Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 4689–4693

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

A comparative study of different curing techniques for SiO_2–TiO_2 hybrid coatings on polycarbonate

L. Sowntharya[1], R. Subasri*

International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Balapur, Hyderabad 500005, Andhra Pradesh, India

Received 30 October 2012; accepted 18 November 2012
Available online 23 November 2012

Abstract

Hybrid nanocomposite coatings derived from titanium tetraisopropoxide and an acrylic modified silane (methacryloxypropyltrimethoxysilane) by sol–gel method was deposited on polycarbonate (PC) by dip coating employing various withdrawal speeds followed by different curing methods. The coatings were cured by thermal, microwave (MW) and ultraviolet (UV) radiations independently as well as in a combined mode and the mechanical and optical properties of the coatings were compared. The pencil scratch hardness of the coatings cured using only UV or MW is lower than that of the substrate scratch hardness, i.e. 2B. Only thermal or MW followed by UV treatment (MW+UV) yields a higher pencil scratch hardness, which is 3H and 2H respectively. The visible light transmittance of all the coatings increased by 1% when compared to that of the bare PC. XRD analysis on the gels revealed the amorphous nature of the coating material under all curing conditions.

Keywords: A. Sol–gel process; B. Nanocomposite; A. Microwave curing; C. Mechanical properties

1. Introduction

Polycarbonate (PC) which belongs to the class of engineering thermoplastics finds application in many fields. The high impact strength and transparency of PC renders it applicable in optical and automobile industries, replacing glass. The main limitation of using these materials is due to their poor scratch and solvent resistances. Improvement of such properties is a major requirement from industries and a scientific challenge [1]. These properties can be improved by loading suitable additives during polymer processing itself, but this method has its own problems like leaching of the additives, change in mechanical properties and also, not economical. An alternative way for this problem is to give a functional protective coating above the substrates [2].

There are several methods of coating like gas phase, vacuum deposition of coating material either by physical vapor deposition (PVD) or chemical vapor deposition (CVD) [3]. Purely inorganic coating materials are used in the above process, which has a problem of high cost and poor adhesion due to its difference in thermal expansion coefficient between the substrate and the coating material. Preparation of organic–inorganic hybrid coating by the sol–gel method is an alternative to gas-phase or vacuum deposition techniques [4,5]. The sol–gel method is economical and can be processed at low temperature. In this process the inorganic backbone is formed by hydrolysis and condensation of the silane precursors and the organic moieties are incorporated into it and help in a network formation when the functional groups are polymerized during curing process.

Plastic substrates are thermo-sensitive and hence, the curing of coatings has to be done at temperature lower than their glass transition temperatures. Conventionally these coatings are cured thermally, which have longer cycle times and high-energy requirements. Thermal curing

*Corresponding author. Tel.: +91 402 444 3567;
fax: +91 402 444 2699.
E-mail address: subasri@arci.res.in (R. Subasri).
[1]Present address: Materials Science Program, Indian Institute of Technology, Kanpur 208016, Uttar Pradesh, India.

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.11.045

occurs by conduction of heat which results in thermal gradient leading to uneven curing. In fact, a fast curing step is a major requirement from a technology development point of view. In view of this, ultraviolet (UV) and microwave curing, which offer several advantages over conventional thermal curing, have drawn attention. UV initiated polymerization is versatile and very fast when compared to thermal curing [6]. The applications of microwave energy have been used extensively in several fields [7]. Rapid volumetric heating in case of microwave curing reduces the cycle time and saves energy. Here, the curing takes place by re-orientation of its dipole moment and hence the heating will be uniformly distributed throughout the material [8]. As the electric field component of the microwave interacts with the molecules of the substrate, there will be a change in the substrate dipole moment. This change will re-orient the position of the molecules in response to the electric field. Microwaves are used in processing of polymer composites [9,10], curing of adhesives based on epoxy, drying of solid materials and also for sintering of ceramics. In order to heat the material using microwaves, microwaves have to be absorbed. Not all materials absorb microwave efficiently and hence, a microwave absorbing additive has to be added to the coating material in order to cure them using microwave. This additive helps in converting the electromagnetic energy to heat loss. The use of carbon black as a microwave absorbing additive in an epoxy adhesive was studied by Soesatyo et al. [8]. Microwave assisted curing was done on inorganic SiO_2 and TiO_2 coatings on PC substrates and its mechanical properties have been studied and reported recently by Dinelli et al. [11].

Although there are quite a few reports on the use of MW for curing of epoxy based composites/coatings [8–10], there are very few for microwave assisted curing of acrylic based resins [12], since acrylic based coatings are more stable toward UV degradation. Hence, in the present investigation, organic–inorganic hybrid nanocomposite coatings were prepared using an acrylic based organically modified silane namely methacryloxypropyltrimethoxysilane (M) along with titanium tetraisopropoxide (T), hereinafter abbreviated as MT. The purpose of using TiO_2 in the multi-metal oxide sol–gel network is that TiO_2 is a good absorber of microwaves [13] and hence, there is no requirement to separately add a microwave absorber in the coatings. In addition, TiO_2 is also a good absorber of UV radiation. Hence, the hybrid nanocomposite coatings can be UV cured also without addition of a photoinitiator. The prepared sol was dip coated on flat PC substrates using different withdrawal speeds and cured by thermal, ultraviolet (UV) and microwave (MW) radiations individually The mechanical and optical properties of the coatings were compared for different curing methods. The dual curing method (microwave followed by UV curing) was also carried out and the results were compared with the curing methods carried out independently.

2. Experimental details

2.1. Chemicals

The organically modified silane precursor methacryloxypropyltrimethoxysilane (MPTMS) with 97% purity was purchased from Gelest Inc., USA, 97% pure titanium (IV) tetraisopropoxide and methacrylic acid (MAA) with 99% purity were obtained from ABCR, GmbH, Germany. Isopropyl alcohol (IPA) with 99.7% purity and hydrochloric acid (HCl) were purchased from Qualigens fine chemicals, Mumbai, India. MilliQ water was used for sol synthesis. All materials were used as-received, without further purification.

2.2. Sol synthesis

In the first step, partial hydrolysis and condensation of the silane precursor (MPTMS) was carried out by adding water and in the presence of an acid catalyst (0.1 N HCl) and the mixture was kept for stirring. Due to the much higher reactivity of titanium (IV) isopropoxide, this component was complexed with methacrylic acid, which was slowly added to the prehydrolysed MPTMS under efficient stirring. The molar ratio of Si:Ti was 3.5:1. The sol was then kept for stirring for 24 h. The sol was appropriately diluted using IPA prior to coating.

2.3. Coating and curing

The PC substrates were rinsed with distilled water and ultrasonicated in an IPA bath and dried. The sol so synthesized was deposited on the cleaned PC substrates of dimensions 5×10 cm^2 (3 mm thick) by dip coating using different withdrawal speeds, 1 mm/s, 3 mm/s, and 6 mm/s. Four sets of such coatings were made and each set was cured by a different method. The first set of coating was conventionally cured by thermal treatment at 130 °C for 1 h and the total cycle time for conventional curing was 4 h. The second and third sets of coatings were either only MW cured or only UV cured respectively. The fourth set of coatings was exposed to microwave on one side followed by UV curing on both sides (MW+UV). UV curing was carried out using a three-medium-pressure-mercury lamp (120 W/cm with total wattage/lamp=12 kW) conveyorized UV curing unit. The belt speed was maintained at 2 m/min during curing. The total time taken for UV curing cycle was 4 min. The light dose as measured by UV radiometer (EIT Inc., USA) was 871 mJ/cm^2 in the UV-C region. Microwave curing was done using a 1 kW domestic Panasonic microwave oven using the maximum power setting for 2 min. Since TiO_2 itself is a good absorber of UV and MW, no external additive was used for enabling UV or MW absorption during the curing.

2.4. Characterization

The viscosities of the sols were determined prior to coating using viscometer (Anton Paar Rheolab QC, Germany, GmbH). The thickness of the coatings was measured using a thickness monitor Filmetrics Inc. F20, USA, which works on the reflectometry principle. This instrument measures the thin-film characteristics by reflecting and transmitting light through the sample and then analyzing this light over a range of wavelength.

The scratch resistance of the coatings was determined by Wolff wilborn pencil tester GEF 720N from Sheen instruments Ltd., as per ISO 15184; the scratched films were then analyzed using optical microscope (Microstructure Olympus Bx51M). The optical transmission of the coating was measured in the visible wavelength range using UV–vis–NIR spectrophotometer (model: Varian Cary 5000i). The crystalline/amorphous nature of the gels derived from sols subjected to the different curing conditions was analyzed using Bruker D8 AXS Advance X-Ray diffaractometer.

3. Microwave theory

Microwaves are electromagnetic waves with a frequency from 300 MHz to 300 GHz. When this electromagnetic field interacts with the molecules, the microwave energy interacts with the material. Most polymer composite materials are non-magnetic and consist of dielectrics and sometimes are conductors. For a conductor, the interaction between microwaves and the materials is determined by the electrical conductivity. For a dielectric, the interaction between the microwaves and the dielectric is dictated by the complex permittivity of the material, ε^* (Eq. (1)) which is also known as the complex dielectric constant:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (1)$$

where ε' is the dielectric constant; ε'' is the dielectric loss of the material; and j is the imaginary part of a complex number.

When an alternating electric field is applied to the material with dipole moments, they try to cancel the field by following the changing direction of the field. The reorientation and the distortion of the dipoles produce frictional heat and hence dissipation of supplied electromagnetic energy takes place. This type of loss of energy is called dielectric loss. Microwave heating of materials is governed by the principle that the dielectric power absorption of the material being processed is proportional to its dielectric loss factor, which determines the rate of conversion of electrical energy into thermal energy in the material. This can be described by Eq. (2) [14]:

$$P = Kf\varepsilon_r E^2 \tan\delta \quad (2)$$

where, K is a constant, f is the frequency, ε_r is the specific inductive capacitance of the dielectric material; $\tan\delta$ is the loss tangent, defined by the ratio of ε'' (dielectric loss) over ε' (dielectric constant) and E is the electric field strength.

4. Results and discussion

4.1. Viscosity and coating thickness

The viscosity of the sol was measured to be in the range of 7–8 m Pa s. The thickness of the coatings was measured and the values are given in Table 1. The thickness of the thermally cured samples was found to increase with increase in withdrawal speed of the coating. The samples exposed to only microwave and UV radiations were seen to have not cured completely and hence the thickness could not be measured, since the measurement technique was through a contact probe. For the samples that were cured by microwave radiation followed by UV curing, the coatings were found to be there was a difference in thickness on both sides, due to the difference in shrinkage during the curing step. The side exposed to both microwave and UV radiations has lower thickness when compared to the side exposed to only UV radiation.

Table 1
Thickness and pencil scratch hardness of MT coatings cured by different methods.

Curing method	Withdrawal speed [mm/s]	Average thickness [μm]	Pencil scratch hardness
Thermal curing	1	2.3 ± 0.2	H
	3	4.6 ± 0.1	2H
	6	7.2 ± 0.07	3H
Only MW	1	-NA-	Lower than the substrate pencil scratch hardness (< 2B)
	3		
	6		
Only UV	1		
	3		
	6		
MW + UV	1	2 ± 0.1	H
	3	3.4 ± 0.3	H
	6	5.8 ± 0.3	2H

4.2. Pencil scratch hardness and visible light transmittance

The results of pencil scratch hardness are given in Table 1. The pencil scratch hardness values depends on the curing method followed, this is evident from the results. The pencil scratch hardness increases with increase in thickness of the coating. The thermally cured samples showed the maximum pencil scratch hardness 3H for 6 mm/s withdrawal speed and the optical micrograph of the scratch on the surface is shown in Fig. 1a. The samples cured by only microwave or UV results in poor pencil scratch hardness, which is even lower than the substrate scratch hardness 2B. These coatings peel out as a wax from the substrate during the pencil scratch hardness testing. Hence, it was seen that only the UV or microwave curing alone cannot improve the mechanical properties of the coatings because of incomplete curing. So, the dual step curing was followed i.e., microwave curing followed by UV curing (MW+UV). Pencil scratch hardness of these coatings were found to have improved to 2H as shown in Fig. 1b when compared to only microwave or UV curing. For very thin coatings, i.e. for ~2 mm thick coatings, the pencil scratch hardness are same. As the coatings become thicker, due to employing of higher withdrawal speeds, the scratch hardness also increase, since it is known that pencil scratch hardness increases with thickness. It can always be seen that the thermally cured coatings are thicker that MW+UV cured coatings, which may be due to large shrinkage occurring in the coatings when MW+UV curing is carried out, due to which the pencil scratch hardness is one order lower than the thermally cured coatings. Nevertheless, it is still possible to achieve a coating with substantial increase in the scratch hardness when compared to the bare substrate by employing the MW+UV curing technique, which is faster than the conventionally cured coatings. Hence, it can be concluded that the MW+UV curing is a time saving process when compared to the conventional thermal curing technique.

The transmittance spectra of the coatings cured by thermal and MW+UV in the visible wavelength are shown in Fig. 2. The average transmittance of the uncoated PC in

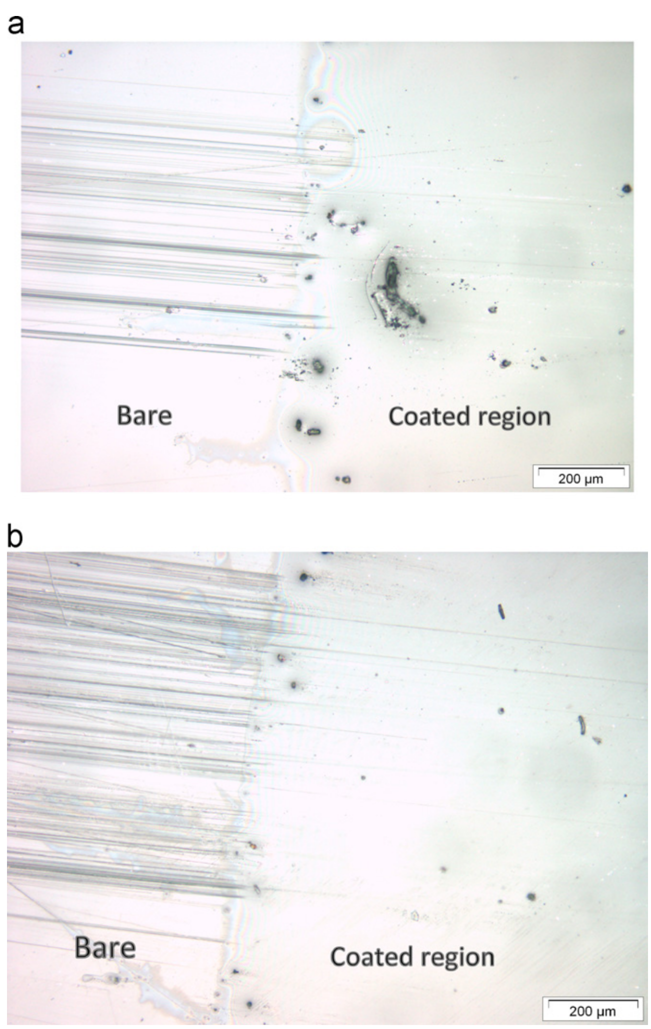

Fig. 1. Optical micrograph of surfaces after pencil scratch test on coatings withdrawn at 6 mm/s speed; scratch direction is from left to right (a) 3H pencil does not cause damage on MT coating cured thermally and (b) 2H pencil does not cause damage on MT coating cured by MW+UV.

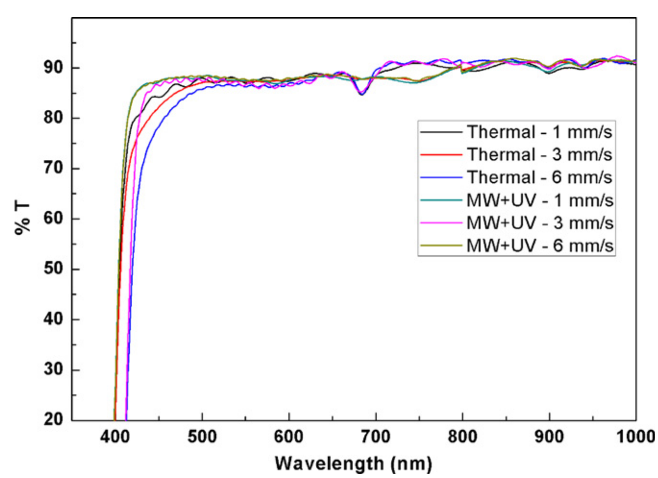

Fig. 2. Visible light transmittance spectra of the MT coatings cured thermally and MW+UV.

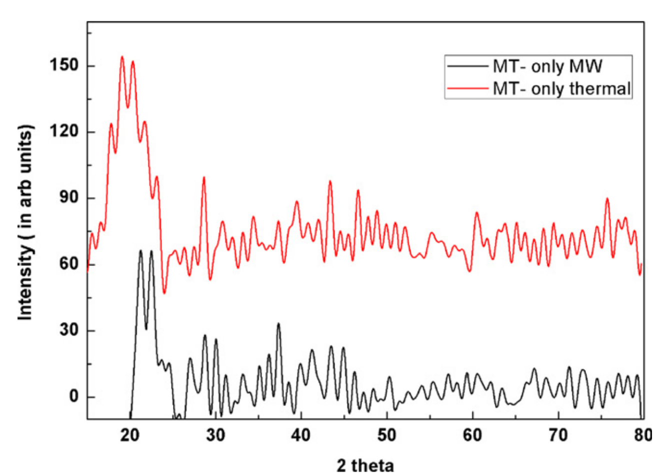

Fig. 3. XRD patterns of the gels obtained from MT cured by only thermal and only the MW method.

the visible region is 87%. The PC with all coatings show nearly 1% improvement in transmittance when compared to that of the bare substrate.

4.3. XRD analysis

The XRD analysis was carried out on the gels obtained from the MT sol which was cured by only thermal treatment at 130 °C for 1 h and only MW radiation. The XRD analysis as shown in Fig. 3 reveals that in both the cases, the coatings are amorphous inspite of the difference in the curing method.

5. Conclusion

Acrylic based organic–inorganic hybrid coating material based on SiO_2–TiO_2 matrix was synthesized by sol–gel route. The effect of different curing methods on the thickness, pencil scratch hardness and visible light transmittance was studied. The pencil scratch hardness of the conventional cured coating was found to be maximum, i.e. 3H for coatings generated using 6 mm/s withdrawal speed and it was found to be maximum when compared to only UV or only MW cured coatings. The coatings cured by only MW and only UV are found not to have dried completely and exhibit poor scratch resistance lower than that of the substrate. Microwave followed by UV curing showed marked improvement in pencil scratch hardness when compared to that of only MW and only UV curing. MW+UV curing takes only 6 min for the completion of the curing process when compared to 4 h cycle time for the conventional thermal curing. The visible light transmittance of the MW+UV curing is same as that of thermal curing and there is a one percent increase when compared to the bare substrate. The XRD pattern of the gels cured by thermal and MW+UV are amorphous in nature. Fine tuning in the dual curing process (MW+UV) to obtain uniform thickness on both sides with further enhancement in mechanical properties will provide a substantial time saving for curing of the coatings and from a technology point of view, will prove to be a very good alternative to thermal curing.

Acknowledgment

The authors gratefully acknowledge Dr. G. Sundararajan, Director and Dr. G. Padmanabham, Associate Director, ARCI, Hyderbad, India for providing constant support throughout the course of this investigation.

References

[1] P. Fabbri, C. Leonelli, M. Messori, F. Pilati, M. Toselli, P. Veronesi, S. Morlat-Thérias, A. Rivaton, J.L. Gardette, Improvement of surface properties of polycarbonate by organic–Inorganic hybrid coating, Journal of Applied Polymer Science 108 (2008) 1426–1436.

[2] N. Nakayama, T. Hayashi, Synthesis of novel UV-curable difunctional thiourethane methacrylate and studies on organic–inorganic nanocomposite hard coatings for high refractive index plastic lenses, Progress in Organic Coatings 62 (2008) 274–284.

[3] S.V. Fortuna, Y.P. Sharkeev, A.J. Perry, J.N. Matossian, I.A. Shulepov, Microstructural features of wear-resistant titanium nitride coatings deposited by different methods, Thin Solid Films 377 (2000) 512–517.

[4] L.Y.L. Wu, G.H. Tan, X.T. Zeng, T.H. Li, Z. Chen, Synthesis and characterization of transparent hydrophobic sol–gel hard coatings, Journal of Sol–Gel Science and Technology 38 (2006) 85–89.

[5] S. Sepeur, N. Kunze, B. Werner, H. Schmidt, UV curable hard coatings on plastics, Thin Solid Films 351 (1999) 216–219.

[6] C.F. Tsang, Investigation into the curing and thermal behaviour of an epoxy-based UV curable coating in microelectronics assembly, Microelectronics International 17 (2000) 27–41.

[7] J.M.R. Belanger, J.R. Jocelyn Pare, O. Poon, C. Fairbridge, S. Ng, S. Mutyala, R. Hawkins, Remarks on various applications of microwave energy, Journal of Microwave Power and Electromagnetic Energy 42 (2008) 2.

[8] B. Soesatyo, A. Blicblau, E. Siores, Effect of rapid curing doped epoxy adhesive between two polycarbonate substrates on the bond tensile strength, Journal of Materials Processing Technology 89–90 (1999) 451–456.

[9] R. Yusoff, M.K. Aroua, A. Nesbitt, R.J. Day, Curing of polymeric composites using microwave resin transfer moulding (RTM), Journal of Engineering Science and Technology 2 (2007) 151–163.

[10] N. Uyanik, M. Karadayi, C. Erbil, Studies on thermal and morphological characteristics of siloxane containing epoxy resins cured by microwave radiation, Surface Coatings International Part B: Coatings Transactions 87 (2004) 91–96.

[11] M. Dinelli, E. Fabbri, F. Bondioli, TiO_2–SiO_2 hard coating on polycarbonate substrate by microwave assisted sol–gel technique, Journal of Sol—Gel Science and Technology 58 (2011) 463–469.

[12] C.P. Lai, M.-H. Tsai, M. Chen, H.-S. Chang, H.-H. Tay, Morphology and properties of denture acrylic resins cured by microwave energy and conventional water bath, Dental Materials : Official Publication of the Academy of Dental Materials 20 (2004) 133–141.

[13] D. Di Claudio, A.R. Phani, S. Santucci, Enhanced optical properties of sol–gel derived TiO_2 films using microwave irradiation, Optical Materials 30 (2007) 279–284.

[14] M. Chen, E.J. Siochi, T.C. Ward, J.E. McGrath, Basic ideas of microwave processing of polymers, Polymer Engineering and Science 33 (1993) 1092–1109.