Silica Reinforced Organic–Inorganic Hybrid Polyurethane Nanocomposites From Sustainable Resource

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Polyol/nanosilica organic–inorganic hybrids (Si/Lpol) were prepared through facile sol–gel chemistry. Tetraethoxyorthosilane (TEOS) and linseed polyol (Lpol) obtained by hydroxylation of linseed oil were used as inorganic and organic precursors, respectively. Si/Lpol was further treated with toluene-2,4-diisocyanate (TDI) to obtain silica embedded polyurethane (Si/LPU). The structure of the organic–inorganic hybrid was confirmed by FTIR, 1H NMR, and 13C NMR spectral analysis. The polyol/nanosilica network shows strong interaction with the remnant polyol backbone through hydrogen bonding, which also has bearing on $T_g$ of polymers. Morphological studies of Si/LPU show the formation of uniform, spherical silica nanoparticles of 2–30 nm size embedded in the polymer matrix. Si/LPU was further reinforced with 2 and 5 wt.-% fumed silica (FS-Si/LPUs); their morphology revealed a carpet layer formation on top of Si/LPU. Thermogravimetric analysis showed improved thermal stability of Si/LPU and FS-Si/LPUs. The polymers exhibit mild to moderate antibacterial behavior against *E. coli* and *S. aureus*, respectively, and will pave way in plethora of biological and chemical applications as coating materials.

Introduction

The development of bio-based polymeric materials with tunable properties poses great challenges to academicians and technologists globally. Such materials offer exclusive advantages of environment affability, cost effectiveness, ease of availability, biodegradability, and sustainability.[1,2] Several bio-based precursors have been modified by conventional reactions, e.g., epoxidation, hydroxylation, acrylation, vinylation, urethanation, and others.[3–9]
Recently, chitosan, starch, cellulose, polycaprolactone, and vegetable seed oil (VSOs) based polymeric resins have been modified by sol–gel and reinforcement techniques to improve their performance as well as broaden their areas of applications.\textsuperscript{[10–17]} These processes involve ambient temperature reactions compared to the conventional high temperature ones. They also result in the improved performance even at low levels of filler reinforcement (≤5 wt.-%) compared to the classical approach of reinforcement of fillers (40–50 wt.-% loading).\textsuperscript{[2]}

VSOs encompass the largest family of sustainable resources. They pose inherently low viscosity, high flexibility, reactive functionalities, enhanced hydrolytic, and thermal stability. In their raw forms they cannot meet the desirable characteristics for various applications; thus they are subjected to several derivatization reactions to broaden their areas of applications which include lubricants, cosmetics, plasticizers, adhesives, coatings, and paints.\textsuperscript{[18,19]} Recently, organic–inorganic hybrid polymers from VSOs have been obtained through sol–gel method with metal alkoxides as inorganic and virgin oil, alkyds, or epoxies as organic precursors.\textsuperscript{[20–24]} Such materials offer cost effectiveness and environment friendliness of VSO derivatives coupled with excellent mechanical properties, hardness, corrosion resistance, flexibility, impact resistance, and higher resilience of coatings attributed to organic and inorganic components, respectively.\textsuperscript{[20–24]} Soucek and coworkers developed linseed and soybean oils derived epoxies, epoxy cyclohexene, and epoxy norbornene–TEOS based organic–inorganic hybrid films. Improved tensile strength, fracture toughness, and other mechanical properties were obtained for an optimum loading of TEOS.\textsuperscript{[14,17,25]} Kobayashi and coworkers have reported nanocomposites from epoxidized oils/3-glycidoxypropyltrimethoxysilane. Good flexibility, hardness, mechanical strength, and high biodegradability were achieved by incorporating the silica network into organic polymer matrix.\textsuperscript{[26]} In another report by Apohan and coworkers, polyurethane–silica nanocomposites showed improved abrasion resistance and higher thermal stability.\textsuperscript{[27]} Organic–inorganic hybrid films with good adhesion, hardness, and tensile strength have been synthesized with castor, epoxidized castor, epoxidized, and hydroxylated soybean oils.\textsuperscript{[23,24]} In this report, oil backbone containing epoxy or hydroxyl groups were condensed with hydrolyzed TEOS resulting in organic–inorganic network. In epoxidized oils, –OH of TEOS oligomers chemically reacted with “latent” hydroxyls formed during ring opening reaction of oxirane ring, which could be a time-consuming process from our understanding due to sluggish reactivity of their internally embedded epoxide groups. The major drawback associated with aforementioned systems is their cumbersome multi-step cure schedule involving elevated temperatures with prolonged time periods.\textsuperscript{[20–24]} This motivated us to develop such hybrids with simple synthesis strategy and curing routes involving lower (or ambient) temperature and time periods en route green chemistry.

In the present work, we report herewith the preparation of organic–inorganic hybrids through simple sol–gel chemistry with linseed oil polyol as organic and TEOs as inorganic precursor (Si/Lpol). The advantage with polyol as organic matrix is the abundance of hydroxyl moieties, their inherent fluidity and improved reactivity over epoxidized oils (that are associated with sluggish reactivity due to internally embedded epoxide groups).\textsuperscript{[28]} It is speculated that the abundance of secondary hydroxyls in Lpol backbone may prove advantageous for negation of alcoholic solvent as generally required in hydrolysis-condensation reactions of TEOs.\textsuperscript{[29,30]}

Si/Lpol was further reacted with toluene-2,4-diisocyanate (TDI) by addition polymerization reaction resulting in the in situ formation of silica incorporated linseed polyurethane (Si/LPU). Morphological studies (TEM) of Si/LPU reveal the presence of nanosilica in the polymer matrix. Si/LPU matrix was further reinforced with fumed silica (2 and 5 wt.-% loading) as fillers due to their similarity with the Si/LPU backbone structure, to further enhance the mechanical properties yielding FS-Si/LPUs (2-Si/LPU and 5-Si/LPU).

Further, experiments are underway to study in detail the effect of the organic–inorganic hybrid microstructure on the coating characteristics of Si/LPU and FS-Si/LPUs matrix and can be found in follow up communication.

**Experimental Part**

**Materials**

Linseed seeds (obtained from local market) were air-dried, ground to powdered form and were further subjected to oil extraction in soxhlet apparatus. Petroleum ether (bp 60–80 °C) was used as solvent in oil extraction. Hydrogen peroxide (30%), sulfuric acid, glacial acetic acid, xylene (Merck, India), tetraethoxyorthosilane (TEOS), and TDI (Merck, Germany) were used as received. Fumed silica was obtained from COBOSIL and was heated at 100 °C overnight prior to use.

**Synthesis of Si/Lpol, Si/LPU, and FS-Si/LPUs**

Lpol was prepared by our previously reported method.\textsuperscript{[19]} TEOS, water, and HCl were mixed in pre-determined ratio at room temperature for 15 min. It was then transferred drop wise (within 20 min) into a four necked round bottomed flask containing Lpol (1 mol), equipped with nitrogen inlet tube, thermometer, and magnetic stirrer under continuous agitation.\textsuperscript{[11]} The temperature of the reaction mixture was maintained at 55 °C for 4–5 h. Three different samples were prepared by varying the amount of TEOS from 0.4, 0.5 to 0.6 mol.
In situ synthesis of Si/LPU was carried out by adding a predetermined quantity of TDI (% by weight) dissolved in minimum amount of xylene, through a dropping funnel within 20 min in the above given reaction mixture of Si/Lpol. The reaction was carried out at ambient temperature under continuous agitation. The progress of the reaction was monitored by hydroxyl value determination and thin layer chromatography (TLC) at regular intervals of time till the completion of the reaction. Similar reaction was also carried out with plain polyol and TDI to develop plain linseed polyol–polyurethanes (LPU). Golden yellow colored LPU, Si/Lpol, and Si/LPU were finally obtained.

Fumed silica (2 and 5 wt.-%) were dispersed in Si/LPU matrix by mechanical agitation using xylene as solvent to prepare FS-Si/LPUs (2-Si/LPU and 5-Si/LPU, respectively). No phase separation was observed even on standing these systems for several days.

**Instrumentation**

FTIR measurements of Lpol, Si/Lpol, and Si/LPU were conducted on Perkin Elmer 1750 FTIR spectrometer (Perkin Elmer Cetus Instrument, Norwalk, CT) using NaCl cell having a wave number resolution of 2 cm⁻¹ at room temperature (28–30°C).

1H NMR and 13C NMR spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer. The samples were dissolved in deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) was used as internal reference.

**Physico-Chemical Analyses**

The determination of hydroxyl value, refractive index, and density involved standard ASTM laboratory methods. Viscosity measurements were performed on Anton-Paar DV2P digital viscometer equipped with a temperature controlled circulating water bath. A concentric cylinder was used to measure the viscosity under shear rate 0.17–68 s⁻¹. The lowest measurable viscosity value is 20 Poise.

Thermogravimetric analysis (TGA) was carried out by TGA 51 (TA Instrument, USA) and DSC 10 (TA Instrument) in nitrogen atmosphere to investigate the thermal degradation pattern of the polymers. The temperature at which the onset of 5 wt.-% loss occurred was taken as the initial thermal degradation temperature.

Morphological studies were carried out by transmission electron microscopy (Morgagni 268-D TEM FEI instrument, Netherlands) on a carbon coated copper grid.

X-ray diffractograms were recorded with an X-ray diffractometer (Philips model PW3710) using Cu Kα radiation.

Anti-bacterial behavior of Si/Lpol, Si/LPU, and FS-Si/LPU was investigated by agar diffusion method with dimethyl sulfoxide (DMSO) as control against standard drug amekasin. [19]

**Results and Discussion**

**Synthesis**

In situ conversion of linseed oil epoxy groups to hydroxyl functionalities was performed yielding polyol. The formation of Lpol follows simple hydroxylation reaction involving an epoxide intermediate through “single-pot, multi-step” reaction strategy [20]. This is evident from the trend followed by epoxide equivalent (EE) values with reaction time (Figure 1). EE values remain fairly high throughout the course of hydroxylation (epoxidation coupled with hydration) reaction in contrast to our previously obtained results [28]. It is assumed that the oxirane ring formed immediately gets consumed in situ through hydration; consequently very low EE value cannot be obtained. These oxirane rings present in oil backbone react with water liberated during epoxidation reaction by Si-O mechanism, leading to its hydration and then hydroxylation forming Lpol with secondary hydroxyl groups located in the middle or in proximity to C₁₈-terminal carbon of the fatty triester chains.

During the synthesis of Si/Lpol, no alcoholic solvent was used as generally required in sol–gel reactions of alkoxides for homogenization due to immiscibility of alkoxides and water. It is believed that the presence of secondary hydroxyls of oil backbone facilitates both homogenization and hydrolysis reactions in the absence of solvent [29,30].

In Si/Lpol, no phase separation occurred up to the addition of sol prepared from 0.5 mol of TEOS, which indicates better compatibility between the constituents. However, beyond 0.6 mol of TEOS, phase separation became visible in Si/Lpol. Thus all further investigative studies were carried out at 0.5 mol of TEOS composition. Figure 2 represents the proposed structure of Si/Lpol and Si/LPU.

Figure 3 illustrates the FTIR spectra of Lpol, which shows bands for –OH (3 449 cm⁻¹), C==C–Hstr (3 009 cm⁻¹), –CH₂–, –CH₃– asym str (2 926 cm⁻¹), –CH₂–, –CH₃– sym str (2 855 cm⁻¹), –C=O–ester (1 743 cm⁻¹), –(C=O–O)str (1 241 and 1 168 cm⁻¹), –O–C–C–str ester (1 098 cm⁻¹), and –C–C– (1 635 cm⁻¹).

Spectra of Si/Lpol (Figure 3) show no significant variation in the values of aforementioned absorption bands as observed previously [29,24]. However, additional bands appear at 487 cm⁻¹ (Si–O–Si bending), 800 cm⁻¹ (Si–O–Si sym str) and 1 086.5 cm⁻¹ (Si–O–Si asym str). [26]
Absorption band generally noticeable in the spectra at 950 cm⁻¹ typical of Si–OH vibrations and also those typical for ethoxy groups of TEOS are not observed in Si/Lpol indicating that i) all SiOH formed after hydrolysis of TEOS get consumed in the formation of nanosilica network and, ii) the polyol matrix does not hinder the hydrolysis or condensation reactions. The chemical reaction of secondary –OH of Lpol with silanol groups at the surface of silica nanoparticles is evident from prominent depression in the absorption band of –OH of Si/Lpol compared to Lpol. The shifting of –OH absorption band from 3 449 to 3 433 cm⁻¹ in Lpol and Si/Lpol, respectively, can be attributed to hydrogen bonding between the polyol modified silica nanoparticles and residual –OH of polyol backbone, which also has bearing on Tgs of polymers, discussed later.[24,32]

¹H NMR and ¹³C NMR spectra of Si/Lpol reveal the presence of characteristic peaks of Lpol as observed earlier.[19] However, the diminished peaks of hydroxyls and the presence of additional peaks at δ = 3.85 ppm (–CH–O–Si–) and δ = 75.2 ppm (–CH–O–Si–) confirm the incorporation of SiO₂ in Lpol backbone.

IR spectra of Si/LPU reveals characteristic peaks at 748 cm⁻¹ (Aromatic ring of TDI), 3 075 cm⁻¹, 1 608 cm⁻¹ (Ar–C=C–H bend, Ar –C=C–Hstr), 2 270 cm⁻¹ (–NCO), 1 738 cm⁻¹ (urethane carbonyl) as also observed in case of plain LPU.[3,18,19,28] ¹H-NMR spectra shows peaks at δ = 2.34 ppm (–CH₃ of TDI), δ = 7.8 ppm (–NH–(C=O)–O–) along with the diminished peaks for –OH groups attributed to the consumption of hydroxyls during urethanation reaction. In ¹³C-NMR spectra of Si/LPU, the presence of characteristic peaks at δ = 18 ppm (–CH₃ of TDI), δ = 160 ppm (–NCO urethane), and δ = 156 ppm (–NH–(C=O)–O–) also confirm the formation of Si/LPU.[3,18,19,28] Detailed discussion provided in following communication.

The spectral analysis thus confirms the formation of organic–inorganic hybrid as Si/Lpol, which was further reinforced with fumed silica by mechanical agitation resulting in the formation of organic–inorganic hybrid nanocomposites (FS-Si/LPUs).

**Physico-Chemical Analyses**

Hydroxyl value decreases from plain Lpol to Si/Lpol indicative of chemical reaction between –OH of Lpol and silanol of SiO₂ while the same from Lpol to Si/Lpol points towards the chemical reaction between –OH of Si/Lpol and...
–NCO of TDI leading to the consumption of hydroxyl moieties of Lpol or Si/Lpol. Refractive index and density also increase from Lpol to Si/Lpol and Si/LPU, which can be correlated to the inclusion of $-\text{O}^{-}\text{Si}^{-}\text{O}^-\text{ in Lpol and urethanation reaction (of Si/Lpol), respectively (Figure 4).}

Figure 5 illustrates the viscosity as a function of temperature and increases monotonically on moving from plain LPU matrix to organic–inorganic nanocomposites with the increase of fumed silica loadings. The presence of siloxane linkages and lack of complete relaxation chains contribute to the solid like response which gives rise in viscosity. It is well known that fumed silica forms three-dimensional network structures, which increases the viscosity of the system.[33] The higher viscosity of the polymers points toward the intercalation of nanoparticles in the polymer matrix, resulting in a higher mechanical integrity of the same.

Thermal Analyses

Figure 6 represents the thermograms of Si/LPU, 2-Si/LPU, and 5-Si/LPU. Si/LPU and FS-Si/LPUs thermograms reveal two stage degradation processes; the onset of first stage of thermal degradation is in the temperature range of 245–260 °C. The second stage degradation starts at 350–380 °C and extends apparently as a singular event over rest of the thermogram in Si/LPU and FS-Si/LPUs. TGA thermograms do not show any significant variation in the thermal stability of Si/LPU and 2-Si/LPU (except 5-Si/LPU) at initial decomposition temperatures. This stage is attributed to the thermal degradation of urethane linkages. At higher temperatures, improved thermal stability of the polymers is evident, which also supports the tethering of silica nanoparticles with polyol backbone. All the systems follow similar degradation mechanisms, as observed in the past.[34] However, at 5-Si/LPU, the onset of first stage decomposition occurs at 245 °C which is due to chemisorbed water as fumed silica is highly hydrophobic in nature. On higher filler content the nanocomposites showed lower thermal stability as also reported by Kashiwagi et al.[34] which can be attributed to their structural inhomogeneity.

$T_g$ of Si/LPU (Figure 7) is observed as 38 °C (well above room temperature), while 2-Si/LPU and 5-Si/LPU show glass transition temperatures as 50 and 53 °C, respectively. Subsequently, an endothermic event becomes evident in DSC thermograms due to configurational changes in polymers, followed by their thermal decomposition (urethane bonds) as observed in TGA and DTA after
240 °C. The increased \( T_g \) values also support the incorporation of silica in linseed polyol–polyurethane matrix since polyol–silica anchorage results in increased crosslinking, reduced specific volume, less motion of chains resulting in increased \( T_g \).

The first stage decomposition corresponding to 20–25% weight loss is attributed to the thermal degradation of urethane linkages while the second stage amounts to the decomposition of the rest of the resin (polyol backbone). The incorporation of nanosilica and FS in Si/LPU matrix is also supported by the amount of residue left at higher temperatures.

**X-Ray Studies**

X-ray diffractograms of Si/LPU, 2-Si/LPU, and 5-Si/LPU recorded in the range of 5–70°, illustrate a broad hump, centered at \( 2\theta \) values = 20, 20 and 18°, respectively as shown in Figure 8. These diffractograms appear identical in nature, even on varying the percentage of silica nanoparticles in the matrix. A preponderant broad hump is indicative of amorphous nature of the resin Si/LPU. Further addition of fumed silica in the polymer matrix also induces no changes in the order of nanocomposites as fumed silica is amorphous in nature.[35]

**Morphology**

Electron micrograph of Si/LPU shows the distribution of silica nanoparticles in LPU matrix indicating homogeneity between the organic and inorganic phases, which prevent the particles from aggregation. TEM micrograph of Si/LPU matrix (Figure 9) shows uniform distribution of unagglomerated, reasonably uniform and spherical silica nanoparticles of size ranging from 2–30 nm dispersed in LPU matrix. As discussed in the previous section, some Lpol segments chemically bonded to silica nanoparticles surface protect the latter from their aggregate formation.[36] Since both the polymer and fillers are amorphous in nature, so there are no crystalline domains but spherulitic structures are evident.

SEM micrograph of 2-Si/LPU show slight aggregation of fillers, which becomes highly pronounced on increasing the filler content up to 5 wt.-% indicating that with higher filler content the compatibility between the organic and inorganic matrix becomes poor because the latter form larger aggregates.

TEM images reveal the presence of carpet layer like structure with the addition of 2 wt.-% filler in Si/LPU matrix. This carpet layer like structure originated from the three-dimensional linkages of fumed silica on the polymer matrix and are like intertwined inorganic components in organic phase, only caused by the reinforcement of nanofillers while silica nanoparticles initially formed in the polyol matrix remain unagglomerated with distinct spherical boundaries and seemingly “peep” out from the filler “cloud.”

**Antibacterial Behavior**

Si/Lpol, Si/LPU, and FS-Si/LPUs show mild antibacterial behavior against *E. coli* while good antibacterial activity against *S. aureus* as shown in Table 1. The reason for the same has been well explained in our previous work reported elsewhere.[19,37] The systems reveal an excellent combination of hydroxyls, urethane, and Si component, which give synergistic effect to denaturation of bacterial proteins, disruption of cell membranes, and decomposition of essential metabolites resulting in overall cessation of cellular activities showing good antibacterial behavior toward *S. aureus*. Another reason may be the small size and large surface area of silica nanoparticles, which makes the antibacterial action more effective.
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Table 1. Antibacterial activity of Si/Lpol, Si/LPU, and FS-Si/LPUs.

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<th>Antibacterial activity</th>
<th>Si/Lpol</th>
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<td>E. coli</td>
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++, Moderately active (16–20 mm); ++++, highly active (21–30 mm).

Conclusion

Organic–inorganic hybrids were synthesized within linseed polyurethane matrix through simple sol–gel chemistry. Spectral studies reveal that the characteristic absorption bands and peaks of the virgin Lpol remain more or less unperturbed even in Si modified Lpol. XRD reveal purely amorphous nature of Si/LPU. TEM images of Si/LPU support the formation of nanosilica of size 2–30 nm. Additional loading of fillers exhibits carpet layer like structure on organic–inorganic hybrid materials, as supported by TEM. The synthesized organic–inorganic hybrid materials exhibit fairly good thermal resistivity and can be safely employed up to 240 °C. They may find application in the field of thermal resistant protective coatings and paints as discovered by our extended studies on the same, which are under the process of communication.


