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Longitudinal polymer gradient materials based on crosslinked polymers

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ABSTRACT

Polymer gradient materials (PGMs) are known to reduce stress concentrations and to increase fracture toughness. The first system we reported for the preparation of longitudinal PGMs was based on poly(-dimethyl siloxanes), covering a relatively low Young's modulus range. In this study, we used two photochemically and one thermally curing polyaddition systems, enabling us to cover a much larger modulus range up to 1300 MPa. Three different gradient structures, hard-soft, hard-soft-hard, and soft-hard-soft, were realized and confirmed by position-dependent UV/Vis absorbance measurements. Tensile testing in dependency on the gradient structure was performed. A comparison with non-gradient samples with discrete composition revealed a significant improvement, specifically in the case of hard-soft-hard gradients. Hence, PGMs are a promising approach for the development of materials with a special mechanical property profile particularly at different temperatures, leading to novel thermoresponsive materials.

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1. Introduction

Understanding biological structuring principles is a key requirement for their adaptation to bio-inspired engineering materials [1,2]. One principle comprises the application of compositional gradients for joining two materials of different stiffness to avoid stress concentrations in the contact zone [3]. Furthermore, gradient materials increase toughness [4,5]. A natural example for a gradient material is the mussel byssus that attaches the mussel in their environment and mediates the mussel soft tissue to the hard surface of rocks [6]. These biogradient fibers possess high strain energies (35–45 MJ/m^3) comparable to that of aramid fibers (50 MJ/m^3) [7,8]. The adaptation of this biological gradient to polymer materials was already envisioned in 1972 [9] but their systematic investigation was limited by the lack of preparation methods [10,11]. Gradient-Interpenetrating Polymer Networks exhibited enhanced fracture strain and energy to break [12,13] as well as better damping properties [14]. Research was also performed in the field of biological and artificial longitudinal gradient materials, meaning a compositional gradient along the length of the sample which was recently reviewed [15].

In general for a polymer gradient material (PGM) a polymer system is required with continuously changing composition accompanied by a changing property such as optical, morphological, and mechanical along the length of the sample. The mechanical properties of polymer networks, such as elastomers or thermosets, can be adjusted by the crosslink density, i.e. the number of active network chain segments per unit volume [16]. In this model, the crosslink density decreases with increasing molecular weight (M_c) segments between crosslinks (Scheme 1).

Askadskii et al. reported on PGMs based on crosslinked poly(-isocyanurate) networks with rigid bulky crosslink points, short flexible linking chains and a continuously changing crosslink density. These materials are able to cover a large range in Young's modulus of 3–2000 MPa [17]. However, the reproducible preparation is inflicted by the application of a complicated two-step procedure with different prepolymers, catalysts, and curing steps up to crosslink-temperatures around 180 °C. Furthermore, the density controlled process is limited to a single gradient structure, rendering only soft-hard PGMs [18].

Recently, we reported on PGMs based on poly(dimethyl siloxane) (PDMS) with high reproducibility on a centimeter scale. As a special feature of the experimental setup, in addition to hard-soft gradients even much more complex gradient structures were realized such as hard-soft-hard or oscillating PGMs. However, the restrictions of PDMS systems are the narrow and low modulus
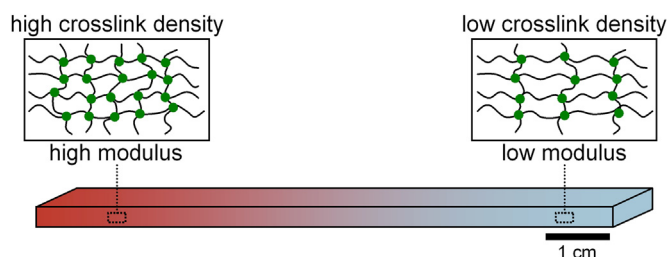
Scheme 1. Concept for the preparation of longitudinal polymer gradient materials. A high crosslink density renders a material with high modulus whereas a low crosslink density confers a low modulus. The continuously changing colour shade reflects a compositional gradient on the centimetre scale in which the crosslink density and thus the modulus continuously changes along the sample length.

range of 0.2–1.8 MPa. Furthermore, the Tg remains in the rubber-like state around −120 °C regardless the composition [15,19,20].

To design more versatile longitudinal PGMs, we wanted to explore longitudinal PGMs made of (1) other polyaddition systems encompassing much higher modulus ranges and involving different chemistry. Specifically, photocrosslinkable acrylate and thiol-ene systems, as well as thermally curing poly(urethane)s were employed. (2) Photochemically curing polyaddition systems deserve a closer look because the fast photoreaction curing step reduces blurring of the desired gradient structure via diffusion. This allows steeper gradients as well as a better controlled over the resulting gradient structures. (3) We restrict this study to off-the-shelf commercially available monomers and prepolymers because these starting materials are readily available which facilitates the reproduction of all PGMs presented outside our lab. Moreover, the statistical evaluation requires a sufficient amount of identical samples. Thus, we were able to investigate the impact of chemistry, composition, and different gradient structures and on the mechanical properties of PGMs, such as overall E-modulus and strain energy determined by standard tensile testing experiments. (4) In continuation of our work on PDMS, we wanted to prepare now PGMs with a rubber to glass transition zone along the sample which might be of interest for thermoresponsive materials, i.e. materials with temperature-dependent mechanical properties.

2. Experimental

2.1. Materials

In this study, we focused on commercially available starting materials which were used as received and listed in Table 1. Here, also details, such as supplier, density, and viscosity, are compiled.

2.2. Sample preparation

Specimens were prepared on a high precision syringe pump system (Cetoni Nemesys) with up to three dosing units [15,19,20]. Each 10 mL glass syringes with luer lock connectors was filled at room temperature (RT) with the liquid components (Table 1). The syringes were mounted and connected by disposable tubing to a custom-designed mixing head with an attached disposable static mixer [15]. PUR components were evacuated at 60 °C overnight prior to use. Due to the differences in the viscosity of each polymer system, different static mixers had to be used [21]. Static mixers with the smallest dead volume but yet sufficient mixing performance were used (Laromer®, PUR, PDMS: Sulzer Quadro™ 15.3/16, dead volume: 1.4 mL; thiol-ene: Sulzer Statomix™ MA 3.0-17-S, 0.3 mL). Gradients were prepared by application of a continuously changing flow rate ratio and constant flow plateaus (Fig. 3, Figures S2, S4, and S6) whereas discrete composition were obtained in the same apparatus by constant flow ratios. The mixtures were cast into rectangular molds of different materials to minimize wetting and demolding problems (Laromer® and thiol-ene: PMMA; PUR: poly(propylene), PDMS: PTFE). The mold (140 × 10 × 1 mm³) was mounted on a linear motion slide (Misumi Europe GmbH) whose motion rate was synchronized with the flow profile. At a total flow rate of 25 μL/s, the mold was uniformly filled in 56 s using a mold movement of 2.5 mm/s. The different offset in time is caused by the combination of mixer type and component viscosity. In the case of butt joint materials, the mold was divided into two sections by a thin Teflon® film divider. After filling each half of the mold, the divider was immediately removed allowing the two mixtures forming a sharp interface by diffusion only (Fig. 5). In the case of photopolymerization, Lucirin®-TPO (from BASF SE, CAS-Nr. 75980-60-8, 2,4,6-trimethylbenzoyldiphenyl phosphine oxide) was added at 2–4 wt.% as specified in Table 1. After processing, the mixtures

Table 1
Compilation of systems, components and properties for the preparation of polymer gradient materials.

System	Component	Supplier	Description[a]	Density[b] (g/L)	Viscosity[b] (mPa s)
Laromer® **1**[c]	LR9007	BASF	Poly(ether acrylate) (*hard*)	1.10	1150
	LR8907	BASF	Poly(ester acrylate) (*soft*)	1.10	1250
Thiol-ene **2**[d]	TMPTA	BASF	Triacrylate (*hard*)	1.10	130
	TPGDA	BASF	Diacrylate (*soft*)	1.04	11
	PMMS SMS-992	Gelest	Thio-Siloxane	0.97	75–150
PUR **3**[e]	Desmophen® VP LS 2249/1	Bayer	Polyol (*hard*)	1.05	1900
	Desmophen® VP LS 2328	Bayer	Polyol (*soft*)	1.06	800
	Desmodur® N 3600	Bayer	HMDI-Cyclotrimer	1.17	1200
PDMS **4**[f]	Alpa-Sil EH	Alpina	H-Siloxane (*hard*)	1.10	10,500
	Alpa-Sil Classic	Alpina	H-Siloxane (*soft*)	1.10	2700
	Alpa-Sil Curing agent	Alpina	Vinyl-Siloxane and Pt-Catalyst	1.05	1050

[a] The exact composition is not disclosed by BASF, Gelest, or Bayer.
[b] Manufacture data sheets.
[c] Photoinitator: Lucirin®-TPO, 4 wt.%.
[d] Photoinitator: Lucirin®-TPO, 2 wt.%; TMPTA: trimethylolpropane triacrylate; TPGDA: tripropylenglycol diacrylate; PMMS: poly[(mercaptopropyl) methylsiloxane] ($M_n \sim 4000–7000$ gmol^{-1}), CAS-Nr. 102783-03-9.
[e] PUR: poly(urethane); Desmophen® VP LS 2249/1, aliphatic highly branched short chain poly(ester) polyol, equivalent weight 110, OH content 15.5%; Desmophen® VP LS 2328, aliphatic linear short chain poly(ester) polyol, equivalent weight 218, OH content 8%; Desmodur® N 3600, polyfunctional aliphatic poly(isocyanate) resin based on hexamethylene-1,6-diisocyanate (HMDI), equivalent weight 183; 0.14 wt.% (VP LS 2249/1) and 0.12 wt.% (VP LS 2328) dibutyl tin dilaureate (CAS-Nr. 77-58-7) was used as catalyst, resulting in a total concentration of 0.05 wt.% in the final polyol/isocyanate mixture. See supporting information for specific mixing ratios.
[f] PDMS: poly(dimethyl siloxane).