MORPHOLOGY AND PROPERTIES OF PREHYDROLYZED EPOXY-SILICA HYBRIDS

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Hybrid organic-inorganic materials combine the best properties of both worlds, flexibility and light weight of polymers with thermal stability and hardness of ceramics. Choice of precursors and the ratio of organic and inorganic phase greatly influences the properties, but the reaction conditions also play a significant role. As the inorganic phase is formed by sol-gel process, through hydrolysis and condensation of metal alkoxides, conditions of hydrolysis – acid or base catalyzed - influence the morphology of the materials. In case of acid catalysis, reaction of hydrolysis is favored, while in base conditions condensation is the faster reaction.

Hydrolysis:	≡Si-OR + H₂O ⇔ ≡Si-OH + ROH	(R = CH ₃ , C ₂ H ₅)
Condensation:	$\equiv Si-OH + XO-Si \equiv \rightarrow XOH + \equiv Si-O-Si \equiv$	(X = R, H)

Epoxy-silica hybrids were prepared from diglycidyl ether of bisphenol A (DGEBA), and modified silicon alkoxide with a reactive epoxy group, 3-glycidyloxypropyltrimethoxysilane (GLYMO) as inorganic precursor, with addition of stoichiometric quantity of a poly(oxypropylene) diamine Jeffamine D230 as a curing agent for epoxy. Prior to mixing with DGEBA and D230, GLYMO was fully hydrolyzed with stoichiometric quantity of water added as 1 M HCl or 1 M NH₄OH. Mixtures were poured into molds and cured immediately either at room temperature for 24 hours or at 60 °C for 1 hour, and then postcured at 120 °C for 24 hours. Fully cured samples were investigated by DMA, DSC, and ball indentation hardness. Morphology was investigated by TEM on JEOL JEM-200CX microscope, under accelerating voltage of 200 kV, on 100 nm thick slices cut from the cured material.

Morphology of hybrid materials depends both on conditions of hydrolysis and cure temperature (Figure 1). Higher temperature of cure speeds up the formation of polymer network and thus stops the reactions of condensation before it can fully advance. Because of this, acid catalyzed sample shows no distinct particles or shapes, and the inorganic phase is uniformly distributed throughout the volume, as was the case for non-hydrolyzed system (not shown). In base catalyzed system small (< 50 nm) silica particles are evenly distributed through the matrix, which probably also contains continuous inorganic phase. At room temperature, longer cure time allows condensation to proceed in both acid and base catalyzed systems, as the amine curing agents acts also as a base catalyst. In the acid catalyzed system very fine silica particles (< 15 nm) have formed uniformly throughout the matrix, while in the base catalyzed system very large and irregular particles have formed locally in the matrix, leaving ample apparently "unfilled" areas.

Hydrolysis of GLYMO visibly improves mechanical properties of hybrid materials, as listed in Table 1. Storage modulus is increased both in glassy and viscoelastic state due to strengthening effect of inorganic network. It is interesting how little influence very different morphologies have on both modulus and glass transition temperature of hybrid materials. Hybrids A25 and B60, having what would seem the most beneficial morphology of small silica particles evenly distributed in the matrix, show the worst values for hardness, but B60 also has the lowest storage modulus and highest indentation creep of all hydrolyzed systems.

Improvement in all properties for A60 system when compared to non-hydrolyzed one shows the positive influence of Si-OH groups formed by hydrolysis, which were able to form hydrogen bonds with polymer matrix further improving interphase contact and thus mechanical properties of the hybrid material.

Table 1. Storage modulus, E', in glassy (above T_g) and viscoelastic (below T_g) state as determined by DMA, glass transition, T_g , as determined by DSC and ball indentation hardness, H, and indentation creep, G

System	<i>E' </i> MPa, 25°C	<i>E′</i> / MPa, 150°C	𝕂̊g / °C	H/Nmm-2	C _I / %
Non-hydr.	2492	37	44	55 ± 3	25,5
A25: Acid-25°C	2889	44	55	39 ± 1	3,2
A60: Acid-60°C	2885	44	62	51 ± 2	4,9
B25: Base-25°C	2888	43	52	56 ± 4	4,2
B60: Base-60°C	2660	43	52	36 ± 1	10,0



, cured at 25 °C/ 24 h B25: base catalyzed, cured at Figure 1. Morphology of all investigated samples