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High refractive index transparent coatings obtained via UV/thermal dual-cure process

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ABSTRACT

Nanostructured organic–inorganic hybrid epoxy coatings containing zirconia domains were obtained via a cationic UV/thermal dual-cure process. Uniform distribution of the in situ generated zirconia within the polymeric network on a nanometric scale (5–25 nm) was demonstrated by AFM and TEM analyses. The UV-cured films showed increase of the refractive index by increasing the zirconium tetrapropoxide content in the photocurable formulation. Coatings with a drastic cut-off in the UV spectra still maintaining transparency in the visible light were achieved. These coatings could find advanced applications as antireflection coatings, or in the optical industry.

1. Introduction

Recently, there has been great interest in the preparation of organic–inorganic hybrid coatings with high refractive index because of their possible applications in lenses, optical waveguide, displays and reflectors [1–3]. The performance of optoelectronic devices such as flat panel displays, photonic circuits and light emitting diodes could be significantly improved when suitable easy to process polymers with high transparency and high refractive index are readily available at low cost [4]; unfortunately most of the organic polymers are characterized by a low refractive index value.

Significant efforts have been made to increase the refractive index by modifying the polymeric molecular structure [5] or by combining polymers with inorganic components to create nanocomposite structures as optically functional materials [6,7].

As inorganic fillers a range of different metal oxides were successfully employed to increase refractive index in polymeric coatings such as TiO_2 [8], ZnO [9] and ZrO_2 [10,11]. In this regard zirconium oxide is a very attractive material for the use as a suitable inorganic component to improve polymeric optical properties: it is characterized by high bulk refractive index (between 2.15 and 2.18) and lack of absorption in the visible light.

Nevertheless, when a photopolymerization technique is used for coating formation, the ZrO_2 UV absorption can compete with the photoinitiator absorption, and consequently a detrimental effect on final reactive group conversion, polymerization rate and mechanical properties of the cured network can be induced.

In our previous investigation, titania domains were formed within the polymeric network through a sol–gel process [12]: an in situ formation of the inorganic domain was achieved, after UV curing, by means of hydrolysis and condensation reactions of the metal alkoxide precursor.

A similar concept is now proposed for the preparation of UV-curable nanocomposite coatings containing zirconia domains within the polymeric network, by following the UV-induced crosslinking reaction, which give rise to the organic polymer by a hydrolysis–condensation (sol–gel process) reaction of a tetraalkoxy-zirconium additive.

It was shown, in previous papers [13–15], that the organic matrix can be obtained by cationic ring-opening polymerization, e.g. epoxy functions initiated by a photogenerated Brönsted acid, and under this acidic condition the alkoxy groups of the metal oxide precursors can be hydrolyzed and further condensed to form the inorganic domains. Therefore both the epoxy ring-opening polymerization and the sol–gel reaction of the ZrO_2 precursor can be acid catalyzed by the UV degradation of an onium salt.

In this paper, zirconium tetrapropoxide was used as inorganic precursor, in the range between 1 and 5 wt%, with the aim to obtain UV-cured high refractive index coatings. The photopolymerization process was investigated by real-time FT-IR analysis and the properties of the UV-cured materials were studied and correlated with the structures.

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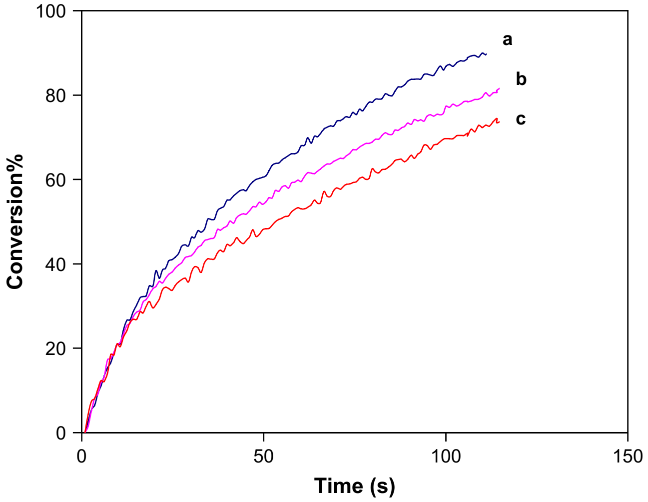

Fig. 1. Real-time FT-IR conversion curves as a function of irradiation time for pure epoxy resin (a) and in the presence of 3 wt% (b) and 5 wt% (c) zirconium tetrapropoxide.

2. Experimental

2.1. Materials

Zirconium tetrapropoxide (ZTP), at 70 wt% solution with 1-propanol, and trimethylolpropane triglycidyl ether (TMP-TGE) were purchased from Aldrich. A commercially available mixture of antimonate sulfonium salts (UVI 6976) were supplied from Dow (the salt is in solution with propylene carbonate at 50% w/w) and it was added to the curable mixtures at a concentration equal to 2% w/w of actual photoinitiator.

2.2. Sample preparation and characterization

The TMP-TGE/$Zr(OPr)_4$ formulations were prepared by adding the inorganic precursor to the epoxy resin in the range between 1 and 5 wt%. Cationic photoinitiator at 2 wt% (as actual photoinitiator content) was added to all formulations.

The obtained mixtures were dissolved in toluene at a concentration of 2 wt% and they were spin-coated on a polished silica wafer substrate at 100–300 rpm for 1 min. Thin films with the average thickness of 500 nm were obtained.

For thick film preparation (around 100 μm) the photocurable formulations were coated on glass substrate by means of a wire-wound applicator obtaining uniform thick films.

The coated films were UV irradiated for 2 min at a light intensity of 30 mW/cm^2 followed by storage in the oven at 100 °C for 4 h in a humid atmosphere (95–98% relative humidity) controlled by a saturated solution of aqueous $NH_4H_2PO_4$, in order to allow the completeness of the sol–gel reaction.

The kinetics of the photopolymerization was determined by real-time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 spectrophotometer. The liquid formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyses in situ the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in the absorbance due to epoxy groups in the region 760–780 cm^{-1}. A medium pressure mercury lamp equipped with an optical guide was used to induce the photopolymerization (light intensity on the surface of the sample is about 30 mW/cm^2). All the conversion curves summarized in a figure were performed on the same day and under the same conditions.

Table 1
Properties of UV-cured films

Samples	Gel content (%)	T_g (°C, DMTA)
TMP-TGE	100	91
TMP-TGE + 3 wt% Zr	100	75
TMP-TGE + 5 wt% Zr	97	75

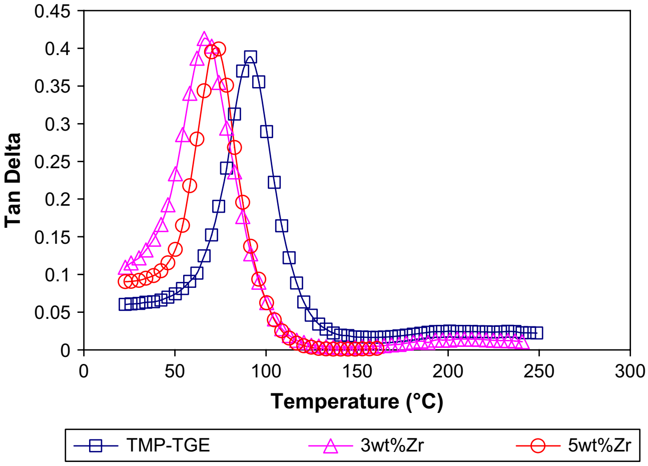

Fig. 2. Tan δ curves (obtained by DMTA) for pure epoxy resin (TMP-TGE) and in the presence of zirconium tetrapropoxide.

The Gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

The AFM measurements were done on the films coated on silica wafer, in the tapping mode using a Dimension 3100 Nanoscope IV (Veeco, USA). A Pointprobe silicon-SPM-sensor (Nanosensor, Germany) with a spring constant of ca. 3 N/m and a resonance frequency of ca. 75 kHz was used. The scan conditions were chosen according to Maganov et al. [16] (free amplitude >100 nm, set-point amplitude ratio 0.5) in order to get stiffness contrast in the phase image that means bright features in the phase image are stiffer than the dark ones.

Samples were prepared for TEM observation by Ar$^+$ ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300 keV transmission electron microscope

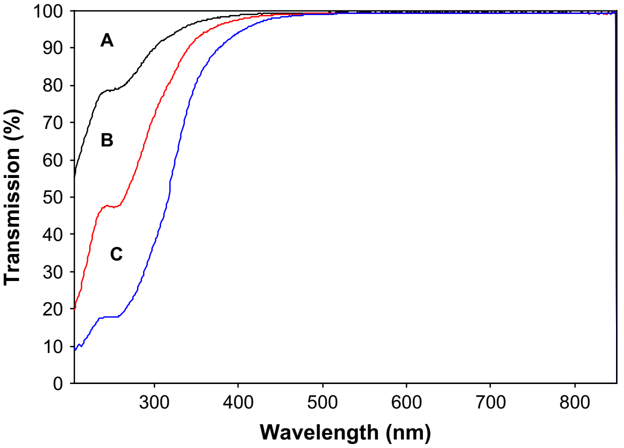

Fig. 3. Absorbance spectra of cured films of pure epoxy resin (A), and of cured formulations containing 3 wt% (B) and 5 wt% (C) zirconium tetrapropoxide.

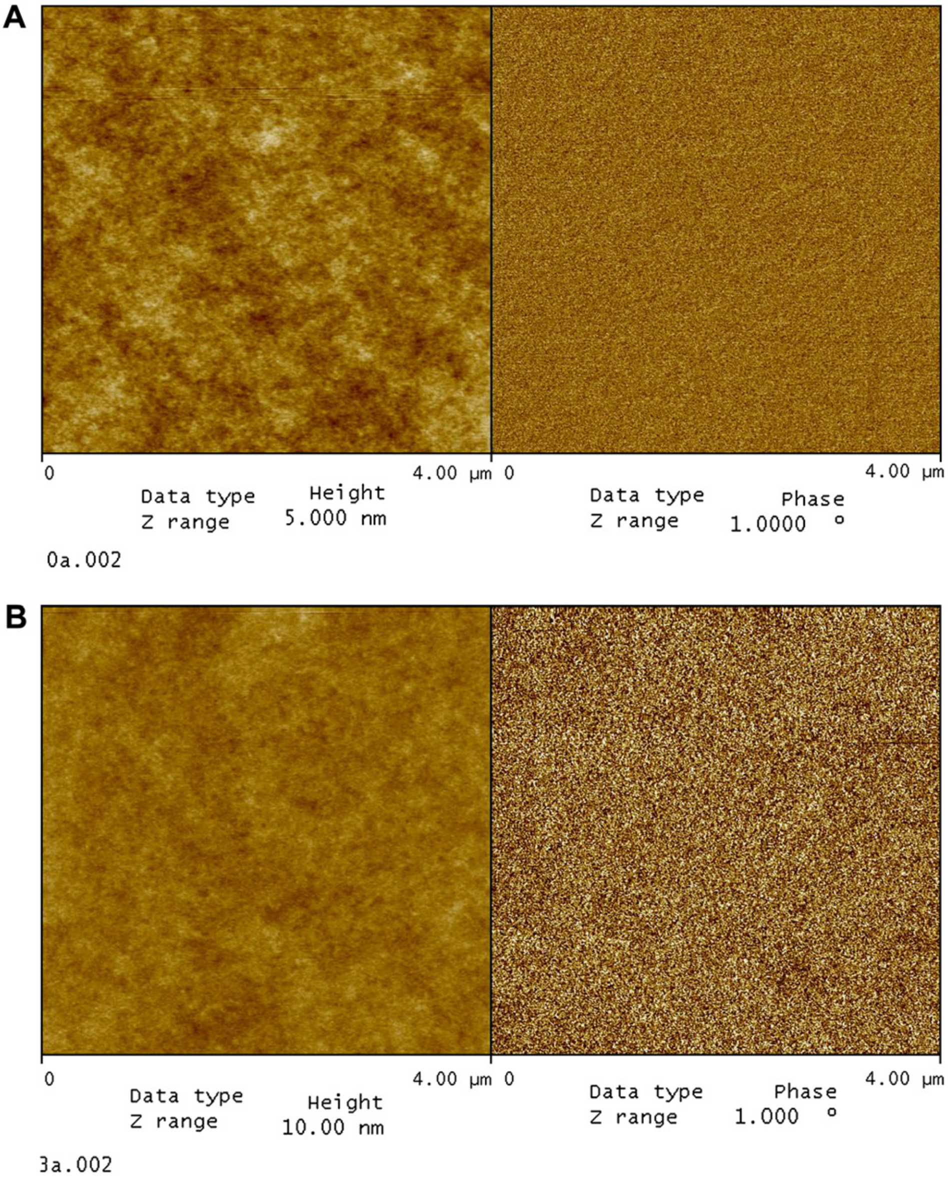

Fig. 4. AFM topography and phase contrast images for (A) pure epoxy-cured film and (B) epoxy/ZrO_2 95:5 wt% cured film.

(TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analysed with the Digital Micrograph program. The TEM observations were always performed using a very low electron flux in order to avoid any structural modification of the sample induced by the electron beam.

The ellipsometric measurements were performed using a variable angle multiwavelength ellipsometer M-2000VI, J.A. Woollam Co. Inc. (USA) in the spectral range from 371 to 1679 nm on films coated on the wafers. It is a Diode Array Rotating Compensator Ellipsometer (DARCE) in PCSA configuration. The ellipsometric WVASE 32 software package was used to evaluate the thickness d and refractive index n of the dry film from obtained ellipsometric experimental data tan ψ (relative amplitude ratio) and δ (relative phase shift) at three angles of incidence (65°, 70°, 75°). The optical two-layer model (Si substrate/SiO_2/polymer) was used for the data analysis. Optical constants of silicon and silicon dioxide at $\lambda = 631$ nm were taken from the literature. First of all, the SiO_2 layer thickness was determined. In order to determine thickness d and refractive index n of the polymer film, ellipsometric data were fitted by means of Cauchy equation over the measured spectral region, where the polymer films are non-absorbing (extinction coefficient $k = 0$). For comparison, the n value at 631 nm was extracted from the data. Additionally, the depolarization degree was measured in order to check the film quality.

Gloss measurements at 60° were measured on cured films according to the standard test method ASTM D2457, by using a Zehntner Testing Instrument (Switzerland) ZGM102.

3. Results and discussion

Real-time FT-IR investigations have been performed following the decrease of the epoxy band, centred at 760 cm^{-1}, during UV irradiation. The conversion curves as a function of irradiation time are reported in Fig. 1 for the pure epoxy resin and for formulations containing increasing amount of zirconia precursor.

From the curves reported in Fig. 1 it is evident that by increasing the amount of zirconia precursor into the photocurable formulation a slight decrease in epoxy group conversion is achieved.

The observed decrease of epoxy group conversion is attributable to the premature formation of ZrO_2 during mixing; zirconium tetrapropoxide is very reactive towards hydrolysis and condensation reactions, and the atmospheric humidity can be enough to cause a fast ZrO_2 formation from the alkoxide precursor.

Zirconia domains, even formed in minimal amount, can compete on UV absorption with the photoinitiator, with a consequent decrease of reactive species formation. A similar behaviour was previously observed when TiO_2 was generated in situ [12] in a similar dual-cure process.

After UV exposure (for 2 min at a light intensity of 30 mW/cm^2) the films were submitted to a thermal treatment in humid atmosphere (at 100 °C in a 95–98% relative humidity atmosphere) to induce the hydrolysis and condensation reactions (sol–gel process) of zirconium tetrapropoxide.

The dual-cured films showed always a high gel content value (above 97%, see Table 1) indicating the absence of soluble fractions. This result is a general indication that good crosslinked network is obtained.

DMTA were performed on dual-cured networks. In Fig. 2, tan δ curves obtained by DMTA are reported for the TMP-TGE cured network and for the polymeric films containing increasing amount of the zirconia precursor. In the T_g region, tan δ shows a maximum which is assumed as the T_g of the cured films [17]. The T_g values for the investigated samples are reported in Table 1.

It is possible to observe a decrease of T_g values in the presence of the inorganic precursor. This result is in accordance with FT-IR data and attributable to the lowering of epoxy group conversion by increasing zirconia precursor concentration in the photocurable formulation; the decrease in crosslinking density is reflected in a flexibilization of the polymer network.

It should also be taken into account the fact that the inorganic precursor is not pure but it is in a 70 wt% solution with 1-propanol. It is well known in literature that alcohol can participate in the cationic chain grown polymerization through a chain transfer reaction with a consequent flexibilization of the polymeric network [18]. Therefore, while the in situ generated ZrO_2 domain should contribute to the increase of the T_g values because of a hindering effect on polymer chain mobility, the alcohol induces a decrease in T_g values because of the flexibilization effect achieved by chain transfer reaction which gives rise to the formation of flexible ether linkages.

All the dual-cured samples are fully transparent to visible light. The transmission spectrum, in the UV–vis region, of the obtained materials is reported in Fig. 3; transparency in the visible light region (400–800 nm) is evident. No significant loss due to scattering was observed in the coatings containing zirconia. It can also be observed that the spectrum shows a decrease in transmittance values in the UV region by increasing the zirconia precursor content in the photocurable formulation.

The transparency in the visible range indicates a uniform distribution of the generated zirconia domains within the polymeric network on a significantly smaller scale than 400 nm. The increase of absorption in the UV region is due to the well known strong UV absorption of ZrO_2.

These results clearly show that by this dual-curing process in the presence of zirconia precursor, it is possible to obtain transparent coatings characterized by a drastic cut-off absorption in the UV region. The strong absorption in the UV region could importantly improve the sun-weathering stability of the UV-cured films. The strong UV-shielding effect on cured samples could be obtained without introducing any UV absorber which would interfere with the UV-curing reaction.

The formation of the inorganic domains in the nanometer range size was further confirmed by AFM and TEM analyses. In Fig. 4A and B, the AFM images, topography and phase contrast of pure epoxy resin and TMP-TGE/ZrO_2 95:5 wt% photocured films, respectively, are reported. In the phase images, the bright (hard) domains were attributed to the zirconia phase generated via sol–gel, while the dark (soft) domains were assigned to the polymeric network.

While the epoxy-cured film shows a complete smooth surface, the cured film containing zirconia shows that the organic and inorganic phases are strictly interconnected with no major macroscopic phase separation that might have occurred during the dual-curing process; the zirconia domains, generated by the sol–gel process, are embedded in the polymeric matrix in the nanoscale range, as it will be further confirmed by TEM analysis.

In Fig. 5 the brightfield TEM micrograph for dual-cured films obtained from the mixture containing 5 wt% of the inorganic precursor is reported. This TEM picture shows that the inorganic phases are well dispersed with no significant macroscopic phase separation; from TEM investigation it is evident that the zirconia domains formed nano-agglomerates of an average size of 5–25 nm.

Even if AFM and TEM analyses were performed on different scales (4 μm for AFM and about 400 nm for TEM), the outcome conclusions clearly put in evidence that the inorganic network was formed within the polymer matrix without any macroscopic agglomeration.

In Table 2 the ellipsometry refractive index values at 631 nm wavelength are reported for dual-cured films obtained from formulations with increasing amount of the inorganic precursor. An increase of the refractive index by increasing the zirconium tetrapropoxide content in the photocurable formulation can be observed. When 5 wt% of the inorganic precursor was added to the epoxy resin, the refractive index of the nanocomposite film reaches the value 1.580 compared to 1.477 for the neat epoxy resin.

Gloss measurements with an incident light at 60° were performed on films coated on glass substrates, in order to quantify the amount of light reflected at the specular angle from the surface; therefore gloss measurements quantify how shiny the surface is.

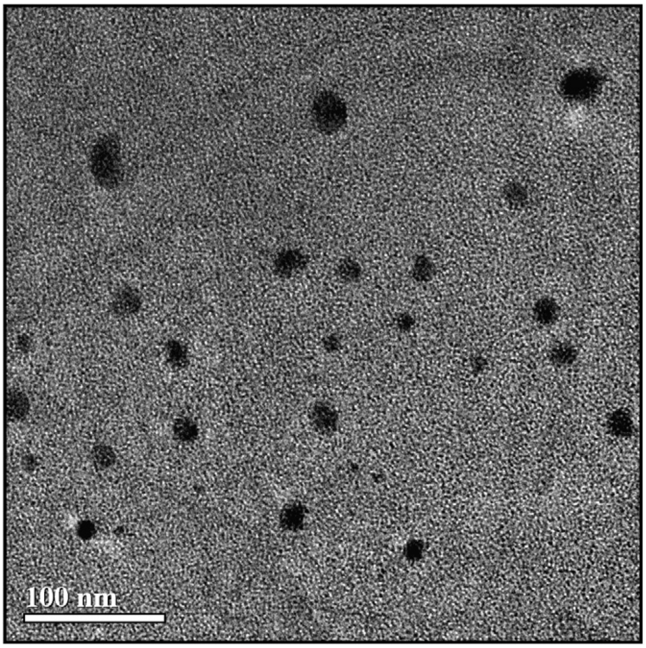

Fig. 5. Brightfield TEM micrograph for dual-cured films obtained from the mixture containing 5 wt% zirconium tetrapropoxide.

Table 2
Refractive index and gloss values of cured films obtained from formulations containing increasing amount of zirconium tetrapropoxide

Samples	n_{631}	Gloss values
TMP-TGE	1477	86.7
TMP-TGE + 3 wt% $Zr(OPr)_4$	1536	73.9
TMP-TGE + 5 wt% $Zr(OPr)_4$	1580	62.5

Gloss values obtained for the dual-cured films are reported in Table 2. It is possible to observe that a decrease in gloss percentage values is obtained by increasing the inorganic precursor content in the photocurable formulation. Gloss values are in accordance with the refractive index values. Polymeric materials with a reduced reflection and higher refractive index are very important as antireflection coatings in applications such as optical industry, displays and solar cells.

4. Conclusions

Hybrid organic–inorganic epoxy coatings containing zirconia domains were obtained through a dual-cure process, which involves first the fast and efficient photopolymerization of epoxy rings and then hydrolysis and subsequent condensation of alkoxy groups of the inorganic precursor. Both the ring-opening polymerization and the sol–gel reaction were catalyzed by the photogenerated Brönsted acid in the presence of a sulfonium salt.

Highly crosslinked coatings were obtained, characterized by a drastic cut-off in the UV spectra but maintaining transparency in the visible region. The transparency in the visible range indicates a uniform distribution of the generated zirconia domains within the polymeric network on a nanometric scale (5–25 nm), as was also demonstrated by AFM and TEM analyses. The UV-cured films showed increase of the refractive index by increasing the zirconium tetrapropoxide content in the photocurable formulation, reaching the value 1.580 in the presence of 5 wt% zirconia precursor. The refractive index increase is concomitant with a decrease in surface coating reflection with a consequent gloss percentage decrease. These coatings could find advanced applications as antireflection coatings, or in the optical industry.

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