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Physico-chemical characterization of hybrid polymers obtained by 2-hydroxyethyl(methacrylate) and alkoxides of zirconium

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Abstract

Hybrid monolithic materials were prepared through polymerisation of 2-hydroxyethyl methacrylate (HEMA) mixed with zirconium alkoxides ($Zr(OBu^n)_4$, $Zr(OPr^n)_4$ and $Zr(OEt)_4$), modified by acetylacetonate groups. The molar ratio HEMA/Zr varied between 1 and 4. Thermo-Gravimetry coupled with Mass Spectroscopy (TG-MS) analyses, ^{13}C MAS NMR and Dynamical Mechanical Thermal Analysys (DMTA) indicated the polymeric chains were interconnected by the inorganic component.

The presence of zirconium alkoxides modified substantially the poly-HEMA properties. Glass transition temperature of hybrid materials derived from butoxy and propoxy was found in the range 50–80 °C, depending on the composition. The typical swelling of p-HEMA in the water, was suppressed by the presence of zirconium compounds. After immersion in distilled water, hybrid polymers showed an initial slight weight increase, followed by a small mass loss, which increases proportionally to the length of alkoxyl group (ethoxide(propoxide(butoxide) and reaches a constant value after about 40 days. The hybrids remained always rigid and transparent. Flexural modulus and strength of about 400–900 and 4–8 MPa were measured.

Keywords: Hybrid polymers; 2-hydroxyethyl(methacrylate); HEMA

1. Introduction

In the last years, the continuous request of materials with improved properties stimulated researchers to develop new classes of polymers for applications, which usual organic macromolecules fail in. At this regard the inorganic–organic materials prepared by sol–gel processes received a remarkable attention [1–6].

When the inorganic and organic components are mixed at nanometric or molecular scale, hybrids with a large variety of composition and properties can be achieved. A well known classification divided hybrids in two classes I and II, depending on whether between inorganic and organic components covalent bonds are absent or not, respectively [4,7]. Since Si–C bonds are stable to nucleophilic attack of water, siloxane based class II hybrids were largely synthesized starting from compounds of general formula $R'Si(OR)_3$. If R' is a polymerizable group, it can copolymerises with other organic monomers [8–13]. This molecular approach for the synthesis had to be adapted for class II inorganic–organic copolymers based on transition metals. The M–Cs (M = Ti, Zr, Nb) bond is not stable and the alkoxides of transition metals are too moisture sensitive. So, the successful strategy was to modify the metal alkoxides by O–donor ligands less hydrolizable than alkoxyl groups and containing a polymerizable functionality: the unsaturated moieties are accessible for copolymerization reactions [14–25]. Among the typical ligands, 2-hydroxyethyl(methacrylate) (HEMA) appeared available at the aim to synthesize a modified monomer precursor, which can yield hybrid network. The large interest in this compound depended on its large use for soft lenses and dental composites. A first attempt was reported from N. Payot et al. [26]: titanium isopropoxide treated with HEMA afforded a polynuclear glycolate complex of titanium, containing no unsaturated ligands, because titanium mediated the C–O bond cleavage of HEMA. Similarly to titanium or niobium, a transesterification occurs between $Zr(OR)_4$ and HEMA, yielding zirconium glycolate

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complexes without any methacrylic moieties. Nevertheless, if acetylacetone is previously added to zirconium alkoxides, modified oxo-alkoxo clusters of polydisperse size can be obtained for low hydrolysis ratios. When these species react with HEMA, the metal modified by acetylacetonate groups is no longer suitable to mediate the C–O bond cleavage of HEMA. The use of strong bidentate complexing ligand, as acetylacetonate, in substitution of a monodentate alkoxy group enabled the charge balance be maintained and extra coordination site be occupied and not available for side reaction [26]. In this case, hybrid molecular precursors containing unsaturated ligands are obtained and available for inorganic–organic materials of class II for non-silicon systems [27]. Indeed, these precursors derived from 2-hydroxyethyl(methacrylate) and zirconium alkoxides modified by acetylacetonate can be easily shaped, and with addition of a typical polymerisation initiator as benzoyl peroxide (BPO) and even without [28], they copolymerise with HEMA or other vynil moieties.

Several monoliths were obtained through this route, starting from ethoxide, propoxide and butoxide of zirconium. In this study, the properties of these hybrid polymers and their behaviour in different environment were compared, with also the aim of a better understanding of the degree of organization of the two components and of their local structures both after preparation and after ageing.

2. Experimental section

2.1. Materials and hybrids preparation

Commercial reagents were used without further purification. 2-hydroxyethyl methacrylate (Fluka) and benzoylperoxide (BDH) were stored at 4 °C until use. Zirconium *n*-butoxide in 80% n-butanol (ABCR) and zirconium *n*-propoxide in 70% *n*-propanol (ABCR) were used as source of inorganic component. Various materials with molar ratio $r = [\mathrm{HEMA}]/[\mathrm{Zr}]$ ranging between 4 and 1 were prepared from reaction mixtures of zirconium alkoxide, acetylacetone ($[\mathrm{acacH}]/[\mathrm{Zr}] = 0.03$ molar ratio) and HEMA (containing 4%wt BPO freshly dissolved). Pale brown solutions, obtained after vigorous stirring, were cast into capped polypropylene tubes (diameter 10 mm and 95 mm length). Polymerisation started after about half an hour at room temperature. The produced monolithic hybrid materials were post-cured at 80 °C for 2 h in oven. Moreover, a trial preparation with zirconium ethoxide (ABCR) was also performed, and the obtained monoliths did not appear completely homogeneous, because zirconium ethoxide is only partially soluble into HEMA. Better results were achieved after preliminary dissolution of zirconium ethoxide into ethanol (from 10 to 20 wt/vol%).

The composition percentage, molar ratio and abbreviation of the prepared hybrid materials are listed in Table 1. Hybrid samples were labelled with the acronyms ZB*r*, ZP*r* and ZE*r* (where $r = 4$, 2, 1) accordingly to the use of butoxide, propoxide or ethoxide Zr-precursors, respectively.

2.2. Characterization procedures

Torsion analysis was carried out by using a PL-DMTA MkIII rheometer (Polymer Laboratories/Rheometrics) in the interval 30–150 °C with a heating rate of 1 °C/min. The reactive solution was inserted between parallel plates, and a disk of 30 mm diameter and about 2 mm thickness was analysed applying a dynamic torsion angle of 1.56 mrads with a frequency of 1 Hz.

^{13}C CP-MAS NMR measurements were performed at the frequency of 100.6 MHz with a AMX400WB spectrometer (Bruker) fitted with a 7 mm MAS probe (Bruker). The samples were finely crushed immediately before the measurements and were spun at 2.5 kHz. A 1H 90° pulse of 5.5 μs and a contact time of 10 ms were used. The spectra were averaged over 2k acquisitions with a recycle time of 4 s.

Thermal analyses were performed on a Netzsch STA 409 simultaneous analyser. Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) were recorded in the range 20–1000 °C both in air and helium flow (100 ml min^{-1}) with a heating rate of 10 °C min^{-1}. Electron impact mass spectra (70 eV) were continuously recorded (scans from 3 to 400 amu) with frequency of 1 scan s^{-1}. From the contribution of all ions detected in each mass spectra, the Total Ion Current (TIC) was plotted vs time (i.e. pyrolysis temperature). The use of TG-MS was already introduced for studying the thermolysis of polysiloxane resins and zirconia gel [29,30].

Dynamic mechanic thermal analysis (DMTA) was performed in shear mode on cured disks of about 9 mm diameter and 2 mm thickness. Two subsequent scans were run up to 150 and 200 °C respectively, with a heating rate of 3 °C min^{-1}. Shear storage modulus (G') and loss modulus (G'') were measured by using a PL-DMTA MkII instrument (Polymer Laboratories) at a frequency of 1 Hz, with a displacement 0.016 mm along the diameter direction. The values of T_g were read off as the temperatures of the peak of loss modulus.

Bending modulus and flexural strength were determined at room temperature on cylindrical samples (70 mm long; diameter of about 9 mm) by using a MTS 810 dynamometer in four points bending configuration (outer distance 40 mm; inner distance 20 mm; loading rate of 1 mm min^{-1}).

Dynamic contact (advancing and receding) angles were measured with a Cahn microbalance model DCA322 by using the Wilhelmy plate technique. Cylinders with diameter of about 9 mm were analysed at a temperature of 20 °C with an immersion and emersion speed of 20 μm sec^{-1} in distilled HPLC water (Merck, Germany).

Water ageing was performed by immersion of disks (about 2 mm thick and about 9 mm in diameter) in distilled water at room temperature up to five months. During this

Table 1
Composition of the hybrid polymers, obtained as crack-free monoliths from zirconium alkoxides and HEMA

Sample	ZB4	ZB2	ZB1	ZP4	ZP2	ZP1	ZE4
HEMA (% by wt.)	53.8	36.1	23.2	58.7	42.3	28.1	63.5
Zr $(OR)_4$ (% by wt)	44.1	62.5	75.8	38.5	55.1	69.3	33.7
BPO (% by wt.)	2.0	1.4	0.9	2.4	1.7	1.1	2.6
$r =$ [HEMA]/[Zr]	3.6	1.7	0.9	3.8	1.9	1	3.9
S of cured materials (% by sect.)[a]	19	27	32	19	29	40	10
S of aged materials (% by sect.)[a]	26	32	51	27	36	48	23

[a] Shrinkage was evaluated on the section (see the text for further explanations).

time, the variation of weight, diameter and thickness was recorded.

3. Results and discussion

3.1. Torsion analysis

In order to investigate the initial stage of radical polymerisation of pure HEMA activated by BPO (4% by wt.), torsion analyses were performed into a plate–plate rheometer. Data showed a narrow peak of loss modulus at about 85 °C and a correspondent sharp increase of the torsion modulus, indicated that polymerisation process started at the same temperature measured by DSC analysis [27]. A sample of fresh solution of ZB4 was analysed in the same conditions. Differently from the pure monomer, the viscosity of the hybrid solution increased continuously with temperature and correspondingly the torsion modulus increased from about 1 kPa to 7 MPa at 40 °C, as shown in Fig. 1. Meanwhile, tan δ (or damping factor) showed initially a peak at 37 °C, probably due to the reaction between the modified zirconium alkoxide and HEMA, whereas from 50 °C, increased because of further condensation and polymerisation processes. The signals above 100 °C could be attributed to phenomena of polymerisation and shrinkage with evolution of volatile species. At the end of the analysis the torsion storage modulus value stabilised at about 45 MPa.

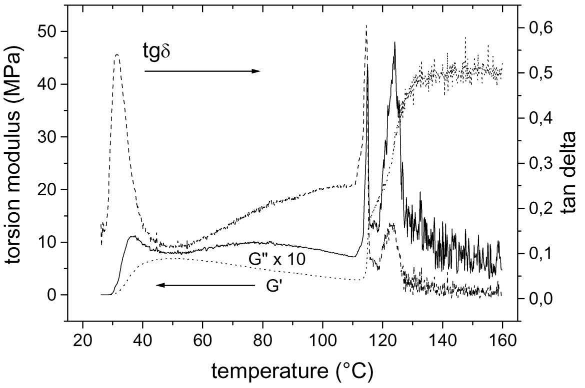


Fig. 1. Torsion storage (G') and loss modulus (G''), and loss factor (tan δ) of the as prepared ZB4 solution heated in plate–plate rheometer.

3.2. ^{13}C MAS NMR measurements

Fig. 2 shows ^{13}C NMR spectra of p-HEMA and of ZB4, ZP4, ZE4 hybrids and the assigned chemical shifts are reported in Table 2, with respect to the HEMA monomer peaks. In the ^{13}C CP-MAS spectrum of p-HEMA, Kiremitci et al.[31] and Miyashita et al. [32] observed the disappearing of the olefinic signals of HEMA monomers at 126 and 136 ppm. They also reported the presence of peaks at ~45 and ~55 ppm, which were attributed to the quaternary carbons and the methylene groups derived from the polymerisation process, respectively. Differently from their conclusions, we assign the strong peak at 43.7 ppm to the CH_2 groups of the main polymer chain (a better magnetic contact), and the weaker feature at 51 ppm to the quaternary carbons. The large and low intensity peak located at 128 ppm, indicated the presence of some amount of unreacted monomer and/or of BPO residuals, whose aromatic carbons fall nearly at the same chemical shift. The downfield peak in the CH_2 region was assigned to CH_2–O– moiety (see the attribution usually made for HEMA monomer). The asymmetry of the CH_3 peak in the region 17–22 ppm could be due to the existence of different stereochemical ordering in p-HEMA. Evidence of different chemical shifts of CH_3 groups due to syndiotacticity in HEMA-based copolymers were recently reported [33,34].

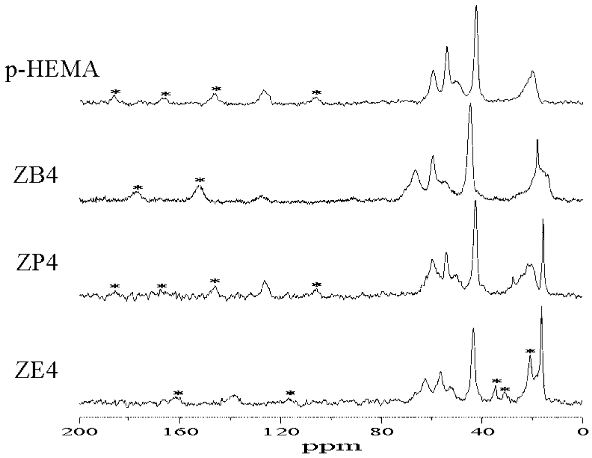


Fig. 2. ^{13}C CP-MAS NMR spectra recorded for p-HEMA, ZB4, ZP4 and ZE4. The spinning sidebands are marked with stars. For the peaks assignment, refer to Table 2.

Table 2

^{13}C MAS NMR chemical shifts of some different carbons of HEMA monomer, p-HEMA and zirconium alkoxide hybrid polymers (ppm from TMS)

Samples	CH_2=	CH_2–O–	CH_2–OH	CH_2 (pol.)	CH_3 (alk.)	CH_3 (HEMA)	C*
HEMA (liq.)	~127	~67	~61	–	–	~18	–
p-HEMA	125.9	59.8	54.3	42.7	–	~21	51.0
ZB4	127.4	66.8	59.6	44.7	18.0	~15	55.8
ZP4	126.5	59.8	54.3	42.6	15.7	~20	51.3
ZE4	138.6	62.7	56.5	43.5	16.4	~18	52.9

The spectra of hybrids were similar to that of p-HEMA, confirming the occurrence of polymerisation of acrylic monomer into polymeric hybrids, unless for the peaks of the alkyl groups of alkoxides (16–18 ppm). Actually, downfield shifts of the $HOCH_2$ peaks were observed in two samples (see Table 2). Evidence of tacticity was also observed in the hybrid polymers, in particular the spectrum of ZP4 displayed a narrow doublet near 21 ppm. It should be also noted that the peak attributable to residual $=CH_2$ was shifted downfield for ZE4. However, a conclusive assignment of this new feature is not yet reached. No evidence of the C=O peak at 177 ppm was found and this could be related to the coordination to zirconium.

3.3. Thermogravimetric and mass analyses

The general pyrolytic behaviour of the cured polymeric samples was well represented by the trends of the TG, DTG and TIC curves. No evolution of HEMA monomer was observed at any temperature. As an example, Fig. 3a shows the TIC curve of the fresh sample ZP1. The parent alcohol (e.g. propanol or butanol) of the zirconium alkoxide and a small amount of alkyl methacrylate (e.g. n-propyl or n-butyl methacrylate) were released in two distinct events, corresponding to the two maxima in the TIC curves, at about 125 and 195 °C. The species formed first at lower temperature through the reaction of a Zr–OR moiety with adjacent Zr–OH or Zr–OR′, where $R = Bu^n$ or Pr^n and $R' =$ methacryloylethoxy, consuming all the available groups. At higher temperature, internal structural rearrangements made other residual groups get closer and available for the reaction. Above 350 °C the decomposition of the overall polymer backbone occurred, resulting in the greatest weight loss.

Decreasing the zirconium alkoxide amount, the two distinct peaks of TIC curve under 300 °C merged into a small single one, due to the simultaneous evolution of parent alcohol and alkyl-methacrylate, (see Fig. 3b for the sample ZP4). The higher content of HEMA in solution favoured a higher degree of substitution of alkoxy groups already before the polymerization. Moreover, the large and intense peak corresponding to the decomposition of the organic polymeric component, was detected just above 300 °C.

TIC curves of the aged samples show trends similar to those of fresh ones (see Fig. 3c for the aged sample ZP1), but the peaks were shifted at lower temperatures. A lot of water and a low amount of parent alcohol featured the first and second peak, respectively. However, alkyl methacrylate was revealed in the evolved gas only at higher temperature during the de-polymerisation process. The relative percentage of the weight loss above 300 °C, attributed to the organic polymeric chains decomposition, increased from about 60% of the fresh materials to 70%, after the ageing.

Both heating and ageing caused shrinkage, which was more pronounced in the samples with the higher percentage of zirconium alkoxides. The percentage of the section variation, $S\%$ was evaluated according to following equation:

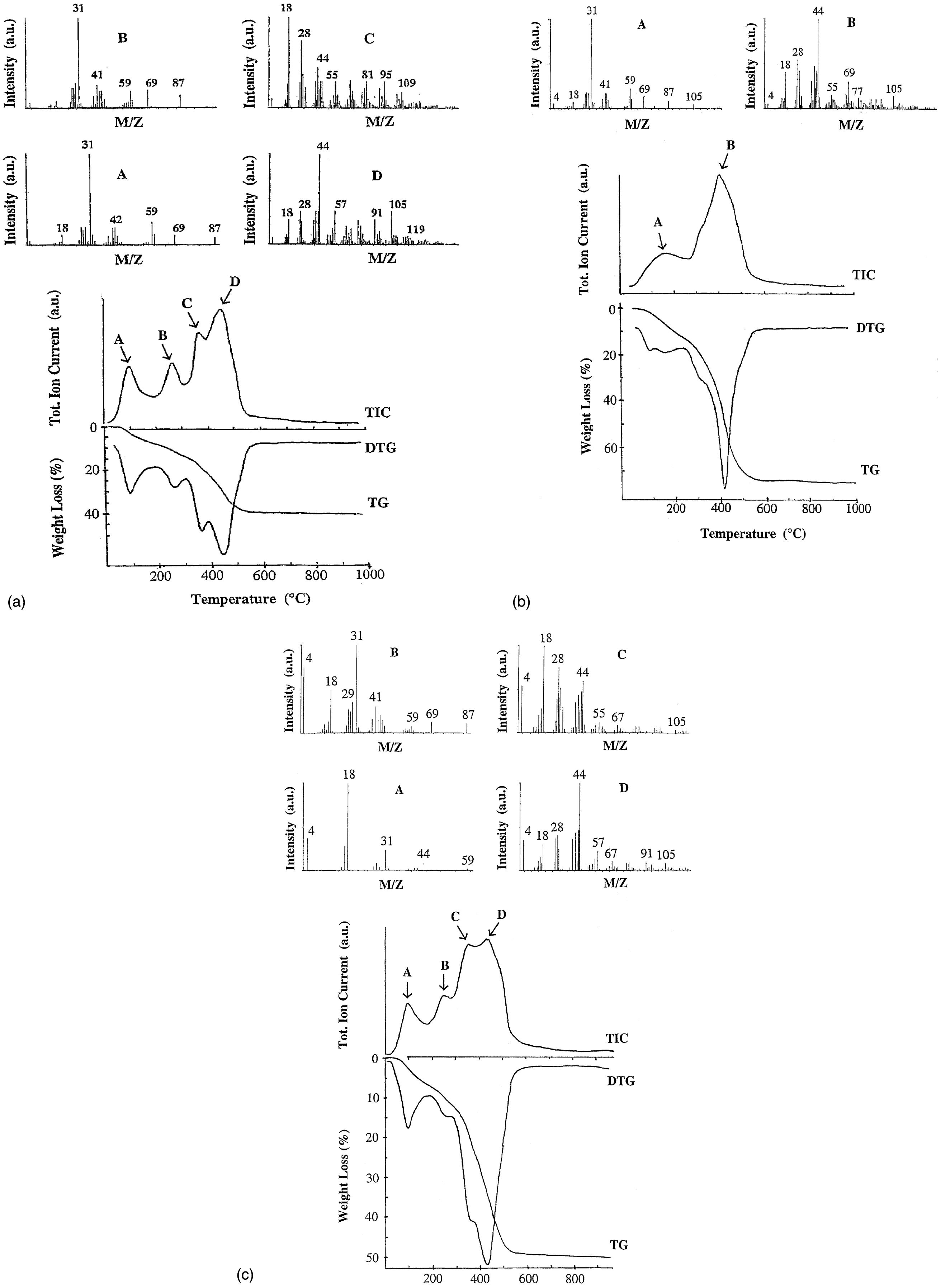
$$S\% = 100(D_t^2 - D_h^2)/D_t^2) \qquad (1)$$

where D_t is the diameter of the polypropylene tube, and D_h the average diameter of the produced hybrid rod. After curing, ZB and ZP hybrid materials showed contraction between 20–40%, whereas shrinkage of 10% was found for cured ZE4, as reported in Table 1. After ageing all hybrid samples showed a further shrinkage of about 25–50%, and the lower the r factor, the higher the shrinkage. On the other hand, pure p-HEMA cured and aged in the same conditions, exhibited lower section shrinkage of 7.8 ± 0.5%, confirming that zirconium alkoxide was the main responsible for the shrinkage of the hybrid materials.

3.4. Dynamic mechanical thermal analysis

Shear storage modulus (G') of hybrid polymers in the glassy region was found ranging between 20 and 50 MPa. By increasing temperature a significant decrease of G' was observed with a sharp drop in the glass transition region, as shown in Figs. 4 and 5 for cured and aged samples. In particular the storage modulus of cured ZB4 (dotted line in Fig. 4a) exhibited a large decrease in the interval 50–100 °C, accompanied by the peak of loss modulus centred at 76 °C, assumed as the glass transition temperature of the material. All ZB and ZP hybrid polymers showed T_g in the range 50–80 °C (see Table 3). These values were lower than that previously measured for dry p-HEMA in bending configuration (84 °C)[29], indicating the relevant influence of the inorganic components on the polymeric backbone.

The peak at about 20 °C, less evident for ZB2 and ZP materials, could be attributed to the presence of organic macromolecules with lower length and/or to the plasticization effect of volatile species. Moreover, a volume



(a)
(b)
(c)

Fig. 3. TG, DTG and TIC curves of fresh ZP1 (a), fresh ZP4 (b) and aged ZP1 (c) samples. Mass spectra recorded at the maximum value of the TIC's peaks are reported in the insets from A to D.

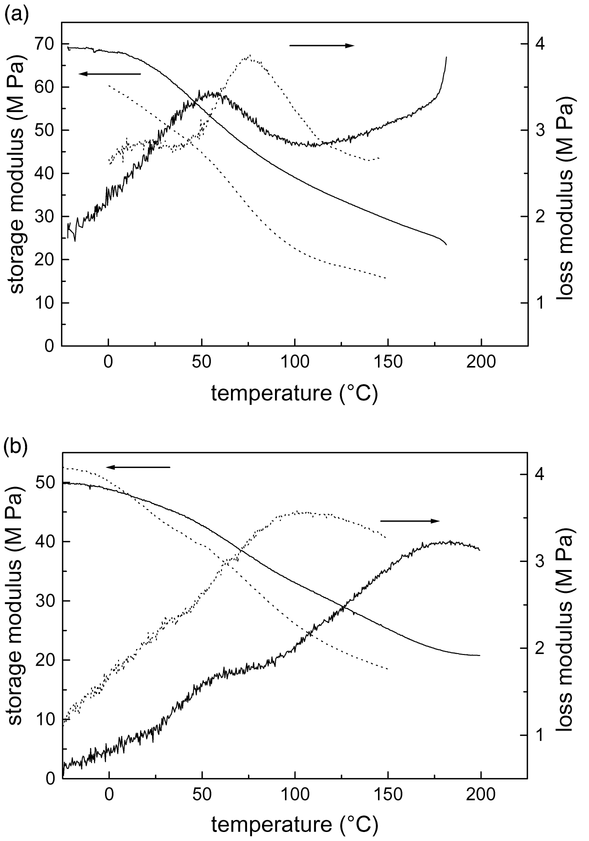


Fig. 4. Shear storage (G') and loss (G'') modulus of ZB4 (a) and ZE4 (b), after curing at 80 °C for 2 h. First (- - -) and second (—) scans are reported.

Table 3
Storage modulus at room temperature (G'_{RT}) and at 100 °C ($G'_{100\ °C}$), and position and intensity of loss modulus peak (G'') of cured hybrid polymers

Cured samples		G'_{RT} (MPa)	$G'_{100\ °C}$ (MPa)	Max G'' (°C)	Max G'' (MPa)
ZB4	1 scan	55	23	76	3.9
	2 scan	64	39	55	3.4
ZB2	1 scan	36	12	73	2.3
	2 scan	47	36	47	3.1
ZB1	1 scan	23	3	59	2.7
	2 scan	31	8	69	1.9
ZP4	1 scan	35	16	59	2.7
ZP2	2 scan	38	34	67	2.6
	1 scan	38	6	67	2.7
ZP1	1 scan	50	–	65	3.3
ZE4	1 scan	45	26	101	3.6
	2 scan	47	33	180	3.2

contraction was measured after heating at 150 °C, (15% for ZB4, 28% for ZB2 and 11% for ZP4), indicating that the higher the inorganic percentage or the longer the alkoxide group, the higher the thermal shrinkage.

In the second DMTA scan (Table 3), all materials showed an increased storage modulus. The maximum of loss modulus of ZB4 and ZB2 decreased and no signal was present at low temperature. For ZE4 sample, the T_g shifted from about 100 °C in the first scan to 180 °C in the second one, meanwhile its storage modulus decreased less than the other materials by increasing temperature.

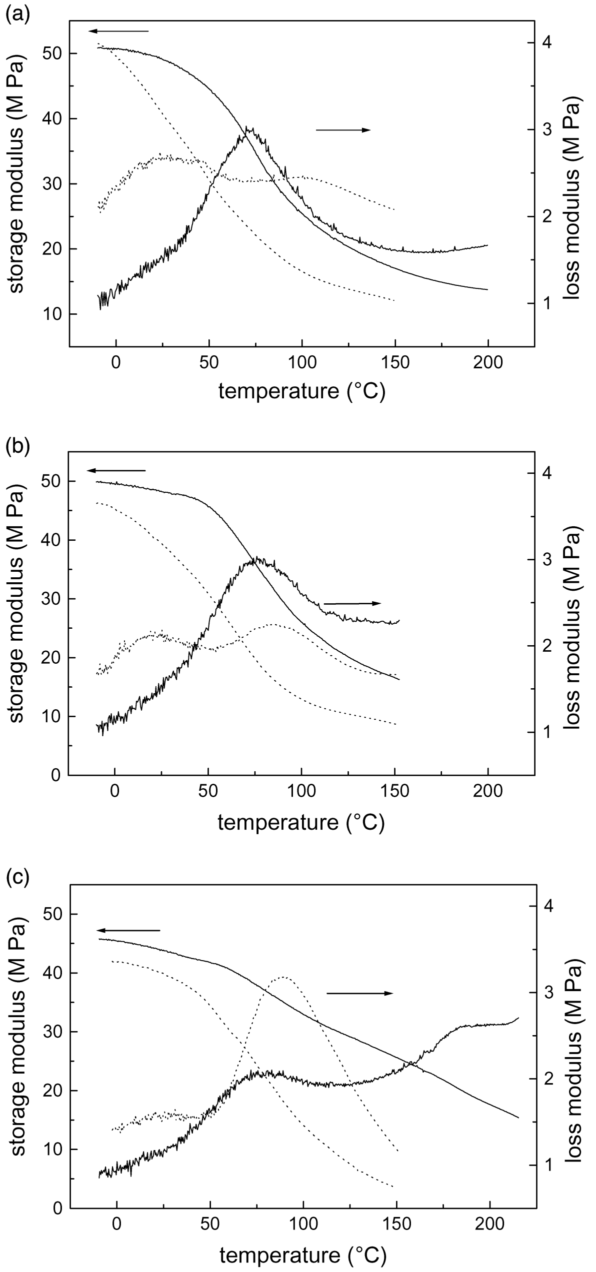


Fig. 5. Shear storage (G') and loss (G'') modulus of ZB4 (a), ZP4 (b) and ZE4 (c) materials aged two years. First (- - -) and second (—) scans are reported.

In Fig. 5a–c, the storage and loss modulus of aged hybrid polymers ZB4, ZP4 and ZE4, are respectively reported. All the materials showed at room temperature in the first scan similar storage modulus (about 40 MPa) and a double peak of loss modulus (at about 25 and 100 °C). A certain plasticization effect was also observed in the first DMTA scan of the aged samples, resulting in a large drop of storage modulus above T_g, down to values of about 10–15 MPa at 100 °C. In the second scan, an increase of storage modulus (about 50 MPa at room temperature) and a single loss modulus peak were observed. In particular, similar T_g was found for aged hybrid polymers with same HEMA/Zr ratio, i.e. 72, 77 and 79 °C for ZB4, ZP4 and ZE4, respectively.

3.5. Flexural measurements

The results of the four points bending tests, performed on cylindrical specimens of cured materials, are reported in Table 4 as average of five specimens. All the samples showed at room temperature a glassy behaviour and a linear elastic $\sigma-\varepsilon$ curve. Flexural modulus of hybrid materials ranged between 400 and 900 MPa depending on the composition. The value of flexural strength, between 2 and 8 MPa, indicated that the hybrids were more brittle than p-HEMA. ZB material exhibited flexural strength about 50% lower than ZP and ZE ones. The higher the percentage and the longer the alkoxy group of inorganic precursor, the lower the flexural strength and the strain at break. In particular, strain at break decreased from about 8% of p-HEMA to about 1% for samples with $r = 4$, or to about 0.5% for those with $r = 2$. An interesting result is that the flexural strength and strain at break of ZE4 (EtOH) sample were about two and four times higher than those of the material produced without any solvent.

3.6. Surface analysis and water ageing

A mean of four measurements of advancing contact angles provided the values of 74 ± 2, 86 ± 1 and 79 ± 3 for ZB4, ZP4 and ZE4 respectively, whereas, the receding contact angles were very low. The existence of hysteresis between the advancing and the receding contact angle indicated that surface was heterogeneous, with both hydrophobic and hydrophilic moieties. On the other hand, during the measurements of dynamic contact angle, p-HEMA exhibited a typical saw-teeth pattern, due to a phenomenon of surface dynamic rearrangement of the outward pointing groups: in order to minimize the free energy of the system at the interface zone with water, the more hydrophilic hydroxyl groups substitute the more hydrophobic methyl ones. The kinetics of this phenomenon was related to the polymer chain mobility, which directly depends on the local glass transition temperature and it was well explained in the paper of Holly and Refojo [36].

Table 4
Average values of flexural modulus (E), flexural strength (σ) and deformation at break (ε)

Samples	E (MPa)	σ (MPa)	ε (%)
ZB4	470 ± 20	4.0 ± 0.6	0.9 ± 0.2
ZB2	445 ± 17	1.8 ± 0.2	0.4 ± 0.1
ZP4	660 ± 20	8.0 ± 0.7	1.2 ± 0.1
ZP2	900 ± 18	4.2 ± 0.3	0.5 ± 0.1
ZE4	570 ± 65	8.3 ± 0.3	1.1 ± 0.2
ZE4 (EtOH)[a]	406 ± 30	18.7 ± 1.1	4.6 ± 0.6
p-HEMA[b]	920 ± 86	75 ± 8	8.2 ± 1.6

[a] Zirconium ethoxide was preliminarly dissolved in ethyl alcohol.
[b] From Ref. [28].

Samples of pure p-HEMA and hybrid polymers with $r = 4$ immersed in distilled water at room temperature exhibited a different swelling behaviour, as shown in Fig. 6a. The higher the HEMA fraction, the higher the initial sorption rate. The sorption rate of hybrid polymers, measured in the first hour and expressed as wt%/min (Table 5), was much lower than that theoretically expected from a linear dependence on the HEMA weight fraction. Moreover, taking into account that the release of species in the first stage is negligible, it can be assumed that the initial water sorption both in the pure polymer and in the hybrid polymers could depend on the hydroxyl HEMA groups. So the percentage of free hydroxylic groups, $\mathrm{OH}_{\mathrm{free}}$, could be estimated by the following equation:

$$\mathrm{OH}_{\mathrm{free}} = \frac{S_{\mathrm{hybrid}}}{\phi \times S_{\mathrm{p-HEMA}}} 100 \tag{2}$$

where ϕ is the weight fraction of HEMA in the hybrids, and S_{hybrid} and $S_{\mathrm{p\text{-}HEMA}}$ are the experimental sorption rate of hybrid and p-HEMA materials, respectively. The hybrid

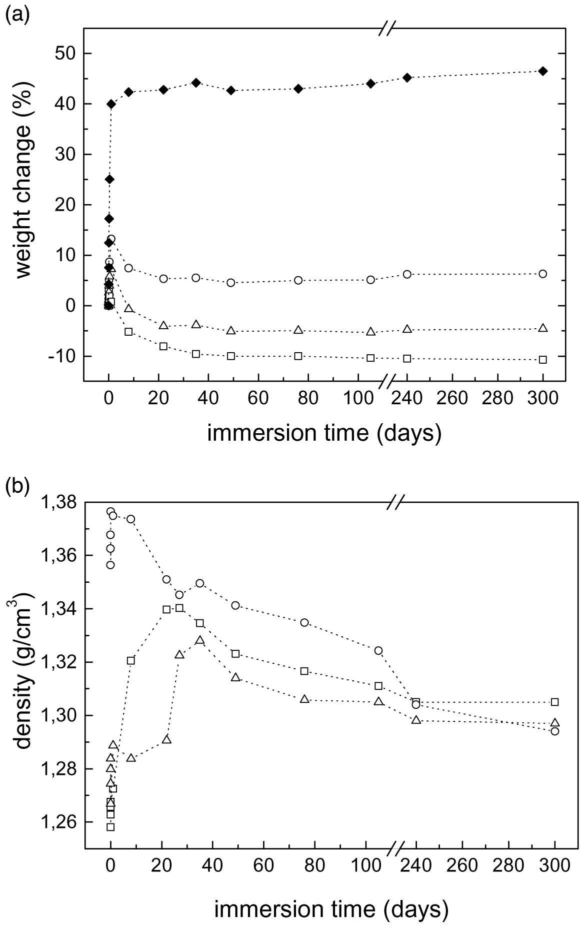


Fig. 6. Behaviour of materials aged two years: (a) weight change during water immersion of p-HEMA (◆) and ZB4 (□), ZP4 (△) and ZE4 (○) hybrid polymers; (b) density variation during water immersion of ZB4 (□), ZP4 (△) and ZE4 (○) hybrid polymers.

Table 5
Sorption rate and weight increase of hybrids polymers and p-HEMA during immersion in distilled water at room temperature

Samples	HEMA fraction by wt.	Sorption rate (%/min)	Weight change after 1 day (%)	Theoretical sorption rate (%/min)[a]	Percentage of free OH (%)[b]	Weight change after 300 days
ZB4	0.55	0.011 ± 0.001	1.8	0.099	11	−11
ZP4	0.59	0.025 ± 0.001	7.2	0.106	24	−5
ZE4	0.64	0.029 ± 0.001	13.1	0.115	25	6
p-HEMA	1.00	0.180 ± 0.025	40.0	0.180	100	45

[a] Theoretical values of hybrids materials were derived from pure p-HEMA with respect to their fraction composition by wt.

[b] The percentage of free OH was evaluated as ratio between experimental and theoretical sorption rate according to Eq. (2) (see text).

polymers exhibited a much lower amount of OH_{free} than expected, suggesting that the unavailable hydroxyl groups of HEMA were tightly bound to the inorganic precursor and providing an indirect measurement of the cross-linking induced by zirconium compounds. This interaction is more intense than that calculated for other hybrid p-HEMA polymers derived from aluminum and iron compounds [37], for which an initial sorption rate of 0.041%/min ($OH_{free} = 40\%$) and 0.095 %/min ($OH_{free} = 88\%$) was measured, respectively.

The pure p-HEMA, like a typical hydrogel, maintained in the wet state a large amount of adsorbed water (45% by wt. at 23 °C, as reported in Table 5), but lower than the value reported in literature (63%, measured at 37 °C)[35]. Moreover, a great increase of size (the volume increase was roughly measured more than 40%) and a decrease of density were observed, similarly to polyglyceryl methacrylate (PGMA) as reported by Refojo [38]. Differently form p-HEMA, the hybrids remained rigid and transparent. ZE4 exhibited swelling as slight as 6 vol% after 100 days, whereas generally a volume contraction of about 10–20% was measured for ZP4 and ZB4 hybrids. Moreover, after about 300 days, the ZP4 and ZB4 samples showed a weight change of −5 and −11%, respectively (Fig. 6a), indicating that the by-products of hydrolysis were driven out.

The densities of dry samples, measured dividing the weight of the specimens by their volume, were 1.26, 1.27, 1.36 and 1.29 g/cm^3 for ZB4, ZP4, ZE4 and p-HEMA, respectively. This latter value was in good agreement with that previously reported in literature for dry p-HEMA (1.283 g/cm^3)[39]. The trend of density for the hybrid materials during the immersion time is shown in Fig. 6b, monitored by measuring the volume and weight variation of the wet samples. It was worth noting that the density attained a similar constant value for all the hybrid samples, after about 250 days. Moreover, the densities of wet samples after 100 days, measured by using n-eptane as reference liquid according to ASTM recommendation [40], were 1.33, 1.30, 1.31 and 1.13 g/cm^3 for ZE, ZP, ZB and p-HEMA, respectively, in good agreement with the data reported in Fig. 6b.

Upon ageing in wet and dry environment or upon heating, the hybrid polymers show a certain degree of shrinkage accompanied by the loss of parent alcohol. So the shrinkage depends on the kind and amount of parent zirconium alkoxides. Finally it should be noted, that these hybrid polymers tend towards a more stable structure.

4. Conclusions

The capability of polymers to incorporate transition metal oxo-clusters, containing unsatured groups, was already reported in literature [41–43]. The two main approaches to the synthesis of hybrid polymers start from structurally well defined clusters with polymerizable groups located at the periphery able to copolymerize with organic monomer, or from molecular precursors of general formula $M(OR)_{4-x}(OR')_x$, (M = Zr, Ti), with R′ = polimerizable organic functionality, which undergo a parallel process of condensation of metal alkoxide and polymerisation of unsaturated moieties. Although the first route offers the advantage to use well-calibrated inorganic nanostructures, which keep their integrity in the final product, it cannot frequently be accessible due to the difficulty to synthesize this kind of metal-oxo-clusters. The second approach is more versatile, provided a proper precursor is available. Accordingly, $Zr(OR)_{4-x-y}(OR')_x(acac)_y$, where R = Bu or Pr or Et and R′ = ethylmethacrylate, was the general formula of the precursors of the hybrid polymers objects of this study. The precursors were prepared mixing $Zr(OR)_{4y}(acac)_y$ and HEMA. The degree of ligands substitution and the number of the HEMA molecules bonded to zirconium have not yet well known, but a certain amount of free organic monomer was supposed to be present in solution, depending on the chosen HEMA/Zr ratio. The so modified zirconium alkoxides, even if much less moisture sensitive than pure alkoxides, can undergo the sol–gel process yielding polydisperse metal-oxo-clusters still containing the methacrylic moieties. At this regard, the knowledge of the chemistry of the structurally defined clusters can be greatly useful. On the base of previously studies regarding the synthesis of carboxylate-substituted clusters of transition metal alkoxides [24], it can be assumed that blocks of different size and shape are obtained controlling two parameters: i) the HEMA/Zr ratio and ii) the kind of OR groups of the parent alkoxide. Both of them determine the degree of ligands substitution and condensation of the inorganic core, with a strong influence on the properties of the final materials. These hybrid blocks copolymerised with the free HEMA, yielding a hybrid polymeric network.

The mechanical properties in the dry state of the HEMA/Zr based hybrids are lower than pure p-HEMA, whatever the composition or the zirconium alkoxide. This result is attributed to the nature of p-HEMA, whose stiffness and strength is largely due to the hydrogen bonds between the polymeric chains. The interaction between HEMA and the zirconium alkoxides, reduced the hydroxyl functionalities of HEMA available for intermolecular hydrogen bonds. This hypothesis is supported by the behaviour of the hybrids in water. In fact p-HEMA behaves as a soft and flexible hydrogel because of the large amount of sorpted water, whereas hybrid polymers exhibited a very low swelling. Although a small shrinkage affected the hybrid polymers, they reached a stable weight and size, maintaining a rigid and transparent structure.

An application of these hybrid polymers as binder of metallic powders in pressureless sintering was recently studied, and in this case the shrinkage is a useful characteristic [44].

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