Studies on Boron Containing Poly(urethane fattyamide)

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Summary: An attempt has been made to synthesize boron containing poly (urethane-fattyamide) [B-PUPGFA] through the incorporation of boron in the backbone of non drying oil such as Pongamia glabra oil derived poly (urethane-fattyamide). The synthesis route involves 50% reduction in the use of harmful volatile organic contents [VOCs] and was carried out in situ by condensation reaction between N, N′-bis (2-hydroxyethyl) Pongamia glabra fattyamide and boric acid without solvent followed by the addition polymerization with toluene diisocyanate in minimum solvent. Spectral (FTIR, 1H-NMR and 13C-NMR), physico-chemical, physico-mechanical and chemical resistance of B-PUPGFA was carried out by standard laboratory methods. The antibacterial performance of B-PUPGFA was done by agar diffusion method against E. coli and S. aureus. The aforementioned performance of B-PUPGFA was compared with Pongamia glabra oil based virgin poly (urethane-fattyamide) [PUPGFA]. It is observed that the incorporation of boron has a significant influence on the overall performance of B-PUPGFA film, which shows antibacterial activity against E. coli and S. aureus. Therefore, B-PUPGFA serves as novel and promising biomaterial candidate for use as anticorrosive and antibacterial coating material.

Keywords: coatings; poly(urethane fattyamide); Pongamia glabra oil; renewable resource; resin; synthesis

Introduction

In recent years, boron containing polymers and their derivatives have gained much attention amongst scientific and industrial community. The incorporation of boron in the backbone of polymers improves thermal stability, mechanical, electrical, antibacterial and antifungal properties, oxidative resistance, flexibility, flame retardancy than their virgin counterparts.[1–6] The boron containing petro-based polymers and their derivatives have found application as fuel cells, light emitting devices, high performance lubricants, radiations, various composites, flame retardants, ceramics and protective materials.[7–15] There is increasing demand to find an alternative of these petro based polymers due to increasing environmental hazards and cost of petroleum resources. Renewable resources such as carbohydrates, starch, proteins, vegetable oils, animal fats and oils have received focused attention as alternatives of petroleum resources due to their ease of availability, inexpensiveness, biodegradability and non toxicity.[16–19] Among them, oils derived from plant and animal sources are an ideal alternative feedstock. They have been extensively used for inks, plasticizers, lubricants, toughening agents, agrochemicals, paints and coatings.[16–21]

To further extend the application of these renewable resources, Sharif Ahmad et al. have focused on converting oils into useful biopolymers.[22–26] In their previous study, they have published work on synthesis and characterization of boron containing

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natural polyols such as castor oil, synthetic oils-based polyols, polyesteramides and developed their polyurethanes. These modified resins have found effective use as anticorrosive and antibacterial coating materials.[27–29]

The objective of the present work is the development of new boron-containing poly (urethane-fattyamide) [B-PGPUFA] from *Pongamia glabra* seed oil (a non drying oil) from simple and shortest route for the synthesis of ambient cured anticorrosive and antibacterial polymeric materials. Literature survey reveals that no work is reported on the same yet.[27–29]

Poly (urethane-fattyamide) consists of alternating short sequence of soft (flexible) polyol fattyamide and hard (rigid) isocyanate segments. It exhibits synergistic properties of both polyurethane and polyamide moieties. They have found application as protective materials.[24,30] Boron is incorporated in the same to improve their film performance and antimicrobial behaviour.

Experimental Part

Materials

Pongamia glabra oil [PO] (extracted and characterized as per our previously reported papers),[31] boric acid [BA], (Merck, India), toluene-2,4-diisocyanate [TDI] (Merck, Germany) and xylene were of analytical grade. N, N′bis (2-hydroxyethyl) *Pongamia glabra* fatty amide [HEPGA] was synthesized according to our previously reported method.[31]

Synthesis

Synthesis of B-Prepolymer

B-prepolymer was synthesized by reacting HEPGA (1.0 moles) and boric acid (0.5 mole). HEPGA was taken in a four necked conical flask fitted with Dean-Stark trap, nitrogen inlet tube, thermometer, mechanical stirrer, and heated at 353 ± 358 K under continuous stirring in nitrogen atmosphere. Boric acid was added very slowly over a period of 900 sec. under continuous stirring at this temperature under N_2 atmosphere. The temperature was raised up to 373 ± 378 K, and by product such as water was removed by vacuum technique. TLC (Thin layer chromatography) and hydroxyl value determination was used to monitor the progress of the reaction. After the completion of the reaction, 1 gm of B-prepolymer was transferred to a closed test tube, dissolved in 20 ml xylene and set aside for 86400 sec. to check the presence of unreacted BA. It was found that no separation occurred in the sample.

Synthesis of B-PUPGFA

In the aforementioned setup, pre-determined amount of TDI (15–30% by weight) along with minimum amount of xylene were added. The reaction was carried out at ambient temperature (301 K–303 K). The progress of the reaction was monitored by the determination of hydroxyl value and TLC at regular intervals of time till the completion of the reaction. Finally, solvent was removed by rotary vacuum evaporator and pure B-PUPGFA was obtained.

Test Methods

Spectral Analysis

FTIR spectra was taken on Perkin Elmer 1750 FTIR spectrometer (Perkin Elmer Cetus Instrument, Norwalk-CT) using NaCl Cell. ^{1}H-NMR and ^{13}C NMR spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer using deuterated chloroform as solvents and tetra methyl silane (TMS) as an internal standard.

Physico-Chemical Analyses

Iodine value, hydroxyl value, refractive index and specific gravity were determined by standard laboratory methods (Table 1).

Physico-Mechanical and Chemical Resistance Analysis

Physico-mechanical tests such as scratch hardness, bending test, impact resistance, and chemical/corrosion tests in water, 5 wt% HCl, 5 wt% NaOH, 3.5 wt% NaCl, xylene and optical properties were

Table 1.
Physico-chemical Characterization of B- prepolymer and B-PUPGFA.

Code* Resin	Hydroxyl value (%)	Iodine value (g I_2/100g)	Specific gravity (g/ml)	Refractive index
B-prepolymer	6.50	43.58	0.8998	1.508
B-PUPGFA-20	3.09	43.22	0.9131	1.617
B-PUPGFA-25	1.79	43.01	0.9228	1.623
B-PUPGFA-30	0. 62	42.98	0.9306	1.635

*Last digit of the resin code indicates % loading of TDI.

performed by standard methods as mentioned in our previous works (Table 2).[24,31] Drying time of B-PUPGFA coatings at ambient temperature (301 K–303 K) were recorded as 900–1200 sec. Thicknesses of these coatings were found within the range of 90–100μm.

Antibacterial Behavior

Antibacterial behavior of the systems was evaluated by agar diffusion method (Table 3).[32] All samples were dissolved in dimethylsulphoxide (DMSO) and were tested against *E. coli* and *S. aureus* using standard drug Amekasin.

Results and Discussion

Synthesis

B-PUPGFA was synthesized through the incorporation of boron in the backbone of non drying oil such as *Pongamia glabra* oil derived poly (urethane-fattyamide). The synthesis was carried out insitu by condensation reaction between N, N′bis (2-hydroxyethyl) *Pongamia glabra* fattyamide and boric acid without any solvent followed by the addition polymerization with TDI in minimum possible solvent (Scheme 1). The synthesis route involves 50% reduction in the use of VOCs.

Spectral Analysis

The presence of peaks in the FTIR spectra (cm^{-1}) at 3339–3333 (NH str. of urethane), 1715.3 (>C=O urethane), 1224.9 (C−N str. urethane), 2271 (free −NCO group), 3077 (ArC=C−H str.), 1540.5, 775.2 (ArC=C), 1322 (−B−O str.) and 667 (−B−O bending) and in the ^{1}H-NMR($CDCl_3$, δ; ppm) at 3.6 ($-C\mathbf{H}_2$ attached to residual −OH group), 4.3 ($-CH_2$ attached to urethane group), 4.1 ($-CH_2$ attached to −O−B), 2.23 ($-CH_3$ of TDI), 7.1–6.9 and 7.99–7.82 (non hydrogen bonded and hydrogen bonded −NH of the urethane), 7.12–7.06 (other ring proton) as well as in the ^{13}C-NMR($CDCl_3$, δ; ppm) at 60–61 ($-CH_2$ attached to −O−B−), 67 ($-CH_2$ attached to urethane group), 134 ($-CH_2$ attached to aromatic ring), 144 (carbonyl of urethane group), 155 (carbonyl of free NCO group), 136, 137, 125.7, 126.5 and 116.2 (other aromatic ring carbon), 17.0 ($-CH_3$ of TDI), confirm the formation of B-PUPGFA.[27–29]

Physico-chemical Characterization

The decrease in hydroxyl and iodine values from B-prepolymer to B-PUPGFA due to the increased loading of TDI can be correlated to the reaction of −OH group with −NCO group of TDI. The increase in the values of specific gravity and refractive index from B-prepolymer to B-PUPGFA

Table 2.
Physico-mechanical Characterization B-PUPGFA.

Resin Code	Drying time (second)	Scratch hardness (kg)	Impact resistance passes (kg/m)	Gloss at 45°	Bending 0.004191 m
B-PUPGFA-20	1200	2.0	3571	65	passes
B-PUPGFA-25	960	2.5	3571	70	passes
B-PUPGFA-30	900	1.9	2678	70	Fail

Table 3.
Chemical/Corrosion resistance tests B-PUPGFA.

Resin Code	H_2O (15 h)	NaOH (5%) (6 h)	HCl (5%) (5 h)	NaCl (3.5%) (10 h)	Xylene (15 h)
B-PGPUA-20	Unaffected	Slight loss in gloss	Slight loss in gloss and adhesion	Unaffected	Unaffected
B-PGPUA-25	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected
B-PGPUA-30	Unaffected	Loss in gloss and swelling	Start swelling	Loss in gloss	Unaffected

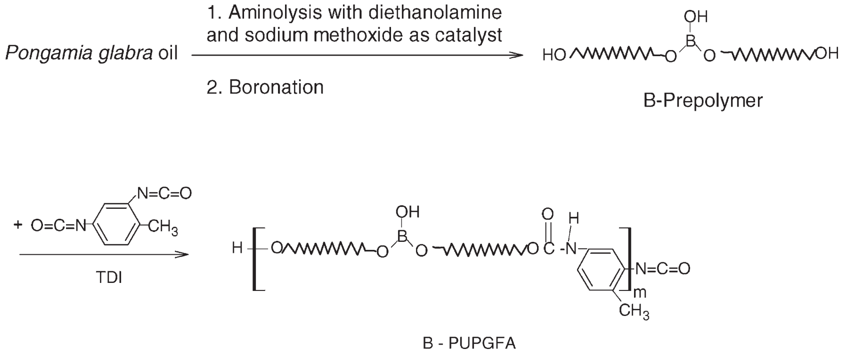
can be correlated to the increase in molar mass of B-PUPGFA with the increase in the loading of TDI (Table 1).

Curing of Film

Curing of the resin is observed as a two-stage process. In the first stage solvent evaporation occurs, which is a physical phenomenon. This is followed by the second stage of curing which is a chemical process involving the reaction of free –NCO groups of B-PUPGFA with moisture present in air leading to the completely cured state. In this reaction, free –NCO groups react with moisture to form amino groups through addition reaction mechanism. The amino group reacts with –NCO group that is present in other polymeric chain of the resin to form a cross-linked structure.[33]

Coating Properties

B-PUPGFA coatings were obtained at room temperature as virgin *Pongamia glabra* oil based poly (urethane-fattyamide). It was found that B-PUPGFA-15 does not attain dry-to-touch stage. However, B-PUPGFA-20, B-PUPGFA-25 and B-PUPGFA-30 become dry-to-touch after 900–1200 sec.; drying time decreases from B-PUPGFA-20 to B-PUPGFA-30 with the increase in the loading of TDI. We understand that optimum crosslinking is achieved only at 15% loading of TDI to attain dry-to-touch stage. The scratch hardness of B-PUPGFA increases from B-PUPGFA-20 to B-PUPGFA-25 and then exhibits a decrease at PUPGFA-30. Systems B-PUPGFA-20 and B-PUPGFA-25 pass bent (0.004191 metre conical mandrel) test as a characteristic of oil based polymers and impact resistance test (3571.6535 kg/m), that can be correlated to the polar nature of poly (urethane-fatty amide) linkage, which provide sufficient adhesion and toughness. However, B-PUPGFA-30 fails aforementioned tests that can be correlated to the overloading of TDI resulting in the predominance of secondary reaction of free –NCO groups (allophanate formation).[33]



Scheme 1.
Synthesis reactions of B-PUPGFA.

The structure becomes excessively crosslinked and deteriorates the physico-mechanical performance of the coatings. The gloss at 45° was found to be in between 75–80 (Table 2).

The chemical resistance tests (Table 3) exhibit that all coating systems show no change in water and xylene up to 15 days. Coatings show slightly lower alkali and acid resistance performance as compared to that of PUPGFA coatings;[30] however, B-PUPGFA-25 coatings were found to be unaffected in aforementioned media. Lower alkali and acid resistance performance of the coatings can be attributed to presence of polar B–O group, which is expected to undergo hydrolysis on exposure to the given media.

Antibacterial Activity

Antibacterial activity of B-PUPGFA was evaluated against *S. aur*eus (gram-positive) and *E. coli* (gram-negative). All the samples were prepared in DMSO that does not show any antibacterial activity against aforementioned bacteria. It was further observed that PUPGFA shows moderate antibacterial activity only against gram negative bacteria (*Salmonella*) [30] while B-PUPGFA shows high activity against *the same (E. coli,* 21-30 mm; inhibition zone) and moderately against gram positive bacteria (*S. aur*eus, 16-20 mm; inhibition zone). It is also observed that the antibacterial activity of B-PUPGFA increases with loading of TDI up to certain limits, thereafter it decreases. The higher antibacterial activity of B-PUPGFA in comparison to those of PUPGFA can be correlated to the presence of boron in B-PUPGFA.

Conclusion

Boron containing poly (urethane-fattyamide) with 25% loading of TDI exhibits higher antibacterial activity, chemical resistance properties as well as physico-mechanical properties compared to reported resins. B-PUPGFA-25 resin has a potential to act as a substitute of petro-based polymers in the antibacterial and corrosion protective paints and coatings. By adopting this method we can use some other non drying oils (insufficient unsaturation for curing) as room temperature cured polymeric resins.

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