

# Development and Characterization of Boron Incorporated Linseed Oil Polyurethanes

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**ABSTRACT:** The aim of this work was to investigate the structures and properties of boron incorporated linseed oil polyols (BPEPs) and their polyurethanes (BPEPUs). Hydroxylation was performed *in situ* using H<sub>2</sub>O<sub>2</sub> and acetic acid; the syntheses of BPEPs and BPEPUs involves polyesterification and polyaddition reactions following "single-pot, multi-step" reactions strategy. Spectral (IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR), physicochemical, thermal (TGA, DSC), physico-mechanical analyses and corrosion/chemical resistance performance of aforementioned resins confirmed the incorporation of boron in polyol and polyurethane backbone. BPEPUs followed a clear cut "three step-ambient temperature" curing strategy. They showed very good resistance to 5 wt % HCl, 3.5 wt %

NaCl (unaffected for 16 and 14 days, respectively), moderate alkali resistance and moderate to good antibacterial activity against *E. coli* and *S. aureus*. Our investigations reveal that (i) the incorporation of boron has significant influence on the structural, physicochemical aspects, physico-mechanical, chemical resistance behavior, and thermal stability of polyurethanes, (ii) boron linkages play dual role, both as cross linker and modifier, and (iii) BPEPUs may serve as efficient corrosion protective material, which may be safely employed upto 230°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 499–508, 2010

**Key words:** synthesis; polyurethane; cross-linking; coatings; TGA

## INTRODUCTION

Vegetable seed oils (VSOs) comprise of triacylglycerols (TAGs) predominantly containing fatty acids (saturated or unsaturated).<sup>1</sup> To produce value added polymeric resins, VSOs undergo several derivatization reactions, about 90% of which occur at carboxyl functionality and the rest at double bonds.<sup>2,3</sup> The chemical reactions involving the latter mainly include vinylation/acrylation, maleinization, hydrogenation, halogenation, ozonolysis, dimerization, metathesis, epoxidation, and hydroxylation.<sup>4–6</sup> The latter two are the most common of the oleochemical reactions involving double bonds of aliphatic chains of oils, yielding TAG epoxies and polyols.

Polyols serve as excellent building blocks of VSO based polyurethanes (PUs), which find applications in the field of elastomers, foams, plasticizers, coatings, and paints. VSO PUs are generally derived from hydroxyl containing monomers and polymers such as fatty amides, polyesteramides, polyetheramides, alkyds, naturally available and synthesized

polyols. The latter may prove as advantageous starting material for VSO PUs due to multitude of hydroxyls and long, aliphatic dangling chains present in their backbone. Furthermore, while the synthesis of PUs from some of the aforementioned resins is overall a cumbersome process involving higher energy and multiple steps, urethanation through polyols is comparatively less energy consuming process in terms of reaction temperature, time and the number of reaction steps involved.<sup>4,5,7–15</sup>

VSO polyols, which usually occur in the form of oil triester, consist of long aliphatic hydrocarbon chains along with hydroxyls, active methylenes, and double bonds. They can be obtained by hydroformylation followed by hydrogenation, epoxidation proceeded by hydration (Generation I polyol), ozonolysis followed by hydrogenation (Generation II polyols), and some other methods.<sup>7–10</sup> Such approaches have been successfully accomplished on oils from seeds of linseed, karanj, soybean, canola, rapeseed, lumbang, rubber seed, and others.<sup>2,16–27</sup>

Like VSOs, the structures of VSO polyols are very complicated and governed by the types, compositions and distributions of fatty acid residues of the starting oils.<sup>8–10,24–27</sup> Similarly, the structures of their derivatives such as PUs are also very complex; their properties depend upon the number, distribution, and site of hydroxyls (in the middle or closer to the end of the chain, which ultimately determines the

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size of dangling chains) present in the fatty triester chains of oil polyols. Interestingly, most of the studies on VSO polyols involve the synthesis, characterization, and structure-property relationships of PUs. Several other modifications of VSO polyols, which are chemically viable and may be commercially valuable, have not been explored, yet. We understand that the complicated structures of polyols limit their further modifications. Recently, only a few publications have appeared on derivatization reactions of polyols viz. acrylic grafted and metalloids incorporated (chemically derived and natural, respectively) polyols and polyurethanes.<sup>9,21,22</sup> The area still holds wide scope for further research investigations.

Metals and metalloids incorporated polymers have attracted much attention over the past five decades. However, research investigations in this field are mainly limited only to petro-based polymers. VSOs based systems are expected to perform better than their aromatic petro-based counterparts owing to their (i) inherent flexibility and (ii) excellent physical and chemical properties viz., improved gloss, enhanced hydrolytic as well as thermal stability attributed to the hydrophobic nature of the constituent triglycerides.<sup>21,28</sup> Literature survey reveals that in the past only a few publications have appeared on metal/metalloid incorporated VSO polyesteramides and polyurethanes.<sup>11–15</sup>

Lately, boron incorporated semi-inorganic polymers (through B–O, B–S, B–N, and B–P bonds) have displayed improved thermal stability, mechanical, electrical, antibacterial, and antifungal properties.<sup>29–32</sup> Such modifications are also limited to petro-based resins only. Thus, from economical and environmental viewpoints, VSOs based polyols may serve as an excellent starting material for aforementioned modification.

This manuscript reports the synthesis and characterization (spectral, physicochemical, physico-mechanical, thermal as well as chemical resistance performance and antibacterial behavior) of boron incorporated polyols (BPEPs) and polyurethanes (BPEPUs) from linseed oil. The synthesis of BPEPs was carried out in the absence of any solvent (by condensation reaction between linseed polyol, phthalic anhydride, and boric acid)<sup>22</sup> whereas that of BPEPUs was accomplished in minimum possible solvent to avoid the harmful effects of VOCs. The results obtained have also been compared with our previously reported work on boron incorporated natural (castor oil) polyols and their boron polyurethanes (BPU).<sup>21</sup> Our studies reveal that (i) BPEPUs exhibit better performance than their castor oil based counterparts, (ii) they may also be safely employed upto 230°C, and (iii) they serve as promising corrosion protective, antibacterial polymeric coating materials.

## EXPERIMENTAL

### Materials

Linseed (seeds obtained from local market) were air-dried, ground to a powdered form, and further subjected to oil extraction in soxhlet apparatus. Petroleum ether (bp 60–80°C) was used as solvent in oil extraction. Hydrogen peroxide (30%), sulphuric acid, glacial acetic acid, boric acid [BA] (Merck, India), phthalic anhydride [PA] (s.d.fine Chem. Ltd., Biosar), and toluene-2, 4-diisocyanate [TDI] (Merck, Germany) were used as received.

### Synthesis

#### Synthesis of linseed polyol

Linseed polyol (LPO) was synthesized according to our previously reported method.<sup>22</sup>

#### Boron incorporated linseed polyester polyol

LPO (1 mol), PA (0.02 mol), and BA (0, 0.06, 0.08, 0.10, and 0.12 mol) were placed in a four necked round bottomed flask fitted with a Dean Stark Trap, nitrogen inlet tube, thermometer, cold water condenser, and magnetic stirrer. The reaction was carried out as per our previously reported method.<sup>22</sup> Same reaction was also carried out without including boron to synthesize linseed polyester polyol (PEP).<sup>22</sup>

#### Boron incorporated linseed polyester polyurethane

PEP and BPEPs were dissolved in minimum amount of xylene and placed in three-necked round-bottomed flask equipped with nitrogen inlet tube, thermometer, cold-water condenser, and magnetic stirrer along with TDI (0.1 mol).<sup>21,22</sup> The reaction was carried out at ambient temperature (28–30°C). The progress of the reaction was monitored by the determination of hydroxyl value and Thin Layer Chromatography at regular intervals of time till the completion of the reaction. Dark brown colored BPEPU were finally obtained.

### Test methods

#### Spectral analyses

FTIR spectra of BPEP and BPEPUs were taken on Perkin Elmer 1750 FTIR spectrometer (Perkin Elmer Cetus Instrument, Norwalk-CT) using NaCl Cell. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer using deuterated chloroform as solvent, and tetra methyl silane as an internal standard.

TABLE I  
Physicochemical Analysis of BPEPUs

Resin code	Hydroxyl value (%)	Iodine value (g I <sub>2</sub> /100g)	Specific gravity (g/mL)	Refractive index	Inherent viscosity (dL/gm)
plain PEPu	22	64	0.920	1.504	1.132
0.06 BPEPU	16	60	0.932	1.513	1.146
0.08 BPEPU	9.5	56	0.936	1.519	1.152
0.10 BPEPU	6.2	51	0.940	1.524	1.158
0.12 BPEPU	3	48	0.944	1.530	1.166

#### Physicochemical analyses

Iodine value, hydroxyl value, refractive index, inherent viscosity, and specific gravity of BPEPs and BPEPUs were determined by standard laboratory methods (Table I).

#### Physico-mechanical and corrosion/chemical resistance performance

BPEPUs (solution in minimum amount of xylene-2 mg/mL) were applied on commercially available mild steel strips of 30 × 10 × 1 mm<sup>3</sup> size for corrosion/chemical resistance tests of their coatings and on strips of size 70 × 25 × 1 mm<sup>3</sup> for the determination of specular gloss at 45° by gloss meter (model RSPT -20; Digital Instruments, Santa Barbara, CA), scratch hardness (BS 3900), bending test (ASTM-D 3281-84) and impact resistance (IS: 101 part 5/sec-3, 1988). Dry-to-touch (DTT) and Dry-to-hard (DTH) times of BPEPU coatings at ambient temperature (28–30°C) were recorded as 15–20 minutes and 7 days, respectively. Chemical/corrosion tests of BPEPUs were performed in tap water, 5 wt % HCl,

5 wt % NaOH, 3.5 wt % NaCl, and xylene by pouring their solutions in 3 inch-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 weight loss (Table II). Thicknesses of these coatings were found within the range of 90–100 μm.

#### Thermal analyses

Thermal analyses were carried out by TGA 51 (TA Instrument) and DSC 10 (TA Instrument) in nitrogen atmosphere to investigate the thermal degradation pattern of the resins.

#### Antibacterial behavior

Antibacterial behavior of the systems was evaluated by agar diffusion method (Table III).<sup>10,22</sup> All samples were dissolved in dimethylsulphoxide and were tested against *E. coli* and *S. aureus* using standard drug Amekasin (30 μg/Disc).

TABLE II  
Physico-Mechanical and Corrosion/Chemical Resistance Properties of BPEPUs

Resins→characteristics↓	Plain PEPu	0.06 BPEPU	0.08 BPEPU	0.10 BPEPU	0.12 BPEPU
SH (kg)	1.0	2.5	2.5	2.7	3.0
IRt (kg/m),14	Pass	Pass	Pass	Pass	Pass
Bend test (1/8 inch)	Pass	Pass	Pass	Pass	Pass
Gloss(At 45°)	75	108	112	122	126
HCl(5 wt %),16 days	a**	a*	a*	a*	a*
NaOH (5 wt %),6 hour	a,c**	a,c	a,c	a,c	a,c
NaCl(3.5 wt %),14 days	a,b**	a,b	a,b	a,b	a,b
Xylene, 3–4 hour	d	d	d	d	d
Water, 60 days	a#	a	a	a	a

SH = Scratch hardness, IRt = Impact resistance.

<sup>a</sup> Unaffected.

<sup>a#</sup> Unaffected 20 days.

<sup>a\*</sup> Appearance unaffected for 16 days in HCl.

<sup>a\*\*</sup> Appearance unaffected for 7 days in HCl.

<sup>b</sup> Loss in adhesion and dissolution after 14 days.

<sup>b\*\*</sup> Loss in adhesion and dissolution after 7 days.

<sup>c</sup> Loss in gloss and adhesion after 6 hrs.

<sup>c\*\*</sup> Loss in gloss, weight and adhesion after 4 hrs.

<sup>d</sup> Swelling and partial dissolution.

**TABLE III**  
Antibacterial Activity of BPEPUs

Antibacterial activity	0.06 BPEPU	0.08 BPEPU	0.10 BPEPU	0.12 BPEPU
<i>E. coli</i>	++	++	++	++
<i>S. aureus</i>	+++	+++	+++	+++

++: Moderately active (16–20 mm).

+++: Highly active (21–30 mm).

## RESULTS AND DISCUSSION

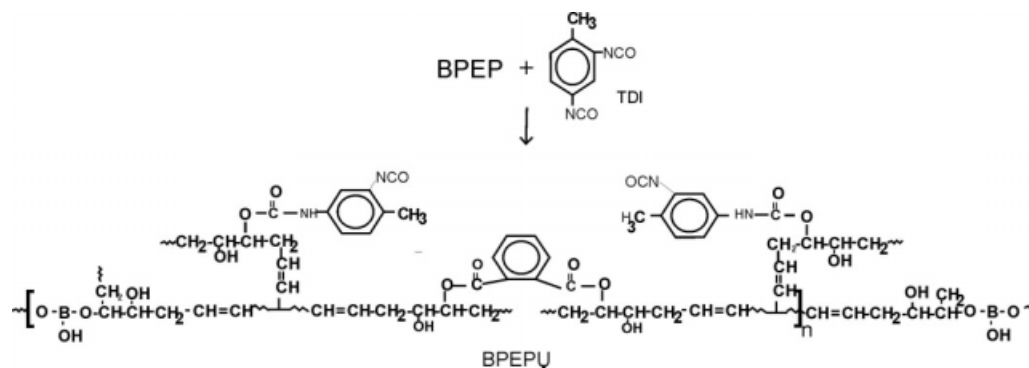
The formation of LPO follows common epoxidation and hydroxylation reactions.<sup>22</sup> The overall strategy involves “single-pot, multi-step” reactions.<sup>2,10</sup> The epoxidised oil reacts with water liberated during epoxidation reaction (at double bonds of oil) by  $SN^2$  mechanism, leading to its hydration and then hydroxylation forming LPO (Generation I polyol).<sup>9,10</sup> Hydroxylation (polyol formation) at unsaturation of oils (by peracids) follows similar mechanism as typical to hydroxylation of alkenes by peracids wherein an epoxide, formed as an intermediate, undergoes acid-catalyzed hydrolysis resulting in the formation 1,2-diols (stereo chemical process) corresponding to anti addition at carbon–carbon double bonds. In Generation II polyols, hydroxyl groups are primary in nature and terminal in location; in the polyols prepared by our method (Generation I polyols), the hydroxyl groups are secondary in nature and located in the middle (or in proximity to C18 –terminal carbon) of the fatty triester chains.<sup>7–10</sup>

The reaction scheme for the synthesis of BPEPs has been provided in our previous publication.<sup>22</sup> PEP, BPEPs, PEPUs, and BPEPUs were synthesized by polyesterification and polyaddition reactions, respectively. The former synthesis reaction, following “single-pot, multi step” reaction strategy, occurs in the absence of any solvent attributed to the inherent free flowing (fluidity) characteristic of polyols, which facilitates homogenous mixing of chain entanglements (formed during polymerization) and ren-

ders solubility.<sup>12–14,21</sup> The synthesis of BPEPUs (Fig. 1) requires minimum amount of solvent owing to their high viscosity and complexity of their inherent structures as discussed previously. Nonetheless, almost 50% reduction in the use of VOCs was achieved in the synthetic approach.

All BPEP samples were obtained as stable, clear free flowing fluids upto higher loading of BA (0.12 moles) even after 30 days, unlike their castor oil based counterparts [BCPEs], which showed separation of white crystals of BA in 0.12BCPE after standing for 20 days.<sup>21</sup> This phenomenon can be well interpreted by understanding the structures of the two polyols. In natural polyol, only one hydroxyl is present in each fatty acid chain [ $-\text{CH}_2-\text{CH}(\text{OH})-$ ]; in LPO, in each chain, at least two hydroxyls are located on adjacent carbons with anti position to each other [ $-\text{CH}(\text{OH})-\text{CH}(\text{OH})-$ ]. In BPEPs, due to the proximity of the hydroxyl groups, BA can possibly react with both inter and intramolecular hydroxyls located on the polyol backbone. Thus, it is speculated that each incorporated  $-\text{B}(\text{OH})-$  moiety is sandwiched between two polyol chains (inter or intramolecular). Because of the higher number of hydroxyls, there is least possibility for  $-\text{B}(\text{OH})-$  to attain terminal position, thus, there is no possible susceptibility to hydrolysis and BA separation. In BCPEs, due to excess of BA (0.12 mol), the incorporated  $-\text{B}(\text{OH})-$  attains terminal position with an easy access to water molecules (formed during polyesterification reaction).<sup>21,22,33</sup>  $-\text{B}$  easily withdraws water molecules toward itself due to its electron deficient nature, imposing strain on the incorporated  $-\text{B}(\text{OH})-$ , which becomes susceptible to hydrolysis resulting in the formation of BA.

BPEPU systems attained much higher viscosity and finally became unbrushable after an optimum loading of TDI. Upto a certain loading of TDI,  $-\text{NCO}$  (TDI) reacts with  $-\text{OH}$  (polyol) and the systems remain in free flowing state. With increased addition of TDI,  $-\text{OH}$ s get consumed and any additional  $-\text{NCO}$  reacts with urethane groups rather



**Figure 1** Reaction scheme for the synthesis of BPEPUs.



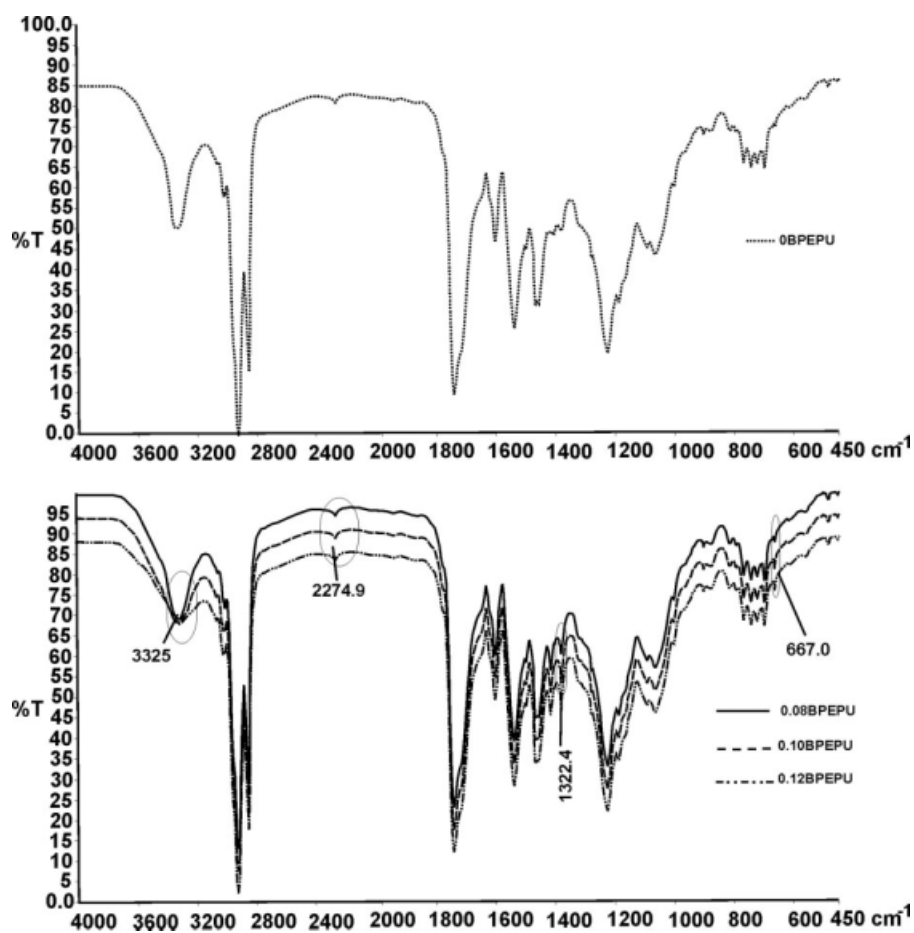


Figure 2 IR spectra of BPEPUs.

than free  $\text{—OH}$  of polyol, forming allophanic acid ester consequently resulting in lumpy aggregate formation (due to these side reactions) leading to their unbrushable state.<sup>21,34,35</sup>

### Spectral analyses

Important IR absorption band assignments for LPO and BPEPs are provided in our previously reported work.<sup>22</sup> Absorption bands at  $1322.4\text{ cm}^{-1}$  ( $\text{—B—O—}$  stretching),  $667.95\text{ cm}^{-1}$  ( $\text{—B—O—}$  bending),  $3325\text{ cm}^{-1}$  ( $\text{—OH}$ ), and  $2275\text{ cm}^{-1}$  ( $\text{—NCO}$ ) respectively, as observed in BCPEs and BPU, are also noticed in BPEPs and BPEPUs (Fig. 2).<sup>21,22</sup> In IR spectrum of 0BPEPU (zero-boron polyurethane), absorption bands characteristic for  $1322.4\text{ cm}^{-1}$  ( $\text{—B—O—}$  stretching),  $667.95\text{ cm}^{-1}$  ( $\text{—B—O—}$  bending), as observed in BPEPs and BPEPUs, are absent here, while bands typical for  $\text{—OH}$  show increased intensity. On incorporation of boron, as in 0.08, 0.10, and 0.12BPEPU, as boron content is increased, the absorption band of  $\text{—OH}$  decreases in depth due to consumption of  $\text{—OH}$  on reaction with BA.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra reveal characteristic peaks for  $\text{—B(—OH)—}$ ,  $\text{—B(—OH)—O—CH—}$ ,  $\text{—B(—OH)—O—CH—CH}_2\text{—}$  and

those typical for urethane linkages at their respective  $\delta$  values (Figs. 3 and 4).<sup>36</sup>

$^1\text{H-NMR}$  spectra also reveals a small peak at  $\delta = 7.89\text{ ppm}$  attributed to free  $\text{—COOH}$  of PA<sup>21</sup>; this peak occurs in the spectra of all BPEP compositions indicating that even at its higher loading (0.12 mol), BA does not react with PA, rather it tends to approach the free  $\text{—OH}$  of LPO. The  $\text{—COOH}$  of PA undergoes esterification reaction only with  $\text{—OH}$  of LPO.<sup>21</sup>

### Physicochemical analyses

Refractive index, specific gravity and inherent viscosity increase while iodine and hydroxyl values show a decrease in trend from BPEPs to BPEPUs.<sup>10,22</sup>

Table I also reveals successive decrease in hydroxyl and iodine values and increase in refractive index, specific gravity and inherent viscosity from BPEPs, 0 to 0.12BPEPU, which can be attributed to the consumption of hydroxyls due to reaction of  $\text{—OH}$  (i) of LPO with BA in BPEPs and, (ii) of BPEPs with  $\text{—NCO}$  of TDI in BPEPUs, respectively, followed by higher crosslinking of polymers.

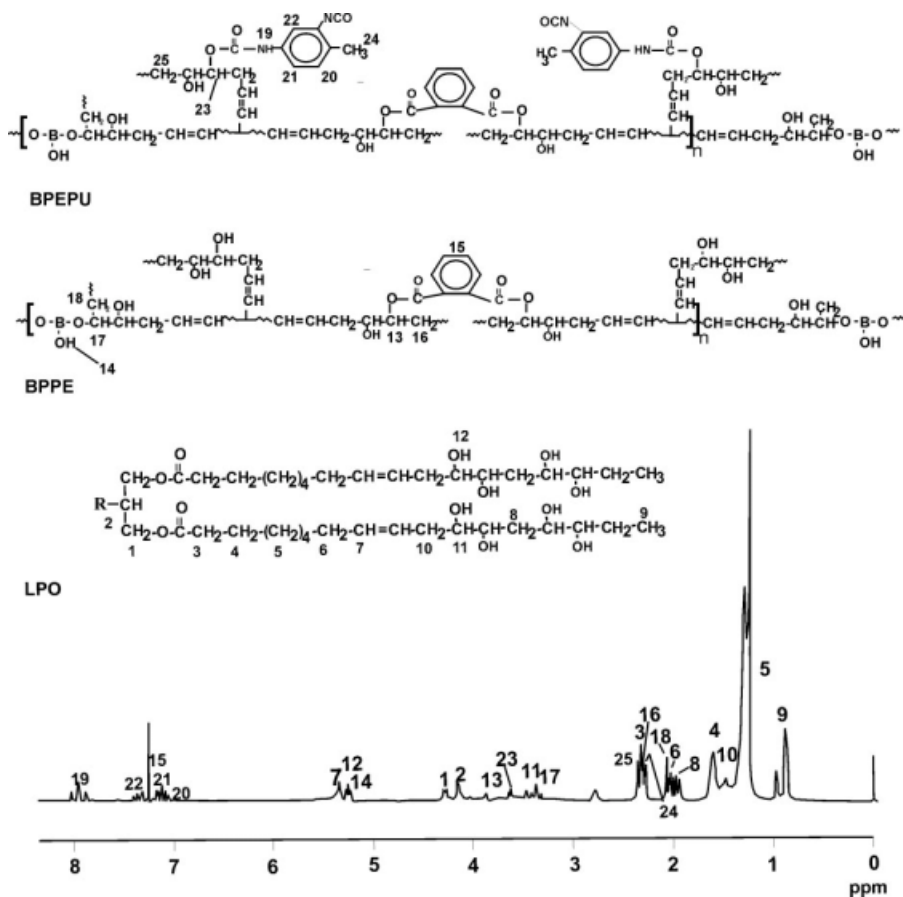


Figure 3  $^1\text{H}$  NMR spectra of BPEPUs.

A closer observation reveals that as compared with their boron incorporated counterparts based on natural polyol, aforementioned physicochemical characteristics for BPEPs and BPEPUs show considerably higher values. As explained earlier, the differences in the structural build-up of synthesized (LPO) and natural (castor oil—CO) polyol highlight higher number of closely situated hydroxyls, with close proximity to each other (inter and intra molecular hydroxyls of fatty triester chains) in the former, providing greater number of crosslinking sites between reactants resulting in denser systems.

### Curing of BPEPUs

BPEPUs follow a clear-cut “three step-ambient temperature” curing strategy, where each step occurs (i) independently (without overlapping or interfering with each other), (ii) in a sequential manner (one after the other), (iii) at ambient temperature, and (iv) each step has an important role in developing a cured thermoset network.

The first step involving solvent evaporation is a purely physical process; the latter two are chemical processes. The second step, proceeding by the reaction of free  $-\text{NCO}$  groups of BPEPUs with moisture,

begins soon after the first; by this time as there is no solvent in the resin, the film starts to set. At the end of this stage, the resin film becomes DTT in 15–20 minutes. The third step follows auto-oxidation at (residual) double bonds of BPEPUs, at the end of which, a completely cured thermoset state (dry-to-hard-DTH) is achieved. Since the latter is a slow process, it is speculated that this step takes almost a week’s time.

### Coating properties

BPEPUs were developed with BA (0, 0.06, 0.08, 0.10, and 0.12 mol) and TDI. To obtain an optimum required content of TDI, the coatings (with varying contents of TDI) were tested for various physico-mechanical and chemical resistance tests. BPEPs were finally treated with this predetermined amount of TDI to prepare BPEPUs. It was noticed that with increased boron content, drying time of coatings decreases and becomes constant at 0.08BPEPU. As discussed below, we understand that increased boron content is accompanied by increased crosslink density and molecular weight of the resins, which also influence their drying times. However, at 0.08BPEPU, the optimum crosslink density required

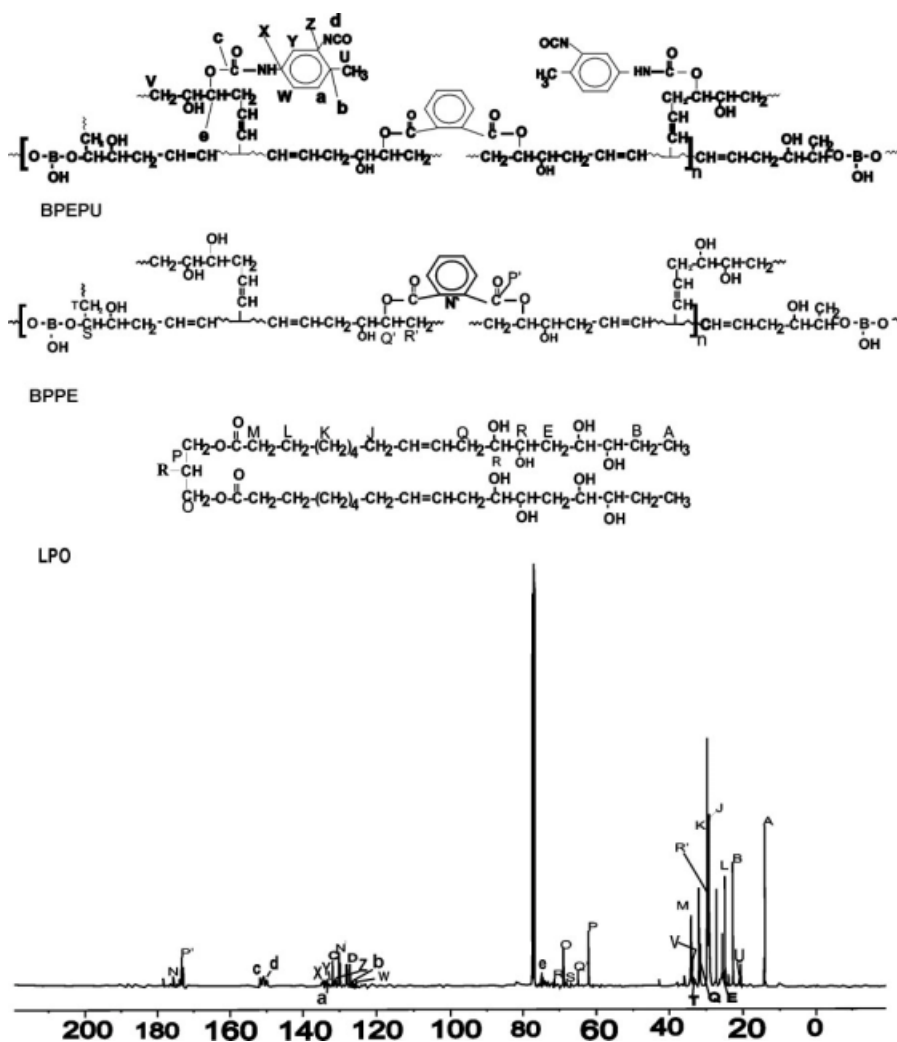


Figure 4  $^{13}\text{C}$  NMR spectra of BPEPUs.

to attain DTT is achieved; consequently, the DTT of BPEPUs also becomes constant beyond this loading of BA.

BPEPUs show higher gloss values, ranging from 75 to 126, from 0 to 0.12BPEPU, compared with castor oil based BPUs (100–110) attributed to the dense structures of the former.

The results of their physico-mechanical and chemical resistance performance have been summarized in Table II. These are the average values obtained after testing five specimen-coated panels for each test.

### Physico-mechanical analyses

As the content of boron increased from 0 to 0.12BPEPU, scratch hardness values increased from 1.0, 2.5 to 3.0 kg; all the systems passed impact resistance (14 kg/m) and bend tests (1/8 inch). The results are indicative of highly cross linked network, with good adhesion to the substrate as well as flexibility (bending ability) of polymeric chains, also evident from the structural build up of the resin, which shows

an excellent combination of moieties, e.g., polyester, polyurethane,  $-\text{O}-\text{B}-\text{O}-$ ,  $-\text{O}-\text{B}(\text{OH})-\text{O}-$ ,  $-\text{NCO}$ , aromatic moieties of TDI and PA, long aliphatic dangling chains of oil triester backbone and crosslinking at unsaturation (Fig. 1). Thus, it is observed that boron incorporated Castor and Linseed polyurethanes show improved performance over plain 0BPEPU (Table II).

### Corrosion/chemical resistance performance

BPEPUs were exposed to different chemical media, e.g., 5 wt % HCl, 5 wt % NaOH, 3.5 wt % NaCl, xylene and tap water to study the corrosion protective behavior of their coatings by recording the visual changes in their appearance, loss in their adhesion to the substrate, loss in their gloss and weight.

It was observed that the coated panels remained unaffected in 5 wt % NaOH and 5 wt % HCl for 6 hours and 16 days, respectively; after this a slight deterioration in the appearance (gloss), adhesion and weight of coated panels was noticed. In NaCl, slight

loss in adhesion of the coatings to the substrate as well as dissolution of coating material could be perceived after 14 days of exposure of coated panels to this medium. In water, no changes could be detected even after 60 days of immersion of coated panels. The uncoated panels showed 59.55 and 0.6526% weight loss in 5 wt % HCl (16 days) and 3.5 wt % NaCl (14 days), respectively, while the coated panels showed 8.8 and 0.0546% weight loss in 5 wt % HCl (16 days) and 3.5 wt % NaCl (14 days), respectively. These results reveal that the coatings act as barrier to the substrate.

Thus, it can be inferred from our results that the increased boron incorporation has significant effect on (i) drying times, (ii) gloss, and (iii) physico-mechanical characteristics (scratch hardness) of BPEPUs as also observed in castor BPU. Similar results were also obtained in case of physicochemical characteristics of aforementioned resins. These results evidently highlight the role of BA both as a cross linker and modifier.  $-\text{O}-\text{B}-\text{O}-$ ,  $-\text{O}-\text{B}(-\text{OH})-\text{O}$  provide additional crosslinking as well as good adhesion of the coatings to the substrate. However, it is also worth mentioning that higher loading of BA has no effect on the chemical resistance performance of BPEPUs and castor BPUs.

Castor oil based BPUs showed higher DTT (5–8.5 hours), whereas BPEPUs achieved relatively much lower DTT (15–20 minutes). Castor 0.06BPU formed a fragile coating over the substrate after a considerable period of time (15 days), whereas 0.06BPEPU formed a tough thermoset network (after 7 days of incubation period). BPEPUs showed higher scratch hardness values (2.75–3.0 kg) in comparison to castor BPUs (1.5–2.0 kg). These results may be corroborated to higher crosslink density due to greater number of closely situated inter and intra molecular hydroxyls in the former.

Corrosion resistance to acid is highly improved in BPEPUs (unaffected in 5 wt % HCl for 16 days, visible deterioration started only after this period) while castor BPUs encountered similar fate only after 3 hours of exposure to the medium. Castor BPUs performed very well in alkaline media (unaffected in 5 wt % NaOH for 50 hours) as compared with BPEPUs (unaffected in 5 wt % NaOH for 6 hours). We understand that there is an optimum amount of modifier required for a particular corrosive media to develop resistance to corrosion; slight variation in this amount may result in drastic alteration in coating performance. BPEPUs have higher number of incorporated  $-\text{O}-\text{B}-\text{O}-$  linkages (more than the optimum required amount), which are more susceptible to alkaline attack than castor BPUs ( $\text{BPEPU}_{\text{OH}} > \text{castor BPU}_{\text{OH}}$ ); consequently, BPEPUs become prone to alkaline hydrolysis readily than acid and exhibit lower resistance to alkaline media than castor

BPUs. Contrarily, higher  $-\text{O}-\text{B}-\text{O}-$  linkages in the former, favor corrosion resistance to acid.

### Antibacterial behavior

Antibacterial activities of BPEPUs are provided in Table III. 0.06BPEP, 0.08BPEP were found to be inactive against *E.coli* and their corresponding BPEPUs were found to be moderately active.<sup>22</sup> 0.10BPEP, 0.12BPEP and their BPEPUs were found to be mildly and moderately active against *E. coli*, respectively. However, all these systems showed higher antibacterial activity against *S. aureus*; 0BPEPU showed mild antibacterial activity. The long hydrocarbon chains of hydroxylated, boronated fatty triester residues of BPEPs as well as urethane and free  $-\text{NCO}$  of BPEPUs cast an inhibitory influence on bacterial activity. Their probable mode of action involves bacterial protein denaturation, damage of lipid complexes in cell membranes or dehydration of bacterial cells; metal/metalloid may reportedly cause the precipitation of bacterial cell proteins.<sup>10,22</sup> These processes accelerated by dehydration of bacterial cells inhibit the overall metabolic activities of bacterial cells; the cells finally become inactive.<sup>12,14,37</sup>

*E. coli* (gram negative) and *S.aureus* (gram positive) show varying response against BPEPs and BPEPUs. It can be correlated to the presence of an outer membrane containing lipopolysaccharide in *E. coli* (absent in *S. aureus*), responsible for protecting the bacteria from several antibiotics, dyes, and detergents, which would normally damage the inner membrane or cell wall peptidoglycan<sup>37,38</sup>; this may be the probable reason here also. Consequently, BPEPs and BPEPUs show high antibacterial activity against *S.aureus* and are inactive to mildly and moderately active against *E. coli*.

### Thermal analyses

TGA and DSC thermograms of BPEPUs provided in Figures 5 and 6, show identical curves attributed to their identical structural pattern as in the case of castor BPUs; the only difference lies in the amount of BA. The onset of degradation in either case occurs at 230°C. The initial weight (2–5%) loss is attributed to the evaporation of the trapped solvent or moisture followed by the degradation of urethane bonds beyond 250°C; this is eventually succeeded by the thermal degradation of aromatic moieties, aliphatic chains of LPO and  $-\text{B}$ -linkages in the second and third step of degradation. It is important to note that plain urethane polymers generally show decomposition of urethane bonds (first stage decomposition) between 150 and 220°C.<sup>39</sup> Here, BPEPUs show slight improvement in their thermal stability attributed to the introduction of boron linkages.



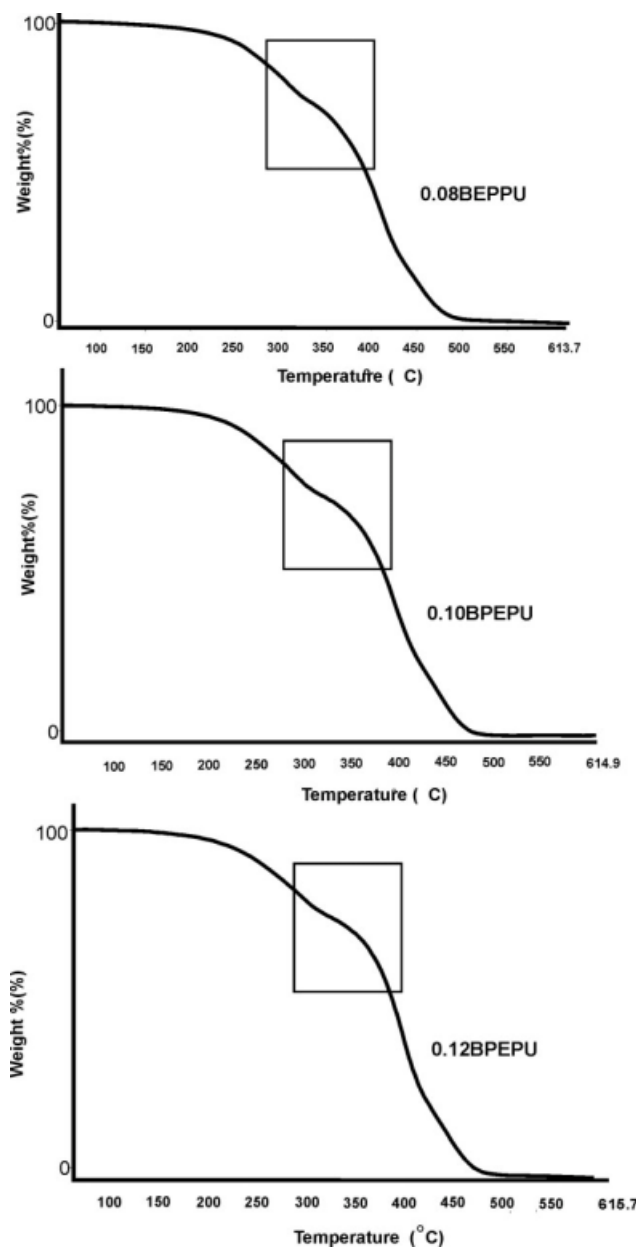


Figure 5 TGA thermograms of BPEPUs.

It has also been observed that petro-based PUs generally show single step degradation while their oil-based counterparts exhibit more than one-step degradation pattern resulting in the formation of isocyanate, alcohol,  $\text{CO}_2$ , primary and secondary amine, and olefin.<sup>21,28</sup>

0.08, 0.10, and 0.12 BPEPUs show 25, 50, and 70 wt % loss at 310, 387, and 414°C, at 312, 396, and 419°C, and at 314, 392, and 408°C, respectively. DSC thermograms show three endothermic peaks at 304, 306, and 308°C, at 325, 328, and 330°C, and at 359, 362, and 365°C, respectively, in 0.08, 0.10, and 0.12BPEPUs proceeded by an exotherm; the former can be inferred as the melting phenomenon pro-

ceeded by some configurational changes in the polymer chains leading to their decomposition marked as an exotherm beyond 400°C. TGA distinctly reveals decomposition after this temperature. Thus, overall, these systems show improved thermal stability and can be safely used upto 230°C.

As reported earlier, 0.08, 0.10, and 0.12 castor BPUs showed 25 wt % loss at 327, 337, and 350°C and 50 wt % loss at 374, 376, and 381°C. The values obtained show that BPEPUs are thermally more stable than CO polyurethanes.

## CONCLUSION

The synthesis of LPO as well as BPEPs follows “single-pot, multi-step” reactions strategy, where each reaction occur independent of each other. BPEPs and BPEPUs serve as an excellent example of metalloids incorporated sustainable resource based polyols and polyurethanes synthesized in minimum solvent. Overall, 50% reduction in the use of VOCs, in the synthetic approach has been achieved. The structures and properties of the resins reveal the dual role of BA, both as a cross linker and modifier. BPEPUs show lower DTT, good gloss and physico-mechanical performance (scratch hardness = 2.5–3.0 kg, impact resistance = 14 kg/m and bending ability = 1/8 inch), better acid resistance and higher thermal stability over their castor oil based counterparts. TGA and DSC thermograms of BPEPUs show identical patterns of their curves even for increased loading of BA. BPEPs and BPEPUs are inactive and mildly to moderately active against *E.coli*; they show high antibacterial activity against *S.aureus*. These systems can be safely employed upto 230°C.

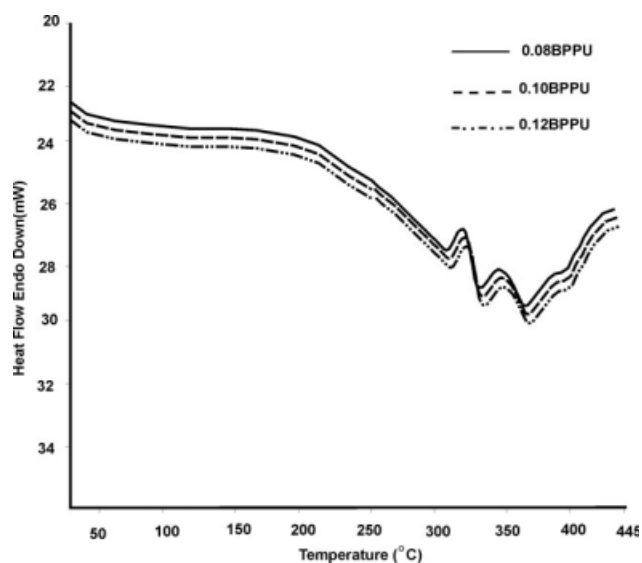


Figure 6 DSC thermograms of BPEPUs.

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