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Linseed polyurethane/tetraethoxyorthosilane/fumed silica hybrid nanocomposite coatings: Physico-mechanical and potentiodynamic polarization measurements studies

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ABSTRACT

The work presents the physico-mechanical properties and potentiodynamic polarization measurements studies of linseed oil based polyurethane/tetraethoxyorthosilane [LPU/TEOS] hybrid and polyurethane/tetraethoxyorthosilane/fumed silica NC [LPU/TEOS/FS] hybrid nanocomposite coatings. The best coating performance was obtained by the inclusion of 2 wt% FS in 2-LPU/TEOS hybrid. 2-LPU/TEOS/FS produced glossy, transparent, flexibility retentive, scratch-resistant and impact resistant coatings at ambient temperature relative to LPU/TEOS coatings. 2-LPU/TEOS/FS showed good scratch hardness (5.5 kg), impact resistance (250 lb/in.), flexibility (1/8 in.) as investigated by standard methods with corrosion rate obtained as 3.567×10^{-4} mm/year and 4.05×10^{-4} mm/year and inhibition efficiency as 99.816% and 99.710% in 3.5% NaOH and 3.5% HCl, respectively.

1. Introduction

Organic–inorganic hybrid [OIH] and nanocomposite [NC] coatings have received much attention during the last decades. By exploiting sol–gel chemistry, the organic phase is bound to an inorganic phase, usually by means of siloxane linkages [1]. The advantages of this technique are the low temperature process, purity of products and the ability to control nano-meter sized internal structure, to form OIH compared to the traditional methods at high temperature. OIH coatings exhibit improved mechanical properties, enhanced adhesion and good corrosion resistance properties [2]. The interaction between the inorganic and organic phases provides increased adhesion, barrier properties, low toxicity, chemical inertness, making them potential candidates for chromate replacement and enables passivation, necessary for increased protection of the substrate [3]. The incorporation of inorganic nanoreinforcements in small amounts introduces drastically improved performance in the final OIH or NC material [4].

Vegetable seed oils (VSO) based polyols consist of long aliphatic hydrocarbon chains usually in the form of oil triester, with hydroxyls, active methylenes and double bonds. VSO polyols serve as important building blocks of OIH due to (i) inherent flexibility, (ii) improved impact resistance, (iii) excellent physical and chemical properties viz., improved gloss, enhanced hydrolytic and (iv) thermal stability, attributed to the hydrophobic nature of the constituent triglycerides [5]. VSO polyols and polyurethanes have been used as organic matrix to produce OIH or NC films and coatings. Such combinations of VSO polyols and polyurethanes coupled with excellent attributes of inorganic components in OIH or NC coating materials are expected to outperform and replace their petro-chemical based counterparts, partially or wholly and may also overcome the drawbacks associated with them such as poor mechanical strength, low T_g, low thermal stability (degradation between 150 °C and 200 °C), helping the augmented utilization of VSO [6–10]. Other major drawback of VSO based OIH is their complex multi-step synthesis and curing process at elevated temperature, with consumption of ample of solvents. This necessitates the development of such OIH through the use of low or no solvents, under mild reaction conditions, utilizing the fluidity characteristics and functional groups present in VSO backbone. Moreover, the inorganic precursors bind the inorganic metal and the organic moiety in a manner that enables passivation for maximum protection of the substrate and increases the adhesion, hardness, flexibility, and impact resistance of films formed with VSO [11].

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In the past, ample of research has been carried out on VSO based OIH and NC. Luca et al. studied the macro- and microscopic properties (adhesion, hardness, swelling in toluene), microstructure (scanning electron microscopy), and T_g of Castor oil [CO] or CO epoxy/tetraethoxyorthosilane [TEOS] as a function of the proportion of inorganic precursor [9]. Martinelli, Gerbase and coworkers performed similar investigations on CO hydroxy/titanium (IV) isopropoxide [TIP] and TEOS [8–10]. The films obtained were microscopically homogenous, and their properties such as hardness, tensile strength and adhesion depended upon the content of inorganic precursor in the hybrid [8–10]. The presence of nano silica particles in waterborne CO-based polyurethane–silica NC improved both the mechanical properties and thermal stabilities of the resulting NC coatings [12]. In a recent publication, Bechi et al. described the adhesion, hardness, microstructure and thermal properties determined as a function of the proportion of VSO to inorganic precursors [13]. Bastürk and coworkers developed methacrylated and phosphorylated epoxidized soybean oil/silica UV curable coating materials. The coatings showed good hydrophobic character, flame retardancy with promising combination of physical and mechanical properties [14]. In our recent publication, we have reported our research findings on Linseed polyol polyurethane/TEOS/fumed silica nano hybrid composites [7]. Literature survey revealed that the electrochemical corrosion studies and physico-mechanical studies of such VSO hybrid coatings have not yet been reported. In an earlier work, Heidarian et al., had studied the anticorrosive properties of CO polyurethane clay NC coatings by electrochemical impedance spectroscopy (EIS) and Tafel polarization method [15]. Ahmad et al. have described the PDP studies on polyurethane fatty amide/TEOS hybrid coatings [11].

Fumed Silica [FS] is an exceptionally pure form of SiO_2, produced by the vapour phase hydrolysis of $SiCl_4$ in a hydrogen–oxygen flame [16]. The process generates particles in the size range from 7 nm to 50 nm, which tend to link together [17] by a combination of fusion and hydrogen bonding to form chain-like aggregates with high surface area [18]. FS is synthetic, amorphous, colloidal silicon dioxide, with unique characteristics such as its extremely small particle size, enormous surface area, high purity and chain-forming tendencies [19]. When immobilized in appropriate solvent, aggregates of silica can interact through hydrogen bonding of surface hydroxyl groups, which results in formation of three dimensional networks. It finds applications in pharmaceuticals, sealants, cosmetics, printing inks, coatings and paints [17,19] and also, it is widely used as filler for strength reinforcement. FS bears advantage of being free from organic residues since obtained by flame process at 1800 °C [20].

In our previous work, we have reported the preparation and properties (spectral and physico-chemical analysis, morphology, thermal stability, antibacterial behavior) of Linseed oil based polyurethane/tetraethoxyorthosilane [LPU/TEOS] and LPU/TEOS/fumed silica NC [LPU/TEOS/FS] [7]. Here, we report our investigations on physico-mechanical and potentiodynamic polarization measurements of LPU/TEOS and LPU/TEOS/FS coatings.

2. Experimental

2.1. Materials

Tetraethoxyorthosilane [TEOS] and toluylene-2, 4-diisocyanate [TDI] (Merck, Germany) were used as received. Fumed silica [FS] was obtained from COBOSIL and was heated at 100 °C overnight, prior to use. Linseed oil polyol was prepared according to our previously reported method. It was obtained from Linseed oil by hydroxylation reaction (peracetic acid procedure) [5,21].

2.2. Preparation of linseed polyurethane/TEOS [LPU/TEOS] hybrids and linseed polyurethane/TEOS/fumed silica (LPU/TEOS/FS) hybrid NC

The preparation of LPU/TEOS and LPU/TEOS/FS is given in an earlier work (supplementary material) [7]. Three different compositions of LPU/TEOS were prepared as 0.4-LPU/TEOS, 0.5-LPU/TEOS and 0.6-LPU/TEOS by varying the amount of TEOS from 0.4 mol, 0.5 mol to 0.6 mol. LPU/TEOS/FS were prepared by the inclusion of 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% of FS (% of FS calculated on the weight of LPU/TEOS). The significant results were obtained at 2 wt% and 5 wt% loading of FS, in 2-LPU/TEOS/FS and 5-LPU/TEOS/FS, (the prefix indicating the amount of inclusion of FS), respectively, which have been described in the manuscript.

2.3. Preparation and testing of LPU/TEOS and LPU/TEOS/FS coatings

Coatings of LPU/TEOS and LPU/TEOS/FS were prepared by brush technique using solvent blend (65 wt% solution in xylene:MIBK; 3:1 v/v) on commercially available mild steel [MS] strips (size $70 \times 25 \times 1\ mm^3$ and $30 \times 10 \times 1\ mm^3$) to evaluate their performance characteristics such as scratch hardness (SH) (M/s Scope enterprises, New Delhi, India), impact resistance (IRt) (M/s Precision Engineer Kothurd, Pune, India), bending ability (BT) (M/s Henry Zubr, New York, USA) and gloss (Digital gloss meter at an angle of 45°) by standard methods. MS strips used were first polished (abraded with emery papers of different grades), followed by thorough rinsing with deionised water, alcohol and acetone and finally dried in air.

All the coatings were prepared at ambient temperature. The photographs of the coatings were taken by Nikon camera (COOLPIX S8100, 12.1 Mpixels). The optical images of the coatings were studied by Lietz Optical Microscope Model (Metallux-3), at 100× and 200× magnifications. Surface morphology of the samples was analyzed by scanning electron microscopy (SEM), JEOL JSM840 scanning electron microscope under thin gold film at Electron Microscopy Centre, AIIMS, New Delhi, India, equipped with digital imaging and 35 mm photography system. The cross hatch adhesion tape tests were performed by cross hatch tester (supplied by CONFORMITY, INDIA; ASTM D-3359-95a). Thickness of these coatings determined by Elcometer Model 345 (Elcometer Instruments Manchester, U K) was found within the range of 70–80 μm. The chemical resistance behavior was investigated by dipping the coated panels in different media. The chemical resistance tests were performed in tap water (Cl–ion 63 mg/l; conductivity 0.953 mS/A), acid (3.5 wt% HCl), alkali (3.5 wt% NaOH), salt (3.5 wt% NaCl) and xylene by pouring their solutions in 3 in.-diameter porcelain dishes. The coated panels were dipped in the aforementioned media; their periodic examination was conducted until coatings showed visual evidence of softening, deterioration in gloss, discoloration or adhesion. Corrosion resistance performance of coatings was evaluated by potentiodynamic polarization measurements in 3.5% HCl, 3.5% NaOH and tap water at room temperature (30 °C) using micro Autolab type III (μ3AVT 70762, The Netherlands) potentiometer by Tafel extrapolation method. Potentiodynamic polarization curves were obtained by using a three-electrode electrochemical cell (EG & G PARC Flat Cell) with platinum gauze as counter electrode, Ag/AgCl as reference electrode and coated and uncoated MS as working electrodes. MS substrate was fitted in electrochemical cell with $1\ cm^2$ area of the sample exposed to the corrosive media. The polarization curves were recorded by sweeping the potential from −100 mV to 100 mV in the noble direction with respect to open circuit potential at a constant scan rate of 0.01 mV/s. GPES softwares were used for data fitting and calculation of results for PDP studies. The linear Tafel segments of anodic and cathodic curves were extrapolated to