

New hybrid organic–inorganic nanocomposites based on functional $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ nano-fillers†

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New hybrid nanocomposites based on a methacrylate functionalized titanium-oxo cluster as nano-cross-linker show improved mechanical properties, optical transparency and photochromic activity.

Organic–Inorganic Hybrid materials (labelled O/I Hybrids) are nanocomposites composed of inorganic and organic phases that can be physically mixed (Class I O/I Hybrids) or covalently connected (Class II O/I Hybrids).¹ The main interest of O/I hybrid materials resides in the infinite choice of chemical combinations, architectures and morphologies that can be designed, and the easy and versatile processing and shaping conditions provided by soft-chemical routes.^{1–4} These possibilities open a land of opportunities for designing tailor made materials which exhibit improved or new properties. Thus, such materials are considered as innovative advanced materials and promising applications are expected in many fields, such as optics, electronics, mechanics, membranes, protective coatings, catalysis, sensors, *etc.*^{5–7}

Common approaches to processing such O/I Hybrid materials based on conventional sol-gel chemistry⁸ lead generally to amorphous materials that are polydisperse in size and composition. Consequently, because these sol-gel derived O/I hybrids generally do not possess perfectly defined structure the understanding of the relationship between structure, functionality and properties is not always straightforward. The use of well defined inorganic bricks (nanobuilding blocks) allows a better definition of O/I Hybrids both in terms of structure and knowledge of the organic–inorganic interface. Indeed, hybrid materials properties and synergy carried by the different components certainly depend on the nature of their components, but they are also heavily influenced by the interaction between these components. Thus a key point for the design of new tailor made hybrids is the tuning of the nature, the extent and the accessibility of the inner interfaces. Such a high level of control can be achieved by using well defined nanobuilding blocks such as metallic-oxo clusters with known reactivity, stability and tunable functionality.^{9–11}

The present work is focused on the synthesis of a new functional oxo-titanium cluster, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$, and its use as a smart nanofiller for polymethacrylates. The resulting hybrid materials combine optical transparency and a very positive reinforcement of their mechanical properties. Moreover, through UV irradiation, the formation of blue domains resulting from the

formation of mixed valence $\text{Ti}^{3+}\text{--Ti}^{4+}$ centres offers possibilities for optical information storage.¹²

The synthesis of the $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$ precursor (labelled $[\text{Ti}_{16}]$) was performed following a previously described procedure which leads to a pure product with a high yield (> 60%) (ESI).^{13,14} Its structure is made of an inorganic core of sixteen TiO_6 octahedra carrying 32 ethoxy surface capping groups that can be selectively transalcoholysed with preservation of the titanium-oxo core.^{15,16} A complete study of the reactivity of $[\text{Ti}_{16}]$ towards transalcoholysis reaction was recently reported.¹⁶ The exchange kinetics and the degree of substitution depend on the nature of the alcohol and on the stoichiometric ratio. Depending on the acidic power of the entering functional alcohol 4, 8 or 16 ethoxy groups can be selectively substituted. In this work the $[\text{Ti}_{16}]$ cluster was post-functionalised with polymerizable ligands in order to connect them with an organic matrix by copolymerisation. The transalcoholysis was carried out by treatment of $[\text{Ti}_{16}]$ in a toluene solution with a strong excess of an aliphatic alcohol terminated ligand, 2-hydroxyethyl methacrylate $[\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}] = \text{HEMA}$. The modification with HEMA proceeded, as expected, with the introduction of eight terminal methacrylate groups producing an octafunctional methacrylate cluster $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ (Fig. 1) whose structure should be analogous to the one of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OPr}^n)_8]$ resolved by X-ray diffraction.¹⁶ Indeed, the quantification of released ethanol by ¹H NMR measurement confirmed the substitution of the 8 ethoxides by ethoxy-methacrylate functions.

The preservation of the titanium-oxo core and the absence of transesterification and methacrylate polymerization during the

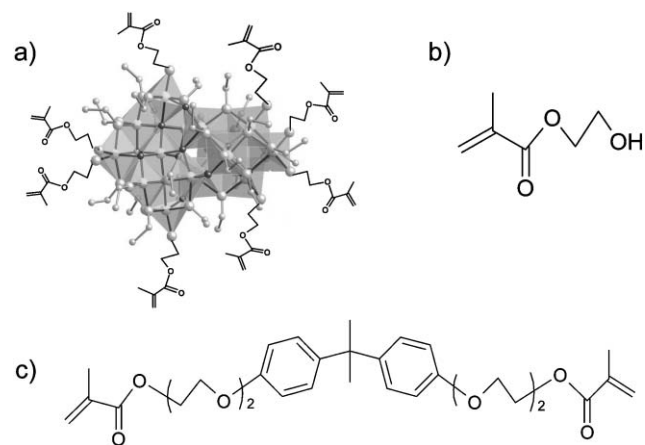


Fig. 1 Inorganic nano-building block structure and organic monomers formulae: a) schematic representation of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$, b) HEMA, c) CD-540.

† Electronic supplementary information (ESI) available: experimental section, spectroscopic data of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{28}(\text{OEMA})_8]$, EPR spectrum of hybrid nanomaterial. See <http://www.rsc.org/suppdata/cc/b5/b502434j> *clems@ccr.jussieu.fr

transalcoholysis step were confirmed by ^{17}O (of ^{17}O enriched specimens), ^1H , and ^{13}C NMR (ESI). In addition, FT-IR spectroscopy showed no complexation of the carboxylate group of HEMA to the titanium atoms (ESI).

The $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ cluster was then copolymerised with methacrylate monomers in order to process the organic/inorganic nanocomposites. The organic matrix component is based on dimethacryloxy-diethoxy-bisphenol A (CD-540) that is known to lead to crosslinked polymers having good mechanical properties. Such polymer matrices are used in industrial applications such as restorative material in dentistry.^{17,18}

$[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ – CD-540 based hybrids were prepared *via* bulk processing conditions through UV initiated free radical polymerisations. The formulations were prepared by using Darocur 1173 as photoinitiator, combined with a methacrylate monomers mixture based on the dimethacrylate monomer, CD-540, a reactive solvent, the hydroxy-ethyl methacrylate, HEMA (2 : 1 wt. CD-540 : HEMA) and various amounts of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ nanobuilding unit (Table 1). It is worth mentioning that the unmodified $[\text{Ti}_{16}]$ cluster is not soluble in the organic medium, while the methacrylate-modification of the cluster leads to a good compatibility.

Comparing the conversion of methacrylate function with various contents of titanium-clusters (Table 1) gives the result that final conversions depend directly on the $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ concentration. The final conversion strongly decreases with increasing content of HEMA modified cluster. As we can see if we compare the conversion of the neat matrix HEMA, *i.e.* > 99%, with the conversion of the corresponding hybrid material containing 19% of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$, *i.e.* 87%.

Because of the large functionality of the methacrylate-modified cluster, *i.e.* 8 functional groups for each $[\text{Ti}_{16}]$, this nanobuilding block should be considered as an efficient crosslinking agent. One consequence of the use of a crosslinking agent is the increase of the medium viscosity during the polymerization kinetics, leading to the gel-point at a lower conversion of reactive species. Consequently, even if the polymerisation rate increases for the gel-effect, the final conversion tends to decrease due to diffusion limitations of propagation.^{19,20†}

The resulting hybrid organic–inorganic materials are fully optically transparent materials, giving evidence of the absence of macroscopic aggregates. However, a transmission electron microscopy experiment performed on photo-polymerised films (Fig. 2) shows the presence of aggregates with sizes ranging from 100 nm to 400 nm as a function of the titanium content.

As shown by dynamic mechanical thermal analysis (DMTA), this new class of hybrid materials based on $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$ –CD-540 copolymers exhibits improved mechanical properties compared to the neat organic matrix.

Table 1 Composition and final conversion of hybrid nanomaterials

Material	CD-540 g (%)	HEMA g (%)	Darocur g (%)	HEMA– Ti_{16} g (%)	Conversion (%)
CDHEMA	2.56 (62.0)	1.28 (31.0)	0.16 (4.0)	—	98.3
HEMA	0.00 (0.0)	3.84 (96.0)	0.16 (4.0)	—	> 99
Ti2.5	2.49 (62.3)	1.25 (31.2)	0.16 (4.0)	0.10 (2.5)	97.0
Ti5.0	2.43 (60.7)	1.21 (30.3)	0.16 (4.0)	0.20 (5.0)	96.1
Ti7.5	2.35 (59.0)	1.18 (29.5)	0.16 (4.0)	0.30 (7.5)	91.3
Ti19.2	0.0 (0.0)	3.08 (76.8)	0.16 (4.0)	0.77 (19.2)	87.0

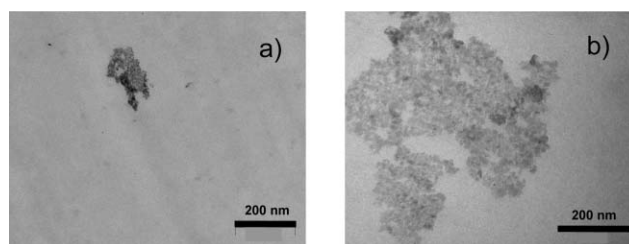


Fig. 2 TEM images of hybrid nanomaterials: a) Ti2.5 and b) Ti7.5.

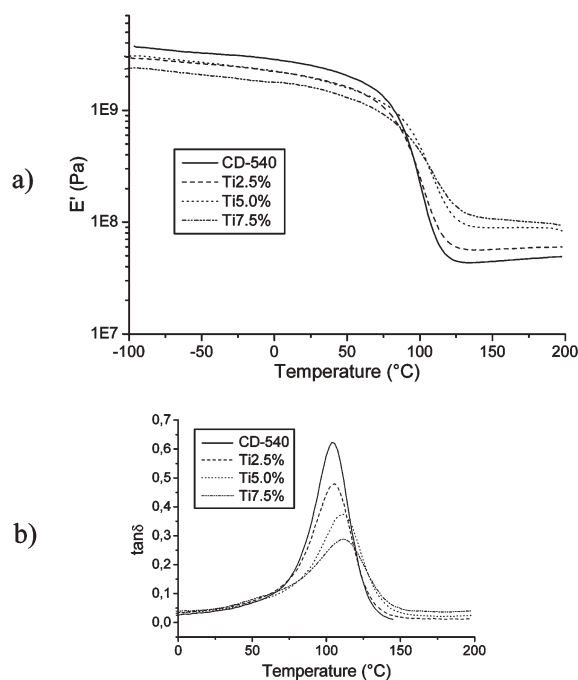


Fig. 3 DMTA analyses of hybrid nanomaterials: a) storage modulus, E' ; b) loss factor, $\tan \delta$.

Dynamic mechanical analyses and data of the nanomaterials are reported in Fig. 3 and Table 2. As expected, at a given frequency, the storage modulus (Fig. 3.a) exhibits a glassy behaviour below 50 °C followed by a large decrease in the glass transition region and a plateau in the rubbery state until 200 °C. The effectiveness of the clusters in enhancing T_g , *i.e.* the temperature of glass transition of nanocomposites, is clearly shown (Table 2). Indeed, increasing the concentration of titanium cluster in the nanomaterials results in increasing the glass transition temperature, even if conversion is lower.

However, simultaneously the amplitude of the loss factor ($\tan \delta$) decreases and its half-width increases, evidencing a distribution of relaxation times of the polymer chains. This effect can be considered as a probe of the network heterogeneity pinpointing that these hybrid nanocomposites display a more heterogeneous distribution of relaxation times than the neat polymer matrix. This effect could be associated with the presence of aggregates visualised by TEM experiments (Fig. 2).

In the rubbery state, the reinforcing effect of the clusters is remarkable even for small contents of HEMA modified titanium-oxo cluster. At 170 °C, the storage modulus, E' , is more than two times higher compared to the neat CDHEMA polymer (Table 2).

Table 2 DMTA analyses of hybrid nanomaterials

Material	HEMA–Ti ₁₆ (%)	T _α ^a (°C)	E' rub ^b (MPa)	h _{max} tan δ ^c	ΔT ^d (°C)
CDHEMA	—	104	46	0.62	13.5
Ti2.5	2.5	105	58	0.48	13.0
Ti5.0	5.0	110	89	0.37	16.6
Ti7.5	7.5	112	105	0.29	19.5

^a Temperature position at 1 Hz of the α-relaxation peak associated with T_g. ^b Rubbery Young modulus determined at T_α +50 K. ^c α-relaxation peak amplitude. ^d Width of the α-relaxation peak at half height.

To the best of our knowledge, for the first time positive effects on the mechanical reinforcement at the rubbery state of hybrid nanocomposites based on nanobuilding blocks are demonstrated.^{21,22} This behaviour can be explained by the analyses of morphologies and analogies with other types of materials containing inorganic clusters. The cluster is an inorganic object with high volume and molar mass covalently bonded to the surrounding polymer medium. Moreover, the cluster is rigid due to the highly polar oxo-bridges between the different titanium atoms. Moreover, [Ti₁₆O₁₆(OEt)₂₄(OEMA)₈] clusters are bulky and heavy objects that decrease the molecular mobility of the polymer matrix, *i.e.* the segmental motions of the polymer networks, in addition to their high functionality leading to a higher crosslink density. The distribution of the functional nanoclusters within the final network, resulting from the copolymerization with the methacrylate monomers, remains under study. In fact, their homogeneous distribution within the heterogeneous polymethacrylate network, *i.e.* similarly dispersed in microgels and in between microgels, or their segregation in the inter-microgel regions could be of importance for explaining the broader distribution of relaxation times (tan δ peaks) as well as the increases of glass transition temperature (considered from T_g) and storage modulus in the rubbery state.

Last but not least, the resulting hybrid materials become dark blue upon UV-Visible irradiation.

This coloration is typical of the absorption created by the intervalence band associated with the photogeneration of localized titanium(III) polarons.^{23,24} Indeed the presence of mixed-valence Ti(III)–Ti(IV) entities has been shown through UV-Visible and EPR measurements (ESI).¹² This photochromic behaviour is reversible in the presence of oxygen which yields the back oxidation of the Ti(III) centers into Ti(IV).

In summary, we have synthesised a HEMA functionalized titanium-oxo cluster which can be dispersed into methacrylate monomers and that does not inhibit polymerisation by UV curing of conventional dimethacrylate monomers. The final nanocomposites are transparent materials based on oxo-titanium clusters covalently bonded to the organic matrix. These nanobuilding blocks act as effective nano-fillers since the thermo-mechanical properties of the nanocomposites are strongly enhanced above the glass transition temperature with respect to the neat polymethacrylate matrix. Moreover, these nanomaterials can be synthesised as transparent thick or thin films which exhibit photochromic properties. The reported synthesis is potentially applicable to other organic vinylic monomers. These types of materials, which present well defined oxo-metallic sites dispersed in an organic medium, can

be interesting for optical devices and further study will be conducted towards the development of their optical properties.

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Notes and references

‡ In addition, such a type of free radical polymerization leads first to microgel formation followed by a macrogelation from connection of the primary microgels. As a consequence, the resulting network is very heterogeneous with highly crosslinked zones (initial microgels) and less crosslinked interparticle zones. In the present case, the presence of the eight functional cluster drastically increases the crosslink density of the nanomaterials with respect to the crosslink density of the matrix based on the difunctional methacrylate monomer, CD-540.

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