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Reactive core/shell type hyperbranched blockcopolyethers as new liquid rubbers for epoxy toughening

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Abstract

Novel reactive core/shell-type hyperbranched blockcopolyethers were tailored as new class of liquid rubbers useful as flexibilizers and toughening agents of anhydride-cured epoxy resins. Anionic ring-opening polymerization of glycidol onto a six-arm star poly(propylene oxide-block-ethylene oxide) afforded hyperbranched polyether cores as macroinitiators for propylene oxide graft copolymerization. The hydroxy end groups of the resulting polyether–polyols have been modified in order to prepare stearate, hydroxy benzoate and epoxy derivatives. The modification afforded reactivity and polarity design which has been the key to improved blend performance with epoxy resins. In comparison to conventional hyperbranched epoxy-terminated polyesters, the influence of molecular architectures on thermal, mechanical and morphological properties of hexahydrophthalic acid anhydride-cured bisphenol-A diglycidylether was examined. As a function of polarity and reactivity design, it was possible to control phase separation and to vary mechanical properties from highly flexible to stiff and tough.

Keywords: Epoxy resin; Hyperbranched polyglycerol; Toughness

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1. Introduction

Epoxy resins are thermosets combining attractive properties, such as high strength and stiffness and excellent dimensional, thermal and environmental stabilities. Epoxy-based materials are being applied as matrix resins of coatings, adhesives and composites. The well-known drawback associated with the application of highly cross-linked thermosetting polymers is related to their inherent brittleness which increases with crosslink density [1]. In order to circumvent this toughness problem, impact modifiers are added to epoxy resins in order to produce multiphase blends with improved toughness/stiffness balance. Two types of impact modifiers are established: epoxy flexibilizers and epoxy toughening agents. Both are miscible with the uncured epoxy resin and should not deteriorate the low resin viscosity required to afford easy processing. In contrast to flexibilizers, toughening agents improve toughness without sacrificing stiffness and glass transition temperature. Prominent impact modifiers are based upon liquid rubbers such as nitrile rubbers which dissolve in the epoxy resin and phase separate during cure [2]. As a function of molecular architectures, their polarity and reactivity are matched with the individual epoxy resin systems. This matching process is very important to achieve phase separation and simultaneous bonding of the dispersed rubber particles to the epoxy matrix without impairing processing [3]. The phase-separated rubber particles function as stress concentrators initiating energy absorbing ‘toughening’ processes due to multiple plastic deformation processes. Since the pioneering advances at B.F. Goodrich Company, low molecular weight butadiene acrylonitrile copolymers bearing carboxyl (CTBN), amine (ATBN) or epoxy (ETBN) reactive end groups have being used extensively [4,5]. Other important liquid rubbers are based upon poly(propylene oxide) [6,7] and poly(tetra-hydrofurane) [8,9]. During recent years, new types of impact modifiers based upon hyperbranched nanometer-scaled polymers, especially polyesters, have been introduced.

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Hyperbranched hydroxy-, carboxy- and epoxy-terminated polyesters give low viscosity blends. A few percent of such polyesters are sufficient to significantly improve toughness without sacrificing stiffness and glass temperature [10,11].

Key features of hyperbranched polymers (HBPs) are the very high degree of branching resulting from branched repeat units and the very high end group functionality located at the surface of the core/shell architectures of this nanometer-scaled polymers. Since their highly branched architecture prevents chain entanglements, HBPs usually exhibit low viscosities in melt and solution as well as high solubility even at elevated molar masses. The multiple end groups, which mainly govern the properties, can be conveniently modified in order to tailor the polymers with respect to the desired application [12,13]. For instance, aiming at an application as toughness enhancer, the polarity of the HBP can be adjusted to provide an initially soluble modifier which phase-separates only during cure. Furthermore, reactive end groups can be incorporated in the hyperbranched material to achieve covalent attachment to the matrix. Additionally, the low viscosity of the resin modified with HBP is expected to preserve good processability in moulding applications. Further applications for HBPs presented in literature to date include the use as rheology modifier for thermoplastics [14,15], compatibilizing agent in polymer blends [16,17], additive in coatings [18,19] as well as adhesives [20] and barrier layer in film packaging [21]. Prominent representatives of HBPs used in thermoset toughening are aliphatic polyesters, commercially available from Perstorp polyols under the trade name of Boltorn. Various end group modifications are available [22]. Månson et al. and later Ratna et al. reported independently on the successful toughening of epoxy resins by epoxy-functional Boltorn. According to these works, K_{Ic} values of the prepared resins were improved up to 300%, depending on the degree of modification of the HBP and the curing cycle [10,11,23,24]. In contrast, Heiden et al. reported only slightly improved toughness when employing hydroxy-terminated Boltorn in epoxy formulations [25].

Most hyperbranched polymers used as epoxy modifiers are being produced by means of random polycondensation of AB_m-type monomers. This mechanism accounts for fairly large polydispersities which increase with increasing molecular masses [26]. Much narrower polydispersities have been obtained when latent AB_m monomers were added slowly to a multifunctional core B_f. The slow addition process offers new opportunities for tailoring novel core/shell type hyperbranched polymers with nanometer size and well defined surface functionalities [27]. Sunder et al. developed a new slow addition process for the anionic ring-opening homo- and copolymerization of glycidol using a polyol-based initiator [28]. Such glycidol polymers, equivalent to polyglycerol, are readily available in large scale using technology established for the production of polyol intermediates for polyurethane chemistry. Hyperbranched polyglycerols were used as polymeric precursors for the synthesis of amphiphilic nanocapsules and nanometer-scaled core/shell-type polymers, which have been applied as new building blocks for hydrogels as well as high loading soluble polymer supports for organic synthesis [29].

The objective of this research was to employ anionic ring-opening copolymerization of gylcidol and propylene oxide to tailor novel readily available nanometer-scaled hyperbranched polyethers with onion-like molecular architectures as new flexibilizers and toughening agents of thermosets. Special emphasis is placed upon polarity and reactivity design, required to achieve good miscibility, low viscosity, interfacial adhesion, and phase separation. The performance of this new type of blend components was examined in anhydride-cured epoxy resins and compared to that of hyperbranched polyesters in order to understand the correlations between molecular architectures and blend performance.

2. Experimental section

2.1. Materials

Bisphenol-A diglycidyl ether (BADGE, EEW = 192 g/equiv., Araldite CY225) and hexahydrophthalic acid anhydride (Hardener HY925) were received from Vantico AG, Switzerland. Liquid six-arm star poly(propylene oxide-block-ethylene oxide) (PPO), supplied by Bayer AG, Germany, (Baygal VP.PU 99IK01 P.64, molar mass of 3300 g/mol) was used as initiator for the polymerization of glycidol and as epoxy modifier. End-tipping with ethylene oxide provided primary hydroxy end groups for PPO. The polymer was dried at 100 °C under reduced pressure prior to use. Boltorn E1, commercially available from Perstorp polyols AB, Sweden, is an epoxy-functional hyperbranched polyester obtained from the acid-catalyzed polymerization of 2,2-bis(hydroxymethyl)propionic acid and modification with epoxidized fatty acid esters. All other compounds were purchased from Sigma-Aldrich and used as received except for glycidol and propylene oxide which were distilled (PO over calcium hydride) prior to use.

2.2. Polymer synthesis

Polymerizations were carried out in a 2 l reactor equipped with a mechanical stirrer and dosing pump under argon atmosphere. Glycidol was polymerized using the slow monomer addition technique in diethylene glycol dimethyl ether (diglyme) as described previously [27]. Glycidol must be added slowly to prevent explosive glycidol bulk polymerization. The monomer/initiator ratio was chosen according to the desired molecular weight of 10,000 g/mol for the product. In order to tailor polymer polarity, propylene oxide was directly polymerized onto the living polyglycerol chain ends in a following reaction step, as described by Sunder et al. [30]. A hyperbranched blockcopolymer consisting of polyglycerol with propylene oxide end-tipping was obtained as a transparent, highly viscous liquid.

2.3. End group modification

36P21 and 35P26. 200 g (12.0 mmol; 1.03 mol of hydroxy groups) of the hyperbranched blockcopolymer was heated together with 83 g (0.50 mol) ethyl 4-hydroxy benzoate at 160 °C for 14 days. A continuous nitrogen stream was applied to remove ethanol formed during the reaction. The amount of ethyl 4-hydroxy benzoate employed aimed at the modification of 49% of the hydroxy end groups to phenol end groups. 2.0 ml dibutyltin dilaurate (DBTDL, 2.1 g, 0.5 wt%) was used as a catalyst. The highly viscous product 36P21 was de-gassed under reduced pressure.

57 g (2.6 mmol; 0.24 mol of hydroxy groups) of the phenol-functionalized HBP 36P21 was then reacted together with 16.4 g (0.055 mol) methyl stearate and 0.3 ml DBTDL as a catalyst (0.3 g, 0.4 wt%) at 160 °C for 6 days. The stoichiometry was set to aim at a conversion of 24.2% of all end groups, resulting theoretically in 21 alkyl chains attached to the HBP. In the beginning, a heterogeneous mixture was formed, which turned into a single phase system after 1 day. The yellow, highly viscous liquid 35P26 was de-gassed under reduced pressure.

22E22 and 6E40. To introduce reactive primary epoxy end groups, 139 g (8.05 mmol; 0.10 mol phenol groups) of the phenol-functionalized blockcopolymer 36P21 (see above) was dissolved in 1.5 l DMF before 194 g (1.4 mol) anhydrous K_2CO_3 and 110 ml (130 g, 1.4 mol) epichlorohydrin were added. The reaction mixture was stirred for 10 h at 60 °C under argon atmosphere. Inorganic salts were filtered off and the solvent was distilled off under reduced pressure. The residue was dissolved in methylene chloride and washed three times with water. After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed in vacuo yielding 22E22 as a viscous, slightly yellow oil.

For comparison, the hydroxy end groups of the six-arm star poly(propylene oxide-block-ethylene oxide) Baygal were transformed completely to phenol moieties. Subsequently, these were epoxidized in the same manner as described above for the hyperbranched blockcopolymer. The resulting epoxy-functional six-arm star PPO 6E4 was obtained as a yellowish viscous liquid.

18E31. 130 g (7.6 mmol; 0.67 mol of hydroxy groups) of the hyperbranched blockcopolymer was reacted with 66 g (0.22 mol) methyl stearate at 160 °C for 8 days. A continuous nitrogen stream was applied to remove methanol formed during the reaction. The amount of methyl stearate employed aimed at the modification of 33% of the hydroxy end groups. 1.4 g dibutyl tindilaurate (DBTDL, 0.5 wt%) was used as a catalyst. The viscous product was degassed in vacuo and was further modified with 47 g (0.28 mol) ethyl 4-hydroxy benzoate, as described above for 36P21. The amount of ethyl 4-hydroxy benzoate was chosen according to the modification of 42% of the original hydroxy groups of the hyperbranched blockcopolymer. Afterwards, the modified hyperbranched polymer was also epoxidized with epichlorohydrin as shown above, affording 18E31 as a viscous orange liquid.

2.4. Polymer characterization

NMR. ^1H NMR and ^{13}C NMR spectra were recorded in deutero chloroform at concentrations of 250 mg/ml on a Bruker ARX 300 spectrometer operating at 300 and 75.4 MHz, respectively.

GPC. The polymers were dissolved in DMF at a concentration of 5 mg/ml. Measurements were performed with a Knauer microgel set C11 using DMF as an eluent at 45 °C and a Polymer Laboratories evaporative mass detector EMD 960 operating at 110 °C. Linear poly(propylene oxide)s 1000, 2000, 4000 (Aldrich), 8000 and 12,000 (ACRO Chemical Co.) were used for calibration.

DSC. Measurements were carried out on a Perkin–Elmer 7 series thermal analysis system in the temperature range from -100 to 20 °C at a heating rate of 10 K/min. The melting point of indium (156 °C) was used for calibration.

Viscosimetry. The viscosities of the liquid polymers and the polymer filled epoxy resins were recorded in bulk with a Brookfield DV-II + viscosimeter in cone-and-plate geometry. The temperature during the measurements was either set to 30 °C for the functional polymers or 80 °C for the epoxy resins, respectively.

2.5. Epoxy blend preparation

22.5 g of each polymeric modifier was mixed with about 240 g bisphenol-A diglycidyl ether (Araldite CY225) at 80 °C and 10 hPa pressure for the duration of 45 min with a Molteni Planimax high shear mixer in order to achieve dissolution and to reduce residual water. Subsequently, ca 190 g of hexahydrophthalic acid anhydride (Hardener HY925) was added and the mixture with an overall weight of 450 g, which was stirred at 80 °C and 10 hPa for another 30 min. The resin was then poured into a mould ($200 \times 200 \times 4$ mm^3) and curing was performed at 120 °C for 2 h, followed by 8 h at 140 °C in a vented oven to produce epoxy blends containing 5 wt% of the polymeric modifier. All blends containing 2.5 or 5 wt% of additive were produced according to this method. The blends containing the HBP 35P26 were pre-gelled in the moulds at 80 °C for 18 h prior to cure. The exact amounts of resin and hardener were calculated separately for each formulation according to the number of reactive end groups of the functional modifier used. A stoichiometric ratio between epoxy groups (either of BADGE or the modifier) and the functional groups reacting with the epoxy groups (anhydride and phenol) was maintained throughout. Characterization by means of TEM and mechanical testing was executed as reported elsewhere [31].

2.6. Dynamic mechanical analysis

Specimens with a dimension of $50 \times 4 \times 2.5\ \text{mm}^3$ were measured by means of temperature sweeps from −100 to 180 °C in a Rheometrics Dynamic Mechanical Analyser RSA II equipped with Dual Cantilever geometry at a frequency of 0.3 Hz, a strain of 0.08% and a scanning rate of 2 K/min.

3. Results and discussion

3.1. Hyperbranched polyether liquid rubbers

The synthesis of the core/shell type hyperbranched blockcopolyethers is based upon Sunder's process combining anionic ring-opening polymerization and slow addition of glycidol and propylene oxide monomers to a polyol-based multifunctional macroinitiator [27]. The reaction scheme and the resulting onion-like copolyethers are displayed in Fig. 1. In a one-pot synthesis, slow-addition glycidol polymerization was initiated by partially deprotonated six-arm star poly(propylene oxide-block-ethylene oxide), abbreviated as 6H3, in order to afford the hyperbranched macroinitiator for the subsequent propylene oxide (PO) graft polymerization. Glycidol must be added slowly to prevent explosive glycidol bulk polymerization and to achieve narrow polydispersities. The monomer/initiator ratio was set to incorporate 90 mol glycerol units/mol and to afford and end group functionality of 96 mol hydroxy groups/mol. Since polyglycerol blocks are highly polar and would render the polymer hydrophilic, polarity design was achieved by grafting propylene oxide onto the hyperbranched core. In earlier research, this approach was used successfully for polarity design of polyols [32]. Thus, the HBP and its derivatives become initially soluble in the epoxy resin to which they are later added. Preferably, the amount of propylene oxide was chosen to incorporate two PO units at each hydroxy end group without altering the total end group content. This synthetic strategy produces the onion-like hyperbranched polyether liquid rubber consisting of a poly(propylene oxide-block-ethylene oxide) core, a hyper-branched polyglycerol block and a shell of poly(propylene oxide) bearing numerous secondary hydroxy end groups. This new polyether liquid rubber is an optically transparent, highly viscous liquid.

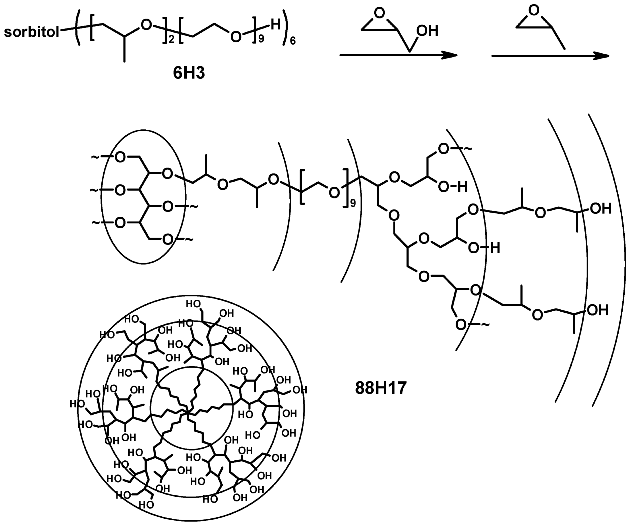

Fig. 1. Reaction scheme: blockcopolymerization of glycidol and propylene oxide on a six-arm star poly(propylene oxide-block-ethyleneoxide) core molecule.

The core/shell-type hyperbranched blockcopolyether has been characterized by means of ^{1}H and ^{13}C NMR spectroscopy, as described by Sunder et al. [34]. The glycidol content was 82 mol/mol giving 88 mol hydroxy end groups/mol. The amount of PO end-tipping was determined to be 1.5 PO units per end group. These values are in good agreement with the theoretical values (i.e. 90 mol glycidol units/mol and two PO units per end group). The molecular weight calculated from the NMR data is therefore 17,100 g/mol, somewhat lower than the theoretical value of 21,000 g/mol. The sample code 88H17 indicates the hydroxy functionality of 88 mol/mol and the molecular weight of 17,000 g/mol. The molecular weight measurement by means of GPC gave a much higher value of 57,000 g/mol. This large deviation of the GPC measurement, which uses a poly(propylene oxide) calibration, is very well in accord with earlier observations that a high degree of branching causes problems when linear polymers are being used for calibration [28]. The increasing viscosity of the reaction medium accounts for larger polydispersities of around 3 with respect to polydispersities of 1.5 for lower molecular weight polyglycerol [34]. It should be noted that this polydispersity of 3 is still much better than that of hyperbranched polymers obtained by means of the 'classical' AB_2 poly-condensations ($M_w/M_n > 5$).

The HBP 88H17 was used as starting material for the preparation of a family of hyperbranched blockcopolyethers by the various hydroxy group conversion reactions displayed in Fig. 2. These modifications on the end groups of the HBP facilitate polarity and reactivity design of the liquid rubbers without altering their macromolecular architecture. The transesterification of hydroxy end groups with methyl stearate was applied to attach non-polar *n*-alkylesters to the hyperbranched blockcopolyethers. Trans-esterification of hydroxy end groups with ethyl-4-hydroxy benzoate on both the non-modified and the alkylester-modified hyperbranched blockcopolyether gave hydroxy benzoate end groups, thus producing novel phenolic hyperbranched blockcopolyethers (samples 41P30 and 36P21, respectively). In another experiment trans-esterification with ethyl 4-hydroxy benzoate was followed by the reaction with methyl stearate resulting in the HBP 35P26, also bearing

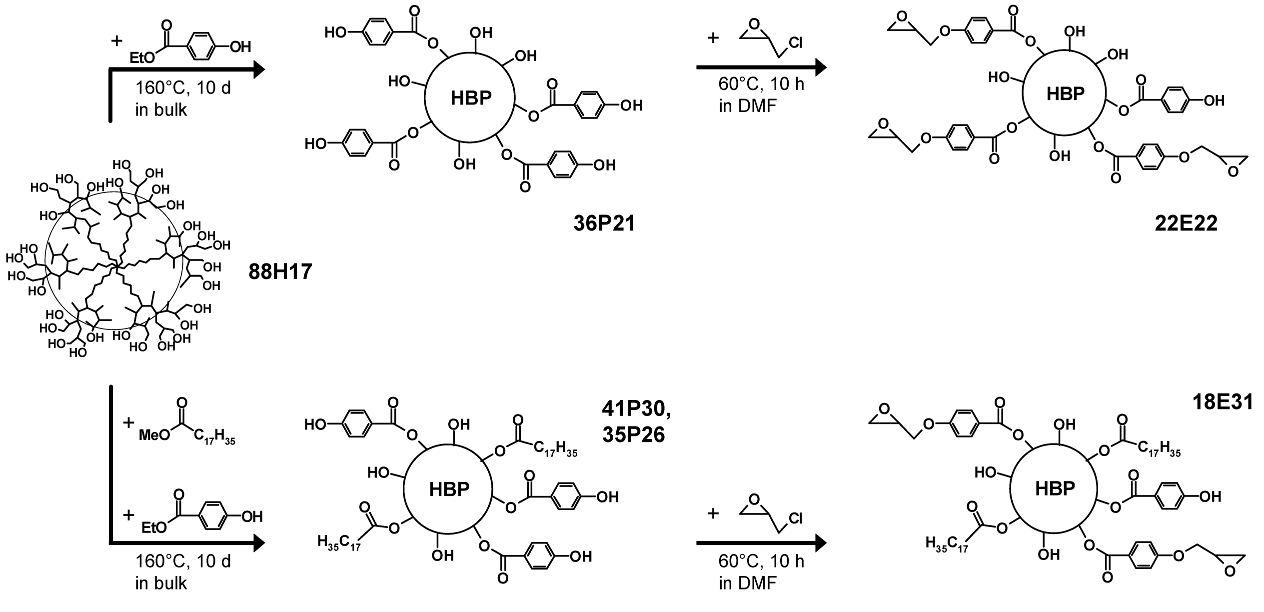

Fig. 2. Reaction scheme: post-polymerization functionalization of hyperbranched blockcopolyethers.

both phenol groups and stearate chains. All reactions were preformed in bulk at elevated temperatures and at hydroxy conversion lower than 100%. Epoxy end groups were introduced by reacting the phenolic end groups with epichlorohydrin in DMF in the presence of potassium carbonate. This one-pot multistep process have yielded hyper-branched blockcopolyethers containing reactive epoxy as well as phenol end groups for 22E22 and additional stearate chains for 18E31.

The functional hyperbranched blockcopolyethers were characterized by means of ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of 88H17, 41P30 and 18E31 are exemplified in Fig. 3. Table 1 lists the different NMR signals and their assignments. The hyperbranched blockcopolyether 88H17 shows two distinct peak groups: (a) represents the polyether backbone with methylene and methine groups next to oxygen atoms; (b) is caused by the methyl protons of propylene oxide units, situated in the core as well as in the outer shell of the HBP. In the spectrum of 41P30, the signals (d–g) represent different parts of the stearate chains as a result of the modification step with methyl stearate. The

Table 1
Assignments of the ^{1}H NMR signals of the hyperbranched blockcopolyether and its derivatives prepared by means of end group conversion

Assignment	Chemical shift (ppm)	Integration (number of H)	Moiety
a	3.50	630	OCH_2; OCH (polyether)
b	0.96	440	CH_3 (PO units)
c	4.93	32	COOCH (end group)
d	2.20	65	OOCCH_2 (α-alkyl)
e	1.52	64	CH_2 (β-alkyl)
f	1.17	960	CH_2 (alkyl-chain)
g	0.80	100	CH_3 (ω-alkyl)
h	7.83	74	o-phenylen
h′	6.80	72	m-phenylen
i	5.14	36	COOCH (end group)
j	3.86	37	OCH_2 (glycidyl)
k	2.82	18	OCH_2 (epoxy ring)
k′	2.68	17	OCH_2 (epoxy ring)

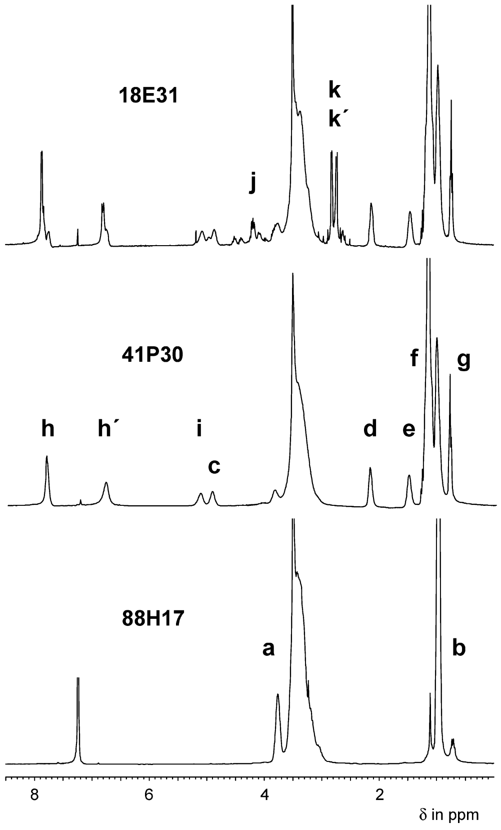

Fig. 3. ^{1}H NMR spectra of the unmodified hyperbranched blockcopolyether (88H17) and its derivatives: 41P30 contains stearate and phenol end groups which are converted with epichlorohydrin to afford the epoxy-functionalized hyperbranched copolyether 18E31.

formation of ester linkages between the hydroxy end groups and the stearate is demonstrated by signal (c). Signal (i) thus represents the ester linkages established between the hydroxy end groups and the benzoate in the second transesterification step. Moreover, the phenylene groups incorporated by the transesterification with ethyl 4-hydroxy benzoate account for both signals (h) and (h′), due to the protons in ortho- and meta-position, respectively. The conversion of the transesterification reactions and hence the number of stearate chains as well as phenol end groups attached to the hyperbranched backbone was calculated from the integrals of the corresponding ^{1}H NMR signals. The integral values are listed in Table 1. Conversions and the number of end groups of the functional HBPs are summarized in Table 2. Epoxidation with epichlorohydrin yields the signals (j), (k) and (k′) caused by the methylene group and the two diastereotopic protons of the glycidyl ether group. Since the integrals from the ^{1}H NMR spectrum overlap with signals of residual DMF, integration of an inverse-gated ^{13}C NMR spectrum was used to determine the degree of epoxidation and the resulting number of epoxy groups. Therefore, Table 1 lists only the idealized integral values for the protons of the epoxy ring, whereas the actual number of epoxy end groups of the various HBPs based on the ^{13}C NMR data is listed in Table 2.

The molecular weights of the functional hyperbranched blockcopolyethers recorded in Table 2 have been calculated by NMR from the molecular weight of the polymeric scaffold, taking into account the gain in molecular weight by the modification of the end groups. GPC over-estimates the molecular weight of the phenolic HBPs by about 100%, as already explained earlier for the unmodified polyglycerol. The change in polarity by the incorporation of stearate chains alters the interactions of the polymers with the GPC column, though, now resulting in under-estimated molecular weights for 35P26, 56H25 and 41P30, respectively. This behaviour was already found in previous works upon examination of various copolymers of glycidol and non-polar glycidyl ethers [33]. Due to the random character of the transesterifications of the polymers, the polydispersities of the functionalised blockcopolyethers are higher than for the corresponding polyglycerol precursor. Furthermore, the partially epoxidized polymers 22E22 and 18E31 tend to crosslink by intermolecular reactions between their epoxy and phenol end groups, thus rendering GPC measurement more difficult.

The low molecular weight six-arm star poly(propylene oxide-block-ethylene oxide) with epoxy end groups (sample 6E4) was prepared in analogous manner for comparison purposes and has been modified in high yields because there exists much less steric hinderance between the end groups. Taking into account the manufacturer data, the epoxy-functional HBP Boltorn E1 by Perstorp appears to possess a rather well-defined architecture (Fig. 4). Burgath demonstrated, however, that the hyperbranched structure of Boltorn E1 is somehow idealistic [34]. Its epoxy groups result from esterification of the hydroxy end groups with epoxidized fatty acids [35].

The functional polymers were further analyzed with respect to glass transition and viscosity. The results are displayed in Table 3. All polymers prepared are viscous liquids at ambient temperature with T_g in the range of -60 to -4 °C, whereas the viscosities differ strongly from 4050 mPa s for the epoxy functionalized six-arm star PPO 6E4 to about 3,200,000 mPa s for the phenol functionalized HBP 35P26 bearing additional alkyl chains. The highest

Table 2
Properties and reaction conditions of hyperbranched polymers used as epoxy modifiers

Sample	6H3	6E4	88H17	36P21	22E22	35P26	56H25	41P30	18E31	E1
M_n (g/mol)[a]	3300	4300	17,100	21,400	22,600	26,300	25,500	30,500	31,200	10,500[c]
M_n (g/mol)[b]	18,600	16,500	57,000	31,300	45,400	11,600	1,300	11,300	n.d.	2500
(M_w/M_n)[b]	1.1	1.3	3	4	5	5	5	4	n.d.	4
OH-functionality (mol/mol)	6	0	88	52	52	34	56	15	15	1[b]
OH-concentration (mmol/g)	1.82	0	5.15	2.43	2.30	1.29	2.20	0.49	0.48	0.10
Alkyl-functionality (mol/mol)	0	0	0	0	0	19	32	32	32	31
Alkyl-concentration (mmol/g)	0	0	0	0	0	0.72	1.25	1.05	1.03	2.95
Conversion to stearate (%)	–	–	–	–	–	90	100	–	–	97
Phenol-functionality (mol/mol)	0	0.6	0	36	14	35	0	41	23	0
Phenol-concentration (mmol/g)	0	0.14	0	1.68	0.62	1.33	0	1.34	0.74	–
Conversion to benzoate (%)	–	(100)	–	84	–	81	–	100	–	–
Epoxy-functionality (mol/mol)	0	5.4	0	0	22	0	0	0	18	11[b]
Epoxy-concentration (mmol/g)	0	1.26	0	0	0.97	–	0	0	0.58	1.05
Epoxy conversion of phenol (%)	–	90	–	–	61	0	–	–	44	–

[a] By ^{1}H and ^{13}C NMR.

[b] By DMF-GPC.

[c] Manufacturer data.

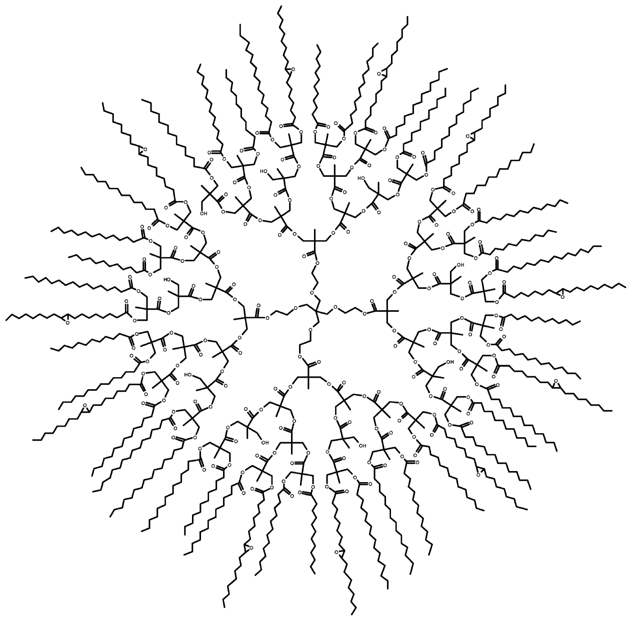

Fig. 4. Idealized chemical structure of Boltorn E1 according to manufacturer data.

glass transition temperatures as well as elevated viscosities were observed for the samples 36P21 and 41P30. Obviously, the many intermolecular hydrogen bonds formed between the numerous phenol groups of the polymers are responsible for these properties. Upon epoxidation of the HBPs, T_g and viscosity of the materials are lowered as the phenol end groups are converted to glycidyl ethers. The viscosities of mixtures of 5 wt% of polymer dissolved in the epoxy resin are only slightly higher than the viscosity of the neat epoxy/hardener mixture at the typical processing temperature of 80 °C. Compared to 69 mPa s for the neat resin, the viscosities of the mixtures are increased by about 20% to values around 80 mPa s.

Table 3
Glass transition temperatures of hyperbranched blockcopolyethers and their solution viscosities in uncured epoxy resins containing 5 wt% of the modifier

Sample	T_g (°C)[a]	Viscosity (mPa s)[b]	Resin-viscosity (mPa s)[c]
6H3	−58	500	77
6E4	−48	1170	69
88H17	−45	26,740	89
36P21	−4	>3,000,000	82
22E22	−40	n.d.	n.d.
35P26	−44	3,200,000	72
56H25	−24	8790	93
41P30	−7	293,000	84
18E31	−57	10,910	n.d.
E1	−49	17,400	81

[a] by DSC.

[b] by Brookfield viscosimetry at 30 °C.

[c] 5 wt%, by Brookfield viscosimetry at 80 °C (neat resin viscosity 69 mPa s); samples printed in bold letters were actually used for epoxy resin modification.

3.2. Morphology of the epoxy blends

The modified materials were prepared by mixing the bisphenol-A diglycidylether (BADGE) and the respective polymeric modifier together with the hardener hexahydrophthalic acid anhydride and casting the homogeneous mixtures into pre-heated moulds. After cure, the morphology of the materials was examined by transmission electron microscopy (TEM).

All epoxy blends comprising the epoxy functional six-arm star PPO 6E4 were transparent materials. Even the blend containing as much as 10 wt% of 6E4 displayed a homogeneous morphology when examined by TEM as shown in Fig. 5a. The epoxy resins containing the functionalised hyperbranched blockcopolyethers 36P21 and 22E22 were transparent materials as well. In the TEM images, however, small particles of around 7 nm size can be observed (Fig. 5b). Addition of the modified hyperbranched blockcopolymer 18E31 to the epoxy resin resulted in opaque materials with large spheres of about 12 μm dispersed in the matrix (Fig. 5c). The epoxy blends with Boltorn E1 are similarly opaque, but in this case the dispersed spheres possess diameters of about 200 nm. This is the case for all different blends which contain E1, even with high loadings up to 10 wt% (Fig. 5d). In contrast to the functionalized polymers mentioned above, these two modifiers bear additional non-polar alkyl chains which are responsible for phase separation during cure. The hyperbranched block copolyether 35P26 bearing alkyl chains as well as phenol end groups, however, does not phase-separate during cure. Even prolonged gelling at 80 °C prior to cure results in a homogeneous morphology. Thus, we conclude that hyperbranched blockcopolyethers with a polar polyglycerol core appear to be soluble in the uncured as well as in the cured epoxy resin, regardless of their end group functionalization. Clearly, the particularly high solubility of such polyethers represents a drawback for the use of these materials as epoxy tougheners because extensive matrix flexibilization is likely to occur. The high molar mass and the aggregation tendency of 18E31, is most probably the reason for the formation of larger phase-separated particles upon addition to the epoxy resins. Heiden et al. reported the formation of single-phase blends when employing hydroxy functional Boltorn polyesters for the toughening of epoxy resins [33]. In contrast to the epoxy-functional Boltorn E1, the HBP Heiden used consisted solely of the unmodified polyester made from 2,2-bis(hydroxymethyl)propionic acid. Boltorn E1, however, bears epoxidized alkyl chains of variable length at every end group and is thus non-polar. Therefore, it phase-separates readily during cure, but is not fully miscible in the uncured resin.

3.3. Dynamic mechanical properties

DMA measurements of the epoxy resins revealed lower glass transition temperatures (T_g) for almost all the samples.

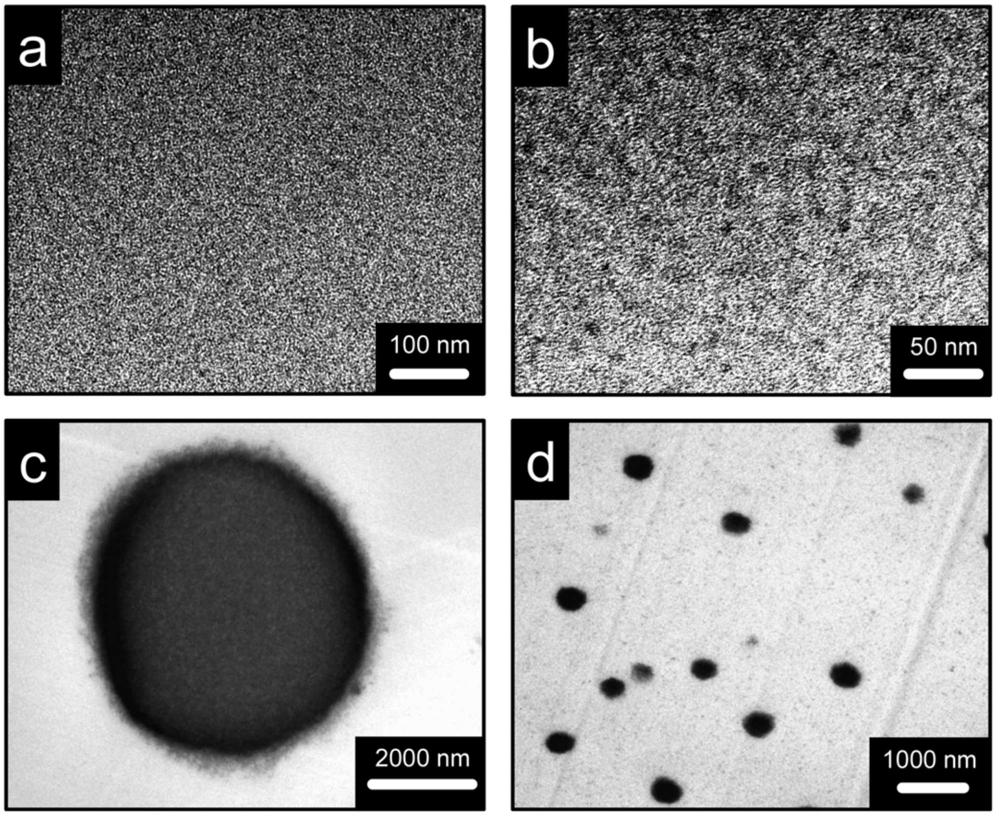

Fig. 5. Transmission electron micrographs of epoxy resins modified with hyperbranched blockcopolyethers and the epoxy-terminated hyperbranched polyester Boltorn E1 (after staining with RuO_4): (a) 10 wt% 6E4, (b) 5 wt% 22E22, (c) 5 wt% 18E31 and (d) 10 wt% Boltorn E1.

Compared to the matrix T_g of 125 °C, the blend T_gs decreased with increasing content of the respective hyperbranched polymer. The lowered T_gs of the blends are due to the low glass transition temperatures of the polymeric modifiers (Table 3) and matrix flexibilization due to the absence or incomplete phase separation during cure. Fig. 6 demonstrates that the glass transition temperatures of the blends with functionalized HBPs are almost unaltered, compared to the neat resin, whereas the T_g of the epoxy resin modified with the epoxy functional six-arm star PPO drops with increasing modifier content. Epoxy resins modified with 35P26, however, possess slightly higher T_gs than the unmodified resin. The small increase of the glass transition temperature is due to the different cure cycle which contains an additional pre-gelling step at 80 °C for 18 h prior to cure (at 120 and 140 °C). Also, it should be noted that epoxy groups can attribute to higher crosslink densities.

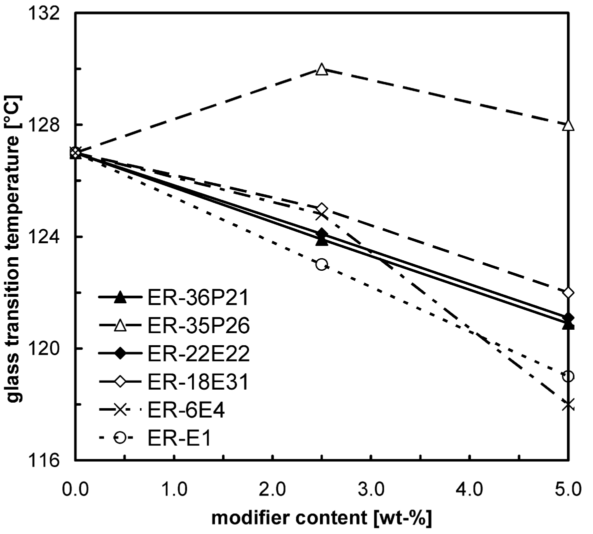

Fig. 6. Influence of modifier type and content on the glass transition temperature of the cured epoxy blends.

3.4. Mechanical properties

The mechanical properties of the epoxy blends containing the various functional polymers were examined by means of tensile testing. Fracture toughness was elucidated in bend-notch geometry.

The tensile moduli of the modified blend materials are generally slightly lowered by the incorporation of the liquid hyperbranched modifiers. Fig. 7 demonstrates a general decrease of about 10% resulting in values around 3000 MPa at 2.5 wt% as well as at 5 wt% loading. Due to its coarse phase structure, the blend containing the functional hyperbranched blockcopolymer 18E31 possesses a significantly lowered stiffness. The tensile strength of all blends, however, is not affected by the addition of the functionalised

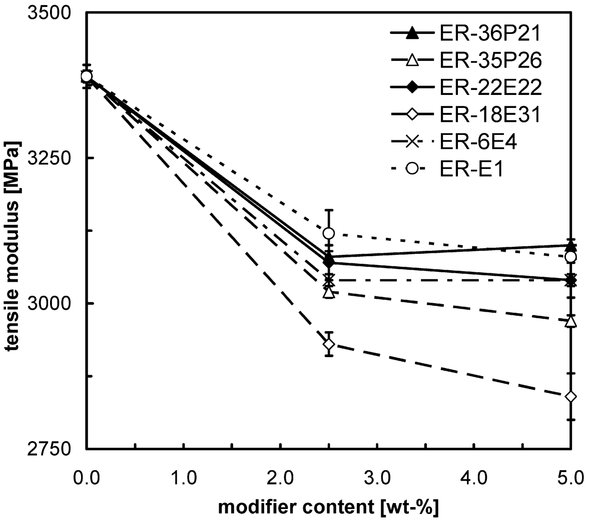

Fig. 7. Tensile modulus of the epoxy blends as a function of the polymeric modifier content.

hyperbranched polymer modifiers. Furthermore, the elongation at break is only slightly lowered when incorporating any of the functionalised polymer modifiers tested.

The fracture toughness of the various blends was measured by means of the critical stress intensity factor K_{Ic}. The transparent materials comprising the homogeneously dissolved functionalized polymers exhibit an almost unaltered toughness with increasing modifier content (Fig. 8). The K_{Ic}-values do not exceed 0.7 MPa m$^{1/2}$ compared to 0.67 MPa m$^{1/2}$ for the neat resin. No difference in the toughening behaviour between the functional six-arm star PPO and the hyperbranched blockcopolymer was detected for the single phase blends. These results are in agreement with observations reported by Heiden et al. on hydroxy-terminated hyperbranched Boltorn polyester in single-phase epoxy blends [33].

The phase-separated blend containing the hyperbranched blockcopolymer 18E31 shows a slight increase in toughness by about 10%. The most successful toughening, however, is achieved when the hyperbranched Boltorn E1 polyester containing epoxidized fatty acid ester end groups is used as modifier of the epoxy resin. The K_{Ic}-value of the blend is improved by 50% compared to the neat resin, using only 5 wt% of the modifier. The enhanced toughening effect originates from the phase-separated morphology with particle sizes of about 200 nm. In general, an optimal particle size can be found for each polymer toughened by liquid rubber particles. The most efficient particle diameters reported for rubber toughened epoxies range between 100 nm and 10 μm, regardless of the chemistry of the modifier [36]. Particles with larger diameters than the maximum value can only contribute to crack bridging, which is a less effective toughening mechanism than the shear yielding initiated by smaller particles [37]. Only in a few cases, interconnected rubber particles with average diameters below 100 nm have been reported to act as efficient stress concentrators and thus are responsible for toughened materials [38,39].

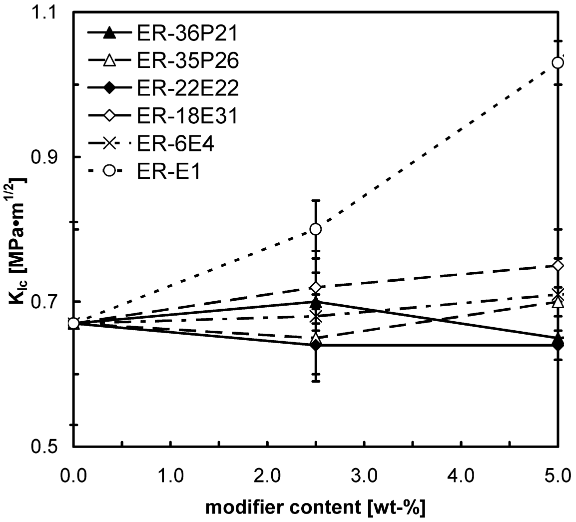

Fig. 8. Fracture toughness, measured as the stress intensity factor K_{Ic}, of the epoxy blends as a function of the polymer modifier content.

4. Conclusions

The one-pot synthesis of hyperbranched blockcopolyether using a six-arm star poly(propylene oxide-block-ethylene oxide) as polyfunctional initiator for gylcidol and propylene oxide graft copolymerization represents a very versatile route to novel hyperbranched copolyether liquid rubber. Characteristic feature of such an onion-like molecular architecture is the presence of an inner polyglycidol block, which gives control on the degree of branching and the resulting end group functionality at the surface of these nanometer-scaled molecular particles. The glycidol addition has increased the number of hydroxy end groups from 6 to 88 mol/mol. Polarity design was performed by means of grafting propylene oxide onto the hyperbranched core and by post-polymerization esterification with stearate and 4-hydroxy benzoate. The reactivity was modified by converting hydroxy end groups into phenol and the corresponding epoxy groups via glycidyl ether formation employing the epichlorohydrin conversion reaction. In spite of high molecular weights of 17,100 g/mol, polarity design afforded good solubility in the uncured epoxy resin. Characteristic feature of all hyperbranched polyesters, polyethers and blockcopolyethers are very low viscosities, similar to that of the neat resin/hardener mixture, at a modifier content of 5 wt%. This is quite advantageous with respect to epoxy processing. Linear polymers of the same molecular weight and polarity give much higher viscosities of the uncured blend which is much more difficult to process. Matching polarity and compatibility between hyperbranched polymers and the epoxy resin is an important requirement to achieve rubber phase separation and interfacial adhesion during cure. Single phase blends and blends containing dispersed discrete nanophases with average diameter below 10 nm fail to enhance toughness and stiffness, although only slightly reduced glass temperatures are observed, as expected for matrix flexibilization. Only the hyperbranched blockcopolyether carrying epoxy, phenol and stearate end groups afforded phase separation of fairly large rubber microparticles with an average diameter around 12 μm. Epoxy-terminated polyesters containing epoxidized fatty esters as end groups give polyester phases with an average size of 200 nm and more effective performance as stress concentrators. More research is required to identify the suitable compatibility match for hyperbranched copolyethers. The versatile synthetic route to hyperbranched blockcopolyether liquid rubbers, combining ring-opening oxiran copolymerization with post-polymerization functionalization offers new opportunities of fine tuning the liquid rubber molecular and to improve the understanding of correlations between liquid rubber molecular design and micromechanics of their epoxy blends.

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