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Sol-Gel Derived Single Layer Zeolite-MgF_2 Composite Antireflective Coatings with Improved Mechanical Properties on Polycarbonate

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Abstract: Single layer antireflective coatings with good optical and mechanical properties are difficult to be obtained on temperature sensitive substrates like plastics. This challenge has been taken up in the present study. Single layer MgF_2 and for the first time, zeolite 4Å and zeolite 4Å - MgF_2 composite antireflective coatings were generated by a wet chemical route on flat polycarbonate sheets and characterized for their reflectance, surface roughness, thickness, porosity, surface morphology and scratch hardness by haze measurement. Autoclaving and boiling water treatment under microwave irradiation were used in case of MgF_2 sols and zeolite/zeolite-MgF_2 coatings respectively. Pure MgF_2 coatings deposited after autoclaving of the MgF_2 sol yielded a low refractive index of 1.28 and an average reflectance of 1.9% vis-à-vis 9.7% reflectance for an uncoated polycarbonate substrate over the wavelength range of 400-1100 nm. Single layer zeolite coatings after a brief treatment in boiling water under microwave irradiation yielded a reflectance of 5.1%. A composite zeolite-MgF_2 coating exhibited a reflectance of 2.8% and the percentage change in haze after crockmeter testing in case of the composite coating was lower than that of a pure MgF_2 coating. This implied that the composite layer had improved mechanical properties combined with good optical properties and could be suitable for practical applications.

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1. INTRODUCTION

Antireflective coatings (ARC) on transparent substrates reduce the reflection loss along the optical surface thereby increasing the transmittance of the incident light. ARCs find lot of applications, e.g. on glass/plastic ophthalmic lenses, display panels, on cover glasses used for solar photovoltaics and solar thermal applications, camera lenses etc [1]. The antireflective property can be achieved by depositing either single layer, multi-layer or graded index antireflection coatings on the substrate. Interested readers may refer to the exhaustive review on antireflective coatings by Raut *et al*. [2]. Usually, a single layer ARC is preferred to be deposited from a technology point of view. Sol-gel technique is one of the versatile methods for depositing ARC in an economical manner [3]. Achieving a good antireflective property with good mechanical property on transparent substrates like glass is relatively easy since one can employ higher heat treatment temperatures for densification and crystallization [4, 5]. The same is a challenge to be achieved on temperature sensitive transparent plastics substrates like polycarbonate (PC), where 130-140^{o}C is the maximum temperature that can be employed for curing/densification. There is an increasing interest to replace glass with transparent plastics like polycarbonate, since plastics are less expensive, more easily formed into complex shapes, lighter in weight and less brittle when compared to glass [6]. The antireflection properties of coatings can be tuned or enhanced by appropriate choice of the coating material. In addition, optimizing the porosity of the coating to achieve ultra-low refractive index has also been employed so as to obtain maximum transmission. MgF_2 has been widely used for generating ARC on glass since it has a very low refractive index of 1.38, which can further be reduced by tailoring the porosity in the coatings [7, 8]. However, when such a porous coating is applied on plastics, the mechanical properties are insufficient to be used for practical applications. MgF_2 along with silica has been investigated for improving the mechanical properties [9]. Zeolites are mesoporous materials with strong inorganic silicate frameworks that have recently been shown to possess good antireflection properties when deposited as coatings, in addition to yielding better mechanical properties. Mostly, the investigations reported are on aluminosilicate-based zeolite as antireflective coatings on glass substrates [10]. To the best of our knowledge, there are no investigations reported so far on single layer, composite

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antireflection coatings of MgF_2 and zeolite 4Å on any transparent substrate, be it glass or plastic. From a careful study of the literature, it could be expected that a single layer composite coating of MgF_2 and zeolite would exhibit good antireflection properties in addition to possessing improved mechanical properties. Hence, the objective of this study was to develop sol-gel derived pure zeolite coatings and MgF_2 coatings along with composite zeolite-MgF_2 coatings on polycarbonate substrates for combining good antireflection and mechanical properties. In order to achieve single layer ARC on polycarbonate which has a refractive index of 1.59, the refractive index of the coating material should be between 1.2-1.3 with a coating thickness of ~140 nm. MgF_2 has a low refractive index of 1.38 and zeolite 4Å, which are mesoporous sodium aluminosilicate materials, have a refractive index of ~ 1.46-1.48. A composite coating of MgF_2 and zeolite was investigated to see if a single layer antireflection coating with improved mechanical properties could be obtained by the sol-gel process.

2. EXPERIMENTAL

2.1. Materials

Zeolite 4Å (sodium alumino-silicate, Sigma-Aldrich, Germany), Methanol (CH_3OH, 99%, Thermo Fisher Scientific India Pvt. Ltd, Mumbai, India), Nitric Acid (HNO_3 ,S.D. fine chemicals Limited, Mumbai, India), magnesium acetate tetrahydrate ($Mg(CH_3COO)_2{\cdot}4H_2O$,99%, Sisco Research Laboratories, Mumbai, India), Hydrofluoric acid (HF,39-43%, Thermo Fisher Scientific India Pvt. Ltd, Mumbai, India), Isopropanol (IPA, 99.7%, Qualigens fine chemicals, Mumbai, India) were used as the starting materials without further purification. Polycarbonate sheets (Lexan grade, GE Plastics) of dimensions 50 mm x 30 mm x 3 mm were used as the substrates.

2.2. Sol Synthesis

2.2.1. Zeolite Sol (Sol A)

0.07 g Zeolite 4Å was dispersed in 50 ml methanol and stirred for 15 min. A polymeric binder cum pore forming agent was added to the above dispersion. The resultant mixture was stirred and peptized using HNO_3 by drop-wise addition to the above mixture with continuous stirring. The sol obtained was then ultrasonicated for 30 min.

2.2.2. MgF_2 Sol (Sol B)

5.36 g of Magnesium acetate tetrahydrate was dissolved in 50 ml of methanol. The above mixture was kept for stirring for 15 min. 2.50 g of Hydrofluoric acid (HF) was separately dissolved in 50 ml of methanol and stirred for 15 min. The HF + methanol mixture was added drop-wise to the ($Mg(CH_3COO)_2{\cdot}4H_2O$) + methanol mixture and the resultant composition was vigorously stirred for 3 hours. The sol so obtained was diluted with 100 ml of methanol in 1:1 volume ratio and then ultrasonicated for 20 min. In order to carry out autoclaving, 50 ml of MgF_2 sol was taken in a 100 ml Teflon-lined autoclave vessel [11]. The vessel was tightly sealed and placed in an air circulating drying oven at 140°C for 24 h. This autoclaved sol was then used for generating single layer MgF_2 coatings. It should be mentioned here that the temperature and duration of autoclave treatment (AT) were optimized independently and the experiments carried out using the optimized parameters only are presented here.

2.2.3. Zeolite-MgF_2 Nanocomposite Sol (Sol C)

Zeolite sol (Sol A) and as-prepared MgF_2 sol (Sol B) were homogenized in a 1:1 volume ratio (optimized after performing experiments using various volume ratios) and stirred for 1 hour. The sol was then ultrasonicated for 20 min before coating deposition.

2.3. Coating and Curing

The PC substrates of 5 cm x 3 cm and 3 mm thickness were cleaned using a 1 wt% Alconox® solution followed by thorough rinsing with de-ionised water. The substrates were ultrasonically agitated for 5 min in IPA followed by drying using moisture-free compressed air. The as-prepared zeolite sol, autoclaved MgF_2 sol and zeolite-MgF_2 nanocomposite sol were dip coated onto the cleaned PC substrates at different withdrawal speeds such as 1 mm/s, 3 mm/s and 5 mm/s. The coated PC substrates were thermally cured in an air circulating drying oven at 130°C for 2 h.

2.4. Microwave (MW) Treatment of the Films

Single layer zeolite coatings and zeolite – MgF_2 nanocomposite coatings obtained on PC substrates were subjected to boiling water treatment [12] in a Panasonic 2.45 GHz, 1.1 kW domestic microwave oven Model NN-K593 MF for 15 min. Figure **1** shows the flowchart of zeolite-MgF_2 composite sol synthesis process and achieving single layer ARC on polycarbonate substrates.

2.5. Characterization

The crystalline nature of the powder samples obtained by heat treatment of the sols at 130°C for 2 h was studied using X-ray diffractometer, (model Bruker Axs D8 Advance). The coating thickness and refractive index were determined using ellipsometric data acquired using a variable angle spectroscopic ellipsometer (J.A. Wollam Inc., USA). The ellipsometric data was analyzed using a standard Cauchy model. The surface morphology and elemental analysis of the coated PC substrates was studied using a scanning electron microscope (SEM, model Hitachi S3400 N). The reflectance of the coatings was measured using a Cary Varian 5000 UV-Vis-NIR Spectrophotometer. The mechanical stability of the coatings was determined using a Crockmeter (SDL Atlas, USA) by rubbing the surface of the coatings for specific number of cycles with a fabric under 9 N load, as per American Association of Textile Chemists and Colorists AATCC test method 8, followed by measurement of

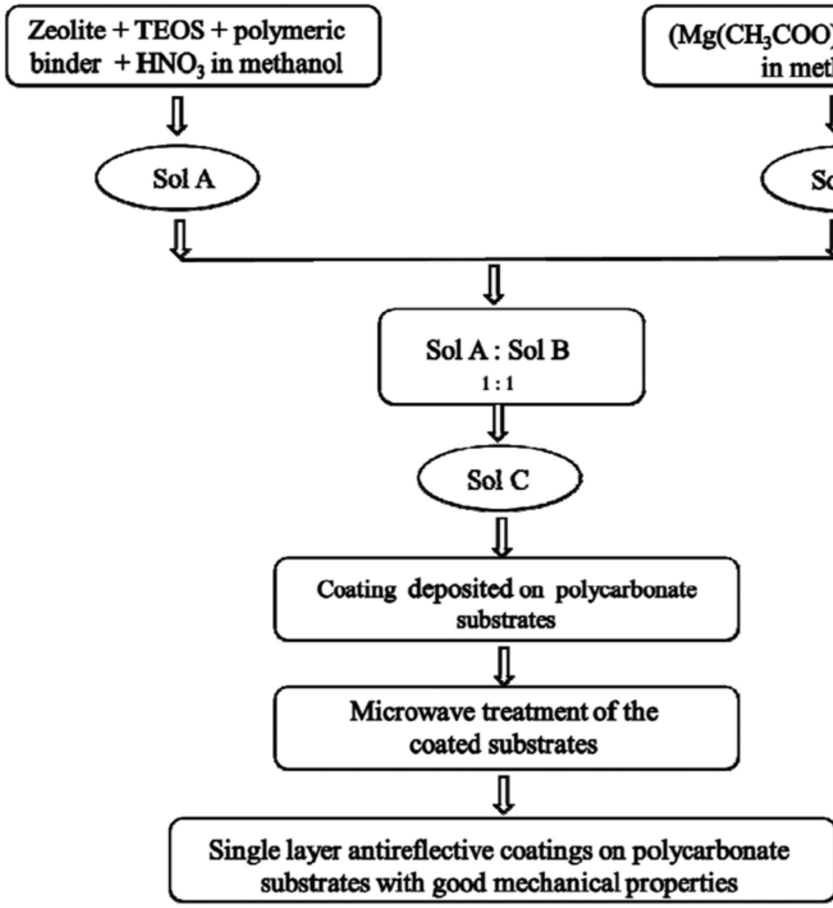


Figure 1: Flowchart showing the zeolite-MgF_2 composite sol synthesis process.

percentage change of haze. The haze of the coatings was measured using Haze-gard dual, BYK-Gardner GmbH, Germany. It should be mentioned here that since the envisaged application of the coatings investigated in the present study is for use in ophthalmic or ophthalmoscopic lenses, the above described testing method was employed by the authors to evaluate the mechanical properties. Water contact angles of the coatings were measured using a Krüss GmbH Germany supplied Drop Shape Analyzer (DSA)-100, The surface roughness of the coatings was analyzed using NTEGRA Aura model (NT-MDT, Russia) Scanning Probe Microscope (SPM).

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction (XRD) Analysis

Powders obtained after heat treatment of the zeolite sol at 130^{o}C, autoclaved MgF_2 sols and zeolite-MgF_2 nanocomposite sol heat treated at 130^{o}C were subjected to XRD analysis and the XRD patterns obtained are shown in Figure **2**. Pattern A in Figure **2** confirms the presence of sodium alumino silicate with the maximum intensity peak matching with the ICDD file 19-1184. Pattern B confirms the completion of reaction of Magnesium acetate and HF by showing the presence of pure MgF_2 with the peaks matching with the ICDD file 01-070-8281. The autoclaving of the MgF_2 sol was found to increase the crystallinity as seen from a decrease in the FWHM of the maximum intensity peak in the XRD pattern obtained from an autoclaved sol when compared to that obtained for an as-synthesized MgF_2 sol (not shown here). XRD pattern (C) confirms the presence of zeolite and MgF_2.

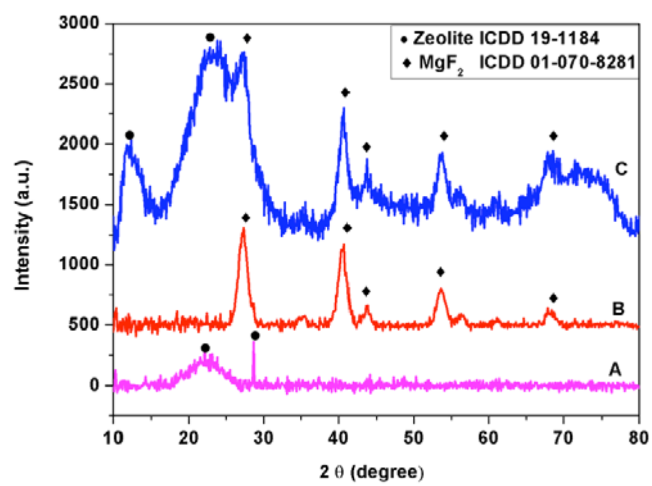


Figure 2: Powder XRD patterns for (A) zeolite sol heat-treated at 130^{o}C; (B) MgF_2 sol autoclaved at 140^{o}C for 24 h and dried at 130^{o}C and (C) heat treated zeolite-MgF_2 composite sol.

3.2. Optical Properties

3.2.1. Effect of Autoclave Treatment for Single Layer MgF_2 Coatings

The average reflectance for the coated PC substrates was measured over the wavelength region 400 – 1100 nm and it was found that autoclave treatment [11] of the MgF_2 sol reduces the percentage average reflectance from 9.7 obtained for a bare PC substrate to a minimum reflectance of 0.134 %, which was observed at a wavelength of 646 nm. This reduction in reflectance for the autoclaved MgF_2 coated sol is due to the increase in porosity and surface roughness induced on the surface of the coated substrate, as confirmed by atomic force microscopic (AFM) and ellipsometric analysis, results of which are shown in the following sections. The effect of autoclave treatment on the reflectance spectra of MgF_2 sol coated PC substrates is shown in Figure **3**.

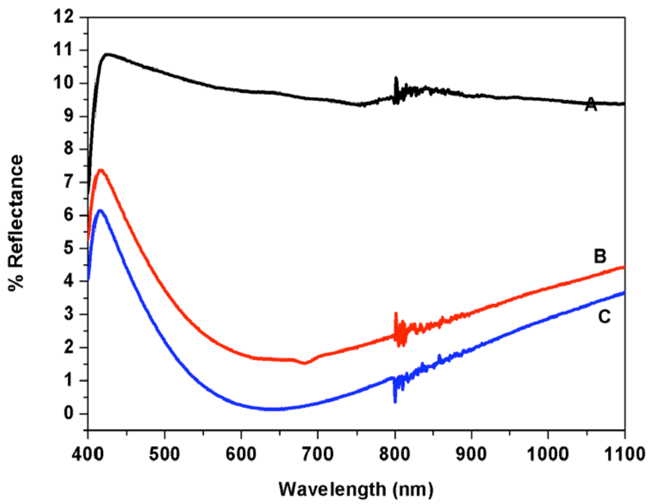


Figure 3: Comparison of the reflectance spectra obtained for (A) bare PC substrate and PC with single layer MgF_2 coatings obtained using a withdrawal speed of 1 mm/s; (B) before autoclave treatment and (C) after autoclave treatment.

3.2.2. Effect of Boiling Water Treatment Under Microwave Irradiation for Single Layered Zeolite and Zeolite-MgF_2 Composite Coatings

The average reflectance for the coated PC substrates were measured over the wavelength range 400 – 1100 nm and it was found that hot water treatment of the zeolite and zeolite-MgF_2 composite coatings reduces the % reflectance. This reduction in reflectance for the hot water treated films is due to the alignment of zeolite crystallites and possible increase in surface roughness [12]. Figures **4-6** show the comparison of reflectance spectra obtained for the bare PC substrate, single layer MgF_2, zeolite and zeolite-MgF_2 composite coatings, after suitable treatments. The reflectance spectra clearly show that the single layered zeolite-MgF_2 coating, though exhibits a higher average reflectance than a single layered MgF_2 coating, still is lower than a single layered zeolite coating.

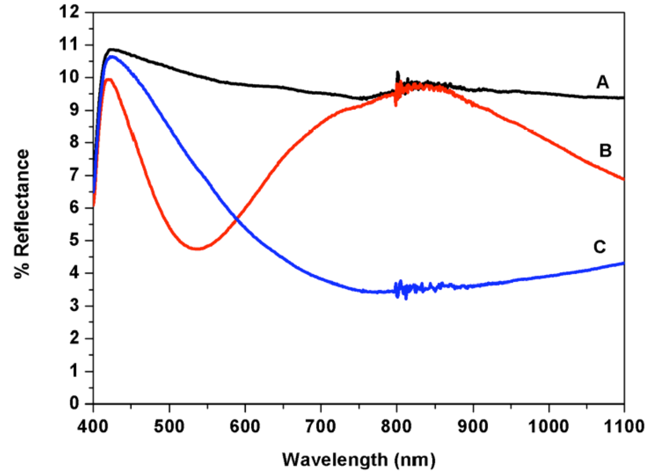


Figure 4: Comparison of the reflectance spectra obtained over 400 - 1100 nm for (A) bare PC substrate with zeolite coatings obtained using a withdrawal speed of 3 mm/s (B) before microwave treatment and (C) after microwave treatment.

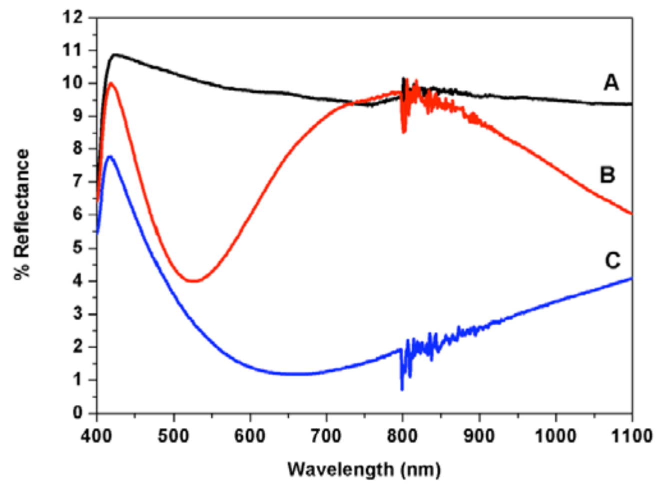


Figure 5: Comparison of the reflectance spectra obtained over 400 - 1100 nm for (A) Bare PC substrate with zeolite-MgF_2 nanocomposite coatings obtained using a withdrawal speed of 5 mm/s (B) before microwave treatment and (C) after microwave treatment.

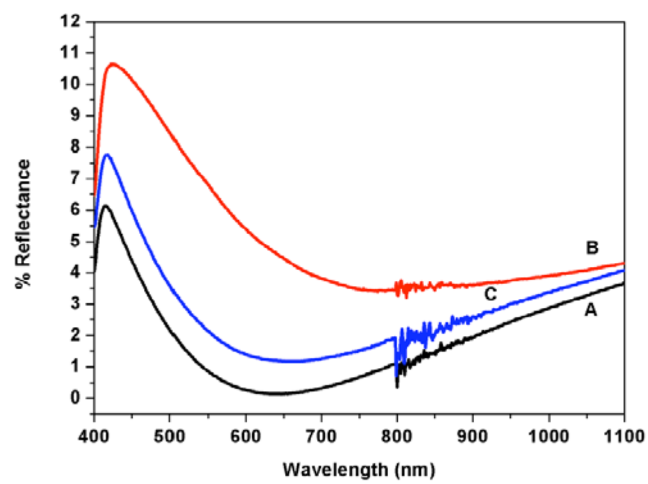


Figure 6: Comparison of the reflectance spectra obtained over 400 - 1100 nm for (A) Autoclaved MgF_2 coatings (B) microwave treated zeolite coatings and (C) microwave treated zeolite-MgF_2 composite coatings.

Table 1: Effect of microwave treatment (MW) and autoclave treatment (AT) on the thickness, surface roughness, refractive index and average percentage reflectance from 400 – 1100 nm of the single layer zeolite 4Å (Z), MgF_2 (M) and zeolite 4Å - MgF_2 (ZM) composite antireflective coatings on PC substrates

Parameters	Thickness (nm)	Surface roughness (nm)	Surface roughness from AFM studies (nm)	Refractive index at 550 nm	Average percentage reflectance from 400-1100 nm
Bare substrate	--		3-6	1.59	9.7
Z before MW	229.13	1.63		1.46	7.9
Z after MW	214.84	2.65	1.5-3	1.40	5.1
M before AT	113.20	2.93		1.39	3.1
M after AT	124.40	12.96	6-12	1.28	1.9
ZM before MW	170.25	0.1		1.46	7.6
ZM after MW	103.27	0.2		1.43	2.8

3.3. Ellipsometric Analysis and Surface Profiles: Thickness and Refractive Index Measurements

The ellipsometric data obtained for the single layered coatings were analysed using the Cauchy model. Table **1** shows the effect of microwave treatment and autoclave treatment on the thickness, surface roughness, refractive index and average reflectance measured over the wavelength range 400 - 1100 nm of the single layered antireflective coatings on PC substrates. A possible schematic of the coating configuration where MgF_2 occupies the space between aligned zeolite crystallites is shown in Figure **7**. The thickness of the zeolite coatings reduced from 229.13 to 214.84 nm and the surface roughness increased from 1.63 to 2.65 nm after microwave treatment in boiling water. The thickness of the MgF_2 coatings was 124.40 nm and the surface roughness increased to 12.96 nm after autoclave treatment of the sol, leading to an increase in the porosity as well. The increased surface roughness along with porosity is in agreement with the Atomic Force Microscopy (AFM) results, which are shown in Figure **8**. The thickness and the refractive index of the zeolite-MgF_2 composite coatings were reduced to 103.27 nm and 1.43 respectively after microwave treatment. Refractive indices as a function of wavelength for the coated PC substrates are shown in Figure **9**. The results of the uniqueness fit as shown in Figure **10** indicated the reliability of the designed optical model used for data analysis.

3.4. Surface Morphology

Surface morphology of microwave treated zeolite coatings, zeolite-MgF_2 nanocomposite coatings and MgF_2 coatings obtained after autoclave treatment of MgF_2 sol as obtained from SEM analysis are shown in Figure **11**. In case of MgF_2 coatings, the surface contains porosity and MgF_2 particles with an average crystallite size of ~ 10 nm are distributed uniformly throughout the surface. Zeolite *4Å* coatings and zeolite *4Å* -MgF_2 composite coatings were rich in aluminosilicate particles on the surface with an average size of 50 nm to 100 nm that were not uniformly distributed throughout the coatings. The aluminosilicate particles on the surface induced surface roughness thereby reducing the reflectance.

3.5. Mechanical Properties of the Coatings

Table **2** compares the change in percentage haze for the coated PC with a bare PC substrate after scratch testing using a crockmeter. The value of % haze after 1000 cycles of rubbing with a fabric showed that the single layered zeolite coatings had the maximum scratch resistance. MgF_2 coatings could not withstand even 10 cycles of the scratch tests whereas, the zeolite-MgF_2 composite coatings were found to have better scratch resistance than a pure MgF_2 coating and could withstand 1000 cycles of the scratch testing with a change in % haze of 3.6.

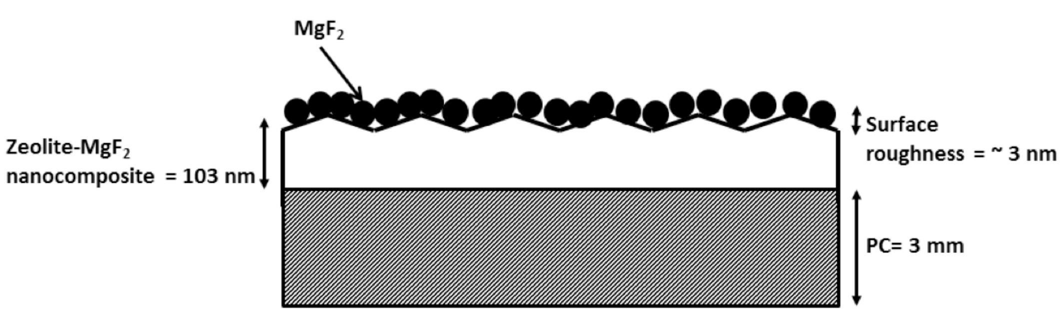


Figure 7: Schematic showing the possible coating configuration of the composite zeolite-MgF_2 coating.

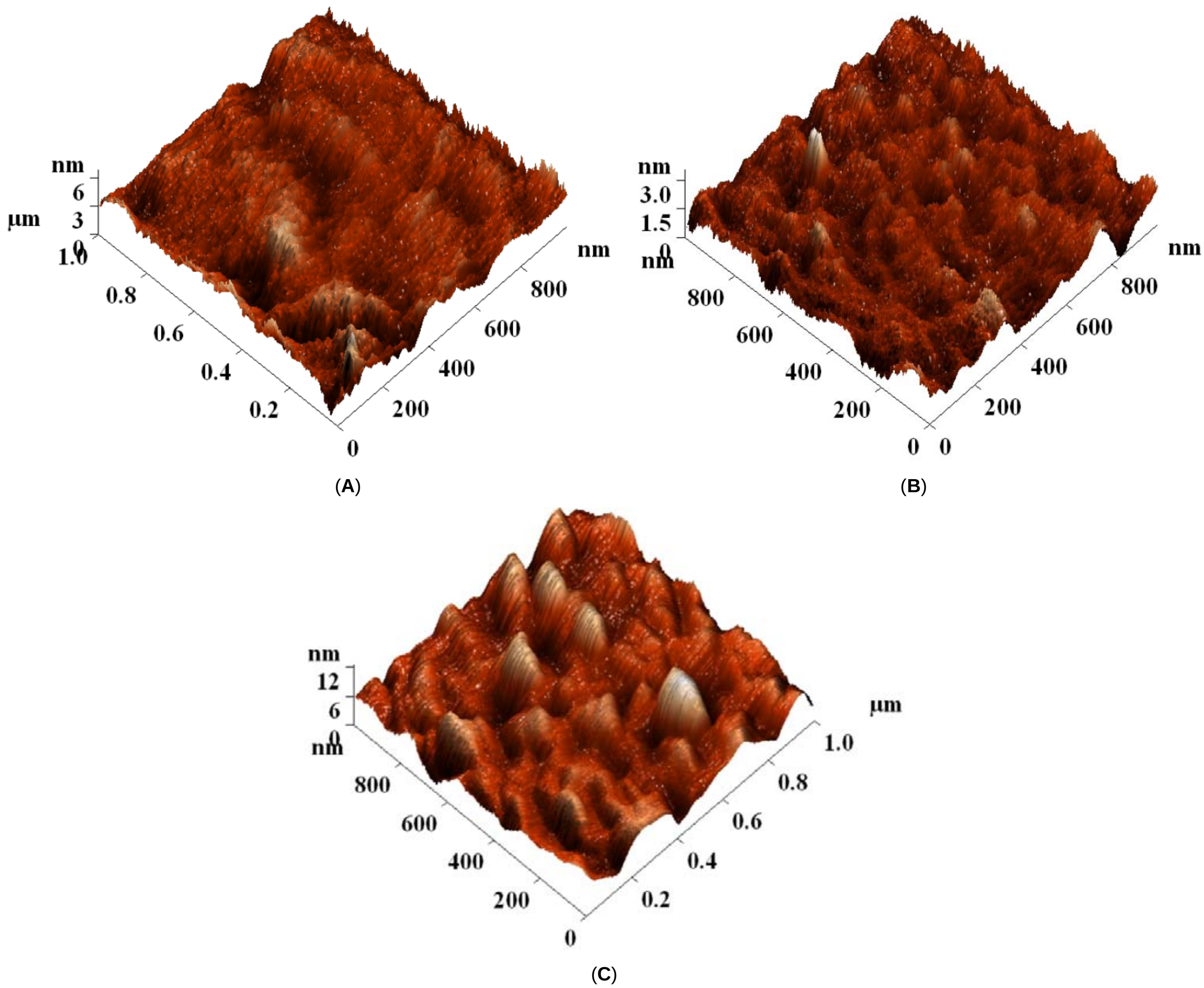


Figure 8: AFM images showing the surface roughness for (**A**) Bare polycarbonate substrate (**B**) microwave treated zeolite coatings and (**C**) autoclaved MgF_2 coating.

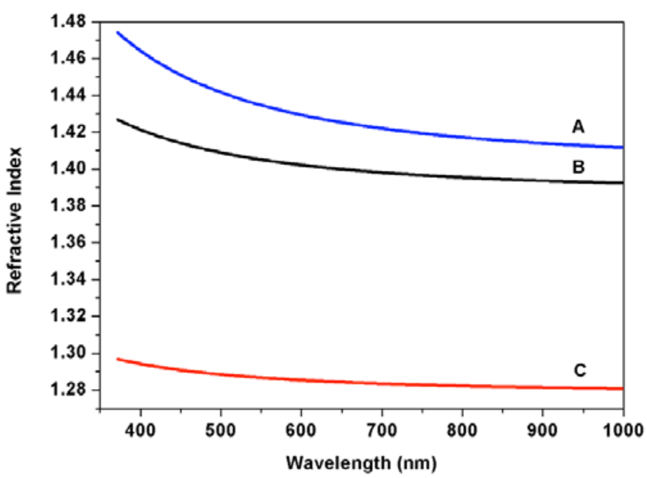


Figure 9: Refractive index as a function of wavelength for (A) microwave treated zeolite-MgF_2 nanocomposite coatings (B) microwave treatment zeolite coatings and (C) autoclaved MgF_2 coatings obtained from the ellipsometric analysis.

3.6. Contact Angle Measurements

The single layered antireflective coatings obtained on the PC substrates are hydrophilic in nature as shown in Figure **12**. The water contact angles obtained for microwave treated zeolite coatings was $27.5^o \pm 2$, was $37.5^o \pm 2$ for autoclaved MgF_2 sol coatings and was $20^o \pm 2$ for the microwave treated zeolite-MgF_2 coatings. The composite coatings are seen to be more hydrophilic than their individual counterparts.

4. CONCLUSION

Dip coated single layer zeolite coatings, MgF_2 coatings, zeolite-MgF_2 composite coatings on PC substrates were characterised for antireflective property as well as their mechanical properties like scratch resistance. The present investigation showed that the optical and mechanical properties of the coatings were improved in the zeolite-MgF_2 composite coatings. Thickness and refractive index of the

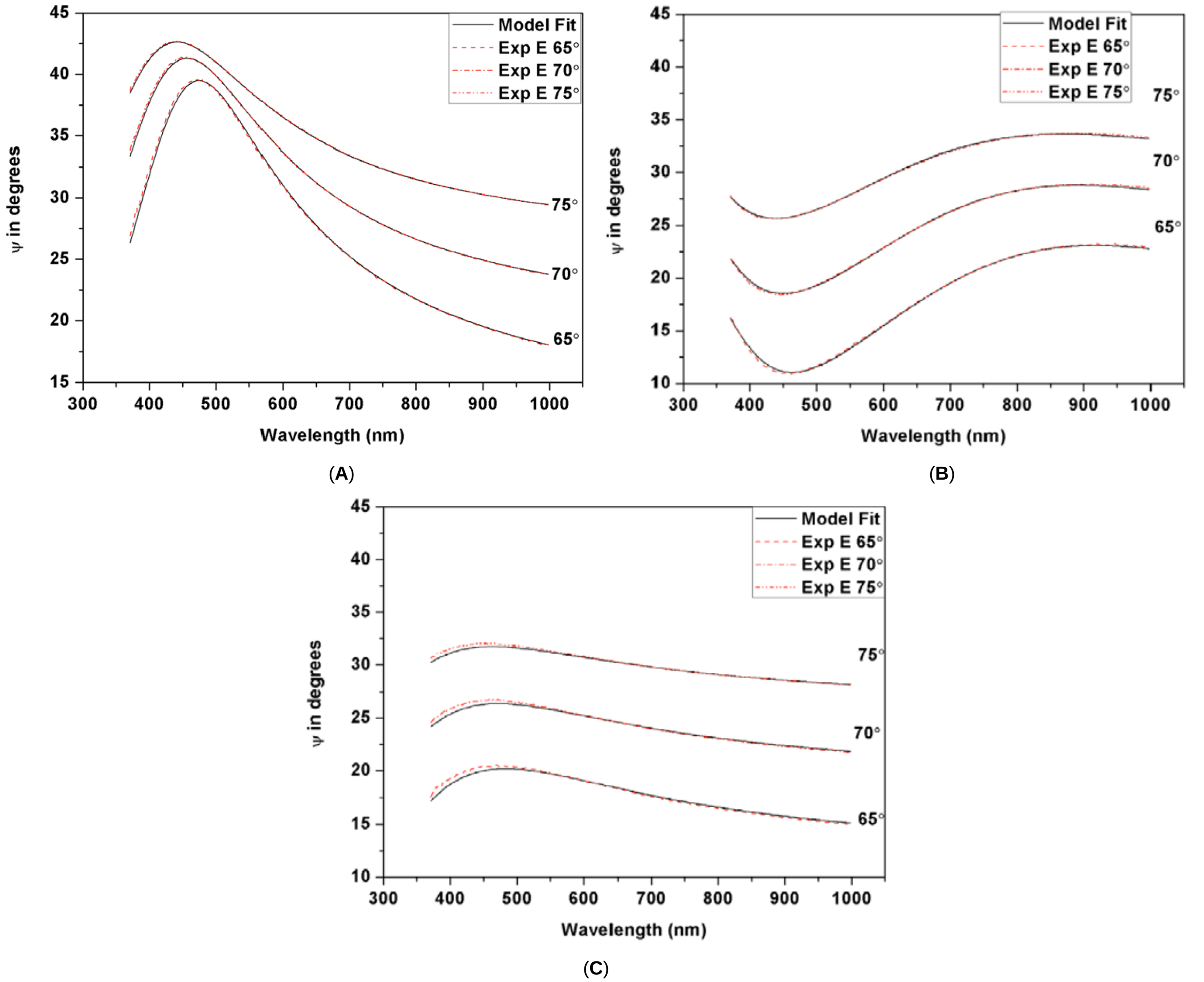
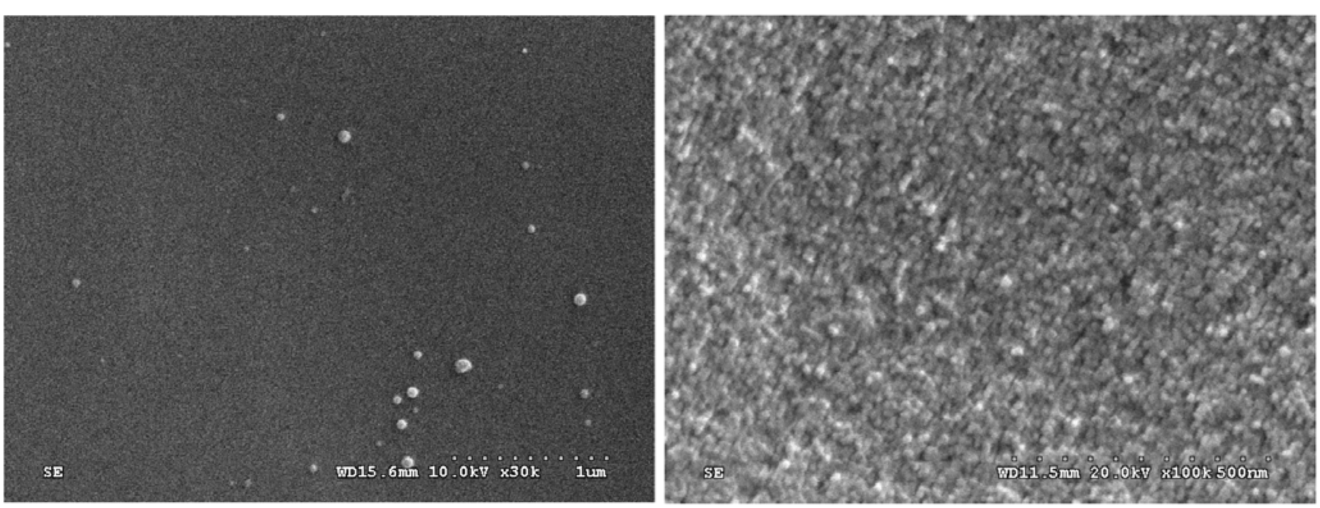
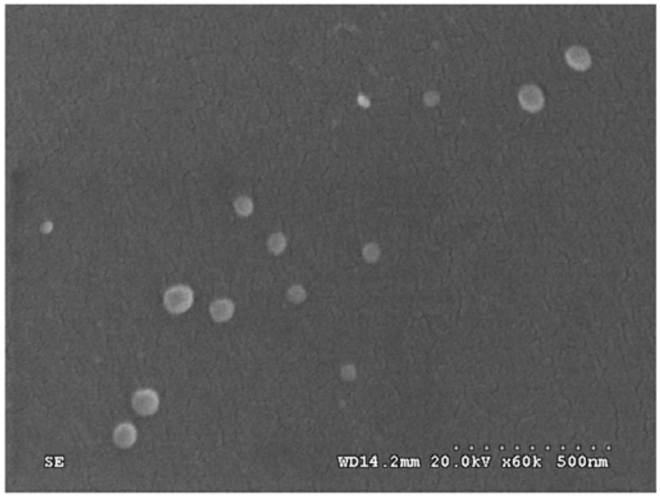


Figure 10: Generated and experimental ellipsometry data for (**A**) microwave treatment zeolite coatings (**B**) autoclaved MgF_2 coatings and (**C**) microwave treated zeolite-MgF_2 nanocomposite coatings obtained from the Cauchy analysis.



(**A**) (**B**)

(Figure 11). Continued.

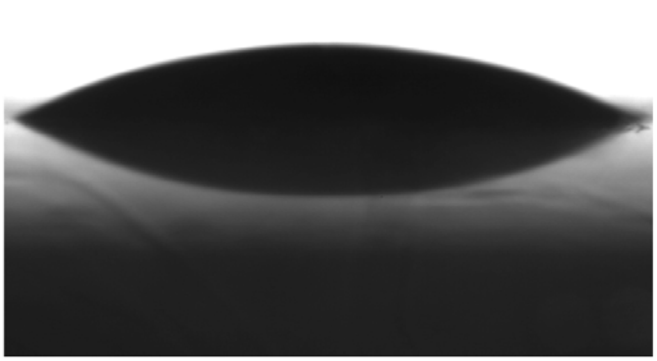


(**C**)

Figure 11: SEM images for (**A**) microwave treated zeolite coatings (**B**) autoclaved MgF_2 coatings and (**C**) microwave treated zeolite-MgF_2 nanocomposite coatings.

Table 2: Comparison of change in Percentage Haze for the Single Layer Zeolite, MgF_2 and Zeolite-MgF_2 Composite Antireflective Coatings with that of Bare PC Substrate

Parameters	No of cycles	Change in % haze
Bare substrate	1000	4.2
Zeolite coatings	1000	1.9
MgF_2 coatings	10	4.4
Zeolite-MgF_2 coatings	1000	3.6



(**A**)

(**B**)

(**C**)

Figure 12: Photographs of the drop shapes after water contact angle measurements for (**A**) Microwave treated zeolite coatings and (**B**) autoclaved MgF_2 coatings and (**C**) Microwave treated zeolite-MgF_2 coatings.

zeolite coatings were found to decrease after a hot water treatment under microwave irradiation in a domestic microwave oven. In case of the MgF_2 coatings, an autoclave treatment was found to increase the surface roughness and porosity leading to an averaged percentage reflectance of 1.9, which was the least among those obtained for the coatings studied. All the coatings obtained on PC substrates were found to be hydrophilic in nature. Pure zeolite coatings were found to possess the best scratch resistance property, while pure MgF_2 coatings were not mechanically stable as evaluated from a crockmeter test. Zeolite-MgF_2 composite coatings were found to possess sufficient scratch resistance along with good optical properties and could be used for practical applications, i.e. for use on ophthalmic or ophthalmoscopic lenses, that warrant sufficient scratch resistance along with very good antireflective property.

The present investigation shows for the first time that cost-effective precursors like the porous silicate based zeolites which have a strong inorganic framework can be used to contain low refractive index materials like MgF_2 in order to generate a single layer antireflective coating with good optical as well as very good mechanical properties on temperature sensitive substrates like plastics. The process of generating the antireflective coatings described herein, i.e. microwave irradiation for a short time is also simple and amenable for scale-up.

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