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Communications

Mechanical Properties of an Inorganic−Organic Hybrid Polymer Cross-linked by the Cluster Zr_4O_2(methacrylate)$_{12}$

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The controlled in situ generation of water in transition-metal alkoxide/carboxylic acid mixtures allows the preparation of carboxylate-substituted metal oxide clusters in very high yields. This approach can also be extended to carboxylic acids with functional groups, such as acrylic and methacrylic acid.[1] Examples of methacrylate-substituted clusters prepared by this method include $Zr_6(OH)_4O_4(OMc)_{12}$ (OMc = methacrylate),[2] $Zr_4O_2(OMc)_{12}$,[2,3] $Ti_6O_4(OEt)_8(OMc)_8$,[4] $Nb_4O_4(O^iPr)_8(OMc)_4$,[5] and several Ti/Zr mixed-metal clusters.[6] We have recently shown that polymerization of 0.5−2 mol % of $Zr_6(OH)_4O_4(OMc)_{12}$ or $Zr_4O_2(OMc)_{12}$ with functionalized olefins (methyl methacrylate, methacrylic acid) as comonomers results in an interesting new class of inorganic−organic hybrid polymers in which the clusters as the inorganic building blocks cross-link the polymer chains very efficiently.[1,3,7] This results in an improvement of the thermal stability of the polymers, and the swelling in organic solvents can be controlled by the kind and proportion of the incorporated clusters. In this communication we report that the mechanical properties of an inorganic−organic hybrid polymer are also greatly improved upon copolymerization with the cluster $Zr_4O_2(OMc)_{12}$.

The synthesis of the alkoxysilane derivatives bis[(methacryloyloxy)propoxycarbonylethyl)](3-triethoxysilyl)propylamine (**1**) and (1,3(2)-bismethacryloyloxypropyl)-(3-triethoxysilylpropylaminocarbonyl)butyrate (**2**) and their sol−gel processing was previously described.[8] Sol−gel processing of the silanes, followed by evaporation of all volatile compounds, resulted in the formation of an oil with a low viscosity for **1** and a viscous resin for **2** (samples **1c** and **2c**).[8] In the latter case, unreacted Si−OH groups were removed by silylation with Me_3SiCl in the presence of 2,4,6-trimethylpyridine. A polysiloxane network is formed during the hydrolytic polycondensation of both compounds, while the methacrylate substituents remain unreacted. Upon irradiation with visible light, the methacrylate groups of the polycondensates were cross-linked, and glassy polymers were obtained. For the determination of the mechanical properties of reference samples, the polycondensates were cast in 25 × 2 × 2 mm dies and photochemically

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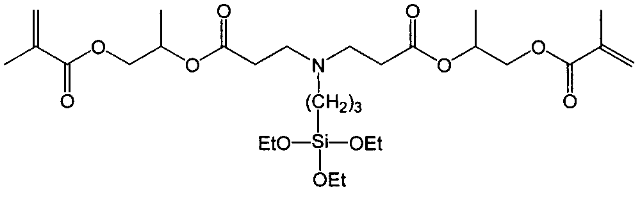

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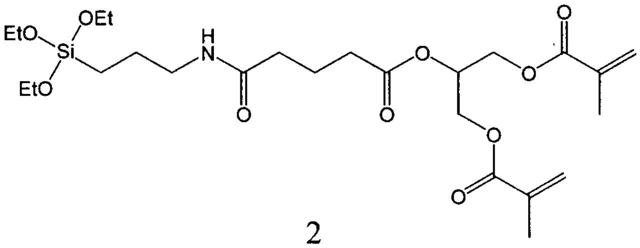

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hardened (samples **1p** and **2p**).[9] The flexural strength and flexural moduli of the test specimens (Table 1) was determined according to ISO 4049. Inspection of Table 1 shows that both the flexural strength and the flexural modulus of the hybrid polymers slightly decrease after storage in water for 1 day.

Photochemical polymerization of the polycondensates **1c** and **2c** was carried out under the same conditions after addition of 10 wt % of $Zr_4O_2(OMc)_{12}$ (samples **1pZr10** and **2pZr10**).[10] While the flexural strength of the cluster-cross-linked polymer **1pZr10** was about the same as that of the undoped polymer, that of **2pZr10** was significantly improved. The increase of the flexural modulus, on the other hand, was much higher for **1pZr10** than for **2pZr10** (Table 1). Another major improvement was that the cluster-cross-linked polymers do not change their mechanical properties upon water storage. No decrease of both the flexural strengths and the flexural moduli was observed (actually a minor increase). We also prepared a sample with a higher cluster proportion (20 wt % of $Zr_4O_2(OMc)_{12}$). This improves the mechanical properties even more, as can be seen from Table 1.

Table 1. Flexural Strengths (FS) and Flexural Moduli (FM) of the Prepared Materials (in MPa)

	1p	**1pZr10**	**2p**	**2pZr10**	**2pZr20**
FS dry[a]	46	47	48	59	70
FS after water storage[b]	31	52	36	60	60
FM dry[a]	1230	1900	1820	2100	2400
FM after water storage[b]	1000	1920	1750	2270	2600

[a] Storage in dry air at 37 °C for 1 day. [b] Storage in water at 37 °C for 1 day.

The results reported in this communication show that cross-linking of organic polymers (or, in the present case, the organic part of hybrid materials) by clusters via covalent bonds leads to a strong increase of both the flexural strength and the flexural modulus of the polymers. The magnitude of the increase depends to some extent also on the kind of polymer. The mechanical properties of the cluster-cross-linked hybrid polymers do not deteriorate upon water storage at 37 °C. This is a surprising finding because one could anticipate some hydrolytic instability of the Zr−methacrylate linkage. The very interesting mechanical properties complement the previously observed favorable thermal and swelling properties of cluster-cross-linked polymers and demonstrate again the usefulness of this new class of inorganic−organic hybrid materials.

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[9] Vivadent Spectramat ($\lambda = 370-500$ nm), light intensity 1000 $mW \cdot cm^{-2}$, 6 min; photoinitiator: mixture of 0.3 wt % campherchinone, 0.6 wt % methyl-4-(*N*,*N*-dimethylamino)benzoate and 0.4 wt % acylphosphine oxide (Lucerin TPO, BASF).

[10] A 10% solution of $Zr_4O_2(OMc)_{12}$ in ethanol was added to **1c** or **2c** (88.7 wt % polycondensate and 10 wt % cluster). After mixing and addition of the photoinitiator (1.3 wt %), the solvent was removed in vacuo. Photochemical polymerization was carried out as for the undoped samples.