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Photochemical [2+2] Cycloaddition of Biobased Latexes for Composites with Microfibrillated Cellulose

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A biobased latex was obtained by copolymerization in emulsion of ethoxy dihydroeugenyl methacrylate (EDMA) and coumarin methacrylate (CMA). Thin films of poly(EDMA-co-CMA) were irradiated with UV light at 365 nm, to promote the [2+2] photocycloaddition reaction of the coumarin moieties. The advancement of the reaction was followed by monitoring the intensity of the UV-Vis absorbance at 320 nm, characteristic of coumarin, after different irradiation times. Complete dimerization of the coumarin moieties could be achieved. A microfibrillated cellulose (MFC) reinforcement was added to the poly(EDMA-co-CMA) latexes to prepare composite materials. The permeability of the composite films to oxygen, before and after crosslinking, was assessed. For the non-crosslinked films, increasing the cellulose content from 5 wt% to 30 wt% decreased the oxygen transmission rate (OTR) by approximately 70%. When 1 wt% CMA moieties were present in the polymer backbone the OTR was approximately 50 % lower with respect to poly(EDMA) composites. A further slight decrease of permeability was observed upon crosslinking of the composite poly(EDMA-co-CMA)/MFC films.

1. Introduction

Replacing oil-based plastics with new materials from renewable resources is a key action for reducing dependency on fossil resources and the related environmental burden. When the renewable resources are derived from non-edible biomass, there is the additional benefit of valorizing otherwise unusable by-products of the agro-food industry, reducing waste. To this aim, increasing attention is being given to cellulose, the most abundant biopolymer on earth, and particularly to microfibrillated cellulose (MFC), which can be obtained not only from wood but also from numerous annual plants (Goncalves et al., 2016). MFC displays very good oxygen barrier properties, which make it an interesting material for packaging applications (Demuner et al., 2019; Nair et al., 2014). MFC films, however, are sensitive to humidity, thus they are often combined with polymers, and particularly thermally or photochemically crosslinked ones, to improve their water resistance; however, MFC aggregate when mixed with apolar polymers or solvents, thus somewhat complex solvent exchange procedures are often involved (Dalle Vacche et al., 2019, 2021; Vitale et al., 2022). The use of polymer matrices in the form of waterborne latexes, that can easily be mixed with MFC in an aqueous dispersion and subsequently crosslinked, is therefore a convenient and environmentally advantageous alternative. Biobased polymer latexes have been prepared by emulsion radical polymerization of vegetable oils and lipids, terpene derivatives, lignin derivatives, proteins, or carbohydrates (Molina-Gutiérrez et al., 2019a). In order to impart the ability to form crosslinks to the polymer latex, an interesting option is the introduction of coumarin functionalities in the polymer structure. Naturally occurring coumarins can be isolated from several plants, particularly of the Apiaceae, Asteraceae, and Rutaceae families. The photoinduced dimerization of coumarin has been known since the beginning of the 20th century, and the structure of the coumarin dimers was elucidated in the 1960s (Anet, 1962; Ciamician and Silber, 1902). Nevertheless, the photochemical [2+2] cycloaddition reaction of coumarin has only been exploited in the last few decades for obtaining polymer networks (Cazin et al., 2021).

Emulsion polymerization of butyl methacrylate in the presence of an acrylated coumarin derivative was performed to obtain coumarin-labeled poly(butyl methacrylate) latex dispersions (Oh et al., 2004), where coumarin acts as an acceptor dye in nonradiative energy transfer experiments. Recently, self-healing bio-based polyurethanes were synthesized by embedding coumarin derivatives into bio-based polyurethanes (Wong et al., 2019). A shape memory polymer was obtained synthesizing a poly(ϵ -caprolactone)/poly(l-malic acid) covalent skeleton with coumarin photoreversible group end-capped dangling chains (Qiu et al., 2021). However, the preparation of biobased polymer latexes bearing coumarin moieties has so far not been widely investigated. In this work, the preparation of a copolymer latex of ethoxy dihydroeugenyl methacrylate (EDMA) and a methacrylate coumarin derivative (CMA) by redox initiated emulsion polymerization, and the study of the [2+2] photocycloaddition reaction leading to cross-linking of the copolymer film, are reported. Furthermore, poly(EDMA) and poly(EDMA-co-CMA) latexes are used for the preparation of composite films containing microfibrillated cellulose and the oxygen barrier properties of the composites are investigated.

2. Materials and methods

2.1 Materials

(4-methyl)coumarin-7-yl methacrylate (94 %, Specific polymers), potassium persulfate (KPS, ≥ 99.0 %, Aldrich), sodium dodecyl sulfate (SDS, >99 %, Aldrich), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$, 99 %, Aldrich), sodium bicarbonate (NaHCO_3 , 99.7 %, Aldrich) were used as received. Deionized water (DIW) ($1 \mu\text{S cm}^{-1}$) was obtained using a D8 ion exchange demineralizer (A2E Affinage de L'Eau). 2-(2-methoxy-4-propylphenoxy)ethyl methacrylate (Ethoxy Dihydroeugenyl MethAcrylate, EDMA) monomer was synthesized as described in previous work (Molina-Gutiérrez et al., 2019c). Microfibrillated cellulose (MFC) Exilva F 01-V (10 wt% in water) kindly provided by Borregaard (Norway), used as filler for the composite materials, is a wood-derived MFC, mainly consisting of fibrils having widths in the 20 nm to 1 μm range, and lengths of ca. 5 to 40 μm , with a small fraction of lower aspect-ratio micrometer-sized fibrils (Cinar Ciftci et al., 2020; Larsson et al., 2019)

2.2 Synthesis of poly(EDMA) and poly(EDMA-co-CMA) latexes

The poly(EDMA) latex was prepared by emulsion polymerization with redox initiation following the procedure previously reported by Molina-Gutiérrez et al. (Molina-Gutiérrez et al., 2019b). To obtain the poly(EDMA-co-CMA) latex, the procedure was slightly modified as follows. Coumarin methacrylate (1 phm) was dissolved in EDMA (15 mmol; 99 phm) and the mixture was purged under argon for 15 min. KPS (2 phm) was dissolved in 9 mL of DIW and placed aside. The emulsion polymerization was carried out in a 50 mL double-walled jacketed glass reactor with a U-shaped glass stirring rod. SDS (4 phm), NaHCO_3 (2.2 phm), $\text{Na}_2\text{S}_2\text{O}_5$ (2 phm) and the rest of the DIW (15 mL) were mixed, placed in the reactor, and purged with argon for 30 min. The reactor was heated to 40 °C and the mixture of monomers was added. Finally, 3 mL of the previously prepared solution of KPS were added in one shot and this was considered as $t = 0$. The rest of the KPS was added over four hours at 1.5 mL h^{-1} . The polymerization proceeded under mechanical stirring at 250 rpm.

2.3 Monitoring of [2+2] cycloaddition by UV-visible spectroscopy

UV-visible spectroscopy was carried out by means of a JENWAY 6850 UV/Vis (Cole-Parmer, UK) UV-visible spectrophotometer. For the analysis, the latexes were dried in a ventilated oven at 80 °C until no change in weight was detected, and then they were dissolved in acetone (at 4 wt% concentration). A drop of the solution was spread on the side of a quartz cuvette and left to dry, obtaining a thin polymer layer. The poly(EDMA-co-CMA) thin coating was then irradiated with UV light using a high-pressure mercury-xenon lamp Lightning Cure LC8 from Hamamatsu equipped with a flexible light guide and an A9616-07 filter with a transmittance wavelength 355-375 nm (transmissive light of 365 nm). An EIT Powerpuck® II radiometer was used to measure the light intensity that was fixed at 36 mW cm^{-2} . UV-vis spectra were taken after given irradiation time intervals.

2.4 Preparation of composites with microfibrillated cellulose

MFC was diluted in demineralized water to a concentration of 0.5 wt% by means of a T 10 ULTRA-TURRAX® homogenizer at approximately 20k rpm. Then, the desired quantity of MFC suspension was added dropwise to the latex and dispersed using a magnetic stirrer for 10 minutes at 1000 rpm. After degassing under vacuum, the film-forming suspension was cast on a Petri dish and allowed to dry overnight under the fume hood. The films were then hot pressed between two silicon-coated glass slides with an applied pressure of 76 mbar at 85 °C for 1.5 hours. Composites with 5 wt% and 30 wt% of MFC (dry weight) were prepared. Part of the composites was exposed to UVA light with an intensity of 20 mW cm^{-2} for 20 min in a 5000-EC UV flood lamp system (Dymax Corporation, Torrington, CT, USA) equipped with a medium intensity mercury bulb (320-390 nm).

2.5 Oxygen permeability measurements

For the oxygen permeability test, the specimens were inserted in a surface reducer with an exposed area of 2.01 cm². Film thickness was measured using a micro caliper, averaging 6 measurements per sample. The oxygen permeability tests were conducted using a MultiPerm permeability analyzer (ExtraSolution S.r.l.). The composite films were analyzed at T = 23 °C and RH = 0 %. The instrument measures and records the instantaneous Oxygen Transmission Rate (OTR), i.e. the flux $J(t)$ of oxygen transported per unit of time through the surface of the tested film. The flux was considered to have reached a steady state (J_{∞}) when the instantaneous OTR did not differ by more than 0.5 % from its average value over more than 100 measurement points. This steady state value was taken as the OTR value of the film. To compare films of different thicknesses the OTR values were normalized with respect to the thickness L of the films; the OTR₂₅, normalized to a thickness of 25 μm, was calculated as follows:

$$OTR_{25} = \frac{OTR \cdot L(\mu m)}{25(\mu m)} \quad (1)$$

The diffusion coefficients D of oxygen in the composite films were estimated using the time-lag method (Beckman et al., 2020), using the equations:

$$D = \frac{L^2}{6\tau_L} = \frac{L^2}{6\mu_1} \quad (2)$$

$$\mu_1 = \int_0^{\infty} (1 - j_N) dt \quad (3)$$

where j_N is the normalized flux (J/J_{∞}). The time-lag τ_L according to the statistical moments method corresponds to the moment μ_1 (Eq. 3), calculated by numerical integration of the experimental OTR curve.

2.6 Optical microscopy

Optical microscopy was performed in reflection mode with an Olympus BX53M microscope (Olympus Italia S.r.l.).

3. Results and discussion

Poly(EDMA) and poly(EDMA-co-CMA) were synthesized in form of latexes by emulsion polymerization, according to the principles of green chemistry. The main co-monomer, EDMA, was derived from eugenol, a natural phenolic compound extracted from clove plant; ethylene carbonate and methacrylic acid used for its methacrylation were not biobased (Molina-Gutiérrez et al., 2019c), but promising routes for their production from biobased sources have been reported (Lebeau et al., 2020; Pescarmona, 2021). The structures of poly(EDMA) and poly(EDMA-co-CMA) are depicted in Figure 1. The solids content of the poly(EDMA) latex was 15 wt% and that of the poly(EDMA-co-CMA) latex was 16.5 wt%.

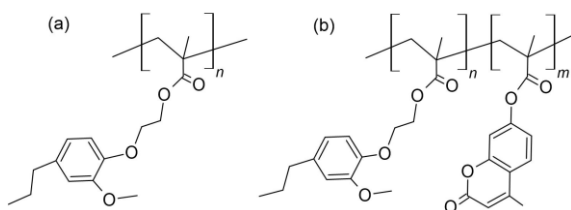


Figure 1. Structure of (a) poly(EDMA) and (b) poly(EDMA-co-CMA)

Upon irradiation with UVA light two adjacent coumarin moieties can undergo a [2+2] photocycloaddition reaction forming a cyclobutane ring, leading to crosslinking of poly(EDMA-co-CMA), as sketched in Figure 2.

Upon drying, the poly(EDMA-co-CMA) latex yielded transparent polymer films that were relatively brittle and could be completely dissolved in acetone. Thin layers of poly(EDMA-co-CMA) cast from acetone (section 2.3) were thus used for the study of the [2+2] photocycloaddition reaction involving the CMA moieties upon exposure to UVA radiation.

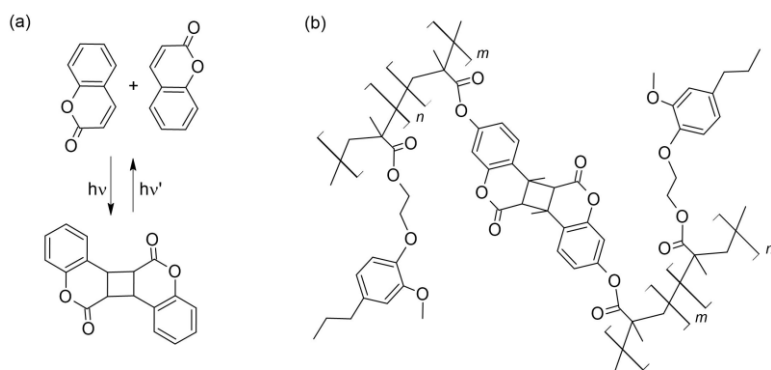


Figure 2. (a) [2+2] photocycloaddition of coumarin, and (b) crosslinking of poly(EDMA-co-CMA).

The advancement of the reaction was followed by monitoring the UV-vis absorbance at 320 nm, which is characteristic of coumarin and decreases proportionally to the extent of photodimerization (Hasegawa et al., 1972). As shown in Figure 3, the absorbance at 320 nm decreased steadily with increasing irradiation time for poly(EDMA-co-CMA), indicating that the photocycloaddition reaction led to the formation of coumarin dimers.

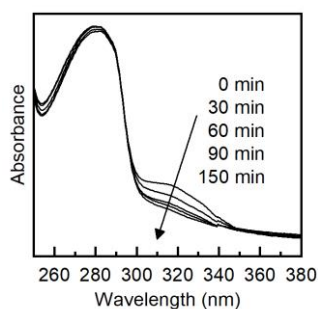


Figure 3. UV-vis absorption spectra of poly(EDMA-co-CMA) at different UVA irradiation times.

A photo of a poly(EDMA-co-CMA) composite with 30 wt% of MFC is shown in Figure 4a, and is representative of the appearance of all the composites prepared in this work. These were translucent, and the surface exposed to air during drying was rough, diffusing light. When the surface was observed by optical microscopy (Figure 4b), the structure formed by MFC was visible. The MFC was well dispersed in the polymer matrix.

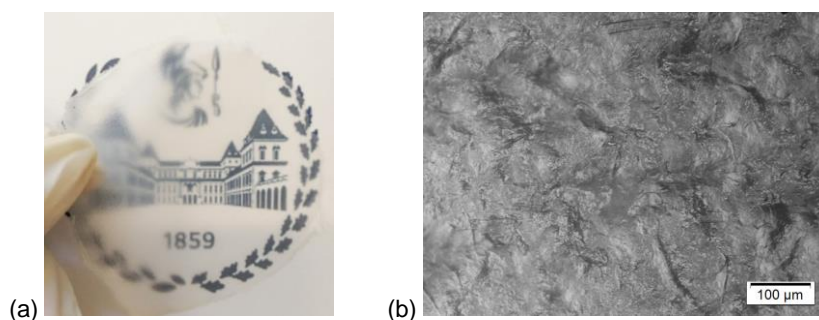


Figure 4. poly(EDMA-co-CMA) composite with 30 wt% MFC: (a) photo and (b) optical micrograph of the surface

With the neat polymer latexes, it was not possible to obtain defect-free films suitable for permeability measurements. Thus, the tests were performed on composite films only. First, the effect of the inclusion of CMA in the polymer structure, and the influence of the MFC weight fraction on the permeability of non-irradiated (thus not crosslinked) poly(EDMA) and poly(EDMA-co-CMA) composite films were assessed. The values of OTR and OTR₂₅ and the values of the diffusion coefficients D estimated with the time-lag method are reported in Table 1.

Table 1: Oxygen transmission rates (OTR) and diffusion coefficients (D) of poly(EDMA) and poly(EDMA-co-CMA) composites before irradiation

	MFC [wt%]	Thickness [μm]	OTR [$\text{cc}/\text{m}^2 \text{ d}$]	OTR ₂₅ [$\text{cc}/\text{m}^2 \text{ d}$]	D [cm^2/s]
Poly(EDMA)	5	143 \pm 1	998	5713	5.5 \cdot 10 ⁻⁸
Poly(EDMA-co-CMA)	5	128 \pm 5	561	2870	3.5 \cdot 10 ⁻⁸
Poly(EDMA)	30	55 \pm 3	823	1816	8.8 \cdot 10 ⁻⁹
Poly(EDMA-co-CMA)	30	52 \pm 4	399	827	7.2 \cdot 10 ⁻⁹

The poly(EDMA-co-CMA) composites showed better oxygen barrier properties than poly(EDMA) composites. Comparing the values obtained for the composites with 5 wt% MFC content, the OTR₂₅ decreased by 50 % when poly(EDMA-co-CMA) was used as matrix, compared to the value obtained using poly(EDMA) as a matrix. For the composites containing 30 wt% of MFC, the presence of the CMA moieties in the copolymer resulted in a decrease of more than 54 % of the OTR₂₅. Comparing the values of the diffusion coefficients, also reported in Table 1, however, the differences between the results obtained with the two polymers are not as pronounced. For the composites with 5 wt% of MFC content, the diffusion coefficient was 36 % lower for the poly(EDMA-co-CMA) composites compared with the poly(EDMA) ones, while for the composites with 30 wt% of MFC, the decrease amounted to only 18 %. The weaker effect of the presence of CMA on the diffusion coefficient with respect to the effect on OTR may imply that CMA improves the barrier properties by also acting on solubility. Indeed, copolymerization with CMA increases the number of polar groups in the polymer matrix and this might result in a decrease in the solubility of non-polar penetrants, such as oxygen. Moreover, the presence of polar groups also favors weak interactions within the copolymer chains, reducing the free volume of the polymer matrix and thus decreasing permeability. When the content of MFC in the composites increased, an improvement of the barrier properties against oxygen was evident for both the poly(EDMA) and the poly(EDMA-co-CMA) composites. Specifically, increasing the MFC content from 5 wt% to 30 wt% resulted in a 68 % decrease of OTR₂₅ for poly(EDMA) composites, and a 71 % decrease of OTR₂₅ for poly(EDMA-co-CMA) composites. Comparing the values of the diffusion coefficients obtained through the time-lag method, the increase of the content of MFC from 5 wt% to 30 wt% caused an 80 % decrease of the diffusion coefficient for poly(EDMA-co-CMA) composites and an 84 % decrease for poly(EDMA) composites. These results confirm that the addition of MFC can decrease permeability by increasing tortuosity.

Finally, the effect on oxygen permeability of crosslinking the poly(EDMA-co-CMA) matrix by UVA irradiation was examined. Crosslinking should cause a decrease in the free volume of the polymeric matrix through the formation of new chemical bonds. Since gas permeation occurs only in the free volume, this process should lead to a decrease in the permeability of the material. The OTR values measured for the poly(EDMA-co-CMA) composites after UVA irradiation are reported in Table 2. When these values are compared with those of the corresponding composites before irradiation, a modest improvement of the barrier properties is shown. The OTR of the composite with 5 wt% MFC only decreased by 5%, while that of the composite with 30 wt% MFC decreased by 25 %.

Table 2: Oxygen transmission rates of poly(EDMA-co-CMA) composites after UVA irradiation

	MFC content [wt%]	Thickness [μm]	OTR [$\text{cc}/\text{m}^2 \text{ d}$]	OTR ₂₅ [$\text{cc}/\text{m}^2 \text{ d}$]
poly(EDMA-co-CMA)	5	128 \pm 5	533	2729
poly(EDMA-co-CMA)	30	52 \pm 4	300	624

4. Conclusions

A novel copolymer of ethoxy dihydroeugenol methacrylate (EDMA) and coumarin methacrylate (CMA) was synthesized by redox-initiated emulsion polymerization. The copolymer, poly(EDMA-co-CMA), having 1 % by weight of coumarin moieties, could be cross-linked by UVA irradiation exploiting the [2+2] photocycloaddition reaction of coumarin. Addition of microfibrillated cellulose (MFC) to poly(EDMA) and poly(EDMA-co-CMA) latexes allows obtaining translucent composite films by simple mixing in aqueous medium. The permeability to oxygen of poly(EDMA-co-CMA) composites was approximately 50 % lower than that of poly(EDMA) composites. For both types of composites, permeability decreased with increasing MFC content. Cross-linking of the poly(EDMA-co-CMA) composites by irradiation with UVA light brought a further slight reduction of permeability.

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References

- Anet, R., 1962. The photodimers of coumarin and related compounds. *Can. J. Chem.* 40, 1249–1257.
- Beckman, I.N., Syrtsova, D.A., Shalygin, M.G., Kandasamy, P., Teplyakov, V.V., 2020. Transmembrane gas transfer: Mathematics of diffusion and experimental practice. *Journal of Membrane Science* 601, 117737.
- Cazin, I., Rossegger, E., Guedes de la Cruz, G., Griesser, T., Schlögl, S., 2021. Recent Advances in Functional Polymers Containing Coumarin Chromophores. *Polymers* 13, 56.
- Ciamician, G., Silber, P., 1902. Chemische Lichtwirkungen. *Berichte der deutschen chemischen Gesellschaft* 35, 4128–4131.
- Cinar Ciftci, G., Larsson, P.A., Riazanova, A.V., Øvrebø, H.H., Wågberg, L., Berglund, L.A., 2020. Tailoring of rheological properties and structural polydispersity effects in microfibrillated cellulose suspensions. *Cellulose* 27, 9227–9241.
- Dalle Vacche, S., Karunakaran, V., Ronchetti, S.M., Vitale, A., Bongiovanni, R., 2021. Nanocellulose from Unbleached Hemp Fibers as a Filler for Biobased Photocured Composites with Epoxidized Cardanol. *Journal of Composites Science* 5, 11.
- Dalle Vacche, S., Vitale, A., Bongiovanni, R., 2019. Photocuring of Epoxidized Cardanol for Biobased Composites with Microfibrillated Cellulose. *Molecules* 24, 3858.
- Demuner, I., Colodette, J.L., Gomes, F.J.B., Oliveira, R.C., 2019. Production and Characterization of Cnf and Lcnf, and Manufacture of Lcnf-nanostructured Packaging Papers. *Chemical Engineering Transactions* 73, 43–48.
- Goncalves, A.P., Cruz, A., Sales, J., Souza, M., Silva, F., Guimaraes, D., Mattedi, S., Jose, N., 2016. Achievement and Characterization of Cellulose Nanowhiskers of Palm (*Elaeis Guineensis*) and Bromelia Fibers (*Neoglaziovia Variegata*). *Chemical Engineering Transactions* 50, 403–408.
- Hasegawa, M., Suzuki, Y., Kita, N., 1972. Photocleavage of coumarin dimers. *Chem. Lett.* 1, 317–320.
- Larsson, P.A., Riazanova, A.V., Cinar Ciftci, G., Rojas, R., Øvrebø, H.H., Wågberg, L., Berglund, L.A., 2019. Towards optimised size distribution in commercial microfibrillated cellulose: a fractionation approach. *Cellulose* 26, 1565–1575.
- Lebeau, J., Efromson, J.P., Lynch, M.D., 2020. A Review of the Biotechnological Production of Methacrylic Acid. *Frontiers in Bioengineering and Biotechnology* 8.
- Molina-Gutiérrez, S., Ladmiral, V., Bongiovanni, R., Caillol, S., Lacroix-Desmazes, P., 2019a. Radical polymerization of biobased monomers in aqueous dispersed media. *Green Chem.* 21, 36–53.
- Molina-Gutiérrez, S., Ladmiral, V., Bongiovanni, R., Caillol, S., Lacroix-Desmazes, P., 2019b. Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates. *Ind. Eng. Chem. Res.* 58, 21155–21164.
- Molina-Gutiérrez, S., Manseri, A., Ladmiral, V., Bongiovanni, R., Caillol, S., Lacroix-Desmazes, P., 2019c. Eugenol: A Promising Building Block for Synthesis of Radically Polymerizable Monomers. *Macromolecular Chemistry and Physics* 220, 1900179.
- Nair, S.S., Zhu, J., Deng, Y., Ragauskas, A.J., 2014. High performance green barriers based on nanocellulose. *Sustainable Chemical Processes* 2, 23.
- Oh, J.K., Stöeva, V., Rademacher, J., Farwaha, R., Winnik, M.A., 2004. Synthesis, characterization, and emulsion polymerization of polymerizable coumarin derivatives. *Journal of Polymer Science Part A: Polymer Chemistry* 42, 3479–3489.
- Pescarmona, P.P., 2021. Cyclic carbonates synthesised from CO₂: Applications, challenges and recent research trends. *Current Opinion in Green and Sustainable Chemistry* 29, 100457.
- Qiu, Y., Munna, D.-R., Wang, F., Xi, J., Wang, Z., Wu, D., 2021. Regulating Asynchronous Deformations of Biopolyester Elastomers via Photoprogramming and Strain-Induced Crystallization. *Macromolecules* 54, 5694–5704.
- Vitale, A., Molina-Gutiérrez, S., Li, W.S.J., Caillol, S., Ladmiral, V., Lacroix-Desmazes, P., Dalle Vacche, S., 2022. Biobased Composites by Photoinduced Polymerization of Cardanol Methacrylate with Microfibrillated Cellulose. *Materials* 15, 339.
- Wong, C.S., Hassan, N.I., Su'ait, M.S., Pelach Serra, M.A., Mendez Gonzalez, J.A., Granda, L.A., Badri, K.H., 2019. Photo-activated self-healing bio-based polyurethanes. *Industrial Crops and Products* 140, 111613.