



## **INFLUENCE OF HYDROLYSIS CONDITIONS ON CURING AND PROPERTIES OF AN EPOXY-SILANE BASED HYBRID MATERIAL**

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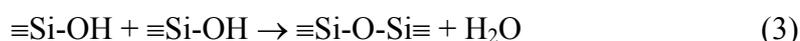
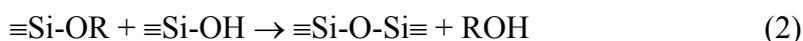
**Abstract:** 3-glycidyoxypropyltrimethoxysilane (GLYMO), an organically modified methoxysilane with a reactive epoxy group linked to silicon atom through a stable Si-C covalent bond, was hydrolysed with varying amounts of water and acid or base catalyst. Reaction was followed by Fourier-transform infrared spectroscopy (FTIR), and it was found that larger content of water and acid conditions favour quick hydrolysis, while in basic conditions hydrolysis proceeds in parallel with condensation of siloxane network. After hydrolysis, epoxy groups were crosslinked with a poly(oxypropylene) diamine, Jeffamine D230, to form an organic-inorganic hybrid material, and the heat of reaction was determined by differential scanning calorimetry (DSC). Epoxy groups have remained stable during hydrolysis, and hydrolysed silanol groups can act as catalysts for the epoxy-amine reaction. Early inorganic condensation in base-catalysed systems can sterically hinder full crosslinking of the organic phase, while presence of chloride ions from acid catalyst (hydrochloric acid) adversely influences thermal stability of such hybrid materials, as determined by thermogravimetric analysis (TGA). Mechanical properties of fully cured hybrid materials were determined by nanoindentation, and glass transition temperature was determined by DSC. Systems hydrolysed with larger amounts of water show poorer mechanical properties, while the most significant improvement in mechanical properties was achieved for an acid-catalysed system.

**Key words:** epoxy-amine resin, mechanical properties, organic-inorganic hybrids, sol-gel

## 1. INTRODUCTION

Organic-inorganic hybrid materials are a class of nanocomposites with inorganic phase formed *in situ* by sol-gel process. This leads to materials with organic and inorganic phase intermingled at nano level, much more homogeneous than those prepared with hard to disperse nano-sized filler [1]. Consequently, the whole volume of hybrid material may act as an interphase, and the hybrid materials are expected to possess superior properties since they unite the qualities of both organic and inorganic phase in synergistic manner [2].

A wide range of hybrid materials can be prepared due to great flexibility of sol-gel process [3], which consists of hydrolysis and condensation of metal alkoxides. These reactions for most commonly used silicon alkoxides (alkoxysilanes) can be simplified as follows [4]:



Here R stands for an alkyl group, usually methoxy (-CH<sub>3</sub>) or ethoxy (-C<sub>2</sub>H<sub>5</sub>). Reactions of hydrolysis (equation 1) and condensation (equations 2 and 3) can be either acid or base catalysed. Acid catalysis favours the hydrolysis, while in base-catalysed systems condensation is the faster step [5].

Presence of covalent bond or hydrogen linkages between the phases increases the strength of interphase, markedly improving mechanical properties of hybrid materials [6]. The covalent bond is most commonly introduced by organically modified alkoxysilanes, since Si-C bond is resistant to hydrolysis and survives the sol-gel process intact [7]. Organic substituent of these alkoxysilanes can contain a reactive group capable of forming the organic phase, thus creating a virtually monophasic material.

In this work, influence of hydrolysis conditions on curing and final properties of epoxy-silica organic-inorganic hybrids formed from 3-glycidyloxypropyltrimethoxysilane (GLYMO) is studied. GLYMO is an epoxy modified alkoxysilane that can undergo both sol-gel reactions of the alkoxy groups and curing of the epoxy functionality with amine, and so form a hybrid network with covalent bonds between organic and inorganic phases.

## 2. EXPERIMENTAL

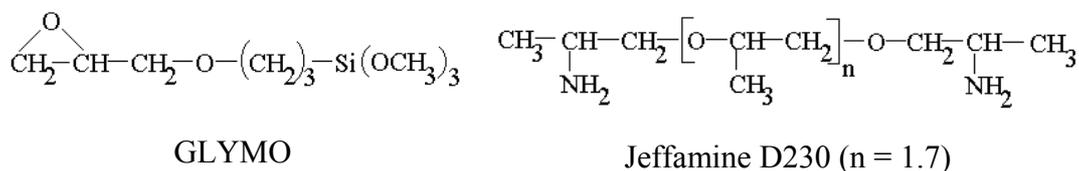


Figure 1 – Chemical formulas of starting materials

3-glycidyloxypropyltrimethoxysilane (GLYMO, 98%, Aldrich Chemicals) was used as the starting compound for synthesis of organic-inorganic hybrid materials. Poly(oxypropylene) diamine Jeffamine D230 (Huntsman Corporation) was used as a curing agent for epoxy group of GLYMO. GLYMO was hydrolysed for 3 h at 60 °C with 1.5 or 3 moles of water per mole of GLYMO, with addition of hydrochloric acid (HCl) or ammonium hydroxide (NH<sub>4</sub>OH) as catalyst. Level of hydrolysis and condensation and stability of epoxy groups of GLYMO was determined by Fourier-transform infrared spectroscopy (FTIR), on

JASCO 615 FTIR instrument. Samples were spread on silicon wafers, and each spectrum from 4000 to 400  $\text{cm}^{-1}$  was averaged over 16 scans at 4  $\text{cm}^{-1}$  resolution. Jeffamine was added to hydrolysed GLYMO in a previously determined stoichiometric amount (ratio of  $-\text{NH}_2$  to epoxy groups 1 : 1) [8]. Sample designations and compositions as well as conditions of cure are given in table 1.

**Table 1:** Sample compositions (expressed in moles per mole of GLYMO), conditions of cure and designations for all investigated systems

Jeffamine	Catalyst	Water	Curing conditions	Designation	
0.5	HCl: 0.0092	1.5	7 days at RT + 24 h / 120 °C	a15	
			24 h / 120 °C	AA15	
	NH <sub>4</sub> OH: 0.0095	3.0	1.5	7 days at RT + 24 h / 120 °C	a30
				24 h / 120 °C	b15
		3.0	1.5	7 days at RT + 24 h / 120 °C	BB15
				24 h / 120 °C	b30

Samples were cured at room temperature for 7 days, and then postcured at 120 °C for another 24 h. Additional samples were cured immediately at 120 °C for 24 h. Reaction of epoxy group with amine was studied by means of differential scanning calorimetry (DSC) with a heating rate of 10 K/min in temperature range 25 – 250 °C, on a Perkin-Elmer Pyris 1 calorimeter equipped with an *intercooler* cooling unit. Measurements were made immediately after mixing with Jeffamine, and again after 24 h of curing at room temperature. Heat of reaction,  $\Delta H$ , was estimated from the area under the exothermic peak. Dynamic DSC experiments were also performed to determine the glass transition temperature,  $T_g$ , of the completely cured material. Samples were heated to 150 °C to erase their thermal history, cooled to –50 °C and immediately reheated to 150 °C, all with the same rate of 10 K/min.

Mechanical properties of fully cured materials in form of self-standing films were determined by continuous nanoindentation testing, using Micromaterials NanoTest nanoindenter, with a maximum load of 20 mN and a load rate of 0.02 mN/s. Thermal stability of fully cured materials was determined by thermogravimetric analysis (TGA), using a Seiko SII Exstar 6000 thermobalance. Samples were heated from room temperature to 1000 °C with a heating rate of 10 K/min in a nitrogen gas flow of 250  $\text{cm}^3/\text{min}$ .

### 3. DISCUSSION OF RESULTS

FTIR spectra of GLYMO hydrolysed for 3 h at 60 °C with 1.5 and 3 mol of water (figure 2) show how choice of catalyst influences the hydrolysis and condensation of alkoxy groups of GLYMO. In acid-catalysed system silanol groups, Si-OH, form immediately and in larger quantities, and the simultaneous decrease of the characteristic  $-\text{CH}_3$  bands confirms that hydrolysis of alkoxy groups takes place. This is much more pronounced for system hydrolysed with 3 mol of water, regardless of catalyst used, since the abundance of water speeds up the hydrolysis. Widening of bands grouped around 1100  $\text{cm}^{-1}$ , which are characteristic for stretching of Si-O bonds (in particular Si-O-Si and Si-O-C bridges), indicates changes due to hydrolysis and condensation of alkoxy groups. Due to overlapping of these bands, it is difficult to determine which bonds form and which disappear. A new band appears as condensation proceeds, shifting from 683  $\text{cm}^{-1}$  to 696  $\text{cm}^{-1}$  for fully condensed system, and it is thus ascribed to Si-O-Si bridges formed by condensation. In base-catalysed systems hydrolysis proceeds simultaneously with condensation, as silanol bands and the band at 696  $\text{cm}^{-1}$  appear at the same time. Characteristic bands for epoxy groups do not disappear

during hydrolysis, and their broadening in comparison with non-hydrolysed GLYMO can be ascribed to influence of hydrogen bonds on the stretching and bending vibrations of the epoxy ring.

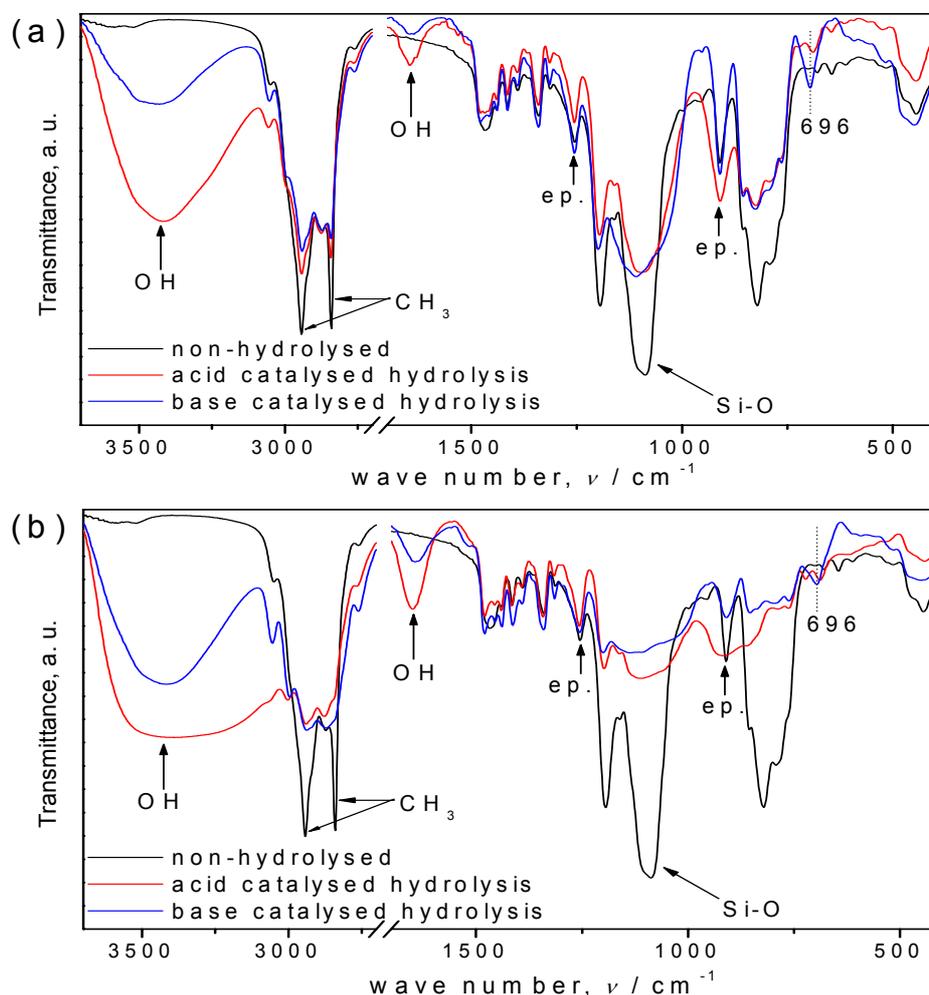


Figure 2 – FTIR spectra of GLYMO hydrolysed for 3 h at 60 °C (a) with 1.5 mol of water and (b) with 3 mol of water, compared with non-hydrolysed GLYMO

Heats of epoxy-amine reaction for hydrolysed systems are comparable with that of non-hydrolysed system (table 2), confirming that epoxy groups survive the sol-gel process intact, as concluded from the FTIR results. The only exception is b30 system, which starts to gel during homogenisation with Jeffamine due to more advanced degree of hydrolysis and condensation in comparison with other systems. As a consequence, a part of epoxy groups is trapped within the inorganic network and unable to react with amine. After 24 h of curing at room temperature all systems have hardened, but acid-catalysed systems show larger residual reactivity of epoxy groups due to a greater flexibility of less condensed inorganic network.

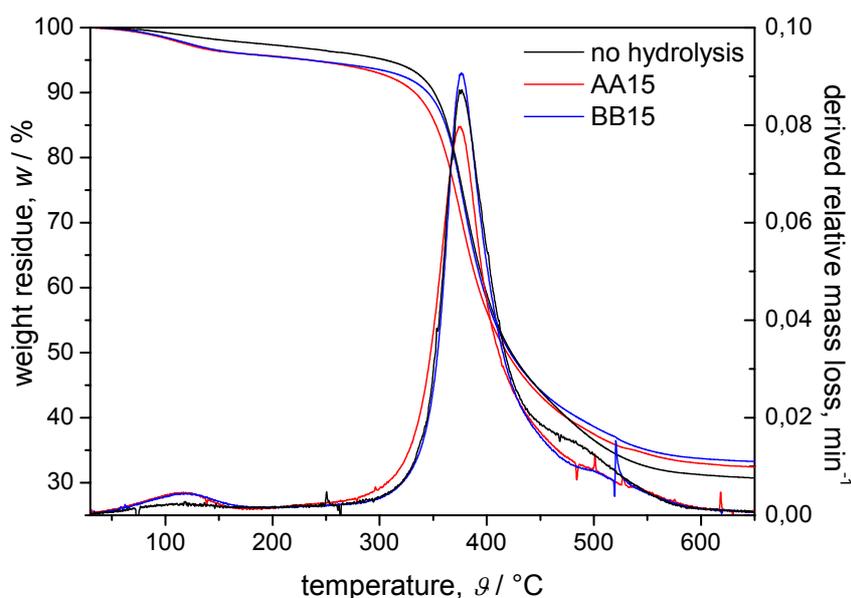
Mechanical properties and glass transition temperatures of hybrid materials from GLYMO hydrolysed with 1.5 mol of water are comparable to those of non-hydrolysed system (table 2). Systems hydrolysed with 3 mol of water have considerably poorer properties, presumably because excess water remains trapped within the hybrid matrix, and b30 also gels too quickly for preparation of samples for mechanical testing. Acid-catalysed systems show better properties than base-catalysed ones, presumably because the inorganic phase is much more finely dispersed and also capable of forming hydrogen linkages with the organic phase due to presence of silanol groups. Systems cured directly at 120 °C (AA15, BB15) also have

better properties than comparable systems cured at room temperature (a15, b15). This can be ascribed to greater degree of crosslinking of the organic phase, which in these conditions forms more quickly than the inorganic one.

**Table 2:** Heat of reaction (measured given time after mixing),  $\Delta H$ , Young modulus,  $E$ , hardness,  $H$ , glass transition temperature,  $T_g$ , onset temperature of the main degradation step,  $T_o$ , temperature of degradation rate maximum,  $T_p$ , and mass fraction of residual char at 1000 °C,  $w$ , for all investigated systems

Systems	$\Delta H / \text{kJ mol}^{-1}$		$E / \text{MPa}$	$H / \text{MPa}$	$T_g / ^\circ\text{C}$	$T_o / ^\circ\text{C}$	$T_p / ^\circ\text{C}$	$w / \%$
	0h	24h						
No hydr.	-104	--	$263 \pm 7$	$62 \pm 2$	17	303	374	29,97
a15	-89	-24	$228 \pm 5$	$55 \pm 2$	10	279	376	27,64
AA15	--	--	$552 \pm 6$	$70 \pm 1$	13	286	375	31,14
a30	-102	-40	$141 \pm 3$	$37 \pm 1$	6	293	374	29,96
b15	-106	-3	$157 \pm 2$	$46 \pm 2$	14	308	376	27,87
BB15	--	--	$230 \pm 6$	$52 \pm 2$	24	305	376	32,21
B30	-43	-3	-- -- --	-- -- --	9	300	378	27,41

Thermal stability of all hydrolysed systems is comparable to the non-hydrolysed one (table 2), with very small variation in temperature of the degradation rate maximum and the quantity of residual char at 1000 °C. Acid-catalysed systems (a15, a30, AA15) show lower onset temperatures for degradation, which is caused by the presence of chlorine from HCl catalyst that remain bound to residual amine groups within the cured material [9]. Chlorine is released by heating, and can then act as chain scission agent, catalysing the start of degradation of organic phase. Somewhat larger weight residues for systems that were immediately cured at 120 °C (AA15 and BB15, figure 3) are most likely due to facilitated evaporation of lower-weight products of sol-gel hydrolysis and residual water from the system during cure at higher temperature.



*Figure 3* – Thermogravimetric curves and curves of derived relative mass loss for systems cured immediately at 120 °C (AA15 and BB15), in comparison with system prepared from non-hydrolysed GLYMO

#### 4. CONCLUSIONS

Hydrolysis of GLYMO does not influence the stability of epoxy groups, as shown by FTIR and DSC. Acid catalysis favours quick hydrolysis of alkoxy groups, while base catalysis leads to parallel condensation and early formation of inorganic siloxane network. The early formation of the inorganic network shows detrimental influence on the reaction of epoxy groups with amine and consequently the final properties of fully cured hybrid materials. Acid hydrolysis improves the mechanical properties of fully cured materials, presumably because the inorganic phase is more finely structured and additionally linked to the organic phase by hydrogen bonds. Immediate cure of hybrid mixtures at 120 °C allows smaller molecules to evaporate more easily, which improves the final properties of the cured material. Residual chlorine from acid catalyst lowers the thermal resistance of fully cured materials.

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