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Hybrid resins from polyisocyanate, epoxy resin and water glass: chemistry, structure and properties

N. Castella · S. Grishchuk · J. Karger-Kocsis · M. Unik

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Abstract Epoxy resin (EP) was selected as potential reactive emulsifier for polyurea-based thermoset resins produced from polyisocyanate/water glass/emulsifier systems. As emulsifier diphenyl-2-ethylhexylphosphate and/or EP served for the initial water-in-oil type emulsions whereby "water" means water glass, and "oil" the organic phase, composed of polyisocyanate and emulsifier, respectively. The EP content of the systems has been varied from 15 to 35 wt% and from 35 to 45 wt% for the hybrid resins with and without DPO emulsifier, respectively. Effects of EP hybridization on the structure, mechanical, thermal and flammability properties of the final polyurea-based systems were studied. EP proved to be a suitable emulsifier based on the fact that the mean size of the polysilicate, generated from the dispersed WG, was markedly reduced. EP could even fully replace the phosphate emulsifier without sacrificing the mechanical properties of the resulting hybrid thermosets. Moreover, the hybridization with EP was accompanied with improved stiffness and fracture toughness.

Introduction

Polyisocyanates are important precursors to produce both linear and crosslinked polymers with tunable properties. Their reaction with di- and polyols result in polyurethanes, with di- and polyamines yield polyureas. The isocyanate group can be transformed to primary amine via the reaction $\text{–NCO} + H_2O \rightarrow \text{–NH}_2 + CO_2$. This reaction is taking place in presence of aqueous media, including water glass (WG) which is a mixture of salts (usually sodium or potassium) of polysilicic acids. As a consequence, WG is an interesting reactant for compounds containing isocyanate groups. Moreover, WG can be considered as an alternative precursor to organosilane compounds to produce polysilicate (silica) in situ via the sol–gel route. The silica particles may be even on nanoscale. Kuan et al. [1] demonstrated that WG can be transferred into nanosilica particles in waterborne polyurethane systems. Researchers of the National Academy of Science of Ukraine used WG to modify the properties of polyurethanes (e.g., [2–5] and references therein). Most of their works focused on the combination of WG with NCO group containing polyurethane oligomers which have some similarity with waterborne polyurethanes. However, the scenario is completely different when apolar polysiocyanates are used instead of polar isocyanate grouped polyurethane oligomers.

WG when dispersed in polyisocyanates results in a highly reactive water-in-oil type emulsion (W/O). This cures very fast into a polyurea-based thermoset. The fast reaction between the water and the isocyanate is controlled by suitable emulsifiers. Commercially available polyurea

N. Castella · S. Grishchuk
Institut für Verbundwerkstoffe GmbH (Institute for Composite Materials), Kaiserslautern University of Technology,
67663 Kaiserslautern, Germany

J. Karger-Kocsis
Department of Polymer Technology, Faculty of Engineering and Built Environment, Tshwane University of Technology,
Pretoria 0001, Republic of South Africa

J. Karger-Kocsis (✉)
Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology
and Economics, 1111 Budapest, Hungary
e-mail: karger@pt.bme.hu

M. Unik
ASAG Umwelttechnik, 47506 Neukirchen Vluyn, Germany

precursor systems are marketed under the trade name 3P resins by Polinvent Ltd. (Budapest, Hungary). They mostly contain phosphates as emulsifiers and thus 'reaction controllers' ([6] and references therein). The designation of 3P is derived from the parent composition: polyisocyanate, phosphate and polysilicate. "Polysilicate" is formed by "hardening" of the dispersed WG phase. 3P resins are gaining acceptance in repair of pipes (canalization) and strengthening of walls (mining industry, tunnels) exploiting the fact that 3P resins cure also under water.

The presence of phosphate is a problematic issue in the 3P systems due to its diffusion in the environment. The European Community Regulation on chemicals and their safe use (REACH—Registration, Evaluation, Authorization and Restriction of Chemical substances—EC 1907/2006) [7] is dedicated to avoid possible contamination of the environment. Accordingly, our strategy was to reduce, or eventually to replace, the phosphate type emulsifiers in polyisocyanate/WG systems. The target emulsifiers should be coreactive, prolong the pot life of the hybrid systems and improve their properties. The present work was focused on the application of epoxy resin (EP) as possible reactive emulsifier for the polyisocyanate/WG systems. 'Reactive' means that the EP is participating in the build-up of the final cross-linked structure. EP has been selected being resistant to strong alkalis (like WG), and via its epoxy groups reactive towards the –NCO groups of the polyisocyanate. It is noteworthy that information on WG/EP/polyisocyanate systems is already available in the literature [8]. The aim of this contribution was to check whether EP works as an 'active emulsifier' in 3P systems. A further aim of this work was to replace the phosphate emulsifier completely by EP. The related resins are termed 2P resins (from polyisocyanate and polysilicate). Effects of the EP hybridization on the structure, mechanical, thermal and flammability properties of the resulting polyurea-based thermosets were determined and discussed.

Chemistry of EP hybridization

The chemistry of epoxies is mainly based on the nucleophilic addition to one of their electrophilic carbons in the epoxy ring with subsequent ring opening. The nucleophilic addition to an epoxide can be base or acid catalyzed. Note that epoxy groups are especially reactive due to their three-membered strained rings. Under basic conditions (provided by the WG media), the ring opening is regiospecific since the nucleophile tends to attack the less hindered carbon, in accordance with standard S_N2 nucleophilic addition reaction process (cf., Fig. 1).

In the 3P chemistry, an amine is obtained from the reaction between isocyanate and WG which is involved in a nucleophilic attack to the less substituted carbon of the epoxide (note that the reaction medium is a strong alkali) causing its opening. As a result an alcohol group is formed (cf., Fig. 1) which can react with the isocyanate via forming a urethane linkage (cf., Fig. 2).

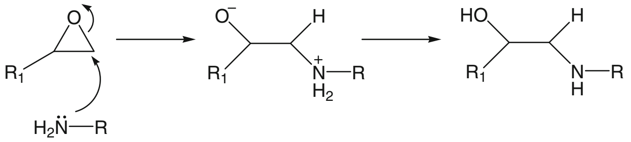

Fig. 1 Nucleophilic addition to an epoxide under basic conditions

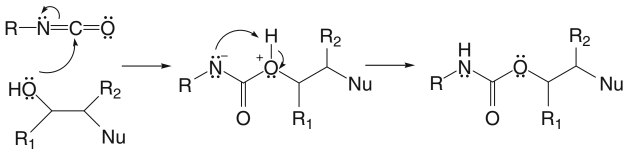

Fig. 2 Urethane linkage formed via the reaction between the hydroxyl formed and the isocyanate

Albeit hydroxide anions of the WG may also react with the epoxide ring yielding a diol (that could react further with isocyanate molecules), the related reaction is less probable when amines are the competing nucleophiles. This is the major reason why no chemical linkage is expected between the polysilicate from the WG and the resulting matrix.

The epoxide group can also react with isocyanate to form oxazolidone linkage as shown in Fig. 3. This cyclic structure of oxazolidone is very stiff which imparts rigidity and excellent thermal properties to the polymer. This reaction occurs only at high temperatures or with basic catalysts.

Isocyanates trimerize by forming isocyanurates under suitable conditions (<120 °C). When isocyanates react with epoxies (especially in presence of amines in the temperature range of 70–150 °C) oxazolidones may also form (Fig. 4) [9–12].

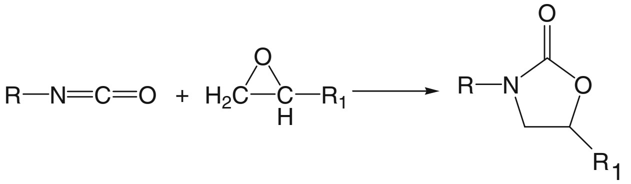

Fig. 3 Formation of oxazolidone by the reaction between isocyanate and epoxide groups

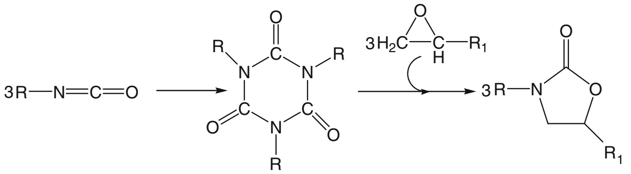

Fig. 4 Trimerization of isocyanates to isocyanurate and the posterior reaction with epoxide yielding oxazolidone

Therefore, EP hybridization is associated with the above outlined reactions which may take place in the initial polyisocyanate/WG systems.

Experimental

Materials

As polyisocyanate compound 4,4′-diphenylmethane diisocyanate in a mixture with its higher functionality prepolymers (PMDI) was used. PMDI (Ongronat® CR-30-60) was purchased from Borsodchem Rt (Kazincbarcika, Hungary) and showed the following characteristics: NCO content 30–31.5 wt%, viscosity: 520–680 mPa s, acidity max. 0.05 wt% and a density of 1.23 g/mL. The WG was Betol 3P (Woellner Silikat GmbH, Ludwigshafen, Germany). It is an aqueous solution (~40 wt%) of sodium silicate ($m\mathrm{Na_2O}\cdot n\mathrm{SiO_2}\cdot x\mathrm{H_2O}$) with viscosity, 600 ± 100 mPa s and "modulus" given by $\mathrm{SiO_2/Na_2O} = 2.0 \pm 0.05$. The bisphenol A based EP, foreseen as reactive emulsifier, was a D.E.R.331 of Dow Deutschland (Schwalbach, Germany). The characteristics of this EP are 22.4–23.6% of epoxide, epoxy equivalent weight (EEW) = 189 g, viscosity 11–14 Pa s and density 1.16 g/mL. As emulsifier for the PMDI/WG systems diphenyl-2-ethylhexylphosphate (DPO) (Lanxess Deutschland GmbH, Leverkusen, Germany) with 8.6 wt% of phosphorous content, 1.086 g/mL density at 20 °C and 22 mPa s viscosity at 20 °C was used. Recall that the emulsifier is responsible for controlling the W/O-emulsion and slowing down the reaction of the polyurea formation. In the final crosslinked product, it works as plasticizer. Using PMDI a crosslinked polyurea-based thermoset will be produced. This proprietary system [13], marketed by Polinvent Ltd. (Budapest, Hungary) is denoted 3P resin (from polyisocyanate, phosphate, and polysilicate).

Preparation of hybrids

The hybrid resins were prepared at room temperature (RT) under air atmosphere. The homogenization of the components was accomplished with a cogged-wheel mixer. The mixing sequence of the components is of great importance for the final hybrid resins. To prepare the EP/3P hybrid resins first, the isocyanate component with the organic phosphate and the EP were mixed (1 min, 1400 rpm). After the homogenization and the degassing of the resulting mixture, WG was added. Since the preparation of epoxy modified 3P resins demanded high mixing speeds, the mixing procedure was carried out at 2000 rpm. The preparation of the 2P/EP hybrid resins was carried out similarly by homogenising the PMDI and the EP for 1 min at 2000 rpm and dispersing the WG during 1 min at 1500 rpm. After mixing and degassing processes the resins were casted in moulds and cured for 20 h at RT and 4 h at 100 °C. Finally, all samples were "dried" for 24 h at 125 °C. The compositions of the 3P/EP and 2P/EP resins are listed in Table 1.

Table 1 Code and composition of the 3P, 3P/EP and 2P/EP resins

	WG, wt%	PMDI, wt%	DPO, wt%	EP, wt%
3P	34	51	15	–
3P/EP—85/15	28.9	43.3	12.8	15
3P/EP—80/20	27.2	40.8	12.0	20
3P/EP—75/25	25.5	38.3	11.2	25
3P/EP—65/35	22.1	33.1	9.8	35
2P/EP—65/35	26	39	–	35
2P/EP—60/40	24	36	–	40
2P/EP—55/45	22	33	–	45

Notes: the WG/PMDI ratio is 1/1.5 in all systems. The 3P/EP combinations represent dilutions of the parent 3P with EP

Testing

The mean particle size and size distribution of the silicate particles were determined using scanning electron microscope (SEM) images (JSM 5400 device of Jeol, Tokyo, Japan). They were taken from the surface of broken compact tension (CT) specimens. The surface was coated with an Au–Pd alloy before SEM investigation. SEM pictures of minimum three showing more than 100 particles were taken into consideration when determining the particle size distribution. The latter was quantified by the mean number- (d_n) and weight-average (d_w) particle diameters, respectively.

The fracture toughness (K_C) and fracture energy (G_C) were measured according to ISO 13586-1 standard. The tests were done with a Zwick universal testing machine type 1445 (Ulm, Germany) at room temperature with a crosshead speed of $v = 1$ mm/min. The CT specimens (dimension: 35 × 35 × 3 mm^3; length × width × thickness) were notched before loading by sawing. The sawn notch of the CT specimens was sharpened by a razor blade. The razor blade, fixed in a rig, was positioned in the notch root before hitting the fixing rig with a hammer. This yielded the desired sharp crack.

The flexural properties, namely, modulus and strength of the hybrid resins, were determined on rectangular specimens (60 × 10 × 3 mm^3; length × width × thickness) in three point bending at room temperature according to EN63. The span length of the specimens was 50 mm, and their loading occurred with deformation rate $v = 1$ mm/min.

Dynamic mechanical thermal analysis (DMTA) were taken on rectangular specimens (60 × 10 × 3 mm^3, length × width × thickness) in three point bending configuration (span length: 50 mm) at 1 Hz using a DMA

Q800 of TA Instruments (New Castle, DE, USA). Tests were performed under displacement control using sinusoidal oscillation and under dynamic conditions in the interval from 20 to 300 °C at a heating rate of 1 °C min^{-1}.

DSC measurements were carried out in a DSC 821 from Mettler Toledo (Giessen, Germany) to determine the glass transition temperature (T_g) of the hybrids. The aluminium pans (40 μL) contained ca. 15 mg samples. Dynamic DSC scans were run with nitrogen purging (30 mL/min). To overcome problems linked with the evaporation of the water in the resins the following heating regime was selected: heating from 25 to 210 °C; holding at 210 °C for 5 min before cooling to RT and reheating from 25 to 350 °C. The heating and cooling rates were 10 °C/min. T_g was read form the thermograms related to the second heating process.

Thermogravimetry (TG) was used in order to determine the changes in the samples weight depending on the temperature. For this purpose, a TG50 from Mettler Toledo (Giessen, Germany) device was used. The sample weight was approx. 30 mg. The measurements were carried out in an open aluminium pan (100 μL) with a heating rate of 10 °C/min from RT to 630 °C under nitrogen purging (30 mL/min).

To test the flammability of the materials the UL 94 (Tests for Flammability of Plastic Materials for Parts in Devices and Appliances) was used. This test covers several types of testing: for our purpose, 94 V flammability vertical test was chosen being a stringent test. In the 94 V flammability test, a specimen is supported in a vertical position and a flame is applied to the bottom of the specimen. The flame is applied for 10 s and then removed until flaming stops at which time the flame is reapplied for another 10 s and then removed. Three specimens for each material were tested.

Results

Morphology

3P/EP

The SEM pictures of the fracture surface of the 3P/EP resins with different compositions are presented in Fig. 5. The change induced by the hybridization of the 3P resin with EP is obvious: the size of the polysilicate particles is markedly reduced. This means that EP worked as additional emulsifier to DPO in the related 3P system. The data related to the dispersion of the polysilicate are summarized in Table 2.

2P/EP

Observing the SEM pictures obtained from the fracture surface of the 2P/EP hybrid samples (cf., Fig. 6), one can clearly see the EP hybridization-induced change in their morphology. When comparing with the reference 3P (Fig. 6a), it is clear that the silicate particle diameter is

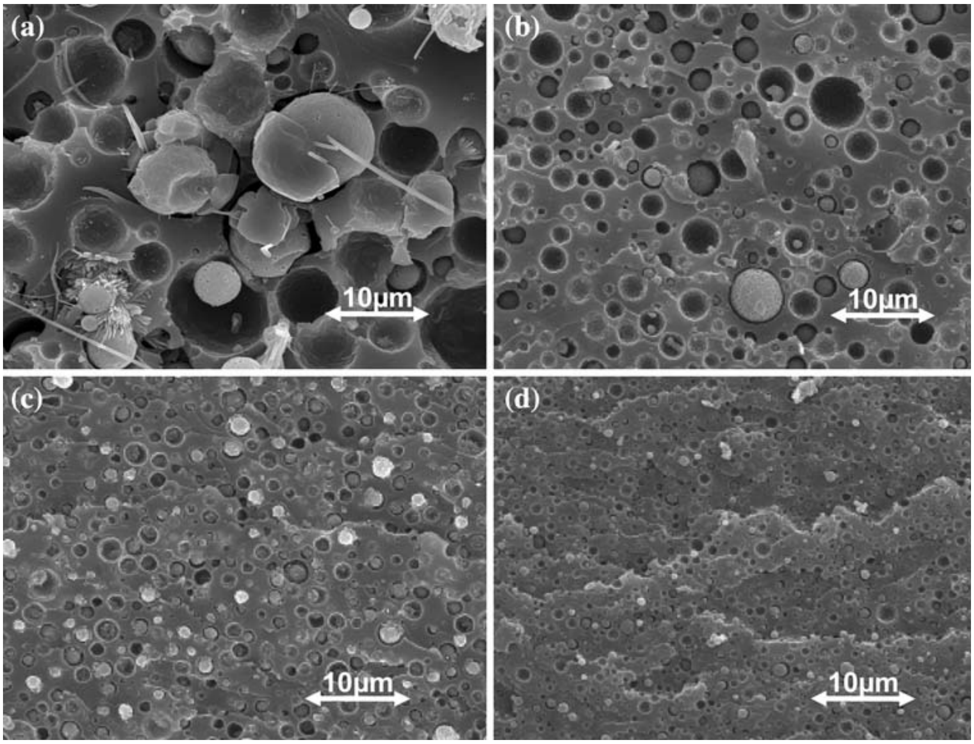

Fig. 5 SEM pictures from the broken surfaces of the reference 3P resin (**a**); 3P/EP 85/15 wt% hybrid (**b**); 3P/EP 75/25 wt% hybrid (**c**); and 3P/EP 65/35 wt% hybrid (**d**)

Table 2 Number-average (d_n) and weight-average (d_w) mean particle size of the 3P/EP hybrid systems and their reference 3P resin

Sample name	d_n, μm	d_w, μm	d_w/d_n
3P	5.0	7.1	1.4
3P/EP 85/15 wt%	1.2	2.0	1.6
3P/EP 80/20 wt%	1.1	1.5	1.3
3P/EP 75/25 wt%	0.8	1.1	1.3
3P/EP 65/35 wt%	0.8	1.1	1.3
2P/EP—65/35 wt%	0.6	0.7	1.2
2P/EP—60/40 wt%	0.5	0.5	1.0
2P/EP—55/45 wt%	0.5	0.6	1.1

drastically reduced from micrometre range to hundreds of nanometre (Fig. 6b–d). This is a clear proof of the emulsifier action of the EP resin as the 2P/EP system contained no DPO.

Characteristics of the polysilicate particle distributions for the 3P, 3P/EP, and 2P/EPs are listed in Table 2. It is the right place to emphasize that the polysilicate particles are not attached to the polyurea matrix, i.e., no chemical reaction took place between the WG and the organic phase components (PMDI, EP). This is in marked contrast to the findings of the Ukrainian researchers [2–5, 8].

Mechanical properties

Fracture toughness and energy

3P/EP The fracture mechanical properties displayed in Fig. 7 show that the novel 3P/EP hybrids possess enhanced fracture toughness (K_C) in comparison to the reference 3P resin. Moreover, K_C increases parallel to the EP content, with the exception of the 3P/EP 85/15 wt% hybrid system. High K_C values are due to the hybridization of the cross-linked polyurea structure via the reaction outlined before. The reduced particle size and the narrow size distribution of the polysilicate are also beneficial to enhance the fracture toughness. Increasing K_C is, however, associated with an adverse effect on the fracture energy (G_C). The latter was reduced compared to that of the reference 3P (cf., Fig. 7).

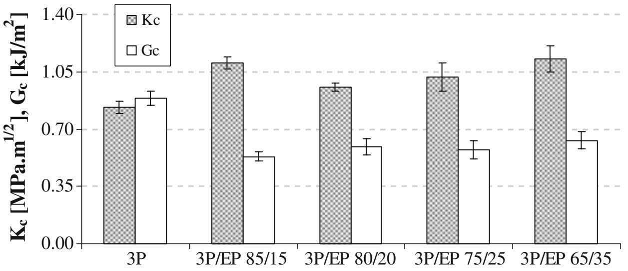

Fig. 7 Fracture toughness (K_C) and fracture energy (G_C) for the 3P/EP hybrids and their reference 3P resin

2P/EP With regard to the fracture mechanical properties displayed in Fig. 8, a significant increase of the fracture toughness (K_C) can be noticed for the 2P/EP hybrids. However, the change in K_C does not follow a clear tendency with the EP resin content. On the other hand, G_C is markedly reduced when comparing to the reference 3P

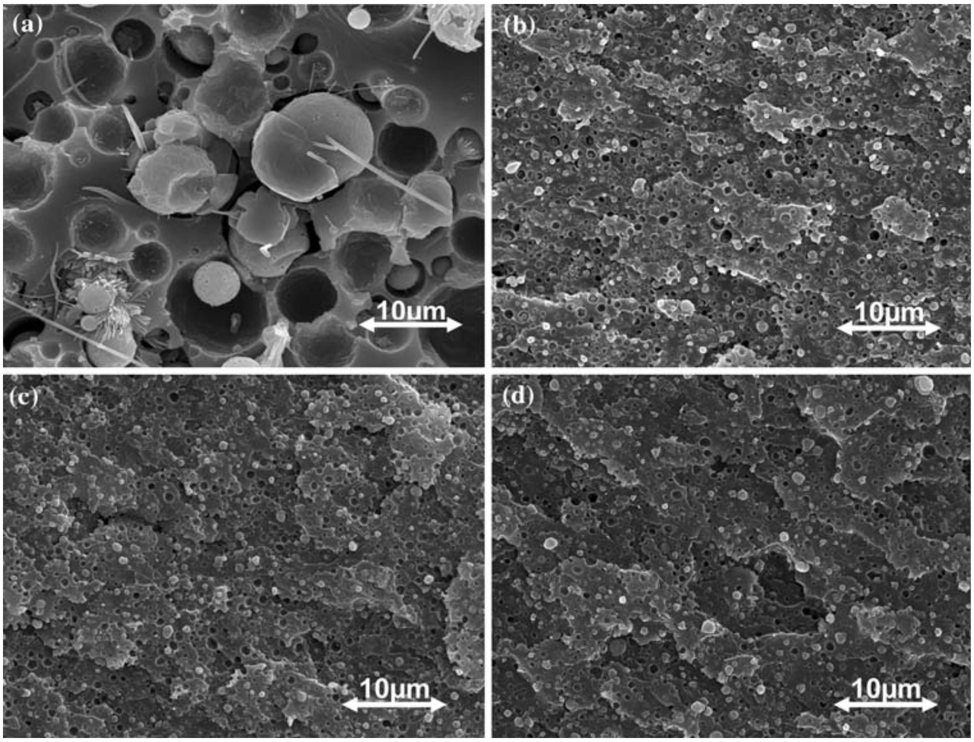

Fig. 6 SEM pictures from the broken surfaces of the reference 3P resin (**a**); 2P/EP-65/35 wt% hybrid resin (**b**); 2P/EP-60/40 wt% hybrid resin (**c**); and 2P/EP-55/45 wt% hybrid resin (**d**)

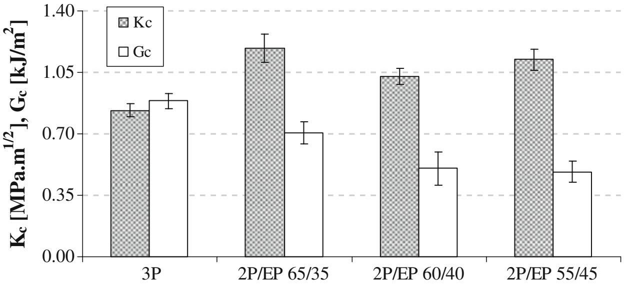

Fig. 8 Fracture toughness (K_C) and fracture energy (G_C) for the 2P/EP hybrids and their reference 3P resin

resin. Moreover, G_C shows a decreasing tendency with increasing EP content.

Flexural properties

3P/EP The flexural tests carried out on the 3P/EP hybrid systems reveal, as expected, that the flexural modulus E_{fm} of the novel hybrids increases with the EP content following the rule of additivity (Fig. 9) in the composition range investigated. The related tendency is less clear for the flexural strength (σ_{fm}), as for all 3P/EP systems quite similar values were measured. However, in general the hybrid systems possess enhanced values of σ_{fm} (cf., Table 3).

2P/EP The flexural properties of the 2P/EP hybrid resins are depicted in Fig. 10. The flexural modulus (E_f) presents a clear growing tendency with increasing EP content, following the rule of addition in the studied composition range. The flexural modulus does not reach the values of the pure EP resin. On the contrary, the flexural strength (σ_{fm}) does show significant changes as a function of the composition. Nonetheless, one can assume that the flexural properties of the 3P resins are in general enhanced when hybridizing with EP (cf., Table 3).

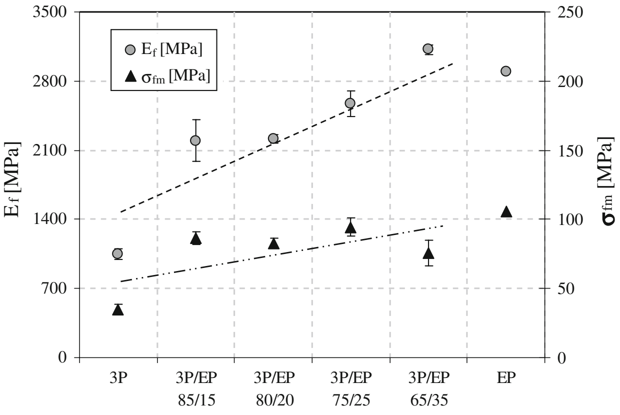

Fig. 9 Flexural modulus (E_f) and flexural strength (σ_{fm}) for the 3P/EP hybrid resins and their references 3P and EP

Table 3 Flexural modulus (E_f), strength (σ_{fm}), strain (ε_m) and standard deviation (s) for the 3P/EP, 2P/EP hybrid resins and their references 3P and EP

Sample name	E_f, MPa	s, MPa	σ_{fm}, MPa	s, MPa	ε_m, %	s, %
3P	1,047	56	34.6	3.9	4.4	0.9
3P/EP 85/15 wt%	2,262	281	82.5	4.6	4.2	0.5
3P/EP 80/20 wt%	2,254	122	80.7	15.8	4.4	1.9
3P/EP 75/25 wt%	2,613	260	81.9	13.7	3.4	0.7
3P/EP 65/35 wt%	3,118	45	75.6	9.3	2.5	0.4
EP	2,900	–	106.0	–	4.0	–
2P/EP 65/35 wt%	2,262	281	82.5	4.6	4.2	0.5
2P/EP 60/40 wt%	2,254	122	80.7	15.8	4.4	1.9
2P/EP 55/45 wt%	2,613	260	81.9	13.7	3.4	0.7

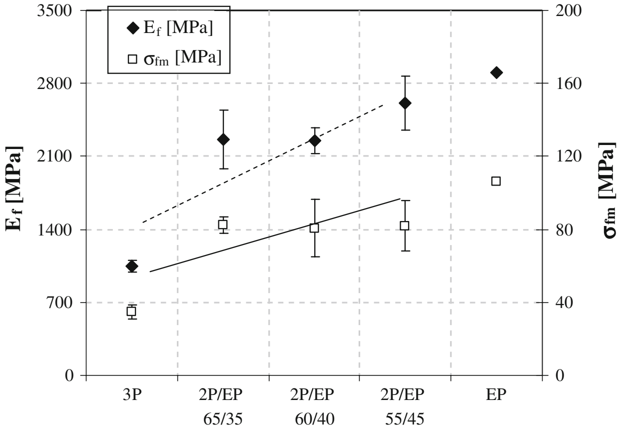

Fig. 10 Flexural modulus (E_f) and flexural strength (σ_{fm}) for the 2P/EP hybrid resins and their references 3P and EP

Dynamic mechanical thermal analysis

3P/EP The DMTA curves shown in Fig. 11 confirm the results obtained in the flexural tests. The higher the EP content, the higher the storage modulus (E') is. For temperatures ranging from 25 to 135 °C E' is markedly higher compared to the reference 3P—again with exception of the

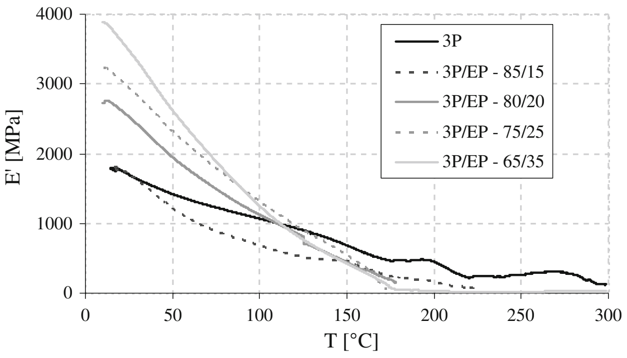

Fig. 11 DMTA results displaying E' versus T for the 3P reference and its 3P/EP hybrids

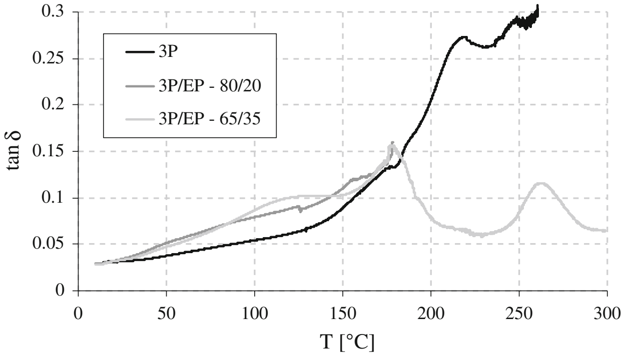

Fig. 12 DMTA results displaying tan δ versus T for the 3P and the 3P/EP hybrids

hybrid system with the lowest EP content. At temperatures around 150 °C the specimens undergo premature failure, apart from the 3P/EP 65/35 wt%, which shows a good thermal resistance at high temperatures.

When taking into account the tan δ versus temperature traces the different behaviour of the novel hybrids in comparison to the reference 3P becomes obvious (Fig. 12). While the 3P resins present a typical broad undefined peak at $T > 200$ °C, the 3P/EP hybrids exhibit minimum three peaks in the tan δ traces of different intensity. The first broad "shoulder" takes place at temperatures from 80 to 120 °C, and it may correspond to the glass transition temperature (T_g) of the amine-cured epoxy fraction. This first "shoulder" is overlapped with a second peak (150–190 °C), which is slightly more intense and may belong to the hybrid components formed between 3P and EP resin (cf., chemical pathways disclosed). The third tan δ peak, which is well resolved, appears at temperatures from 250 to 275 °C and corresponds to the T_g of the polyurea phase. Because of the premature failure of the specimens only the sub T_g relaxation peaks could be observed for the 3P/EP 80/20 hybrid system.

2P/EP The 2P/EP hybrid systems show alike viscoelastic behaviour to the 3P/EP hybrid systems. The DMTA traces, displayed in Fig. 13, confirm the tendency observed before by the flexural tests: the 2P/EP hybrids possess higher storage modulus (E') as the EP content increases. The storage modulus of the hybrid systems drops along with the temperature increase, until reaching values close to zero at $T \sim 180$ °C. Differently from the 3P/EP systems, the 2P/EP hybrid resins owe an improved resistance to high temperatures. It is noteworthy to say that the storage modulus of the 2P/EP hybrids is notably higher than for the 3P/EP hybrids (cf., Fig. 11). This fact is mostly related to the chemical reactions occurring due to EP hybridization and partly due to the absence of the phosphate which acts as plasticiser.

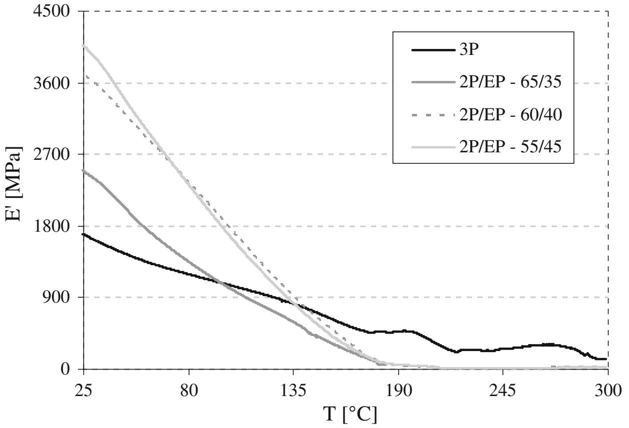

Fig. 13 DMTA results displaying E' versus T for the 3P reference and its 2P/EP hybrids

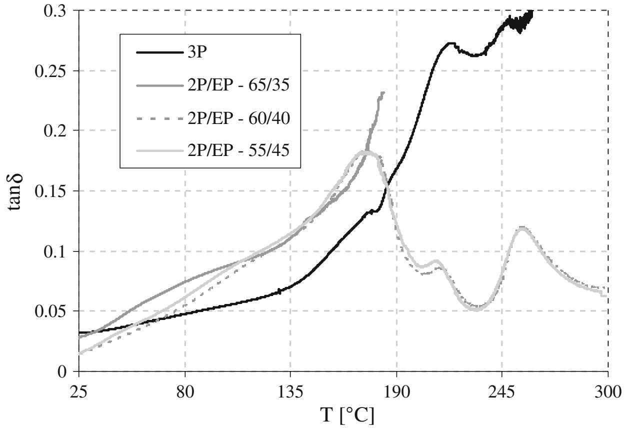

Fig. 14 DMTA results displaying tan δ versus T for the 3P and the 2P/EP hybrids

Considering the tan δ versus T traces in Fig. 14, one can observe an increase in the damping factor tan δ at $T \sim 180$ °C. This relaxation peak, traced to the outcome of the reactions between epoxy and isocyanate groups, is overlapped with a further peak of lesser intensity at $T \sim 230$ °C. Moreover, a third peak in the tan δ curve is noticeable at $T \sim 260$ °C. These results, obtained also for the 3P/EP hybrid systems, were confirmed by DSC tests. It is the right point to remark that, the EP content did not affect significantly the course of the damping factor as a function of T. On the other hand, the 2P/EP hybrid resins show different viscoelastic behaviour than the reference 3P resin. Changes induced due to the absence of the organic phosphate are also patent in the 2P/EP hybrid systems. The broad shoulder at 120 °C disappeared and a single peak with a tan δ maximum at 175 °C became observable for the 2P/EP hybrid systems. This can be traced to the formation of a phase based on the favoured reactions between the epoxide and isocyanate groups being no more influenced by the organic phosphate.

Thermal properties

3P/EP

The thermal degradation of the 3P/EP hybrid resins, presented in Fig. 15, show that the EP conferred to the hybrid systems an additional thermal stability at higher temperatures. The 3P/EP hybrid systems begin to experience a certain mass loss at $T < 250$ °C while at the same temperature the reference 3P resin has already lost more than 20% its weight. One can observe that the 3P/EP systems are stable for a wide range of temperatures before suffering a drastic mass loss ($T \sim 350$ °C). On the contrary, the reference 3P undergoes several degradation steps. In general, the higher the EP content of the hybrid systems the better is the resistance to thermal degradation. As listed in Table 4, one can see that the temperature at which the 5% of the mass is lost is higher for the hybrids with larger EP content. On the other hand, the final residue is slightly lower for these 3P/EP hybrids compared to the reference 3P.

2P/EP

The thermal degradation of the 2P/EP hybrid resins is depicted in Fig. 16, one can observe that the 2P/EP hybrids owe a very similar thermal behaviour independently of the EP content. The first mass loss process is observed at $T \sim 200$ °C, corresponding to the water evaporation contained in the matrix and hydrolysis products, followed by a drastic second mass loss at $T \sim 390$ °C due to the destruction of the organic matrix. When comparing the TGA response of 2P/EP systems those of the phosphate containing 3P/EP (cf., Fig. 15), it becomes clear that the systems without phosphate withstand to higher temperatures than those with phosphate. However, the residue at the end of the process, as well as the temperature at which the specimen loses its 5% of the mass ($T_{5\%}$) are very similar for both systems (cf., Table 4). On the other hand, when comparing the novel 2P/EP hybrid systems to the reference 3P, one can clearly see that the hybridisation with EP resulted in enhanced thermal stability.

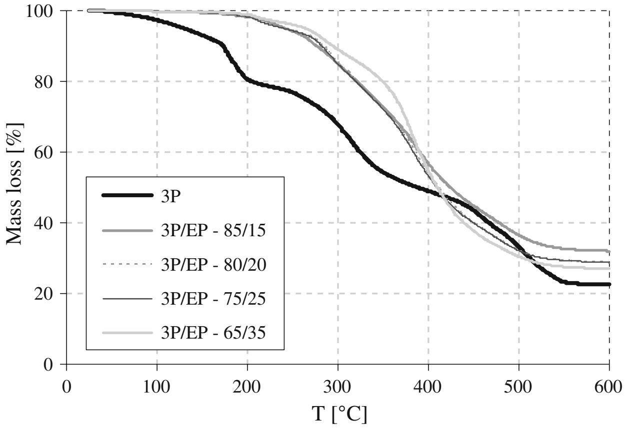

Fig. 15 Mass loss versus T for the 3P/EP hybrid resins and their reference 3P

Table 4 $T_{5\%}$ (°C) and residue (%) for the 3P/EP hybrid resins

Sample name	$T_{5\%}$, °C	Residue, %
3P/EP 85/15 wt%	242	32
3P/EP 80/20 wt%	241	29
3P/EP 75/25 wt%	240	29
3P/EP 65/35 wt%	264	27
2P/EP—65/35 wt%	250	27
2P/EP—60/40 wt%	232	27
2P/EP—55/45 wt%	249	27

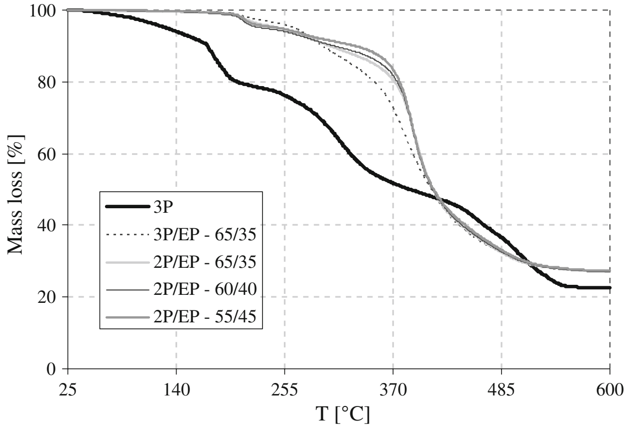

Fig. 16 Mass loss versus T for the 2P/EP hybrid resins and their reference 3P

DSC traces

3P/EP In Fig. 17 are presented those DSC traces, which were obtained from the second heating scans. One can observe a strong endothermic peak at temperatures ranging

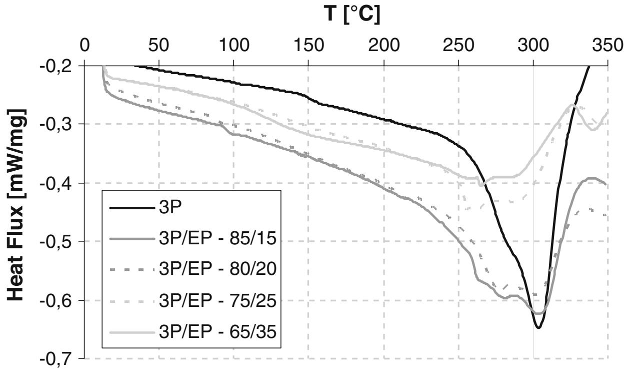

Fig. 17 DSC curves for the 3P/EP hybrid resins and the reference 3P

from 250 to 300 °C belonging to the evaporation of the organic phosphate present in the matrix. As mentioned before, this is superimposed to the T_g transition. This peak is narrow and pronounced for the reference 3P resin. However, in the 3P/EP hybrids with increasing EP content the endothermic absorption broadens and decreases since higher EP ratios in the 3P/EP hybrid systems imply less phosphate content. Moreover, at $T > 300$ °C an exothermic peak is observed corresponding to the destruction processes of the organic matrix. It is worth to remark that three different transitions were determined for the 3P/EP hybrid resin, which confirmed the results obtained by the DMTA (cf., Fig. 12). The T_g of the 3P/EP epoxy hybrids shift to lower temperatures as the EP ratio in the 3P/EP hybrid systems increases (cf., Table 5).

2P/EP The DSC curves depicted in Fig. 18 show, as expected from the DMTA data, three transition temperatures. The transition temperature of the hybrids decreases with increasing EP content (cf., Table 5). A characteristic attribute of the 2P/EP systems is that they do not possess the intense endothermic peak characteristic of the systems with phosphate (3P and 3P/EP). This is an important fact that accentuates the influence of the organic phosphate emulsifier on the crosslinking and destruction processes that take place at high temperatures.

Table 5 Transition temperatures (T_g) for the 3P/EP hybrid resins

Sample name	T_g transitions, °C
3P/EP 85/15 wt%	95/187/259
3P/EP 80/20 wt%	85/153/257
3P/EP 75/25 wt%	76/144/250
3P/EP 65/35 wt%	67/105/243
2P/EP—65/35 wt%	84/121/209
2P/EP—60/40 wt%	79/107/202
2P/EP—55/45 wt%	65/104/200

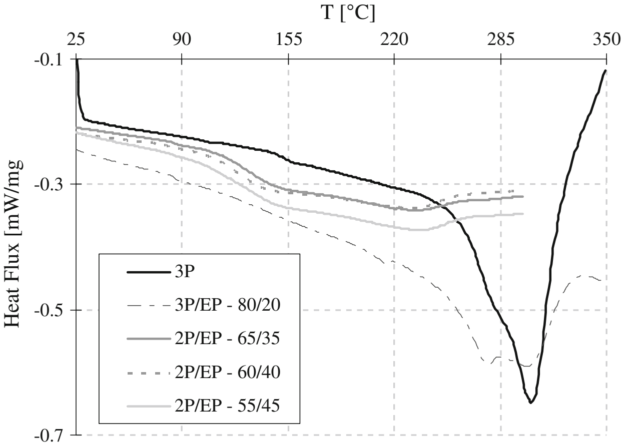

Fig. 18 DSC curves for the 2P/EP hybrid resins and the reference 3P

Flammability

3P/EP The flammability tests performed on the 3P/EP hybrid resins give a qualification of V-2 according to the UL 94 flammability test. The flammability of the hybrid resins is enhanced by the addition of EP. The specimens burned up to 2 min after applying the flame and dropped flaming drips. Therefore, one can assume that the hybridization of the 3P resins with EP did not maintain the outstanding good fire resistance of the reference 3P resin (V-0).

2P/EP The flammability tests performed on the 2P/EP hybrid resins give a qualification of V-1 according to the UL 94 flammability test. The specimens burned about 30 s in average after applying the flame but did not drop any flaming drip. The flammability of the hybrid resins is enhanced by the addition of EP compared to the excellent flame resistance of the reference 3P resin. However, when comparing to the 3P/EP systems, its flammability is reduced in absence of the organic phosphate.

Summary

This work was devoted to study the effect of EP as reactive emulsifier for polyisocyanate/polysilicate/phosphate (3P) and polyisocyanate/polysilicate (2P) resins. The polyurea-based 3P and 2P resins were produced from water-in-oil type emulsions composed of WG (“water”) and polyisocyanate + emulsifier (“oil”). The results achieved can be summarized as follows:

- Incorporation of EP in a reference 3P resin reduced the mean particle size of the polysilicate derived from the WG. Accordingly, EP worked as additional emulsifier to phosphate in the reference 3P resin. EP overtook the role of emulsifier in the related 2P systems, which was confirmed by a pronounced reduction of the mean particle size of the polysilicate.
- DMTA and DSC results suggested that the hybrid resins have a complex chemical build up containing such domains in the polyurea matrix which were formed by epoxide/amine, and epoxide/isocyanate, respectively.
- The static flexural (stiffness and strength) and dynamic-mechanical properties (stiffness) of both 3P and 2P resins were improved by the EP hybridization. The EP hybridization increased the fracture toughness at cost of the fracture energy.

- The thermal degradation started later and the char yield slightly decreased with increasing EP content for both the 3P/EP and 2P/EP systems. The flame resistance of the EP-containing hybrids remained below that of the 3P reference.

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