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INFLUENCE OF PRECURSOR HYDROLYSIS ON MORPHOLOGY AND PROPERTIES EPOXY-BASED ORGANIC-INORGANIC HYBRID MATERIALS

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Epoxy resins are high-performance polymer materials with wide application, ranging from bulk materials to protective coatings and high-performance binders. In order to further improve their already excellent properties, epoxy resins are being modified by admixture nanofillers, whose relatively large contact surface increases matrix-filler interactions [1]. But this also causes nanofillers to easily aggregate, which makes their homogeneous dispersion in the resin difficult. To avoid aggregation, an alternative approach of synthesis by formation of inorganic phase (filler) *in situ* by sol-gel process has been used. Materials prepared in this manner are called organic-inorganic hybrid materials [2]. Presence of covalent or hydrogen bonds between organic and inorganic phase improves interphase contact and end-properties of hybrid materials [3].

Sol-gel process consists of hydrolysis and condensation reactions of metal (most frequently Si) alkoxides [4]:

Hydrolysis: $\equiv\text{Si-OR} + \text{H}_2\text{O} \Leftrightarrow \equiv\text{Si-OH} + \text{ROH}$ $(\text{R} = \text{CH}_3, \text{C}_2\text{H}_5\ldots)$

Condensation: $\equiv\text{Si-OH} + \text{XO-Si}\equiv \rightarrow \text{XOH} + \equiv\text{Si-O-Si}\equiv$ $(\text{X} = \text{R}, \text{H})$

These reactions can be either acid or base catalysed. Acid catalysis favours hydrolysis while base catalysis promotes condensation. Morphology and properties of hybrid materials can therefore be influenced by variations in reaction conditions, and also by modifying the ratio of organic and inorganic phase. This can easily be achieved by addition of either organic or inorganic monomers. To achieve covalent bonding between phases, organically modified silicon alkoxides, R'-Si(OR)_3, are used, where R' represents a reactive organic group linked to silicon by a Si-C covalent bond which is resistant to hydrolysis [2].

Epoxy-silica hybrid materials were prepared from diglycidyl ether of bisphenol A (DGEBA), with modified silicon alkoxide with a reactive epoxy group, 3-glycidyloxypropyltrimethoxysilane (GLYMO) as inorganic precursor. Stoichiometric quantity of a poly(oxypropylene) diamine Jeffamine D230 was added as a curing agent for epoxy. Prior to mixing with DGEBA and D230, GLYMO was fully hydrolysed with stoichiometric quantity of water (1.5 mole per mole of GLYMO) added as 1 mol/dm^3 HCl or 1 mol/dm^3 NH_4OH. Hybrid materials were cured either 24 hours at room temperature or 1 hour at 60 °C, and postcured 24 hours at 120 °C to complete the organic cure. Fully cured samples were investigated by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and ball indentation hardness. Properties of all investigated materials are given in table 1.

Morphology of hybrid materials was found to depend both on hydrolysis conditions and cure temperature. Base catalysis, as expected, caused formation of larger inorganic particles inside epoxy matrix, which is especially pronounced in case of material cured at 25 °C. Materials cured at 60 °C show finer morphology compared to those cured at 25 °C, since higher temperature favours formation of polymer network over condensation of inorganic phase [5]. Hybrid materials prepared from hydrolysed GLYMO show visibly improved mechanical properties. Storage modulus as determined by DMA is increased both in glassy and viscoelastic state due to strengthening effect of inorganic network, and very different morphologies are shown to have comparably small influence on both modulus and glass transition temperature of hybrid materials. Hybrids that contain small silica particles evenly distributed within the matrix show the worst values for hardness, contrary to nanocomposites formed by admixture of preformed nanoparticles [6]. Truly hybrid system prepared from acid-catalysed GLYMO and cured at 60 °C shows improvement in all properties when compared to non-hydrolysed one. This indicates positive influence of silanol Si-OH groups formed by hydrolysis. Presence of uncondensed silanol groups enabled formation of additional hydrogen bonds with polymer matrix, further improving interphase contact and consequently mechanical properties of the hybrid material. On the other hand, residual HCl in the material can act as a centre of chain-scission [7], and these materials were found to start degrading at somewhat lower temperatures. Therefore, it is proposed that use of a different acid catalyst could be used to improve the mechanical properties without a detrimental influence on thermal properties.

Table 1. – Glass transition, T_g, as determined by DSC, storage modulus, *E'*, in glassy (below T_g) and viscoelastic (above T_g) state as determined by DMA, ball indentation hardness, *H*, onset temperature of degradation, T_o, in nitrogen as determined by TGA and morphology as determined by TEM.

System	T_g / °C	*E'* / MPa, 25°C	*E'* / MPa, 150°C	*H* / Nmm^{-2}	T_o / °C	Morphology
Non-hydr.	44	2492	37	55 ± 3	312	Homogeneous
Acid-25°C	55	2889	44	39 ± 1	306	Particles < 15 nm
Acid-60°C	62	2885	44	51 ± 2	310	Homogeneous
Base-25°C	52	2888	43	56 ± 4	312	Particles ~ 1 µm
Base-60°C	52	2660	43	36 ± 1	314	Particles < 50 nm
Unmod. epoxy	89	2599	14	59 ± 1	313	Homogeneous

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