## CHARACTERIZATION OF ORGANIC-INORGANIC HYBRIDS PREPARED FROM POLY(METHYL METHACRYLATE) AND ORGANICALLY MODIFIED Si – ALKOXYDE

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Organic-inorganic hybrid materials were prepared by the sol-gel process. Simultaneous polymerizations of methyl methacrylate (MMA) and an organically modified silicon alkoxyde, 3-glycidyloxypropyltrimethoxysilane (GLYMO), were performed. Poly(oxypropylene)diamine was used as a curing agent.

Prepared hybrid materials were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and by transmission electron microscopy (TEM).

Inorganic phase formed as a result of GLYMO hydrolysis and condensation in the sol-gel process influences the glass transition temperature and improves the heat resistance of hybrid materials.

Key words: organic-inorganic hybrids, sol-gel, PMMA

#### **1. Introduction**

In the last decade, organic-inorganic hybrids became a fascinating new field of research in materials science. One of the main reasons for this is the chance of obtaining the desired and sometimes unique end properties, which can be hardly reached if only organic and/or inorganic components are used<sup>1</sup>. In polymer matrices small amounts (several %) of nanometer-sized particles can considerably influence the end properties of these systems. One of the most common ways for nanoparticle preparation is the sol-gel process<sup>2-10</sup>. The inorganic nanostructures can either be formed *in situ* simultaneously with organic polymer or they can be first prepared and then added to polimerizable monomers or to polymer solution.

The presence of covalent bonding between organic and inorganic components reinforces interaction between components and improves the properties of hybrid materials<sup>2</sup>.

Hybrid materials based on  $SiO_2$  and acrylic polymers, such as poly(methyl methacrylate), PMMA, were successfully prepared via sol-gel process. Simultaneous polymerizations of organic monomer and hydrolysis and condensation of tetraethoxysylane were peformed<sup>11-13</sup>.

In this work organic-inorganic hybrid materials were prepared by the simultaneous polymerizations of methyl methacrylate (MMA) and an organically modified silicon alkoxyde, 3-glycidyloxypropyltrimethoxysilane (GLYMO), with varying MMA/GLYMO molar ratio. Poly(oxypropylene)diamine (D230) was used as epoxy ring-opening reagent.

# 2. Experimental

### **2.1. Preparation of organic-inorganic hybrids**

Prior to the preparation of the organic-inorganic systems there were a number of preliminary studies which are worth noting<sup>14</sup>. Separately, the polymerization of MMA, the inorganic polymerization of GLYMO by sol-gel process (hydrolysis and condensation reactions), as well as reactions in the systems MMA/D230 and GLYMO/D230 were studied.

Based on the aforementioned preliminary studies<sup>14</sup> the detailed procedure of synthesis of organic-inorganic hybrids can be described as follows: GLYMO was prehydrolyzed with H2O (molar ratio GLYMO:H2O=1:1,5) . Acetic acid was used as a catalyst. This solution was stirred at room temperature for 1h then mixed with D230 (molar ratio Glymo: D230=1:1) and stirred for another 30 min.Various amounts of MMA were then added to the solution. AIBN was used as initiator of MMA polymerization. Numbers in the sample designations (hybrids H3, 5, 7, 9 in Table 1) represent approximate weight percent of inorganic phase calculated as SiO<sub>1,5</sub>. The mixtures were left for 24 h at room temperature and then cured at  $65^{\circ}$ C for 24 h and post-cured at  $140^{\circ}$ C for 12 h.

	GLYMO	H <sub>2</sub> O	CH <sub>3</sub> COOH	D230	MMA
Sample	<i>n</i> /mol	<i>n</i> /mol	<i>n</i> /mol	<i>n</i> /mol	<i>n</i> /mol
Н3	1	1,5	0,0092	1	15,09
H5	1	1,5	0,0092	1	7,08
H7	1	1,5	0,0092	1	3,64
H9	1	1,5	0,0092	1	1,74

**Table 1:** Compositions and labels of investigated systems

#### **2.2.** Characterization

The infrared spectra of investigated systems were recorded by a Fourier transform infrared (FTIR) spectrometer (Bruker Vertex 70) equipped with an attenuated total reflection (ATR) accessory with a diamond crystal. 16 scans were collected for each measurement over the spectral range of 400-4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

Dynamic differential scanning calorimetry (DSC) measurements were done on a Netzsch thermo analyzer STA 409. To determine the glass transition temperature, Tg, of hybrids samples were heated from room temperature to 200°C at 10°C/min.

Weight loss of fully cured samples, weighing approximately 15 mg, was measured by thermogravimetric analysis (TGA), using a Perkin Elmer thermobalance TGS-2. The samples were heated from room temperature to 1000°C at a heating rate of 10 °C/min in the synthetic air atmosphere (gas flow of 150 cm<sup>3</sup>/min).

To verify the morphology of the cured samples the materials were investigated by means of transmission electron microscopy (TEM), in JEOL 200 CX microscope with 120 kV acceleration voltage.

Solubility of samples was studied in tetrahydrofurane, THF.

#### **3. Results and Discussion**

The results of FTIR analysis of hybrid H5 are given in Figure 1, a-c. Similar results were obtained for other hybrids. For comparison, FTIR spectra of MMA, PMMA, GLYMO and D230 are given as well.



a) **Figure 1.** FTIR spectra of hybrid H5. Sample is post-cured at 140°C for 12 h.



Figure 1. FTIR spectra of hybrid H5. Sample is post-cured at 140°C for 12 h.

As seen, the sharp band at 1637 cm<sup>-1</sup>, which is characteristic of C=C bond<sup>15</sup>, is disappearing as a result of MMA polymerization. Bands between 1000 and 1200 cm<sup>-1</sup> are characteristic for Si–O–Si bond and broad peak between 3100 and 3600 cm<sup>-1</sup> is characteristic for silanol –OH groups. The appearance of new bands, at ~1560 cm<sup>-1</sup> and 1510 cm<sup>-1</sup>, which are characteristic for –C=(O)–NH– and band at ~1050 cm<sup>-1</sup> which is characteristic for –Si–O– C bond<sup>17</sup>, is observed.

Figure 2 shows the dynamic DSC thermograms of the PMMA and hybrid materials. As seen, relatively small changes in the glass transition temperature,  $T_g$ , were observed. The decrease of  $T_g$  in hybrids H3 and H5 in comparison to the PMMA can be caused by remain products of sol-gel process (water and alcohol) which act as plasticizers. In hybrid materials with higher content of inorganic phase (H7 and H9) glass transition was not observed. It could indicate a good interference between organic and inorganic phase. Similar results are reported in the literature<sup>16</sup>.



Figure 2. DSC thermograms of PMMA and hybrid systems. The glass transition is seen.

Results of TGA analysis are shown in Figure 3. The temperature at the maximum rate of weight loss was determined from the first derivation of the TGA curves (see Figure 3b) and summarized in Table 2.



Figure 3: TGA (a) and DTGA (b) thermograms of investigated systems.

As expected, the increase in the GLYMO content in hybrid systems results in the increased weight residue after thermal degradation. Shape of DTGA curves for hybrids (Fig. 3b) imply on complex mechanism of thermal degradation. In hybrid materials H7 and H9, the onset temperature of degradation is shifted toward lower values in comparison with the systems H3 and H5. This could be caused by higher concentration of poly(oxypropylene) chains which are more prone to degradation than inorganic part or PMMA matrix<sup>18</sup>. In hybrid materials the temperature of the maximum degradation rate is higher than the latter for PMMA (Table 2). Presumably, the inorganic part of hybrid material can act as a mass transport barrier for volatile degradation products<sup>3</sup> and can reduce or prevail the negative influence of polymer part on heat resistance of material.

Sample	$\mathcal{G}_{max}$ /°C
PMMA	378,1
Н3	452,8
H5	458,3
H7	445,2
Н9	447,3
GLYMO/D230	429,8
GLYMO	276,2

**Table 2:** Temperature of maximum degradation rate,  $\mathcal{G}_{max}$ 

It should be noted that all hybrid materials were optically transparent indicating no phase separation of the organic and inorganic phases<sup>19,20</sup> at a scale smaller than the wavelength of visible light, that is 400 nm. To verify the morphology of the cured samples hybrid materials H3 and H7 were characterized with TEM (Figure 4 and 5). The TEM images showed quite homogenous distribution of components in the whole volume of material. Rare aggregates of inorganic particles smaller than 400 nm are observed.



Figure 4. TEM image of hybrid H3.

**Figure 5.** TEM image of hybrid H7.

Prepared samples were held in tetrahydrofurane, THF, for 60 days. PMMA is completely soluble, while inorganic systems (cured GLYMO and the system GLYMO/D230) are almost entirely insoluble. Hybrid materials are partially soluble in THF (between 4 and 20 mass %) what can be attributed to noncrosslinked structures.

Solubility results indicate that prepared hybrid materials are interpenetrating networks, IPN, i.e. combination of soluble linear (PMMA, D230) or grafted polymers (aminolyzed PMMA) and network structures. The latter could be an organic-inorganic network as a result of covalent bonding of PMMA to inorganic structures obtained by sol-gel process or a full IPN of crosslinked PMMA and inorganic network.

# 4. Conclusion

Poly(methyl methacrylate)-silica hybrids were prepared by a simultaneous polymerization of methyl methacrylate and 3-glycidyloxypropyltrimethoxysilane, using a poly(oxypropylene)diamine as a crosslinking agent. Prepared hybrid materials were studied by FTIR, DSC, TGA, TEM and solubility in tetrahydrofurane.

- FTIR results indicated complete polymerization of MMA in investigated systems.
- Hybrids have lower glass transition temperature than PMMA or the glass transition is not detectable.
- TGA analysis in synthetic air atmosphere showed better thermal stability of hybrid materials compared with PMMA
- The TEM images showed homogenous distribution of components in whole volume of material. Rare aggregates of inorganic particles smaller than 400 nm are observed.
- Solubility results indicated that prepared hybrid materials are interpenetrating networks, IPN, i.e. combination of soluble linear (PMMA, D230) or grafted polymers (aminolyzed PMMA) and network structures. The latter could be an organic-inorganic network as a result of covalent bonding of PMMA to inorganic structures obtained by sol-gel process or a full IPN of crosslinked PMMA and inorganic network.

## References

- 1. U. Schubert, N. Hüsing, A. Lorenz, Chem. Mater., 7 (1995) 2010.
- 2. L. Matějka, O. Dukh, J. Kolařík, *Polymer*, **41** (2000) 1449.
- 3. B.M. Novak, Adv. Mater. 5 (1993) 422.
- 4. E. Girardreydet ,T.M. Lam , J.P. Pascault, Macromol. Chem. Phys., 195 (1994) 149.
- 5. J.E. Mark, J. Appl. Polym. Sci., 58 (1995) 1135.
- 6. C.L. Jackson, B.J. Bauer, A.I. Nakatani, J.D. Barnes, Chem. Mater., 8 (1996) 727.
- 7. J.E. Mark, *Polymer* **38** (1997) 4523.
- 8. D.W. Mccarthy, J.E. Mark, D.W. Schaefer, J. Polym. Sci. Part B-Polym. Phys., 36 (1998) 1167.
- 9. L. Matejka, O. Dukh, J.Kolarik, Polymer, 41 (2000) 1449.
- 10. W. Zhou, J.E. Mark, M.R. Unroe, F.E. Arnold, J. Appl. Polym. Sci., 79 (2001) 2326.
- 11. C.A. Avila-Herrera, O. Gomez-Guzman, J.L. Almaral-Sanchez, J.M. Yanez-Limon, J. Munoz-Saldana, R. Ramirez-Bon R, J. Non-Cryst. Solids, **352** (2006) 3561.
- 12. J.M. Yeh,C.J. Weng, W.J. Liao, Y.W. Mau, Surface & Coatings Techn., 201 (2006) 1788.
- 13. J.M. Yeh, C.F. Hsieh, C.W. Yeh, M.J. Wu, H.C. Yang:, Polym. Intern., 56 (2007) 343.
- 14. T.Vrabec, *Diploma Thesis*, University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, 2007. (Croatian)
- B. Kaczmarczyk, B. Morejko-Buž., A. Stolarzewicz, *Fresenius' J. Analyt. Chem.*, 370 (2001) 899.
- 16. J. Habsuda, G.P. Simon, Y.B. Cheng, D.G. Hewitt, D.R. Diggins, H. Toh, F. Cser, *Polymer*, **43** (2002) 4627.
- 17. C. Wu, T. Xu, W. Yang, Europ. Polym. J., 41 (2005) 1901.
- 18. J. Pospíšil, S. Nešpurek, Progress Polym. Sci., 25 (2000) 1261.
- 19. H.K. Schmidt, J. Sol-Gel Sci. Technol., 8 (1997) 557.
- 20. C.J.T. Landry, B.K. Coltrain, J. A. Wesson, N. Zumbulyadis, J.L. Lippert, *Polymer*, **33** (1992) 1496.