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Developments of Organic-Inorganic Hybrid Free Radical-Cationic Dual Cured Coatings

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Abstract

Organic-inorganic nanocomposite hybrid coatings were prepared through a dual-cure process involving free-radical and cationic photopolymerization of a methacrylic-epoxy functionalized resin and subsequent condensation of organo-alkoxysilane inorganic precursor. All the formulations investigated gave rise to photocured films characterized by a high gel content values. A lower decrease on glass transition temperature is observed in the presence of MEMO or GPTS compared with a monofunctional methacrylic monomer. The dual-cured hybrid films were optically transparent evidencing that the organic-inorganic phase separation is in the scale of smaller than 400 nm. The formation of nanometric size inorganic domains (in the range between 10-30 nm), both in the presence of MEMO or GPTS as silica precursor, were further confirmed by TEM analysis.

Keywords

Organic-inorganic hyrbid coatings, free-radical and cationic UV curing, nanocomposites.

1. Introduction

Polymeric nanocoatings have drawn considerable attention in recent years, due to the improvements in various properties including scratch resistance, abrasion resistance, heat stability as well as other mechanical properties [1-3].

Inorganic particles are currently used for the reinforcement of polymeric matrices to decrease shrinkage on curing, to improve thermal conductivity and to enhance mechanical properties [4].

The use of inorganic particles in the nanoscale range is particularly attractive with the aim of improving the polymer properties by controlling the degree of interaction between the polymer and the nanofiller [5]. One major problem with nanosized particles is their homogeneous dispersion within the organic matrix avoiding macroscopic phase separation. The bottom-up approach of nanofiller generation in situ via the sol-gel process is an interesting method to overcome this problem.

The sol-gel process mechanism involves a series of hydrolysis and condensation reactions starting from a hydrolysable multifunctional alkoxysilane as precursor for the inorganic domain formation [6]. In previous studies we reported the preparation of organic-inorganic nanocomposite hybrid coatings through a dual-cure process, involving radical or cationic photopolymerization and subsequent condensation of alkoxysilane groups [7-9]. The photopolymerization technique is becoming increasingly important in the field of coatings; 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: this should lead to a silica phase strictly interconnected with the polymer matrix achieving the formation of a hybrid coating. Many researchers have obtained organic-inorganic hybrid films using low molecular weight organoalkoxysilane as the precursor for the sol-gel reactions [11, 12].

In fact, a bottom-up approach can be followed with the inorganic domain formation starting from a bifunctional molecular precursors $(RO)_3Si–X–A$ bearing a hydrolyzable alkoxysilane group $(RO)_3Si$, and an organic functionality (A) capable of undergoing polymerization or crosslinking reactions. The hybrid polymers are formed by a combination of sol-gel processing and organic polymerization reactions.

Another kind of hybrid materials are the radical-cationically photopolymerizable systems. These systems may incorporate the advantages of both kinds of polymerization to obtain a unique material. There has been developed several hybrid UV curing systems using mixtures of certain acrylates and either epoxides [14], vinyl ethers [15], or oxetanes [16]. One of the main advantages of those systems is that the oxygen inhibition of free-radical polymerization is greatly reduced and this fact allows obtaining higher photopolymerization rates and conversions, as well as reducing costs by eliminating the necessity of nitrogen blanketing normally used in radical photopolymerizations. Besides, these hybrid systems incorporate the advantages of both kinds of polymers in one material, for instance, the excellent mechanical and optical properties of epoxy polymers, with the rapidity of curing and variety of properties than can be achieved by polymerizing different types of acrylates. It has also been reported the synthesis of hybrid monomers containing both functionalities, free radically and cationically polymerizable groups as very interesting way to combine the properties of these two types of photopolymerization [17,18].

We reported in a previous investigation, the synthesis of hybrid acrylate-silicone-epoxy monomers, their photocuring and characterization [13]. Due to the excellent mechanical and optical properties of the films obtained, as well as the high reactivity shown by those hybrids monomers it was decided to use them in the preparation of organic-inorganic photocurable coatings.

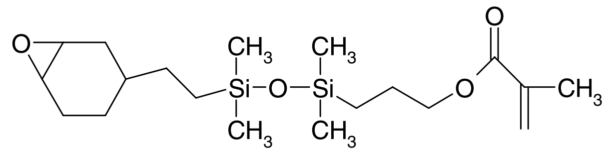
The aim of this work was to investigate the previously synthesized methacrylic-silicone-epoxy hybrid monomers as starting materials for the preparation of organic-inorganic hybrid coatings, using organoalkoxysilane as inorganic precursors. The chosen alkoxysilane was either 3-glycidoxypropyltrimethoxysilane (**GPTS**) or methacryloyloxypropyl-trimethoxysilane (**MEMO**), and the cured films were characterized.

2. Experimental

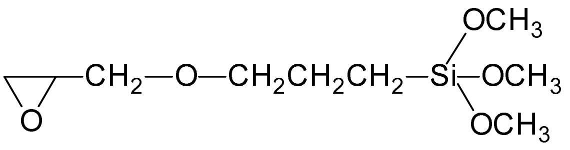
2.1 Materials

The starting monomer was 1-(3´,4´-Epoxycyclohexyl)ethyl-3-methacryloxypropyl tetramethyl disiloxane (**EM2Si**), synthesized as previously reported [13]. 3-glycidoxypropyltrimethoxysilane (**GPTS**, by Aldrich) or methacryloyloxypropyl-trimethoxysilane (**MEMO**, by Aldrich), were used as organoalkoxysilane inorganic precursors. Both radical (Darocur 1073 from Ciba) and cationic (triphenylsulfonium exafluoroantimonate, UVR6196, DOW) photoinitiator were used at 2 wt% each. The chemical structures of the materials employed are reported in Table 1.

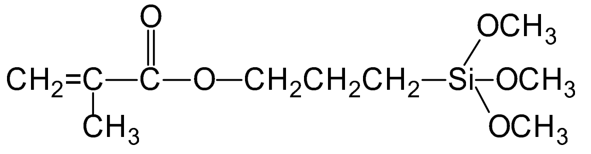
Table 1: Chemical structures of monomer and alkoxysilane inorganic precursors



EM2Si



GPTS



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2CH_2CH_2{-}Si(OCH_3)_3$

MEMO

2.2 Sample preparation and characterization

Organic-inorganic hybrid films obtained via dual-cure process were prepared by adding to the hybrid monomer (EM2Si) the inorganic precursors GPTS or MEMO at different concentration. An amount of 2 wt-% of the radical and of the cationic photoinitiator were added to the obtained mixtures and the formulation were 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 obtaining a film of about 100 µm. The subsequent hydrolysis and condensation reaction was performed by storing the photocured films in an oven at 80°C for 4 hours in a chamber with constant humidity (95-98% relative humidity) controlled by a saturated solution of aqueous $NH_4H_2PO_4$. The obtained samples after thermal treatment appeared transparent.

The gel content was determined on the cured films by measuring the weight loss after 24 hours extraction with chloroform at room temperature. Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration. 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.

Samples were prepared for TEM observation by Argon 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 (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed 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.

3. Results and Discussion

Organic-inorganic hybrid coatings were prepared starting from the hybrid methacrylic-epoxy monomer EM2Si. Either GPTS or MEMO were employed as inorganic precursors; these molecules contain on one side an organic group that can copolymerize with one side of the monomer, and on the other hand they contain alkoxysilane groups that can give rise to silica by hydrolysis and condensation reactions.

The organic-alkoxysilane additive was added in the range between 20 and 40 wt%, the investigated compositions are reported in Table 2.

The organic polymer network was obtained, under UV conditions, both by cationic ring-opening polymerization of epoxy group and radical chain grown addition on methacrylic double bond. While the radical UV-curing is started by a photochemical cleavage of the suitable photoiniatitor, cationic photopolymerization is initiated by a photogenerated Brönsted acid in the presence of onium salt. In this acidic conditions alkosysiloxane groups react with water-moisture, and generate silanol groups that subsequently condense to form siloxane crosslinks. The occurance of the sol-gel reaction was confirmed by the char content evaluated by TGA analysis.

Table 2: Formulation compositions taken under investigations

Sample	**Monomer EM2Si**	**MEMO**
R	100	0
RM20	80	20
RM30	70	30
RM40	60	40
Sample	**Monomer EM2Si**	**GPTS**
RG20	80	20
RG30	70	30
RG40	60	40

Table 3: properties of cured networks

Sample	**Tg °C (DMTA)**	**% gel**
R	127	98
RM20	108	98
RM30	95	99
RM40	88	98
RG20	100	97
RG30	97	98
RG40	95	98

All the formulations investigated gave rise to photocured films characterized by a high gel content values (>98%, see Table 3) indicating the formation of a completely insoluble network and therefore confirming the efficiency of the dual-cure process.

Dynamic mechanical analysis were performed on dual cured films: DMTA analyses allow the evaluation for the storage modulus (E'), loss modulus (E'') and tanδ in a large temperature interval. Therefore, this technique gives a complete characterization of the thermal and viscoelastic properties of the material. The glass transition temperature for the cured film is defined as the peak of tanδ curve.

The Tg data for dual cured films are reported in Table 3. The copolymerization of a monofunctional alkoxyde monomer will induce a decrease on Tg values because of a reduction on crosslinking density. As a reference we characterized the cured film EM2Si containing 40 wt% of butyl methacrylate, therefore the same molecule as MEMO without the alkoxysilane groups. The Tg of cured films was around 70°C, and this put in evidence the important role of the alkoxysilane groups on increasing the crosslink density of the cured films. The hydrolysis and condensation reactions will induce the formation of an inorganic network strictly interconnected with the organic one.

The strong and extensive interfacial interactions between the organic and inorganic phase can restrict the segmental motion of the polymeric chains, increase the crosslinking density in the polymer network and a less Tg value decrease will be achieved. In any case, gel content is always high indicating the formation of a complete insoluble network.

Thermal stability of hybrid systems was determined by TGA analyses. The TGA curves of pure cured resin and in the presence of increasing amount of MEMO are shown in Figure 1, while the TGA curves for the pure monomer compared with the films containing increasing amount of GPTS are reported in Figure 2. The TGA values for the 10% and 50% weight loss and for the non-volatile part or char content are reported in Table 4.

The behaviors are similar with the two different silica precursors, and the data indicate that by increasing the organoalkoxysilane content in the photocurable formulation, the thermal stability of the films was increased; in all cases the thermal degradation occurs in one step.

The hybrid materials also show a higher char content (or reduced weight loss) at 700°C as silica precursor content increased. The char content values are close to the theoretical content of silica calculated from the initial composition according to the sol-gel reaction (see Table 4). The theoretical silica content was calculated supposing a complete methoxysilane groups condensation.

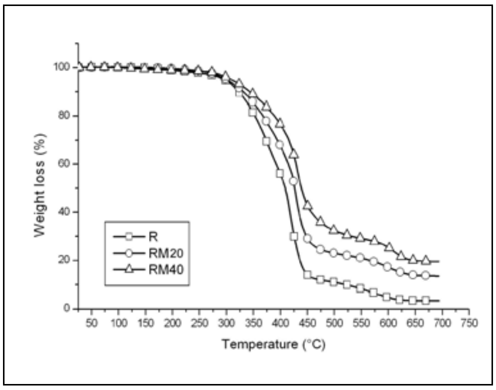


Figure 1: TGA curves for the EM2Si cured film and in the presence of increasing amount of MEMO

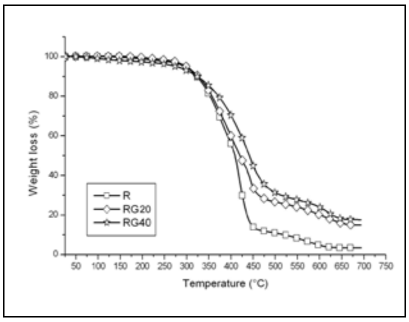


Figure 2: TGA curves for the EM2Si cured film and in the presence of increasing amount of GPTS

Table 4: TGA data for the cured samples

Sample	**T10** **°C**	**T50** **°C**	**Char (%)**	
			Ther.	**Exp.**
R	322	373	-	4
RM20	331	394	4.4	13
RM40	343	415	9.4	19.7
RG20	326	379	4.7	15
RG40	324	400	10	18

The dual-cured hybrid films were optically transparent; this can be an evidence that the organic-inorganic phase separation is in the scale of smaller than 400 nm. The formation of inorganic domains in the nanometer range size were further confirmed by TEM analysis.

In Figure 3 and 4 the bright field TEM micrograph for cured films obtained respectively from the mixture containing 40 wt% MEMO and 40% GPTS are reported. These images show that in both cases the organic and inorganic phases are strictly interconnected with no macroscopic phase separation, which might have occurred during the dual-curing process; the silica domains, generated by the sol-gel process, are embedded in the polymeric matrix on nanometric scale 5-10 nm, and it seems there is not any difference on using either a methacrylic or a glycidyl alkoxysilane precursor.

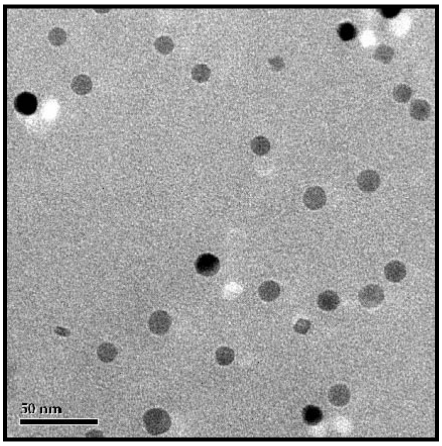


Figure 3: TEM in the presence of MEMO

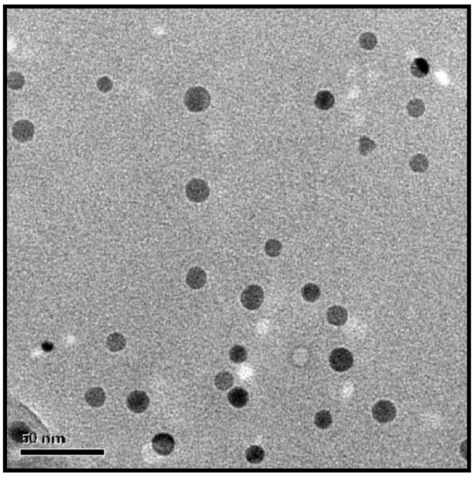


Figure 4: TEM in the presence of GPTS

Conclusions

Organic-inorganic hybrid coatings were prepared starting from a synthesized hybrid methacrylic-epoxy oligomer (EM2Si) and using low molecular weight organoalkoxysilane as inorganic precursor. The hybrid coatings were formed by a combination of sol-gel processing and organic polymerization reactions.

All the formulations investigated gave rise to transparent photocured films characterized by a high gel content values.

TGA analyses showed a slight increase on thermal stability for hybrid cured films by increasing the GPTS or MEMO content in the photocurable formulations; very similar behavior was observed for the two different inorganic precursors.

TEM analysis showed the formation of inorganic domains in the nanometer range size in the range between 10-30 nm, both in the presence of MEMO or GPTS as silica precursor.

References

1. Hajji P., David L., Gerard J.F., Pascault J.P., Vigier G., J. Polym. Sc. Polym. Phys., (1999), 37, 3172.
2. Liu L. M., Qi Z., Zhu X.G., J. Appl. Polym. Sc., 1999, 71, 1133.
3. Cho J.D., Ju H.T., Hong J.W., J. Polym. Sc. Polym. Chem., (2005), 43, 658.
4. Bondioli F., Cannillo V., Fabbri E., Messori M., J. Appl. Plym. Sc., (2005), 97, 2382.
5. Ajayan P.M., Schadler L.S., Braun P.V., "Nanocomposite Science and Technology", (2004)Wiley New York.
6. Bandyopadhyay A., Bowmick A.R., De Sarkar M., J. Appl. Polym. Sc., (2004), 93, 2579.
7. Malucelli G., Priola A., Sangermano M., Amerio E., Zini E., Fabbri E., Polymer, (2005), *46*, 2872.
8. Amerio E., Sangermano M., Malucelli G., Priola A.. Voit B., Polymer, (2005), *46*, 11241.
9. Amerio E., Sangermano M., Malucelli G., Priola A., Rizza G., Macrom. Mat. and Eng., (2006), 291, 1287.
10. Fouassier J.P., Rabek J.C., in "*Radiation Curing in Polymer Science and Technology*", Elsevier, London, 1993 Vol. I.
11. Zhang X., Wu Y., He S., Yang D., Surf. Coat. Tech., (2007), 201, 6051.
12. Ochi M., Takahashi R., Terauchi A., Polymer, (2001), 42, 5151.
13. Acosta Ortiz R., Sangermano M., Bongiovanni R., Garcia Valdez A.E., Berlanga Duarte L., Ivon Patricia Saucedo L., Priola A., Prog. Org. Coat., (2006), 57, 159.
14. Dean K., Cook W.D., Macromolecules, 2002, 35, 7942.
15. Decker C., Decker D., J. Macromol Sci: Pure & Appl Chem. (1997), A34 (4) 605-625.
16. Osama M., U.S. Pat. Appl. Publ. (2004), US 2004225074.
17. Hideyuki I., Atsushi K., N. Tadatomi, J.Polym Sci: Polym Chem, 1996, 34 217.
18. Sangermano M., Malucelli G., Priola A., Manea M., Progress in Organic Coatings (2006), 55(3), 225.