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# Synthesis and Characterization of Boron Incorporated Polyester Polyol from Linseed Oil: A Sustainable Material

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**Summary:** Polyols obtained from seed oils have established themselves as excellent building blocks of polymers, viz. polyurethanes. In this work, a novel attempt has been made to incorporate boron in the backbone of polyol [LPO] derived from linseed oil. Furthermore, LPO was treated with phthalic anhydride [PA] and boric acid [BA] (in different molar ratios) to obtain boron incorporated linseed polyester polyols [BPPEs] through solvent less synthesis process. BPPEs were characterized by spectroscopic techniques (IR, $^1$H NMR and $^{13}$C NMR) to confirm the incorporation of boron and also to elucidate their structures. Physico-chemical characterization and antibacterial behavior of BPPEs was also investigated. It is speculated that these resins may serve as excellent raw materials for adhesives, coatings and as antibacterial agents.

**Keywords:** differential scanning calorimetry; NMR; polyesters; resins; synthesis

## Introduction

Vegetable seeds oils (VSOs) have been established as the singular largest family of sustainable resources yielding polymers viz. alkyds, polyepoxies, polyesters, polyamides, polyesteramides, polyethers, polyetheramides, polyurethanes, IPNs and several vinylated, maleinated and acrylated polymers. These polymers, obtained by various chemical modifications of virgin VSOs, find versatile end use applications as inks, plasticizers, cosmetics, foams, coatings, paints and as antimicrobial agents.[1–3] Polyols are also emerging as one such class of polymers. However, most of the studies on VSOs derived polyols are limited to polyurethanes with applications in foams, plasticizers and coatings.[4–9] The topic still holds wide scope for further research investigations.

The past five decades have witnessed extensive investigations of metal and metalloid incorporated commercial polymers. However, only a few publications have appeared on metal/metalloid incorporated polyesteramides and polyurethanes obtained from VSOs.[10–13] In the past, boron incorporated semi-inorganic polymers (through B-O, B-S, B-N and B-P bonds) with improved thermal stability, mechanical, electrical, antibacterial and antifungal properties have also been reported.[13–15] Such modifications are also limited only to petro-based resins.[14,15] Thus, arguably, from socio-economical and environmental viewpoints, VSOs based polyols may serve as an excellent starting material for aforementioned modification.

In our previously reported papers we have carried out the synthesis and characterization of acrylated and metalloid incorporated polyols (chemically derived and natural, respectively).[13,16] In this work, we proposed to carry out the synthesis and characterization of boron-incorporated polyol derived from linseed oil [LPO]. LPO was treated with PA and BA in different molar ratios to obtain boron incorporated linseed polyester polyol [BPPE]. The structural elucidation of BPPE was accomplished by IR and NMR ($^1$H and $^{13}$C) spectroscopic techniques.

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Physico-chemical characterization was carried out by standard laboratory methods. Antibacterial behavior of aforementioned resins was also investigated against *E. coli* and *S. aureus*. Some of these results have also been compared with our previously reported similar work on boron incorporated natural polyol [BCPE], *i.e.*, oil obtained from seeds of *Ricinus communis* or castor.[13]

## Experimental Part

### Materials

Linseed (obtained from local market) was air-dried. Seeds were ground to powdered form and were further subjected to oil extraction in soxhlet apparatus. Petroleum ether (BP 60–80 °C) was used as solvent in extraction procedure. Hydrogen peroxide (30%), sulphuric acid, glacial acetic acid, boric acid [BA] (Merck, India) and phthalic anhydride [PA] (s.d.fine chem. ltd., Biosar), were used as received.

### Synthesis

#### Synthesis of LPO

Oil, glacial acetic acid and $H_2O_2$ (with a few drops of sulphuric acid) were mixed under strong mechanical stirring in a three necked round bottomed flask equipped with cold water condenser, nitrogen inlet tube and thermometer. The ratio of double bonds: acetic acid: $H_2O_2$ was kept as 1**:** 0.5**:**1.5. After mixing, the temperature of the reaction mixture was raised to $70 \pm 5$ °C and maintained at this value for the required time period. The ethereal solution of the final product (LPO) was washed with sodium bicarbonate aqueous solution, distilled water and sodium chloride aqueous solution and was further dried over anhydrous sodium sulfate. Ether was removed from LPO in a rotary vacuum evaporator at $45 \pm 5$ °C. A golden yellow colored LPO was finally obtained.

### Linseed Polyester Polyol (PEP)

LPO (1.0 mol) and PA (0.02 mol) were placed in a four necked round bottomed flask fitted with a Dean Stark Trap, nitrogen inlet tube, thermometer and magnetic stirrer. The reaction mixture was heated to 115 °C–130 °C and refluxed until the theoretical amount of water was collected in Dean Stark Trap. The progress of the reaction was monitored by thin layer chromatography (TLC). The reaction mixture was visually observed for any changes in its clarity and viscosity. After the completion of the reaction, a dark brown colored PEP was finally obtained.

### Boron Incorporated Linseed Polyester Polyol (BPPE)

LPO (1.0 mol), PA (0.02 mol) and BA (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 and magnetic stirrer. The reaction mixture was heated to 120 °C–140 °C and refluxed until the theoretical amount of water was collected in Dean Stark Trap. The progress of the reaction was monitored by TLC. The reaction mixture was visually observed for any changes in its clarity and viscosity. After the completion of the reaction, a dark brown colored BPPE was finally obtained.

### Test Methods

FTIR spectra of PEP and BPPE were taken on Perkin Elmer 1750 FTIR spectrometer (Perkin Elmer Cetus Instrument, Norwalk-CT) using an NaCl Cell (a thin film of the resin was applied on NaCl cell). $^1$H-NMR spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer using deuterated chloroform and DMSO as solvent, respectively and tetra methyl silane (TMS) as an internal standard. Differential Scanning Calorimetry (DSC) analysis was carried out by DSC 10 (TA Instrument, USA) in nitrogen atmosphere. Physico-chemical analyses *viz.* Iodine value (IV), Hydroxyl value (HV), Refractive index (RI), Inherent viscosity (InV) and Specific gravity (SG) involved standard laboratory methods. Antibacterial behavior of the systems was evaluated by agar diffusion method (Table 3).[22] All samples were dissolved in dimethylsulphoxide (DMSO) and were tested against *E. coli* and *S. aureus* using standard drug Amekasin (30 μg/Disc).

## Results and Discussion

The reaction schemes for the synthesis of LPO and BPPEs have been provided in Figure 1. 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 of 1,2-diols (stereochemical process) corresponding to anti addition at carbon-carbon double bonds.[17,18] Here, epoxide formed as an intermediate cannot be isolated as a single, separate component. Rather, at any specific time during the progress of the reaction, epoxidized oil occurs mixed with oil, hydrated epoxy species and hydroxylated oil. Contrarily, in our previously published work,[17] oil based polyol was formed by a clear-cut, two-stage process-epoxidation followed by hydration, where oil epoxy formed could be well isolated and characterized at the end of former reaction.

The synthesis of PEP and BPPEs follows polyesterification reaction. The reaction was carried out in the absence of any solvent attributed to the inherent free flowing characteristic of polyol, which facilitates fluidity, renders solubility and homogenous mixing of chain entanglements (formed during polymerization) at the reaction temperature. All BPPE samples were obtained as clear free flowing fluids even upto higher (0.12 mol) loading of BA unlike BCPE, which showed separation of white crystals of BA in 0.12BCPE

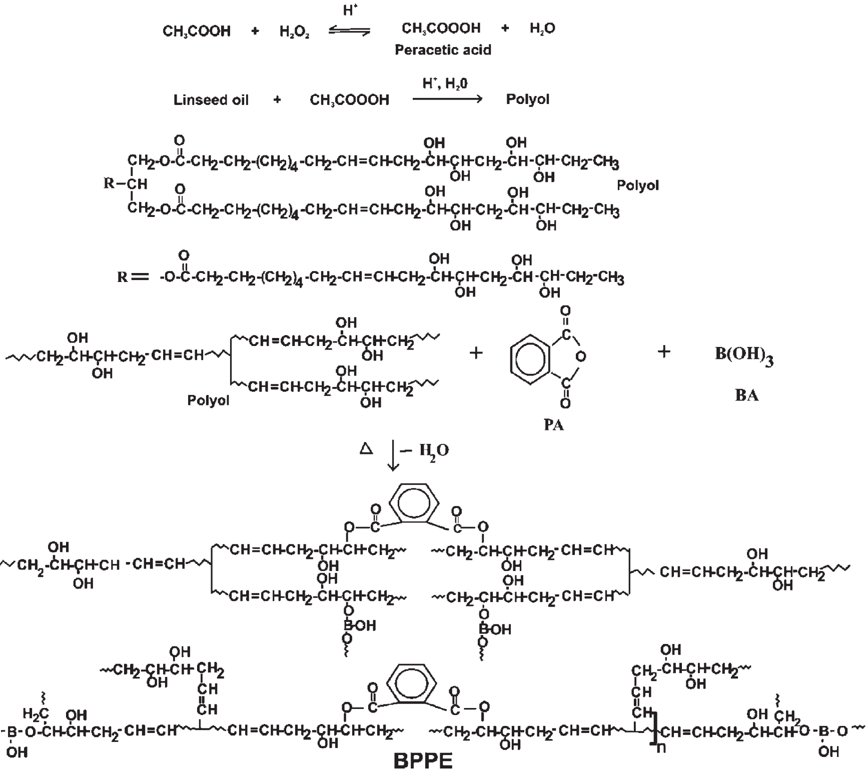

*Figure 1.*
Reaction scheme for the synthesis of LPO and BPPE.

after standing for 20 days. In latter system, it can be speculated that due to excess of BA (0.12 mol), the incorporated –B(–OH)- attains terminal position with an easy access to water molecules (formed during polyesterification reaction).[13,19] –B– easily withdraws water molecules towards itself due to its electron deficient nature, imposing strain on the incorporated –B(–OH)–, which becomes susceptible to hydrolysis resulting in the formation of BA. In BPPEs, contrarily, the entire BA is consumed by reaction with excess of hydroxyls, consequently such state is not observed here.[19]

In natural polyol, only one hydroxyl is present in each fatty acid chain [–$CH_2$–CH(OH)–], while in LPO, in each chain, (atleast two) hydroxyls are located on adjacent carbons with anti position to each other[–CH(OH)–CH(OH)–]. In oil-based polyols, the number of hydroxyls on each chain as well as their stereochemistry is also variable depending upon the hydroxylating agents and other reaction conditions.[12,13,21]

In BPPEs, BA is capable to react with both inter and intramolecular hydroxyls located on the polyol backbone. Thus, each incorporated –B(–OH)-moiety is sandwiched between two polyol chains (inter or intramolecular). Due to higher number of hydroxyls, the chances of –B(–OH)- attaining terminal position are negligible, thus there is no possible susceptibility to hydrolysis and BA separation, and BPPEs remain as clear free flowing fluids even upto higher (0.12 mol) loading of BA.

The structures of the final products have been ascertained with the help of spectral analyses (discussed below).

## Spectral Analyses

IR absorption band assignments for LPO and BPPEs have been provided in Table 1.

***Table 1.***
IR absorption bands of Polyol and BPPE

| IR ($cm^{-1}$) | Polyol | BPPE |
|---|---|---|
| –C=C–H Str | 3009 | 3008 |
| –$CH_2$, –$CH_3$ assym str | 2925.2 | 2928 |
| –$CH_2$, –$CH_3$ sym str | 2855.4 | 2856 |
| –C=O ester | 1742.2 | 1748 |
| –(C–C(=O)–O str | 1241, 1167.2 | 1241.9,1167 |
| –O–C–C str (ester) | 1104.3 | 1106 |
| –C=C– | 1632 | 1636 |
| OH | 3439.4 | 3445 |
| B–O str* | | 1335.0 |
| B–O bending* | | 648.0 |

*[12,13,17,20].

Additional bands for –B–O– stretching and bending at 1334 $cm^{-1}$ and 645 $cm^{-1}$, respectively, which are absent in IR spectra of PEP, are observed in BPPEs. $^1$H-NMR and $^{13}$C-NMR spectra reveal characteristic peaks for –B (–OH)–, –B (–OH)–O–CH– and –B (–OH)–O–CH–$CH_2$– (also absent in PEP) at their respective $\delta$-values (Figure 2 and 3) along with those typical of all other component functional groups of BPPEs.[12,13,20]

$^1$H-NMR spectra also reveals a small peak at $\delta = 7.96$ppm attributed to free –COOH of PA; it is noteworthy that this peak (of same intensity) occurs in the spectra of all BPPE compositions indicating that even at higher (0.12 mol) loading of BA, it does not react with PA, rather it tends to approach the free –OH of LPO. The –COOH of PA undergoes esterification reaction only with –OH of LPO.

## Physico-Chemical Analyses

IV, HV, RI, InV and SG of BPPEs are provided in Table 2. It is observed that HV decreases on successive increase in BA content in BPPEs, which can be attributed to the reaction of PA and BA with –OH of LPO. IV decreases while RI, SG and InV increase on successive addition of BA supporting the increased molar mass of BPPEs on the incorporation of –B–.

It is interesting to note that compared to similar boron incorporated systems based on natural polyol, aforementioned physico-chemical characteristics show considerably higher values. As explained earlier, the structural build-up of synthesized LPO reveals higher number of closely situated hydroxyls with close proximity to the hydroxyls of other (inter and intra molecular) chains allowing for higher cross-linking between constituents resulting in denser systems with high molar mass.

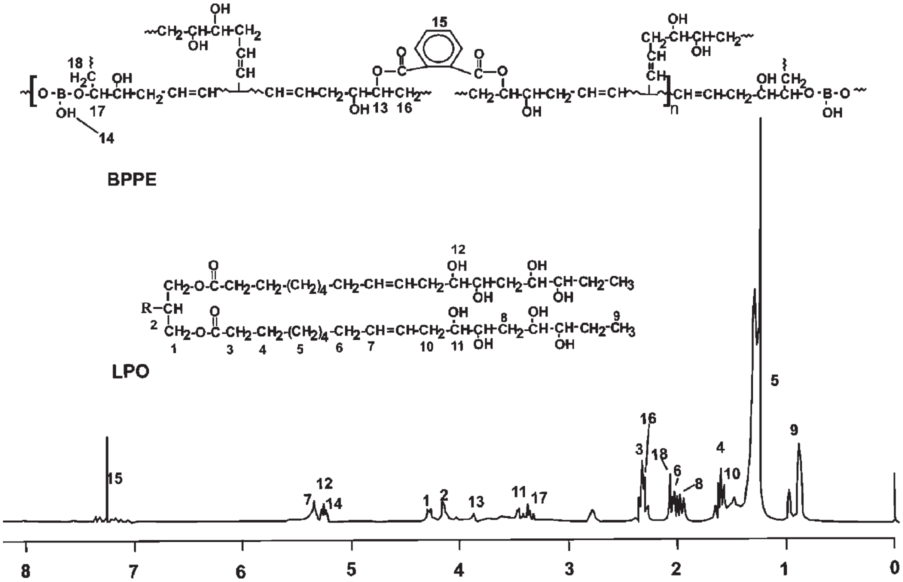

**Figure 2.**
$^1$H NMR spectra of BPPE.

## DSC

In DSC thermogram of plain polyol[17] (Figure 4), first (small) and second (broad) endotherms are centered at 152 °C and 164 °C, respectively; an exotherm starts to appear beyond 250 °C–260 °C. The former may be attributed to some configurational changes taking place within the resin prior

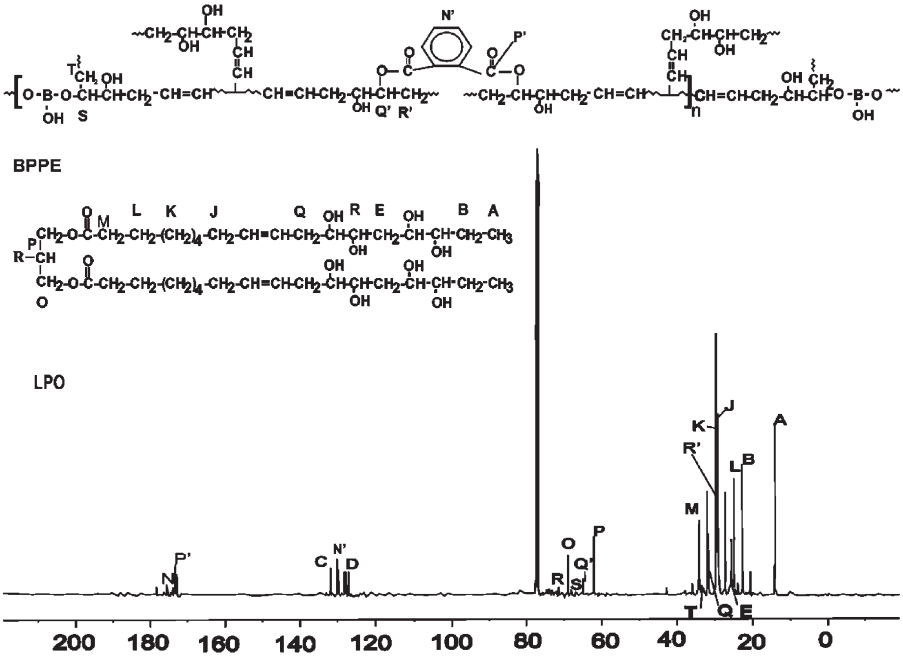

**Figure 3.**
$^{13}$C NMR spectra of BPPE.

***Table 2.***
Physico-chemical analysis of BPPEs.

| Resin Code | Hydroxyl Value (%) | Iodine Value (g $I_2$/100g) | Specific Gravity (g/ml) | Refractive Index | Inherent Viscosity (de/g) |
|---|---|---|---|---|---|
| 0.06 BPPE | 19.22 | 65 | 0.9131 | 1.488 | 1.134 |
| 0.08 BPPE | 14.45 | 62 | 0.9156 | 1.489 | 1.138 |
| 0.10 BPPE | 9.77 | 58 | 0.9181 | 1.491 | 1.140 |
| 0.12 BPPE | 7.22 | 55 | 0.9186 | 1.494 | 1.145 |

The values of the aforementioned parameters for physico-chemical analyses given in Table 2 are the average values of three consecutive analyses of each resin, for each parameter, with experimental error permissibility of ±0.05.

to the onset of degradation under the influence of higher temperatures; this is eventually followed by an exotherm, which highlights decomposition of the resin beyond 250 °C–260 °C.

In the DSC thermogram of 0.12BPPE (Figure 5), an endotherm appears at 156.85 °C, followed by endotherms at 349.56 °C and 382.56 °C; this later merges with an exotherm beyond 400 °C. The former endotherm is expected to highlight melting phenomenon while the latter can be attributed to define some configurational changes that generally take place within polymeric chains (after melting), under the effect of high temperature. Since the second endotherm immediately merges with an exotherm, it can be conceived that these configurational changes are followed by thermal degradation of the resin.

It can be inferred that the incorporation of boron has a pronounced effect on thermal behavior of the resin only at higher temperatures. While in plain polyol an exotherm starts to appear beyond 250 °C–260 °C, in BPPE, it is visible only at 400 °C.

### Antibacterial Studies

Anti bacterial activity of BPPEs is provided in Table 3.

0.06BPPE and 0.08BPPE were found to be inactive while 0.10BPPE and 0.12BPPE were found to be moderately and highly active against *E.coli*. However, all these systems showed higher antibacterial activity against *S. aureus*. The long hydrocarbon

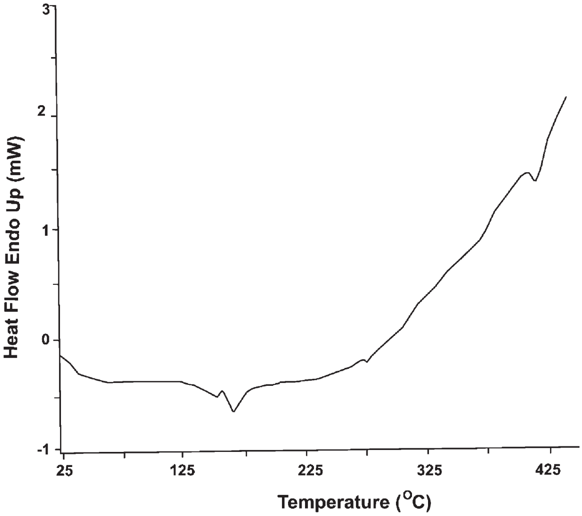

***Figure 4.***
DSC thermogram of plain polyol.

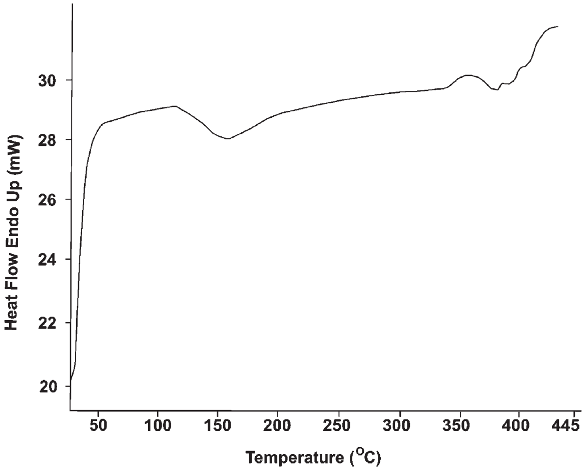

***Figure 5.***
DSC thermogram of 0.12BPPE.

***Table 3.***
Antibacterial Activity of BPPEs.

| Antibacterial activity | 0.06 BPPE | 0.08 BPPE | 0.10 BPPE | 0.12 BPPE |
|---|---|---|---|---|
| E.Coli | – | – | + | ++ |
| S.aureus | +++ | +++ | +++ | +++ |

–: Inactive (0.9 mm), +: Mildly active (10–15 mm), ++: Moderately active (16–20 mm), +++: Highly active (21–30 mm)

chains of hydroxylated and boronated fatty triester residues of BPPEs 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;[17] metal/metalloid may cause the precipitation of bacterial cell proteins. These processes accelerated by dehydration of bacterial cells inhibit the overall metabolic activities of bacterial cells, making them inactive.[10,11,22]

*E. coli* (gram negative) and *S. aureus* (gram positive) show varying response against BPPEs, which can be correlated to the presence of outer membrane containing lipopolysaccharide in the former. This outer membrane is responsible for protecting the bacteria from several antibiotics, dyes and detergents, which would normally damage the inner membrane or cell wall peptidoglycan [22] and this, may be the probable reason here also. Consequently, BPPEs show high antibacterial activity against *S.aureus* and are inactive to mildly active against *E.coli*.

## Conclusion

BPPEs serve as excellent example of metalloid incorporated sustainable resource based polyols synthesized for the first time. These systems were synthesized in the absence of any solvent taking advantage of the inherent fluidity of oil polyol, thus cutting off the use of harmful volatile organic compounds (VOCs). Spectral analyses confirm the structure of BPPEs. DSC themogram shows endotherms and exotherm that signify some configurational changes that take place within the resin under the influence of high temperature, followed by thermal degradation of polymer beyond 400 °C. BPPEs show mild to moderate antibacterial activity against *E.coli* while they are highly active against *S.aureus*. These systems may find applications as antibacterial coatings, paints, tougheners for commercial epoxies, lubricants, adhesives and as cementing agents.

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