



Development of functional polyurethane-cenosphere hybrid composite coatings from ricinus communis seed oil

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ABSTRACT

The usage of castor seed oil (CSO) as a sustainable and non-toxic biodegradable substitute for non-eco-friendly petroleum-based chemicals must be considered. This renewable feedstock (seed oil) is vital for developing polymeric organic coatings. This report investigates the one-spot synthesis of castor seed oil, 1,1,1-Tris(hydroxymethyl) propane (cross-linker), Isophorone diisocyanate, and cenosphere nanoparticles incorporated within the polymer matrix. The hybrid coatings were characterised using FT-IR, NMR, FESEM, and XRD. The FT-IR spectrum showing the presence of absorption peaks at 1350 cm^{-1} , 1102 cm^{-1} , and 1000 cm^{-1} , which represent the (Al=O), (SiO-Si), and (AlO₄) functional groups, respectively confirms the modifications carried out on the cenosphere fly ash nanoparticles. The thermal stability of the synthesised composites was evaluated on a thermogravimetric analyser (TGA). The TGA thermograms showed improved thermal stability as the percentage composition of CFA material increased in the coating system. The antimicrobial activity indicates that the PU-CFA composite bettered resistance toward *Staphylococcus aureus* and *Escherichia coli*.

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Introduction

The growing environmental concern (such as oil spillage, gas flaring, or industrial cum domestic waste) and the consistent fluctuating pricing surrounding the use of petroleum-based feedstock cannot be overstressed. The world economy cannot rely on this depleting natural and non-biodegradable resource material hence, the need to substitute this energy-

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driving and products feedstock with a sustainable, eco-friendly resource material like proteins, natural rubber, cellulose, starch and vegetable seed oils (VSOs) [1–2]. Vegetable seed oils {like soybean oil (SBO), linseed oil (LSO), *Thevetia peruviana* seed oil (TPSO), *Moringa oleifera* seed oil (MOSO) etc.} have successfully been used to prepare biodiesel, bone regeneration, elastomers, flooring materials, diluents, soaps, cosmetics, plastics, medical devices, lubricants and coatings [3–5]. However, the quest to develop more functional urethane coating systems from VSOs base monomers is unending. Modifications like hydroformylation, partial glyceride (PG) formation, epoxidation, aminolysis, and transesterification are ways of creating reaction sites on most triglyceride molecules (i.e. polyol) for urethanation reaction [4]. Castor seed oil (Ricinun communis seed oil {RCSO}) is a cheap, non-drying and non-edible triglyceride used to prepare various urethane coatings without prior modification. The "resident" hydroxyl functional group on its 90% ricinoleic fatty acid chain provides the natural reaction site for polymerisation. The fact that the C-12 hydroxyl group is evenly distributed within the RCSO triglyceride molecule creates a uniform crosslinking structure of synthesised polyurethane, improving mechanical properties [5–6]. RCSO has been used in preparing various resins. Karakaya et al. [7] described how ricinoleic fatty acid on RCSO trans-esterified dipentaerythritol in a one-step polymerisation reaction, forming a low viscosity air drying hyperbranched resin. This resin showed excellent flexibility, adhesion, gloss, and formability. In this work, we synthesised organic coating systems in a one-step reaction of RCSO, 1,1,1-Tris(hydroxymethyl)propane (TMP), and isophorone diisocyanate and subsequently fortified with a nanomaterial (cenosphere). TMP in this system provides matrix crosslinking within the polymer structure. This multi-functional organic compound (TMP) has been used as a precursor for the syntheses of alkyd, epoxides (ethoxylated and propoxylated derivatives), and other polyols. These polyol monomers/derivatives influence coating properties [8]. The coating property influence of inorganic nanoparticles (ZnO, SiO₂, TiO₂, Al₂O₃ etc.) and their hybrid forms must be emphasised. They provide combinational properties of organic and inorganic constituents, with an orientation towards improving coating properties like flame retardancy, conductivity, hardness, fluorescence, and antimicrobial properties [3,9]. Fly ash, a by-product of coal-fired industrial plants (about 80%) comprising a high percentage of silica (SiO₂) and alumina (Al₂O₃), has been used as a filler for polybutadiene rubber. This low-cost inorganic waste particulate matter continues to generate hazardous pollutants in various sites where coal is being used to provide electricity [10–11]. The poor management of fly ash is responsible for its anthropogenic effects on human health. Cenosphere is a vital fraction/component of fly ash; its hollow spheres are filled with inert gas and copious quantities of SiO₂ and Al₂O₃ [12]. Industries use this multi-functional filler with low-density and lightweight material to resist corrosion and reinforce materials like thermoplastics and thermosetting. In the petroleum industry, the cenosphere plays a vital role in the drilling processes (like reducing the density of petroleum cement). In the paint and coating industries, the cenosphere help in controlling infrared radiation, which limits thermal conductivity [13]. This research work attempts to investigate the influence of this filler on the properties of the synthesised coating composites. Field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) analysis, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (¹HNMR), water contact angle, and antimicrobial sensitivity test of the coating films were also evaluated.

Experimental

Materials and methods

Ricinun communis seeds were obtained from the Federal Polytechnic, Ado-Ekiti, Ekiti State, Southwestern Nigeria. The harvested seeds were handpicked to separate them from foreign materials, and the harvested seeds' pericarp (seed coats) were removed by cracking. The seeds were ground and subjected to solvent extraction in a Soxhlet apparatus with n-hexane as the solvent. Acetone, 1,1,1-Tris(hydroxymethyl)propane (TMP), Isophorone diisocyanates, and 4 methyl –2-pentanone were obtained from Sigma-Aldrich, USA. N-hexane was obtained from were obtained from S.D. Fine Chemicals, Mumbai, India. The Whatman filter paper was obtained from Whatman International Limited, Maidstone, England. Fly ash grade 5–150 μm was obtained from Swift Services, Hyderabad, Telangana State, India (Schemes 1 and 2).

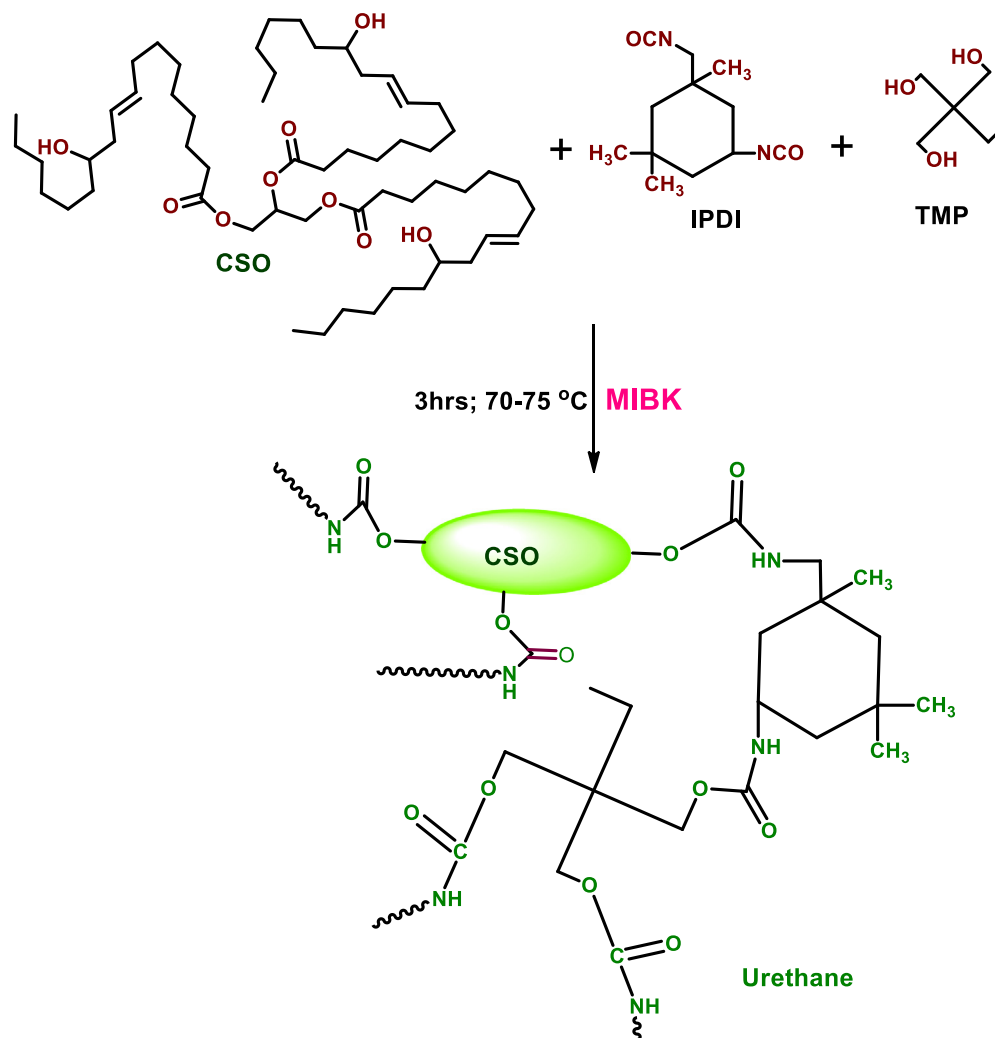
Preparation of cenosphere fly ash nanoparticles

The cenosphere fly ash was subjected to 1000 °C in an oven for 3 h to remove aluminium nanoparticles and other impurities. 70 g of this product was treated with 94 g of limestone and 42 g of soda ash. This mixture was kept in a muffle furnace for 3 h at 1000 °C. The obtained product (clinker) was treated with 5% NaOH solution in a ratio of 1:3. The slurry was subjected to continuous stirring for half an hour at 90 °C in a covered 500 ml beaker.

The product from the last step (sodium aluminate solution) was filtered using Wattman filter paper No 1, followed by batch washing with hot distilled water. This was then desalinated by adding saturated lime milk at 1000 °C for 1 hour. Aluminium hydroxide was prepared by passing carbon dioxide gas through this solution. Finally, it was sintered at 1000 °C for 3 h.

Preparation of ricinun communis seed oil polyurethane (RCSO-PU) and its composites

RCSO (4 g), 0.60 g of 1,1,1-Tris(hydroxymethyl)propane (TMP), and calculated percentages of cenosphere fly ash nanoparticles (CFA) were weighed and dissolved in about 6 ml of 4-methyl pentan-2-one. This mixture was placed in an ultrasonic

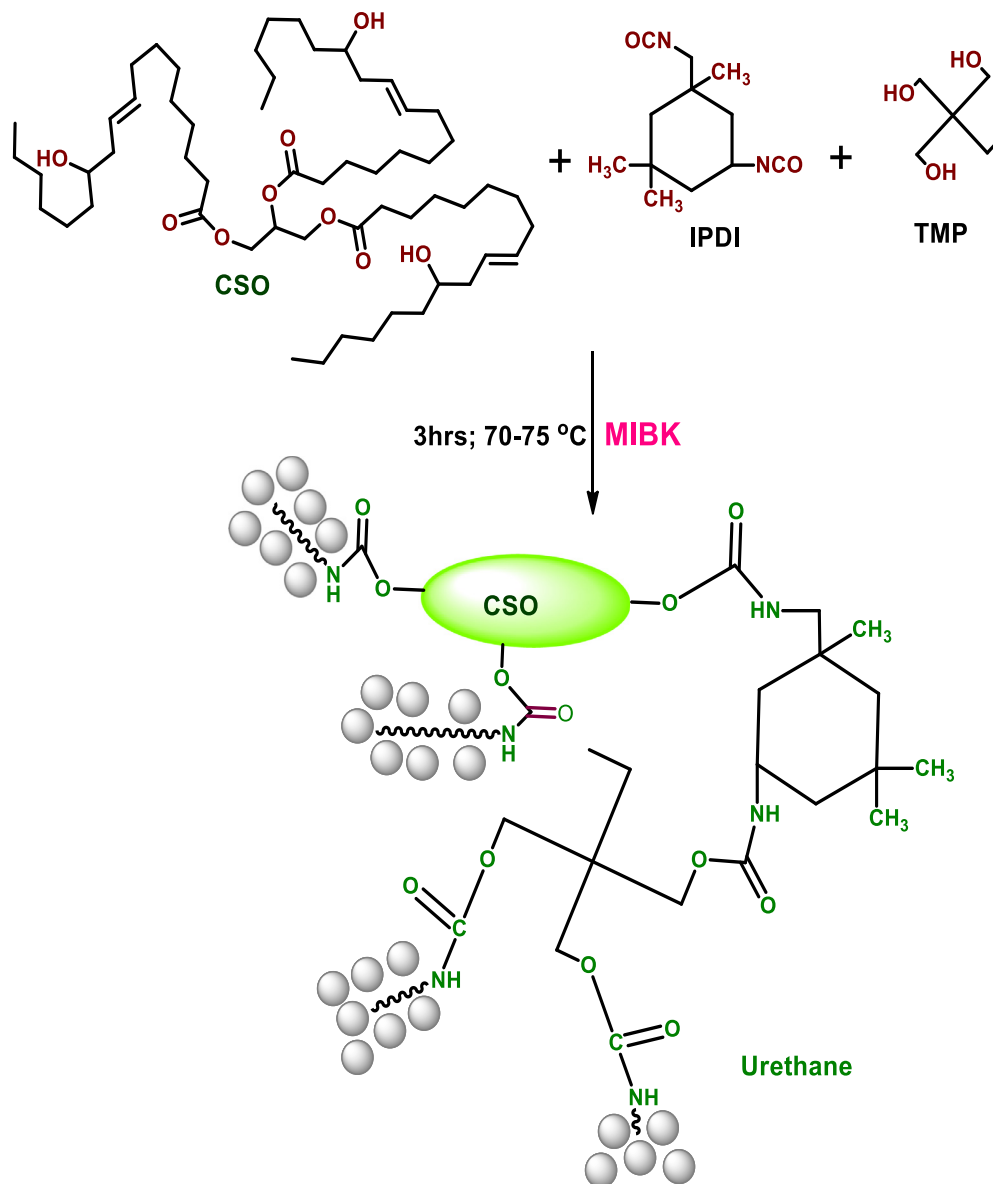


Scheme 1. Synthesis of RSCO-PU.

bath for three hours at 60 °C. A 50 ml three-neck round bottom flask fitted with a nitrogen gas inlet, thermometer, and dropping funnel; dissolved 5.20 ml of Isophorone diisocyanates (IPDI) in 4 ml of 4-methyl pentan-2-one was added under stirring. The sonicated mixture was discharged into the round bottom flask drop wisely. The content of the three-neck flask was allowed to react at 78 °C for 3 h. The reaction progress was monitored by thin-layer chromatography. The pristine and hybrid composite coating films were obtained by casting on tin foil and allowed to cool at ambient temperature. The 6 μm cured films were removed by amalgamation with mercury to get free films. These films are coded as RSCO-PU (pristine) and RSCO-PU-CFA (0.1 wt%, 0.2 wt%, 0.3 wt%).

Instrumentation

The chemical structures of synthesised hybrid polyurethane composites were confirmed on FTIR, ^1H NMR and ^{13}C NMR. Scanning eight (8) times, Perkin Elmer spectrum 100 spectrometer (PerkinElmer Inc. USA) FTIR was used to validate the functional groups in the synthesised films. ^1H NMR and ^{13}C NMR spectra were respectively recorded on Varian VXR-Unity 200 MHz spectrometer and Bruker UXNMR 400 MHz spectrometer using CDCl_3 or $\text{DMSO}-d_6$ as a solvent and tetramethyl silane (TMS) as an internal standard. The acid, hydroxyl, and saponification values of RSCO were determined by using the ASTM D1639-90 [14], ASTM D1957-86 [15], and Jacob's (1973) [16] procedures. The solubility behaviour of castor seed oil and the prepared urethane composite was investigated in DMSO, xylene, chloroform, acetone, MIBK, DMF, and ethanol [17–18]. The thermogravimetric analyser (TGA) TA Q500 (TA Instruments, Inc) with a heating rate of 10 °C/min under an N_2 atmosphere was used to evaluate the synthesised films' thermal stability thickness the coating on the panels was obtained



Scheme 2. Synthesis of RCSO-PU-CFA.

from Elcometer. The morphology of the synthesised hybrid composites (PU-CFA) films was studied using the SEM Hitachi-S520 (Oxford link ISIS-SEM model). Siemens D-5000 X-ray diffractometer with Cu $K\alpha$ radiation of a wavelength of 1.54 nm was used to analyse the XRD patterns of CFA and PU-CFA. Water contact angle measurements were carried out on Goniometer (model-IL4201 DSA) from Krüss GmbH, Germany. In-vitro antimicrobial activity of the synthesised polymers was examined and tested against Gram-positive organisms; *Bacillus subtilis* (MTCC 441), *Staphylococcus aureus* (MTCC 96), and Gram-negative organisms; *Escherichia coli* (MTCC443), *Klebsiella pneumonia* (MTCC 618) [2]. The prepared nutrient agar was suspended in distilled water (1000 mL) and heated to boiling until it dissolved utterly; the medium and Petri dishes were autoclaved at a pressure of 15 lb./in² for 20 mins. The medium was poured into sterile Petri dishes in a laminar airflow chamber under aseptic conditions. When the medium in the plates solidified, 0.5 mL (approx. 10^6 CFU ml⁻¹) of a culture of test organism was inoculated and uniformly spread over the agar surface. The sterile L-shaped rod-embedded polymer samples with 2 cm × 2 cm (approx.) samples were washed with double distilled water, placed on the medium, and incubated at 37 °C (bacteria) for 24 h. Antimicrobial evaluations were performed based on the formation of inhibition zone loss of organism growth beneath and surrounding the films placed on an agar medium. Three replicates were maintained for each treatment. MTCC is a microbial-type culture collection in IMTECH (CSIR LAB) Chandigarh, India [2,19].

Table 1Physicochemical properties comparison between castor oil, soybean oil, *Thevetia oleifera*, Linseed oil and *Moringa oleifera*.

Physicochemical properties	RCSO	SBO [20]	TPSO [2]	LSO [19]	MOSO [18]
Acid value (mg KOH/g)	0.852	0.4	2.3	8.3	3.5
Saponification value (mg KOH/g)	182	159.4	193.6	160	180.31
Iodine value (g _I /100 g)	79.09	109.00	74.9	181	80.1
Viscosity [(cSt) at 40 °C]	198.5	N.D	35.1	N.D	60
Refractive index (40 °C)	1.4723	1.473	1.4411	1.478	1.450
Moisture content (%)	0.3	0.8	N.D	18	N.D
Hydroxyl value (%)	165	N.D	3.1	0.3	N.D

N.D: Not Determined.

Table 2

Physicochemical evaluation of CSO and PU-CFA solubility property.

Sample	DMSO	Xylene	Chloroform	Acetone	MIBK	DMF	Ethanol
RCSO	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Partially Soluble
PU-CFA	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Not Soluble

Results and discussion

Physicochemical analysis of RCSO

Table 1 compares the physico-chemical structural indices such as acid, iodine, saponification and hydroxyl values of RCSO with that of Soybean oil (SBO), Linseed oil (LSO), *Thevetia peruviana* seed oil (TPSO), *Moringa oleifera* seed oil (MOSO). RCSO, like SBO, TPSO, and MOSO, is categorised as non-drying seed oil because its iodine value is less than 115 g_I/100 g. The 0.852 mg KOH/g acid value of RCSO is low compared to that of LSO, MOSO, and TPSO. A lower acid value of RCSO indicates fewer free fatty acids that undergo rancidification upon exposure to air, light, moisture, or bacterial action, reducing the shelf life [21]. The high saponification value (182 mg KOH/g) suggests using RCSO to produce shampoos, liquid soaps, and shaving creams. The refractive index (1.4723) reflects the oil saturation level. The solubility properties of RCSO were examined in various solvents like acetone, diethyl ether, toluene, methanol, ethanol, chloroform, MIBK, dimethylformamide (DMF), xylene, and DMSO. The test was performed by taking 0.1–0.2 g of RCSO and PU-CFA sample in 10 ml of solvent, stirring well for up to 15 mins, and heating if necessary. RCSO, like LSO, MOSO, and SBO, etc., have excellent solubility in all the solvents (**Table 2**). Pictorial representation (i.e. transparency retention) of the coatings under investigation is presented in **Fig. 1**. The films all showed bright clarity, but as the percentage composition of CFA increases, a faint yellowish colouration is observed mainly in **Figs. 1B, 1C, and 1D**. The composites' clarity and non-foggy picture suggest an even distribution of the nanoparticles.

Spectroscopic characterisation of RCSO

The FTIR spectrum of RCSO in **Fig. 2A** shows the various functional groups present in the oil. The characteristic broad absorption band of a secondary -OH functional group on the ricinoleic fatty acid chain is 3410 cm⁻¹. The stretching asymmetric and symmetric methylene (CH₂) bands appear respectively at 2926 cm⁻¹ and 2854 cm⁻¹. The respective strong stretching frequency of ester carbonyl (C=O) and C-O was observed at 1710 cm⁻¹ and 1210 cm⁻¹. Alkene bending (=C-H) and stretching (C=C) vibrations resonate at 869 cm⁻¹ and 1621 cm⁻¹. These RCSO FTIR vibrational peaks are typical for most fatty acids except for the presence of the -OH functional group present in ricinoleic fatty acids.

Spectroscopic characterisation of RCSO-PU and RCSO-PU-CFA

Fig. 2B presents the FTIR spectrum of pristine synthesised urethane (RCSO-PU). The stretching absorption bands 3349 cm⁻¹ and 1718 cm⁻¹ represent urethane N-H and C=O, respectively, and the disappearance of the isocyanate (-NCO) peak within the region of 2100–2270 cm⁻¹ confirms the complete urethanation reaction of the coating system [3] -NH of amide and fatty acid alkene =CH bending vibrations occurs at 1510 cm⁻¹ and 812 cm⁻¹ respectively. In **Fig. 2C**, absorption peaks at 1350 cm⁻¹ correspond with (Al=O) stretching peaks. Also, the AlO₄ and Si-O-Si stretching peaks were observed at 1000 cm⁻¹ and 1102 cm⁻¹, respectively, confirming the formation of the hybrid polyurethane with CFA nanoparticles (PU-CFA). Similar peaks present in **Fig. 2B** are also present in **Fig. 2C**.

The proton NMR spectrum of the pristine polyurethane (PU), as presented in **Fig. 3**, further confirms the formation of the polyurethane. The hydrogen linked to the urethane functional group (-N-H) confirms the polyurethane formation is observed at $\delta = 7.11$ ppm, 7.55 ppm, and 6.76 ppm [1,2,3]. The observed variations of this chemical shift are due to their different

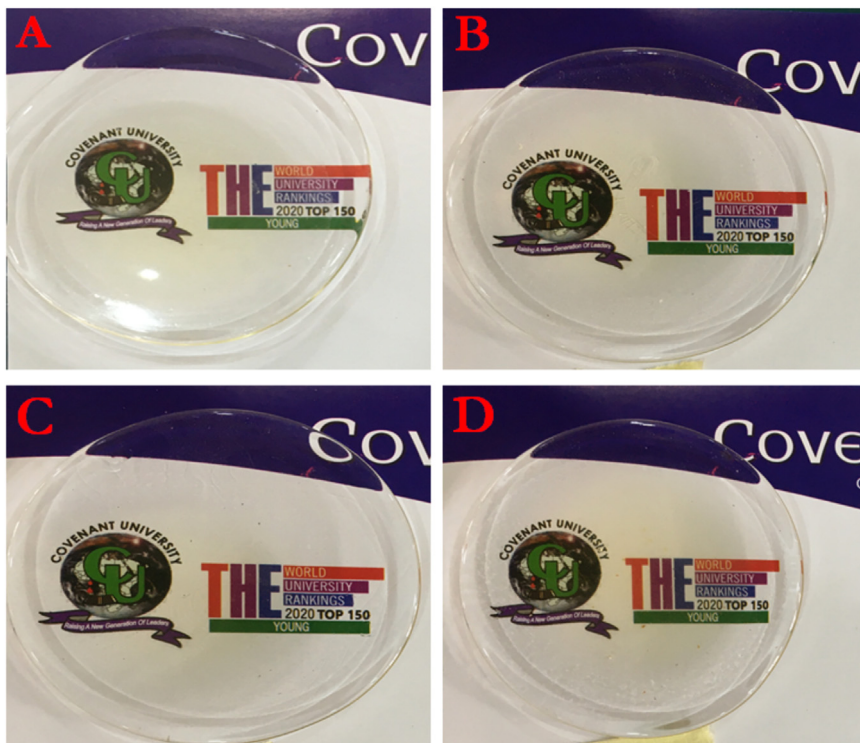


Fig. 1. Photograph showing transparency retention test.

chemical environments. The fatty acid chain's methyl ($-CH_3$) terminal protons, TMP and IPDI are observed at $\delta = 0.88$ ppm, 0.83 ppm, and 0.87 ppm, respectively. The hydrogen of the methine group ($=CH$) appears at $\delta = 5.36$ ppm.

The structural reassertion of the synthesised urethane is presented in Fig. 4 (^{13}C NMR). The chemical shift at 22.7 ppm - 38.5 ppm represents various methylene carbon ($-CH_2-$) on the fatty acid chain of the seed oil as well as that of the cyclohexyl ring of the isophorone diisocyanate. The fatty acid terminal methyl carbon ($-CH_3$) resonates at $\delta = 14.1$ ppm while the double carbon ($-C=C-$) on the fatty acid chain was observed at 122.4 ppm and 133.5 ppm. The structure's urethane amide carbonyl linkages ($-OOC-NH-$), which represent the principal signal for urethane formation, were observed from 155.6 ppm to 158.6 ppm.

Morphology analysis

The FESEM-EDX analysis carried out shows the surface morphology and the elemental composition of the Cenosphere fly ash nanoparticle and PU-CFA as demonstrated in Fig. 5. Fig. 5A, B, C, and D show the FESEM image of CFA, PU-CFA, EDX of CFA and EDX of PU-CFA respectively. The FESEM of PU-CFA shows the even distribution of the CFA nanoparticles within the polymer matrix of the urethane films (Fig. 5D and E). The films' non-agglomeration accounts for the composites' uniform evaluation of the test samples. The EDX percentage weight of carbon in PU-CFA is observed to have increased from 15.3 Wt.% to 40.2% in CFA. In the EDX of PU-CFA, there is a decrease in the percentage weight of oxygen, aluminium and silica from 43.9 Wt.%, 13.8 Wt.% and 15.6 Wt.% to 38.7 Wt.%, 2.8 Wt.%, and 4.6 Wt.%, respectively, compared to the EDX of CFA. The observed differences in the EDX results confirm the formation of hybrid coating composites (PU-CFA).

Thermogravimetric (TGA) and differential thermogravimetric (DTA) analyses

The TGA provide information on several polymeric phenomena, which include percentage weight loss, desorption of contaminant, degradation, and sorption of gases. The thermal stability studies of the synthesised coating films {PU (Pristine), PU-CFA (0.1 wt%) and PU-CFA (0.2 wt%)} were evaluated in a nitrogen atmosphere at a heating rate of 10 °C/min. The overlaid thermograms (TGA and DTA) are presented in Figs. 6 and 7, respectively. Peculiar to polyurethane coatings systems, these thermograms showed three (3) stage degradation steps (T_{1MAX} , T_{2MAX} and T_{3MAX}), corresponding to that of urethane, urea, and ester segments of the coating system [21]. Seed-oil polyurethane coatings systems usually have low thermal stability, which may be due to urethane bonds present in the system. The usual onset dissociation of the urethane bond at about 220 °C [21] is improved by doping the polymeric matrix with cenosphere material (Table 3). PU-CFA (0.1 wt%) and PU-CFA (0.2 wt%) respectively have onset degradation values at 282.57 °C and 287.41 °C; these values show better thermal

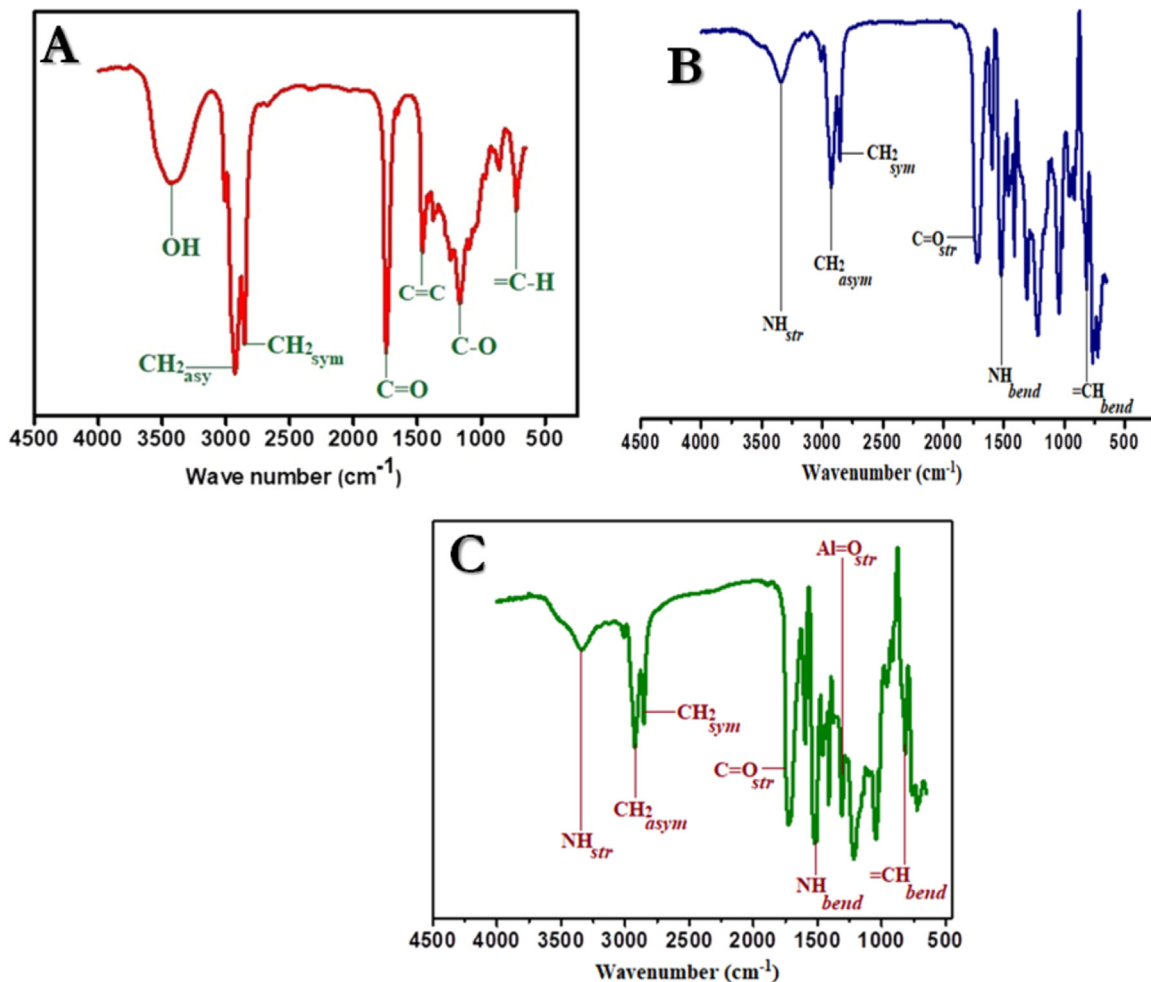


Fig. 2. (A) FTIR spectrum of the RCSO. (B) FTIR spectrum of RCSO-PU. (C) FTIR spectrum of RCSO-PU-CFA.

Table 3

Thermogravimetric comparison between PU and its hybrid forms.

Sample codes	T_{ON} (°C)	T_{1MAX} (°C)	T_{2MAX} (°C)	T_{3MAX} (°C)	T_{END} (°C)	Weight Loss (°C)		
						25%	50%	75%
A	234.14	332.61	385.88	478.69	534.38	467.73	400.92	348.31
B	282.57	333.42	389.10	481.11	541.64	472.97	406.69	351.62
C	287.41	332.62	387.49	477.08	531.96	473.60	415.76	361.54

A = PU (Pristine), B = PU-CFA (0.1 wt%), C = PU-CFA (0.2 wt%).

stability than that of the pristine urethane film (234.14 °C) (Fig. 6). The incremental weight loss percentage values at 25%, 50%, and 75% (Table 3) indicate the stabilisation tendencies of the doped material as its percentage content increases in the urethane system.

Water contact angle

The hydrophobicity test of prepared polyurethane (PU) and its hybrid forms (PU-CFA 0.1 wt% and PU-CFA 0.2 wt%) are presented in Fig. 8. The water contact angle of the coating films under study increases as the weight percentage of CFA increases in the polymer matrix. PU-CFA 0.2 wt% film has the highest value of 80.3°, while the pristine urethane has the least value (74.2°). This observation corroborates the research findings of Yao et al. (2015) [22].

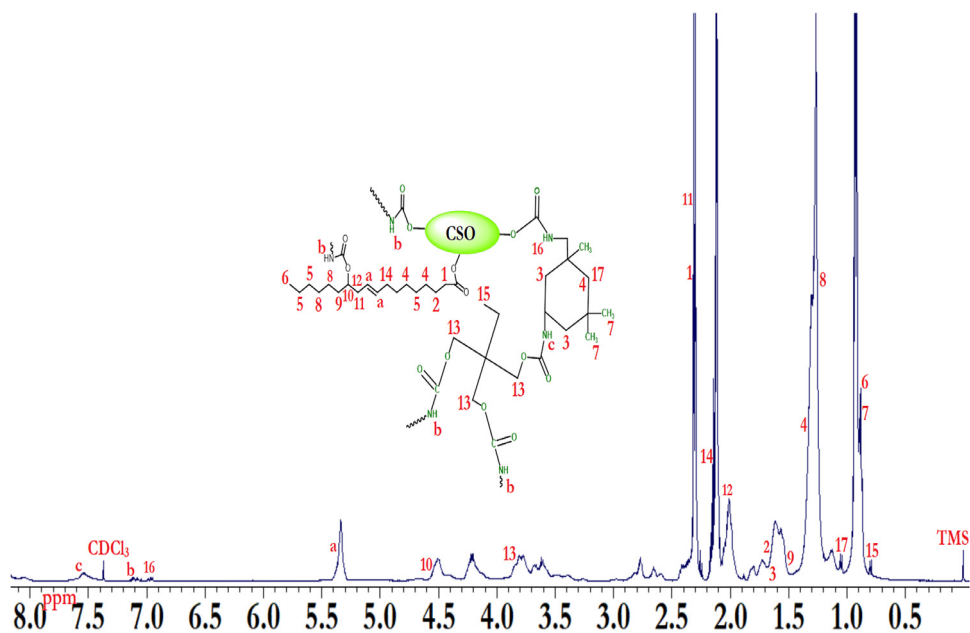


Fig. 3. ^1H NMR spectrum of RCSO-PU.

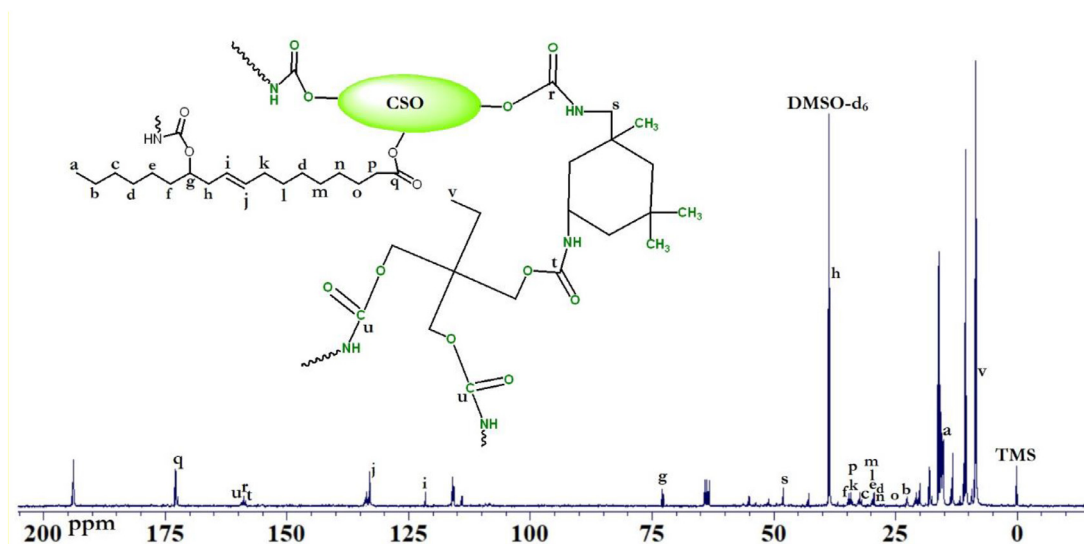


Fig. 4. ^{13}C NMR spectrum of RCSO-PU.

Antimicrobial evaluations

The antimicrobial activities of the pristine (PU) and the CFA-doped urethane systems are presented in Table 4. The activities of the polyurethane films were examined on common pathogenic organisms like *E. coli*, *Klebsiella pneumonia* (gram-negative), *Staphylococcus aureus*, and *Bacillus subtilis* (gram-positive) [2,23]. Czapek–Dox medium was used to grow all the bacterial and fungal stains. The formation of the inhibition zone beneath and in the surroundings of the coating films was used to estimate the microbial activities of the films. The films under investigation all showed zero activity for *Bacillus subtilis*. The hybrid composite films (PU-CFA 0.1wt% and PU-CFA 0.2 wt%) displayed the most active inhibition zones on *E. coli* and *Staphylococcus aureus* organisms. Notably, these hybrid films showed poor activities for *Aspergillus niger*.

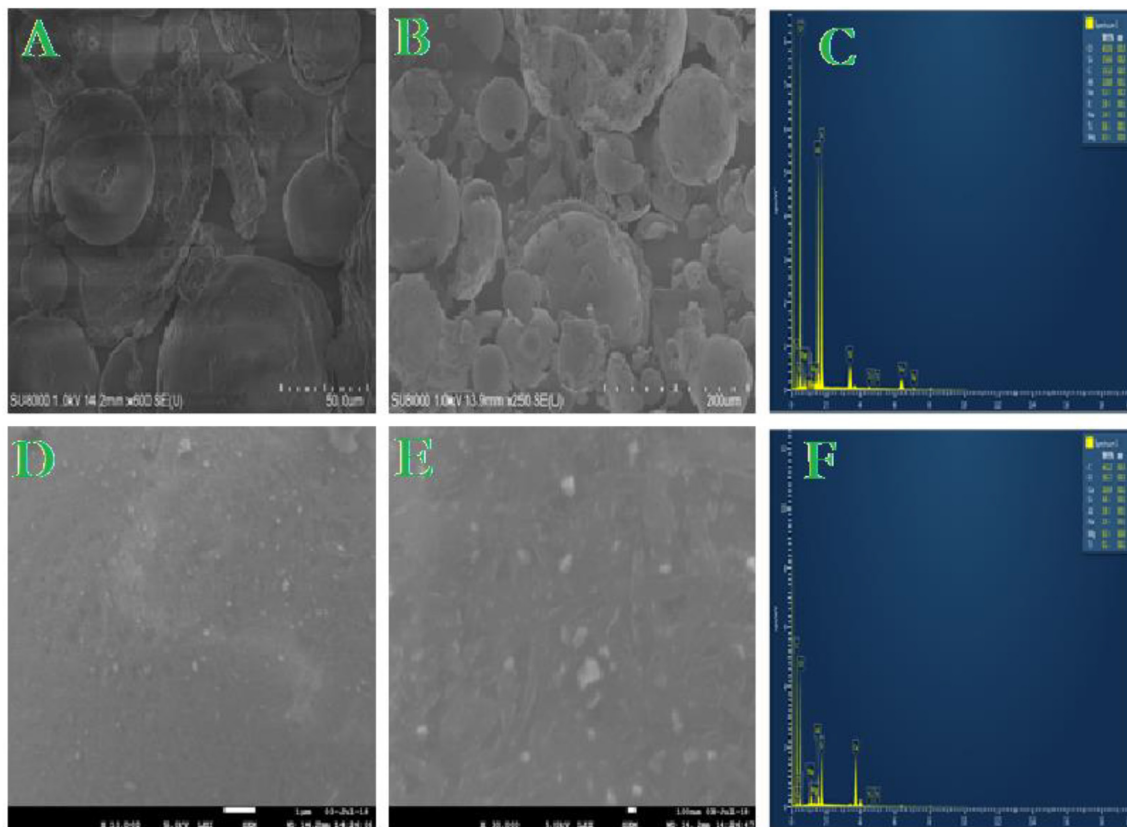


Fig. 5. The FESEM micrograms of A= CFA 50 μm , B= CFA 200 μm , and C= CFA-EDX, D= PU-CFA 0.1 wt%, E = PU-CFA 0.2 wt%, F = PU-CFA 0.1 wt%-EDX.

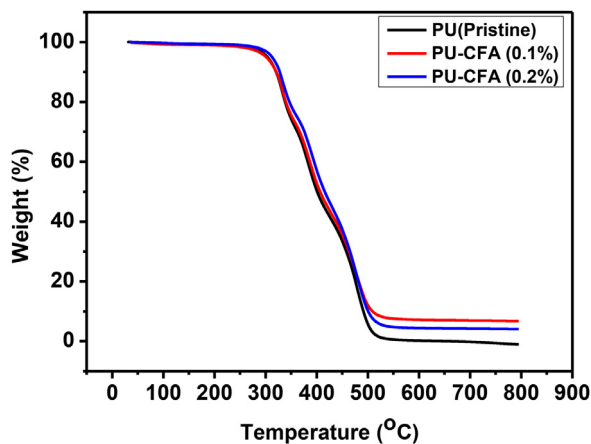


Fig. 6. TGA thermograms for synthesised PU and its hybrid forms.

Table 4
Antimicrobial activities of PU and PU-CFA hybrid coatings.

Samples	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>B. Subtilis</i>	<i>A. Niger</i>
PU	+	++	+	-	-
PU-CFA 0.1 wt%	++	+++	++	-	+
PU-CFA 0.2 wt%	+++	+++	++	-	+

- Inactive.
+ Poorly active.
++ Mildly active.
+++ Moderately active.

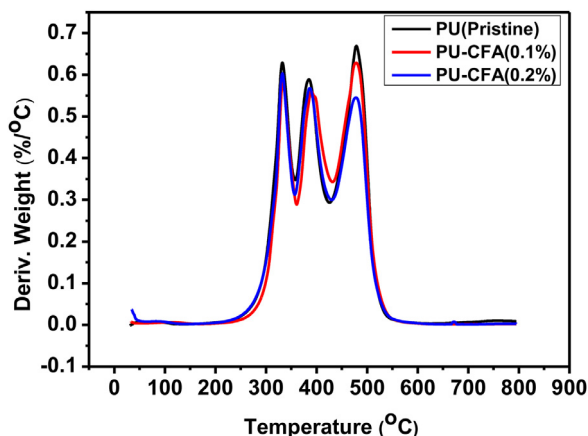


Fig. 7. Overlay DTA thermograms for synthesised PU and its hybrid forms.

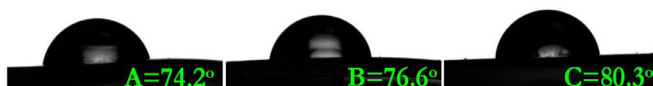


Fig. 8. Contact angle of A= PU, B= PU-CFA 0.1 wt%, C= PU-CFA 0.2 wt%.

Conclusion

Incorporating CFA within the one-pot polymer matrix of PU (RCSO, TMP, and IPDI) was successful. Spectroscopic analysis like the FT-IR and NMR confirms the pristine and hybrid PU formation. The ultrasonication machine facilitates uniform dispersion of the nanoparticles within the polymer matrix. The air-drying hybrid composites prepared from RCSO-based urethane showed improved thermal stability, antimicrobial (except *B. subtilis*), and water contact angle properties. PU-CFA 0.2 wt% film showed a water contact angle of 80.3° compared with 74.2° for the pristine film. The pristine and hybrid films displayed poorly and mild activities for *Pseudomonas aeruginosa*, which is better than that prepared by Kenawy et al. [23].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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