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Preparation and characterization of hybrid nanocomposite coatings by photopolymerization and sol–gel process

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Abstract

Organic–inorganic nanocomposite hybrid coatings were prepared through a dual-cure process involving cationic photopolymerization of epoxy groups and subsequent condensation of alkoxysilane groups. The kinetics of the photopolymerization and condensation reactions were investigated; suitable conditions for obtaining a complete conversion of both reactive groups were found. The obtained films are transparent to visible light. The T_g values of the hybrids increase by increasing the TEOS content in the photocurable formulation. Also, a significant increase in surface hardness could be obtained for the hybrid systems. AFM analysis gave evidence of a strong interaction between the organic and inorganic phase with the formation of silica domains in the nanoscale range.

Keywords: Hybrid nanocomposites; Cationic photopolymerization; Sol–gel process

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1. Introduction

Organic–inorganic nanocomposites hybrid coatings are nanophase separated metal-oxo clusters connected to a continuous organic polymer network via a phase coupling agent [1–3]. These materials have drawn considerable attention in recent years due to improvements in various coating properties including resistance to scratching, abrasion, heat stability, as well as other mechanical properties [4,5].

An interesting method for obtaining these hybrid materials is the in situ sol–gel process, which allows to obtain silica domains into the polymer network [6]; it involves a series of hydrolysis and condensation reactions starting from a hydrolysable multifunctional alkoxysilane as precursor for the inorganic domain formation [7]. The use of suitable coupling agent permits to obtain a strictly interconnected network preventing macroscopic phase separation. The coupling agent provides bonding between the organic and the inorganic phases, therefore, well-dispersed nanostructured phases may result [8].

In this context, we considered the preparation of such hybrid materials by combining the sol–gel reaction with a photopolymerization process; this allows putting together the advantages of both the curing methods. The photopolymerization technique is becoming increasingly important in the field of coatings [9]; it induces the polymer formation with a fast transformation of the liquid monomer into a solid film with tailored physical–chemical and mechanical properties. It can be considered an environmental friendly technique, due to the solvent free process usually carried out at room temperature [10].

The UV-induced crosslinking reaction might be followed subsequently by a hydrolysis-condensation (sol–gel process) of the tetraalkoxysilane and condensation with the alkoxysilane groups of the coupling agent: this leads to a silica phase strictly interconnected with the polymer matrix.

In a previous paper [11] we investigated hybrid organic–inorganic nanocomposites coatings containing PEO segments linked to an acrylate network and tetraethoxysilane as silica precursor. Pursuing this research we have now focused on the preparation of organic–inorganic hybrid epoxy coatings through cationic UV curing.

The epoxy resin was photocured in the presence of glycidoxypropyltrimethoxysilane (GPTS) as coupling agent and tetraethoxysilane (TEOS) as organic precursor for the ceramic phase. The mixtures were firstly subjected to UV-curing involving ring-opening polymerization, then to a thermal condensation of the alkoxysilane groups; under acidic conditions, the siloxane groups can react with the atmospheric

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moisture to generate silanol groups which can then condense to form siloxane crosslink. The properties of the cured systems were evaluated and correlated to their structures.

2. Experimental

2.1. Materials

1,6-Hexanedioldiglycidyl ether by EMS (Switzerland, RV1812, HDGE) was used as epoxy resin, 3-glycidoxypropyltrimethoxysilane (GPTS, by Aldrich) was used as coupling agent, and tetraethoxysilane (TEOS, by Aldrich) was the organic precursor for the ceramic phase. A commercially available mixture of antimonate sulfonium salts (UVI 6976) was supplied from Dow: it is given as solution with propylene carbonate (50% w/w) and it was added to the curable mixtures at a concentration equal to 2% wt/wt.

2.2. Preparation of the hybrid samples

The UV curable formulations were prepared by adding to the HDGE monomer GPTS (20 wt%) and TEOS (from 10 to 50 wt%). The relative weight compositions for the different mixtures are reported in Table 1.

An amount of 2 wt% of cationic photoinitiator was added to the obtained mixtures and the formulation was applied to a glass substrate using a wire-wound applicator. The photochemical curing was performed by using a fusion lamp (H bulb), with radiation intensity on the surface of the sample of 280 mW/cm^2 and a belt speed of 6 m/min. The subsequent hydrolysis and condensation reaction was performed by storing the photocured films in an oven at 100 °C for 4 h in a chamber with constant humidity (95–98% relative humidity) controlled by a saturated solution of aqueous $NH_4H_2PO_4$.

2.3. Characterization techniques

The kinetics of the photopolymerization were determined by real-time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument. 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 analyzes 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 of the epoxy groups in the region 760–780 cm^{-1}. A medium pressure mercury lamp equipped with an optical waveguide was used to induce the photopolymerization (light intensity on the surface of the sample of about 10 mW/cm^2). Variation in the experimental conditions (light intensity, humidity, temperature) caused slight differences in the kinetic curves. For this reasons all the conversion curves summarized and compared in one figure were performed on the same day and under the same conditions, thus good reproducibility was obtained.

Table 1
Weight percentage composition of the photocurable formulations

Sample	HDGE	GPTS	TEOS
HDGE	0.8	0.2	0
HDGE + 10% TEOS	0.72	0.18	0.1
HDGE + 30% TEOS	0.56	0.14	0.3
HDGE + 50% TEOS	0.4	0.1	0.5

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.

DSC measurements were performed under nitrogen flux, in the range between −80 and 150 °C, with a DSCQ 1000 of TA Instruments equipped with a low temperature probe. TGA analyses were performed using a LECO TGA-601 instrument in the range between 30 and 700 °C, with a heating temperature of 10 °C/min in air. 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 pencil hardness was evaluated on photocured films according to the standard test method ASTM D 3363.

Contact angle measurements were performed with a Krüss DSA10 instrument, equipped with a video camera. Analyses were made at room temperature by means of the sessile drop technique. Three to five measurements were performed on every sample and the values were averaged. The measuring liquid was double distilled water ($\gamma = 72.1$ mN/m).

XPS analyses were performed using AXIS ULTRA instrument (Kratos Analytical, England). X-Ray-source: Mono-Al K$\alpha_{1,2}$, power of the X-ray source: 300 W at 20 mA, analyzer: pass energy 160 eV (survey spectra) and 20 eV (highly resolved spectra), charge compensation switched on. All survey spectra were formally charge-compensated using the C 1s peak of the saturated hydrocarbons as reference (BE = 285.00 eV). The correct BE for the charge reference peak was determined from the deconvoluted high-resolution C 1s spectrum. Negative values of charge compensation indicate an overcompensation guaranteeing unadulterated peak shapes.

The AFM measurements were done on the films coated on glass substrates in the tapping mode using a Dimension 3100 Nanoscope IV (Veeco, USA). A Pointprobe silicon-SPM-sensor (Nanosensor, Germany) with spring constant of ca. 3 N/m and resonance frequency of ca. 75 KHz was used. The scan conditions were chosen according to Maganov [12] (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 dark ones. In order to remove any dust and surface attached impurities, the films were rinsed with ethanol and air dried before analysis.

3. Results and discussion

Organic–inorganic hybrid coatings were prepared from HDGE, as epoxy resin, in the presence of TEOS, as organic precursor of the silica network, and GPTS as coupling agent. The organic matrix was obtained by cationic ring-opening polymerization of HDGE, initiated by a photogenerated Brönsted acid.

Under acidic conditions, siloxane groups react with water or moisture and generate silanol groups that can then condense to form siloxane crosslinks [13]. Therefore, both the HDGE ring-opening polymerization and the sol–gel reaction of TEOS, can be acid catalyzed by the UV degradation of an onium salt, as recently reported in literature [14].

GPTS can act as a coupling agent, copolymerizing on the one hand with the organic matrix through its epoxy group, and condensing on the other hand with the silica network through its methoxy groups after hydrolysis. The addition of the GPTS coupling agent induces a strong chemical interaction between the organic and inorganic moieties, which is crucial for the formation of the nanocomposite films.

3.1. Kinetic measurements

The photopolymerization kinetics were monitored by real-time FT-IR. The conversion curves as a function of irradiation time for the pure monomer and the hybrid systems are reported in Fig. 1.

While the plateau value gives the final epoxy group conversion, the slope of the curve gives an indication of the polymerization rate. It is possible to observe that the presence of TEOS does not affect the final epoxy conversion, which goes to full conversion in all cases. On the other hand, a slight increase on the photopolymerization rate with increasing TEOS content is evident. In the presence of 30 and 50% TEOS content the kinetic curves overlap perfectly.

This result can be explained by taking in account that under the acidic conditions obtained by the sulfonium salt photodegradation, the atmospheric moisture is already enough to yield a certain degree of TEOS hydrolysis. The hydrolysis product is ethanol, which can interact with the carbocationic growing chain through a chain transfer mechanism [15] enhancing the polymerization rate slightly. In fact, Penczek and Kubisa have shown that in the presence of alcohols the polymerization rate of epoxide monomers can undergo an acceleration effect [16]. They have proposed an 'activated monomer mechanism'. According to this mechanism there is a rapid exchange of proton when the propagating oxonium chain end reacts with an alcohol. A following transfer from the growing chain to the monomer will thereafter start new chains. This mechanism was confirmed in cationic UV curing by Crivello [17].

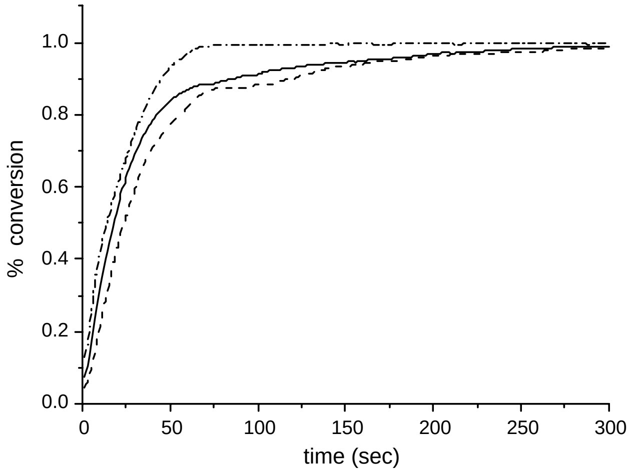

Fig. 1. Real time FT-IR kinetic curves for HDGE (—), and for hybrid systems containing 10% TEOS (– – –), 30% TEOS (· · ·) and 50% TEOS (– · –).

After photopolymerization, the condensation reaction was followed by measuring the weight loss due to the alcohol evaporation. The maximum of the condensation curves was achieved after a 4 h treatment in an oven at 100 °C under constant humidity (95–98% relative humidity).In all the investigated systems the experimental weight loss was lower but very close to the theoretical values. The difference between the experimental and theoretical values could be due to the premature hydrolysis obtained during photopolymerization.

3.2. Mechanical and viscoelastic properties

A pure epoxy network and hybrid films containing different amounts of TEOS, in the range between 10–50 wt%, were prepared by UV-thermal dual-curing.

In Table 2, the gel content for the pure epoxy resin and for the hybrid systems is reported. The data indicate that the thermal treatment after UV curing induces an increase in gel content leading finally to a completely insoluble network. The films are fully transparent to visible light; this indicates an uniform distribution of the generated silica phase within the polymeric network on a significantly smaller scale than 400 nm. This was confirmed by AFM investigation (see below).

Thermal and dynamic-mechanical analyses were performed on cured films. While DSC analysis gives information about the thermal behavior, DMTA analyses allow the evaluation for the elastic and viscous components of the modulus of the material in a large temperature interval. Therefore, this technique gives a complete characterization of the thermal and viscoelastic properties of the material.

In Fig. 2, DMTA thermograms for cured systems are reported. In the T_g region a strong decrease of E' is evident, while tan δ shows a maximum which is assumed as the T_g of the cured films. A shift towards higher temperature is observed for tan δ peak with increasing amount of TEOS, confirming the increase on T_g values observed by DSC analyses. From the T_g data reported in Table 2, it can be observed that the T_g values obtained by DMTA are higher than those obtained by DSC; similar results were reported previously and are attributed to a frequency effect [18].

Table 2
Properties of cured films

Sample	Gel content% after UV	Gel content% after thermal	T_g °C DSC	T_g °C DMTA
HDGE	98	100	−38	−2
HDGE + 10% TEOS	84	97	−34	0
HDGE + 30% TEOS	75	96	−16	3
HDGE + 50% TEOS	61	98	−12	10

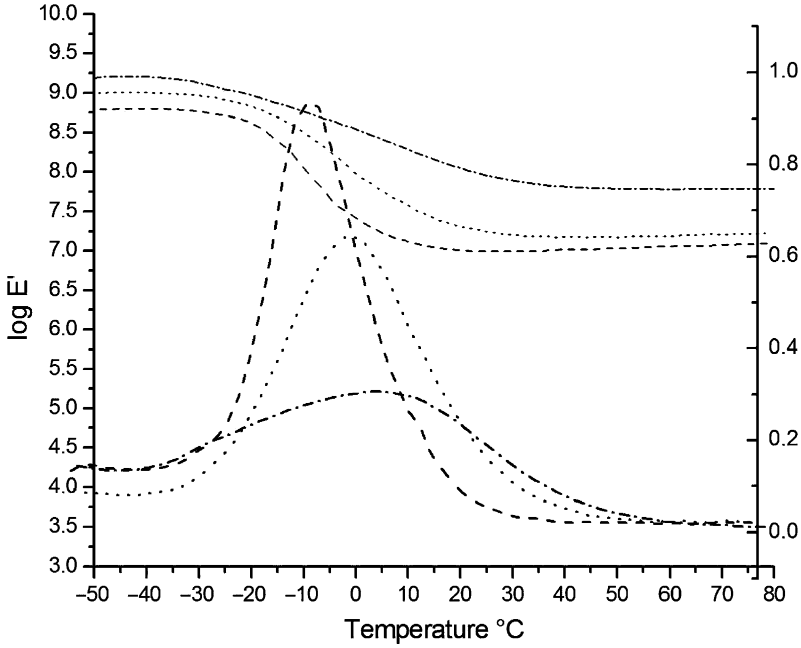

Fig. 2. DMTA curves for cured hybrid films containing 10% TEOS (– – –), 30% TEOS (· · ·) and 50% TEOS (– · –).

DMTA thermograms evidenced also a tan δ peak broadening with increasing amount of TEOS; this is a common behavior for composites [17]; in addition, an increase in storage modulus above T_g in the rubbery plateau is observed with increasing TEOS content.

Both, the increase in T_g values and in modulus, can be attributed to strong and extensive interfacial interactions between the organic and inorganic phase. In fact the inorganic silica particles, formed during the sol–gel process, can restrict the segmental motion of the polymeric chains, and increase the crosslinking density in the polymer network.

3.3. Surface properties

The SiO_2 formation induces also a modification of the surface properties of the cured films, with an increase in pencil hardness by increasing the silica content. The data are reported in Table 3 and they show an increase from 5B for the pure cured epoxy network to 3H for the film obtained in the presence of 50% TEOS. These results are particularly interesting in coating applications; in fact by increasing the surface hardness of the coatings it is possible to induce a related increase in scratch resistance. Therefore, by this method the scratch-resistance of coatings can be strongly improved.

This hardness increase for the hybrid systems can be attributable to the increase in modulus and to the presence of hard silica domains generated after thermal treatment, which tend to segregate towards the film surface.

The later is confirmed by the water contact angle values, reported in Table 3, which show an increase of surface hydrophilicity with increasing amount of TEOS in the photocurable mixtures. This behavior is attributable to a segregation effect of the polar SiO_2 domains toward the air interface of the film.

The silica enrichment of the top-layer of the film was also confirmed by XPS analysis. From the XPS data reported in Table 3, it is possible to observe that by adding TEOS the silica content (mass conc.) on the surface of the film increased considerably from 5.42 (due to the GPTS) to 6.32%. One has to note that already the GPTS led to a significant enrichment of silica on the surface since based on the bulk concentration only about 2.6 mass% Si can be expected in the pure HDGE sample. Carbon content goes down a little in the presence of TEOS while the oxygen remains constant, which is understandable because oxygen is introduced also by TEOS.

3.4. Morphology

In Fig. 3 the AFM image, topography and phase contrast, is reported for the cured film obtained from the formulation containing 50% TEOS. The bright (hard) domains were attributed to the silica phase, while the dark (soft) domains are assigned to the polymeric network, characterized by a low

Table 3
Surface properties of cured films

Sample	Pencil hardness	Adv. contact angle θ (°)	XPS elemental mass%		
			C	O	Si
HDGE	5B	70	57.2	33.9	5.42
HDGE + 10% TEOS	3B	68	–	–	–
HDGE + 30% TEOS	2H	55	–	–	–
HDGE + 50% TEOS	3H	50	56.6	33.8	6.32

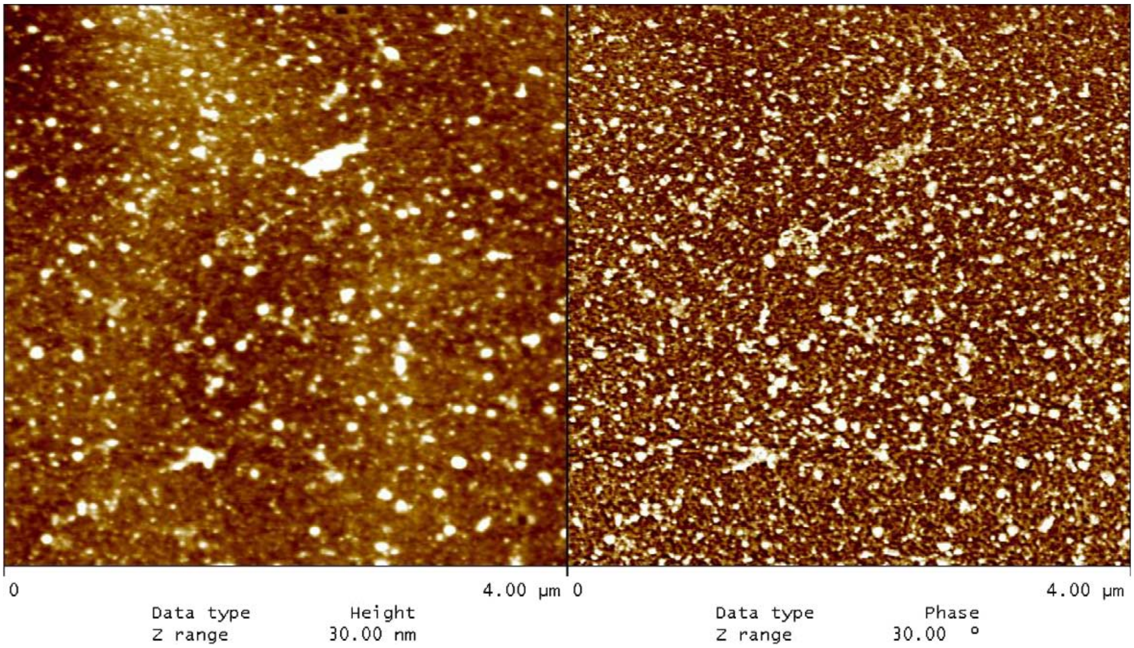

Fig. 3. AFM topography and phase contrast image for the hybrid systems containing 50% TEOS.

T_g (−38 °C). This image 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 silica domains, generated by the sol–gel process, are embedded in the polymeric matrix with an average size around 20 nm.

The strong interactions between the organic and the inorganic network were possible only due to the presence of GPTS as coupling agent. By avoiding macroscopic phase separation, it was possible to obtain hybrid materials in the nanoscale range; this offers the possibility to prepare coatings transparent to visible light with improved mechanical properties and increased hardness.

3.5. TGA characterization

The thermal stability of the hybrid systems was determined using a thermogravimetric analyzer. The TGA curves of pure epoxy resin and in the presence of increasing amount of TEOS are shown in Fig. 4. The TGA values for the 10 and 50% weight loss and for the non-volatile part or char content are reported in Table 4.

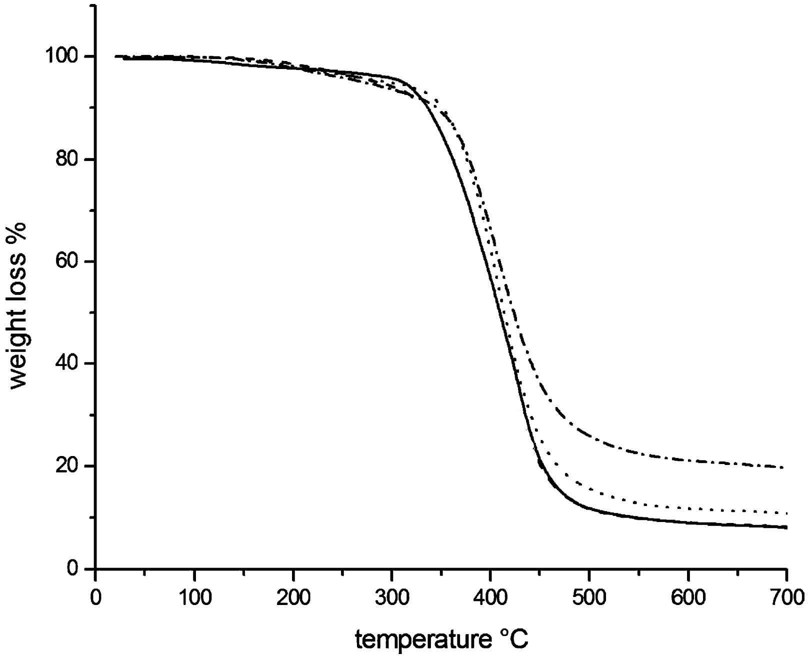

Fig. 4. TGA curves for cured films HDGE (—), and for hybrid systems containing 30% TEOS (· · ·) and 50% TEOS (– · –).

Table 4
Thermal properties for cured films

Sample	10% weight loss	50% weight loss	Char content %
HDGE	336	410	8
HDGE +30% TEOS	351	413	10
HDGE +50% TEOS	340	423	20

These data indicate that with increasing amount of TEOS in the photocurable formulation slightly the thermal stability of the pure epoxy network is slightly enhanced. In all cases the thermal degradation occurs in one step, which is mainly due to the degradation of the cross-links.

The hybrid materials also show a higher char content or reduced weight loss at 700 °C as TEOS content increased. While the pure epoxy network shows a char content of 8%, in the presence of 30 wt% TEOS, the char content increases to a value of 10% and reach 20% in the cured film obtained in the presence of 50 wt% TEOS. These char content values are in good agreement with the theoretical content of silica, as calculated from the initial composition and according to the proposed sol–gel reaction.

4. Conclusions

Epoxy organic–inorganic hybrid systems were prepared through a dual cure process, which involves first the photopolymerization of epoxy rings and then hydrolysis and subsequent condensation of alkoxysilane groups. Both, the ring-opening polymerization and the sol–gel reaction, were catalyzed by the photogenerated Brönsted acid in the presence of a sulfonium salt. Under acidic conditions, siloxane groups can react with atmospheric moisture to generate silanol groups, which can then condense to form siloxane crosslinks.

Completely insoluble coatings transparent to visible light were obtained after UV curing and a subsequent thermal treatment under controlled constant humidity.The kinetics of photocuring were followed by real-time FT-IR, indicating a complete epoxy group conversion after two minutes of irradiation The condensation reaction was followed by weight loss (due to alcohol evaporation) and the maximum conversion was achieved after 4 h at 100 °C.

The T_g values of the hybrid films increase with increase of the TEOS content. This behavior can be explained by assuming an increase of constraints of the polymer segments in the network, due to the siloxane condensation reaction. An increase in storage modulus is also observed, with increasing TEOS content, even in the rubbery plateau region.

An evident hardness increase is obtained in the hybrid systems and is attributable to the increase in modulus as well as to the presence of the hard silica domains on the film surface generated after thermal treatment. The surface segregation of silica domains was demonstrated by contact angle measurements and by XPS analyses.

AFM analysis gave evidence of a strong interaction between the organic and inorganic phases with the formation of silica domains in the nanoscale range.

In conclusion cationic photopolymerization and subsequent sol–gel process is a suitable method to obtain hybrid nanocomposites coatings transparent to visible light with improved dynamic-mechanical characteristics and increased hardness.

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