

Preemptive Healing through Supramolecular Cross-Links

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ABSTRACT: The ability of highly cross-linked thermoset materials to relax stresses by network chain segment mobility above or just below T_g is generally limited. We describe materials in which some of the cross-links have been replaced by dimers of quadruple hydrogen-bonding ureidopyrimidinone (UPy) moieties, which act as reversible cross-links. Materials based on mixtures of ϵ -caprolactone and L-lactic acid, and containing different ratios of covalent and UPy dimer cross-links, were synthesized, and their thermal and mechanical properties were tested by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The presence of reversible cross-links results in superior relaxation of stresses even below T_g , as witnessed by the creep and stress relaxation behavior. These properties bode well for potential applications, e.g., in coatings technology.

Introduction

Hydrogen-bonded dimers of ureidopyrimidinone (UPy, of general structure **1**, Figure 1)¹ have been used in various supramolecular polymers with unique properties. In numerous studies in polymer chemistry,^{2,3} biomedical applications,^{4–6} and materials science,^{7,8} UPy units act as robust, selective, and directional hydrogen-bonding systems. Their high dimerization strength ($\Delta G^\circ_{\text{dim}} = -35$ kJ/mol in chloroform) is intermediate between the bond strength of covalent and of most other noncovalent bonds.^{9,10} In UPy-based materials, mobility and stability are often combined: in some of them one can switch dynamics by a change in temperature or solvent. The factors that govern the kinetics and thermodynamics of the often complex equilibria involved have also received continuous attention. UPy dimerization can be influenced by electron-donating or -withdrawing groups and the stacking of UPy dimers onto each other can be tuned with more or less bulky groups on the UPy core.³

Here we report on the mechanical properties of polymeric networks in which part of the cross-links are UPy-based rather than covalent in order to assess their ability to relax stresses *preemptively*, that is, before buildup of stresses may lead to mechanical failure. These materials, schematically depicted in Figure 1, combine stiffness with stress-relaxing properties. Usually, stress relaxation in covalent networks is very limited because of topological constraints imposed by the network.¹¹ UPy groups have been used in acrylate networks to allow fast relaxation of stresses at elevated temperatures in materials designed to display shape memory properties.⁸ Our interest is in the slower relaxation of stresses at room temperature. To this end, we introduced the noncovalent UPy cross-links in polyester–polyurethane networks, which were inspired by the two-component polyester–polyurethane systems that constitute some of the most important

commercial coatings. In these two-component systems, OH-terminated polyesters react with oligomeric isocyanates to form a covalent polyurethane network, with resistance to solvent and chemicals, shape retention, and the impossibility to be melted. During the curing stage of a coating, mechanical stresses can arise, which have been identified as a major cause for failure of the coating.^{12–17} If the coating is applied on a metal substrate, an important cause of stress is the differential thermal contraction between the coating and the substrate. Other factors also contribute to the stress, including an increase in density upon cross-linking and shrinkage due to the evaporation of solvent. Deformation of the substrate (e.g., tight bends) can also induce stresses concentrated in areas of highest deformation.¹⁸

In order to combine stiffness with flexibility, many coatings are designed to have glass transition temperatures of 40–50 °C. The materials investigated in the current study were designed to have similar glass transition temperatures. In contrast to this, dissociation of UPy dimers was shown to result in a rheological transition around 70–80 °C in molten polyesters.³ The main aim of this study is to investigate the possibility for the latter process to improve stress relaxation at temperatures below the glass transition. To this end, materials with varying content of UPy cross-links were characterized by DSC and DMA, and their relaxation behavior was studied by means of creep and stress relaxation tests.

Experimental Section

Chemicals. All monomers and catalysts as well as *n*-hexyl isocyanate and hexamethylene diisocyanate were purchased from Aldrich or Fluka and used as received, except ϵ -caprolactone, which was distilled from CaH₂ under reduced pressure before use. Solvents were purchased from Aldrich or Biosolve or Cambridge Isotope Laboratories (CDCl₃).

Characterization. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 400 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm relative to the solvent peak.

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Gel permeation chromatography (GPC) was performed on a Shimadzu LC-10ADvp, using a Shimadzu SPD-M10A vp photodiode array detector at 254 nm and a PLgel 5 μ m Mixed C ($200\text{--}2 \times 10^6$ g mol $^{-1}$) column in series with a PLgel 5 μ m Mixed D ($200\text{--}4 \times 10^5$ g mol $^{-1}$) column. THF was used as the mobile phase (1 mL min $^{-1}$, room temperature). All molecular weight values were calculated with respect to polystyrene standards and are uncorrected. Sample concentrations were 1–3 mg mL $^{-1}$ in the eluent solvent.

Preparation and Testing of Coatings. Aluminum plates used as the coating substrate were thoroughly cleaned with isopropanol or acetone and dusted with a pressurized nitrogen stream immediately before use. Coatings were applied as 120 μ m films to the metal plates using a doctor blade, at a coating speed of 12.5 cm min $^{-1}$ on an Erichsen Testing Equipment with a Coat-master 509 MC controller. For each sample, the binder was mixed with some NMP several hours before application. Before application, the isocyanate was added, and the viscosity was adjusted with additional solvent. The panels were then baked for 1 h at 100 $^{\circ}$ C. Adhesion and flexibility of the coating were qualitatively tested by double-bending the substrate in both directions and following the appearance of crazing or cracks within the coating. Acetone double rubs were used to obtain a comparative measure of solvent resistance. When more than 100 double rubs were applied and no significant damage on the coating was noticed, the test was considered successful. For water staining tests, an aqueous methylene blue solution was applied to the coating film and left to soak overnight, in order to see incorporation of water or the dye into the film.

Preparation of Free-Standing Films. Free-standing films were prepared by dissolving the functionalized triols, cross-linker, and catalytic DBTDL in CHCl $_3$ and casting the mixture into

a silanized glass mold (height: 1.3 mm). The mixture was then cured at 50 $^{\circ}$ C for 3 h and subsequently dried under reduced pressure at 100 $^{\circ}$ C for 12 h. Dry film thicknesses typically ranged between 450 and 550 μ m. We refer to the cured films as **F4-*u***, with *u* referring to the percentage of UPy cross-links; e.g., **F4-47** refers to polyol **2** prefunctionalized with 47% **3**, the remaining 53% of the initial hydroxyl groups being cross-linked with uretdione diisocyanate. Films of **F4-100** were obtained from a concentrated solution in CHCl $_3$, which was cast on a silanized Petri dish and allowed to slowly evaporate. All films were dried in vacuo at 100 $^{\circ}$ C for 12 h after curing or evaporation.

Differential Scanning Calorimetry (DSC). Thermal properties (T_g) of the free-standing films were investigated with differential scanning calorimetry on a Perkin-Elmer differential scanning calorimeter Pyris 1 with a Pyris 1 autosampler and a Perkin-Elmer CCA7 cooling element under a nitrogen atmosphere with heating and cooling rates of 10 $^{\circ}$ C min $^{-1}$ (samples of 10–15 mg were measured). The temperature range was from -20 to 120 $^{\circ}$ C.

Dynamic Mechanical Thermal Analysis (DMTA). Mechanical properties were tested in tensile mode on a TA Instruments Q800 series DMA with a gas cooling accessory (GCA) under a nitrogen atmosphere (free-standing films) for the determination of T_g and cross-link density (XLD). The dimensions of the specimens tested were 12 mm \times 6 mm \times 0.5 mm. The dynamic tests for the determination of T_g were performed at a heating rate of 3 $^{\circ}$ C min $^{-1}$ and a frequency of 1 Hz. The temperature range was from -20 to 140 $^{\circ}$ C. The creep measurements were performed at different temperatures (10 $^{\circ}$ C, 14 $^{\circ}$ C below the T_g of each UPy containing material and 16 $^{\circ}$ C above the T_g) at a stress of 0.5 MPa and a creep time of 60 min, followed by a recovery time of 20 min. Each measurement was performed twice. Stress/strain tests were also conducted at 30 $^{\circ}$ C with a strain rate of 1% min $^{-1}$. In all cases a preload force of 0.01 N was applied.

Synthesis and Analytical Data. Isocyanate **3** was synthesized and reacted according to a previously published procedure.⁵ All newly synthesized polymers were obtained via the following procedure (Scheme 1): Monomers and initiator were mixed at 90 or 120 $^{\circ}$ C under nitrogen without any solvent. After addition of the catalyst the mixture was allowed to react overnight at 90 or 120 $^{\circ}$ C. As the catalyst, 0.01 equivalent of Sn(Oct) $_2$ relative to the initiator was added as a 0.2 M solution in dry toluene. The degree of conversion can easily be monitored by 1 H NMR. After full conversion, the reaction mixture was diluted with CHCl $_3$, filtered through a glass filter, and precipitated into an 8-fold volume of heptane. The precipitated polymer was rinsed with heptane and dried in vacuo. Subsequent functionalization with isocyanate **3** followed reported procedures.⁵ The degree of functionalization was measured by comparison of the

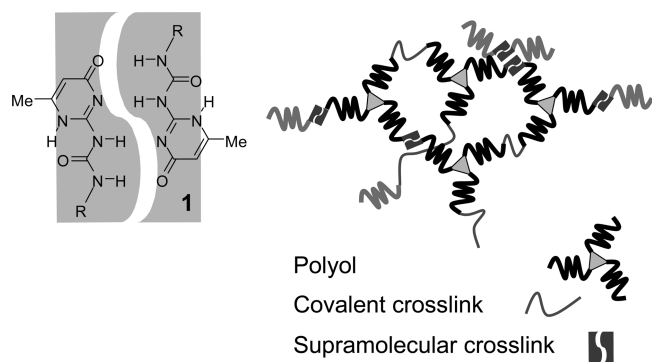


Figure 1. Dimer of ureidopyrimidinones **1** and schematic of networks with covalent and noncovalent cross-links.

Scheme 1. (a) Initiators, Monomers, and Catalyst Used for the Synthesis of Star Polyester **2**; (b) Noncovalent Cross-Linker **3** and Covalent Uretidione Cross-Linker Desmodur N3400

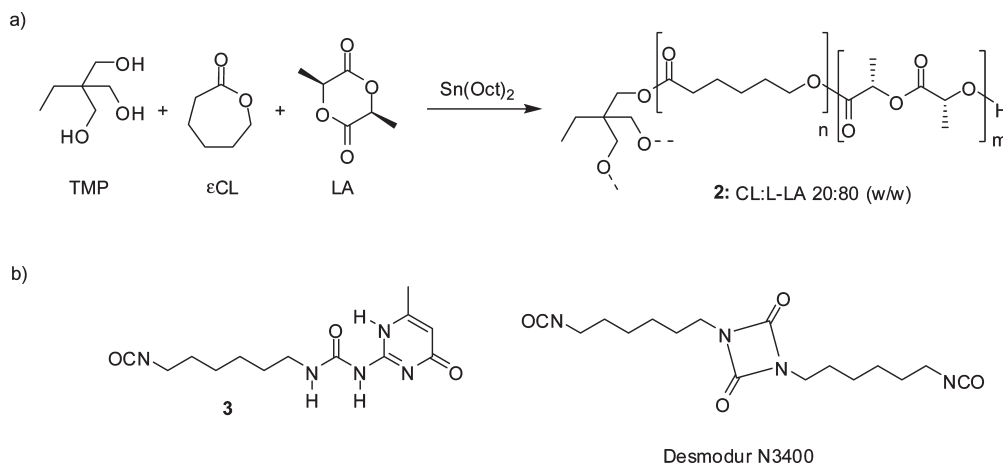


Table 1. Summary of Properties of the Prepared Free-Standing Films

coating	<i>u</i> (%)	Desmodur N3400 cross-linker ratios (w/w) ^a	DSC <i>T</i> _g (°C)	DMA <i>T</i> _g (°C)	storage modulus <i>E'</i> (MPa) ^b	cross-link density (mol cm ⁻³)
F4-0	0	0.462	34	44	7.19 (117 °C)	739 × 10 ⁻⁶
F4-10	10	0.406	38	48	4.24 (122 °C)	604 × 10 ⁻⁶
F4-20	20	0.332	39	50	2.96 (123 °C)	299 × 10 ⁻⁶
F4-30	30	0.294	42	54	2.24 (127 °C)	224 × 10 ⁻⁶
F4-40	40	0.218	44	53	0.74 (126 °C)	74 × 10 ⁻⁶
F4-47	47	0.196	42	brittle ^c		
F4-53	53	0.155	36	brittle ^c		
F4-100	100	0	6	brittle ^c		

^a 10% excess of the covalent cross-linker was used in all cases. ^b Storage modulus (and respective temperature) measured 73 °C above *T*_g. These values were used for the calculation of XLD. ^c Brittle specimens that could not be tested on DMA.

integrals of the ¹H NMR signals of the aromatic UPy proton and the TMP methyl group.

Triol 2. ¹H NMR (400 MHz, CDCl₃, δ): 5.12 (m, 10H, α-LA), 4.40–3.96 (m, 10H, ε-CL, TMP–CH₂–O), 2.39–2.30 (2 × m, 4H, α-CL), 1.66 (m, 8H, β-CL, δ-CL), 1.61–1.44 (m, 36H, β-LA, TMP–CH₂–CH₃), 1.40 (m, 4H, γ-CL), 0.88 (bt, 3H, TMP–CH₃). NMR: *M*_n = 1.1 kg mol⁻¹, GPC (THF): *M*_n = 1.8 kg mol⁻¹, PDI = 1.3.

In order to have a maximum flexibility with respect to parameters such as *T*_g, cross-link density, ratio of covalent vs supramolecular cross-links, volatile organic compounds (VOC) content, etc., we decided to use a polyol made by cationic ring-opening polymerization (ROP) of cyclic esters, using trimethylolpropane as trifunctional initiator (TMP, Scheme 1a). Monomers that can easily be polymerized by ROP include ε-caprolactone (CL) and its derivatives as well as lactides (Scheme 1a), the cyclic dimers of both enantiomers of lactic acid. The homopolymer of the former monomer has a *T*_g of –60 °C, and the latter have *T*_g's of +60 °C. Poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) are highly crystalline polymers,¹⁹ but poly(rac-lactic acid) (PRLA) and copolymers of lactides and ε-caprolactone are fully amorphous. This characteristic and the possibility to copolymerize both monomers in any ratio allows tailoring of the *T*_g of the polyol and hence of the final coating. We aimed for final *T*_g values between 10 and 40 °C and synthesized a polyester **2** with a CL:LLA ratio of 20:80. This material would give, according to the Fox equation, a *T*_g of +26 °C for a long, non-cross-linked polymer. Reaction of TMP with lactide and ε-caprolactone in the presence of catalytic Sn(Oct)₂²⁰ reproducibly gave **2** in high yield and good purity. UPy units with a variety of R groups have been reported in the literature. Compound **3**, a synthon which is easily synthesized on kilogram scale, was used to functionalize the polyol. Compound **3** is insufficiently soluble for use in the very concentrated mixtures of polyol and covalent cross-linker. Thus, triol **2** was functionalized with variable amounts of **3** in dilute solution prior to formulation of the curable mixture. The materials thus obtained all have good solubility in CHCl₃, NMP, and THF. As covalent cross-linker, a nonvolatile dimer uretdione, Desmodur N3400 (Scheme 1b), was used instead of the widely available but toxic and volatile hexamethylene diisocyanate (HDI). The dimer offers the advantage over the more commonplace trimeric isocyanurate that it has the same cross-link functionality and geometry as the UPy dimer, so the overall cross-link density (equating a UPy dimer to a covalent cross-link) remains unchanged when the ratio of covalent to reversible cross-linkers is varied. A slight excess (equivalent to a total NCO/OH ratio = 1.1) of covalent cross-linker was used in all cases to compensate for possible losses of isocyanate through hydrolysis and urea formation.

Mixtures of polyols and isocyanates were cured in *N*-methylpyrrolidone (NMP) and tetrahydrofuran (THF); chloroform was used in a number of control experiments. When low-boiling solvents THF or chloroform are used for preparing thick, free-standing films, cure temperatures of 50 °C are necessary in order to get uniform materials. In that case, we used dibutyltin(II) dilaurate (DBTDL) as a catalyst in order to get full conversion within reasonable times.

Results and Discussion

Tests on a Metal Substrate. Cross-linked films **F4** with varying amounts of UPy cross-links (10%, 20%, 30%, 40%, 47%, and 53%) were prepared from a concentrated NMP solution on aluminum plates. Mixtures of polyol and isocyanate containing from 30% (m/m) solvent in the case of **F4-0** to 60% for **F4-53** were applied to the substrate using a doctor blade to give wet film thicknesses of 120 μm and were cured in an oven at 100 °C for 1 h. Using attenuated total reflection infrared spectroscopy (ATR-IR), full conversion was found to be reached after 20 min, when the isocyanate band at 2262 cm⁻¹ had disappeared.

The resulting films (see Supporting Information, Table S11) were colorless and highly transparent; they displayed medium gloss and had dry film thicknesses of 40–60 μm. They were all hard, showed good adhesion to the substrate—also when the latter was bent—and did not show any tack. An acetone double rub test (ADR)²¹ showed that the films with *u* = 0% up to *u* = 40% of UPy-functionalized end groups easily withstood the solvent action (more than 100 double rubs), whereas the coatings above *u* = 47% (**F4-47** and **F4-53**) slowly dissolved in acetone. Although on statistical grounds one can expect a covalent network to subsist at this ratio of supramolecular cross-links, it fails to sufficiently reduce swelling of the coating with solvent, rendering it vulnerable to the mechanical stresses of rubbing.

Preparation of Free-Standing Films. In order to get insight into the mechanical properties and more specifically the stress relaxation potential of the UPy-containing coatings, free-standing films **F4-0** to **F4-53** were prepared (see Table 1). In addition, the fully noncovalent material **F4-100** was prepared in a similar way without any covalent cross-linker. The challenges of preparing a free-standing film are different from the requirements for a coating on a surface. Film thickness can be much higher, but adhesion to the substrate must be weak in order to detach the film from its mold. This conflicts with the requirement of good wetting of the substrate, which a uniform film presupposes. Silanized glass proved to give a good compromise, and we used glass plates of different sizes to make molds in which the reaction mixtures were cast. Wet thicknesses exceeding 1 mm were used in order to obtain dry films of 500 μm. These films have to be uniform in thickness and must not contain any entrapped bubbles (from air entrapment or isocyanate hydrolysis), as these make the films unsuitable for mechanical testing. We found that this can be best achieved using chloroform as solvent and curing the materials at 50 °C for 3 h in the presence of catalytic amounts of DBTDL. The cross-linked films were then dried under vacuum at 100 °C for 12 h. These materials showed a tendency toward haziness and yellowing in the case of higher UPy contents. Above *u* = 47%, the materials were too brittle to be analyzed by DMA.

Glass Transition Temperatures. The properties of the films are summarized in Table 1. The glass transition temperatures

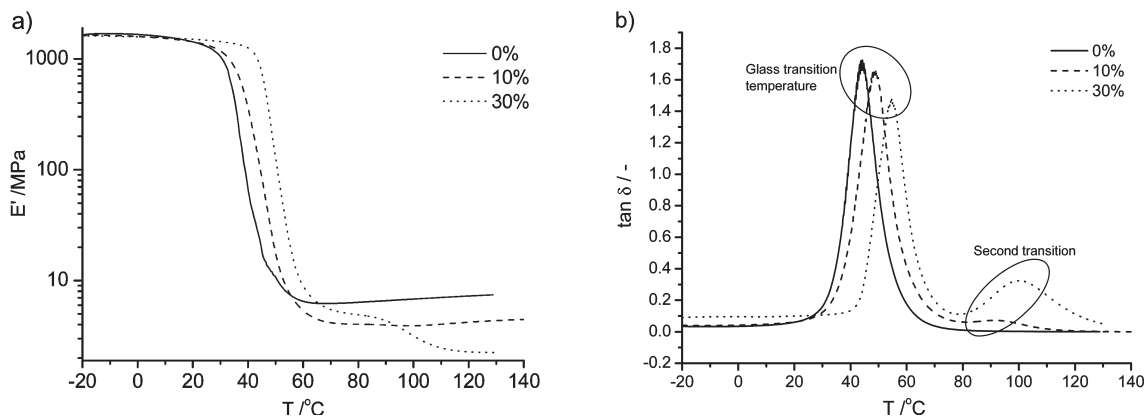


Figure 2. Dynamic scans on DMA of **F4-0**, **F4-10**, and **F4-30** (heating rate $3\text{ }^{\circ}\text{C min}^{-1}$, frequency 1 Hz): (a) storage moduli vs temperature and (b) loss tangent vs temperature.

measured by DMA increase by about $10\text{ }^{\circ}\text{C}$ from the fully covalent film to $u = 40\%$. DMA was used in tensile mode (heating rate $3\text{ }^{\circ}\text{C min}^{-1}$, frequency 1 Hz), and T_g values were measured taking the maximum in the loss tangent ($\tan \delta$) as the T_g value. The glass transition temperatures measured by DSC shift from 34 to $44\text{ }^{\circ}\text{C}$ when the amount of UPy content in the materials is increased from 0% to 40% (see Supporting Information). This effect is presumably due to the presence of stiff UPy units in the polyester phase. Results from DSC and DMA differ by about $10\text{ }^{\circ}\text{C}$, but the increase of the glass transition temperature with UPy content correlates very well between both techniques. As opposed to all partially covalent materials, the purely UPy film **F4-100**, when aged at room temperature for a week, shows a glass transition at $6\text{ }^{\circ}\text{C}$ (Supporting Information) while a melting transition is observed at $55\text{ }^{\circ}\text{C}$ in the first heating run. Second heating runs or fresh films do not display this endothermic peak. A transition at similar temperatures has been reported for non-cross-linked supramolecular polymer systems based on oligocaprolactones.³ On all other materials studied, aging did not induce any crystallinity, nor did a second heating run differ significantly from the first one.

These findings point to marked differences in morphology: even if crystallization is slow and incomplete, molecules in thermoplastic **F4-100** have enough mobility to rearrange and crystallize. Covalent cross-links impede any such movements above T_g and restrict motion strongly enough to keep the materials fully amorphous during preparation and result in approximately $25\text{ }^{\circ}\text{C}$ higher glass transition temperatures.

Mechanical Properties by DMA. Figure 2 presents the results of dynamic heating tests by DMA (T_g values presented in Table 1) on selected films. Figure 2a illustrates the evolution of the tensile storage moduli E' with temperature. As the materials go from the glassy to the rubbery state, the tensile storage moduli E' drop by more than 2 orders of magnitude. Fully covalent **F4-0** (Figure 2a) displays a minimum in the storage modulus, after which it shows the expected slow but constant increase due to entropic elasticity. However, the presence of supramolecular cross-links induces a second, weaker softening at higher temperatures. At low u values, the change is more conspicuous in the loss tangent than in E' , as it exhibits a second maximum. This transition will be referred to as “the second transition”. Beyond this second transition, the storage modulus shows again entropic hardening for the lower u values. Incidentally, for the materials with the highest UPy contents that could be measured, E' continues to decrease, a trait characteristic of un-cross-linked materials.

The closeness of the two transitions causes the absence of a clear minimum in the storage modulus above T_g , which is generally used to calculate the cross-link density (XLD) of the network (see Figure 2b). One way to circumvent this problem is to consider exclusively the covalent cross-links and to calculate XLD values well above the second transition. The cross-link density was calculated using eq 1, derived from the kinetic theory of rubber elasticity.²²

$$E' = 3\nu_e RT \quad (T \gg T_g) \quad (1)$$

where E' is the tensile storage modulus, ν_e is the calculated cross-link density (XLD) measured in mol cm^{-3} , R is the universal gas constant, and T the temperature in K. In order to make sure that a realistic temperature is utilized for the determination of XLD, the storage modulus was measured $73\text{ }^{\circ}\text{C}$ above the T_g of each material, well beyond the second transition. For $u = 0\%$, a XLD of $739 \times 10^{-6}\text{ mol cm}^{-3}$ was found, in excellent agreement with the value of $\sim 900 \times 10^{-6}\text{ mol cm}^{-3}$ expected for a material with a density close to unity and a cross-link molecular weight, M_c , of 1.1 kg mol^{-1} . When the u value increases, the XLD decreases, with a drop of an order of magnitude close to $u = 33\%$. A critical value of XLD of $\sim 1 \times 10^{-6}\text{ mol cm}^{-3}$ (1 kg mol^{-1} for the molecular weight between cross-links) coincides with the threshold for material strength (i.e., the onset of excessive brittleness) as well as a plateau in the storage modulus above the second transition. This is in good agreement with the expectations from a statistical argument: given the functionality of the binder and the cross-linker, there will on average be less than two covalently linked chain ends in each binder molecule above $u = 33\%$ and an infinite covalent network does not subsist at higher u values.

Creep/Stress Relaxation Measurements and Stress/Strain Curves. Creep measurements were conducted at stresses in the linear viscoelastic region (0.5 MPa , see the Supporting Information) at different temperatures for times up to 60 min . The specimens were allowed to recover for another 20 min after stress removal.

Above T_g , in the rubbery state, creep behavior (Figure 3c) is strongly dependent on UPy content. When measured at $16\text{ }^{\circ}\text{C}$ above T_g (Table 1), equilibrium elongation increases strongly with increasing fraction of UPy cross-links. Whereas the fully covalent material (**F4-0**) shows 18% final strain, this value is ~ 3.5 times higher (64%) for the sample with 30% UPy content (**F4-30**). The strains reflect the differences in covalent cross-link density in the materials and roughly correspond to the elastic moduli determined with DMA determined $73\text{ }^{\circ}\text{C}$ above the T_g of each material. The rate of creep in the

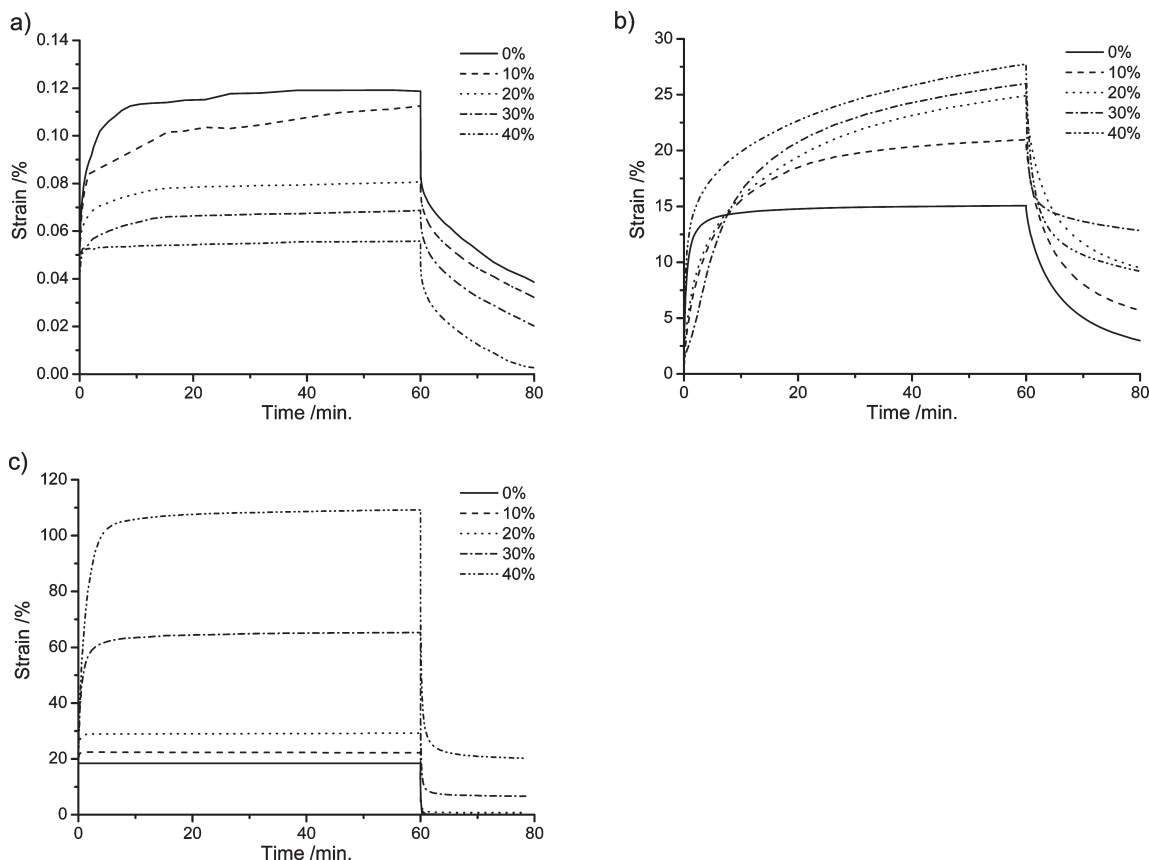


Figure 3. Creep measurements at 0.5 MPa stress at (a) 10 °C, (b) 14 °C below T_g , and (c) 16 °C above T_g of films **F4-0** to **F4-40**.

UPy containing samples is much slower than in the fully covalently cross-linked material, which essentially shows an instantaneous response to the applied stress, while **F4-40** requires ~ 1.2 min to reach 50% of its final strain.

After stress removal, the fully covalently cross-linked material exhibits nearly instantaneous recovery as the elastic network regains its equilibrium shape. Like in the creep part of the experiment, recovery of the UPy containing materials is much slower and is not complete after 20 min. When the creep and creep recovery experiments are plotted on a logarithmic time axis (see Supporting Information), it is clear that initial rates of creep and recovery increase with UPy content. However, it is also evident from the plot that the behavior of the materials cannot be fitted with a single relaxation time over the time course of the entire experiment. Attempts to fit creep and creep recovery behavior of the UPy containing materials simultaneously with a single set of four parameters using a rheological model consisting of a Maxwell and a Kelvin–Voigt element in series (Burger's model)^{23,24} gave moderately good fits and showed that the relaxation times increase with increasing UPy content. The fitting procedure resulted in a steadily increasing value for the viscosity η_2 of the dashpot in the Kelvin–Voigt element with UPy content. As a result, the relaxation time of this element increased from 5 s for **F4-10** to 51.6 s for **F4-40**. Both creep and recovery behavior of the UPy containing material can be considered to be the result of the combination of a purely elastic component from the covalent network and a viscoelastic component originating in dissociation and recombination of UPy groups. In molecular terms, this corresponds to dimers opening and each UPy half finding a different partner under stress. The current materials are therefore mechanically analogous to the very lightly cross-linked rubbers studied

by Ferry, which show viscoelastic behavior of which the viscous component finds its origin in slow relaxation of entanglements between cross-links.²⁵

For preemptive relaxation of stresses in coatings, creep behavior close to room temperature is of particular interest. In order to compare materials with different UPy contents, creep was measured at a fixed distance from T_g (14 °C below the T_g of each material) instead of at a fixed temperature. Also here, the presence of UPy cross-links results in higher strains, although the differences are much smaller than above T_g (see Figure 3b). The fully covalent material ($u = 0\%$) is elongated up to a strain level of 14% at $T_g - 14$ °C. Equilibrium strain is reached after a relatively short time, with 50% of the final strain reached after 1 min. The strain recovered for the most part after release of stress. UPy-containing materials elongate to significantly higher strains (up to 26% strain reached for the $u = 40\%$) because at these temperatures the noncovalent UPy cross-links are unable to sustain stress at the time scale of the experiment and the covalent part of the network has a lower cross-link density than in the fully covalent material.

When stress is removed, recovery is slow for the fully covalent cross-linked material, but after longer times almost fully recovers to its original dimensions. The UPy-containing materials display faster recovery up to a specific level due to the relaxation of the covalent network. In addition, the presence of UPy groups leads to a very slow recovery process above this level. It is expected that the presence of the noncovalent bonds will not allow for a full recovery, inducing a certain amount of irrecoverable creep.

Finally, deeper in the glassy state, creep was measured at constant temperature (10 °C). Under these conditions, final strains are small, and they are reversed compared to the values at higher temperatures because the UPy containing

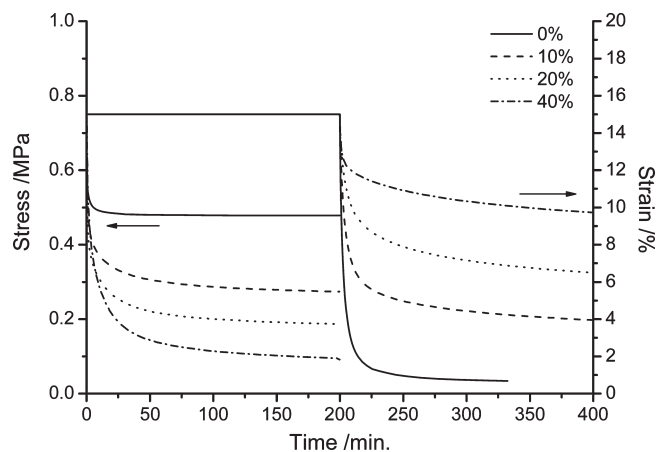


Figure 4. Stress relaxation measurements at 15% strain at 14 °C below the glass transition temperature ($T_g - 14$ °C) of films **F4-0** to **F4-40**.

materials are further below their T_g than the covalent material. The fully covalent cross-linked material shows creep up to 0.12% strain after 60 min (Figure 3a), while the material containing 40% UPy cross-links has only 0.05% strain after this amount of time. The recovery time of 20 min is barely adequate to see full recovery of the covalently cross-linked material after the stress has been removed. Although the UPy containing materials were extended to lower strains, their creep behavior is similar to that of the fully covalently cross-linked material ($u = 0\%$). The creep behavior is governed by very limited relaxations due to residual chain mobility in the glassy state. For this reason, after stress removal the materials show very slow recovery.

In addition to the creep tests, stress relaxation measurements were conducted at a temperature 14 °C below the T_g of each UPy-containing material. Stress at a constant strain of 15% was monitored for 200 min. Then, in the absence of any external stress, strain recovery was followed for another 200 min (Figure 4). For the fully covalent cross-linked material, the stress required to maintain the material at 15% constant strain decays with time, starting at a value of 0.9 MPa and equilibrating at a value of almost 0.5 MPa. This result is in excellent agreement with the creep measurement at the same temperature: a maximum strain of 14% was reached at a stress of 0.5 MPa.

Higher UPy contents result in lower stresses required to maintain the materials at the same constant strain: incorporation of UPy moieties into the networks allows for effective stress relaxation. The materials show that at higher UPy contents the behavior becomes more thermoplastic-like. This is also evidenced by the strain recovery recorded when stress was released. The fully covalent cross-linked material recovers almost completely. For the UPy containing materials ($u = 10\text{--}40\%$) the strain decays only slowly and does not fully recover. This again is in very good agreement with the creep measurements (see also Figure 4), showing that the presence of UPy groups slows down the recovery of the materials after stress removal in the same way creep is slowed down by the supramolecular cross-links.

Figure 5 illustrates the stress/strain curves obtained at 30 °C at an elongation rate of $1\% \text{ min}^{-1}$. At low UPy contents, the supramolecular units make the material stiffer and, above all, notably tougher. When 20% of the cross-links are supramolecular ones, the fracture energy of the material approximately triples with respect to the fully covalent polymer. However, higher UPy contents render the material brittle; above 40% the materials cannot be tested any more

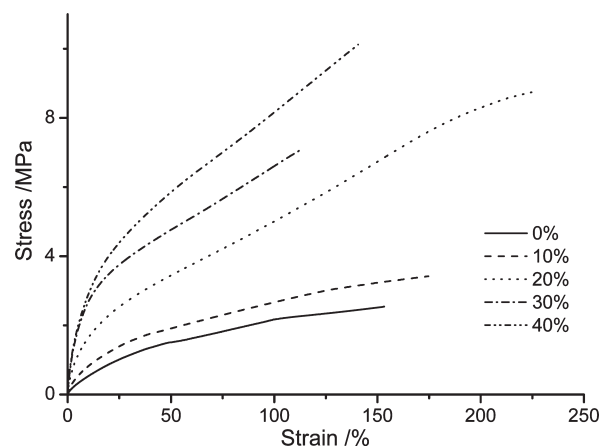


Figure 5. Stress/strain curves of films **F4-0** to **F4-40** at 30 °C, measured at a strain rate of $1\% \text{ min}^{-1}$.

on DMA. The toughening effect of UPy on our polyester–polyurethane networks is an encouraging side effect of the design of stress-relaxing networks. The precise reasons for this toughening as well as for the following embrittlement remain elusive: T_g values do not decrease above the optimum UPy contents around 20%.

It could prove very interesting to investigate more thoroughly the incorporation of higher UPy contents in order to shed some light not only on the embrittlement but also on the evolution of the glass transition temperature of the UPy-containing materials.

Conclusions

In this paper, we have established that UPy units can conveniently be incorporated into polyester–polyurethane networks, such as the ones used in coatings for metals. These networks interestingly combine properties unique to typical thermoset materials, such as resistance to solvent swelling, with some typical features of thermoplastic materials. Surprisingly, the incorporation of the UPy groups improves the material strength and toughness of the polyurethane coatings rather than impairing their mechanical properties. Furthermore, we showed that the UPy's induce an additional relaxation mechanism, with characteristic times longer than the ones of Rouse-like motions. This relaxation mechanism leads to softening of the materials above T_g .

Remarkably, the presence of UPy groups leads also to higher creep compliances below T_g . The latter property makes these materials potentially useful for application in industrial coatings because mechanical tensions which are present within the material due to film shrinkage during the curing stage or deformation of the substrate can be relaxed thanks to the nature and composition of the network. This type of preemptive healing is completely autonomous, as no external stimuli such as excessive heating, light, or chemicals are necessary for the material to recover from internal stresses. Furthermore, the healing mechanism we describe here could potentially be repeated indefinitely. We are currently investigating in greater depth the underlying mechanisms by which the UPy groups lead to improved stress relaxation below T_g and look into the scope for variations and applications.

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Supporting Information Available: Additional calorimetric and mechanical characterization of films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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