Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 4245–4252

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of addition of surface modified nanosilica into silica–zirconia hybrid sol–gel matrix

L. Sowntharya[1], Ravi C. Gundakaram, K.R.C. Soma Raju, R. Subasri*

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

Received 21 July 2012; received in revised form 12 October 2012; accepted 15 October 2012
Available online 10 November 2012

Abstract

An organic–inorganic hybrid sol (MZ) comprising a methacrylate functionalized silane matrix (M) and zirconium-n-propoxide (Z) was prepared using sol–gel technique. Two methodologies were adopted to modify the hybrid sol for generating nanocomposite coatings viz., (a) addition of acrylic surface modified silica nanoparticles (N) of diameter ~20 nm to the sol to enhance their compatibility with the hybrid sol–gel matrix and (b) in-situ formation of a three dimensional silica network by addition of tetraethoxy silane (T) to the sol MZ. In the first methodology, the sols were prepared with six different weight ratios of the nanoparticles to the sol, i.e. 0, 0.01, 0.05, 0.1, 0.25 and 1 which were labelled as MZ+Nx where $x=0$, 1, 2, 3, 4 and 5 respectively. The prepared sols were dip coated on 100 mm × 100 mm polycarbonate substrates followed by thermal curing at 130 °C. The coatings were characterized for their mechanical properties like pencil scratch hardness, scratch resistance using scratch tester, nanoindentation hardness, and abrasion resistance as well as visible light transmittance. FT-IR studies were also carried out on heat-treated gels derived from the sols. A maximum pencil scratch hardness of 3H was obtained for the MZ+T coatings and these coatings withstood a critical load of 4.3 ± 0.7 N before failure during scratch test. The maximum nanoindentation hardness of 3.8 ± 0.01 GPa was obtained for the MZ+N5 coatings. The abrasion resistance of MZ+T coatings was higher when compared to MZ+N0 and MZ+N5 coatings. The scratch and nanoindentation hardness were seen to be better for an in-situ formed –Si–O–Si– network in the hybrid sol when compared to those obtained from coatings generated by external addition of acrylic surface modified silica nanoparticles. The difference in properties was attributed to the level of interaction between the nanoparticles and hybrid sol–gel matrix.

Keywords: A. Sol–gel process; B. Nanocomposites; C. Mechanical properties; E. Functional application

1. Introduction

Transparent polymers such as polycarbonate (PC), polymethyl methacrylate (PMMA), and polyethylene terephthalate (PET), which have excellent toughness and processability, have been widely used for optical lenses, goggles, windows, head lamp covers of automobiles, display panels and so on. However, the quality of these polymeric materials can easily be deteriorated by surface scratches, greatly limiting their applications [1]. The surface of plastics can be protected by depositing a hard coating using different techniques like gas phase, vacuum deposition and sol–gel method [2,3]. Among these methods, the organic–inorganic hybrid coating materials prepared by sol–gel route have drawn considerable attention because of their unique low temperature processing characteristics, which make them useful for coating on temperature sensitive plastic substrates. These hybrid coating materials are developed to achieve specific properties that organic or inorganic materials cannot provide independently [4].

Recently, studies on incorporation of nano-structured inorganic particles into a hybrid matrix to improve the modulus, scratch and abrasion resistance of the coating material have been reported [5,6]. The nanoparticles can be

---

*Corresponding author. Tel.: +91 40 24443567; fax: +91 40 24442699.
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 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.276

incorporated using two methods, i.e. either in-situ building up within the hybrid matrix by addition of fully hydrolysable silane precursors like tetraethoxysilane (TEOS) [7,8]/tetramethoxysilane (TMOS) or by external addition and homogeneous dispersion of nanoparticles into the hybrid matrix [9]. The properties of the resulting nanocomposites can be tailored by controlling the degree of interaction between the hybrid matrix phase and the nanoparticles. It is expected that when strong interfacial adhesion between two phases is formed, the hybrid materials exhibit a stable, homogeneous microstructure without macro-phase separation that in turn helps in achieving improved material properties.

The successful application of nanoparticles depends upon both the synthesis methodology and the nature of surface of these nanoparticles. The major problem in dispersing the nanoparticles into an organic–inorganic hybrid matrix is the aggregation which results in poor mechanical properties of the coatings. Also, increase in concentration of the nanoparticle rapidly increases the sol viscosity, which affects the critical thickness of the coating [10]. In order to overcome these problems, the surface of the nanoparticles has to be modified so as to improve their interaction with the matrix. In some of the previous investigations, the effect of addition of different concentrations of colloidal silica nanoparticles in the hybrid matrix on mechanical properties of coatings has been reported [2,5,6,9]. However, there is no systematic study reported on the addition of surface (acrylic) modified silica nanoparticles into a silica–zirconia hybrid matrix that has a polymerizable acrylic group and its effect on the mechanical properties of the coatings derived from the nanocomposite sol.

In this investigation, we report on the effect of incorporating acrylic modified nanosilica into an organic–inorganic hybrid sol–gel matrix with emphasis on mechanical properties of the coatings derived from the sols. A hybrid matrix derived from methacryloxypropyltrimethoxysilane (MPTMS) along with zirconium-n-propoxide was chosen. The effect of homogeneous dispersion of surface modified silica nanoparticles on the mechanical properties of coatings has also been compared with coatings where an in-situ generated silica network obtained by addition of TEOS co-precursor to the hybrid matrix. The generated coatings were characterized for thickness, pencil scratch hardness, scratch test, nanoindentation hardness, abrasion resistance, visible light transmittance and properties were compared. The interaction of the nanoparticle with hybrid matrix was seen to affect the mechanical properties of coatings.

2. Experimental details

2.1. Materials

The organically modified silane methacryloxypropyltrimethoxysilane (MPTMS) and the metal alkoxide Zr-n-propoxide (both of 97% purity) were purchased from Gelest Inc., USA, and 98% pure tetraethoxy orthosilicate (TEOS) was purchased from Kemphasol, Mumbai, India. Methacrylic acid (MAA) with 99% purity was obtained from ABCR, GmbH, Germany. Nanocryl® C150, an acrylic modified silica nanoparticle dispersion having a mean particle diameter ~20 nm, was obtained from Nanoresins AG, 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

MPTMS in conjunction with zirconium-n-propoxide (MZ) sol was synthesized using the following procedure. The sol preparation involved two parts; in the first part, the organically modified silane (MPTMS) was hydrolysed and allowed for partial condensation by the addition of water in the presence of an acid catalyst 0.1 N HCl and kept for stirring. Zr-n-propoxide was highly reactive and hence, was complexed with MAA, which formed the second part. After 30 min, the second part was added dropwise into the first part. The molar ratio of Si to Zr was maintained as 1:0.3. The sol was diluted by 40% by weight using IPA. The prepared MZ sol was used as the stock sol. By using the first methodology, six sols were prepared by dispersing Nanocryl® C150 into the stock sol in different weight ratios as 0, 0.01, 0.05, 0.1, 0.25, 1 and the sols were labelled as MZ+N0, MZ+N1, MZ+N2, MZ+N3, MZ+N4 and MZ+N5 respectively.

Only one sol was prepared by adopting second methodology, where the inorganic silane precursor TEOS was added to MPTMS in the ratio 0.18:1 during the hydrolysis of MPTMS that takes place in the first part. Rest of the procedure was the same as that used for MZ sol, including the dilution step. This sol was labelled as MZ+T. Seven sols were prepared in total during this investigation by adopting two different methodologies.

2.3. Generation of the hard coatings

The PC substrates were cleaned with 0.3% surfactant solution of Alconox® and rinsed with copious amounts of distilled water followed by rinsing with IPA and then dried. The seven sols so synthesized were deposited on the cleaned PC substrate of size 100 mm × 100 mm × 3 mm by the dip coating technique using a single dip at different withdrawal speeds (1 mm/s, 3 mm/s and, 6 mm/s). The coatings were cured conventionally in an oven at 130 °C for 1 h. The coatings were labelled same as that of their respective sols.

2.4. Characterization

Several methods were employed to characterize the mechanical properties of the coatings. The thickness of the coatings was measured using a thickness monitor using Filmetrics Inc. F20, USA, which works on the reflectometry principle. 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 analysed using optical microscope (Microstructure Olympus Bx51M).

Nanoindentation studies were carried out using an MTS (now Agilent) Nanoindenter, model XP. As-coated samples were sliced into coupons of approximately 1 cm × 1 cm and mounted on metal cylinders such that the coated surface faces the indenter, which were then inserted into the sample holder. All studies were carried out in the displacement-control mode. The continuous stiffness measurement (CSM) technique was used to measure the hardness and elastic modulus as a function of depth. The load at the final depth of indentation was held for duration of 30 s. The samples were indented to depths of 500 nm, which was decided based on the coating thickness, since it is generally accepted that when the depth of indentation is 1/10th or less of the coating thickness, the substrate effect can be avoided.

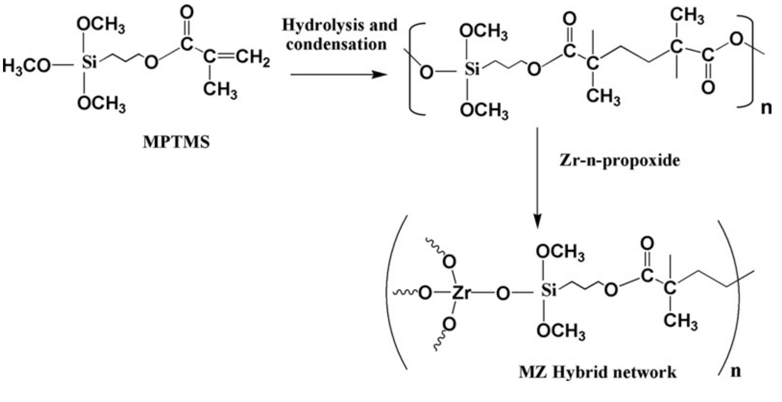
Scratch tests were carried out on a CSM make REVETEST scratch tester by using a Rockwell diamond scratch indenter having tip radius $R=200\ \mu m$ where the load increases progressively from 0.9 to 200 N to a length of 6 mm, while the sample moves at constant velocity of 1.2 mm/min.

The abrasion resistance of the coatings was measured by Taber abrader (Taber industries, 5155) using CS-10F wheel under 2 × 250 g load in accordance with ASTM D1044. The optical transmission of the coating was measured in the visible wavelength range using UV–vis–NIR spectrophotometer (model: Varian Cary 5000i). The Fourier-transformed infrared (FTIR) spectra were recorded on gel powders obtained from the sols heat treated under same conditions as that of the coatings, using Spectrum OPUS (Bruker Optics, Germany) spectrometer in the range 400–4000 cm^{-1}. The heat treated gel powders were mixed with KBr powder in the weight ratio of 1:100. The fine powder was then compacted as a pellet and used for FT-IR studies.

3. Results

3.1. Interaction of surface modified nanoparticles with hybrid matrix

The hydrolysis and condensation reactions of the organically modified silane precursor MPTMS are basic sol–gel sub-processes and interested readers can refer to [11,12]. The formation of the MZ hybrid network by interaction of MPTMS (M) with zirconium-n-propoxide (Z) is shown in Eq. (1). When silica nanoparticles with no surface modification are directly loaded into hybrid matrix comprising MPTMS, it has been reported that there will be phase separation and agglomeration of the particles [13]. This is due to incompatibility of the silica and acrylic groups from MPTMS [13]. Hence, in order to enhance the compatibility between the nanoparticles and the matrix, it is appropriate to introduce a surface modification in the nanoparticles. Usually, surface modification is carried out using the same organic group that is present as the polymerizable group in the organic–inorganic matrix, so that there is compatibility between the organic groups from the nanoparticle and the hybrid sol–gel matrix. Nanocryl® C150 is such a surface modified silica particle available commercially, where the surface modification is effected by acrylic groups. Nanocryl® C150 is a trimethylol propane triacrylate suspension containing 50 wt% silica nanoparticles. The surface of the silica particle is modified with acrylic functional group to make it compatible with the organic phase obtained from MPTMS. When the acrylic surface modified silica nanoparticles are added to the hybrid sol, there will be an interaction between the acrylic groups in the sol with that of the same acrylic functional groups on the nanosilica surface. The representation of the surface modification of silica particles and their interaction with the hybrid network is shown in Eq. (2)



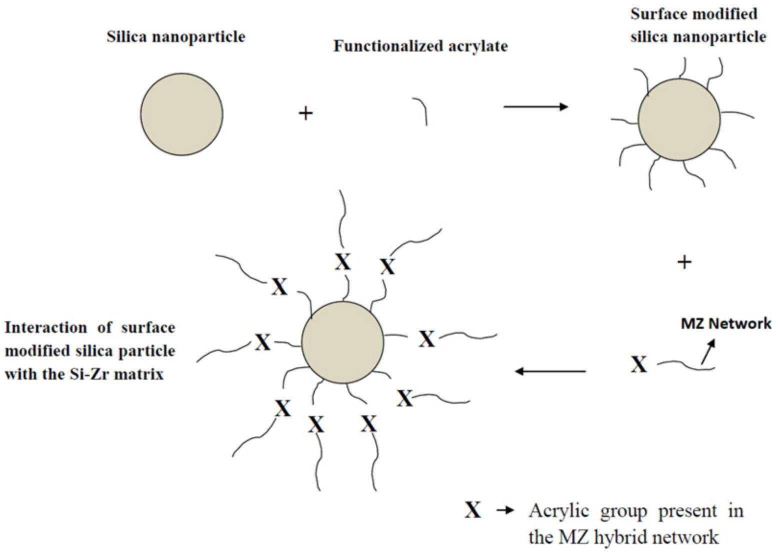


Table 1
Comparison of coating thickness obtained at various withdrawal speeds.

Sample code	Withdrawal speed [mm/s]	Average thickness [μm]
MZ+N0	1	2.0
	3	4.0
	6	7.0
MZ+N1	1	2.3
	3	4.4
	6	6.4
MZ+N2	1	2.8
	3	6.3
	6	–
MZ+N3	1	2.5
	3	5.8
	6	–
MZ+N4	1	2.4
	3	5.2
	6	9.5
MZ+N5	1	6.3
	3	Coatings got cracked after curing
	6	
MZ+T	3	13

Table 2
Pencil scratch hardness of the coatings.

Sample code	Average thickness [μm]	Pencil scratch hardness
MZ+N0	7	3H
MZ+N1	6.4	3H
MZ+N2	6.3	2H
MZ+N3	5.8	2H
MZ+N4	5.2	H
MZ+N5	6.3	2H
MZ+T	13	3H

3.2. Coating thickness

Thickness of the coatings was found to increase slightly with the increase in the weight per cent of Nanocryl® C150 when compared to coatings generated without Nanocryl® C150 for the same withdrawal speed. However, all the mechanical property testing was carried out on the coatings of same thickness obtained from different sols. For MZ+N5 sol, the coatings were found to crack beyond 6.5 μm thickness. The coating thickness from MZ+T sol was higher and found to be 13 μm. The thickness values obtained for the coatings generated using different withdrawal speeds are given in Table 1.

3.3. Analysis of mechanical properties of the coatings

The mechanical properties of the coatings were evaluated by pencil scratch hardness, scratch test, nanoindentation hardness and abrasion resistance measurements.

3.3.1. Pencil scratch hardness

The results of the pencil scratch hardness measurements are shown in Table 2. The value decreases with the increase in nanocryl weight ratio. This may be explained in terms of the interaction of the nanoparticles with the organic–inorganic hybrid matrix. Even though, the nanoparticles used are surface modified, if the nanoparticles are not homogeneously distributed and dispersed in the hybrid matrix, this may lead to phase separation resulting in poor scratch resistance [9]. The scratch hardness is lower for MZ+N4 when compared to other coatings. For MZ+T coatings, the silica network is generated in-situ by hydrolysis and co-condensation of TEOS [11,12] with MPTMS during the hydrolysis and condensation of MPTMS. This enhances the interaction between organic and inorganic domain and these coatings exhibit same scratch resistance as that of the MZ+N0, i.e. pure MZ coatings.

3.3.2. Scratch test

The coatings were subjected to a scratch test with a progressively increasing load from 0.9 to 200 N. The first and second critical load values (LC1 and LC2) that correspond to failure and detachment of the coatings respectively are plotted in Fig. 1 for different samples. The experiment was carried out at three places and the average values of LC1 and LC2 were calculated and depicted in the plot.

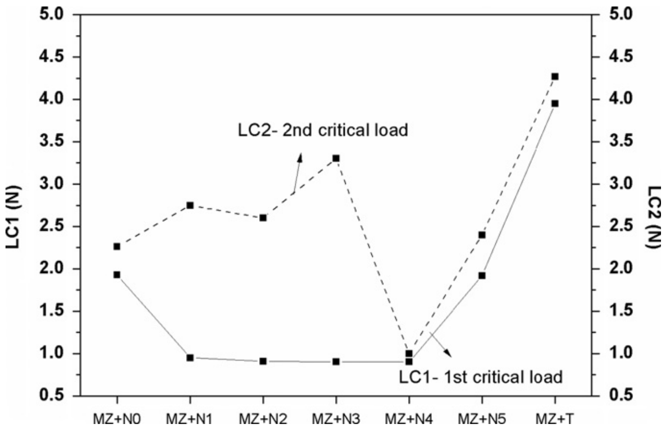


Fig. 1. First and second critical load on the coatings during scratch testing.

Scratch resistance is evaluated on the basis of critical load, crack formation and recovery [10]. The coatings with excellent scratch resistance will evidence high critical load, low cracking tendency and high recovery. The coatings with in-situ generated silica network (MZ+T) showed enhanced scratch resistance when compared to other coatings where nanoparticles were added externally. Also, the critical load values of MZ+T are two times than that of MZ+N0 coatings. For the Nanocryl® C150 added coatings, the first critical load is very less and same for all the ratios except MZ+N5, whereas the LC2 is comparatively higher which proves the good adhesion strength of these coatings. The SEM images captured after the scratch test for MZ+N0, MZ+N5 and MZ+T coatings are shown in Fig. 2, where the load increases progressively from right to left.

3.3.3. Nanoindentation hardness

The nanoindentation hardness test was carried out for all the samples, since it is an intrinsic property and gives an indication of the hardness despite the coating thickness. The samples were indented to a depth of 500 nm at 10 places.

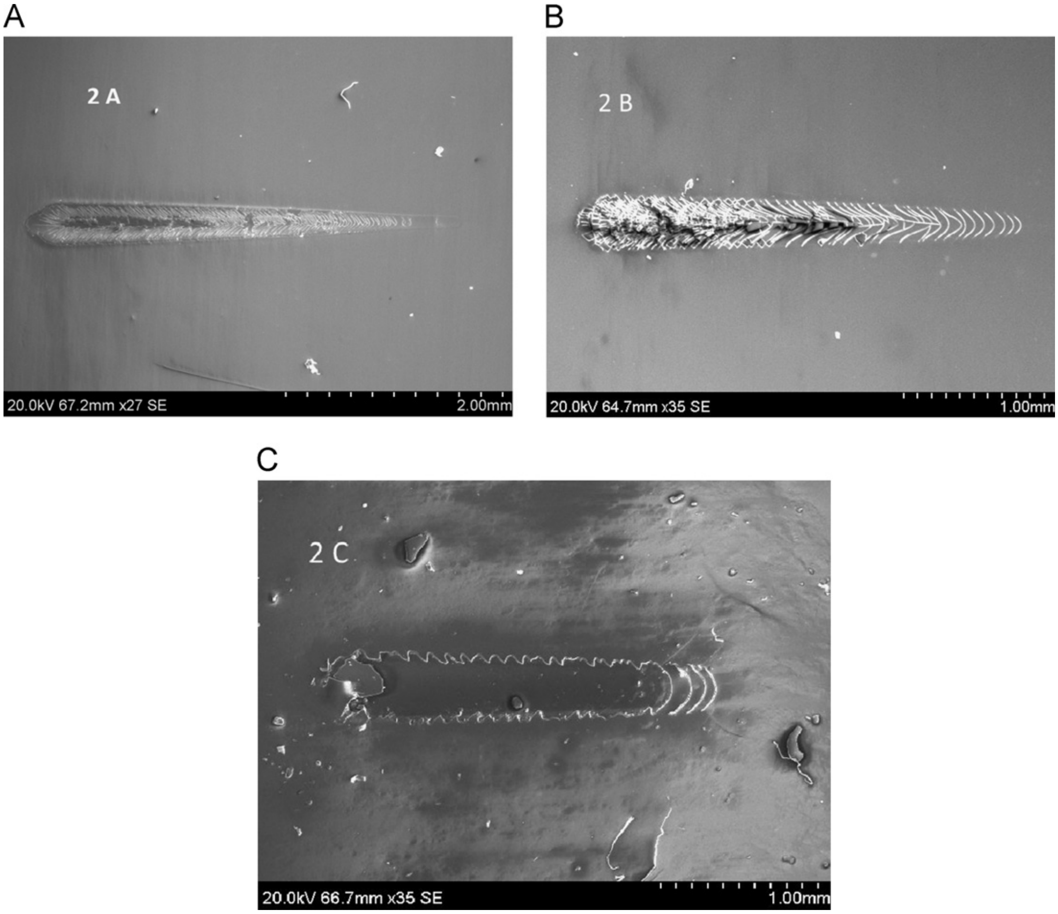


Fig. 2. SEM images of the scratch on (A) MZ+N0; (B) MZ+N5; and (C) MZ+T coatings.

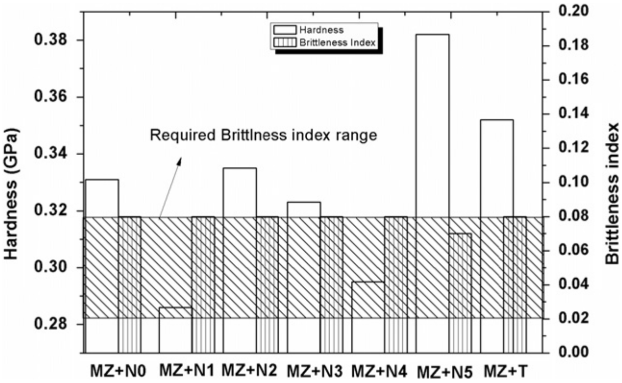


Fig. 3. Comparison of nanoindentation hardness and brittleness index at a depth of 500 nm.

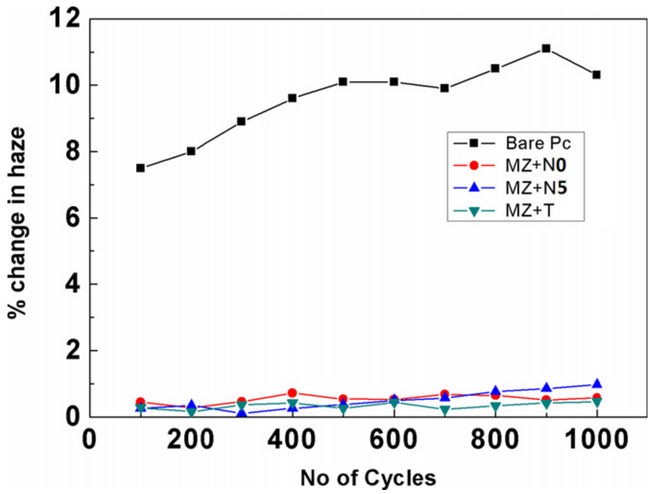


Fig. 4. Comparison of abrasion resistance of a bare PC with that of MZ+N0, MZ+N5 and MZ+T coatings.

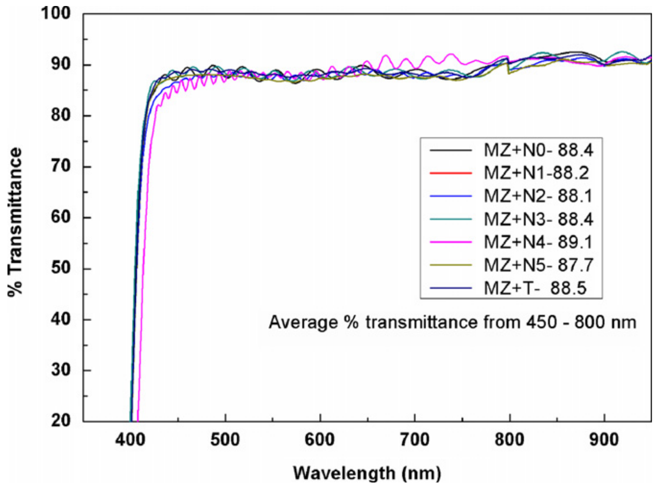


Fig. 5. Visible light transmittance spectra of all the coatings with average transmittance values included for the coatings over the wavelength range 450–800 nm.

The average hardness and brittleness index values were determined and compared in Fig. 3. The abrasion resistance of the coatings depends on the hardness and brittleness index of the coating material. Brittleness index is the ratio of hardness to Young's modulus [14]. For the coating to have better abrasion resistance, the nanoindentation hardness has to increase while keeping a low value of brittleness index. The brittleness index and Vickers hardness of polycarbonate are reported as 0.06 and 0.15 GPa in the literature [14]. Any coating with hardness more than 0.15 GPa and brittleness index within the range 0.06–0.08 will have good mechanical properties and can be judged as useful for hard coating applications on PC. This property can be further enhanced by addition of nanoparticles like silica or zirconia.

In the present investigation, the brittleness index calculated for all the coatings falls within the required limit. Maximum hardness and low brittleness index of 0.07 were obtained for MZ+N5 coatings, where the weight ratio of the Nanocryl® C150: hybrid sol is more. After MZ+N5, the MZ+T coatings exhibit higher nanoindentation hardness but the brittleness index is 0.08. The hardness value was found to reduce for the coatings with lower weight ratio of Nanocryl® C150. This may be due to poor/non-homogeneous dispersion of nanoparticles into the sol, though being surface modified.

3.3.4. Abrasion resistance

The abrasion resistance study was carried out only for the samples that exhibited comparatively higher scratch resistance and nanoindentation hardness. Accordingly, the coatings from MZ+N0, MZ+N5 and MZ+T sols were chosen and studied using a Taber type abrader with CS-10F wheels under 2 × 250 g load. The test was carried out for 1000 cycles and the change in haze was measured after every 100 cycles. The percentage change in haze was plotted against the number of cycles for each sample and compared with that of bare PC as shown in Fig. 4. A lower change in haze is an indication of good abrasion resistance. The change in haze after 1000 cycles was found to be lower for MZ+T coatings. Though during the initial stages of testing, i.e. up to 500 cycles, the change in haze values were lower for MZ+N5 coatings. After 1000 cycles, MZ+T coatings show the least change in haze when compared to the other coatings studied. Hence, it may be concluded that MZ+T coatings have slightly better abrasion resistance because of higher critical load during scratch test as well as least change in haze during taber testing. However, it should be mentioned that under the testing conditions employed in the present investigation, all coatings show $<2\%$ haze change, and can be acceptable for automotive glazing applications.

3.4. Visible light transmittance

The transmittance spectra of all the coatings in visible wavelength region are given in Fig. 5. The transmittance of the uncoated PC in this region is 87%. The PC with all coatings shows ~1–2% improvement in transmittance

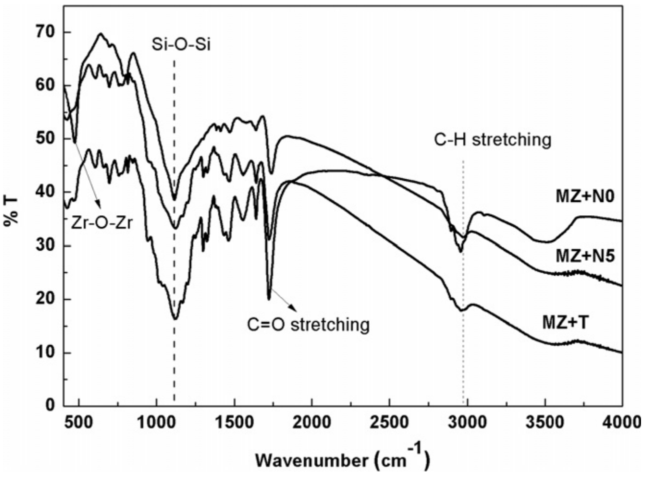


Fig. 6. FT-IR transmission spectra over the spectral range 500-4000 cm^{-1} for MZ+N0, MZ+N5 and MZ+T coatings.

when compared to that of the bare substrate. A higher transmittance of ~89% is obtained for MZ+T and MZ+N4 coatings.

3.5. Analysis of chemical structure by FTIR studies

The FT-IR transmission spectra of the heat-treated gels derived from MZ+N0, MZ+N5 and MZ+T sol over the spectral range 500–4000 cm^{-1} are shown in Fig. 6. The peaks obtained at 3500 cm^{-1} and 2900 cm^{-1} can be assigned to Si-OH absorption and C–H stretching respectively [15]. C=O stretching peaks are observed at 1720 cm^{-1} for all the gels. The C=O stretching is more in case of MZ+N0. A peak at the wave number 1640 cm^{-1} can be assigned to C=C stretching. The reduction in this peak indicates the polymerization of methacrylate group [16]. A broad absorption peak obtained near the wave number 1110 cm^{-1} corresponds to –Si–O–Si bond. The intensity of this peak is more in case of MZ+N0. The wave numbers that correspond to –Si–O–Zr and Zr–O–C stretching are 965 and 1556 cm^{-1}, respectively [17] and these peaks are absent in MZ+N5. Instead of those there is a new sharp peak at 489 cm^{-1} representing –Zr–O–Zr– formation in MZ+N5 that indicates phase separation of zirconia from the hybrid network.

4. Discussion

The mechanical properties of the coatings can be correlated with the interaction of the added nanoparticles with the matrix. This is also a crucial factor in influencing the phase morphology of the hybrid. The addition of nanosilica particles into the hybrid matrix produces a deterioration of scratch resistance properties of the coatings. The presence of nanosilica leads to high stress concentration around the silica particles themselves, which makes the matrix weak. The weak compatibility between the matrix and the nanosilica leads to poor interfacial properties. On the other hand, when the silica inorganic network is generated by adding TEOS (MZ+TEOS) to the hybrid sol, the coatings were able to withstand the scratch up to a maximum first critical load 4.3 N. This is due to the enhanced interaction between the organic and inorganic phase.

The reduction in the abrasion resistance of the coatings for MZ+N5 is due to the formation of silica clusters with increase in the weight ratio of Nanocryl® C150:hybrid sol. When TEOS is added during the condensation of MPTMS, the three dimensional silica networks with superior abrasion resistance and homogeneously developed nano-structured morphology are formed.

The nanoindentation hardness is higher for the MZ+N5 than MZ+T coatings, whereas the scratch resistance and the abrasion resistance are higher for MZ+T. This may be justified as the nanocryl weight ratio is more in case of MZ+N5 and the indentation hardness is a material intrinsic property [18] and also governed by nature and the extent of hybrid interface. An evident improvement in modulus is obtained for MZ+N5 which results in higher indentation hardness. The FTIR studies showed that the Si–O–Si network formation is less for MZ+N5 coatings due to poor interaction of the acrylic modified silica with the organic matrix. Hence, the scratch and abrasion resistances of these coatings during prolonged testing are lower than those derived from MZ+T sol.

5. Conclusion

Acrylic based organic–inorganic hybrid coating material based on SiO_2–ZrO_2 matrix was prepared by the sol–gel route. The effect of addition of silica nanoparticles and in-situ generation of silica network by TEOS addition on mechanical properties of the coatings was studied. The in-situ generation of –Si–O–Si network was found to result in enhanced mechanical properties. The modification of the surface of the silica with functional methacrylate group helps in increased interfacial bonding between the organic and inorganic phases in case of MZ+N5 coatings. These coatings exhibited the maximum nanoindendation hardness of 0.38 GPa when compared to 0.15 GPa of the substrate. The brittleness index is also low, i.e. 0.07 for the same coatings. The scratch and abrasion resistances were found to be the maximum for MZ+T coatings. From FTIR studies, it was evident that the formation of silica network is less in case of MZ+N5. The rate of polymerization is more in case of MZ+N0 and hence, more Si–O–Si networks are formed. The visible light transmittance was found to be two per cent more than that of the bare substrate for MZ+N4 but this coating exhibited poor mechanical properties. MZ+T coatings were seen to exhibit better mechanical properties and high enough transmittance when compared to other coatings studied in the present investigation. MZ+T coatings could be adjudged as a promising sol composition for application as hard coatings on PC.

Acknowledgement

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

References

[1] S.W. Kim, Characterization of UV curable hybrid hard coating materials prepared by sol–gel method, Journal of Chemical and Engineering 28 (2011) 298–303.

[2] 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.

[3] H. Schmidt, Transparent inorganic/organic copolymer by sol–gel process, Journal of Sol–Gel Science and Technology 1 (1994) 217–231.

[4] Y-H Han, A. Taylor, M.D. Mantle, K.M. Knowles, UV curing of organic–inorganic hybrid coating materials, Journal of Sol–Gel Science and Technology 43 (2007) 111–123.

[5] M. Spirkova, A. Strachota, L. Brozova, J. Bruz, M. Urbanova, J. Baldrian, M. Slouf, O. Blahova, P. Duchek, The influence of nanoadditives on surface, permeability and mechanical properties of self-organized organic–inorganic nanocomposite coatings, Journal of Coatings Technology and Research 7 (2010) 219–228.

[6] H. Schmidt, Nanoparticles by chemical synthesis, processing to materials and innovative applications, Applied Organometallic Chemistry 15 (2001) 331–343.

[7] B. Ramezanzadeh, M. Mohseni, A. Karbasi, Preparation of sol–gel-based nanostructured hybrid coatings; Part 1: morphological and mechanical studies, Journal of Materials Science 47 (2012) 440–454.

[8] Y. Ma, M. Kanezashi, T. Tsuru, Synthesis and characterization of hydrophobic silica using methyltriethoxysilane and tetraethorthosilicate as a co-precursor, Journal of Sol–Gel Science and Technology 53 (2010) 93–99.

[9] M. Sangermano, M. Messori, Scratch resistance enhancement of polymer coatings, Macromolecular Materials and Engineering 295 (2010) 603–612.

[10] E. Amerio, P. Fabbri, G. Malucelli, M. Messori, M. Sangermano, R. Taurino, Scratch resistance of nano-silica reinforced acrylic coatings, Progress in Organic Coatings 62 (2008) 129–133.

[11] C.J. Brinker, G.W. Scherer, Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing, Academic Press, 1990, p. 790.

[12] J. Livage, C. Sanchez, Sol–gel chemistry, Journal of Non-Crystalline Solids 145 (1992) 11–19.

[13] D.L. Chandler, A New Approach to Scratch Resistance, MIT News Office, August 17, 2011 (Recent access: October 4, 2012).

[14] L. Hu, X. Zhang, Y Sun, R.J.J. Williams, Hardness and elastic modulus profiles of hybrid coatings, Journal of Sol–Gel Science and Technology 34 (2005) 41–46.

[15] W.L. Walton, R.B. Hughes, Infrared spectra of α, β-unsaturated esters, Journal of the American Chemical Society 79 (1957) 3985–3992.

[16] S.K. Medda., D. Kundu, G. De, Inorganic–organic hybrid coatings on polycarbonate. Spectroscopic studies on the simultaneous polymerizations of methacrylate and silica networks, Journal of Non-Crystalline Solids 318 (2003) 149–156.

[17] R.M. Almeida, A.C. Marques, Characterization of sol–gel materials by infrared spectroscopy, in: S. Sakka (Ed.), Handbook of Sol–Gel Science and Technology, Springer Science+Business Media, Inc, New York, 2005, pp. 65–89.

[18] Linda Y.L. Wu, E. Chwa, Z. Chen, X.T. Zeng, A study towards improving mechanical properties of sol–gel coatings for polycarbonate, Thin Solid Films 516 (2008) 1056–1062.