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Research Article

Toward UV-Triggered Curing of Solvent-Free Polyurethane Adhesives Based on Castor Oil

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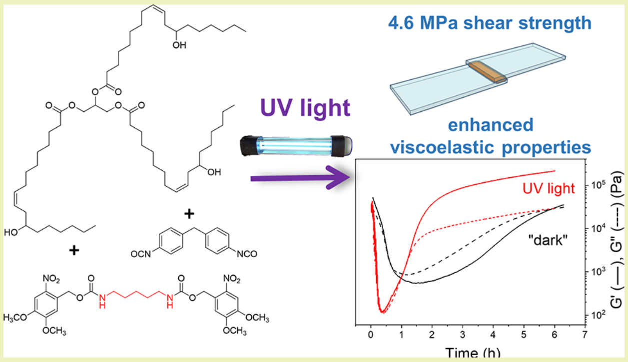
ABSTRACT: An *o*-nitrobenzyl-protected precursor was used as a phototrigger for the release of the diamine cadaverine in polyurethane adhesives based on castor oil as a renewable source of polyol and organic diisocyanates. This resulted in formulations with suitably controlled curing by photoactivation. This material shows faster curing when UV light is applied as compared to curing in the absence of irradiation, which was in situ monitored by rheological measurements. In addition, the adhesion performance is superior, reaching lap shear strength values of up to 4600 kPa, which is unprecedented for bio-based adhesives. On one hand, the in-depth chemical characterization with FTIR spectroscopy revealed that the slow release of cadaverine yields a well-balanced urethane/urea composition with direct impact on adhesion properties. The photocured bioadhesive was shown to bond a variety of surfaces, such as polyethylene or even wood. On the other hand, the direct one-time addition of cadaverine yields a material with approximately the same viscoelastic properties, which were achieved almost immediately as a consequence of the favored fast formation of urea bonds in detriment of urethanes, however, lacking adhesion properties.



KEYWORDS: *adhesion, bio-based adhesive, cadaverine, castor oil, photorelease, rheology*

INTRODUCTION

One of the pillars of modern chemistry and chemical product design is sustainability. The replacement of non-renewable raw materials with renewable feedstock is in the focal point of these efforts. This is, for example, reflected in a steadily increasing interest in environmentally friendly adhesive formulations from renewable resources with improved and tunable functional properties that can be adapted to the demands of the most diverse final applications.[1] These efforts are showcased in the development of bioadhesives,[2−4] which can be grouped broadly into formulations based on vegetable oils, proteins, carbohydrates, lignocelluloses, and tannins. Recently, adhesives prepared with CO_2-derived poly(propylene carbonate) have been formulated. This could also contribute to climate change mitigation.[5−7] Preferentially, the resulting green formulations should be devoid of organic volatile solvents, which constitute an environmental hazard. Noteworthy in this context is that vegetable oils not only provide an integrative reactive component of bioadhesive formulations but also constitute the fluid medium for the polymerization processes that lead to the adhesive polymer network. Among the adhesives prepared from such natural resources, polyurethanes are among the most widely studied ones.[1,8−13] Besides, polyurethanes, based on vegetable oils, have been demonstrated to exhibit low ecotoxicity and high biodegradability.[14]

Polyurethanes that are derived from renewable resources exhibit suitable properties for using them as adhesives and coatings for wood and chipboard, plastic, or metal surfaces.[5−9] However, their functional performance has still ample room for improvement to turn them into serious alternatives to their purely synthetic counterparts. One of the most notorious technological aspects of successful adhesive formulations is the curing process. The control of curing has direct implications on the rheological properties and the ultimate adhesion strength, and thus, it is a worthwhile starting point for the further optimization of polyurethane adhesives.

The moisture-curing ability of polyurethanes is well known, and the resulting compositional changes may lead to differences in mechanical and adhesion properties that can impact the performance.[10] However, this process happens

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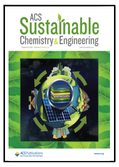
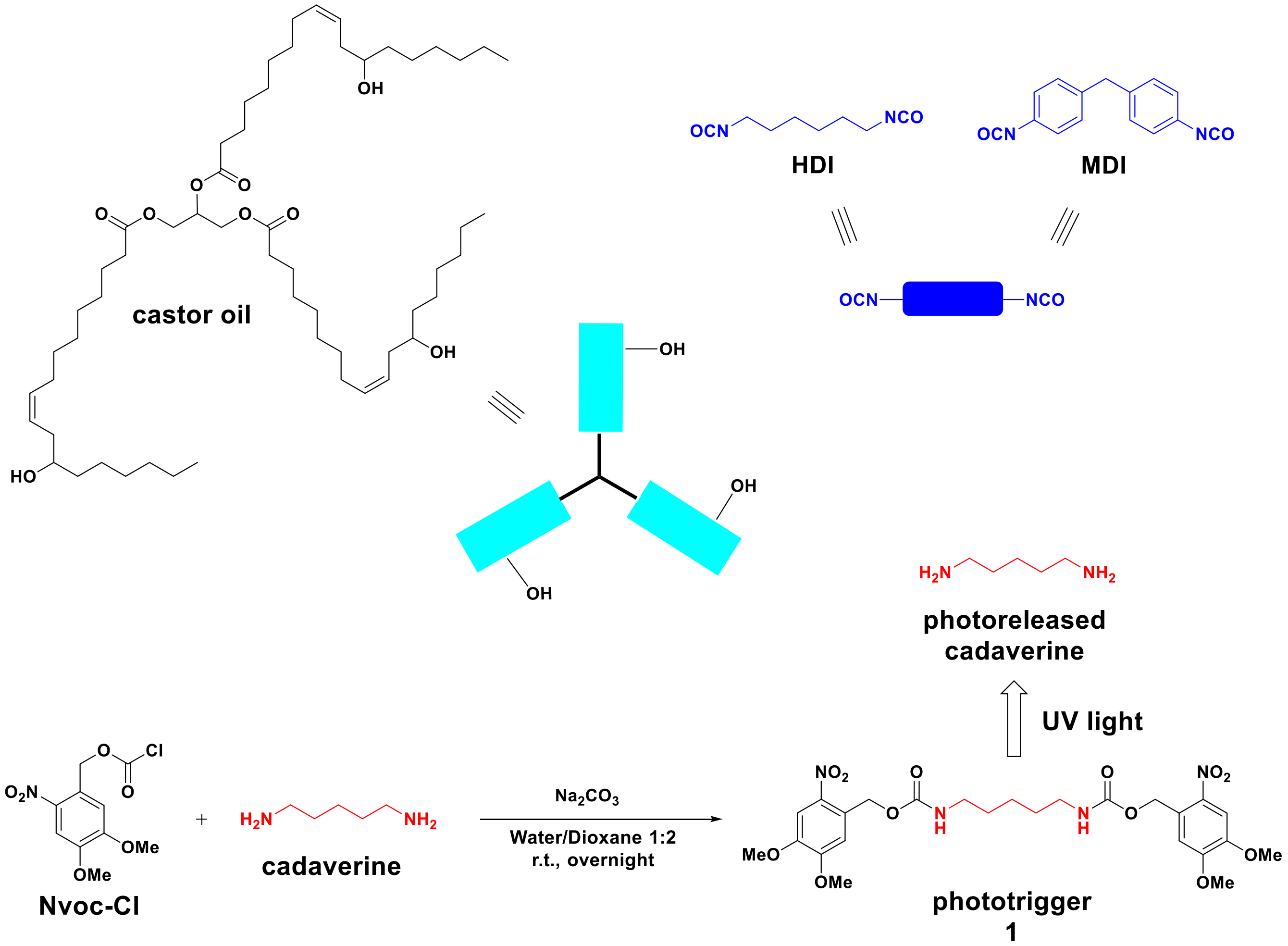


Scheme 1. Chemical Structures of the Components Used for the Formulation of UV-Curable Adhesives and Synthesis of 1



spontaneously, lacking the feature of control or external triggering. In some cases, the undesirable use of non-renewable and/or environmentally harmful compounds such as hardeners or cure initiators and accelerators is necessary to tune the required functional properties during curing.[15,16] Another proposed methodology to activate/control the curing process is thermal activation by thermo-reversible blocking techniques, for example, by acting on the isocyanate groups in the case of polyurethanes,[17,18] which have demonstrated excellent performance in CO_2-derived adhesives.[6,7] However, in general, the unblocking of reactive groups requires high temperatures (333−473 K),[6,7] which may compromise the final functional properties of the adhesive.

The exploitation of light as an external stimulus for triggering the curing process is especially appealing because it offers the possibility of spatiotemporal control under mild conditions, such as room temperature. Photocurable synthetic adhesives and resins have been employed in biomedicine or dentistry[19−21] or more technologically oriented applications.[22−24] However, the implementation in formulations of bio-sourced adhesives is rather underexplored.[25,26]

Building on earlier observations that diamines can function as efficient crosslinking agents of polyurethane- and polyurea-based adhesives,[23,27,28] we anticipated that the photorelease of the biogenic amine cadaverine (1,5-pentanediamine) would be beneficial for controlling and/or triggering the curing of polyurethane/polyurea adhesives. As model systems for our study, we focused on formulations of castor oil with commonly employed organic diisocyanates (HDI or MDI); see structures in Scheme 1. Amines can be masked with several photoremovable protection groups, such as *o*-nitrobenzyl systems, which have found applications in the most variable contexts, including photocaging of bioactive compounds, photolithography, or light-triggered organocatalysis.[29] The *o*-nitrobenzyl chromophore can be tuned by appropriate substitution to exhibit UV/vis absorption that extends up to 400 nm. A nowadays commonly applied variant is the 6-nitroveratryloxycarbonyl (NVoc) group, which has been chosen for the present work. The photolysis of this chromophore is known to proceed uniformly, yielding the released compound and an *o*-nitrosobenzaldehyde derivative.[30−32]

The photorelease of the diamine cadaverine from compound **1** provides an efficient crosslinking agent, which should aid the curing of polyurethane adhesive formulations including castor oil as a renewable polyol source (see structures in Scheme 1). In this work, we demonstrate the feasibility of such a strategy for triggering the light-induced curing of highly potent bioadhesives.

EXPERIMENTAL SECTION

Materials. Castor oil was purchased from Guinama (Valencia, Spain). The fatty acid profile and the main physical properties can be found elsewhere.[33] 1,6-Hexamethylene diisocyanate (HDI), 4,4′-methylenediphenyl diisocyanate (MDI), 6-nitroveratryloxycarbonyl

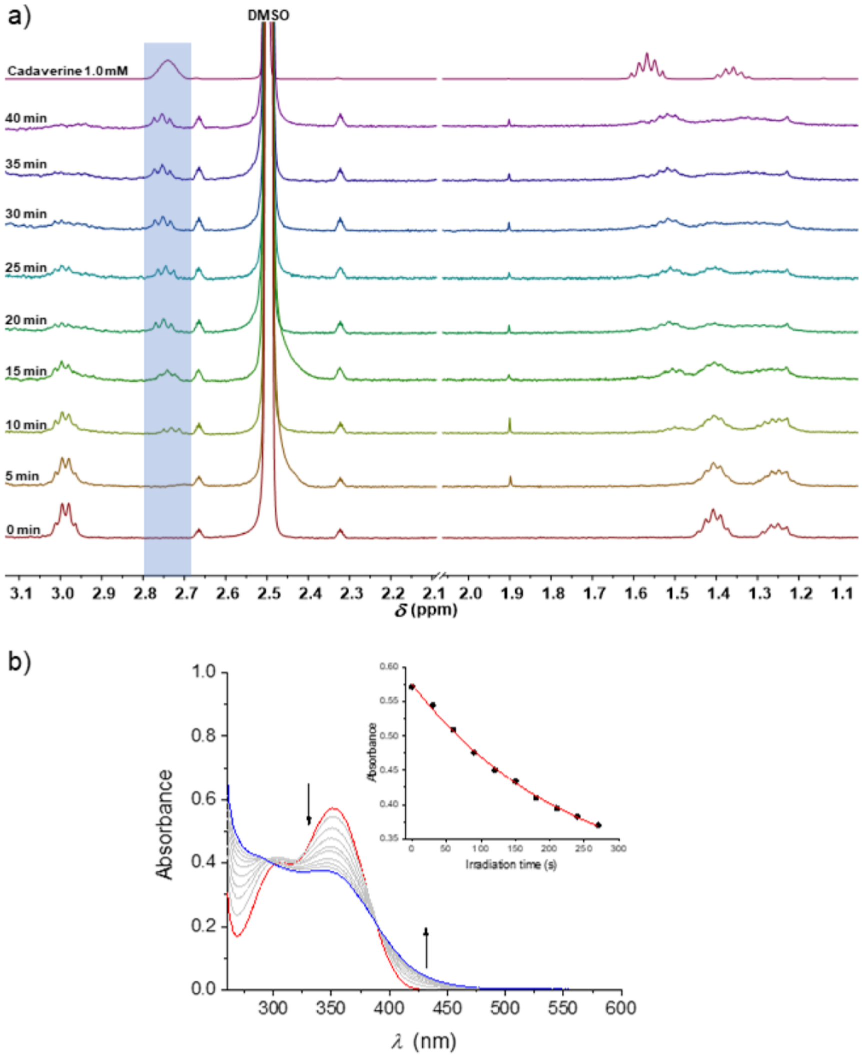


Figure 1. (a) Photorelease of cadaverine on light irradiation (ca. 22 mW cm^{-2} at >340 nm) of **1** (1.16 mM), monitored by ^{1}H NMR spectroscopy (partial spectra, focusing on the aliphatic region, are shown) in DMSO-d_6 at 298 K. (b) UV/vis absorption spectral changes on irradiation (ca. 1.8 mW cm^{-2} at 352 nm) of **1** (48 μM) in DMSO. Inset of panel (b): temporal development of the photoreaction.

chloride (NVoc-Cl), and cadaverine (cad), solvents, and other general reagents, used for synthetic procedures, were acquired from Merck−Sigma-Aldrich (Darmstadt, Germany).

Synthesis of 1. *Bis(4,5-dimethoxy-2-nitrobenzyl)pentane-1,5-diyldicarbamate (1).* An oven-dried 100 mL round-bottom flask was charged with cadaverine (198 mg, 1.94 mmol), anhydrous sodium carbonate (411 mg, 3.88 mmol), and Milli-Q water (15 mL). The mixture was stirred at room temperature, and a solution of NVoc-Cl (1070 mg, 3.88 mmol) in 1,4-dioxane (30 mL) was added dropwise into the aqueous solution under stirring at room temperature. The reaction mixture was protected from light and vigorously stirred for 18 h, then diluted with dichloromethane (20 mL), and poured into an aqueous sodium bisulfate solution (20 mL, 1 N). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried over anhydrous sodium sulfate and then concentrated in vacuo to give a pale-yellow solid as a crude product. The crude was sonicated with cold methanol (10 mL) for 20 min, filtered, washed several times with small portions of cold methanol, and dried in vacuo, giving pure compound **1** (970 mg, 86% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.68 (s, 2H), 6.99 (s, 2H), 5.47 (s, 4H), 4.95 (s, 2H), 3.97 (s, 6H), 3.94 (s, 6H), 3.21 (m, 4H), 1.55 (m, 4H), 1.38 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 156.0, 153.4, 148.1, 139.9, 128.0, 110.4, 108.2, 63.6, 56.4, 40.8, 29.5, 23.5. HRMS (ESI, NaI additive, positive mode): calcd for $[M + Na]^+$ $C_{25}H_{32}N_4O_{12}Na$, 603.1909; found, 603.1900. FTIR (Nujol): ν (cm^{-1}) 3315, 2725, 1696, 1520, 1456 (S), 1373, 1328, 1271, 1220, 1154, 1063, 982, 878, 790, 726. The NMR and FTIR spectra are shown in the Supporting Information (Figures S1−S4).

Preparation of Adhesives. The formulation of the UV-sensitive bioadhesives was carried out according to the following protocol. First, **1** was grinded in a quartz mortar, aiming to reduce particle size, and then properly dispersed in castor oil (0.2/0.8 **1**/castor oil molar ratio, equivalent to 0.1/0.6 $-NH_2$/$-OH$ molar ratio, assuming castor oil is composed of 100% ricinolein), using ultrasonication for approximately 20 min. Afterward, either HDI or MDI at 1/1.05 (castor oil + **1**)/diisocyanate molar ratio (equivalent to 1.3/1 ($-NH_2$ + $-OH$)/$-NCO$ molar ratio) was added, and the blend was manually stirred. For comparison, samples with the same ($-NH_2$ + $-OH$)/$-NCO$ molar ratio but prepared with unprotected cadaverine were also formulated.

Instrumental Analyses. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker ADVANCE 400 (400 MHz) spectrometer (Bruker, Bremen, Germany). The temperature was actively controlled at 298 K. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS). Mass spectra were recorded with a Bruker microTOF LC using the ESI-TOF method in the positive ion mode and NaI as an additive. Fourier transform infrared (FTIR) spectroscopy measurements were performed using a FT/IR 4200

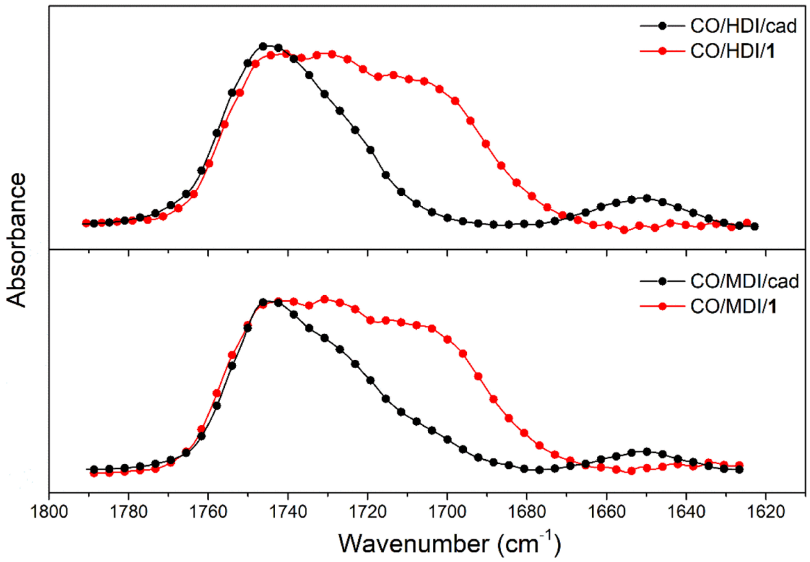


Figure 2. FTIR spectra in the 1790−1625 cm^{-1} window of formulations with castor oil (CO), HDI/MDI, and **1** (+UV light irradiation) or cadaverine (cad).

spectrometer (Jasco, Tokyo, Japan). The spectra were recorded in the 400−4000 cm^{-1} wavenumber range, with a 4 cm^{-1} resolution.

Photorelease of Cadaverine from 1. Photorelease was followed by ^{1}H NMR spectroscopy in dimethylsulfoxide-d_6 (DMSO-d_6) Samples of **1** (1.16 mM) were irradiated directly in the NMR tube, using a xenon lamp (L.O.T.-ORIEL GmbH & Co. KG, Darmstadt, Germany) with a 340 nm long-pass filter, providing an intensity of ca. 22 mW cm^{-2}. An analogous experiment, monitoring the UV/vis absorption spectral changes (Varian Cary 50 Bio spectrophotometer), was done with a diluted solution of **1** (48 μM) in dimethylsulfoxide (DMSO). A Luzchem LZC-4V photoreactor with UV-A lamps (1.8 mW cm^{-2} at 352 nm) was employed in this case.

Rheological Characterization. The phototriggered curing process of castor oil-based polyurethanes was in situ monitored in an Ares G2 rheometer (TA Instruments, New Castle, DE, USA), equipped with a 200 W high-pressure Hg lamp (Omnicure S2000, Waltham, MA, USA) and a 320−500 nm light filter (TA Instruments, New Castle, DE, USA) and supplying ca. 180 mW cm^{-2} intensity to the sample. A transparent acrylic top plate−stainless-steel bottom plate geometry (20 mm diameter, 0.5 mm gap) was employed for this purpose. The time-dependent evolution of the linear viscoelastic functions in small-amplitude oscillatory shear (SAOS) tests was followed under UV irradiation at room temperature (295 ± 1 K) during 6 h or 12 h periods at a constant oscillation frequency of 0.1 rad s^{-1}. In addition, the whole mechanical spectra of adhesive samples for different light exposure times were obtained by performing frequency sweep tests within the 100−0.03 rad s^{-1} range. In all cases, the applied strain was ensured to be within the linear viscoelastic regime throughout the test. Samples not submitted to UV light exposure were also characterized following identical protocols. Aiming to evaluate the curing shrinkage, the "autogap" function was activated, whereby the rheometer modifies the gap according to changes in the axial force. No significant gap modification was detected throughout the curing tests.

Adhesion Tests. In order to test the performance of the photocurable bioadhesives on different surfaces, polyethylene (PE) or oak wood segments of around 2 mm × 25 mm × 100 mm were used. The lap shear strength of the different adhesive joints was measured in an AG-IS universal testing machine (Shimadzu, Kyoto, Japan) by following ASTM-D3163 and ASTM-D906 standards for polyethylene and wood specimens, respectively. The specimens for adhesion tests were prepared as follows: A small portion of the adhesive sample was poured onto the surface of the segment, and then, another segment was placed above. UV light irradiation was applied using either the 150 W xenon lamp (L.O.T.-ORIEL GmbH & Co. KG, Darmstadt, Germany) with a 340 nm long-pass filter, providing an intensity of ca. 22 mW cm^{-2}, or the 200 W high-pressure Hg lamp (Omnicure S2000, Waltham, MA, USA) with a 320−500 nm light filter (TA Instruments, New Castle, DE, USA), supplying ca. 180 mW cm^{-2} intensity. A very thin slice of adhesive (∼0.1 mm) was applied in all cases to prepare the specimens for the adhesion tests. This ensured sufficient UV light penetration. For the sake of comparison, specimens were also tested without UV light exposure. At least three tests were performed for each sample, and standard deviations were calculated.

RESULTS AND DISCUSSION

Photorelease of Cadaverine from 1. The photoactivatable trigger **1** was first tested for its capability to release cadaverine on irradiation with UV light (>340 nm). The course of the photoreaction was followed by ^{1}H NMR spectroscopy. In Figure 1a, the partial nuclear magnetic resonance (NMR) spectra at varying irradiation times are shown ([**1**] = 1.16 mM); see Figure S5 for the full-range spectra. It can be observed that the signals of **1** vanish, and new resonance signals of the released cadaverine appear with time in the aliphatic region (between 1 and 3 ppm) of the ^{1}H NMR spectrum. From the initial slope of the kinetic curve (see Figure S6 in the Supporting Information), a rate of ca. 2.9 × 10^{-2} mmol L^{-1} min^{-1} can be extrapolated. This is a relatively slow release, but this turned out to be a key point for the formation of highly adhesive polymer networks, as will be discussed below. In an additional experiment, in the micromolar concentration range ([**1**] = 48 μM), the evolution of the UV/vis absorption spectra was followed (see Figure 1b). The spectral changes correspond to the typically observed ones for NVoc photodeprotection, and they feature a clear isosbestic point, hinting at the uniformity of the implied photoreaction.

Implication of Cadaverine Photorelease in the Polymer Network Formation. Having established the release of cadaverine under UV light irradiation of **1**, the implication and role of the diamine in the formation of the polymeric network were investigated. For this purpose, FTIR spectroscopy was selected as the method of choice. The carbonyl group signals constitute a sensitive indicator for the nature of functional groups [urethane NH−(C═O)−O vs

Table 1. Deconvolution Results for Adhesive Formulations Comprising the Castor Oil (CO), Isocyanate Component (HDI or MDI), and Amine Source (cad or **1**)

	CO/HDI/cad	CO/HDI/**1**	CO/MDI/cad	CO/MDI/**1**
fraction[a] C═O triglyceride	0.68	0.39	0.55	0.40
fraction[a] urethane NH−(C═O)−O	0.25	0.50	0.35	0.48
fraction[a] urea NH−(C═O)−NH	0.07	0.07	0.10	0.11
ratio urethane/urea	3.6	7.1	3.5	4.4
ratio H-bonded/non-bonded urethane	0.6	1.9	1.2	3.2
ratio H-bonded/non-bonded urea	56.6	<0.1	8.9	0.1

[a] The values indicate the proportion of the different kinds of carbonyl groups in relation to the total number of carbonyl groups, which were estimated from the relative areas of the deconvoluted FTIR absorption bands.

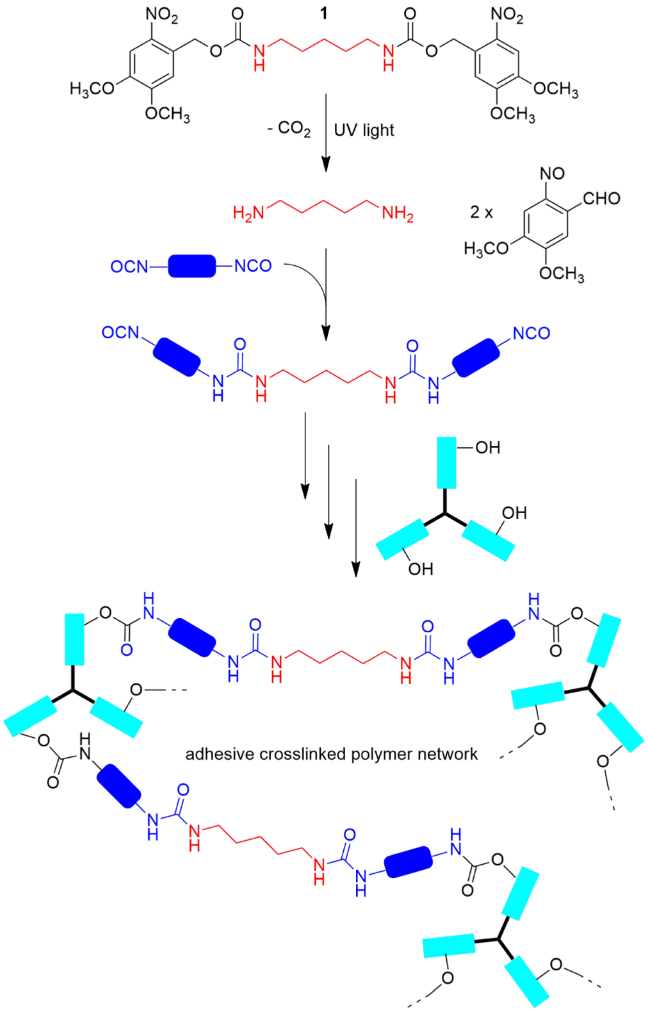
urea NH−(C═O)−NH] that are formed during the curing process and their supramolecular association (H-bonded vs non-bonded).[34,35] The results for the deconvolution of the FTIR spectral window between 1790 and 1625 cm^{-1} (see spectra in Figure 2), following a previously described procedure,[34] are summarized in Table 1 for selected formulations cured for 3 h. The spectra were normalized before their deconvolution, taking into account that systems with protected and unprotected cadaverine must have the same number of methylene groups.

The relative distribution of urethane and urea functional groups was analyzed for the one-time addition of cadaverine and for the time-controlled release of the diamine via photolysis of **1**, implying either HDI or MDI as a diisocyanate component. The urethane/urea ratio is significantly lower for the direct addition of cadaverine as compared to that for the photocured material. This is reasoned with the rapid reaction of the isocyanate groups with the diamine upon one-time addition, which leads to a significant amount of linear polyureas and a fast and drastic reduction of isocyanate groups that are available for polyurethane formation. However, when the diamine is photoreleased slowly, the isocyanate is always in excess, and the formation of monourea is more likely (see Scheme 2). The non-reacted isocyanate groups are available for the slower reaction with the hydroxyl groups of castor oil,[36] leading to a higher urethane/urea ratio and more effective crosslinking. Likewise, diisocyanates may react through one NCO group with the OH groups of castor oil and then from urea with photoreleased cadaverine, thus leading to similar polymer products as those shown in Scheme 2.

Another interesting point, which is of importance for the rheological properties and adhesion performance of the formulation, is the supramolecular interaction in the polymer network by means of H-bonding between −NH groups and carbonyl oxygen atoms. In the instant of polyurea formation, on direct addition of cadaverine, a high amount of urea is involved in H-bonding, but much less urethane groups are implicated in this interaction. Hence, it appears that interchain polyurea interactions and domain formation apply. However, this situation reverts for the photocured material. Hydrogen bonding between urethanes that are formed in a significant amount due to the less-competitive low steady concentration of photoreleased diamine becomes determinant and dictates the higher order organization of the polymer network; see below for the implications of this observation in the rheology and adhesion performance of the materials.

Rheological Monitoring of the Phototriggered Curing Process. The evolution of both the storage (G') and loss (G'') viscoelastic moduli with curing time during UV light exposure of castor oil-based polyurethane formulations, using HDI or MDI, is presented in the Figure 3a,b, respectively. The absence of **1** expectedly results in the light-insensitive and relatively slow formulation of polyurethanes. This is reflected in similar G'' values for the irradiated and non-irradiated HDI-based formulations. Furthermore, the curing process resulted in negligible values of the elastic modulus (G') during the monitored time window of 6 h. These observations change dramatically with the addition of **1** as a phototrigger. Due to the colloidal suspension characteristics, the incorporation of **1**

Scheme 2. Chemical Mechanisms of Curing and Network Formation Upon UV Light Exposure of the Formulated Adhesives[a]



[a] The shown formation of the polymer network is a title of example (see the main text).

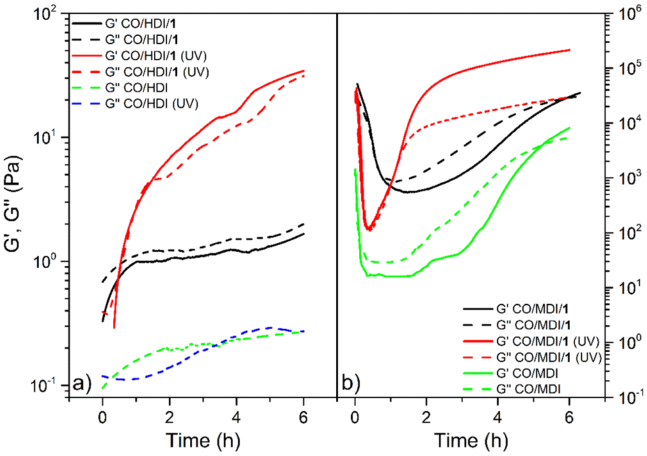


Figure 3. Influence of UV light irradiation on time-dependent viscoelastic functions for (a) HDI-containing castor oil-based formulations and (b) MDI-containing castor oil-based formulations, in the presence or absence of **1**. UV denominates the application of ultraviolet light. Note that the initial decrease in both moduli in panel (b) is attributed to the presence of MDI crystals, which disappear with progressing polymerization. CO: castor oil.

increases the viscoelastic moduli of the sample by around 1 order of magnitude from the early stages of the curing process, also enhancing the viscoelastic character (see Figure 3a). The curing process is relatively slow and limited to the reaction of HDI with castor oil, since the cadaverine remained protected in the absence of UV light. Indeed, it is the UV light exposure that dramatically increases the SAOS functions of the sample. Thus, both viscoelastic moduli experience a fast increase during the first 2 h of UV light exposure due to the photoinduced release of cadaverine, which activates the curing process by controlled urea bond formation (see Scheme 2). After 6 h, both SAOS functions reached values around 1 order of magnitude higher as compared to the non-irradiated sample after the same time. Moreover, the viscoelastic functions further increased over time, reaching G' and G'' values of around 10^4 and 10^3 Pa, respectively, after 12 h of irradiation, also enhancing the elastic character (see Figure S7 in the Supporting Information).

However, despite the favorable effect of the cadaverine photorelease, the curing time scale is still long for a practicable photocurable adhesive. This time scale can be significantly shortened using a more reactive aromatic diisocyanate.[34] The replacement of HDI with MDI leads to a faster and much more noticeable increase in the viscoelastic functions (see Figure 3b). Besides, once more the viscoelastic moduli were augmented by the simple inclusion of compound **1**. The higher reactivity of MDI is showcased by the G' value of the formulation without application of UV light irradiation. After 6 h, a 4-orders-of-magnitude higher G' value in comparison to that achieved with HDI was observed (see Figure 3b). As for HDI, the exposure to UV light triggers the increase in both viscoelastic moduli and the enhancement of the elastic behavior. Nonetheless, the results are considerably more promising, as reflected in the 1-order-of-magnitude difference between G' and G'' for the irradiated sample. This implies an enhanced relative elasticity, resulting in the formation of a stiffer system, that is, an already hardened adhesive.

The evolution of the rheological properties of the photocurable bioadhesives has likewise been followed by frequency sweep experiments, performed during the course of the UV-induced curing process (Figure 4). The frequency dependence of both SAOS functions clearly demonstrates that the UV light exposure (12 h) drives HDI-based systems from a liquid-like response, which remains invariable for the non-irradiated sample (Figure 4a), to a gel-like response with a well-developed G'-plateau (Figure 4b). However, only an incipient gel was obtained after 6 h of UV light irradiation, showing a rheological response quite close to that of a critical gel.[37] On the other hand, UV light-irradiated MDI-based adhesives showed gel-like characteristics almost from the beginning, already exhibiting a critical gel response in the first 30 min of curing and a predominant elastic response within the full frequency range studied after 2 h (Figure 4d), which was

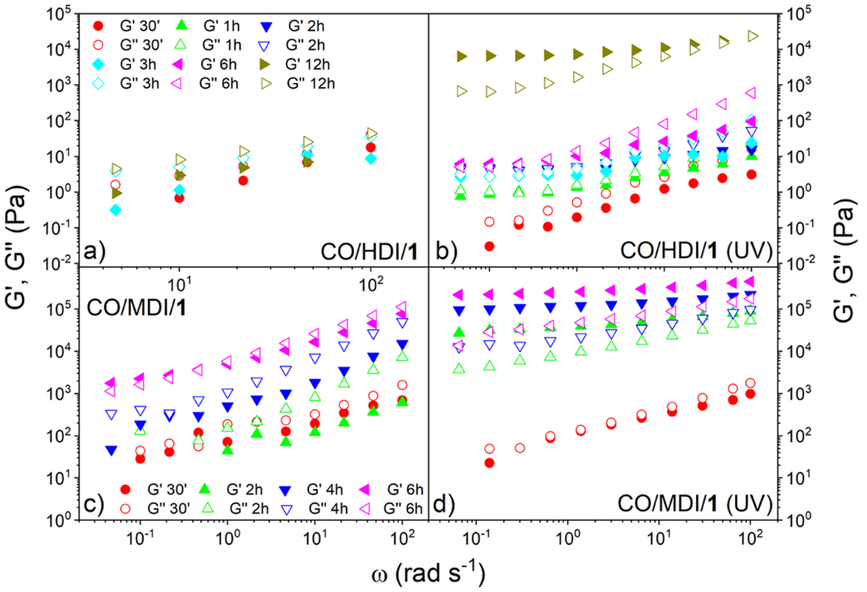


Figure 4. Evolution of the SAOS functions with frequency along the curing process for both HDI- and MDI-containing castor oil-based adhesives without (a,c) or with (b,d) UV light irradiation. CO: castor oil.

not achieved for the non-irradiated adhesive even after 6 h of curing (Figure 4c).

The UV photocurable castor oil-based polyurethane adhesives have also been compared with those containing non-protected cadaverine, that is, replacing **1** by the direct addition of cadaverine (see Figure S7 in the Supporting Information). As expected, no significant time evolution of the SAOS functions was observed in this case, resulting in high G' and G'' values from the beginning, that is, in the order of 10^4 Pa for both G' and G'' for HDI-based formulations and 10^6 Pa (G')−10^5 Pa (G'') for MDI-based formulations. These figures are very similar to those achieved after 12 and 6 h of the photoinduced curing process in HDI- and MDI-based formulations (containing **1**), respectively; see the Supporting Information. This can be explained by considering the lower reactivity of hydroxyl groups with isocyanates as compared to amines,[36] which favors the almost instantaneous formation of urea bonds in detriment of urethanes (see the Results and Discussion given above) and results in the instantaneous formation of gel-like systems. However, these did not prove to yield adhesives (see below). Therefore, the photorelease of protected cadaverine may be proposed as an efficient tool to control the curing kinetics and to balance the formation of urea and urethane bonds that dramatically influence the adhesion properties, as will be discussed in the following section.

Adhesion Performance of Photocurable Castor Oil-Based Polyurethanes. Due to the higher reactivity of MDI compared to HDI and the negligible adhesion performance of HDI-based polyurethanes, with or without irradiation (see adhesion strengths in Table 2), the effect of UV irradiation on the shear strength of adhesive joints has mainly been analyzed for MDI-based polyurethanes. Table 2 summarizes the shear strength values of adhesive/PE joints exposed to different irradiation scenarios, along with the predominant type of failure. As previously reported,[10] curing of a MDI/castor oil-derived polyurethane yields a considerably tough adhesive joint (evaluated after 24 h of curing), due to the slow reaction between castor oil hydroxyl groups and MDI isocyanates (with or without the addition of **1**). Nonetheless, an even improved adhesion performance can be obtained in a much shorter time by means of UV curing, as shown in the present work. The adhesive shear strength was demonstrated to be UV light intensity-dependent, in line with the light-triggered nature of the curing. Thus, 5 h of exposure under 20 mW cm^{-2} UV light was necessary to achieve a similar shear force value (ca. 1200 kPa) as observed for no UV light exposure after 24 h (ca. 1500 kPa). However, only 2−3 h under 180 mW cm^{-2} UV light was sufficient to achieve the same adhesion performance (1100−1400 kPa). Moreover, 4 h of exposure at this higher UV intensity led to an outstanding adhesion performance with a shear strength value of ca. 4600 kPa. To the best of our knowledge, such a high value has never been obtained before for bio-based polyurethane adhesives on polyethylene, and it is close to the values obtained for other plastic substrates.[6] This shear strength is also comparable or even better than that reported for commercial adhesives based on neoprene, photocurable acrylics, rosin resin, or other polyurethane and vinyl dispersions in water.[38−40] Photocuring can even be achieved when using non-transparent adhesion surfaces. Surprisingly, the exposure of wood−adhesive−wood joints to UV light, basically acting only at the edges of the specimen (due to the strong impediment to UV light penetration in this substrate), still produced good adhesion results (ca. 2000 kPa shear strength) at relatively short irradiation times (4 h at 180 mW cm^{-2} intensity). This fact and the achieved consistency suggest that these systems could also be applied as a coating in this type of non-transparent surfaces. These results highlight the excellent response of bio-based adhesives for different surfaces.[5−9] Finally, it is worth mentioning that no adhesive properties were obtained by the direct addition of neat cadaverine to MDI- or HDI-based formulations. Therefore, the direct formation of polyureas does not yield a macromolecular chemical structure with a substantial bonding ability, whereas the gradual photorelease of cadaverine does. This result unambiguously indicates that a sensitive balance of urea and urethane formation is required to achieve optimum adhesion.

Table 2. Adhesion Performance of Selected Castor Oil (CO)-Based Polyurethanes Submitted to Different UV Light Irradiation Protocols[a]

formulation	substrate	UV intensity (mW cm^{-2})	time (h)	lap shear strength (kPa)
CO/HDI/**1**	PE	non-irradiated	168	122 ± 41[a]
	PE	180	3	
CO/MDI	PE		24	727 ± 196[a]
CO/MDI/**1**	PE	non-irradiated	24	1534 ± 533[a]
	PE	20	3	338 ± 84[a]
	PE	20	4	566 ± 91[a]
	PE	20	5	1164 ± 221[b]
CO/MDI/**1**	PE	180	2	1104 ± 185[a]
	PE	180	3	1430 ± 262[a]
	PE	180	4	4600 ± 777[a,b]
	oak wood	180	4	2010 ± 302[a]
CO/MDI/cad	PE	non-irradiated		no adhesion

[a] Types of failure: (a) cohesive and (b) substrate.

CONCLUSIONS

The formulation of castor oil, an organic isocyanate component, and a photoactivatable precursor for a diamine yields polymeric networks with significant adhesive strength upon UV light irradiation. The use of castor oil as a renewable polyol source provides an interesting basis for a sustainable approach toward bioadhesives, especially when combined with the described photocuring. The relatively slow release of cadaverine as diamine on light irradiation of an NVoc-protected precursor yields a well-balanced distribution of urea and urethane functionalities, whose supramolecular organization via H-bonding is of benefit for arriving at materials of outstanding adhesion performance. This is opposed to the one-time addition of cadaverine, which provides merely gel-like behavior. The photorelease of protected cadaverine leads to a much sharper increase in the viscoelastic moduli during the first hours of the curing process than that observed for the same non-irradiated samples. The values of the viscoelastic functions of the photocured adhesives are several orders of magnitude higher and evidence much more enhanced elastic characteristics, which is especially favored when using MDI as diisocyanate. Hence, the photorelease of cadaverine in castor oil-based polyurethanes can be proposed as an efficient method to trigger a balanced and suitable curing process, ultimately yielding outstanding adhesion performance in polyethylene and wood substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c02461.

^{1}H and ^{13}C NMR spectra and FTIR spectrum of **1** and additional rheological data (PDF)

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Notes

The authors declare no competing financial interest.

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