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New hyperbranched polyether containing cyclic carbonate groups as a toughening agent for epoxy resin

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Abstract

Hyperbranched polyglycerol containing terminal five-membered cyclic carbonate groups has been obtained by anionic polymerization of glycidol and then in the reaction of its terminal vicinal hydroxyl groups with dimethyl carbonate in the presence of potassium carbonate. The remaining OH groups of the polymer were protected in the reaction with acetic anhydride to reduce polymer hydrophilicity and increase miscibility with the epoxy resin. A strong decrease in viscosity was observed after esterification, from 73 to 3.6 Pa s. The product (HBPG **3**) was used for modification of the bisphenol A based epoxy resin. The epoxide–cyclic carbonate compositions were cured using a polyamine hardener (TETA) in a one-step procedure. Thermal and mechanical properties of the cured compositions were characterized and compared with the parent epoxy resin. The optimal mechanical properties were obtained for the compositions containing HBPG **3** when phase separation takes place. The mechanical properties are discussed in terms of the morphology observed by SEM.

Keywords: Hyperbranched polyglycerol; Modified epoxy resin; Phase separation

1. Introduction

Epoxy resins combine attractive properties such as high strength and good dimensional, thermal and environmental stabilities. They also exhibit good thermomechanical properties and excellent processability [1]. The main disadvantage associated with the application of these highly crosslinked thermosetting polymers is related to their inherent brittleness, which increases with crosslink density [1].

The application of epoxy thermosetting materials is limited by their poor toughness properties, which affect the durability (impact strength, fatigue behavior, damage tolerance). To eliminate this, tougheners are usually added. Commercial tougheners such as rubber, thermoplastic or glass particles can affect the resin T_g to various degrees, but they always limit the processability of the resin systems and can be filtered out during impregnation of the composite fiber structure [2].

Hyperbranched polymers (HBP) and dendrimers have a high potential as additives and modifiers in engineering materials [2]. However, the synthesis of dendrimers often involves tedious multiple steps of protection/deprotection procedure and complicated purification. For these reasons they are not commonly used. In contrast to dendrimers, hyperbranched polymers can be prepared according to a one-step synthetic procedure [3].

The specific advantages of the hyperbranched polymers and their influence on mechanical properties in the modification of thermoset resin systems have been discussed in detail by Månson et al. in Ref. [2].

Several HBP systems have already been applied for modification of epoxy resins. In most cases the authors use commercially available materials [2,4–11] or present low cost synthetic pathways to the new hyperbranched polymers [12–16]. A majority of HBPs contains ester linkages, both aliphatic and aromatic ones. Examples of polyether branched structures

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are relatively rare [17]. The outer sphere of the macromolecules usually consists of hydroxyl [2,8,9,11], phenolic [18], alkyl [2,19] or epoxy groups [2,10,13,17]. In the literature described systems HBP/epoxy were mostly cured with multifunctional amines or cyclic anhydrides. However, there were also examples of the cationic photopolymerizations [18,19]. The HBP/epoxy mixtures can form fully soluble systems or show phase separation during the curing process, showing more efficient toughening properties [2,20].

Only few HBPs form a separate phase during cure, especially those containing long non-polar alkyl chains. However, they are not fully miscible with the uncured epoxy resin [8].

Five-membered cyclic carbonates can readily react with primary amines forming β-hydroxyurethanes [21]. The transesterification of 1,2-diols with ethylene carbonate or dialkyl carbonate is a convenient method of obtaining cyclic carbonate derivatives [22]. The other, very effective method is the addition of carbon dioxide to an epoxide in the presence of KI and crown ether [20]. Recently, cyclic carbonate derivatives of soybean oil have been successfully applied for the toughening of epoxy resins [20].

The objective of this work was the synthesis of a new hyperbranched polyether containing cyclic carbonate functionalities and the use of it for the modification of diglycidyl ether of bisphenol A (DGEBA). In our approach, the cyclic carbonate synthesis was carried out under mild conditions without any solvent, using HBPG and dimethyl carbonate. The effect of cyclic carbonate–HBPG content on the curing behavior, as well as thermal and mechanical properties of the epoxy resin/HBPG composition has been studied and discussed.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) (Epidian 5 of EN = 0.49 val/100 g) was purchased from Organika Sarzyna S.A. (Poland). Acetic anhydride, dimethyl carbonate, glycidol, potassium, trimethylolpropane (TMP) and triethylenetetraamine (TETA) were purchased from Aldrich. Tetrahydrofuran was distilled prior to use over potassium benzophenone ketyl. All the chemicals were used as received.

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard. FTIR spectra were recorded on a Biorad FT-IR Spectrometer FTS165. Mechanical properties were determined on Instron 5566. The Brinell hardness tests were performed using a 10 mm diameter hardened steel ball with a 600 N load applied for a period of 15 s. Glass transition temperature (T_g) was calculated from the inflection point in the break in the heat flow curves. DSC studies were performed over the temperature range from −100 °C to +120 °C using a Perkin Elmer Pyris 1 calorimeter at a heating rate of 20 °C/min for samples of 10–25 mg mass. Scanning electron microscopy (SEM) was done using a LEO 1530 apparatus (at 20 kV). SEM specimens were etched and carbon coated. Viscosity of the branched polymers was measured using the Mettler RM180 rheomat at 40 °C with shear rate 9.9 1/s and at 70 °C with shear rate 99 1/s. Measurements of the molecular weight were performed with GPC LabAlliance apparatus using water (HBPG **1**, HBPG **2**) or chloroform (HBPG **3**) as an eluent at 35 °C using poly(oxyethylene) glycol (HBPG **1**, HBPG **2**) or polystyrene (HBPG **3**) for the calibration.

2.3. Mechanical properties tests

Tensile strength was measured on dumb-bell shaped type IV samples according to standard ASTM D-638. The samples were obtained by the die-casting method. Measurements were carried out at ambient temperature using a constant crosshead speed of 2 mm/min and the gauge length of 45 mm. Minimum 5 specimens were tested in each case to obtain an average value. Flexural strength was measured with samples of $120 \times 5 \times 2.5$ mm^3 according to the standard ASTM D-790, using the same machine at a crosshead speed 2 mm/min. The flexural strength was performed using a 3-point bending method. In this work the flexural strength was reported as the load at yield measured at 5% deformation of the outer surface for the samples that did not break or at break. Impact resistance of the samples was determined by a Charpy impact strength method (ASTM D-256, Method B). Results are presented as the energy to break per fractured area.

2.4. Epoxy number (EN) and carbonate groups content determination

The epoxy number was determined by standard titration with hydrogen chloride in dioxane [23]. The results were calculated and corrected accordingly to the results of titration of phenyl glycidyl ether as a standard sample.

The molar content of carbonate groups in HBPG **3** was calculated from calibration curves obtained for propylene carbonate and ethyl acetate. The calibration curves were prepared for chloroform solutions in the range of 0.005–0.3 mol/dm^3 at 1800 cm^{-1} for propylene carbonate and 1736 cm^{-1} for ethyl acetate.

2.5. Preparation of hyperbranched polyglycerol *1*

HBPG **1** was prepared by a modified procedure previously reported by Sunder et al. [24]. In a 750 ml three-neck flask equipped with a magnetic stirrer, nitrogen inlet and distillation condenser 50 g (0.373 mol) of TMP followed by 4.4 g (0.112 mol) of potassium was placed. The mixture was stirred at 60 °C under nitrogen for 1 h until potassium dissolved in the reaction mixture. The temperature was increased to 95–100 °C. The solution of glycidol (96%) 288 g (3.70 mol) in 1000 ml of dry THF was then introduced with the rate of 30 ml/h by an infusion pump (Ascor Ap22). The remains of THF were removed under vacuum leaving 310 g (92%) of the HBPG **1** as pale yellow viscous oil.

The ^{1}H NMR and FTIR data of **1** match the characteristics given in Ref. [24].

2.6. Reaction of HBPG 1 with dimethyl carbonate

To a 1000 ml three-neck flask equipped with a magnetic stirrer, reflux condenser and thermometer, 423 g (5.29 mol of hydroxyl groups) of HBPG **1** was added followed by 133 g (1.48 mol) of dimethyl carbonate and 9.85 g (0.07 mol) of K_2CO_3. The reaction mixture was stirred at 80 °C for 5.5 h. When the absorption band at 1755 cm^{-1} corresponding to linear carbonate groups in the FTIR spectrum disappeared, methanol and unreacted dimethyl carbonate were removed under reduced pressure. The remaining oil was taken up into dichloromethane and potassium carbonate was filtered off. Evaporation of the solvent yielded 536 g (96%) of light yellow oil of HBPG **2** with cyclic carbonate terminal groups.

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 4.91 (br s, CH_{2cyc}), 4.73 (br s, OH), 4.51 (br s, CH_{2cyc}), 4.27 (br s, CH_2CHCH_{2cyc}), 3.9–3.1 (m, OCH and OCH_2 in hyperbranched structure), 1.25 (br s, CH_3CH_2), 0.78 (br s, CH_3CH_2). FTIR (KBr) (cm^{-1}) = 3380 (OH), 2878 (CH), 1791 ($C{=}O_{cyc}$), 1100 (C–O–C).

2.7. Protection of remaining hydroxyl groups in the HBPG 2

In a one-neck 1000 ml flask equipped with a magnetic stirrer and reflux condenser 411 g (approx. 2.9 mol of hydroxyl groups) of HBPG **2** was dissolved in 440 g (4.3 mol) of acetic anhydride. The catalyst – anhydrous zinc chloride (1.64 g, 12 mmol) was added and the reaction mixture heated overnight at reflux. Then the post-reaction mixture was cooled down, and acetic anhydride as well as acetic acid was removed under vacuum. The remaining oil was taken up into dichloromethane, washed with 20% $K_2CO_{3\ aq}$ and with brine, dried with magnesium sulfate and evaporated to dryness. The reaction yielded 516.8 g (96.5%) of HBPG **3**.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.15–4.95 (m, CH_{2cyc}), 4.76 (br s, OH), 4.44 (br s, CH_2CHCH_{2cyc}), 4.23 (dd, CH_2CHCH_{2cyc}, $J_1 = 3.3$ Hz, $J_2 = 11.7$ Hz), 4.05 (dd, CH_2CHCH_{2cyc}, $J_1 = 6.4$ Hz, $J_2 = 11.7$ Hz), 4.0–3.1 (m, hyperbranched structure), 2.00 (s, CH_3CO), 1.99 (s, CH_3CO), 1.32 (br s, CH_3CH_2), 0.78 (br s, CH_3CH_2). FTIR (KBr) (cm^{-1}) = 2877 (CH), 1800 ($C{=}O_{cyc}$), 1741 ($C{=}O_{ester}$), 1107 (C–O–C).

2.8. Curing of epoxy/HBPG compositions

In each experiment a sample consisted of commercial epoxy resin Epidian 5, HBPG **3** and polyamine curing agent (TETA). The curing process was performed by a one-step method. The epoxy resin was mixed with HBPG **3**, heated at 80 °C for 15 min and then the amine was added. After mixing, the resulting composition was degassed and poured into a steel mold, degassed again and cured at room temperature for 12 h and then heated at 80 °C for 2 h. Table 1 shows the composition of the epoxy/HBPG mixtures and corresponding amounts of curing agent.

Table 1
The composition of the investigated HBPG/epoxy samples and the corresponding amounts of TETA used for curing

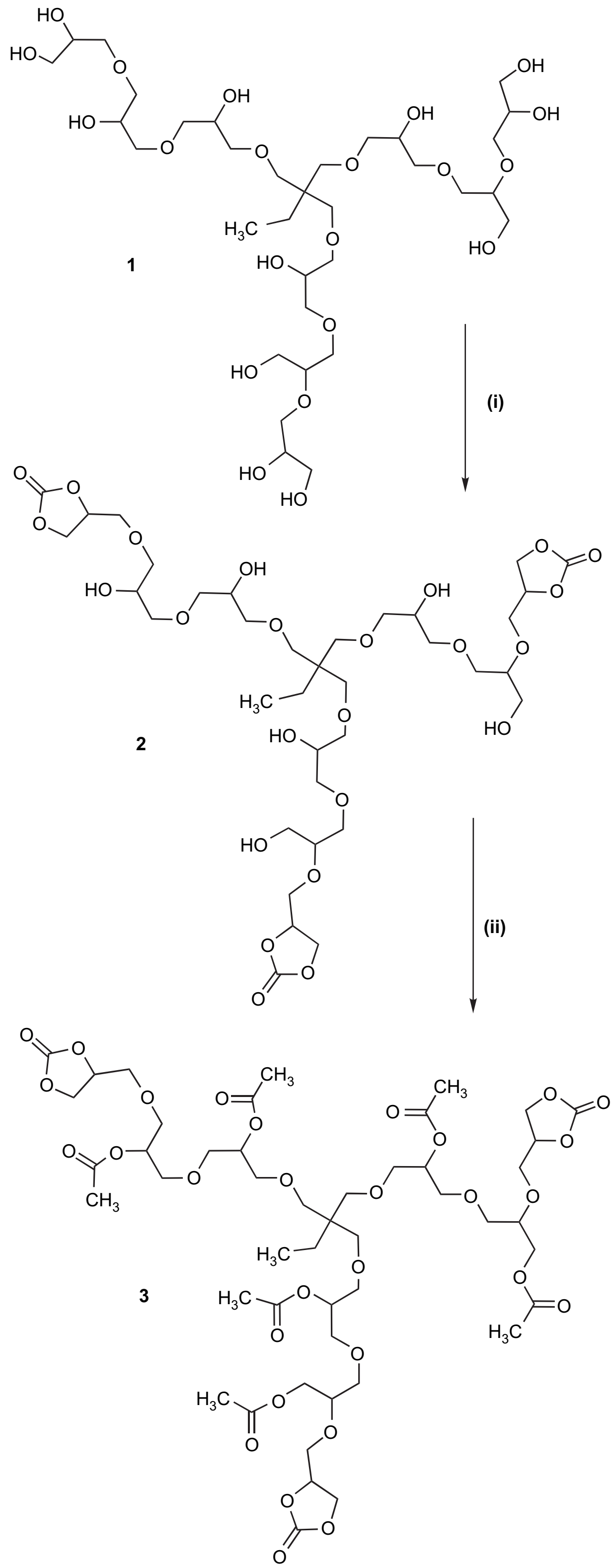
Sample	HBPG **3** [g]	DGEBA – Epidian 5 [g]	TETA [g]
			Equimolar TETA amount
1	0	60	7.14
2	6	54	6.76
3	12	48	6.38
4	24	36	5.63
			10% TETA excess
5	6	54	7.44
6	12	48	7.02
7	24	36	6.19
			20% TETA excess
8	6	54	8.11
9	12	48	7.66
10	24	36	6.75
			25% TETA excess
11	6	54	8.45
12	12	48	7.98
13	24	36	7.03

3. Results and discussion

3.1. Synthesis of hyperbranched polyglycerol with terminal cyclic carbonate groups

The hyperbranched polyglycerol (HBPG **1**) presents a good base for further modifications due to the simplicity of the synthesis and dendrimer-like properties. It was synthesized by anionic polymerization of glycidol, according to the modified procedure reported by Sunder et al. [24]. As the core of the molecule, partially deprotonated trimethylolpropane was used.

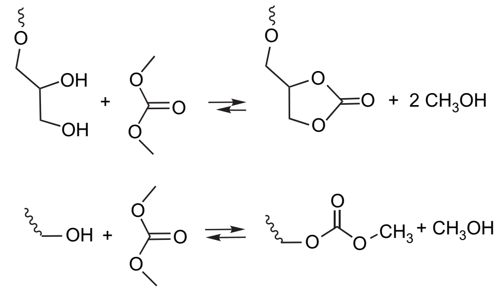
Further modification consisted in the optimization of the reaction of HBPG **1** with dimethyl carbonate (DMC) to introduce the cyclic carbonate groups to the molecule and esterification of the remaining hydroxyl groups with acetic anhydride (Scheme 1). The reaction of the HBPG **1** with dimethyl carbonate was carried out at 75–80 °C in the presence of a catalytic amount of potassium carbonate. At the beginning both cyclic and linear carbonates are present in the reaction mixture (Scheme 2). As the cyclic product is thermodynamically more stable and the formation of linear product is reversible, it is possible to obtain HBPG **2** containing solely cyclic carbonate groups. The reversibility of the formation of linear carbonate is strongly bound with the presence of methanol in the reaction mixture. Methanol generated in the reaction is kept in the reaction flask by the reflux condenser. The reaction progress was monitored by FTIR spectroscopy controlling the absorption bands at 1791 cm^{-1} characteristic for the cyclic carbonate and 1750 cm^{-1} characteristic for the linear carbonate groups. The optimized reaction mixture consisted of HBPG and DMC in which the molar ratio of the hydroxyl groups to the DMC was equal 4.25 to 1. The removal of methanol and the remains of DMC from the reaction mixture yielded the product HBPG **2** containing cyclic carbonates in the outer sphere



Scheme 1. Synthesis of carbonated hyperbranched polyglycerol. (i) DMC, K_2CO_3, (ii) $(CH_3COO)_2O$, $ZnCl_2$.

and free hydroxyl groups inside the sphere of the branched molecules.

Fig. 1 shows the ^{1}H NMR spectrum of HBPG **2** containing cyclic carbonate and OH groups. In the range of 5.0–4.0 ppm the signals of the protons of a cyclic carbonate ring can be clearly seen. The single proton of the substituted carbon atom of the ring appears as a multiplet at 4.27 ppm. The methylene group protons of cyclic carbonates appear in the spectrum as a set of two pairs of doublets located at 4.91 and 4.51 ppm. The signals of the CH_2 groups attached to the ring are overlapped by a strong multiplet corresponding to protons of the hyperbranched structure in the range of 4.0–3.0 ppm. There are also signals of the hydroxyl protons at 4.73 ppm and the signals at 1.25 and 0.78 ppm which can be assigned to the protons of the core TMP. The amount of cyclic carbonate and free hydroxyl groups was estimated from the ^{1}H NMR spectrum to be in average 2.5 cyclic carbonates and 8 hydroxyl groups per molecule. The ^{13}C NMR spectrum shows the carbonyl carbon signals at 158 ppm.



Scheme 2. Formation of cyclic and linear carbonates.

Fig. 2 shows the FTIR spectra of the starting HBPG **1** (line a), the fully substituted HBPG with linear and cyclic carbonate groups (line c) and the expected product HBPG **2** containing solely cyclic carbonate groups (line b). The absorption bands of the cyclic carbonate carbonyl groups appear at 1791 cm^{-1}, whereas the linear carbonate groups appear at 1750 cm^{-1}. It is to underline that the products represented by the spectra b and c can be easily converted to each other according to Scheme 3.

The final step of the modification was the reduction of hydrophilicity of the obtained molecules. The HBPG **1** and HBPG **2** are not miscible with the epoxy resin. To achieve effective toughness improvement of the HBPG/epoxy resin, the polymeric additive must be soluble and precipitate during the curing process in the form of nano- or microparticles. In case of heterogeneous systems obtaining evenly distributed

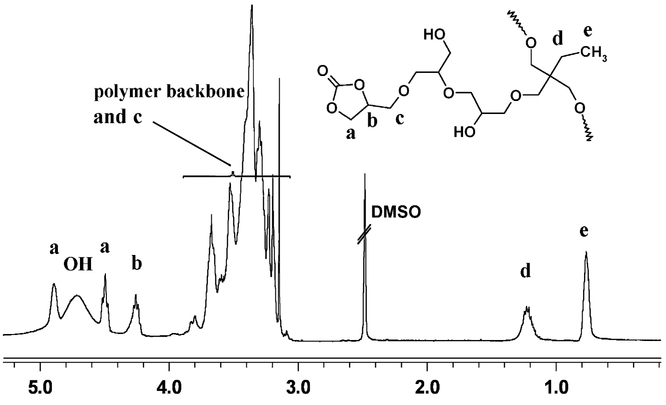


Fig. 1. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of the HBPG **2**.

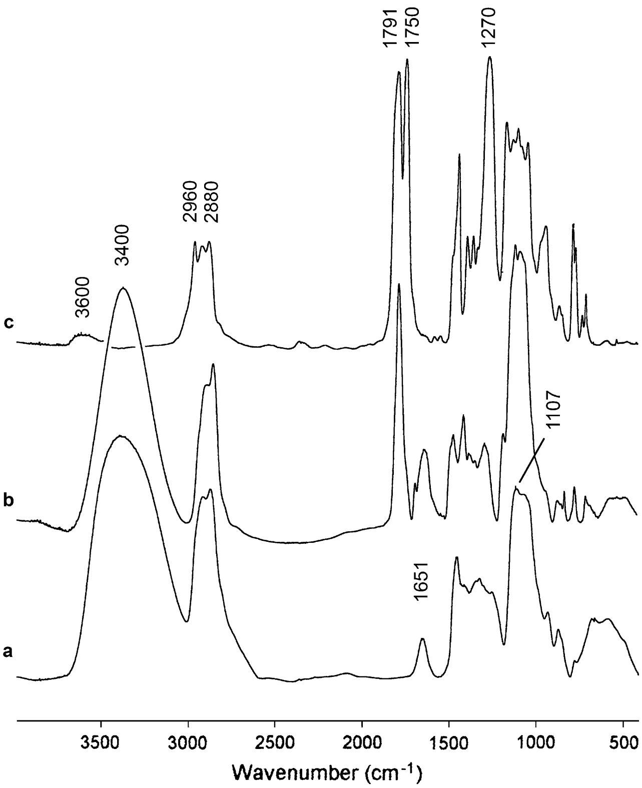
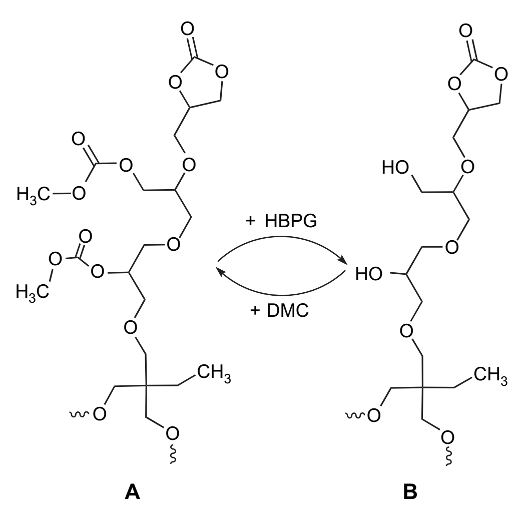


Fig. 2. FTIR spectra of the HBPGs: (a) HBPG **1** before the modification, (b) HBPG **2**, (c) HBPG containing both linear and cyclic carbonate groups.

nanoparticles is highly questionable. This goal has been achieved by the reaction of the remaining OH groups of HBPG **2** with acetic anhydride.

In the ^{1}H NMR spectrum of HBPG **3** additional signals at 2 ppm corresponding to acetyl protons appeared indicating the substitution of residual OH groups. In the ^{13}C NMR spectrum there are signals corresponding to carbonyl carbon atoms of cyclic carbonates at 155 ppm and acetyl groups at 177 ppm.

Fig. 3 shows the FTIR spectrum of the final product HBPG **3**. The absorption bands of cyclic carbonate and acetyl carbonyl groups are present at 1800 and 1741 cm^{-1}, respectively. The absorption band characteristic for hydroxyl groups, clearly seen in the FTIR spectrum of carbonated HBPG **2**, almost disappeared in this case.



Scheme 3. Transformation between HBPG structures containing both cyclic and linear carbonate groups A and solely cyclic carbonates B (HBPG **2**).

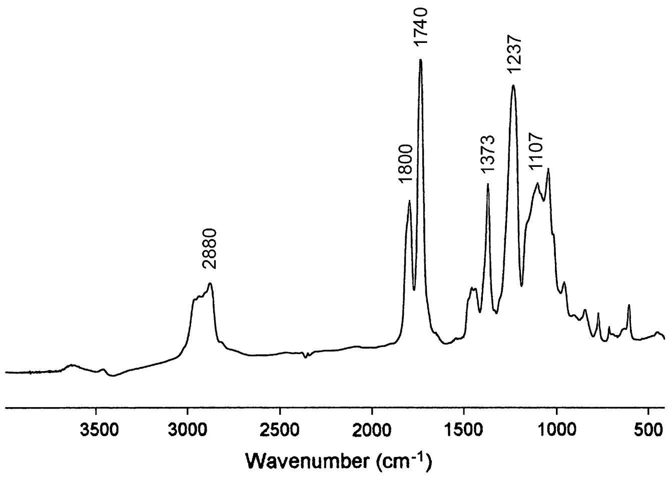


Fig. 3. FTIR spectrum of the HBPG **3**.

In addition to the spectral data, the cyclic carbonate and ester group concentrations in the final product were calculated from FTIR spectra using calibration curves (see Section 2). The data showed the concentration of 0.176 mol of cyclic carbonates per 100 g of HBPG **3**. It means that ca. 43% of the hydroxyl groups were transformed into cyclic carbonate and 57% into ester groups. Taking into account the molecular weight of the starting HBPG **1** and concentration of cyclic carbonate and acetyl groups, the average molecular weight of HBPG **3** was calculated to be ca. 1700. Such a hyperbranched oligomer contained in average 2.8 cyclic carbonate groups per molecule, which is close to the estimation made for HBPG **2** from ^{1}H NMR spectrum.

The GPC analysis of the polymers showed the molecular weights close to the calculated ones and relatively narrow dispersities (Table 2).

The high viscosity (62 Pa s at 40 °C) of HBPG **1** is the limiting property for its technical applications. A similar result of 73 Pa s was obtained for the viscosity of HBPG **2**. The increase in viscosity may be explained by the formation of stronger hydrogen bonds between carbonyl and hydroxyl groups. In contrast, HBPG **3**, due to OH group protection, shows a significant drop in viscosity down to 3.6 Pa s at 40 °C (6 Pa s at 25 °C). Thus, the viscosity of the hyperbranched oligomer with blocked hydroxyl groups was much lower than that of the epoxy resin (25 Pa s at 25 °C). This is quite advantageous with respect to epoxy resin processing. Linear polymers of the same molecular weight and polarity exhibit much higher

Table 2
The GPC characteristics of the synthesized polymers

Sample	M_n	M_w	D
HBPG **1**	1037	1390	1.34
HBPG **2**	856	1143	1.34
HBPG **3**	1282	1798	1.40

viscosity and uncured compositions containing such modifier are much more difficult to process.

The viscosity of the HBPs decrease significantly above 70 °C – at this temperature hydrogen bonding is not efficient any more. The viscosities measured at 70 °C for HBPG **1**, HBPG **2** and HBPG **3** were 5.1, 6.3 and 0.4 Pa s, respectively.

3.2. Curing of the epoxy resin/HBPG compositions with TETA

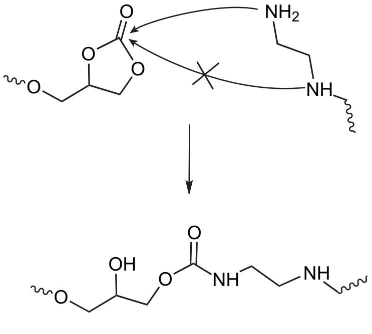
It was found that HBPG **3**, containing in a proper balance polar, lipophilic and hydrophilic functionalities, is miscible without limits with bisphenol A based epoxy resin and moreover, five-membered carbonate groups present in the oligomer **3** readily react with primary aliphatic amines [20].

Scheme 4 shows one of the possible reactions, which takes place during the curing process. The cyclic carbonate groups react with primary amine groups of the hardener leading to urethane derivatives, but do not react with secondary amines. In contrast, epoxy groups of diglycidyl ether of bisphenol A readily react with both primary and secondary amine groups.

The reaction rate of the cyclic carbonates with an amine hardener is slower than that of epoxy groups [20]. Therefore, part of the primary amine groups expected to react with cyclic carbonates reacts with epoxy groups leaving part of the carbonate groups unreacted, as can be seen in Fig. 4(b). This might result in lowered crosslinking density and decrease in mechanical strength of the sample. In contrary, the increased toughness strongly depends on the formation of microparticles, which contain unreacted and partially reacted HBPG **3**. Thus, it was reasonable to investigate the influence of the amount of TETA on the formation of the second phase and the mechanical properties of the cured compositions.

A set of the epoxy/HBPG compositions was prepared and cured with TETA. The compositions contained 10, 20 or 40 wt.% of HBPG **3**. TETA was used in an equimolar (calculated for all the epoxy and carbonate groups) amount or in excess (10–25 mol%) (Table 1).

The curing of these compositions can be performed in a one-step procedure (when all the reagents are mixed together) or a two-step method (when first HBPG **3** is reacted with the amine hardener used in an amount calculated for both epoxy and cyclic carbonate groups, then the resulting adduct is added to the epoxy resin and the curing process is continued).



Scheme 4. Formation of β-hydroxy-urethane groups in the reaction of cyclic carbonates with primary amine groups.

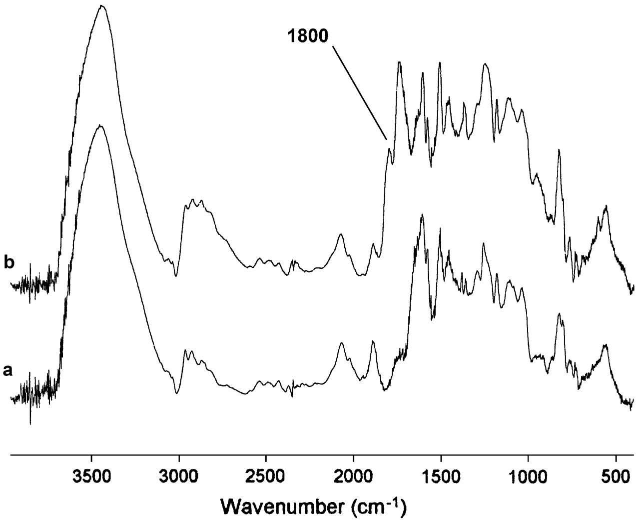


Fig. 4. FTIR spectra of the cured epoxy compositions: (a) without HBPG **3**, (b) with 40% of HBPG **3** for stoichiometric amount of TETA.

In the first case, at the beginning, a homogeneous mixture of the epoxy resin, HBPG **3**, and amine hardener is obtained. The more reactive epoxy groups start forming networks with polyamine. The unreacted HBPG **3** is not soluble in such a partially cured composition and precipitates in the form of small domains. The previously homogeneous system becomes heterogeneous. Indeed, it was found that this procedure led to the ivory opaque products. All the experiments described in this work were performed according to a one-step procedure.

The glass transition temperature (T_g) of the cured systems with HBPG **3** was determined by DSC. The registered $T_g = -30$ to -35 °C could be assigned to unreacted HBPG, independently on the amount of amine hardener used. The second T_g, characteristic for epoxy network, was 75–80 °C.

In case of the two-step procedure, due to the lack of competition between epoxy and carbonate groups, all of the carbonate groups containing an additive are incorporated into the network. The resulting samples do not show phase separation, therefore no toughness improvement is observed [20].

3.3. SEM analysis

The formation of a new phase can be observed in the SEM images. Fig. 5 shows the images of the fractured surfaces of the modified epoxy resins: (a) sample 11 (see Table 1) containing 10% of HBPG **3** cured with 25% excess of TETA, (b) sample 12 containing 20% of HBPG **3** cured with 25% excess of TETA and (c) sample 13 containing 40% of HBPG **3** cured with 25% excess of TETA. In the pictures (b) and (c) particles of HBPG **3** can be observed. As can be seen the modified resin formed spherical domains of the hyperbranched polymer dispersed within the continuous epoxy resin phase. Uniform distribution of the HBPG particles throughout the matrix is very important for toughening. It allows the yielding process to operate throughout the matrix [25]. The size and number of the

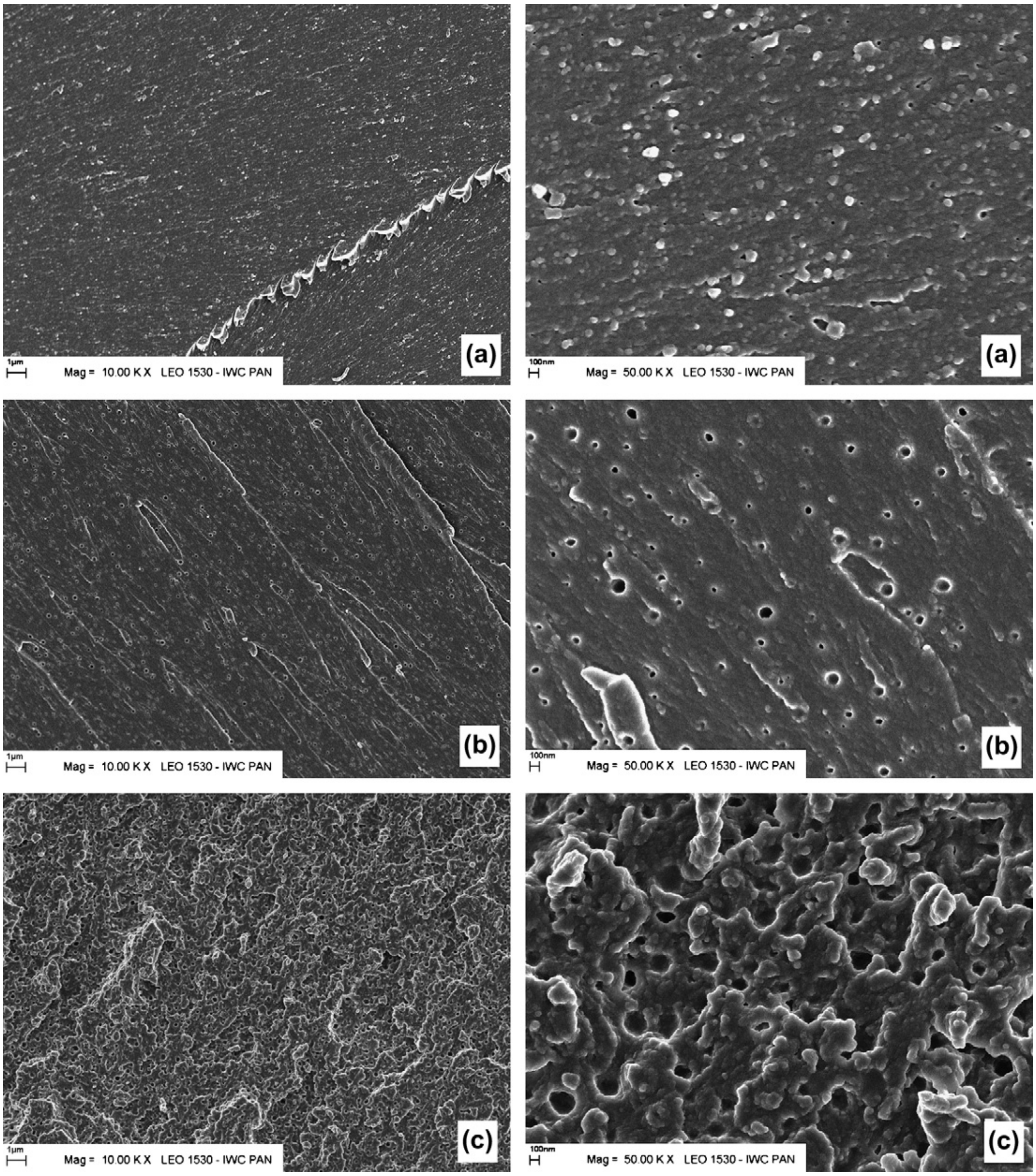


Fig. 5. Images of the fractured surfaces of the modified epoxy resins at 10 000 and 50 000× magnification: (a) sample 11 containing 10% of HBPG **3** cured with 25% excess of TETA, (b) sample 12 containing 20% HBPG **3** cured with 25% excess of TETA, (c) sample 13 containing 40% of HBPG **3** cured with 25% excess of TETA.

particles depend on amount of the modifier and are higher for larger amount of HBPG used.

Table 3 shows the size of the domains depending on the amount of the reagents used in the composition. It can be seen that the lower HBPG **3** content and higher hardener concentration resulted in a smaller size of the particles. In the latter case a greater part of HBPG is incorporated into the resin matrix. The application of the highest amount of HBPG **3** and lowest amount of the hardener led to the formation of the biggest particles (sample 3, 350 ± 50 nm). The HBPG domains did not undergo cavitations, suggesting good adhesion between HBPG **3** and the epoxy resin matrix. A certain amount of the cyclic carbonate, present in the outer sphere can react with the epoxy resin via amine hardener and effectively lock the domains in the matrix and ensure an efficient stress transfer between the HBPG and the epoxy resin. A similar phenomenon was reported by Boogh and coworkers for HBP containing in the outer sphere reactive epoxy groups [6]. Moreover, due to the presence of cyclic carbonate and β-hydroxy-urethane groups,

Table 3
The size of the HBPG particles depending on the composition

Sample	HBPG **3** [%]	Particle size [nm]
		Equimolar TETA amount
2	10	65 ± 20
3	20	130 ± 50
4	40	350 ± 50
		25% TETA excess
11	10	30 ± 20
12	20	70 ± 60
13	40	180 ± 60

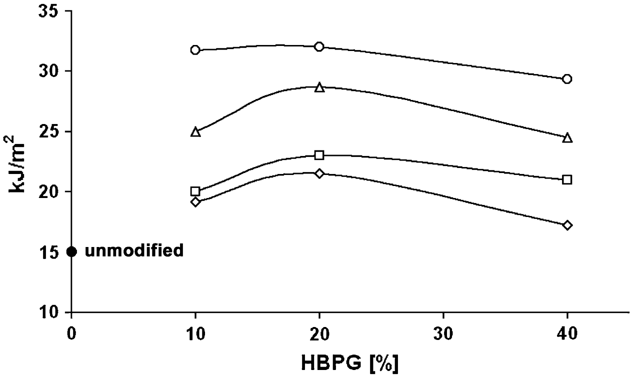


Fig. 6. Impact strength of the epoxy/HBPG **3** compositions cured with TETA. ◇-Equimolar amount, □-10%, △-20%, ○-25% excess of TETA for different amount of HBPG **3**.

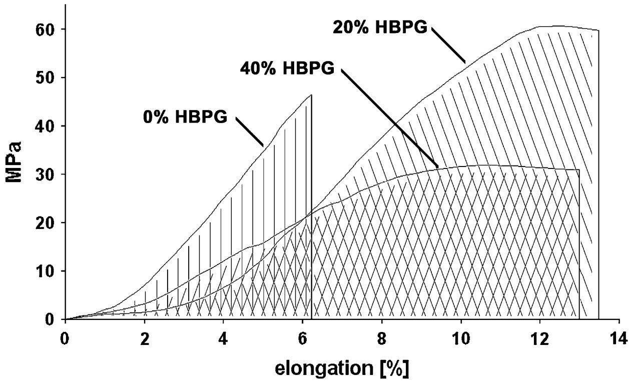


Fig. 7. Stress–strain curves for the HBPG **3** modified epoxy resin cured with TETA (20% excess).

additional, physical crosslinking takes place by the formation of hydrogen bonds between OH and carbonyl groups of the composition.

3.4. Mechanical properties

The modification of the epoxy resin with HBPG **3** strongly influences the mechanical properties of the cured resin. It was found that all samples exhibited higher impact strength than the unmodified resin. The impact tests were performed by the Charpy's method. The results are presented in Fig. 6. It can be seen that both concentration of HBPG and amount of the curing agent influence the impact strength. Phase separation is an important factor affecting the impact strength. Samples containing 20 and 25% of an excess of TETA showed phase separation and the highest impact strength was observed for compositions containing 20% of HBPG. The most probable toughening mechanism of the cured resin containing domains of HBPG is shear yielding. This very efficient impact energy absorbing mechanism (due to the irreversible nature of plastic deformation) also constitutes an efficient barrier to the propagation of crazes, delaying material failure. Contrary to crazing, which is also partially responsible for higher impact strength, shear yielding does not induce any significant material volume variation.

Table 4
Tensile strength of the HBPG **3** modified epoxy resin cured with TETA

HBPG **3** content [%]	Tensile strength [MPa]	Elongation at break [%]
Equimolar TETA amount		
0	46.6 ± 0.7	6.5
10	57.3 ± 0.8	12.5
20	51.2 ± 4.4	8.0
40	30.4 ± 0.4	18.5
10% TETA excess		
10	54.9 ± 1.6	12.5
20	54.8 ± 2.9	12.0
40	29.0 ± 3.2	14.5
20% TETA excess		
10	61.5 ± 2.2	16.0
20	58.9 ± 1.0	13.5
40	30.1 ± 0.4	13.0
25% TETA excess		
10	59.7 ± 3.8	13.0
20	57.6 ± 2.7	17.0
40	31.6 ± 1.4	16.0

It was found that the epoxy resin containing up to 20% of HBPG cured with TETA also exhibited higher tensile strength than that of the unmodified resin. For a higher concentration of hyperbranched polyglycerol the tensile strength remained at the level lower than that of the unmodified epoxy resin, whereas the elongation at break increased within the amount of the modifier (Table 4). This indicates that for higher than 20% concentration of HBPG plasticization of the cured resin takes place in significant extent. Similar effect was observed by Fröhlich et al. for the resin containing the functional hyperbranched block copolymer (polyether with epoxy and fatty acid ester groups). The presence of 2.5 and 5% of the modifier led to significantly lowered stiffness of the resin [17].

The surface area below the stress–strain curves, visualized in Fig. 7, represents the amount of work required to break a sample. By simple comparison, it can be seen that the samples containing 20% of HBPG **3** require more than twice as much work to break the sample as that of unmodified resin. The addition of 40% of HBPG reduces this value significantly, but still is higher than that of unmodified resin.

The flexural strength of the obtained samples is shown in Fig. 8. The HBPG **3** modified samples indicated lowered values of flexural properties than those of unmodified epoxy

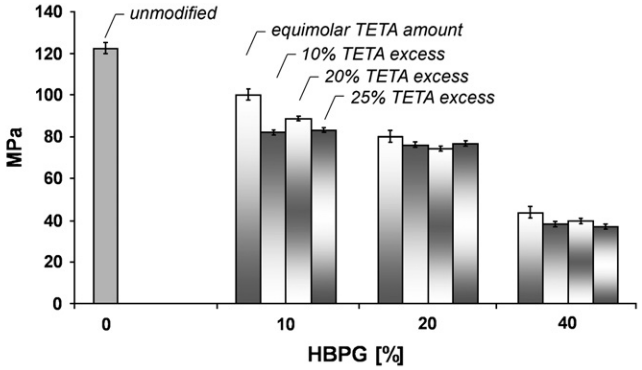


Fig. 8. Flexural strength of HBPG **3** modified epoxy resin cured with TETA.

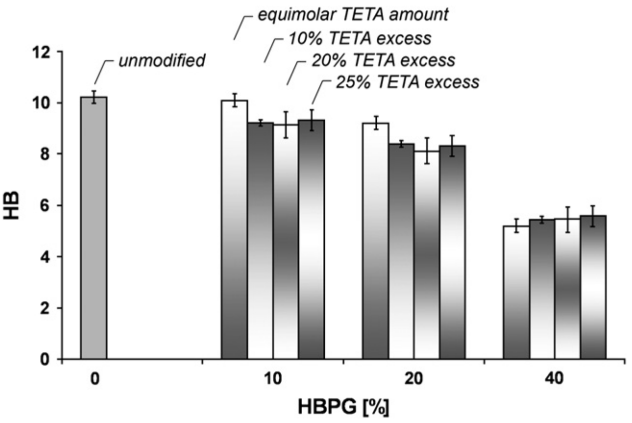


Fig. 9. Influence of the addition of HBPG **3** on the Brinell hardness of the samples.

resin. The reduction of those values was proportional to the amount of HBPG added and did not depend on the hardener excess.

Fig. 9 shows the influence of the addition of HBPG **3** on the Brinell hardness of the samples. The presence of 10% of the modifier to a small degree reduces the hardness of the cured samples. For higher amounts of HBPG **3** a drop of hardness was observed.

The observed toughening is in accordance with the results reported by Boogh [6] and Fröhlich [17], in which the enhanced toughening effect was observed for phase-separated morphology with particle size of 100–200 nm. To attain phase separation, they introduced epoxidized fatty acid ester end groups into commercial hyperbranched polyester. Long aliphatic chains reduce hydrophilicity and epoxy groups enable partial introduction into the epoxy resin network. It is also known that the most efficient particle diameters for rubber used as toughener is in the range 100 nm–10 μm. Larger particles can only contribute to crack bridging. This mechanism is less effective than shear yielding contributed by smaller particles [25].

4. Conclusions

New synthesized hyperbranched polyglycerol with cyclic carbonate terminal groups is an effective low viscosity toughener for epoxy resin when aliphatic polyamine is used as a hardener. The simple method of selective introduction of cyclic carbonate groups into the outer sphere makes this HBPG an attractive material of improved impact strength. This multifunctional HBPG used in our study causes phase separation during the curing of the completely homogeneous composition at room temperature. For samples exhibiting phase separation the highest impact strength was observed. The amounts of modifier and the excess of hardener influence the secondary phase structure, which in turn determines the mechanical properties of the cured resin.

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