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Synthesis of Castor Oil based Pristine and Silver Nanoparticle Embedded Polyurethanes and their Characterization by Thermal and Antibacterial Activity Analysis for Biomedical Applications

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Ecofriendly and sustainable pristine and silver nanoparticle embedded polyurethanes (PUs)/polyureas were synthesized by using the renewable castor oil as the main component, 1,6-hexane diol, poly(propylene glycol) and poly(propylene glycol)-*bis*-2-amino propyl ether as chain extenders, trimethylolpropane/or glycerol as cross linkers and toluene diisocyanate and dibutyltindilaurate as curator and catalyst, respectively. The prepared PUs were characterized for their thermal degradation by simultaneous TGA/DTA, structural features by FT-IR and antibacterial activity against *Bacillus subtilis* and *E. coli*. The onset degradation temperature (265-269 ºC) of the PUs was much lower than the onset weight loss temperature of castor oil. In air, the thermal degradation was exothermic at temperatures beyond 300 ºC. Unlike the pristine PUs, AgNPs embedded PUs displayed antibacterial activity and comparatively lower degradation temperature due to the catalytic effect of silver nanoparticles (AgNPs). These PUs may be used for various biomedical applications such as antibacterial foam, antibacterial scaffold, body implant, food packaging, wound dressing, *etc*.

Keywords: Castor oil based polyurethane, Urea-link, Antibacterial activity, Thermal analysis, Silver nanoparticle.

INTRODUCTION

Polyurethanes (PUs), a major family of versatile polymers are prepared from the petroleum derived chemicals such as polyol and a polyisocyanate (di- or tri-) and a chain extender such as 1,4-butane diol or 1,6-hexane diol *via* step growth polymerization [1-8]. The polyol, and the diisocyanate and chain extenders generate the soft and hard segments as micro domains in PU chain, respectively [5,8]. These imparted PUs a wide spectrum of physico-chemical, mechanical and structural properties such as low flexibility, high tensile strength, good tear, abrasion and solvent resistances, *etc.* which made their extensive diverse applications in different manipulated forms such as rigid and flexible foams, fibre, adhesive, sealants, coatings, elastomers, *etc*. The hard segments, provide physical crosslinks *via* H-bonding to impart properties ranging from elastomeric to rigidity depending upon its contents. Polyurethane occupies almost 5% of global polymer product and are used in our daily life for different uses such as furniture, construction, footwear, automotive and transportation, electronics, heat insulation, packaging, biomedical, *etc*. [9-11] and many of these PU products have poor biodegradability. Polyurethane is also used as a biomaterial in the preparation of implants and medical devices since decades owing to their biocompatibility, tailorable chemical and physical forms and hydrolytic biodegradability. Polyurethanes can be modified by the introduction of biomolecules (polysaccharides, proteins, lipids) that can enhance their biocompatibility (cell, blood or tissue compatibility). Some of the biomedical applications of PUs include antibacterial surfaces and catheters, drug delivery vehicles, vascular stents, surgical dressings/pressure sensitive adhesives, tissue engineering scaffolds and electrospinning, nerve generation, cardiac patches, dressings, artificial organs and PU coatings for breast implants. Polyurethane structures with precise tissue biomimicking can be obtained with adequate adhesion, proliferation and differentiation of many types of cells [10-13].

But the high rising costs of petrochemical feedstock, dwindling fossil fuel sources and the enhanced global desire for environmentally friendly green products have created a thrust to use renewable resources for manufacturing ecofriendly PU. The current varieties of biomass available have extended the diversity of starting materials for the development of bio-based

PUs with advanced properties such as controlled biotic and abiotic degradation. In this direction vegetable oils have been identified and investigated as one of the most promising raw materials out of all agricultural feed stocks to produce bio based polyol for PU manufacture due to their abundance, inherent biodegradability and low price [4-6,10,14-19]. Among the vegetable oils, castor oil is only one of the oils which naturally contains hydroxyl groups [19], and hence it can be directly used as a polyol for PU preparation with a uniform integrated network and good mechanical properties. Even though significant research on renewable PU has been reported, renewable PU are still a niche market till now and account for only 0.1% in the approximately 20 million tons of PU produced per year [20]. Castor oil is one of the major natural vegetable oils that is widely used in chemical industries specifically for the production of PUs [21-25]. The castor oil triglyceride is characterized by the presence of 18 carbon ricin oleic acid to the extent of 90% and this contains a double bond at the 9th and 10th carbon and an alcohol functional group on the 11th carbon. Typically, the castor oil contains about 2.7 hydroxyl groups per triglyceride and it also has a low hydroxyl number [21]. Polyurethanes market size exceeded US $ 59.5 billion, globally in 2018 and is estimated to grow at over 5.8% CAGR between 2019 and 2026 [26-28].

EXPERIMENTAL

Castor oil purchased from local shop was dried under vacuum at 60 ºC and used. 1,1,1-trimethylolpropane (Cross linker, TMP), poly(propylene glycol) (PPG, M_n: 2000), poly(propylene glycol)-*bis*-2-amino propylether (PPG-*bis*-2-APE, M_n:2000) and 1,6-hexane diol (chain extenders) (Sigma-Aldrich) were dried under vacuum at 40 ºC and used. Silver nitrate (Himedia), sodium borohydride ($NaBH_4$, NICE), dibutyl tin dilaurate (DBTDL catalyst, Aldrich), dimethyl formamide (DMF, NICE), nutrient broth and Mueller Hinton Agar (HI MEDIA) were used as received. Neem leaves were collected from a local neem tree to prepare the leaf extract in water. Since > 90% of castor oil is glyceryl triricinoleate, its structure is given in Fig. 1 along with the structures of other chemicals used to synthesis PU in the present work.

The hydroxyl value of castor oil was determined as reported procedure [29] and the determined hydroxyl value was 164.1. The proportions of different components used to synthesis PUs (PU-1 to PU-7) are furnished in Table-1. Silver nitrate and sodium borohydride solutions of concentration 0.002 M were prepared in Millipore water and used throughout the experiments. Mother cultures of *Escherichia coli* and *Bacillus subtilis* were cultured from glycerol stock of our Institute's microbiology lab as per the standard procedure.

Preparation of neem leaf extract: Fresh neem leaves were collected and washed in running water to remove dirt and dust from the surface of leaves. The leaves were then washed with Millipore water, air dried and powdered. Neem powder (20 g) were added to 100 mL of distilled water and boiled for 15 min. The extract was cooled, filtered and stored for further use.

Synthesis of polyurethane (PU): Castor oil based PUs with different formulations were synthesized as per the composition shown in Table-1. A known amount of the dried castor oil was taken in a disposable plastic beaker or ice cream paper

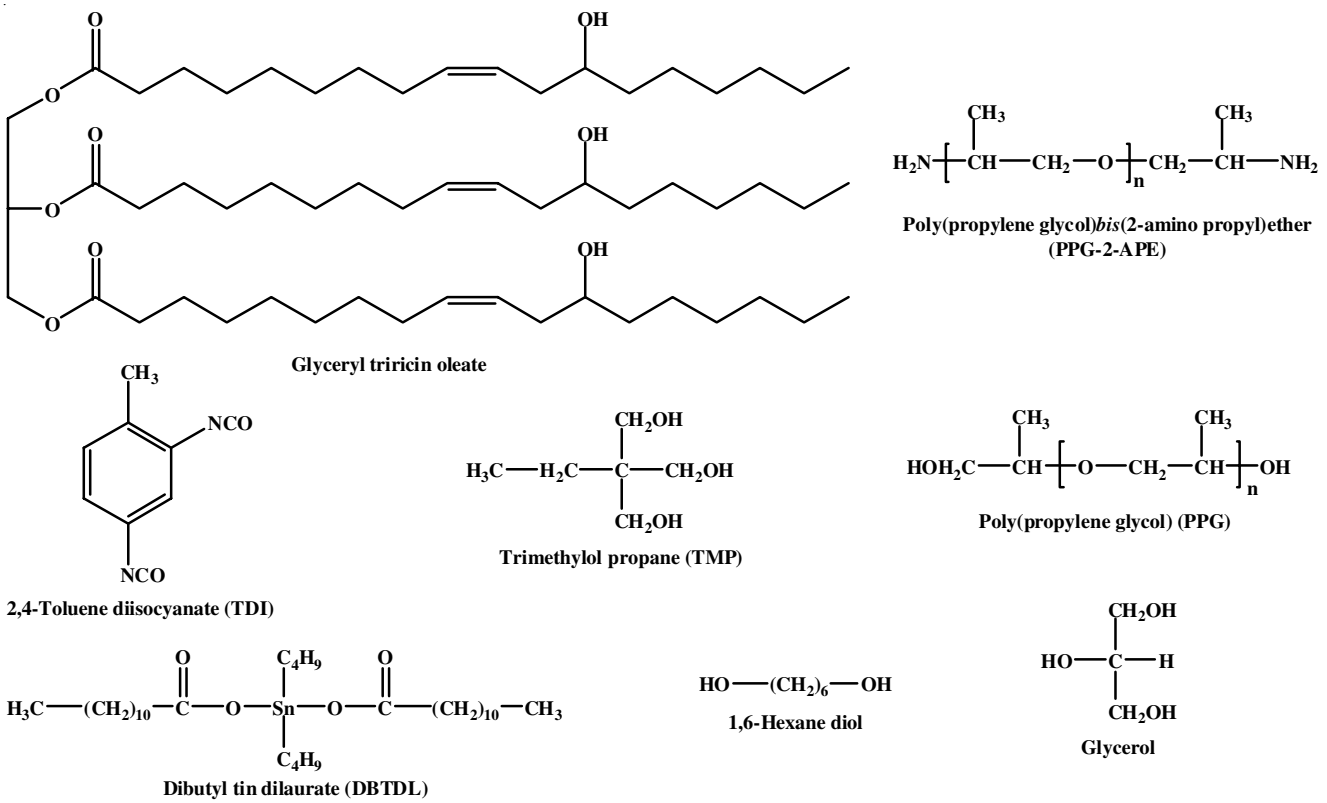


Fig. 1. Chemical structures of castor oil and other chemicals used in the synthesis of polyurethane

TABLE-1
COMPOSITIONS OF INGREDIENTS FOR POLYURETHANES, PU-1 TO PU-7

PU sample	Castor oil (g)	TMP (g)	1,6-Hexane diol (g)	PPG (g)	Glycerol (g)	PPG-*bis*-2-APE (g)	DBTDL (g)	TDI (g)
PU-1	5.0	0.001	0.02	–	–	–	0.045	1.310
PU-2	5.0	0.001	–	–	–	0.035	0.045	1.310
PU-3	5.0	–	0.02	–	0.00068	–	0.045	1.303
PU-4	5.0	–	–	–	0.00068	0.035	0.045	1.303
PU-5	5.0	0.001	–	0.6060	–	–	0.045	1.303
PU-6	5.0	–	–	0.6060	0.00068	–	0.045	1.303
PU-7	7.3	0.0007	0.01	–	–	–	0.045	0.680

cup. To this a known amount of dry TMP, 1,6-hexane diol and a drop of DBTDL were added and homogenized by mixing at 45 ºC. The viscous mass thus obtained is deaerated under vacumm in a desiccator to remove the entrapped air bubbles. Then a calculated quantity of TDI equivalent to the sum of the hydroxyl values of the all ingredients in the chosen composition was added and mixed thoroughly using a glass rod and then deaerated under vacuum for 1 min at room temperature and allowed to cure at room temperature (33 ºC) for 12 h. The cured PU was peeled out from the container cup. The PUs thus prepared for various compositions are designated as PU-1 to PU-7 and were used for characterization.

Silver nanoparticle (AgNP) embedded PU: AgNP was incorporated into the synthesized PU by both chemical and biological methods [30-32] *via* inter matrix synthesis approach [33,34].

Chemical method: A small piece of PU (0.504 g) was cut from each of the prepared PU samples and immersed in 4 mL of DMF/water (3/1 v/v) in a 20 mL stoppered tube and allowed to swell overnight. To this 2 mL of ice cold silver nitrate solution (0.002 M) was added and left aside for 2 h. Then the tube was cooled in an ice bath and 5 mL of ice cold $NaBH_4$ solution was added and incubated under dark condition at room temperature. The silver ions imbibed in to the PU matrix were reduced to nano silver as per the following chemical reaction:

$$AgNO_3 + NaBH_4 \longrightarrow Ag + ½\ H_2 + ½\ B_2H_6 + NaNO_3$$

and get embedded into the PU indicated by the dark brown colour. AgNP embedded PU-1 to PU-6 prepared using $NaBH_4$ reduction were designated as Ag-C-PU-1 to Ag-C-PU-6.

Biological method: About 0.504 g from each of the synthesized PU samples were immersed in 4 mL of DMF + water (3:1 v/v) in separate test tubes covered with black papers. To each of the test tube 2 mL of ice cold silver nitrate solution (0.002 M) was added and allowed to equilibrate for 4 h in ice bath. To this 5 mL ice cold neem leaf extract was added and incubated. The silver ions penetrated into the matrix of the PU were reduced to nano Ag and get entrapped into PU and the PU and the solution become mild dark brown in colour due to the formation of AgNPs [17]. AgNP embedded PU-1 to PU-6 prepared using neem extract were designated as Ag-P-PU-1 to Ag-P-PU-6.

Antibacterial activity: The PUs synthesized were cut into 15 mm diameter disks (of thickness 3 mm) using a 15 mm cylindrical paper punching machine and the cut samples were then vacuum dried overnight at 60 ºC and then sterilized both by immerzing in 70% ethanol for 30 min and exposing to UV radiation on both of their sides for 15 min.

Culture media preparation: The pure cultures of Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli* species were collected from the glycerol stock from our microbiology laboratory and their sub-culture were prepared in nutrient broth and incubated for 24 h and stored.

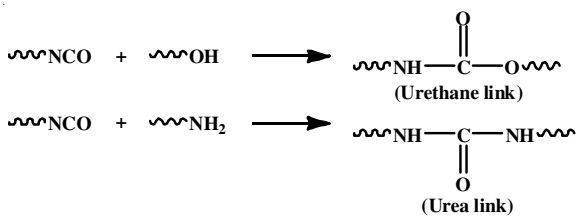
Antibacterial activity by agar disk diffusion method: The media Mueller-Hinton agar was prepared and autoclaved as per standard procedure. Sufficient quantity of the prepared agar was taken in sterile petri dish of diameter 10 cm under sterile and aseptic conditions and allowed to solidify under Laminar air flow chamber. The thickness of the agar taken in the petri dish was around 4-6 mm. Then the sub-cultured microbes namely *Bacillus subtilis* and *Escherichia coli* were inoculated on the surface of Mueller-Hinton agar plate evenly *via* streaking the microbial broth suspension using a sterile cotton swab in 3 planes to cover the entire surface uniformly by the microorganism and allowed to dry for 5 min. Using a sterile knife, a small circular pit of diameter < 5 mm and depth < 1 mm was created on the agar surface to introduce the sterilized virgin and AgNP embedded PU samples. Then the petri dish was incubated for 24 h at 37 ºC. The antibacterial AgNP from PU diffuses into the agar medium and inhibits the proliferation and growth of microorganism. The zone of inhibition was measured.

Simultaneous thermogravimetric-differential thermal analysis (TGA-DTA): Simultaneous TG/derivative thermogravimetry (DTG) and DTA were performed in nitrogen (& air) in the temperature range 27-650 ºC at a heating rate of 10 ºC per min on NETZSCH STA 2500 Regulus (GERMAN) for a sample size 3-9 mg using alumina crucibles as sample holder and reference. The thermograms were analyzed and overlayed using the proteous software supplied with the equipment. The flow rate for nitrogen (99.999%) and air (N_2/O_2, 80/20) as purge gases was 60 mL/min. The flow rate of protective nitrogen gas was 40 mL/min. Temperature calibration was done using the pure metals In, Ag, Au, Cu, Al, *etc*. as standards. The thermal stabilities of PUs were determined by the measuring their onset degradation temperatures from the TG/DTG traces.

RESULTS AND DISCUSSION

Polyuretane reaction with castor oil: Hydroxyl (-OH) and amino ($-NH_2$) functional groups will react with isocyanate

(-NCO) to form urethane and urea linkages respectively as shown below:



In formulations PU-2 and PU-4 (Table-1), a diamino chain extender namely PPG-*bis*-2-APE has been used instead of 1,6-hexane diol. A diamino chain extender will give urea linkage and hence PU-2 and PU-4 are poly(urethane/urea) polymers and other formulations are pure PUs. The chemical reactions involved in their formation are furnished in Fig. 2. The hydrolytic stabilities of urea and urethane linkages are roughly nearer to that of peptide bonds in protein and hence they hydrolytically biodegrade under biological and soil environments. Since castor oil based PUs also contains ester links, they are also hydrolytically biodegradable. On these grounds, the PU-1 to PU-7 made in present study may be assumed to be ecofriendly biodegradable PUs. But their rate of biodegradation is affected by cross-links and other structural features.

FT-IR (ATR) spectra of castor oil and PU: FT-IR spectra of castor oil and representative FT-IR spectra of castor oil based PU are shown in Fig. 3. The assignment of peak frequencies [35-41] taken from the recorded FT-IR spectra of PU samples prepared from castor oil, TDI, chain extenders, TMP, *etc*. are furnished in Table-2. FT-IR spectra of PU samples do not show any band in the frequency regions 2313-2260 cm^{-1} confirming the absence of isocyanate group, which indicated the completion of urethane and urea links forming reactions. The IR absorption frequencies in Table-2 also revealed the presence of the most important stretching frequencies due to $>CH_2$, urethane (-N-H & -NH-C(=O)-O-), >C=O (urethane & ester, carbonyl), C-N, C-O and C-O-C groups/bonds [35-41] in the PUs.

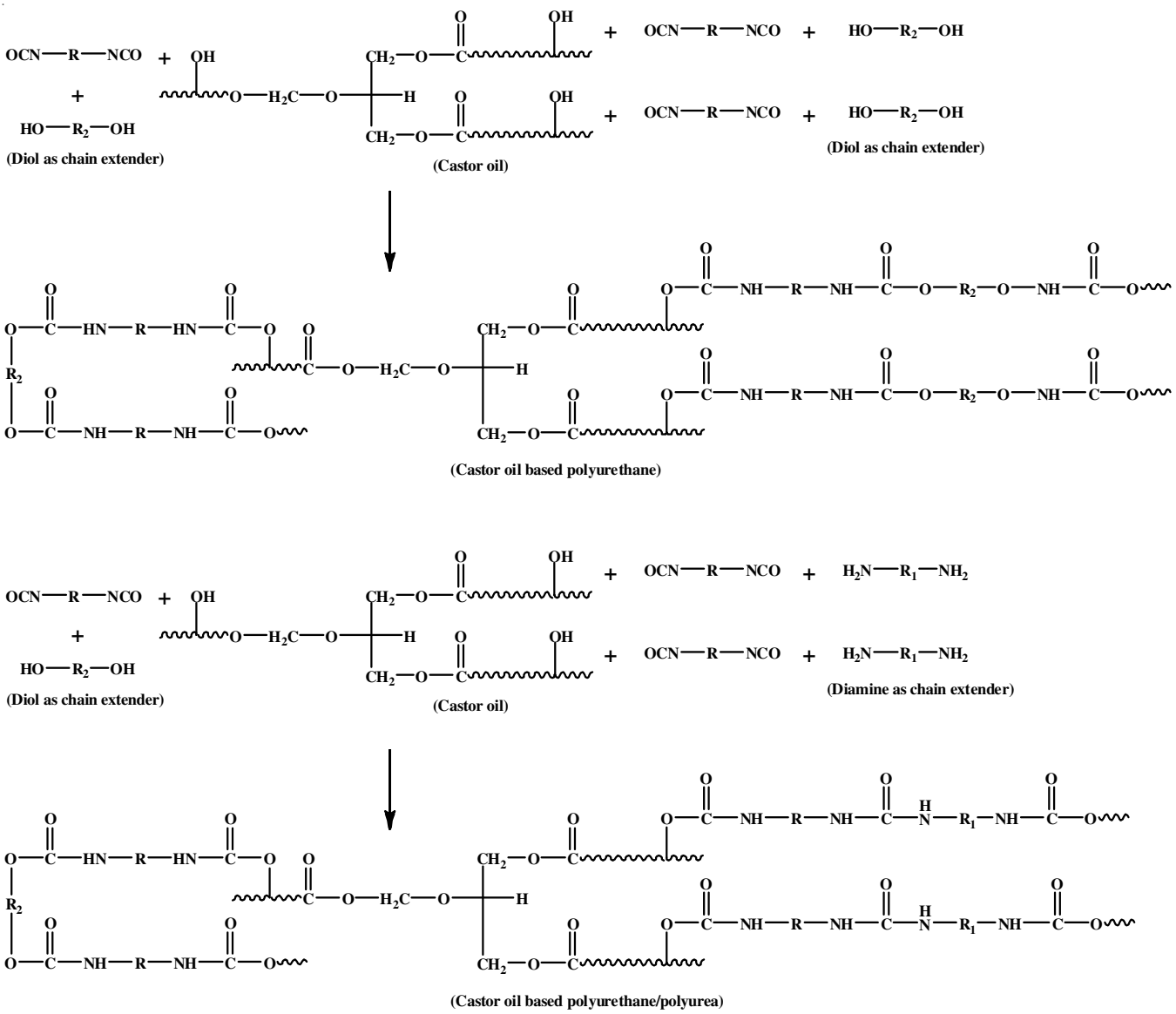


Fig. 2. Chemical reaction showing the formation of PU and poly(urethane/urea) polymers from castor oil

TABLE-2
ABSORPTION FREQUENCY ASSIGNMENT IN THE FT-IR SPECTRA OF CASTOR OIL AND PUs [35-41]

Sample	Peak frequency (cm^{-1})	Functional group or bond assigned
Castor oil [35-39]	3416.96 (broad)	O-H stretching
	3008.08 (weak)	C-H stretching (in *cis* C=C-H)
	2975.1 & 2854 (strong)	Assymmetric& symmetric C-H stretching of $>CH_2$ group
	1742.7 (strong)	Ester carbonyl >C(=O)-O-
	1461.1(strong)	C=C
	1165, 1095	>C-O & C-O-C stretching vibrations in the ester links (>C=(O)-O-C-)
	721	Overlapping of $>CH_2$ rocking vibration and out of plan vibration of *cis* disubstituted olefins
	1241, 1165	C-O stretching in ester function
	1091.7, 1032	C-H deformation and C-O stretching vibrations in fatty acid esters
PU samples (PU-1 to PU-7) [18,39-41]	3308-3363	N-H stretching
	3009	C-H stretching in C=C-H
	2916-2983 & 2848-2857	Asymmetric and symmetric stretching of $>CH_2$ group
	1733-1741	Ester and urethane carbonyl -C(=O)-O-; -NH-C(=O)-O-
	1090-1116, 1040, 1017	C-O and –C-O-C- stretching vibrations
	1533-1560	C-N stretching and N-H bending (amide II)
	1460	C=C stretching
	1225-1275	C-N stretch and N-H bending (amide II)

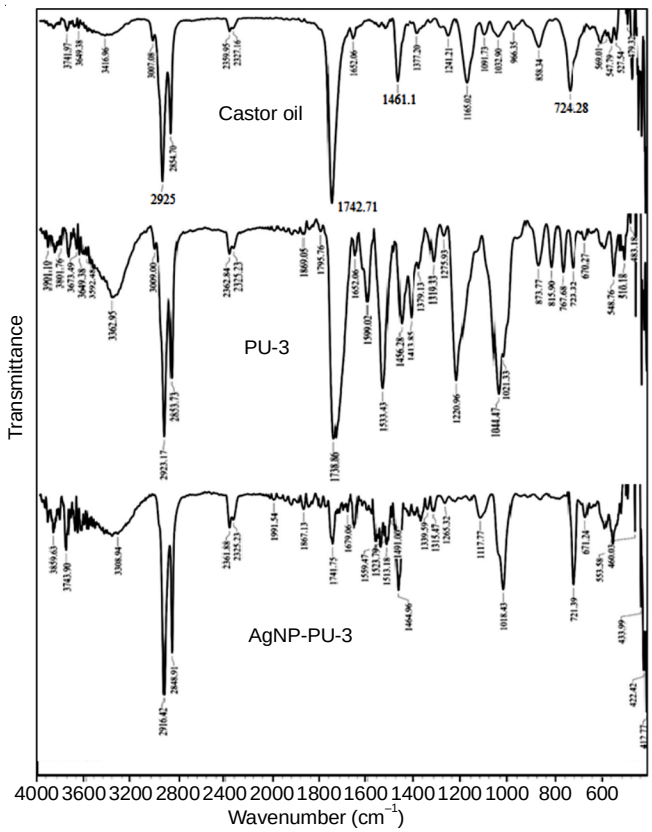


Fig. 3. FT-IR spectra (ATR) of castor oil, PU-3 and AgNP embedded PU-3

Antibacterial activity of PUs: The agar diffusion test results for antibacterial activity of virgin and AgNP embedded PUs with *B. subtilis* and *E. coli* are shown in Figs. 4 and 5 respectively. Analysis of these figures indicated that virgin PUs do not show any zone of inhibition implying no antibacterial activity. But in AgNP embedded PUs diameter of zone of inhibition (Figs. 4 and 5) was clearly seen showing antibacterial action against both the bacteria. It is believed that the high surface area AgNPs can interact with DNA, cell membrane and cellular proteins leading to the death of bacterial cells [34,42].

Simultaneous TGA-DTA studies: Thermal degradation of PU occurs in multistep due to a multitude of physical and chemical processes [43]. The thermal stability of PUs is related to the nature and structures of hard segment, soft segment and chain extender, on the molar ratio of the hard segment to soft segment and also, on the extent to which the hard and soft segments are phase separated into microdomains. Thermal stability of PUs depends strongly on urethane groups per unit volume and on the equilibrium between polymerization and depolymerization of functional groups or linkages [*e.g.*, -NH-C(=O)-NH-; -NH-C(=O)-O-, -C(=O)-O-] present in the polymer chains [44]. The thermal stability of the synthesized PU was analyzed by simultaneous thermogravimetric-differential thermal analysis in air/or nitrogen atmospheres. The TG/DTA and DTG traces of synthesized PUs of typical composition are shown in Fig. 6. The shape of TGA/DTG curves for the prepared PUs indicated three major degradation steps in nitrogen atmosphere. The first stage of degradation observed in the range 265-271 ºC was due to urethane/or urea bond *via* their dissociation to isocyanate and alcohol, the formation of primary amines and a terminal olefinic group, and the formation of secondary amines and CO_2, and fragmentation of ester groups [6-8,44-46]. The second major degradation that occurred in the temperature range 338-342 ºC was attributed to the decomposition of soft segments. The third step degradation in the temperature range 439-450 ºC was associated with the decomposition of segments from the remaining structure of castor oil or might be due to a more likely C-C bond cleavage. In fact the temperature for third step degradation of PU samples nearly matches with that of pure castor oil. The onset weight loss temperature of castor oil in nitrogen was 370 ºC.

The residual weights at 600 ºC for synthesized PUs in the TG traces (Fig. 6a) under nitrogen were in the range 3.2% to 4.9% and for castor oil it was zero. But the residual weight in air at 600 °C for PU of typical composition (PU-3) was reduced to 0.59% (Fig. 7) due to oxidative degradation.

The TG/DTG traces (Fig. 7) of virgin PU-3 in air showed a four step degradation with more prominent fourth step in

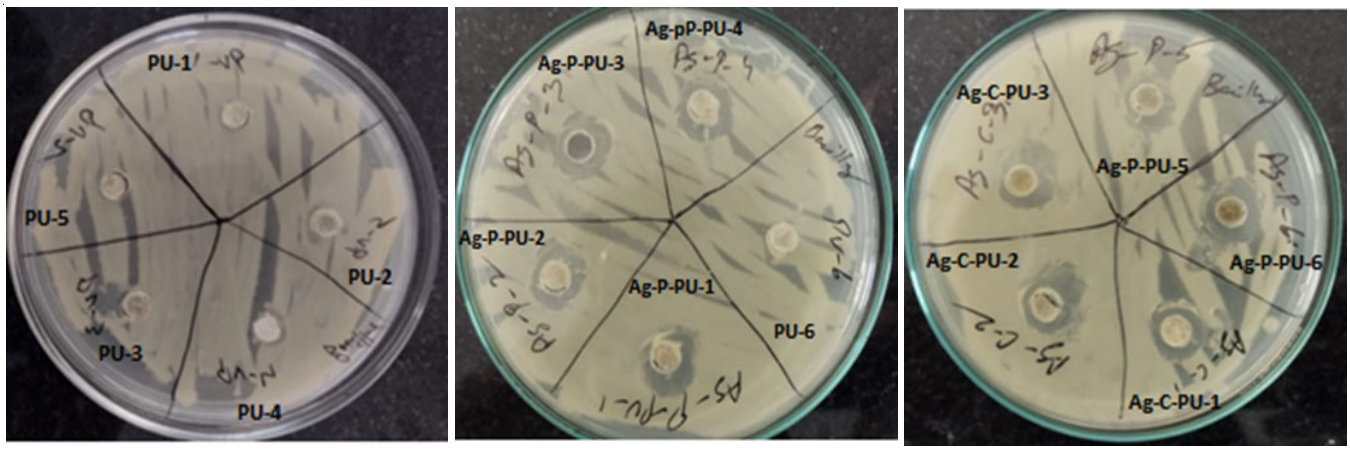


Fig. 4. Agar diffusion tests for virgin PUs (PU-1 to PU-6) and AgNPs embedded PUs [*via* chemical (Ag-C-PU-1 to Ag-C-PU-6) and biological (Ag-P-PU-1 to Ag-P-PU-6), methods) with *Bacillus subtilis*

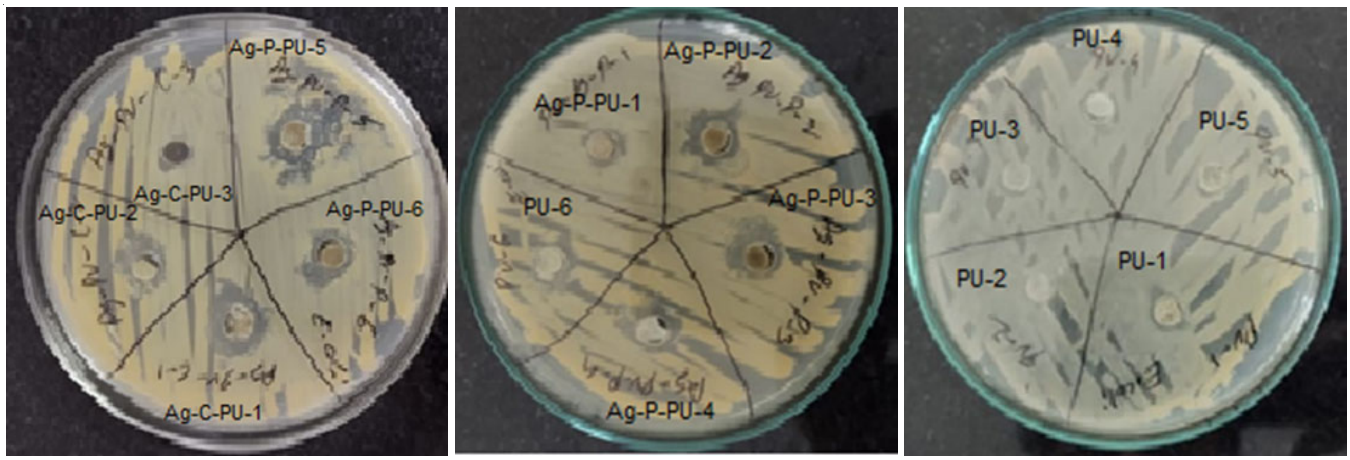


Fig. 5. Agar diffusion tests for virgin PUs (PU-1 to PU-6) and AgNPs embedded PUs [*via* chemical (Ag-C-PU-1 to Ag-C-PU-6) & biological (Ag-P-PU-1 to Ag-P-PU-6) methods] with *E. coli*

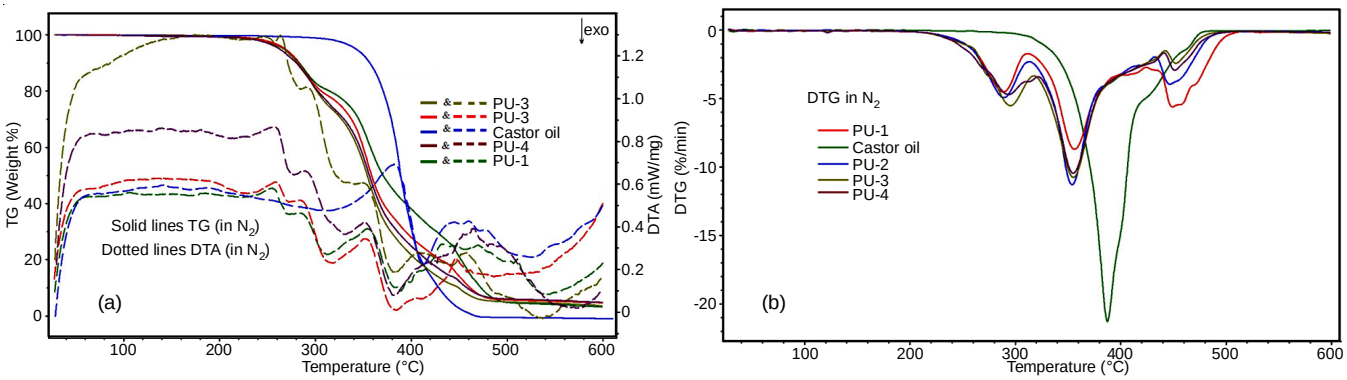


Fig. 6. TG/DTA (a) and DTG (b) thermograms for castor oil and polyurethanes, PU-1 to PU-4 in N_2

the high temperature region (around 595 ºC) and this may be due to thermooxidative degradation of the residual products formed in the previous step. In air the onset degradation temperature of virgin PU-3 is reduced only by 2-3 ºC compared to that in nitrogen (Fig. 7). But in the thermograms of AgNP embedded PU in air the thermo-oxidative degradation temperatures of all the four steps were lowered (Fig. 7) and this was more significant in third and fourth step degradations. This was more likely attributed to the catalytic effect of AgNPs on thermo-oxidative degradation.

The DTA traces of PUs in air showed exotherms at temperatures beyond 300 ºC due to oxidative degradation and the rate of weight loss is less in air compared to that in nitrogen for the temperature range 350 to 550 ºC. The very broad exotherm (Fig. 8) observed around 500 ºC in DTA of virgin PU-3 in air become comparatively narrower and sharper multiple exotherms

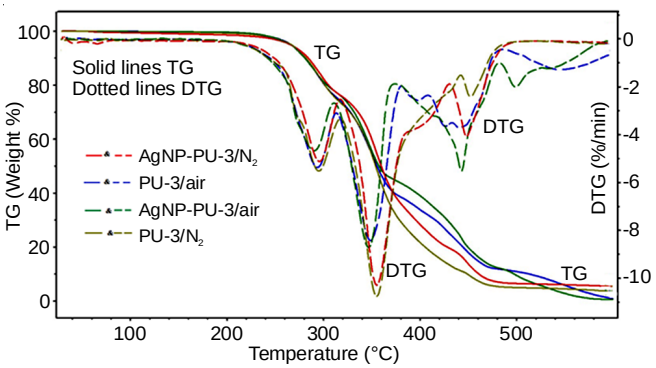


Fig. 7. Representative TG and DTG traces of virgin and AgNP embedded PU-3 in air and N_2

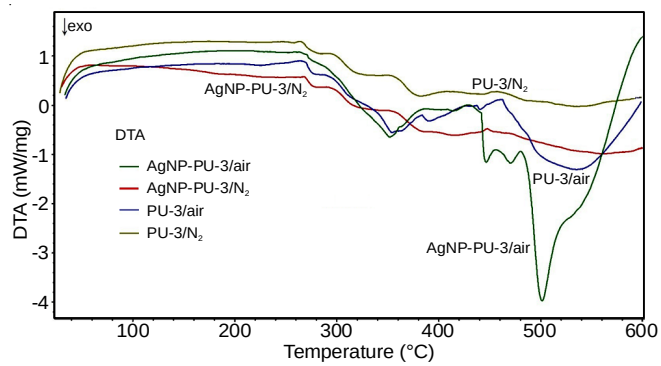


Fig. 8. Representative DTA thermograms for virgin and AgNP embedded PU-3 in air and N_2

in AgNPs embedded PU. This may be primarily due to the catalytic effect of the dispersed AgNPs in the PU, which can provide more active sites for the reactions to occur at a faster rate. It is to be noted that the heterogeneous catalysts are considered to be more active, efficient and selective compared to the homogeneous catalysts [47]. The multiple endotherms observed in DTA for PU-1 to PU-4 samples under nitrogen (Fig. 6a) were attributed to the endothermic weight loss degradation steps involving cleavage of urethane/urea, ester links, C-C bonds, *etc.* observed in TGA [6-8,44-46].

Conclusion

In present study, the castor oil based polyurethanes (PUs) were synthesized using TDI (as curator), TMP/or glycerol (as crosslinker), PPG, 1,6-hexane diol and PPG-2-APE (as chain extenders) and DBTDL as catalyst. The FT-IR spectra of PUs indicated the presence of characteristic absorption frequencies of PUs and absence of stretching frequency around 2260 cm^{-1} corresponding to isocyanate (-NCO) group. The latter indicated the formation of polyurethane/polyurea links in the prepared PUs. These PUs were embedded with AgNPs *in situ via* chemical as well as biological methods to impart antibacterial activity. Agar diffusion tests on the PUs with *Bacillus subtilis* and *E. coli* showed zone of inhibition for the AgNP embedded PUs which was not observed in pristine PUs, demonstrating the antibacterial activity of AgNP incorporated PUs. The onset degradation temperatures for all the prepared PUs were in the range around 265-271 ºC and this was very much lower than the initial weight loss temperature (370 ºC) of pure castor oil. Incorporation of AgNP into PU not only inculcated antibacterial activity but also enhanced their thermoxidative degradation. Since the urethane, urea and ester links in the synthesized PUs are inherently susceptible to hydrolytic degradation under soil and biological environments and the renewable and ecofriendly castor oil has been used as main raw material in the prepared PUs, they may find promising biomedical applications as transdermal batches in wound healing, scaffold in tissue engineering, antibacterial foams, body implants, food packaging films, antibacterial coatings, *etc.*

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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