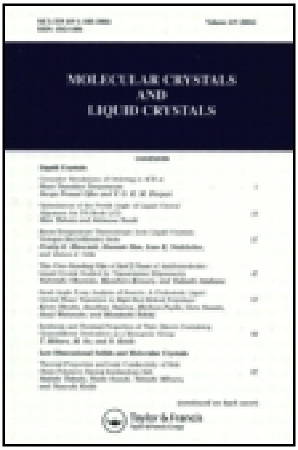

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Formulation of Thermally Cured Organic-Inorganic Superhydrophilic Coating for Antifogging Optical Application

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Formation of coatings with combined properties of being superhydrophilic/superhydrophobic are of immense applications in the field of optics. In our present work, we have developed a transparent, organic/inorganic hybrid coating by mixing appropriate ratios of organic silanol coupling agents and monoacrylates to impart strong adhesion to the substrate, and inorganic components comprising of a hybrid mixture of silica-titania, and certain vinyl components as well as hydrophilic surfactants for improved antifogging behavior. Polycarbonate lens or glass slides, as substrates were dip coated into the hybrid precursor solution at a suitable withdrawal rate of 5 cm/min to form uniform and crack free film of thickness 458 nm. The sequential process of drying of the coated films involved thermal curing at varied temperature and time in the presence of an appropriate thermal initiator, dicumyl peroxide. The surface chemistry and thermal behavior along with the superhydrophilicty and fogging behavior of the coated substrates were assessed by respective ATR-IR, ^{29}Si NMR, TGA/DSC analysis and AFM measurements. The remarkabale observation was that the composite of

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organic-inorganic mixture exhibited desired properties of being superhydrophilic as well as antifogging on the substrate by curing at appropriate temperature of 50°C for 24 hr and 120°C for 8 hr, respectively.

Keywords: antifogging; hydrophilic; organic/inorganic coating; transparent

INTRODUCTION

In the filed of optics, the design of a protective coating onto a lens surface with dual imperative properties of being superhydrophilic and antifogging is of immense importance. The superhydrophilic property of the surface allows water to spread uniformly under the humid conditions, rather than remaining as droplets. In the past decade, many reports are available on the formation of superhydrophilic coatings with titanium dioxide and also with subsequent inclusion of silicon dioxide in the same [1,2]. But, those coatings suffer from a disadvantage that only under UV illumination they behave as superhydrophilic film and then restore back to the normal phase with high contact angle to water [3,4].

Several other trials have involved the formation of antifogging layers on polymer films with only temporary effects [5,6]. Sol-gel process is a chemical technology, which can be very well employed to prepare inorganic as well as organically modified inorganic materials via hydrolysis and condensation of metal alkoxides [7,8a]. Based on the contention that by employing only metal alkoxides as starting material, it is difficult to form crack free thin films.

Many studies have been undertaken to form thin optical quality films by employing certain silanol coupling agents and colloidal silica [8b]. Many different combinations of alkoxides and organoalkoxysilanes have also been prepared to produce coatings with improved mechanical properties such as abrasion resistance and high chemical stability [9,10]. From our laboratory, we have previously reported surface sulfonation of colloidal silica for superhydrophilic applications, where the vinyl-terminated silica was sulfonated by an addition reaction of chlorosulfonic acid [11] and have also proposed an alternative sulfonation route to generate superhydrophilic surfaces by using mercapto functionalized mesoporous silica [12].

Very recently, we have also developed a technology for the formation of transparent and abrasion resistant coating onto the polycarbonate lens surface [13]. Hence, in order to impart the combined properties to make a surface well versed with antifogging behavior as well as superhydrophilic which must be long lasting, we have formulated an organic-inorganic coating mixture. In the present paper, our main aim was to develop a coating onto the optical lens with desired properties of being superhydrophilic, antifogging and abrasion resistant. Hence, mainly we opted for an anionic coagulant material of sulfonate compound. The organic components were chosen such that they could impart strong adhesion to the substrate and must be solvent resistant. The performance of the coating was assessed by spectroscopic analysis in terms of surface chemistry, whereas optical transparency and thermal behavior were assessed by UV-Vis spectrometer and TGA/DSC analysis, respectively.

EXPERIMENTAL

Preparation of Coating Solution

The coating solution comprised of suitable ratios of organic and inorganic components. The first coating solution was prepared by hydrolysed tetraethylorthosilicate (TEOS), $TiCl_4$, and sulfonate salt compound together in the presence of an ionic or non-ionic surfactant. The final mixture thus formed was denoted as mixture 1. To mixture 1, polyvinyl alcohol, polyvinyl pyrrolidine, polyethylene glycol methacrylate, sodium dodecyl sulfate (anionic surfactant), polyoxyethylene sorbitan monolaurate were added to confer additional hydrophilicity. The final mixture was denoted as mixture 2. For the preparation of organic composite, solutions with the desired amounts of TEOS and 3-methacryloxypropyltrimethoxysilane (MPS) were hydrolyzed in ethanol-water mixture for 24 hr under stirring. On the subsequent day, the desired amount (similar to the amount taken for TEOS and MPS) of methyl methacrylate [9] and 0.2% of dicumyl peroxide (as thermal initiator) were added. Both, the mixture 2 and inorganic mixture were mixed and further stirred for homogeneous mixing with no phase separation. The desired well cleaned substrates, polycarbonate lens (from SMC Tech., South Korea) and glass slides (cleaned for 24 h in oxidizing solution of hydrogen peroxide/water/ammonia) were dip coated into the composite mixture and dried at 50°C for 24 hr and 120°C for 8 hr. All the reagents and solvents were obtained from Sigma-Aldrich, unless otherwise stated.

Characterization

The chemical nature of the coating was characterized by ATR-IR (Attenuated Total Reflectance, Sens IR Tech, USA) spectroscopy by employing the composite mixture coated glass slide as substrates. The wetting behavior of the coating was examined by measuring the contact angle of the coated and uncoated glass slide in contact angle goniometry (DSA100, KRUSS GmbH). Chemical reaction of the hybrid system was monitored by ^{29}Si NMR spectroscopy (BRUKER, AM-300). Light transmittance of the coated films was measured by using an UV-Vis spectrometer (SPECTRONIC, GENESYS). The coating thickness and roughness of the coated film on a glass slide were assessed by contact AFM mode (Model Nanoscope IIIA, Digital Instruments). Thermal analysis of the composite mixture was done by DSC/TGA analysis (TA Instrument 2050) under air atmosphere. The TGA of the as prepared composite organic-inorganic mixture was carried out under air atmosphere from 30 to 1000°C with a heating rate of 10°C/min. Also, to have an estimate of the thermal stability of the composite and the weight loss, DSC analysis was carried out to a maximal temperature of 350°C with a heating rate of 10°C/min (air atmosphere). To determine the thermal stability of coating, the coated substrates were kept in hot water (100°C) for 30 min and were then wiped off and checked for antifogging behavior by placing the coated substrate over a beaker containing hot water (100°C) or in the refrigerator for 10 min.

For examining the resistance of coating to water and various organic solvents, the composite coated lens were washed 3–4 times with water, ethanol, methanol, acetone and isopropyl alcohol and tested for the antifogging behavior. To test the adhesion of film on the substrates, the coated film was cross-cut into 1 × 1 cm square. A pressure sensitive scotch tape (3M) was then uniformly applied to the surface and after a time gap of 5 min, the tape was removed with maximal force. Subsequently, the coating was applied for the measurement of antifogging behavior and light transmittance.

RESULTS AND DISCUSSION

Characterization of Hybrid Organic-Inorganic Coating

As it is evident from the composition of the hybrid mixture, there are various different constituents. To achieve the ultimate goal of forming a transparent, superhydrophilic and anti-fogging coating along with strong adherence to the substrate, different constituents were chosen based on their chemical nature and fundamental properties. A mixture of TEOS-titanium chloride-sulfonate salt was chosen for certain basic reasons such that, silica-titania have been conventionally employed to form anti-reflective, crack free and hard transparent films on optical surface. As an initial step, we tried forming film of the above composition on both lens and glass surface by dip coating at a rate of 5 cm/min; though hydrophilicity (contact angle $> 10^{\circ}$) and antifogging was achieved the film was not strongly adherent to the surface. Hence, as a further step to improve the hydrophilic behavior and to attain superhydrophilicity, certain other constituents and surfactants like polyvinyl alcohol, polyvinyl pyrrolidine, polyethylene glycol methacrylate, sodium dodecyl sulfate (anionic surfactant), non-ionic polyoxyethylene sorbitan monolaurate (Tween-20) and commercially available super wetting agent were also included. It is worth mentioning at this point that there was inclusion of certain other chemical constituents and surfactants to achieve good superhydrophilic property, as the presence of sulfonate salt compound was not sufficient to lower the contact angle with water to be less than 10°. In continuation, we could not achieve the formation of strongly adherent film. Based on the previous report [9], third mixture comprising of TEOS-MPS-methyl methacrylate and a thermal initiator were included into the previous mentioned coating solution to achieve strong adherence to the substrates.

It was observed that the final hybrid solution coated on the cleaned glass substrate was transparent and colorless with little bit of glossy appearance (this characteristic had no effect on the transparency of the film or visibility of lens). Figure 1 shows the typical optical transparency of organic-inorganic hybrid mixture on the glass substrate in

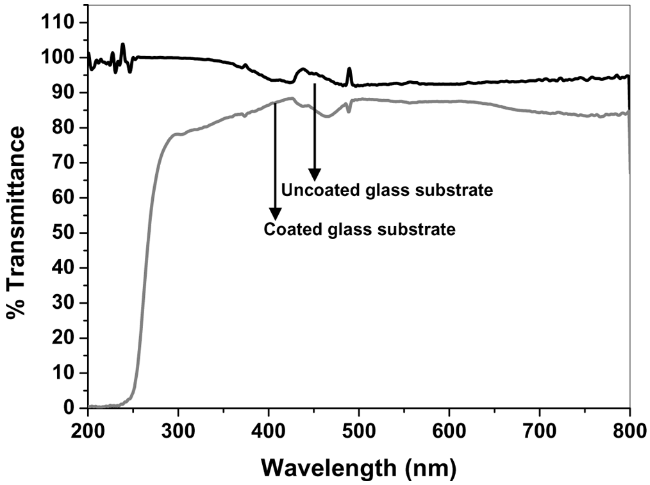


FIGURE 1 Optical transparency of organic-inorganic hybrid mixture on the glass substrate in the visible region (300–800 nm). On comparison with the uncoated substrate, the organic-inorganic coated substrate exhibited 80% of light transmittance in the visible region.

the visible region (300–800 nm). The final coating on the glass substrate displayed optical transparency of 80% when compared to the bare substrate indicating that there was no macrophase separation between organic and inorganic components, and the crack free coatings were obtained after sequential drying at varied temperatures at different intervals of time. The glossiness of the film and lower transmittance in the visible region could be attributed to light scattering by the agglomerated inorganic particles in the hybrid coating films [13] and presence of yellow tinge in the coating, respectively. The coated film on the glass substrate which was eventually tested for abrasion resistance also exhibited similar percentage of light transmittance (data not shown). The film thickness and surface roughness of the film on the glass substrate were calculated from AFM measurement in contact mode. The film thickness was estimated to be around 458 nm with an average surface roughness of less than 150 Å.

It is a well known phenomenon that wetting of solid surfaces with liquid depends upon their surface chemistry [14]. The hydrophilic property of coated film was confirmed by contact angle measurement with water. The substrates utilized were hybrid film coated glass substrates. Figure 2(a) and (b) show the photographs on the behavior of water droplet on a bare surface and hybrid mixture coated slide. The contact angle of bare glass surface was 80° and that of the coated substrate was 7.5°. This behavior indicates the superhydrophilic nature of the hybrid organic-inorganic coating. The observed hydrophilicity can be attributed to the presence of surface sulfonate groups in the coating in conjunction with the presence of hydrophilic super wetting agent and other surfactants. The reason for introduction of certain other surfactants like, SDS and Tween-20 and vinyl reagents such as polyvinyl alcohol and polyvinyl pyrrolidine was to confer additional hydrophilicity to the coating. The presence of commercially available super wetting reagent (Q2 5211) resulted in further decrease in the contact angle with water and formation of a highly condensed network through condensation of tetrafunctional alkoxysilanes, as can be seen from ^{29}Si NMR data shown later in the text (Fig. 6). Figure 3(a) shows comparative photographs of the superhydrophilic behavior of coating on the surface of optical lens, when it was kept under fogging atmosphere (either in refrigerator for 10 min or under hot vapor steam) and uncoated lens treated under similar conditions. The photograph of the lens surface (uncoated) looks translucent and hydrophobic due to large water droplets formed on the surface. On the other hand, the organic-inorganic hybrid coated lens surface (coated) appears to be transparent and clear without any fog formation with the presence of a thin film of water, indicating the antifogging and superhydrophilic nature

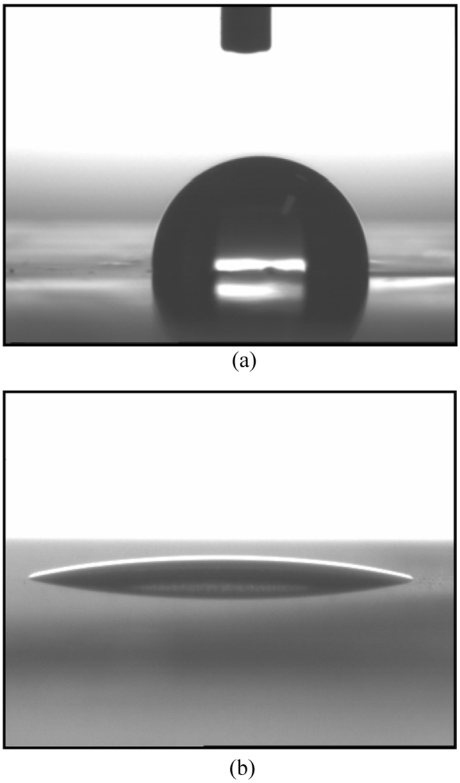


FIGURE 2 Photographs of behavior of water droplet on a bare glass surface (a) and hybrid mixture coated glass surface (b) The contact angle of bare glass surface was 80° and that of the coated substrate was 7.5°.

of the coating. To assess the stability of film under harsh environmental conditions such as hot water treatment, the hybrid mixture coated lens was dipped in hot water (100°C) for 30 min and was analyzed for antifogging behavior. It was interesting to note that still the coated lens retained the desired characteristics and there was no change in the superhydrophilic nature, as canbeseen from Figure 3(b). It is also desirable to state that thus formulated coating on both the lens and glass surface was resistant to attack of organic solvents such as ethanol, methanol, acetone and isopropyl alcohol. Even after washing the surface with the above mentioned solvents, the coated surface exhibited the properties such as antifogging and superhydrophilicity.

The peel resistance test was carried out by using 3 M scotch tape to test the adhesion of the film to the substrate, as per the reported

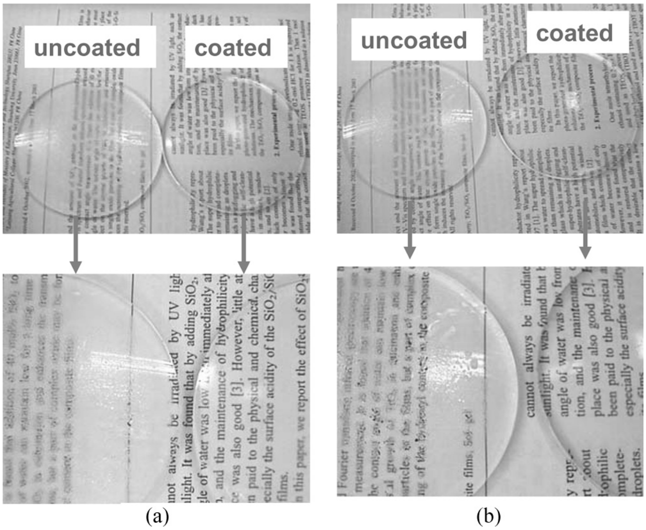
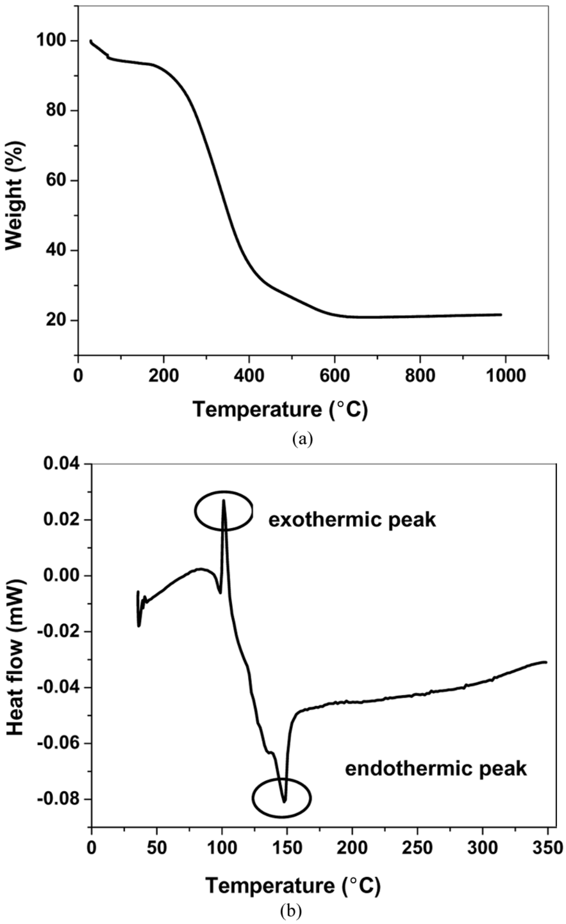


FIGURE 3 (a) Comparison of the fogging behavior between the uncoated and hybrid mixture coated lens. (b) Photograph demonstrating the stability of the hybrid mixture coated lens in terms of antifogging behavior.

procedure [15]. It was observed that peeling of the tape from the coated surface with a high force had no drastic influence on the surface characteristics of the film. The coated film still exhibited good antifogging behavior. The good adhesion of the coated film to the substrate was due to the formation of Si−C bond between the organic and inorganic components in the composite, as can be seen in Figure 5 and as also evident from ^{29}Si NMR spectrum (Fig. 6) of the composite mixture, which reveals the presence of a strong interconnecting network between organic and inorganic components. Moreover, the presence of organic phase prevented any crack formation during the drying step. Our results also indicate that the acrylic based organic-inorganic hybrid coatings must be fully polymerized in order to achieve good abrasion resistance and over curing must be avoided.

Thermal Behavior of Film Precursor

As thermogravimetric analysis is often utilized to determine a suitable temperature profile for curing a sol-gel coating, both TGA and DSC analysis of the coating mixture was carried out. The representative TGA and DSC curves are reported in Figure 4(a) and (b). In the TGA curve, the initial and slow weight loss below 200°C can be



(a)

(b)

FIGURE 4 (a) TGA analysis of organic-inorganic composite mixture. It is apparent from the curve that there was no significant weight loss up to 200°C, which reveals that the composite is stable. Gradual weight loss from 200° can be due to pyrogenic destruction of organic component. (b) DSC analysis of organic-inorganic composite mixture. The exothermic peak at 110°C indicates condensation reaction between the organic and inorganic components and evaporation of water and organic solvents. The endothermic peak around 150°C is considered to be due to evaporation of adsorbed water in the pores of very small radius and the starting stage of decomposition of the organic components.

attributed to evaporation of water and thermal decomposition of organic solvents [16]. It is also apparent from the curve that there was no significant weight loss up to 200°C, which reveals the stability of composite mixture. From Figure 4(a), it can be seen that as the temperature rises from 240°C, there is a significant weight loss from 90 to ~30% revealing the pyrolytic decomposition of organic component. Figure 4(b) shows the DSC curve of the organic-inorganic composite. The exothermic peak at 110°C indicates condensation reaction between the organic and inorganic components and evaporation of water and organic solvents. The endothermic peak around 150°C is considered to be due to evaporation of adsorbed water in the pores of very small radius and also indicates the starting stage of decomposition of the organic components. Hence from TGA and DSC curves, it is apparent that the composite mixture exhibits good thermal stability over to a temperature as high as 200°C and can be very well utilized to form an optical coating.

Chemical Reactions of the Organic-Inorganic Composite

It is a reported phenomenon that complete homogeneity in the hybrid mixture of organic-inorganic solution, leads to the formation of desired characteristics of the film in terms of being optically transparent and thermally stable [13]. Hence, the chemical feature of the film was investigated by ATR-IR spectroscopy and ^{29}Si NMR was carried out to monitor the reaction between organic and inorganic precursors. Figure 5 shows the Fourier transform infrared spectrum of the composite film. The wide absorption band centered at 3397 cm^{-1} is due to Si–OH or Ti–OH residues in the film [17]. The absorption peak around 930 cm^{-1} corresponds to Si–O–Ti stretching vibration indicating the generation of Si–O–Ti in the system [2]. The band located around 657 cm^{-1} can be due to Si–C stretching vibration, which shows that the organic and inorganic components in the composite are connected by chemical Si–C bond [16]. The wide overlapping band centered at 1091 cm^{-1} may result from the superposing effect of Si–O O (1054 cm^{-1}), Si–O–C (1100 cm^{-1}) and C–O–C (1000–1300 cm^{-1}) [16]. The sharp band at 2973 cm^{-1} can be attributed to the presence of aliphatic CH groups [18]. The aggregated bands in the region of 1350–1440 cm^{-1} were due to the presence of alkane –CH bending [18] and sulfonate moiety (1028 cm^{-1}) [19] in the hybrid system which was mainly responsible for imparting hydrophilic characteristic to the film. It is a reported phenomenon that alkoxy groups of silanol coupling agents (Si–OR') hydrolyze quickly with water in suspensions to form silanol groups (Si–OH), which in turn condense with each other and produce dimers and large oligomers [8b]. Hence, to have an estimate of the cross linking behavior of the hydrolyzed inorganic components, ^{29}Si NMR of the final organic-inorganic mixture was carried

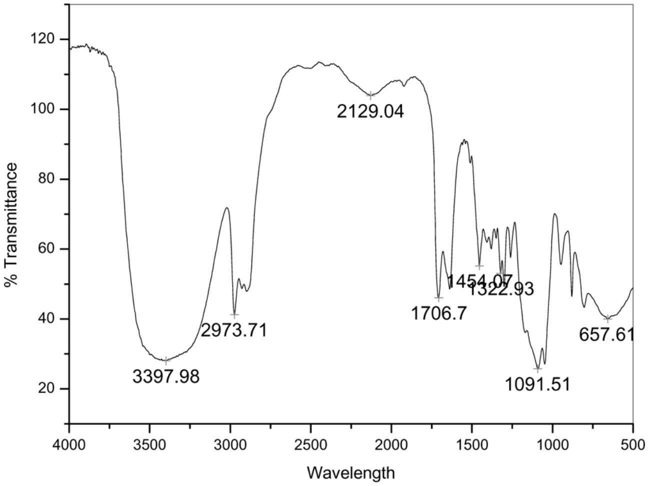


FIGURE 5 ATR-IR spectrum of organic-inorganic film coated on a glass substrate. The spectrum reveals the presence of sulfonate peak at $1028\,\mathrm{cm}^{-1}$. The Si–C stretching vibration around $657\,\mathrm{cm}^{-1}$ shows that organic and inorganic components in the composite are connected by chemical Si–C bond.

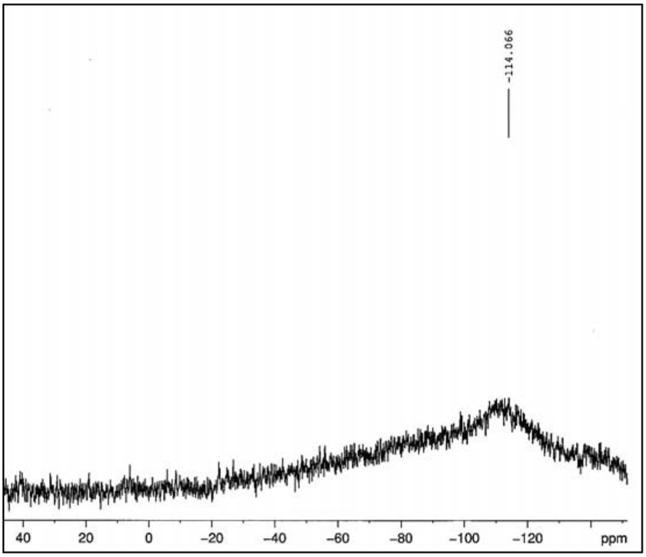


FIGURE 6 ^{25}Si-NMR spectrum of organic-inorganic composite mixture. A single broad peak in the region of −105 to −120 indicates the presence of larger oligomers with two or three siloxane bonds due to condensation of tetrafunctional alkoxysilanes.

out. The notations of Si environments in NMR spectroscopy are represented in Figure 6. In the NMR spectrum, a single broad peak is observed in the region of -105 to -120, which can be attributed to the presence of larger oligomers with two or three siloxane bonds due to condensation of tetrafunctional alkoxysilanes. The hydrolyzed silanol groups could have aroused from different components in the mixture such as, TEOS, MPS and from one of the components of super wetting agent (methyl(propyl hydroxide, ethoxylated)bis(trimethyl siloxy)silane). This finding indicates that a condensed network was produced, which contributed to the formation of strongly adherent coating onto the substrate.

Hence, based on the present study it is worth mentioning that the formulated coating can be very well applied as antifogging, superhydrophilic and stable coating for optical lenses.

CONCLUSION

The experimental results reveal that organic-inorganic formulation as prepared in our present study can be successfully employed to produce thin optical films under appropriate curing conditions. The coated film possessed good qualities such as optical transparency, crack resistant and excellent adhesion. The hydrophilic surfactants can be introduced into the hybrid system by following the conventional sol-gel process as an initial step for the formation of a ternary silica-titania-salt system with subsequent addition of organic counterpart comprising of certain silanol coupling agents and acrylates for imparting strong adhesion of the film to the substrate. It was also apparent that the final composite mixture exhibited desired properties of being antifogging, superhydrophilic and organic solvent resistant, which are the major pre-requisites for the development of a high grade optical coating. Hence, the formulation prescribed in our present paper can be very well employed for optical applications.

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