

XAFS structural investigation on inorganic-organic thin layers embedding different zirconium oxoclusters: effect of concentration and post-treatment

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One of the most effective approaches for the development of particle-reinforced polymers is based on organically-modified molecular clusters, which constitute structurally well-defined nanosized building blocks (NBB) [1]. In this approach, clusters bearing polymerizable surface ligands with typical diameters in the 0.5–1.5 nm range are polymerized in the presence of organic co-monomers [2,3]. The resulting inorganic-organic hybrid polymers have interesting properties which can be traced back to the combination of efficient crosslinking by the multifunctional clusters and the (nano-)filler effect of the clusters [4].

In the present work, such hybrid polymers in the form of thin layers were prepared by:

- thiol-ene free radical polymerization of the thiol-functionalized oxocluster $\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{MP})_{24}\cdot 4(\text{MPA})$ (**Zr12**), ($\text{MP} = \text{HS}-(\text{CH}_2)_2-\text{C}(\text{O})\text{O}^-$; $\text{MPA} = \text{HS}-(\text{CH}_2)_2-\text{C}(\text{O})\text{OH}$) and a 1:1 molar ratio mixture of acrylic and thiol-functionalised monomers in three different cluster : (monomers mixtures) weight ratios: 5, 10, 20%.
- free radical polymerization of the zirconium methacrylate-functionalized oxocluster $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ (**Zr4**), ($\text{OMc} = \text{CH}_2=\text{C}(\text{CH}_3)\text{H}_2-\text{C}(\text{O})\text{O}^-$) and PMMA in three different cluster: MMA ratios: 1: 50, 1:100, 1:200.

These materials were analyzed by EXAFS spectroscopy in order to determine whether the clusters retain their structures even after polymerization with the chosen monomers. This is a crucial point, since many properties of these hybrid materials are dependent on the presence of the structurally intact oxoclusters.

A further goal of the performed investigations was to analyse the structure of the cluster in the polymer matrix after different post-treatment (thermal heating at temperature of 100, 150 and 200°C; UV treatment for 6 h; storage in water for 24 h), to investigate its behaviour under harsh treatment conditions.

To this aim, 14 different samples were analysed, whose preparation, main features and compositions are summarized in the following table:

Sample labeling	Description	Substrate	Analysed cluster and edge
1_TH10_NOS	Polyacrylate matrix embedding Zr12-SH cluster produced by photothiolene TH10 10% wt Zr12	self-supported	Zr12 Zr K (17998 eV)
2_TH20_NOS	Polyacrylate matrix embedding Zr12-SH cluster produced by photothiolene TH20 20% wt Zr12	self-supported	Zr12 Zr K (17998 eV)
3_TH5_NOS	Polyacrylate matrix embedding Zr12-SH cluster produced by photothiolene TH5 5% wt Zr12	self-supported	Zr12 Zr K (17998 eV)
4_PEGDA3_NOS	Polyacrylate matrix embedding Zr4 cluster produced by photoactivated polymer PEGDA 3 5% wt Zr4	self-supported	Zr4 Zr K (17998 eV)
5_PEGDA4_NOS	Polyacrylate matrix embedding Zr4 cluster produced by photoactivated polymer PEGDA 4 10% wt Zr4	self-supported	Zr4 Zr K (17998 eV)
6_PEGDA5_NOS	Polyacrylate matrix embedding Zr4 cluster produced by photoactivated polymer PEGDA 5 15% wt Zr4	self-supported	Zr4 Zr K (17998 eV)
7_Zr_100_4_TQ	PolyMethylMethAcrylate matrix embedding Zr4 cluster (100:1) produced by photoinitiator 4.18% wt	Soda lime glass	Zr4 Zr K (17998 eV)
15_Zr50_4_TQ	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt	Soda lime glass	Zr4 Zr K (17998 eV)
17_Zr50_4_200	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt, with thermal treatment (200°C 5h)	Soda lime glass	Zr4 Zr K (17998 eV)
18_Zr50_4_150	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt, with thermal treatment (150°C 5h)	Soda lime glass	Zr4 Zr K (17998 eV)
19_Zr50_4_100	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt, with thermal treatment (100°C 5h)	Soda lime glass	Zr4 Zr K (17998 eV)
21_Zr50_4_UV	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt, with UV treatment (6h)	Soda lime glass	Zr4 Zr K (17998 eV)
22_Zr50_4_H2O	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt, with swelling in H₂O.	Soda lime glass	Zr4 Zr K (17998 eV)
23_Zr4cry100_4_TQ	Zr4 crystal melted in PolyMethylMethAcrylate matrix (1:100) produced by photoinitiator 4.18% wt.	Soda lime glass	Zr4 Zr K (17998 eV)
24_Zr4cry200_4_TQ	Zr4 crystal melted in PolyMethylMethAcrylate matrix (1:200) produced by photoinitiator 4.18% wt.	Soda lime glass	Zr4 Zr K (17998 eV)
28_Zr4cry100_4_100	Zr4 crystal melted in PolyMethylMethAcrylate matrix (1:100) produced by photoinitiator 4.18% wt, with thermal treatment (100°C 5h)	Soda lime glass	Zr Zr K (17998 eV)
31_Zr50_4_250	PolyMethylMethAcrylate matrix embedding Zr4 cluster (50:1) produced by photoinitiator 4.18% wt, thermal treatment (250°C 5h)	Soda lime glass	Zr Zr K (17998 eV)

X-Ray absorption measurements at the Zr K-edge were performed during 9 shifts of beamtime at the European Synchrotron Radiation Facility on the Italian beamline BM08 GILDA. Due to the low Zr concentration, the analyses were performed by choosing the fluorescence detection mode at room temperature. The monochromator was equipped with (311) Si crystals with the second crystal bent in order to focus the beam in the horizontal plane on the sample at each point of the spectrum. Figure 1 shows the XANES spectra of polymethacrylate-embedded clusters produced by photothiolene with 5, 10 and 20% wt Zr₁₂, where _NOS denotes self-supported samples and _S with glass substrate. The spectra of crystalline Zr₁₂ and zirconium metal are also shown for comparison.

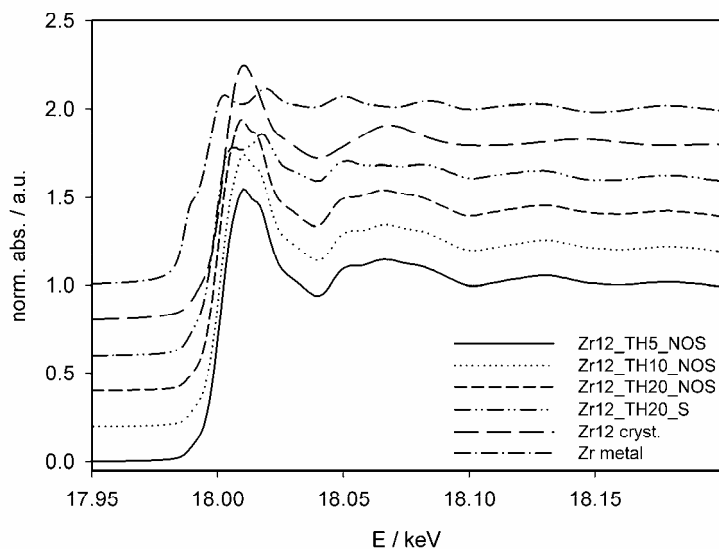


Figure 1: XANES spectra of the embedded **Zr₁₂** cluster together with the spectra of crystalline **Zr₁₂** and metallic zirconium. The spectra were shifted for clarity.

As can be seen from the XANES spectra, by the process of embedding the cluster into the matrix, its structure is altered, while the oxidation state remains +IV. Preliminary EXAFS results indicate a decomposition of the cluster, since additional Zr-shells in comparison to the crystalline cluster are necessary to obtain a good fit. Detailed analysis of the EXAFS data is currently carried out and can not be presented in this report due to a lack of time between the measurements and the analysis.

The data quality was excellent and makes forthcoming measurements at GILDA desirable.

In conclusions, the main results which have been obtained by this first preliminary experiment are the following:

- 1- the feasibility of EXAFS measurements in fluorescence mode on Zr-based inorganic-organic hybrid materials has been demonstrated
- 2- EXAFS is a powerful tool to investigate the structure of different Zr based oxoclusters also after their embedding in a polymer matrix
- 3- the Zr₄ and Zr₁₂ oxoclusters retain their structural integrity once embedded in the polymer matrix
- 4- harsh post-treatment conditions (temperature, storage in water, exposure to UV radiation)

References

1. Functional Hybrid Materials, Edited by P.G. Romero and C. Sanchez, Wiley, 2004
2. S. Gross, G. Trimmel, U. Schubert, V. Di Noto. *Polym Adv Techn* 2002; 13: 254
3. S. Gross, V. Di Noto, G. Kickelbick, U. Schubert, *Mat Res Soc Symp Proc* 2002, 726, Q4.1.1-Q4.1.9
4. F. Faccini, H. Fric, U. Schubert, K. Müller, E. Wendel, H. Bertagnolli, A. Venzo, S. Gross in press in *J. Mater. Chem.*