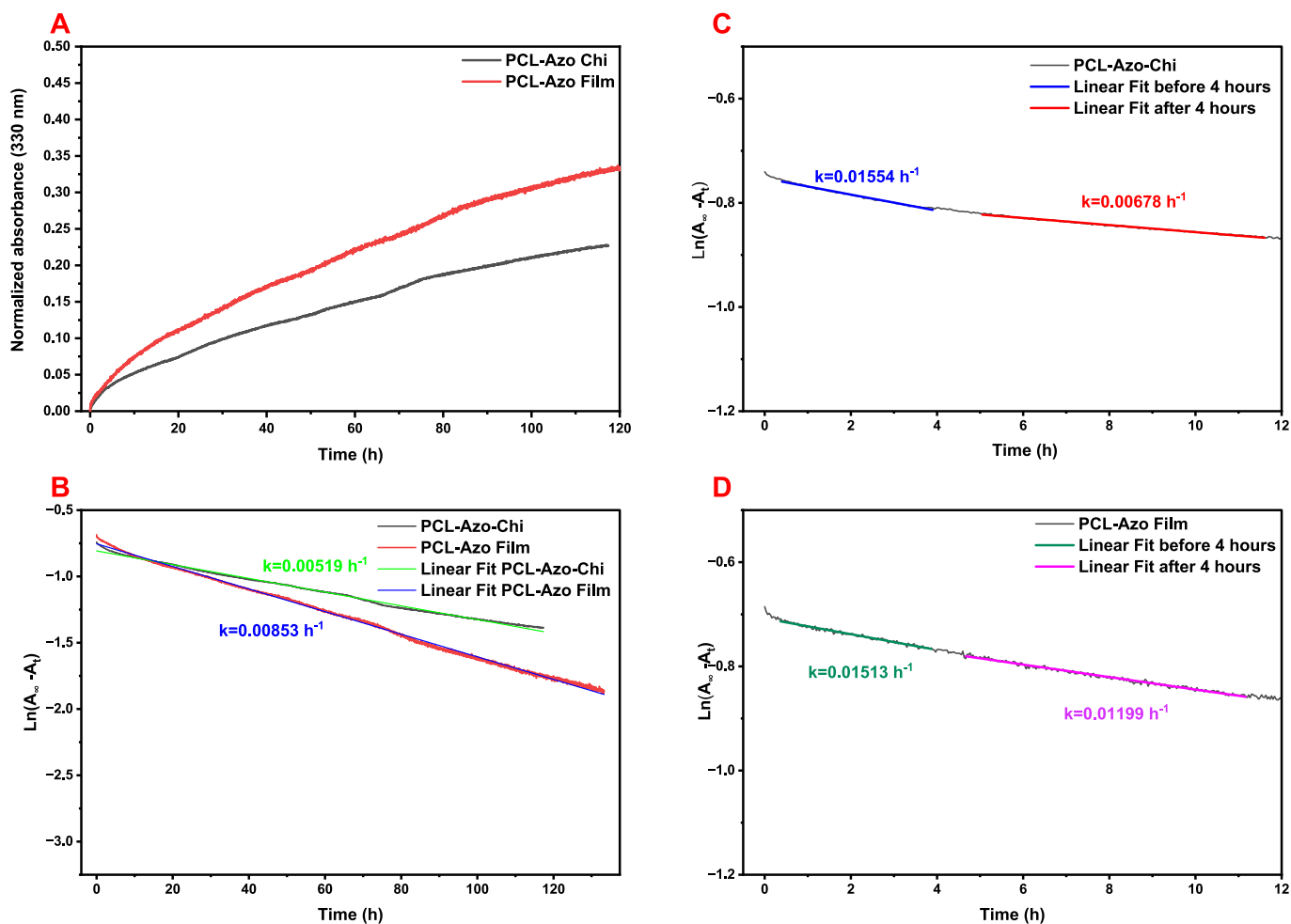


Fig. 15. Thermal *Cis*-to-*Trans* back-isomerization kinetics of PCL-Azo film and PCL-Azo-Chi composite monitored by UV-Vis spectroscopy at 330 nm after UV irradiation (365 nm, 1 min). (A) Evolution of normalized absorbance over time. (B) Global pseudo-first-order kinetic fitting for both materials. (C) Early-stage kinetic fitting (0–12 h) for PCL-Azo-Chi composite. (D) Early-stage kinetic fitting (0–12 h) for PCL-Azo film. The extracted kinetic parameters are presented in Table 7.

isomerization dynamics are not initially altered by the composite matrix. This initial fast step likely corresponds to the relaxation of azobenzene moieties situated in microenvironments with higher free volume, where localized mobility remains unrestricted.

Once these highly mobile populations discharge, the kinetics progressively diverge. At longer relaxation times (>4 h), the process slows considerably, yielding a second-stage rate constant of 0.01199 h^{-1} for the film and a markedly lower 0.00678 h^{-1} for the composite. This pronounced reduction suggests that the remaining *Cis* isomers in the composite reside in highly restricted domains in PCL-Azo-Chi composite. In these regions, the chitosan-containing nanofibrous matrix and localized intermolecular interactions impose severe steric and diffusional limitations on the segmental mobility required for molecular rearrangement. Consequently, Chitosan might extend the lifetime of *Cis* isomer by kinetically restricting the degrees of freedom available for back-isomerization within the confined polymer environment.

The slower thermal relaxation observed in the PCL-Azo-Chi composite is attributed to interactions between chitosan and the PCL-Azo system, which can restrict molecular mobility within the nanofiber matrix. The polycationic nature of chitosan is known to influence polymer organization and viscoelastic properties, thereby hindering conformational rearrangements. [32] In this context, chitosan may interact with the azobenzene moieties through hydrogen bonding or other noncovalent interactions, extending the lifetime of the *Cis* state through confinement effects within the polymeric matrix. This confinement decreases the degrees of freedom of the azobenzene units, limiting the molecular motions required for efficient thermal *Cis-to-Trans* back-isomerization. [53]

Additional intermolecular interactions involving the polymeric nanofiber matrix may further contribute to this effect. Hydrogen bonding between hydroxyl groups of chitosan and the $\text{N}=\text{N}$ moiety of the azobenzene derivative [54] as well as van der Waals interactions with the PCL backbone, can modify the local chemical environment and reduce molecular freedom. As previously reported, the incorporation of chitosan and the solid-state confinement of azobenzene-based systems increase the viscoelastic response of the medium, thereby restricting molecular mobility and slowing *Cis-to-Trans* isomerization kinetics. [52,55] Therefore, the prolonged thermal relaxation observed for the PCL-Azo-Chi composite is more accurately associated with kinetic hindrance caused by matrix confinement and reduced configurational freedom, rather than intrinsic stabilization of the *Cis* isomer. This behavior is particularly relevant for long-term molecular solar thermal energy storage applications, where extending the lifetime of the metastable photocharged state is highly desirable. In a broader context, recent advances in azobenzene-based MOST materials have highlighted the importance of both molecular design and device integration for achieving practical solar thermal storage. A comprehensive review by Xu et al. has underscored the critical role of polymer architecture, cycling stability, and solid-state confinement in determining real-device performance. [56] In parallel, the development of phase-change azobenzene derivatives capable of simultaneously storing photon energy and phase-transition enthalpy has demonstrated that molecular engineering strategies can substantially boost the total stored energy density. [57] Compared to these approaches, the present work offers a distinct and complementary pathway: by embedding azobenzene units within a transparent biopolymer nanofiber composite, we achieve optical accessibility, robust cycling performance over 100 charge-discharge cycles, and extended *Cis*-state lifetime, all within a processable and sustainable platform.

To evaluate the emission quantum yields of PCL-Azo, the PCL-Azo-Chi composite, and the corresponding blank samples, emission spectra were recorded upon excitation at 300 nm (Fig. 16). Based on these measurements, the emission quantum yield of azobenzene within the different polymeric matrices was estimated. In all cases, the emission quantum yield of azobenzene was found to be lower than 10^{-6} , in good agreement with previously reported values for azobenzene-based

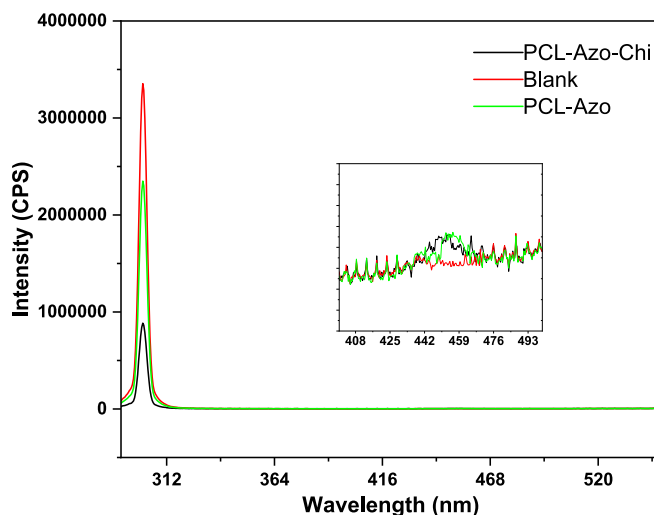


Fig. 16. Emission spectra of PCL-Azo film and PCL-Azo-Chi composite.

systems. [58] This extremely low emission efficiency indicates that nonradiative decay pathways strongly dominate the excited-state deactivation process, which is consistent with the well-known photoisomerization behavior of azobenzene derivatives. Notably, a comparison of the absorbed photon flux reveals that the PCL-Azo-Chi composite absorbs a higher number of photons than the PCL-Azo film under identical excitation conditions. This enhanced absorption can be attributed to a combination of factors, including the intrinsic absorption of chitosan at 300 nm and the increased optical transparency of the composite, which promotes more efficient light penetration and light-matter interaction within the material. As a result, a larger fraction of incident photons can effectively interact with the azobenzene moieties embedded in the composite matrix.

3.7. Computational analysis

Fig. 17 shows the optimized *Cis* and *Trans* conformations of azobenzene, PCL-Azo, and PCL-Azo in the presence of chitosan (Chi). For all three systems, the *Trans* isomer corresponds to the most stable geometry, characterized by a $\text{C}=\text{N}=\text{N}=\text{C}$ dihedral angle close to 180° . In contrast, the *Cis* conformations exhibit dihedral angles of approximately 9° , with slight deviations observed in the presence of chitosan (Fig. 17c). A perfectly planar *Cis* configuration (0° dihedral angle) is sterically inaccessible due to repulsion between adjacent hydrogen atoms on the phenyl rings. The *Trans-Cis* isomerization energies ($\Delta E_{\text{Trans-Cis}}$), reaction enthalpies ($\Delta H_{\text{Trans-Cis}}$), and Gibbs free energies ($\Delta G_{\text{Trans-Cis}}$) calculated for the three model reactions are summarized in Table 8. Comparable thermodynamic values were obtained for R1 (azobenzene) and R2 (PCL-Azo), with $\Delta E_{\text{Trans-Cis}}$ values of approximately 12 kcal mol^{-1} . In contrast, the *Trans-Cis* isomerization in R3 (PCL-Azo in the presence of chitosan) is less energetically favorable, with $\Delta E_{\text{Trans-Cis}}$ values in the range of 6 to 10 kcal mol^{-1} . This trend indicates that interactions with chitosan reduce the thermodynamic driving force for *Trans-to-Cis* isomerization of PCL-Azo. In particular, the $\Delta H_{\text{Trans-Cis}}$ values become less favorable in the presence of chitosan, reflecting stabilization of the *Trans* state through intermolecular interactions. Nevertheless, entropic contributions partially compensate for this effect, so that the overall $\Delta G_{\text{Trans-Cis}}$ remains negative, allowing photoisomerization to proceed while increasing the relative stability and lifetime of the *Cis* isomer. These results are consistent with the experimentally observed slower thermal back-isomerization kinetics in the PCL-Azo-Chi composite.

The interaction energy between PCL-Azo and chitosan (Chi) was also calculated for both the *Trans* and *Cis* conformations of PCL-Azo

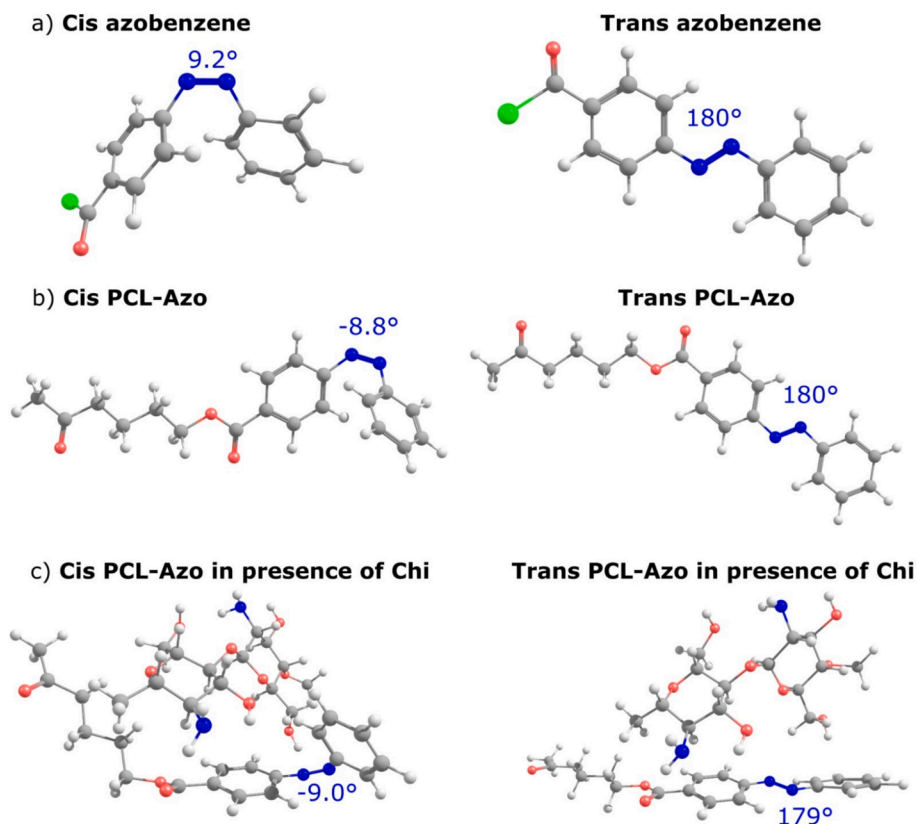


Fig. 17. Optimized *Cis* (left) and *Trans* (right) geometries of (a) azobenzene, (b) PCL-Azo in the absence of chitosan, and (c) PCL-Azo in the presence of chitosan.

Table 8

Thermochemical outcomes for the *Trans*–*Cis* isomerization energy reaction of azobenzene and PCL-Azo in the absence and presence of chitosan (Chi).

	Azobenzene (R1) (kcal mol ⁻¹)	PCL-Azo (R2) (kcal mol ⁻¹)	PCL-Azo in presence of Chi (R3) (kcal mol ⁻¹)
$\Delta E_{trans-cis}$	12.1	12.2	5.9
$\Delta H_{trans-cis}$	12.1	12.2	5.9
$\Delta G_{trans-cis}$	12.6	12.8	10.0

interacting with Chi. For the *Trans* conformation, a favorable interaction energy of $2.4 \text{ kcal mol}^{-1}$ was obtained, whereas for the *Cis* conformation the interaction energy was positive ($7.6 \text{ kcal mol}^{-1}$), indicating an energetically unfavorable interaction. The nature of these interactions was further analyzed using noncovalent interaction (NCI) analysis, as shown in Fig. 18. In both systems, the interaction interface between PCL-Azo and Chi is dominated by weak dispersive interactions, represented

by green regions, which are characteristic of van der Waals forces. However, a clear difference is observed between the two conformations. When Chi interacts with the *Cis* conformation of PCL-Azo (Fig. 18a), a larger number of repulsive regions (yellow surfaces) appear at the interface. In contrast, for the *Trans* PCL-Azo–Chi system (Fig. 18b), two localized attractive interactions (blue regions) are observed. These correspond to a hydrogen bond between the carbonyl group of the PCL-Azo moiety and the amino group of chitosan, as well as a nonconventional hydrogen bond involving the π -system of the azobenzene ring and a hydrogen atom from a chitosan hydroxyl group. The presence of these stabilizing interactions rationalizes the more favorable interaction energy calculated for the *Trans* conformation and explains the preferential interaction of chitosan with *Trans*-PCL-Azo over its *Cis* counterpart. Overall, these computational results support the experimental observations by highlighting the critical role of steric confinement. The substantial repulsive regions observed at the interface of the *Cis* PCL-Azo–Chi system (Fig. 18a) indicate that the rigid chitosan matrix imposes severe spatial restrictions on the metastable state. Rather than

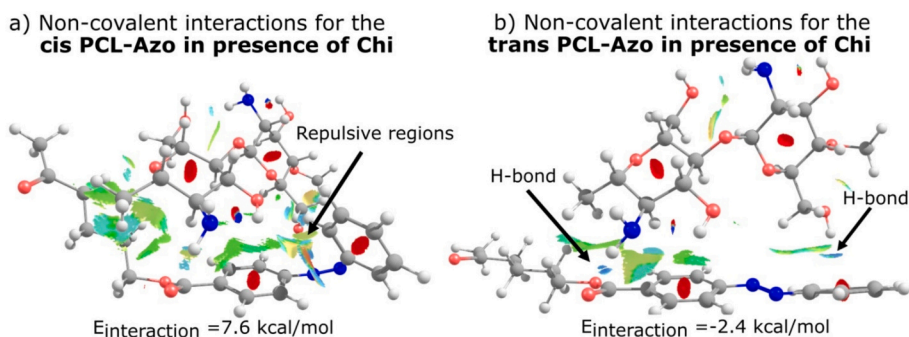


Fig. 18. Non-covalent interaction of *Cis* (a) and *Trans* (b) PCL-Azo in presence (b) of Chi.

thermodynamically suppressing the back-conversion, this tight molecular environment acts as a physical barrier, kinetically trapping the azobenzene moiety and severely hindering the large-scale conformational rearrangement necessary to reach the transition state. This matrix-induced restriction of molecular mobility provides a robust structural explanation for the significantly slower thermal back-isomerization and extended *Cis*-state lifetime experimentally observed in the composite system.

The DFT model employed in this work represents a simplified local molecular environment composed of one azobenzene-modified caprolactone unit interacting with two glucosamine units. Therefore, the calculations do not explicitly account for macroscopic effects associated with polymer chain length, chain entanglement, semicrystalline domains, long-range cooperative interactions, or the heterogeneous morphology of the electrospun nanofiber matrix. Expanding the quantum mechanical model to incorporate these extended macromolecular features would render the calculations computationally prohibitive at the employed level of theory. Consequently, the calculated thermodynamic parameters should be interpreted qualitatively rather than as an exact representation of the bulk material. Despite these limitations, the model provides valuable molecular-level insight into the local non-covalent interactions and confinement effects introduced by chitosan, which reduce the molecular degrees of freedom of the azobenzene moieties and contribute to the experimentally observed extension of the *Cis*-state lifetime in the PCL-Azo-Chi composite system.

While the developed nanofiber matrix exhibits excellent optical properties and kinetic stabilization, the terminal-group functionalization of high-molecular-weight PCL (80,000 g/mol) inherently limits the macroscopic energy storage capacity. Based on our computational analysis (Table 8), the enthalpy of isomerization for the azobenzene core is ≈ 50.6 kJ/mol (12.1 kcal mol⁻¹). Consequently, the theoretical energy density of the pure chromophore is approximately 242 J/g. At our theoretical loading of 0.0425 wt%, the estimated energy storage density of the bulk composite is restricted to ≈ 0.1 J/g. This value is low compared to state-of-art bulk phase-change MOST materials, which can exceed 200 J/g [56,57]; however, this extreme dilution is a critical factor in achieving the reported 87% optical transmittance. High chromophore loadings in solid-state matrices often lead to aggregation and phase separation, which induce severe light scattering and opacity. Consequently, this system serves as a proof-of-concept demonstration that biopolymer impregnation can yield a transparent, confinement-driven platform, establishing a baseline for future iterations that utilize side-chain functionalized polymers to increase loading without sacrificing optical clarity.

To experimentally verify this macroscopic energy storage, Differential Scanning Calorimetry (DSC) was performed on the UV-irradiated composites. However, no exothermic heat release corresponding to the *Cis*-to-*Trans* back-isomerization was observed during the thermal cycles (Fig. S9). This lack of a measurable signal is a direct consequence of the system's architectural limits. Specifically, the combination of a minimal absolute stored energy (≈ 0.1 J/g) and a release of over an extended, confined timeframe ($t_{1/2} > 133$ h) yields a continuous instantaneous heat flow that falls completely below the detection threshold of standard calorimetric instrumentation.

4. Conclusions

The development of transparent, photoactive nanocomposites was successfully achieved by integrating azobenzene-functionalized polycaprolactone (PCL-Azo) nanofibers with a chitosan matrix. Optimizing the electrospinning parameters yielded uniform, low-diameter nanofibers (133.25 ± 22.8 nm), increasing the specific surface area and facilitating efficient vacuum-assisted polymer infiltration. This pore-filling strategy effectively minimized refractive index mismatches within the fibrous network, enabling high optical transmittance ($\sim 87\%$ at 600 nm) while preserving the structural integrity and reversible

Trans-Cis-Trans photoisomerization capabilities of the solid-state platform.

Crucially, the composite matrix significantly modulates the thermal back-isomerization kinetics of the azobenzene units, substantially extending the lifetime of the metastable *Cis* state. This delayed relaxation is driven by severe space-confinement rather than thermodynamic stabilization. The rigid chitosan-filled nanofibrous architecture imposes a prominent physical barrier, drastically restricting the molecular degrees of freedom required for large-scale conformational rearrangement. Computational noncovalent interaction (NCI) analysis mathematically validates this steric trapping, demonstrating substantial repulsive interactions at the matrix interface that kinetically hinder the back-conversion process.

While the terminal-group functionalization strategy limits the macroscopic energy storage capacity to approximately 0.1 J/g, this extreme chromophore dilution represents a deliberate trade-off required to prevent aggregation and achieve exceptional optical clarity. Consequently, this system serves as a highly stable, transparent, and confinement-driven proof-of-concept for molecular solar thermal (MOST) energy storage. It establishes a robust structural baseline for future designs utilizing side-chain functionalized polymers to increase energy density without sacrificing the high visible-light transmittance essential for adaptive coatings and optically functional platforms.

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CRediT authorship contribution statement

Sebastián Castillo: Writing – original draft, Methodology, Investigation. **Óscar Ramírez:** Methodology, Formal analysis. **Galder Kortaberria:** Supervision, Investigation, Formal analysis. **Angie Carolay Forero-Giron:** Investigation. **Diego Cortés-Arriagada:** Investigation. **Nancy Pizarro:** Investigation. **César Saldías:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization. **Ángel Leiva:** Supervision, Project administration, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.reactfunctpolym.2026.106857>.

Data availability

Data will be made available on request.

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