

# Hybrid Thermosets from Polyisocyanate/Water Glass/Emulsifier Systems: Effects of Melamine-Formaldehyde Resin

Núria Castellà,<sup>1</sup> Sergiy Grishchuk,<sup>1</sup> Jozsef Karger-Kocsis,<sup>2,3</sup> Martin Schehl<sup>1</sup>

<sup>1</sup>Institut für Verbundwerkstoffe GmbH (Institute for Composite Materials), Kaiserslautern University of Technology, D-67663 Kaiserslautern, Germany

<sup>2</sup>Faculty of Mechanical Engineering, Department of Polymer Engineering, Budapest, University of Technology and Economics, H-1111 Budapest, Hungary

<sup>3</sup>Polymer Technology, Faculty of Engineering and Built Environment, Tshwane University of Technology, Pretoria 0001, South Africa

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**ABSTRACT:** Melamine-formaldehyde resin (MF) was selected as potential reactive emulsifier for polyurea-based thermoset resins produced from polyisocyanate/water glass (WG)/emulsifier systems. As emulsifier tricresyl-phosphate and/or MF served for the initial water-in-oil type ("water" = WG; "oil" = polyisocyanate + emulsifier) emulsions. The MF content of the systems has been varied ( $\leq 15$  wt %) and its effect on the structure, mechanical, thermal and flammability properties of the final polyurea-based thermosets studied. It was found that MF is a suitable

emulsifier, which can fully replace the phosphate without negatively affecting the properties of the resulting hybrid thermosets. Moreover, hybridization with MF was often accompanied with pronounced improvements in fracture mechanical and static flexural properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 7–14, 2011

**Key words:** thermosetting hybrid resins; dispersions; particle size distribution; flame retardance; structure-property relations

## INTRODUCTION

Polyisocyanates are highly reactive components which may enter in different reactions resulting in linear and crosslinked polymers, such as polyurethanes, polyisocyanurates, and polyureas. The latter compounds form by reactions between  $-NCO$  and  $-NH_2$  groups. Primary amines can be produced via the reaction  $-NCO + H_2O \rightarrow -NH_2 + CO_2$  from polyisocyanates, as well. This reaction is taking place in presence of aqueous media, like water glass (WG). Accordingly, WG is an interesting reactant in the polyisocyanate chemistry.<sup>1–5</sup> Note that WG is a mixture of salts (usually sodium or potassium) of polysilicic acids.

WG, when dispersed in polyisocyanates with a functionality of higher than 2, yields highly reactive water in oil type emulsion (W/O). This cures very fast into a polyurea-based thermoset. The rapid reaction between the water and the isocyanate can

hardly be controlled unless a suitable emulsifier is used. Commercially available systems, as 3P resins of Polinvent Ltd, Budapest, Hungary, contain phosphates as emulsifiers and thus "reaction controllers".<sup>6</sup> Note that the designation of 3P is derived from the related composition: polyisocyanate, phosphate and polysilicate. "Polysilicate" is formed by hardening (silicification) of WG. The related resins are gaining acceptance in repair of pipes (canalization) and strengthening of walls (mining industry, tunnels). Such applications are favoured by the fact that 3P resins cure also in and under water. Attempts were already made to improve the thermal, mechanical and fracture mechanical properties of the corresponding polyurea based thermosets. "Nanomodification" by incorporating nanoscaled water dispersible alumina proved to be less promising<sup>7</sup> than the hybridization concept targeting the polyurea-type matrix.<sup>8–10</sup>

The presence of phosphate is a problematic issue in the 3P systems due to its diffusion, "leakage". Following the European Community Regulation on chemicals and their safe use registration, evaluation, authorization and restriction of chemical substances (REACH) (EC 1907/2006),<sup>11</sup> which calls for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified,

Correspondence to: S. Grishchuk (sergiy.gryshchuk@ivw.uni-kl.de).

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vivid search started to find suitable emulsifiers for the polyisocyanate/WG systems. Our intention was to replace or at least reduce the amount of the present organic phosphate being not environmental benign. The new emulsifiers should be coreactive, prolong the pot life of the hybrid systems and enhance or maintain their properties. Accordingly, the present work was focused on the application of emulsifiers of coreactive nature for the polyisocyanate/WG systems. "Reactive" means that the related emulsifiers should be chemically built in the final cross-linked structure.

For that purpose, we have selected water-free melamine-formaldehyde resin (MF) which is resistant to strong alkalis (like WG) and via its methylol groups reactive towards the  $\text{-NCO}$  groups of the polyisocyanate. So the aim of this contribution was to check whether MF can replace phosphate and thus overtake the role of an "active emulsifier" in 3P systems. A further aim of this work was to determine whether the incorporation of MF is accompanied with improvement with respect to the mechanical and thermal properties of the corresponding hybrid resins.

Due to the poor solubility of MF in aqueous media attempts were made to replace the phosphate emulsifier completely by MF. The related resins are termed 2P resins (from polyisocyanate and polysilicate).

When MF is dispersed in isocyanate, the hydroxyls from the methylolated melamine react with isocyanates to produce urethane crosslinking sites between the final polyurea and MF.

Among other possible, but less probable reactions, the reaction between the amines (formed thanks to the reaction of isocyanates with WG) with the hydroxyls of the methylolated melamine is noteworthy.<sup>12–15</sup> However, this reaction is practically inexistent since first, the majority of the amine formed will react with isocyanates to form the polyurea matrix, and second, the MF crosslinking reaction according to Scheme 2 is negligible at room temperature (while it increases exponentially with temperatures above 100°C). Therefore, the crosslinking via amines occurs mainly during curing of the resin.<sup>16–21</sup>

## EXPERIMENTAL

### Materials

The silicate source (Inosil Na-5120 waterglass (WG) of sodium silicate type) was donated by ASAG Umwelttechnik (Neukirchen-Vluyn, Deutschland). This WG had a "modulus", i.e.  $\text{SiO}_2/\text{Na}_2\text{O} = 2.02 \pm 0.02$ , and a viscosity:  $600 \pm 100$  mPa·s ambient temperature. As polyisocyanate source 4,4'-diphenylmethane diisocyanate (PMDI) was used. Ongronat<sup>®</sup> CR-30-60 PMDI 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. For the PMDI/WG system tricresylphosphate (TCP) (Disflamoll TCP, Lanxess Deutschland GmbH, Leverkusen, Germany) was used as an emulsifier; phosphorous content: 8.4 wt %; density: 1.18 g/mL at 20°C; viscosity: 69 mPa s at 20°C. MF (HIPE<sup>®</sup>ESIN MF 100C) was purchased from Agrolinz Melamine International Italia S.r.l (Castellanza, Italy). This MF was a white powder of  $\sim 0.6$  kg/dm<sup>3</sup> bulk density and with less than 2.0 wt % of volatile content. Note that MF is soluble at room temperature in water and water/alcohol mixtures.

### Sample preparation

The 3P/MF hybrid resins were prepared first by homogenising the TCP and the PMDI for 1 min at 1400 rpm with a cogged-wheel-mixer. Subsequently MF was dispersed in the PMDI/TCP mixture for 1 min at 2000 rpm with the same mixer and degassed under vacuum. WG was added and dispersed in the final system for 1 min at 800 rpm with the mixer. The MF content in the 3P resins was varied, viz. MF was applied in 15, 10, 5, 2.5, 1, 0.5 wt % MF considering the total resin content.

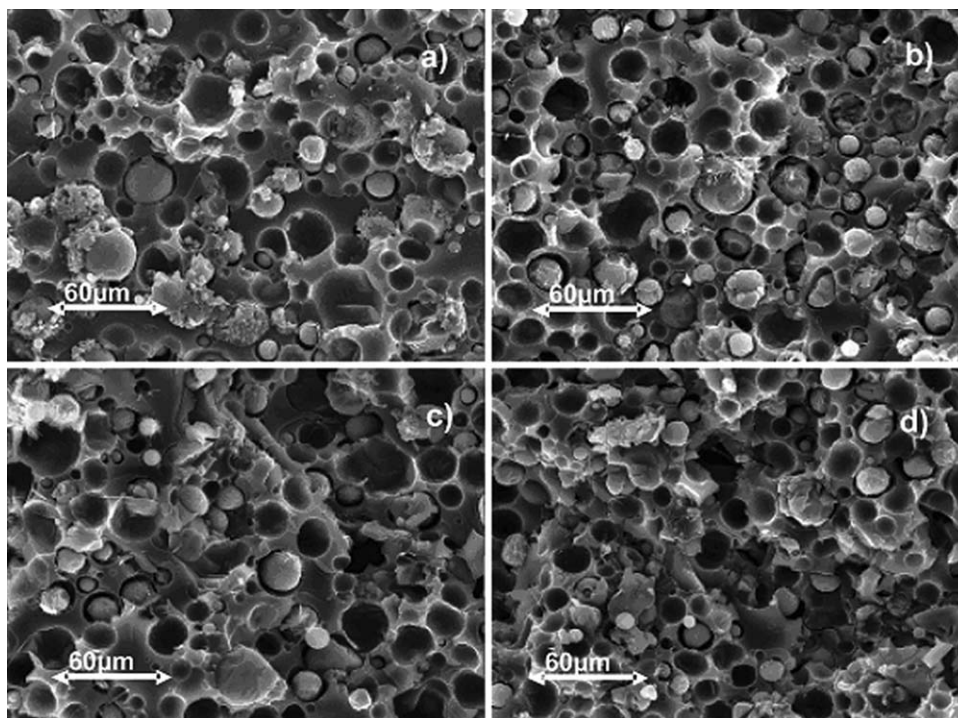
Attempts were also made to fully replace the TCP in the recipe. The corresponding systems were termed to 2P resins (from polyisocyanate and polysilicate). The 2P/MF hybrid resins were produced as follows: different amounts of MF (0.5, 1, 2.5, 5, 10, and 15 wt % of the total sample weight) were dispersed in PMDI with a cogged-wheel mixer for 1 min at 2000 rpm and then the air bubbles were removed under vacuum. Afterwards WG was added and dispersed for 1 min at 800 rpm.

The resulting mixtures, 3P/MF and 2P/MF, were both degassed in vacuum. Their curing regime was 20 h at RT and 4 h at 100°C.

### Tests

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 diameter respectively.

The fracture toughness ( $K_{Ic}$ ) and fracture energy ( $G_c$ ) were measured according to ISO 13586-1 standard. The tests were done with a Zwick universal



**Figure 1** SEM pictures from the broken surfaces of the reference 3P resin (a), 3P/MF-1% hybrid resin (b), 3P/MF-5% hybrid resin (c), 3P/MF-10% hybrid resin (d).

testing machine type 1445 (Ulm, Germany) at room temperature with a crosshead speed of  $v = 1$  mm/min. The CT specimens (dimension:  $35 \times 35 \times 3$  mm<sup>3</sup>; length  $\times$  width  $\times$  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 ( $60 \times 10 \times 3$  mm<sup>3</sup>; length  $\times$  width  $\times$  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 ( $60 \times 10 \times 3$  mm, length  $\times$  width  $\times$  thickness) in three point bending configuration (span length: 50 mm) at 1 Hz using a DMA Q800 of TA Instruments (New Castle, DE). Tests were performed under displacement control using sinusoidal oscillation and under dynamic conditions in the interval  $T = +25^\circ\text{C} \dots +250^\circ\text{C}$  at a heating rate of  $1^\circ\text{C min}^{-1}$ .

The resins were subjected to thermogravimetric analysis (TGA) in a TG50 device of Mettler Toledo (Giessen, Germany). The TGA experiments were conducted under nitrogen atmosphere in the temperature range  $T = 25^\circ\text{C} \dots +600^\circ\text{C}$  with heating rate  $20^\circ\text{C/min}$ .

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, 94V flammability vertical test was chosen being a stringent test. In the 94V 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 AND DISCUSSION

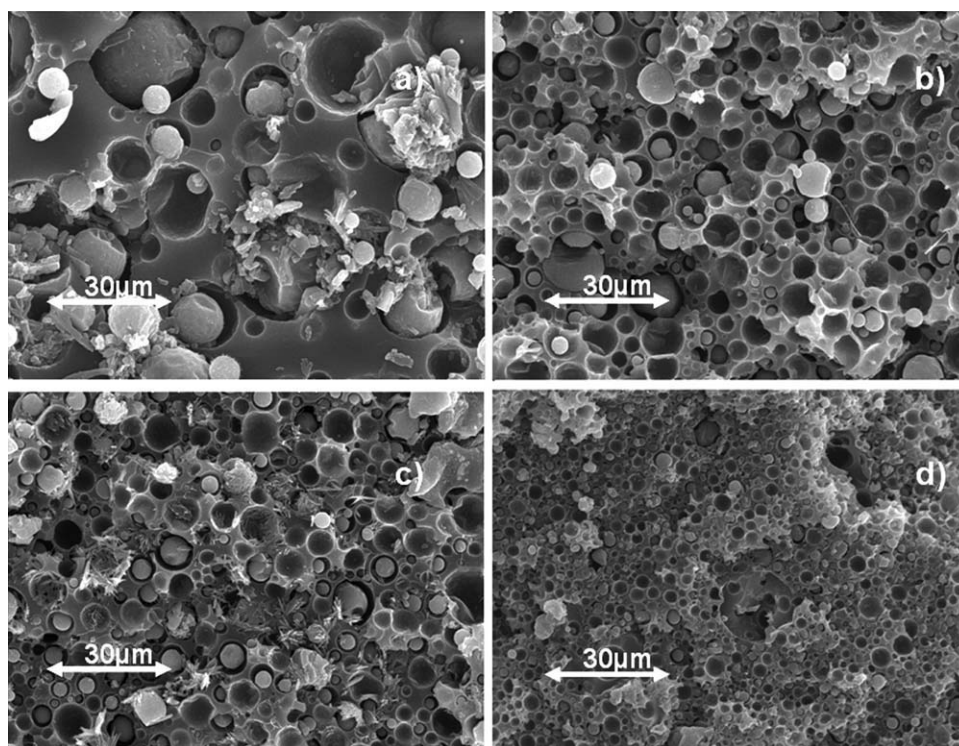
### Polysilicate dispersion

#### 3P/MF

The morphology of the 3P/MF hybrid systems, studied from the SEM pictures of the fracture surfaces (cf. Fig. 1), reveal no apparently influence of the MF.

**TABLE I**  
Number- ( $d_n$ ) and Weight-Average ( $d_w$ ) Mean Particle Size of the 3P Reference and 3P/MF Hybrid Systems

MF wt %	0 (3P)	0.5	1	2.5	5	10	15
$d_n$ (μm)	11.2	12.7	10.9	11.2	11.0	9.7	7.5
$d_w$ (μm)	15.5	17.9	13.8	16.1	15.9	12.7	10.7
$d_w/d_n$	1.4	1.4	1.3	1.4	1.5	1.3	1.4



**Figure 2** SEM pictures taken from the fracture surfaces of the 3P resin sample (a), 2P/MF-1% hybrid resin (b), 2P/MF-5% hybrid systems (c), 2P/MF-10% hybrid systems (d).

Considering the morphology of the reference 3P and those of the 3P/MF hybrids, one can see that neither the particles size nor the distribution of the polysilicate particles altered by the hybridization of the initial 3P resin with MF. However, when inspecting more accurately, one can observe that increasing MF contents reduce slightly the mean particle size diameter and that the 3P/MF hybrids as well as, the reference resin 3P, possess similar broad particle distributions (cf. Table I). Table I indicates that the amount of MF in the hybrid resins had little influence on the polysilicate particle distribution.

#### 2P/MF

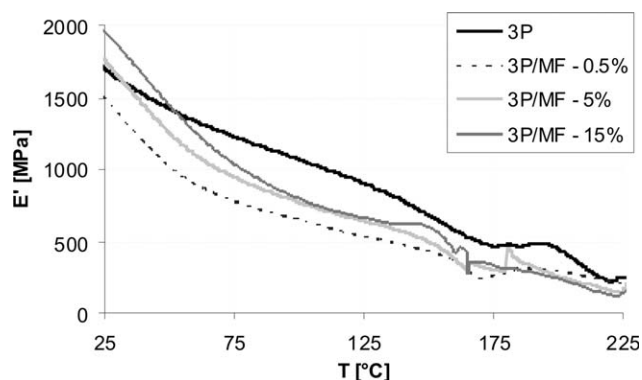
The SEM pictures obtained from the broken surface of the 2P/MF systems are presented in Figure 2. The substitution of the phosphate by the MF reduced

**TABLE II**  
Number- ( $d_n$ ) and Weight-Average Diameter ( $d_w$ )  
of the Polysilicate Particles in the 3P Reference  
and 2P/MF Hybrid Systems

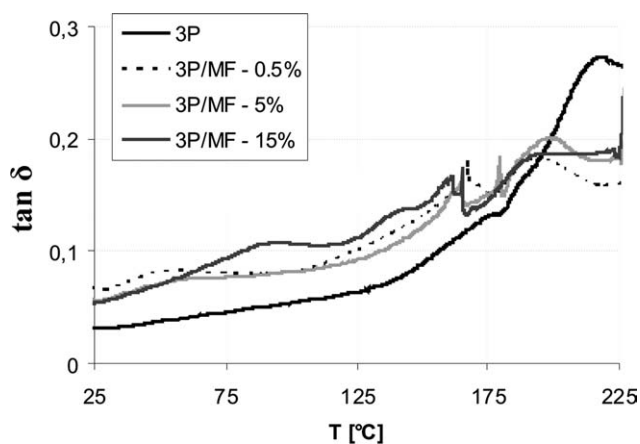
MF wt %	0 (3P)	0.5	1	2.5	5	10	15
$d_n$ ( $\mu\text{m}$ )	11.2	3.9	4.0	4.7	3.9	2.6	6.2
$d_w$ ( $\mu\text{m}$ )	15.5	5.5	5.6	7.2	5.3	2.7	8.8
$d_w/d_n$	1.4	1.4	1.4	1.5	1.3	1.1	1.4

substantially the particle size of the polysilicate in comparison with the reference 3P resins. The reference 3P resin had an average particle size diameter of 10  $\mu\text{m}$ , while for the 2P/MF hybrid systems this was reduced to its half, however, with some exceptions (cf. Table II). Moreover, the substitution of the phosphate by MF did not broaden the polysilicate distribution.

Attention should be paid to the fact that the system 2P/MF-10% owes a very small particle size and a narrower distribution compared to the other hybrids. This is well reflected in Figure 2d.



**Figure 3** DMTA results displaying  $E'$  vs.  $T$  for the 3P reference and 3P/MF hybrids.

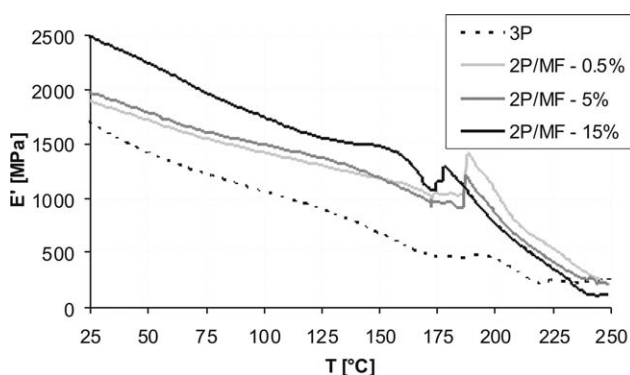


**Figure 4** DMTA results displaying  $\tan \delta$  vs.  $T$  for the 3P reference and 3P/MF hybrids.

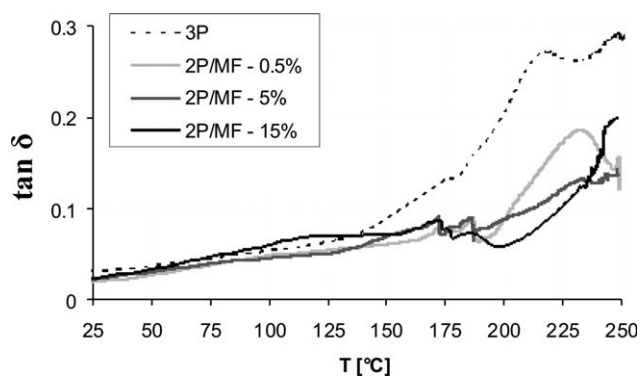
### DMTA response, phase structure

The DMTA tests results in form of storage modulus vs. Temperature ( $E'$  vs.  $T$ ) traces are given in Figure 3 for the 3P and the 3P/MF hybrid resins. The storage modulus ( $E'$ ) is mostly improved by the addition of MF in the systems, however only at room temperature. At higher temperatures the reference 3P resin exhibits higher stiffness than the 3P/MF versions. At temperatures around 150°C the 3P/MF specimens undergo a brusque discontinuity caused by premature failure. For the reference 3P resins such failure takes place at temperatures above 180°C.

Inspecting the mechanical loss factor ( $\tan \delta$ ) vs.  $T$  traces for the reference 3P and its 3P/MF hybrids depicted in Figure 4, one can observe that the 3P/MF hybrid resins present two broad "shoulders" in the  $\tan \delta$  traces at temperatures from 50 to 100°C and a second one from 130 to 160°C. Further, a not well resolved relaxation peak is also observed at temperatures from 180 to 210°C. Unfortunately, the premature failure of the specimens at  $T > 150^\circ\text{C}$  hampers its detection.



**Figure 5** DMTA results displaying  $E'$  vs.  $T$  for the 3P reference and 2P/MF hybrids.



**Figure 6** DMTA results displaying  $\tan \delta$  vs.  $T$  for the 3P reference and 2P/MF hybrids.

The DMTA traces in form of  $E'$  vs.  $T$  for the 3P and the 2P/MF hybrid resins are depicted in Figure 5. The stiffness ( $E'$ ) increases with increasing MF content in the systems and it was higher than that of the 3P resin. One can recognise an abrupt discontinuity in the  $E'$  traces at  $T$  around 180°C for the 2P/MF systems as well as for the 3P reference resin due to the failure onset in the specimens at high temperatures.

In the  $\tan \delta$  vs.  $T$  traces, depicted in Figure 6, one can not clearly discern the glass transition temperature ( $T_g$ ), when assigned to the highest peak temperature of the  $\tan \delta$  vs.  $T$  traces. However, despite of the premature failure, the 2P/MF-0.5% and 2P/MF-5% hybrid resins show a reasonably definite peak at temperatures ranging from 200 to 250°C and a second broad and less resolved peak of low intensity centred at  $T \sim 175^\circ\text{C}$ . For the other hybrids, containing larger amounts of MF, the  $\tan \delta$  peak at high temperatures is not well resolved.

### Flexural and fracture mechanical properties

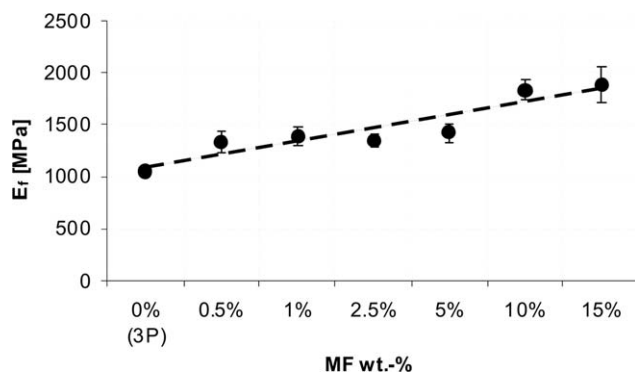
#### 3P/MF—mechanical properties

The fracture energy ( $G_c$ ) and fracture toughness ( $K_{Ic}$ ) for the 3P/MF hybrid resins are summarized in Table III. The hybridization of the 3P resins with MF

**TABLE III**  
Fracture Toughness ( $K_{Ic}$ ) and Fracture Energy ( $G_c$ )  
for the 3P Reference and 3P/MF Hybrids

	$K_{Ic}$ (MPa m <sup>1/2</sup> )	$s$ (MPa m <sup>1/2</sup> )	$G_c$ (kJ m <sup>2</sup> )	$s$ (kJ m <sup>2</sup> )
3P	0.83	0.04	0.89	0.04
3P/MF-0.5%	0.91	0.04	1.26	0.09
3P/MF-1%	0.89	0.02	1.36	0.06
3P/MF-2.5%	0.90	0.02	1.18	0.03
3P/MF-5%	0.97	0.02	0.99	0.04
3P/MF-10%	0.87	0.02	0.83	0.05
3P/MF-15%	0.85	0.02	0.72	0.03

$s$  represents the standard deviation.



**Figure 7** Changes in the flexural modulus as a function of the MF content for the 3P based systems.

did have an effect on the fracture properties. Beholding the changes of the fracture properties for the hybrids with different MF content, one can see that the fracture energy of the hybrids is improved in relation to the reference. A  $G_c$  increase was found for all the hybrids up to an MF content threshold of 10 wt % MF, where  $G_c$  is slightly lower than the reference 3P afterwards. It is noteworthy that  $G_c$  decreases with the MF content of the hybrid resins. This could be related to the diminished polysilicate particle size (cf. Table I) with increasing MF content which affects the failure mode. On the other hand,  $K_c$  does not appear to be influenced by the hybridization with MF or by its amount. However, in general the fracture properties of the novel hybrid resins experienced a modest improvement.

The flexural properties of the 3P/MF hybrid resins were positively influenced by the incorporation of MF (cf. Figure 7). Satisfactory results on the flexural properties were obtained from the hybridization of the 3P resins with MF. Increasing amounts of MF improve markedly the flexural modulus ( $E_f$ ). In general, the increase of  $E_f$  is parallel to the increase in MF. The strength passed a maximum whereas the flexural strain decreased as a function of MF wt.-% content (cf. Table IV).

**TABLE IV**  
Flexural Modulus ( $E_f$ ), Strength ( $\sigma_{fm}$ ), Strain ( $\epsilon_m$ ) and Standard Deviation ( $s$ ) for the 3P Reference and 3P/MF Hybrids

	$E_f$ (MPa)	$s$ (MPa)	$\sigma_{fm}$ (MPa)	$s$ (MPa)	$\epsilon_M$ (%)	$s$ (%)
3P	1047	56	34.6	3.9	4.4	0.9
3P/MF-0.5%	1335	107	37.0	2.4	3.8	0.1
3P/MF-1%	1383	87	37.4	1.8	3.5	0.2
3P/MF-2.5%	1349	58	31.6	7.9	2.7	0.7
3P/MF-5%	1424	94	34.6	4.7	2.9	0.4
3P/MF-10%	1833	100	37.8	3.7	2.5	0.3
3P/MF-15%	1891	173	35.9	2.9	2.4	1.0

**TABLE V**  
Effects of the Compositional Changes on the Fracture Toughness ( $K_c$ ) and Fracture Energy ( $G_c$ ) for 2P/MF Hybrids in Comparison with 3P Reference (cf. Table III)

	$K_c$ (MPa m <sup>1/2</sup> )	$s$ (MPa m <sup>1/2</sup> )	$G_c$ (kJ m <sup>2</sup> )	$s$ (kJ m <sup>2</sup> )
3P	0.97	0.06	1.10	0.09
2P/MF-0.5%	0.81	0.03	0.93	0.06
2P/MF-1%	0.83	0.02	0.85	0.06
2P/MF-2.5%	0.82	0.01	0.75	0.04
2P/MF-5%	0.91	0.03	0.80	0.07
2P/MF-10%	0.84	0.03	0.60	0.02
2P/MF-15%	0.97	0.06	1.10	0.09

### 2P/MF—mechanical properties

The results of the fracture tests carried out on the 2P/MF hybrid resins are summarized in Table V. According to the results obtained, the substitution of the phosphate by the MF improved the fracture energy ( $G_c$ ) of the hybrids only for MF contents lower than 2.5 wt %. With increasing MF amount in the hybrid systems  $G_c$  decreased. On the other hand, the fracture toughness ( $K_c$ ) was only slightly influenced by the amount of MF introduced. It is the right place to remark that, the system 2P/MF-10% gave comparable  $K_c$  and  $G_c$  results with the 3P reference.

The flexural properties of the 2P/MF hybrids presented in Table VI reflect how the replacement of the phosphate by MF improves the stiffness of the systems in comparison to the 3P reference resin. The flexural modulus  $E_f$  and strength ( $\sigma_{fm}$ ) increase with increasing MF content, however, at expenses of the flexural strain ( $\epsilon_M$ ). This is comprehensible since larger amounts of MF confer higher rigidity to the samples and therefore they undergo smaller deformation at a given loading.

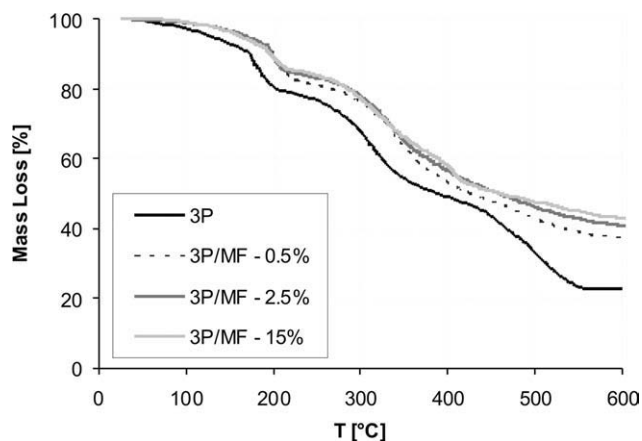
### Thermal and flame resistance behaviour

#### 3P/MF—thermal properties

The thermal degradation behaviour of the 3P/MF hybrid resins, as well as their reference 3P, is shown

**TABLE VI**  
Flexural Modulus ( $E_f$ ), Strength ( $\sigma_{fm}$ ) and Strain ( $\epsilon_m$ ) for the 3P Reference and 2P/MF Hybrid Resins (cf. Table III)

	$E_f$ (MPa)	$s$ (MPa)	$\sigma_{fm}$ (MPa)	$s$ (MPa)	$\epsilon_M$ (%)	$s$ (%)
3P	1047	56	34.6	3.9	4.4	0.9
2P/MF-0.5%	1463	147	40.5	1.4	4.2	0.1
2P/MF-1%	1375	95	37.4	1.9	3.5	0.3
2P/MF-2.5%	1661	133	40.3	2.5	3.1	0.4
2P/MF-5%	1618	174	44.2	3.9	3.3	0.2
2P/MF-10%	2029	147	47.9	2.3	2.9	0.2
2P/MF-15%	2085	113	51.8	5.3	2.9	0.3



**Figure 8** Mass loss vs.  $T$  for the 3P reference and 3P/MF hybrid resins.

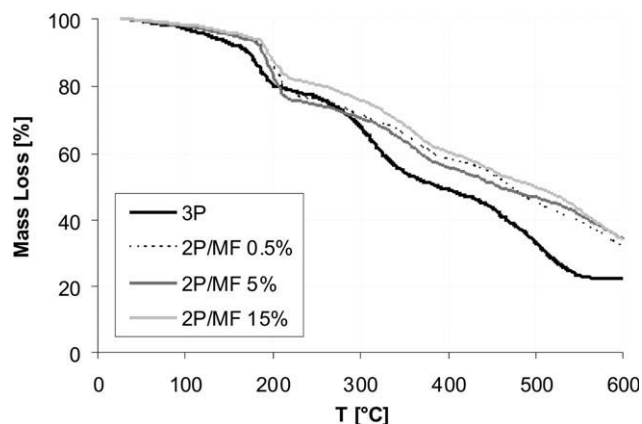
in Figure 8. When comparing the TG traces of the hybrids with that of the 3P reference, one can observe that the degradation steps for both resemble to one another, at least, from RT to 400°C. However, the degradation processes of the hybrids 3P/MF take place in general at higher temperatures. At temperatures above 400°C the reference 3P undergoes a considerable mass loss, while the 3P/MF hybrids continue to lose mass at a moderate rate.<sup>22</sup>

Observing more accurately the temperature at which the 5% of the mass is lost ( $T_{5\%}$ ), one can clearly see that this ranges from 145 to 180°C for the corresponding 3P/MF hybrids, while for the 3P reference the 5% of the mass is lost at the early temperature of 125°C (cf. Table VII). Similarly, the residue remaining after the degradation process is significantly higher for the 3P/MF hybrids, increasing along with the MF content, than for the reference 3P, which is approximately a 23% of the initial specimen mass. To sum up we can assert that the hybridization of the 3P resins with MF had a positive influence on the thermal behaviour.

The flammability test for the 3P/MF hybrid resins, according to the 94UL standards for vertical burn (94V), give a classification of is V-0. The total flaming combustion time was zero, the specimens did not burn with flaming combustion after the flame application and they did not drip flaming particles that ignite the cotton. The results obtained from the

**TABLE VII**  
 $T_{5\%}$  (°C) and Residue (%) of the 3P/MF Hybrid Resins as a Function of Their MF Content

MF (wt %)	0.5	1	2.5	5	10	15
$T_{5\%}$ (°C)	167	145	170	178	169	163
Residue (%)	37	39	41	43	43	43



**Figure 9** Mass loss vs.  $T$  for the 3P reference and 2P/MF hybrid resins.

flammability test showed that 3P/MF hybrid resins are good fire resistant materials.

#### 2P/MF—thermal properties

TGA curves depicted in Figure 9 show the thermal behaviour of the 2P/MF hybrids with different MF content. The response of the diverse hybrids seems not to be influenced by the MF content, since they do not differ one from another in a great extent, yet the 2P/MF-10% system presents a markedly different behaviour (cf. Table VIII). The 2P/MF hybrid systems are stable at temperatures below 200°C, as seen before in the DMTA analysis, before they suffer a brusque loss of mass. Nonetheless, the continuous mass loss is not as severe as for the reference 3P, which at temperatures above 300°C exhibits a second remarkable mass loss. Therefore, the substitution of the phosphate by MF appears to influence positively the thermal resistance of the novel hybrids.

The flammability tests, conducted on the 2P/MF hybrid resins, showed that the specimens did not burn with flaming combustion after the flame application as well as they did not burn with flaming or glowing combustion up to the specimen holding clamp. Moreover the 2P/MF resins did not produce flaming particles that ignite the cotton. The total flaming combustion time was zero or 1 s for some specimens; therefore the classification of

**TABLE VIII**  
 $T_{5\%}$  (°C) and Residue (%) of the 2P/MF Hybrid Resins as a Function of their MF Content

MF (wt %)	0.5	1	2.5	5	10	15
$T_{5\%}$ (°C)	160	143	147	159	126	171
Residue (%)	32	34	34	34	20	34

the 2P/MF resins according to the 94UL standards is V-0. The results obtained from the flammability test showed that 2P/MF resins are good fire resistant materials and that the substitution of the phosphate (which is an active flame retardant additive) by MF resin is straightforward also in terms of fire resistance.

### CONCLUSION

This work was devoted to study the effect of MF 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 MF in a reference 3P resins slightly reduced the mean particle size of the polysilicate derived from the WG. So, MF worked as additional emulsifier to phosphate in the reference 3P resin. MF fulfilled the role of emulsifier in 2P systems. This was confirmed by a pronounced reduction of the mean particle size of the polysilicate.
- The fracture mechanical and static flexural properties of both 3P and 2P resins were mostly improved by MF hybridization. The change in the related properties as a function of MF was not always linear.
- The thermal degradation was delayed; the char yielded increased with increasing MF content for the 3P/MF systems. This was less prominent for the 2P/MF companions. The flame resistance of the hybrids was not affected by MF incorporation.

### References

1. Stoye, D., Ed. *Paints, Coatings and Solvents*; VCH: Weinheim, Germany, 1993; p 94.
2. Mamunya, Ye. P.; Iurzhenko, M. V.; Lebedev, E. V.; Ischenko, S. S.; Boiteux, G.; Seytre, G. *J Non-Crystalline Solids* 2007, 535, 4288.
3. Mamunya, Ye. P.; Shtompel, V. I.; Lebedev, E. V.; Pissis, P.; Kanapitsas, A.; Boiteux, G. *Eur Polym J* 2004, 40, 2323.
4. Pizzi, A.; Walton, T. *Holzforschung* 1992, 46, 541.
5. Pizzi, A.; Valenzuela, J.; Westermeyer, C. *Holzforschung* 1993, 47, 69.
6. Erdélyi, S.; Karger-Kocsis, J.; Nagy, G. *J Macromol Sci B* 2007, 46B, 21.
7. Castellà, N.; Grishchuk, S.; Karger-Kocsis, J. *Plast Rubber Compos* 2007, 36, 122.
8. Karger-Kocsis, J.; Erdélyi, S.; Nagy, G. *J Appl Polym Sci* 2007, 103, 853.
9. Grishchuk, S.; Castellà, N.; Karger-Kocsis, J. *Eur Polym J* 2007, 43, 1245.
10. Karger-Kocsis, J. *Express Polym Lett* 2007, 1, 122.
11. REACH—European Community Regulation. Available at [http://ec.europa.eu/environment/chemicals/reach/reach\\_intro.htm](http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm)
12. Wieland, S.; Pizzi, A.; Grigsby, W.; Warnes, J.; Pichelin, J. *J Appl Polym Sci* 2007, 104, 2633.
13. Despres, A.; Pizzi, A.; Delmotte, L. *J Appl Polym Sci* 2006, 99, 589.
14. Simon, C.; George, B.; Pizzi, A. *J Appl Polym Sci* 2002, 86, 3681.
15. Wieland, S.; Pizzi, A.; Hill, S.; Grigsby, W.; Pichelin, J. *J Appl Polym Sci* 2006, 100, 624.
16. Ege, S. *Química Orgánica—Estructura y Reactividad*. Editorial Reverte, 2000; Vol. 1–2.
17. Stevens, M. P. *Polymer Chemistry. An Introduction*; Oxford University Press: New York-Oxford, 1990.
18. Bauer, D. R. *J Appl Polym Sci* 1982, 27, 3651.
19. Scheepers, M. L.; Gelan, J. M.; Carleer, R. A.; Adriaensens, P. J.; Vanderzande, D. J. *Vib Spectrosc* 1993, 6, 55.
20. Wilson, R. C.; Pföhl, W. F. *Vib Spectrosc* 2000, 23, 13.
21. Anderson, D. G.; Netzel, D. A.; Tessari, D. J. *J Appl Polym Sci* 1970, 14, 3021.
22. Costa, L.; Camino, G. *J Therm Anal* 1988, 34, 423.