

Fire-Retardant Hybrid Thermosetting Resins from Unsaturated Polyesters and Polysilazanes

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ABSTRACT: This introduces an organic–inorganic thermosetting hybrid resin system based on unsaturated polyester and polysilazanes. It shows the chemical modification of unsaturated polyester structures by end capping to enable the combination of both components. In general, halogen-free unsaturated polyesters are not fire-retardant and have to be equipped with additives. Fillers and intumescent additives are preponderantly used in today's fire-retardant formulations. In contrast to these fire-retardants, polysilazanes act as ceramizing agents. Polysilazanes are suitable fire-retardants for resin transfer molding due to their low viscosity. Both burning behavior and glass transition temperature (T_g) are investigated as important application properties. In contrast to state-of-the-art fire-retardant formulations polysilazane-based thermosetting hybrid resins burn with high intensity and fast extinction. Therefore, total heat and smoke emission is decreased. The formation of ceramic structures during burning results in high residual mechanical properties and a low mass loss. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40375.

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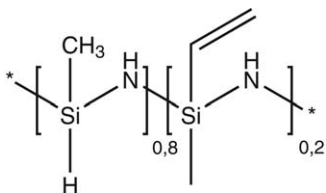
INTRODUCTION

Unsaturated polyester resins (UPRs) are one of the most versatile classes of thermosetting polymers. Due to their low raw materials and production costs, their easy processing and versatility of properties, this class is widely used as fiber reinforced plastic (FRP) in several applications.^{1,2} UPR contains in particular the predominantly linear unsaturated polyester and the reactive diluent as main components. Unsaturated polyesters are synthesized by condensation polymerization of unsaturated dicarboxylic acid, typically maleic acid, maleic anhydride (MA), or fumaric acid (FA), and dihydroxy compounds (diols), for example, 1,2-propylene glycol (PG).³ A wide range of physical and chemical properties can be achieved by combining different diols. In addition, saturated dicarboxylic compounds like ortho-, tere-, isophthalic, or adipic acid are used to modify the FRP and resin properties.⁴ For UPRs, styrene is mainly used as a reactive diluent. In addition to styrene, yet less relevant methyl methacrylate and other reactive monomers can also be used as single reactive diluents or in combination with styrene. FRPs from UPRs are processed by hand or spray lay-up, hot pressing, resin transfer molding (RTM) and several other processing techniques. UPRs are also used in adhesives or coatings.

UPRs can be processed under room temperature, they are low viscous and can be cured in short time cycles. State-of-the-art

formulations show at least two major disadvantageous properties: compared to other thermosetting resin types, UPRs result in brittle parts and show insufficient fire-resistance.^{5–7} UPRs are typically cured by radical copolymerization of a reactive diluent and a linear unsaturated polyester building a three-dimensional network. This copolymerization is initiated by free radicals formed by thermal or radiation labile compounds, especially peroxides. A broad range of initiators allow to cure UPRs at low (even below 0°C) or high temperatures (>200°C).^{8,9} Polysilazanes are polymers based on repeating units connected by silicon–nitrogen bonds. The polysilazanes used in this study are synthesized in anhydrous liquid ammonia using different organically substituted dichlorosilanes.^{10,11} For a combination with unsaturated polyesters, a vinyl-substituted polysilazane has been used (Kion HTT 1800, see Scheme 1). HTT 1800 shows the constitutive repeating unit from 20 mol % vinylmethyl silazane and 80 mol % monomethyl silazane. Polysilazanes are widely used as precursors for different kinds of Si–C–N ceramics. These materials are used in electronic elements, structural ceramics or precursor coatings.¹²

The combination of organic polysilazanes with different organic polymers and crosslinkers for precursor coatings¹³ as well as polysilazane-modified thermosetting hybrid resins based on polycyanurates¹⁴ were reported. Polysilazanes show high reactivity



Scheme 1. Repeating unit of Polysilazane Kion HTT1800.

against moisture, oxygen, acids, and peroxides due to a higher bond enthalpy between silicon and oxygen. Therefore, direct combinations of polysilazanes with state-of-the-art thermosetting resins have to be tested in terms of reactivity. In this study, the combination of polysilazanes and unsaturated polyesters as matrix resin for FRPs was investigated. Background of this study was the development of RTM processable unfilled fire-retardant UPR-based FRPs. Aspects are the reactivity between polysilazanes and unsaturated polyesters, the chemical modification of the UP structure, the processing behavior of the organic/inorganic hybrid thermosetting resin by RTM, and the resulting FRP properties. The characterization was done by dynamic mechanical analysis (DMA), cone calorimetry, and UL-94 fire test.

EXPERIMENTAL

Materials

FA (trans-1, 2-ethylenedicarboxylic acid, food grade), glycidyl methacrylate (GMA, oxiran-2-ylmethyl 2-methylprop-2-enoate, 97%), and hydroquinone (HQ, benzene-1, 4-diol, 99%) were bought from Sigma Aldrich in given purity. Maleic anhydride (MA, furan-2, 5-dione, 97%), dipropylene glycol (DPG, 4-oxa-2, 6-heptandiol, 99%), neopentyl glycol (NPG, 2, 2-dimethyl-1, 3-propanediol, 99%), and hydroxyethyl methacrylate (HEMA, 2-hydroxyethyl 2-methylprop-2-enoate, 97%) were bought from Alfa Aesar, PG (propane-1, 2-diol, 99%) from AppliChem. Phthalic anhydride (PA, 2-benzofuran-1,3-dione, 99%) was purchased from ABCR. Dipropoxylated bisphenol-A (Dianol 320, 1,1'-(isopropylidenebis(*p*-phenyleneoxy))di-2-propanol) came from Seppic. The polysilazane Kion HTT 1800 was provided by Clariant Produkte (Deutschland). HTT 1800 was purified by vacuum distillation of low molecular weight fractions, all other reagents were used without further purification. For determination of unsaturated polyester acid values a 0.1 *N* methanolic solution of potassium hydroxide (0.1 mol/L, AVS TITRIMORM, $t = 1.002$) from VWR International was used. For reinforcement of RTM plaques a woven 0°/90° carbon fiber fabric from SGL Carbon type KDK 8058 (160 g/m²) was used.

Investigation of Critical Reactions Between Polysilazanes and Unsaturated Polyesters

Due to expected reactivity of polysilazanes with unsaturated polyester functional end groups a classification of hydroxy, carboxy, and ester groups was done by simple mixing and evaluation of the gas emission behavior. The emission of ammonia is characteristic for the reaction of polysilazanes with fumaric acid, diethyl fumarate, and ethylene glycol as reference substances. The calculation of stoichiometric ratios of the reactants was done at the base of typical unsaturated polyester values (COOH- and OH-value).

Unsaturated Polyesters and Their Chemical Modification

For organic/inorganic hybrid resin based on polysilazanes and UPRs, two basic formulations were selected to show the general behavior and the properties of the resulting FRPs. The basic formulations are technically oriented on state-of-the-art commercial compositions. The first formulation (system 1) is based on a repeating unit from 1 mol MA, 0.5 mol PA, 0.84 mol PG, and 0.75 mol DPG. System 1 represents a broadly used industrial composition with typical unsaturated polyester properties. The second basic formulation (system 2) contains 1 mol FA, 0.4 mol NPG, 0.606 mol Dianol 320, and 0.05 mol PG. This formulation represents a resin with higher mechanical stiffness and higher thermal stability.

Both formulations were synthesized in bulk. All reagents were placed in a four-necked flask equipped with Vigreux's column, distillation apparatus, thermo couple, and mechanical stirrer. To prevent crosslinking by radicals formed from oxygen at high temperatures, the reaction was done under a slight nitrogen stream (99.999% N₂, app. 0.6 L/min) using Schlenk technique. Additionally, 500 ppm HQ as inhibitor was added. The condensation polymerization starts at about 135°C. The reaction mixture is slowly heated up to 150°C. At around 140°C, first water distillation can be observed. From that point on the temperature control was changed from bulk temperature to gas phase temperature. The maximum of the reaction temperature was set to 190°C (bulk). The gas phase temperature was limited to 90°C to prevent distillation of diol compounds. The reaction was controlled by determination of acid value (defined as a number of mg potassium hydroxide needed for the neutralization of 1 g of unsaturated polyester). The condensation reaction was stopped when reaching an acid value of ~25 mg KOH/g. After the condensation polymerization of the basic unsaturated polyester the carboxy end groups are end capped with different reagents. As end capping reagents 1-octanol, HEMA, and GMA were evaluated. The stoichiometric amount of end capping reagent was calculated by real and theoretical acid value (0 mg KOH/g). The calculated mass was added to the basic unsaturated polyester and the reaction mixture was heated again to 190°C. Due to the reaction equilibrium the real acid value cannot reach 0 mg KOH/g. Condensation was done until the acid value had been stable within two hours. After end capping procedure acid values between 2 and 9 mg KOH/g could be observed. Additionally, the melt viscosity of the unsaturated polyesters were determined by cone-plate experiment using a Brookfield CAP 2000+ Viscometer (Cap 03: $\beta = 0.45^\circ$, $r = 0.953$ cm) at 150°C. The characteristic properties of modified unsaturated polyesters are presented in Tables I (system 1) and II (system 2). After the condensation polymerization, the modified unsaturated polyester was filled in brown glass bottles and solved in 50 wt % styrene.

Combination of Polysilazanes and Modified Unsaturated Polyester

Combination of polysilazane HTT 1800 with modified UPR was done in 500 mL mixing beakers. In some cases, during stirring a gelation could be observed. The gel could be resolved by continuous stirring for a few minutes. During mixing a reaction of polysilazane and residual-free reactive end groups of UPR could

Table I. Properties of Modified Unsaturated Polyester System 1

| Properties | End capping reagent | | |
|--|---|------------------------------|------------------------------|
| | 1-Octanol | HEMA | GMA |
| Acid value before end capping (mg KOH/g) | 22.99 | 25.99 | 25.00 |
| Acid value after end capping (mg KOH/g) | 9.3 | 17.6 | 2.19 |
| Melt viscosity at 150°C (mPa s) ^a | 593 (10000 s ⁻¹) ^b | 990 (10000 s ⁻¹) | 564 (10000 s ⁻¹) |

^a Measured with Cone-Plate set up.^b Shear rate speed.

be observed by an innocuously gassing. After mixing of the components and adding 1.5 wt % of tert-butyl peroxy (2-ethyl) hexanoate the ready-for-curing mixture was degassed in a desiccator at 400–500 mbar to remove residual ammonia.

Manufacturing of RTM Panels

The described mixture of polysilazane and modified UPR could be easily processed in a RTM unit. 12 layers of a woven 0°/90° carbon fiber fabric KDK 8058 (SGL Carbon, 160 g/m²) were used as reinforcement. A RTM mold of rectangular geometry with 3 mm deep cavity was used. The curing mixture could be easily infused under slight pressure (1 bar) and a dwell pressure of 2 bar. The curing was done for 1 h at 160°C and for 1 h at 180°C. After cooling the RTM samples could be easily demolded.

Characterization

DMA measurements were performed using a Dynamic Mechanical Analyzer Solid Analyzer 3-RSA 6 from Rheometrics Scientific. As test device a three-point bending setting with a span of 40 mm was used. The calibration was done in accordance to the producer's recommendation. Temperature scanning (30–200°C) was done with a constant heating rate of 4 K/min. The oscillation frequency was set to 1 Hz. Sample specimens had a size of 45 mm × 6 mm × 3 mm. The determination of glass transition temperature (T_g) was evaluated by $\tan \delta$ peak value, which is the ratio of loss modulus (E'') and storage modulus (E') [eq. (1)].

$$\tan \delta = \frac{E''(\omega)}{E'(\omega)} \quad (1)$$

Cone calorimetry measurements were used to evaluate the burning behavior of hybrid resin composites. Standardized samples of 100 mm × 100 mm × 3 mm were used in accordance with ISO 5660 at a heat flux of 50 kW/m² (testing specification from railway standard DIN CEN/TS 45545-2).^{15,16} As test device a Cone Calorimeter (2002) from Fire Testing Technologies was

used. For the evaluation of burning behavior the main parameters Time To Ignition (TTI), peak of heat release rate (HRR_p), maximum average rate of heat emission (MARHE), total heat release (THR), total smoke release (TSR), and mass loss (Δm) were determined and interpreted. The samples were placed in a sample holder with a retainer frame, resulting in 88 cm² of the sample surface being exposed to the radiation from the cone heater. From each material two samples were tested. The mean values are based for the evaluation of burning behavior in general but they show a distinct tendency. Therefore given data represents values for the respective sample with lowest fire retardancy.

Additionally to the cone calorimetry measurements the hybrid resin composites were characterized in accordance with UL-94 V standard with a sample thickness of 3.0 mm. Test procedure and conditions are given in the literature.^{17,18}

The thermal degradation of cured neat UPRs (without fiber reinforcement) was followed by monitoring weight loss corresponding to temperature under oxidizing atmosphere. The samples were weighed in ceramic crucibles and tested without further treatment. As test device a Mettler TGA/SDTA 851^e was used. The measurement was performed from 25 to 800°C using a heating rate of 10K/min under an air stream of ~0.015 L/min.

RESULTS AND DISCUSSION

Chemical Modification of Unsaturated Polyesters

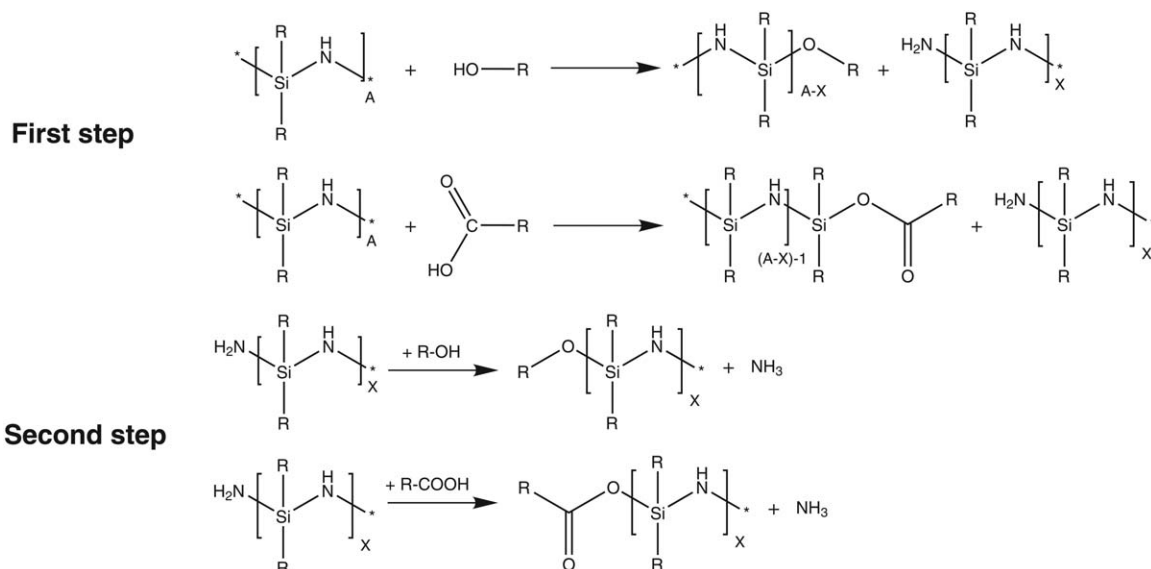
Polysilazanes show a high reactivity against O-nucleophiles. Therefore, reactions with hydroxy and carboxy end groups of the unsaturated polyesters have to be considered. These reactions are characterized by the emission of ammonia while forming Si–O bonds.

Essential for the development of an unsaturated polyester/polysilazane resin is the knowledge of the reaction intensity for each kind of functional polyester end group. To avoid a gelation

Table II. Properties of Modified Unsaturated Polyester System 2

| Properties | End capping reagent | | |
|--|---|------------------------------|------------------------------|
| | 1-Octanol | HEMA | GMA |
| Acid value before end capping (mg KOH/g) | 15.00 | 22.94 | 23.50 |
| Acid value after end capping (mg KOH/g) | 6.93 | 8.73 | 5.3 |
| Melt viscosity at 150°C (mPa s) ^a | 5787 (1600 s ⁻¹) ^b | 2155 (4000 s ⁻¹) | 2098 (4000 s ⁻¹) |

^a Measured using Cone-Plate set up.^b Shear rate.



Scheme 2. Schematic reaction of polysilazanes and unsaturated polyester end groups (hydroxy and carboxy).

during mixing, a reactivity study of unsaturated polyester with polysilazane was done with model substances (fumaric acid, diethyl fumarate, and ethylene glycol). The acid groups almost immediately started to react with HTT 1800 in an exothermic reaction under formation of foam, which cannot be accepted in hybrid resin (see Scheme 2).

Hydroxy groups also show a high reactivity with polysilazanes but much slower and with lower intensity than acids. In consequence, further research was concentrated on acid group end capping. In contrast to carboxy and hydroxy groups, ester groups do not react with polysilazanes. Therefore, the combination of unsaturated polyesters and polysilazanes is indeed possible, but requires a modification especially on the carboxy end groups (see Scheme 2).

Furthermore, the knowledge of potential chemical reactions of polysilazanes with peroxide initiators during the compounding process is important. An experimental study carried out by C. Caspari shows that the reactivity of polysilazanes and peroxides is correlated with the oxidizing potential of peroxide species. The oxidizing potential shows the following trend: peroxy acids > alkyl hydroperoxides > diacyl peroxides > peresters > alkyl peroxides.¹⁹ By choosing the initiator one has to consider the half-life temperature to set up proper curing conditions. In this study, a perester (tert-butyl peroxy-2-ethylhexanoate) was used to initiate the curing process.

Thermo-mechanical Analysis

To investigate the influence of polysilazane in organic/inorganic hybrid resins the glass transition temperature (T_g) was determined by DMA for 0 and 33 wt % of polysilazane for two unsaturated polyester systems. This investigation allows an evaluation of end capping reagent effects in terms of thermo-mechanical properties. By using DMA the differences in network formation can also be observed and correlated to the resin structure. Furthermore, T_g is an important property for application. Table III shows the composition of RTM plaques based on system 1 (standard formulation for UPR) and the resulting T_g . Due to system incompatibility of modified UPR and polysilazane caused by the high residual acid value after end capping of unsaturated polyester no RTM plaques for HEMA modified unsaturated polyester system 1 can be produced. Therefore, this formulation could not be used for further developments.

Figure 1 shows the DMA curves for RTM plaques 1a to 2b. The graph shows that the polysilazane (RTM-1a) weakens the network in comparison to the neat UPR (RTM-1b). This is assured by a broader glass transition and a 25 K decrease in T_g . Comparing the neat resin samples RTM-1b and 2b, a softening effect on network formation is evident. This effect results in a decreased T_g (about 10 K) for 1-octanol compared to GMA. 1-octanol acts in the network as a long side chain and does not allow an ideal network formation while GMA contains a

Table III. Composition of RTM Plaques for System 1 and Results from DMA Measurement

| Sample | Unsaturated polyester system | End capping reagent | HTT 1800 (wt %) | T_g (°C) |
|--------|------------------------------|---------------------|-----------------|------------|
| RTM-1a | 1 | 1-Octanol | 33 | 100 |
| RTM-1b | 1 | 1-Octanol | 0 | 125 |
| RTM-2a | 1 | GMA | 33 | 138 |
| RTM-2b | 1 | GMA | 0 | 136 |

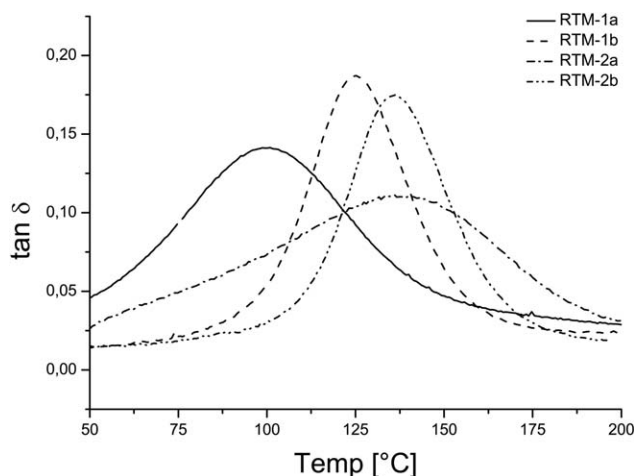


Figure 1. DMA curves for RTM-1a (-), RTM-1b(--), RTM-2a(-.-), and RTM-2b (-.-).

reactive double bond which incorporates in the network during curing. Comparing RTM-2a and 2b no difference in T_g can be observed, but the conspicuously changed relaxation behavior (glass transition takes place between 50 and 180°C) evinces a more inhomogeneously crosslinked network.

DMA measurements were done for system 2- (UPR with higher T_g) based hybrid resin RTM plaques as well. Table IV shows the composition and the measured T_g .

Figure 2 shows the DMA curves for RTM plaques referring to Table IV. As expected, the comparison of system 1 and 2 results in ΔT_g of 30–35 K which is related to stiffer unsaturated polyester building blocks in system 2. In the same manner as for system 1, a large decrease in T_g can be observed for 1-octanol end capped unsaturated polyester system 2 in combination with HTT 1800. DMA results show a ΔT_g of ~50 K for this system. For HEMA or GMA end capped resins combined with HTT1800 a drop in T_g of ~30 K could be measured. In all system 2 plaques a decrease in crosslink density and a broader glass transition peak was observed when HTT 1800 was used.

The evaluation of the thermo-mechanical properties of system 1 and 2 shows that end capping is reasonable to increase the compatibility of polysilazanes and modified UPRs with acceptable thermo-mechanical properties comparable to standard UPRs.

Burning Behavior

Cone calorimeter measurements allow the observation of several aspects of burning at a time, e.g., TTI or THR. This method is

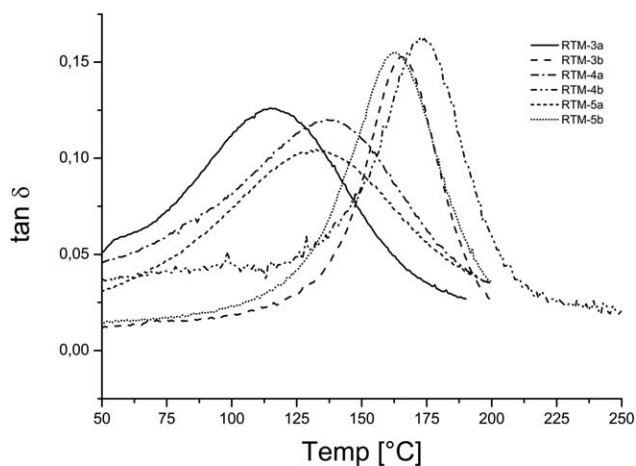


Figure 2. DMA curves for RTM-3a (-), RTM-3b(--), RTM-4a(-.-), RTM-4b (-.-), RTM-5a (-.-), and RTM-5b(-.-).

likely used in research and development, due to the holistic burning process approach as a function of time and its simultaneous measurement of smoke and heat. Table V shows the cone calorimeter measurement data for all RTM plaques.

No serious differences between type of end capping reagent and resin type can be observed in the measurement data. In general, these results show the different fire-retarding mechanisms with polysilazanes in comparison to other state-of-the-art methods, e.g., adding of filler (aluminum trihydroxide), phosphorous, and/or intumescent additives.²⁰ In contrast to these mechanisms, polysilazanes act as char increasers by forming ceramic structures during burning. The resulting ceramic is non-flammable and delivers a high mechanical stiffness in comparison to carbon char. Therefore, polysilazanes are promising in various application fields, especially for construction purposes, where a residual mechanical stiffness is advantageous. In detail, polysilazane/unsaturated polyester hybrid systems reinforced with carbon fibers show only a mass loss of ~30 wt %. Another positive effect is the low smoke emission during fire. Usually, high smoke emission is a major disadvantage of unsaturated polyester-based FRPs. Due to its toxicity smoke is a major hazard in case of fire for humans and much more hazardous than flames and heat. In the UK (2010/11) 34 % of all fire-related deaths result from gas or smoke inhalation. Additionally, 18 % of deaths cannot be related to fire or smoke separately. In contrast, only 24 % of deaths result from burning.²¹

In addition to cone calorimeter measurement, the RTM plaques were also characterized using UL-94 V fire test. The test results

Table IV. Composition of RTM Plaques for System 2 and Results from DMA Measurement

| Sample | Unsaturated polyester system | End capping reagent | HTT 1800 (wt %) | T_g (°C) |
|--------|------------------------------|---------------------|-----------------|------------|
| RTM-3a | 2 | 1-Octanol | 33 | 115 |
| RTM-3b | 2 | 1-Octanol | 0 | 165 |
| RTM-4a | 2 | HEMA | 33 | 137 |
| RTM-4b | 2 | HEMA | 0 | 171 |
| RTM-5a | 2 | GMA | 33 | 133 |
| RTM-5b | 2 | GMA | 0 | 161 |

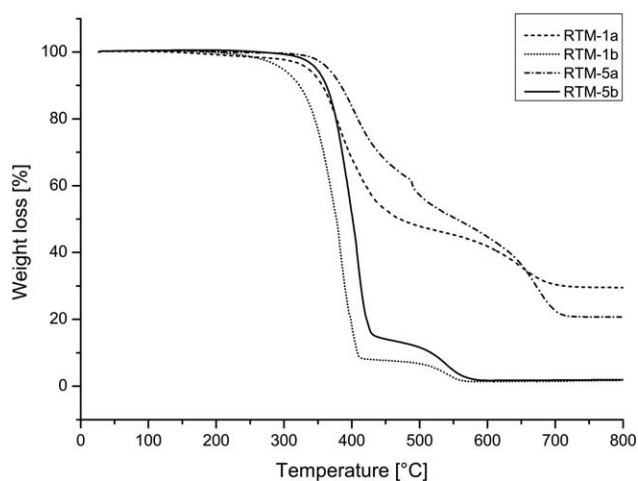
Table V. Results from Cone Calorimeter Measurements for RTM-1 to -5 at 50 kW/m² Heat Flux

| Sample | UL-94 classification | Appearance of residual char |
|--------|----------------------|-----------------------------|
| RTM-1a | Failed | Not delaminated |
| RTM-1b | Failed | Delaminated |
| RTM-2a | Failed | Not delaminated |
| RTM-2b | Failed | Delaminated |
| RTM-3a | Failed | Not delaminated |
| RTM-3b | Failed | Delaminated |
| RTM-4a | Failed | Not delaminated |
| RTM-4b | Failed | Delaminated |
| RTM-5a | Failed | Not delaminated |
| RTM-5b | Failed | Delaminated |

are shown in Table VI. Due to a quick and fast burning behavior without extinguishing of flames after flaming, all RTM samples failed the UL-94 V classification independent if polysilazane is added or not. Because UL-94 V classification considers only the flaming and burning behavior, the char forming mechanism of polysilazanes takes no effect on classification. In consequence the new hybrid thermosetting resins are not suitable for applications which have to pass UL-94 V testing.

This behavior was expected. During cone calorimeter measurements the specimens ignited quite fast (TTI). The influence of polysilazane becomes obvious by observing the residual char. The burned laminates are delaminated for all unmodified samples, while for all polysilazane modified RTM samples the laminated structure remained stable. The residual laminated structure leads to a higher residual strength of the burned component. As mentioned before, this behavior could be of interest for several construction purposes.

During the synthesis of unsaturated polyesters and during end capping a slight extent of diols was used. Due to the fact that the end capping reaction cannot be driven to an ideal acid value of 0 mg KOH/g a small amount of monomeric substances has

**Figure 3.** TGA results for neat resins (without reinforcement) RTM-1a/1b and RTM 5a/5b.

to be taken into account. This extent of monomers could be the answer for the fast ignition and the quick burning behavior. To check this, two different pairs of resins (RTM-1a/1b and RTM 5a/5b) had been picked out and were additionally characterized by Thermo-Gravimetric Analysis (TGA). No significant differences were expected due to more or less comparable chemical and physical behavior of the different hybrid resin systems. Therefore, no complete characterization of all RTM systems was done. The results of TGA measurements are shown in Figure 3.

For both resin systems the TGA showed no significant mass loss up to 250°C. Therefore, the influence of the extent of monomeric substances does not lead to a significant weight loss or to a faster decomposition of the cured resin. There is no correlation between monomer extent and fast ignition during the fire testing. In detail, TGA showed that there is a large increase on the residual char using the organic/inorganic hybrid resins which can be correlated to the residual char from cone calorimeter measurement. The unmodified UPRs decompose without forming a significant amount of char. Due to the crosslinked end capping of RTM-5 (GMA) the onset temperature of

Table VI. Results from UL-94 Characterization

| Sample | UP system | End capping reagent | HTT 1800 (wt %) | Mass (g) | Thickness (mm) | TTI (s) | HRRp (kW/m ²) | MARHE (kW/m ²) | THR (MJ/m ²) | TSR (m ² /m ²) | Δm (%) |
|--------|-----------|---------------------|-----------------|----------|----------------|---------|---------------------------|----------------------------|--------------------------|---------------------------------------|----------------|
| RTM-1a | 1 | 1-Octanol | 33 | 35.32 | 2.7 | 33 | 344/696 | 283 | 32 | 1160 | 32 |
| RTM-1b | 1 | 1-Octanol | 0 | 38.13 | 3 | 44 | 438/348 | 236 | 51 | 1900 | 51 |
| RTM-2a | 1 | GMA | 33 | 39.11 | 2.8 | 39 | 727 | 268 | 37 | 1310 | 29 |
| RTM-2b | 1 | GMA | 0 | 39.16 | 3 | 45 | 375/378 | 236 | 51 | 2020 | 51 |
| RTM-3a | 2 | 1-Octanol | 33 | 37.96 | 2.8 | 36 | 630/536 | 285 | 37 | 1300 | 33 |
| RTM-3b | 2 | 1-Octanol | 0 | 37.02 | 3 | 47 | 309/391 | 230 | 48 | 2100 | 50 |
| RTM-4a | 2 | HEMA | 33 | 39.67 | 2.9 | 48 | 772 | 269 | 41 | 1365 | 31 |
| RTM-4b | 2 | HEMA | 0 | 37.02 | 3 | 47 | 309/391 | 230 | 48 | 2100 | 50 |
| RTM-5a | 2 | GMA | 33 | 37.53 | 2.8 | 49 | 655 | 250 | 37 | 1270 | 30 |
| RTM-5b | 2 | GMA | 0 | 41.68 | 3 | 53 | 396/332 | 229 | 61 | 2740 | 52 |

decomposition is much higher than for the uncrosslinked end capping with 1-octanol in RTM-1.

Both fire test methods and the TGA showed that hybrid resin FRPs are burning fast and show high char residue. So the total heat emission is drastically reduced. Yet, high intensity of burning and short TTI are two inappropriate properties compared to state-of-the-art fire-retardant mechanisms, which leads to fail several common test procedures.

CONCLUSIONS

In this research the development of unsaturated polyester/poly-silazane hybrid thermosetting resins was presented. Aim of this development was to increase the fire retardancy of UPRs without fillers for RTM processing. Because of the high reactivity of polysilazanes against standard unsaturated polyester end groups—especially COOH groups—a chemical modification was necessary to develop an appropriate hybrid resin system with good processing properties. End capping procedures as chemical modification for carboxylic groups were developed. Crosslinkable end capping reagents are important to obtain satisfying properties in cured FRPs. Indeed, the selection of end capping reagents has to meet condensation polymerization conditions: The reagents have to be stable up to 195°C and need to have a boiling point above this temperature. Considering condensation behavior, processing and FRP properties HEMA and GMA are very promising end capping reagents.

Vinyl containing polysilazanes are crosslinkable with styrene and unsaturated polyesters. Their weakening effect on network results in a certain decrease of thermo-mechanical properties, especially T_g . A variation in unsaturated polyester basic formulations allows customization of properties. The resulting reduction in T_g by using polysilazanes as a hybrid component is about 30 K. UPRs used in this study are able to balance this, so that RTM plaques with satisfying technical properties result.

The most important effect of polysilazane hybrid resins is their high fire retardancy in comparison to unmodified UPRs. In difference to state-of-the-art fire-retardants polysilazanes result in flammable products with low TTI and fast burning behavior, which is of course disadvantageous. Also the very common UL-94 classification was failed for all samples. Nevertheless, this kind of protection leads to an increased char formation (formation of ceramic products), smoke suppression and total heat reduction. Beneficial for this material is a high mechanical stiffness of the burned FRPs, which will be of interest for various applications fields, especially construction purposes, where residual mechanical properties are necessary. Its low smoke emission is essential for life and safety of humans and animals.²²

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