EXAFS AS POWERFUL ANALYTICAL TOOL FOR THE INVESTIGATION OF INORGANIC-ORGANIC HYBRID MATERIALS

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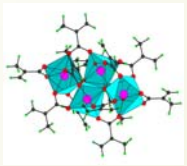
ABSTRACT: The inherent complexity of inorganic-organic hybrid materials derives from the intimate combination, *at a molecular level*, of components which may strongly differ from a chemical and structural point of view. On account of this, the characterisation of inorganic-organic hybrid materials arises several issues, since these materials can be characterized by interpenetration of the phases, motional and/or compositional heterogeneity and absence of long range order (amorphous nature), thus making ineffective typical materials characterization methods such as X-ray diffraction. In this framework, it assumes particular relevance the resort to not conventional characterization methods. Since not only the structural, but also the functional properties of the final hybrid materials are strongly dependent on the structure and on the chemical nature of the embedded cluster, it becomes crucial to asses whether the cluster has retained its structural integrity and chemical composition (in terms of oxidation state and chemical environment of the different species) once embedded in the polymer. At this regard, analytical methods delivering information on the local structure of the cluster are required to assess the structural integrity of the cluster itself. Long range order techniques like XRD fail due to the small cluster sizes and to the lack of long range order, once they are embedded in the matrix. Therefore other spectroscopic methods need to be applied to investigate the structure of the embedded clusters. Structural information on these systems can be conveniently obtained by using X-ray absorption fine structure (XAFS) spectroscopy, which enables the selective determination of the short range order around a specific atom. This method based on the absorption of X-rays by a particular atom is a powerful tool for determining the local atomic environment of a specific atom regardless of the physical state of the sample.[29] Extended X-ray absorption fine structure (EXAFS) spectroscopy provides information on the coordination number, the nature of scattering atoms surrounding the absorbing atom, the interatomic distance between the absorbing atom and the backscattering atoms, and the Debye-Waller factor, which accounts for the disorders due to static displacements and thermal vibrations. In the paper, the XAFS characterisation of different hybrid systems, obtained by copolymerisation of the thiol functionalized Zr oxocluster $Zr_{12}(\mu_3\text{-}O)_8(\mu_3\text{-}OH)_8(MP)_{24}\cdot 4(MPA)$, MPA = HS-$(CH_2)_2$-C(O)OH; MP = HS-$(CH_2)_2$-C(O)O$^-$ and of the zirconium oxocluster $Zr_4(\mu_3\text{-}O)_4(McO)_{12}$ with acrylic resin mixtures is thoroughly discussed. The main results which have been obtained by this first preliminary experiments are the following: a) the feasibility of EXAFS measurements in fluorescence mode on Zr-based inorganic-organic hybrid materials has been demonstrated; b) EXAFS is a powerful tool to investigate the structure of different Zr based oxoclusters also after their embedding in a polymer matrix; c) the Zr4 and Zr12 oxoclusters retain their structural integrity embedded in the polymer matrix.

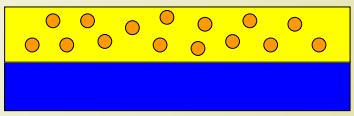
synthesis and characterisation of the inorganic-organic hybrid materials

Zr4 + PEGDA



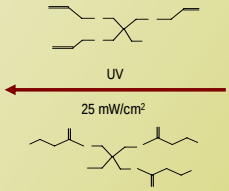
UV
25 mW/cm²

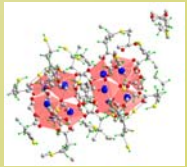
Poly(ethylene gycol)
diacrylate



I/O hybrid thin layer

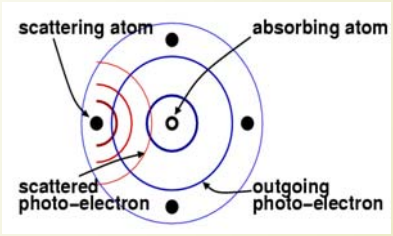
Zr12 + acrylate mixture





Zr12-SH

XAFS background and characterisation



Basic principle of X-ray absorption fine structure (XAFS) spectroscopy:

1) Ejection of a 1s (K-edge) or 2p (L_{III}-edge) photoelectron by a X-ray photon
2) Backscattering of the photoelectron wave at neighbour atoms
3) Interference of the outgoing and backscattered wave at the X-ray absorbing atom

⇒ Modulation of the X-ray absorption coefficient: Oscillatory fine structure

→ Extended X-ray Absorption Fine Structure (EXAFS)

The EXAFS equation:

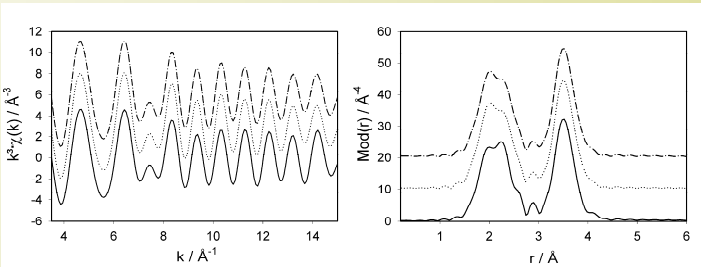
$$\chi(k) = \sum_j \frac{N_j}{k r_j^2} S_0 F_j(k)\, e^{-2\sigma_j^2 k^2}\, e^{-\frac{2r_j}{\lambda}} \cdot \sin\left[2kr_j + \varphi_{ij}(k)\right]$$

F_j: Backscattering amplitude of neighbours j
N_j: Number of atoms of type j
R_j: distance of atoms of type j
σ_j: Debye-Waller factor

Complete structural characterization of the short range order possible

Due to ts short range sensitivity, EXAFS spectroscopy is a powerful tool to analyze amorphous materials or cluster structures without any long-range order. It allows the identification of changes to the cluster which can appear during the incorporation into the matrix by comparison with the crystalline cluster structure and XRD-data thereof.

Zr4 + PEGDA

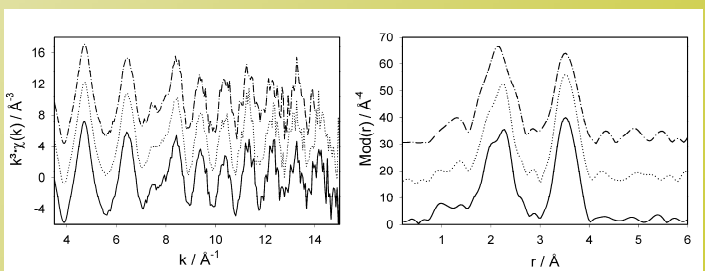


Sample	Absorber-Backscatterer	N(Bs)	R(Bs) / Å	σ / Å²
Zr4_PEGDA_5 %	Zr-O	7.5	2.22	0.025
(solid line)	Zr-Zr	0.5	3.24	0.015
	Zr-Zr	2.0	3.54	0.009
Zr4_PEGDA_10%	Zr-O	7.5	2.23	0.025
(dotted line)	Zr-Zr	0.5	3.25	0.021
	Zr-Zr	2.0	3.53	0.008
Zr4_PEGDA_15%	Zr-O	7.5	2.23	0.025
(dotted dashed line)	Zr-Zr	0.5	3.29	0.012
	Zr-Zr	2.0	3.53	0.009

Comparison with crystalline Zr4 structure: Distances and coordination numbers are comparable

⇒ Zr4-Cluster remains intact after the incorporation.

Zr12-SH + acrylate mixture



Sample	Absorber-Backscatterer	N(Bs)	R(Bs) / Å	σ / Å²
Zr12_Acrylate_5	Zr-O	2.0	2.11	0.005
(solid line)	Zr-O	6.0	2.26	0.012
	Zr-Zr	4.0	3.53	0.012
Zr12_Acrylate_10	Zr-O	2.0	2.10	0.007
(dotted line)	Zr-O	6.0	2.25	0.012
	Zr-Zr	4.0	3.53	0.012
Zr12_Acrylate_20	Zr-O	2.0	2.12	0.011
(dotted dashed line)	Zr-O	6.0	2.25	0.018
	Zr-Zr	4.0	3.52	0.014

Comparison with crystalline Zr12 structure: Distances and coordination numbers are comparable

⇒Zr12-Cluster remains intact after the incorporation.

Conclusions

- Methacrylate- and thiol-modified zirconium oxoclusters were used as inorganic building blocks for the preparation of (meth)acrylate inorganic-organic hybrid materials
- In the case of the Zr12-SH cluster, the presence of the thiol groups around the oxoclusters was exploited to embed the zirconium oxocluster both into a poly(methacrylic acid) and in a mixed acrylate matrix by photo-activated thiol-ene polymerization of the cluster with an excess of methacrylic acid.
- EXAFS: the cluster structure remains intact after the incorporation into the matrix, EXAFS is a very useful tool for structural investigations of hybrid materials without short range order.

Acknowledgments

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