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Chapter I

A concise explanation about the perspective towards some production of biologically significant compounds with heterocyclic moiety

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Chapter I

Section A

(Humic Acid: A Rarely Explored, Robust, Green Catalyst for Solvent-Free Synthesis of 4*H*-Benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate and Benzo[*d*]thiazole)

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Chapter I

Section B

(Beta – Cyclodextrin (β-Cyclodextrin) mediated Solvent-Free Synthesis of 3,3'-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) and 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol))

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Chapter II

General Introductory part

(Wide-ranging analysis of polymeric exploration, synthesis and evaluation)

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Chapter II

Background of the Present Study

(Wide-ranging analysis of polymeric exploration, synthesis and evaluation)

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Chapter II

Section A

(Synthesis and Performance Evaluation of Castor oil – Styrene Co - polymer: an Outstanding Multipurpose Directional Lubricant Additive)

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Chapter II

Section B

(Evaluation and Synthesis of Environmentally Benign multifunctional additives for lube oil)

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Chapter II

Section C

(Synthesis of behenyl acrylate and citral based polymers: A comparative study on their performances as biodegradable multifunctional lube oil additives)

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REPRINT OF SOME PUBLISHED PAPERS

Research on Chemical Intermediates
https://doi.org/10.1007/s11164-024-05237-1

Humic acid: a rarely explored, robust, green catalyst for solvent-free synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate and benzo[*d*]thiazole

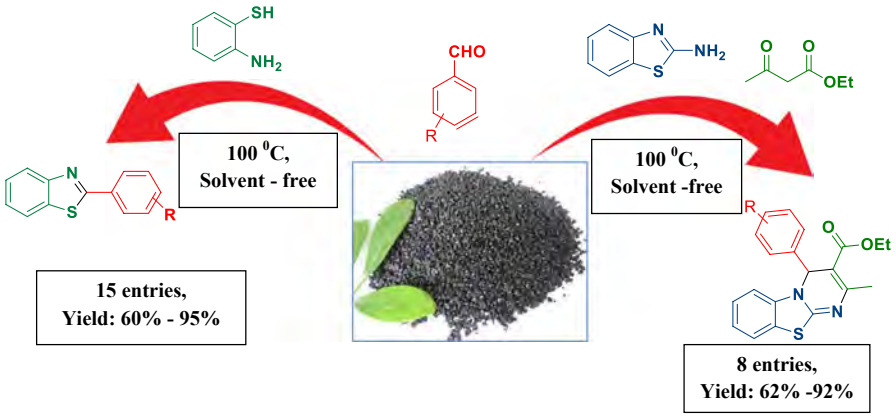
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Received: 1 November 2023 / Accepted: 22 January 2024
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Abstract

Humic acid, a rarely used non virulent, easily accessible, inexpensive, environmentally benign, high molecular weight polymer, because of its extraordinary catalytic activity has been explored for the synthesis of functionalised 4*H*-benzo[4,5] thiazolo[3,2-*a*]pyrimidine-3-carboxylate and its derivatives along with functionalised benzo[*d*]thiazole. Environmental friendliness, low catalyst loading, outstanding yield, magnificent functional group forbearance and renewability up to fifth run without any noteworthy loss of its activity at the finishing point of reaction, are the cue significances of these methods.

Graphical abstract



Keywords Aldehydes · Benzo[*d*]thiazole · Heterocycles · Humic acid and Thiazolo[3,2-*a*]pyrimidine

Extended author information available on the last page of the article

Published online: 20 March 2024

Introduction

In the past several decades, research practices in chemistry are constantly evolving through overcoming the rigidities such as, fixed reaction patterns, systematic approaches inside the confines of a laboratory. In order to make any system sustainable, attempts should be made to keep the laboratory experimental conditions in accordance with the environment, surrounding us. Therefore, any alteration, innovation or discovery, made in the system must be handled with great care and consideration to ensure its suitability to the surroundings. The continuous environmental degradations and it is already visible devastating impacts have made the researchers and scientists to be focused on to the suitability of their research like never before. As a consequence, like any other procedures, organic synthesis must look at the sustainability aspect through the application of innovative and greener protocols that avoid the use of hazardous solvents, toxic chemicals, poisonous catalysts, and harsh reaction conditions. Use of such substances can result in massive environmental pollution and damage to the nature, during the synthesis of chemical components, particularly organic molecules. For that reason, organic synthetic methodologies must attempt to replace the traditional solvents and catalysts (wherever possible) with appropriate alternatives. The need to keep the drug industry flourishing through maintaining the sustainable protocols makes it worthwhile to pursue chemical synthesis.

Solvent-free protocols are greener and one of the best solutions to these environmental issues, since they can eliminate most of the flaws like pyrophoric property of harmful and hazardous solvents with high volatility and poor recovery. There are ample scopes in future, for further more detailed inspection of the solvent-free pathway, basically, as a part for synthesizing of organic molecules through greener methodology. Due to such factors, solvent-free pathways of organic synthesis have become very much popular in recent years. The aim of this initiative is to enhance earthly consciousness above a number of hazardous chemicals and substitution of harmful solvents and substituting those using greener products to progress towards green chemistry [1–14].

Generally, high molecular weight materials are very much useful for organic synthesis because of their low toxicity, ease of separation, easy recovery and reusability. Among them humic acid is very rarely used, nontoxic, easily accessible, inexpensive, environmentally benign, high molecular weight polymer with extraordinary catalytic activity. Humic acid is derived primarily from biodegradation of dead and decreased organic materials and obtained mostly in peat, soil, coal, upland streams, dejected lakes and well water. It is interesting and essential catalytic activity is exhibited owing to the presence of wide range of most ample functional groups, e.g. carboxyl (–COOH) and phenolic hydroxyl (=CH–OH) group in its structure. However, a careful review of the literature reveals that, only a few articles have reported the application of catalyst. Therefore, there is an enormous scope of further detailed exploration of its catalytic venture in multidirectional protocols of biosynthesis. Low catalyst loading, outstanding yield and significant functional group toleration are some of the extraordinary

characteristics of humic acid in its catalytic approach. Another important convenience about humic acid is its renewability. Structure of humic acid is shown below (Fig. 1) [6, 15, and 16].

The previously reported humic acid mediated solvent-free production of multiple collection of functionalised bis(indolyl)methanes, bis(pyrazolyl)methanes, biscoumarins and bis-lawsones by the reaction of vast range of aldehydes with Indole, 3-methyl-1-phenyl pyrazolone, 4-hydroxy coumarin and 2-hydroxy naphthalene-1,4-dione respectively [6]. Another previously reported humic acid catalysed reaction was one pot, three components, water mediated preparation of 5-substituted 1*H*-tetrazoles, from a number of aldehydes, hydroxylamine hydrochloride in presence of sodium azide [15]. Again, humic acid was used as a support of Pd/Ni bimetallic catalyst for Heck coupling reaction, in one of the previous studies [16].

4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine is a very essential compound under the highly important branch of fused heterocycles, with a vast pharmacological [17], pharmaceutical [18] and industrial [18] properties. It consists of a large number of biological activities, such as, antibacterial [18], anti-tumour [18], anti-inflammatory [18], antiviral [18], anticonvulsant [18], anticancer [18], antifungal [18] or fungicidal [19], antiallergic [19], antimicrobial [19], antimycobacterial [19], antiproliferative [19], anticoagulant [20], antiherbicidal [20], antituberculosis [21] . It can be used as a salient synthon to design various modern medicinal drugs [22] for synthesizing a number of biologically active compounds [23] and natural products [10]. It is a remarkable optical liquid [13] with electronic properties [13] and used as dyes[24] and fluorescent [16] materials. This compound is so much useful for constructing medicines, associated with human and cattle contagious disorder such as, AIDS, hepatitis B and C, tuberculosis and bovine viral diarrhoea, drug resistant cancers i.e. leukaemia, carcinoma, melanoma and multi drug resistant tumours, which has no definite remedy or effective availability of vaccines till date [15].

It is very well known fact, that, heterocyclic and polycyclic compounds, containing nitrogen, sulphur and oxygen (N, S, and O respectively) are very much flexible and necessary framework for designing a variety of drugs [25]. Some basic skeletal structures of such bioactive drugs are shown below (Fig. 2). Benzothiazole and its derivatives, the important part of heterocyclic [17] and polycyclic compounds [17], represent a number of biological [26], medicinal [27], pharmacological [18],

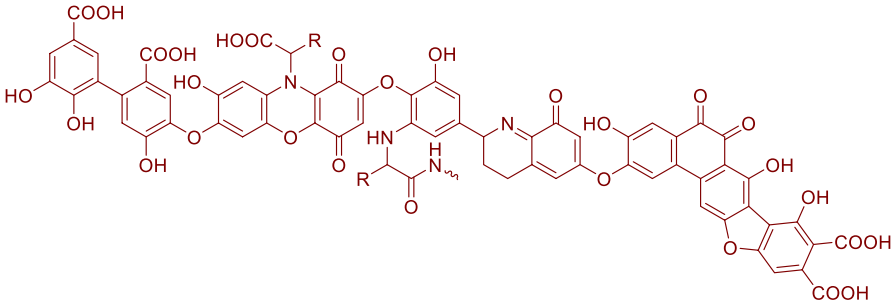


Fig. 1 Structure of humic acid

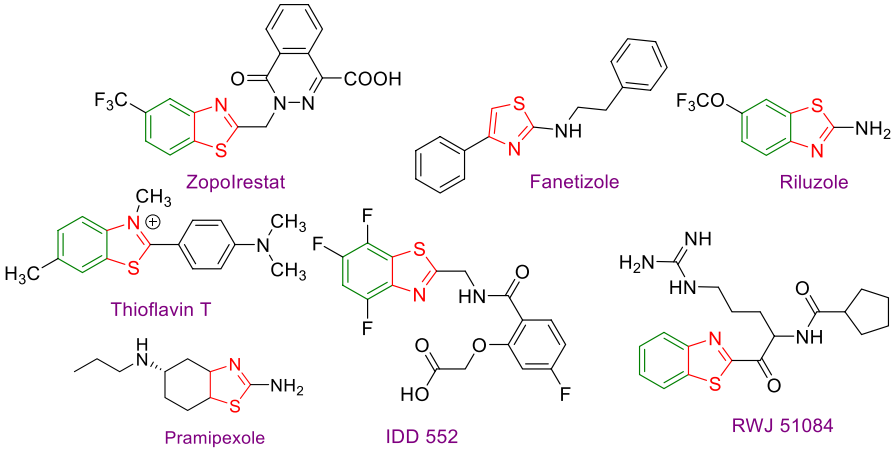


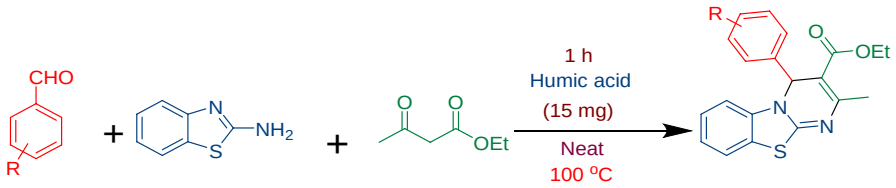
Fig. 2 Some examples of biologically active drugs

pharmaceutical [28] significances like analgesic [19], antiepilepsy [29], antilateral sclerosis [21], antihypertensive [19], anti HIV [19], antiulcer [19], anti diabetic [30], anti Parkinson [31], antithrombotic [19], antihistamine [32], antiemetic [24], antianxiety [33], antistress [34], antiglutamate [23], antiparasitic [22], antihelminthic [35]—etc. They are used in autoimmune diseases [21]. Benzothiazoles are extensive important class of pervasive heterocyclic moieties [36] and exist as molecules or molecular framework in many bioactive natural products [28], e.g. vitamin B_{12} [16]. They have huge applications in material sciences [28] or material chemistry [28] as the primary components of materials with optical or electronic belongings [37] and also used as ligands of transition metals and intermediates of organic reactions [38]. They play an important role as ligands in asymmetric transformations [30]. It has great application prospect in synthesis of variety of agrochemical compounds [30]. They are pharmacophores and applied in variety of modern drug discovery and development like omeprazole (proton-pump deterrence), candesartan and telmisartan (AT1 receptor nemesis), mebendazole (drug to prevent parasitic worm infection), dabigatran (direct thrombin inhibitor), flunoxaprofen (NSAID) and riluzole (sodium channel barricade and drug to fend off amyotrophic lateral sclerosis)—etc. [31]. Benzothiazole derivatives are also present in Fanetizole (anti-inflammatory agent), UDP-galacto-pyranose mutase inhibitor, κ and μ narcotic receptor and small molecular somatostatic receptor subtype 5 (SST5R) antagonists –etc. [39]. It can act as efficient enzyme inhibitor, e.g. it is very popular inhibitor of Chemokin receptor ($CXCR_3$) [30], Lymphocyte tyrosine kinase (LCK) [32], Glycinamide ribonucleotide transformylase (GARTfase) [41], Topo isomerase-1 [19], Aldol reductase [42], HIV reverse transcriptase [19]—etc. Some derivatives of benzothiazole behave as plant growth regulators [43], photosensitizes, LTD_4 receptors [22], potent cationic Trypsin receptor [34] and chemosensor [44] for a range of analytes. They are actively used in corrosion science [45]. These compounds are especially found in the moieties, which can conduct the life cycles in various cells [32]. They act a very significant role in metabolic process, taking place in living organisms [24]. They

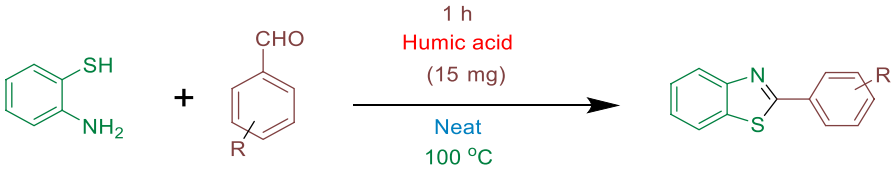
have vast industrial significances [11]. In industry, they are used as antioxidants [17], vulcanization accelerators [22], dopants in light emitting organic electroluminescent devices, i.e. nonlinear optical luminescent [17]. They can exhibit florescent properties [17] and so, they are used in designing sensor molecules of specific categories [17]. They can form the compounds with cytotoxic activities [19] and imaging agent for Ca^{2+} channel antagonist [17].

4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate was synthesized previously by using the catalysts like; magnetic nano catalyst (nano—kaoline or hydrated aluminium silicate Al_2O_3, $2SiO_2$, $2H_2O$)/Ti^{4+}/Fe_3O_4 [18], nano-Co-[4-chlorophenyl-salsylaldimine-pyranopyridine dione]Cl_2 or nano-Schiff base complex [46], DBU and CPB (cetyl pyridinium bromide) [19], phosphorus containing ionic liquids [17], Fe_3O_4@nano-cellulose/Cu(II) [47], Fe_3O_4@SiO_2-$TiCl_3$ nano particles [48], nano cellulose/BF_3/Fe_3O_4 [21], nano-$TiCl_2$/cellulose [20], L-proline [49], Lewis acid, covalently grafted over sulfonic acid functionalised carbon@titania composites [50], ager [51], ammonium chloride [23], microwave over *p*-TSA clay [52], MgO or 12-tungstophosphoric acid [53], chitosan [54], phosphoric acid supported on alumina (H_3PO_4-Al_2O_3) [55], Mg–Al–CO_3 and Ca–Al–CO_3 hydrotalcite [56], TBAHS [57] – etc.

Benzo[*d*]thiazole was synthesized previously by using the catalysts like; amino quinolone B,B-diphenyl complex as the photocatalyst [58], enzyme like Trypsin, Lipase, Bovin—etc. [26], H_2SO_4, HCl, H_3PO_4, HF—etc. traditional acid catalysts [27], Bronsted acid surfactant combined ionic liquids [36], I_2 in TBHP (Tert butyl hydroperoxide) [59], Cu(II)-Glycerol/MCM-41 (nanocatalyst) [24, 88], mesoporous titania—alumina mixed oxide [60], magnetic Co-doped $NiFe_2O_4$ [40], nano composite, mesoporous silica supported samarium [61], Ag_2O (in microwave) [62], epichlorohydrin cross linked *β*-cyclodextrin (*β*-CD polymer) [63], YCl_3 [64], UIO-66-NH_2 derived Bronsted acid catalyst [65], nanosealed UIO-66-NH-RSO_3H catalyst [57], ZnO nanoparticles [66], iron catalyst [41], ruthenium silicate zeolite [25], vanadium and molybdenum Schiff base complexes [32], fluorescein (photocatalyst i.e. visible light in presence of O_2) [37], fluorinated phosphoric acid [38], camphor sulfonic acid [33], hydrotalcite, visible LED light in photosensitizer [67], laccase/DDQ [68], NH_2-MIL-125(Ti) metal–organic framework [69], tin modified mono ammonium phosphate fertilizer ($SnCl_2$ in MAP) or SnP_2O_7 in EtOH [70], hybrid crystal $H_3N(CH_2)_4NH_3SiF_6$ (monoalkyl ammonium hexafluorosilicate) [35], $NiFe_{2-x}Eu_XO$ nanostructured catalyst [71], TiO_2 nanoparticle in H_2O_2(in P_{25} nanoparticles) [31], mesoporous poly(melamine–formaldehyde) [42], water(H_2O) [72], magnetic nanoparticles supported tungsto silicic acid [73], iron phthalocyanine [39], NaY zeolite functionalised by sulfamic acid/$Cu(OAC)_2$ or NaY zeolite-$NHSO_3H$/$Cu(OAC)_2$ as hybrid catalyst [29], oxalic acid: L-proline [44], solid acid supported on magnetic nanoparticles (solid acid catalyst [Fe_3O_4@SiO_2@$(CH_2)_3$NPC-SO_3H]Cl) [74], MIL-101(Fe)hexagonal microspindle [22], functionalised magnetic core shell nanoparticles, containing I_3^-, i.e. [Fe_3O_4@SiO_2@$(CH_2)_3NMe_3^+$]I_3^- [75], chitosan-SO_3H [76], $H_3N(CH_2)_5NH_3BiCl_5$ [77], copper containing nano silica thioalated dendritic material [45, 89], two dimensional Bi_2WO_6 nanosheets as a sturdy catalyst (towards photocatalyzation) [43], phosphoric acid supported on alumina



Scheme 1 Humic acid mediated synthesis of functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine



Scheme 2 Humic acid mediated synthesis of functionalised benzo[*d*]thiazole

(H_3PO_4/Al_2O_3) [55], CuI [78], $VOSO_4$ catalyst in ethanol [79], calcinized egg shell [30], copper(II)-diaminosarcophagine functionalised SBA-15 [34], proline-based ionic liquid catalyst [80], nano-titania-supported sulfonic acid catalyst (n-TSA) [81], tBuONa [82], visible light photo catalyst [83], i.e. CdSe nanocomposites, made by monmorillonitrile (MMT) [75], SiO_2-HNO_3 [84], Ag_2O_3/Celite [85], $Fe_3O_4/SiO_2/(CH_2)_3NMe_3^+ Br^-$ core shell nanoparticles [86], $CuFe_2O_4$ nanoparticle catalyst [87]—etc.

Metal catalysts are very much expensive, hazardous, dangerous, poisonous, fatal, toxic, and huge time consuming to be prepared. Ionic liquids are also very much expensive, auto toxic, especially for human and aquatic organisms. Moreover, ionic liquids have their limited solubility and they cannot be removed by distillation. Therefore, we have chosen humic acid since; it is much superior in its catalytic approach with respect to the other mentioned catalysts. This makes the overall methodology of those reactions is superior in greener and environmentally more sustainable approach with respect to their previous studies.

The discussion, presented in the previous paragraphs, indicates the points of interests to synthesize compounds, containing benzothiazole moieties with a large no. of conveniences. The target compounds in this experiment, were functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine along with its derivatives in addition to functionalised benzo[*d*]thiazole and its derivatives. The present study utilized humic acid as significant greener catalyst and used some greener pathway like, solvent-free methodology (Schemes 1, 2). Scheme 1 shown here, the reaction of benzaldehyde, 2-aminobenzothiazole andethyl acetoacetate; along with the formation of functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine; on the other hand, Scheme 2 shown below, the reaction of benzaldehyde and 2-aminothiophenol; along with the formation of functionalised benzo[*d*]thiazole; in presence of humic acid catalyst, under absolute solvent—free condition.

Experimental

General information

All the compounds were acquired from commercial suppliers and used without further purification. All the products were purified by column chromatography on silica gels (60 – 120 Mesh, SRL, India). For TLC, Merck plates coated with silica gel 60, F254 were utilized. ^{1}H NMR,^{19} F and ^{13}C NMR were recorded using 400 MHz, 376 MHz and 100 MHz, respectively, on Bruker AV 400 NMR spectrometer using TMS as internal standard. Splitting manners of protons were explained as s (singlet), d (doublet), t (triplet) and m (multiplet).

General procedure for the synthesis of 4H-benzo[4,5]thiazolo[3,2-a]pyrimidine

A mixture of 2-aminobenzothiazol (1 mmol), benzaldehyde (1 mmol),ethyl acetoacetate (1 mmol) and humic acid (15 mg) was blended at 100 °C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept track of using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was annihilated to room temperature and ethyl acetate (5 mL) was added to the reaction mixture and the catalyst was separated by easy filtration and was extracted with ethyl acetate twice (2 × 20 ml). Amalgamated extracts were cleaned with distilled water, dried over anhydrous Na_2SO_4 and concentrated. The primitive product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate−petroleum ether). The products obtained were known compounds and were recognized by their colour, melting point and NMR spectroscopy.

General procedure for the synthesis of benzo[d]thiazole

A mixture of 2-aminothiophenol (1 mmol) benzaldehyde (1 mmol) and humic acid (15 mg) was blended at 100 °C for 1 h in open air in a reaction vessel (50 mL) using a magnetic stirring bar. The reaction progress was kept an eye on using TLC with a mixture of ethyl acetate and petroleum ether as the eluent medium. After finishing of the reaction, the mixture was annihilated to room temperature and ethyl acetate (5 mL) was added to the reaction mixture and the catalyst was separated by smooth filtration technique and was extracted with ethyl acetate twice (2 × 20 ml). Amalgamated extracts were washed with purified water, dried over anhydrous Na_2SO_4 and concentrated. The primitive product was decontaminated by passing through a column packed with silica gel (eluent: ethyl acetate−petroleum ether). The products obtained were known compounds and were recognized by their colour, melting point and NMR spectroscopy.

Spectral data of some compounds

The NMR data of Ethyl 2-methyl-4-(3-nitrophenyl)-4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate, the desired product of the model reaction, is given below:

^{1}H NMR (400 MHz, DMSO-*d6*) δ (ppm): 1.085 (t, $J=7$ Hz, 3H), 2.419 (s, 3H), 4.026 (q, $J=6.8$ Hz, 2H), 6.662 (s, 1H), 7.175 (t, $J=7.6$ Hz, 1H), 7.282 (t, $J=7.6$ Hz, 1H), 7.511 (d, $J=8$ Hz, 1H), 7.576 (t, $J=8$ Hz, 1H), 7.737 (d, $J=7.6$ Hz, 1H), 7.827 (d, $J=7.6$ Hz, 1H), 8.058 (d, $J=8$ Hz, 1H), 8.315 (s, 1H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ (ppm): 14.448, 23.774, 56.338, 60.227, 102.428, 112.873, 122.225, 123.246, 123.478, 123.809, 124.861, 127.510, 130.956, 133.875, 137.646, 143.997, 148.160, 155.598, 163.556, and 165.707.

The NMR data of 2-(3-Nitrophenyl)benzo[*d*]thiazole, the desired product of the model reaction, is given below:

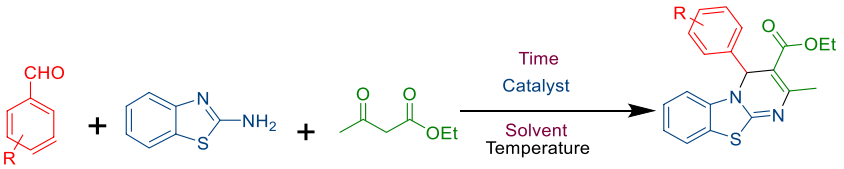
^{1}H NMR (400 MHz, CDCl3) δ (ppm): 7.456 -7.476 (m, 1H), 7.551 (d, $J=0.8$ Hz, 1H), 7.694 (t, $J=8$ Hz, 1H), 7.954 (d, $J=8$ Hz, 1H), 8.120 (d, $J=8$ Hz, 1H), 8.325 (s, 1H), 8.424 (d, $J=8$ Hz, 1H), 8.935 (m, 1H).

^{13}C NMR (100 MHz, CDCl3) δ (ppm): 121.840, 122.348, 123.761, 125.189, 126.041, 126.842, 130.113, 133.004, 135.187, 135.309, 148.773, 153.954, and 164.899.

Result and discussion

Catalyst, solvent and temperature are important driving components of any chemical reactions. So, it is necessary to maintain properly, the extent of catalyst, solvent and temperature throughout the target synthetic procedure. 1 mmol of benzaldehyde, 1 mmol of 2-aminobenzothiazole and 1 mmol ofethyl acetoacetate were taken as reactants to undergo model reaction (Scheme 1). We started our optimization technique (Optimization procedure of Scheme 1, has been shown in Table 1, below, in details), at first, with solvent, in presence of 30 mg of catalyst and next, it was observed that, refluxing with water, methanol and ethanol, the yield of the product was extensively low (Table 1, entry 1, 2, and 3). After that, by refluxing for 6 h continuously, the yield of the product was 50% with DMF (Table 1, and entry 4). When we carried out the same reaction, under neat condition, at 100 °C, with same amount of catalyst, then the yield of the product was enhanced up to 95% (Table 1, entry 5). Then we started the optimization of catalyst by lowering the quantity as, 25 mg, 15 mg, 10 mg and 5 mg (Table 1, entry 6, 7, 8, and 9). As a result, we observed that, 15 mg of catalyst was enough to carry out this pathway and the yield of the product was 92% (Table 1, and entry 7). On the other hand, the reaction could never be undergone in devoid of catalyst (Table 1, and entry 10). After that, by lowering the temperature up to room temperature, the yield of the product was reduced gradually (Table 1, entry 11, 12 and 13). Next, we kept track of the required time, for proceeding of the reaction and we found that, 1 h is sufficient for obtaining the maximum amount of product, under the indistinguishable reaction condition (Table 1, entry 15).

Table 1 Optimization of reaction condition (Scheme 1)



Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (h)	Yield (%)[a]
1	Water	30	reflux	6	trace
2	Methanol	30	reflux	6	30
3	Ethanol	30	reflux	6	42
4	DMF	30	reflux	6	50
5	Neat	30	100	6	95
6	Neat	25	100	6	94
7	Neat	15	100	6	92
8	Neat	10	100	6	49
9	Neat	5	100	6	43
10	Neat	Nil	100	6	–
11	Neat	15	70	6	77
12	Neat	15	50	6	65
13	Neat	15	rt	6	trace
14	Neat	15	100	3	92
15	**Neat**	**15**	**100**	**1**	**92**

The bold part signifies the optimized conditions

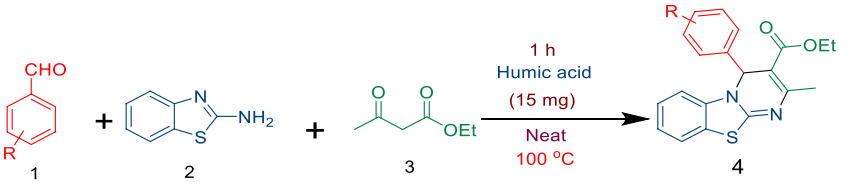
Reaction of benzaldehyde (1 mmol), 2-aminobenzothiazole (1 mmol) andethyl acetoacetate (1 mmol)

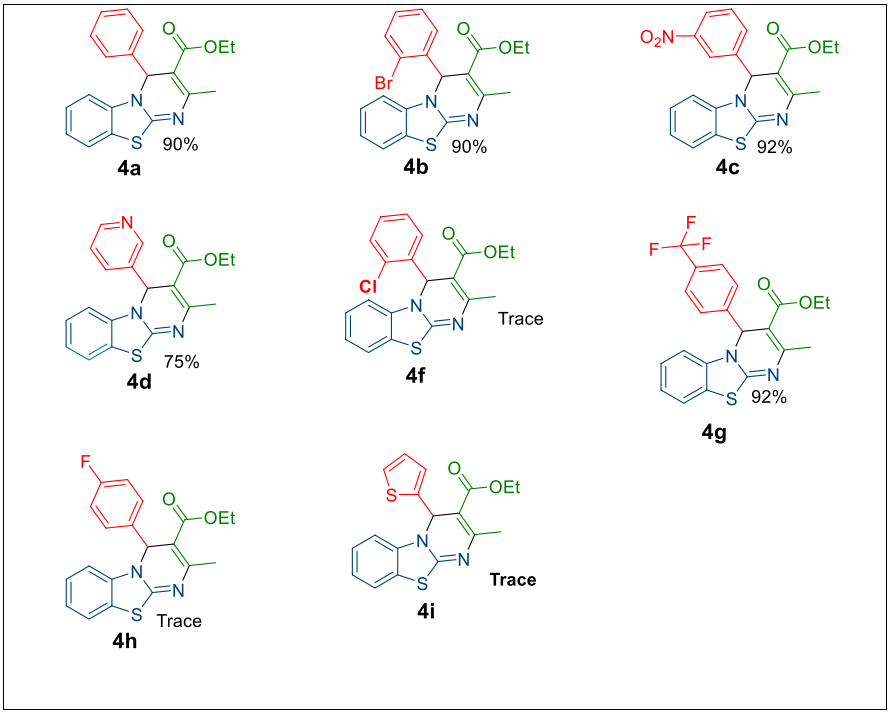
[a]Isolated yield was extracted through column chromatography

To perform in detailed study of our schemes, functionalised aldehydes were treated with 2-aminobenzothiazole andethyl acetoacetate (Scheme 1), under optimized condition and a variety of a number of 4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate derivatives were constructed. The resulted compounds have been tabulated in Table 2.

It was observed that, when electron withdrawing groups, especially nitro and trifluoromethyl were present in aldehyde, the product yield was very good (Table 2, entry 4c, g, respectively). But it was observed that, when aldehyde contained heterocyclic moiety, like thiophene, the product yield was not good (Table 2, entry 4i). However, aldehyde with heterocyclic moiety, like pyridine, produced the products with medium yield (Table 2, entry 4d). On the other hand, electron withdrawing groups like bromo, at ortho position, gave good yield (Table 2, entry 4b). On the contrary, electron withdrawing group chloro at ortho position and that of fluoro at para position, gave poor yield of the product (Table 2, entry 4f, h, respectively).

Table 2 Synthesis of functionalised thiazolo[3,2-*a*]pyrimidine derivatives (Scheme 1)

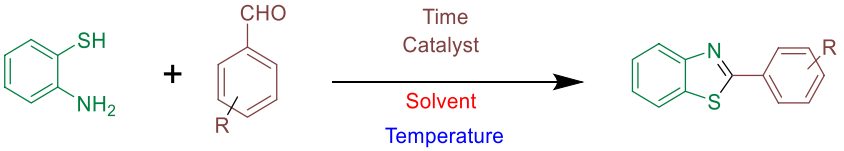




Reaction of aldehydes (1 mmol), 2-aminobenzothiazole (1 mmol), ethylacetoacetate (1 mmol) and humic acid (15 mg), under solvent-free condition for 1 h

In Scheme 2, we took 1 mmol of 2-aminothiophenol and 1 mmol of benzaldehyde as reactants to undergo model reaction (Scheme 2). In the screening method of this reaction, (Optimization procedure of Scheme 2, has been shown in Table 3, below, in details), at first we choose solvent, in presence of 30 mg of catalyst, refluxing with water, DMF, methanol and ethanol the yield of the product was very low (Table 3, entry 1, 2, 3, 4). By maintaining of 100 °C temperature continuously for 4 h, the yields of the product were 50% and 32% with PEG-200 and DMSO, respectively (Table 3, entry 5, and 6).When we underwent the same reaction in neat condition, at 100 °C, with same amount of catalyst, then the yield of the product was enhanced up to 98% (Table 3, entry 7). Then we initiated the optimization of catalyst, by reducing the amount of catalyst (Table 3, entry 8, 9, 10, 11). Thus, it was observed that, 15 mg of catalyst was enough to carry out this procedure and the yield of the product was 97% (Table 3, entry 9). On the other hand, the reaction could never be

Table 3 Optimization of reaction condition (Scheme 2)



Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (h)	Yield (%)[a]
1	Water	30	reflux	4	–
2	DMF	30	reflux	4	42
3	Methanol	30	reflux	4	trace
4	Ethanol	30	reflux	4	30
5	PEG-200	30	100	4	50
6	DMSO	30	reflux	4	32
7	Neat	30	100	4	98
8	Neat	25	100	4	98
9	Neat	15	100	4	97
10	Neat	10	100	4	88
11	Neat	5	100	4	82
12	Neat	Nil	100	4	–
13	Neat	15	70	4	87
14	Neat	15	50	4	81
15	Neat	15	rt	4	Trace
16	Neat	15	100	2	97
17	**Neat**	**15**	**100**	**1**	**97**

The bold part signifies the optimized conditions

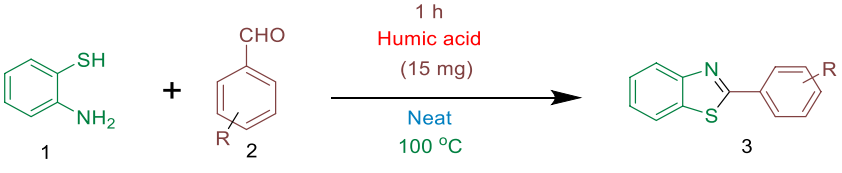
Reaction of benzaldehyde (1 mmol) and 2-aminothiophenol (1 mmol)

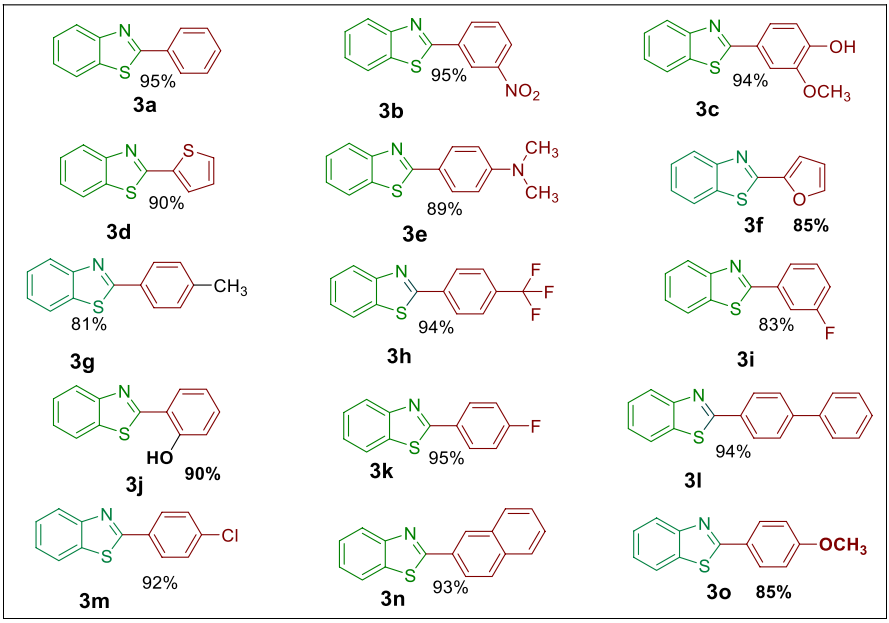
[a]Isolated yield was extracted through column chromatography

feasible to perform in devoid of catalyst (Table 3, entry 12). After that, by lowering the temperature, the yield of the product was reduced frequently (Table 3, entry 13, 14, 15). Next, we kept an eye on the required time for proceeding of the reaction and we discovered that, 1 h is sufficient for gaining the maximum amount of product, under exactly the same reaction condition (Table 3, entry 17).

To go through the detailed study of scheme 2, functionalised aldehydes were treated with 2-aminothiophenol (Scheme 2) under optimized condition and a variety of a number of benzo[*d*]thiazole derivatives were prepared. The resulted compounds have been tabulated in Table 4. From this table, it was observed that, when electron withdrawing groups i.e. nitro at meta position, fluoro, chloro, trifluoromethyl and biphenyl at para position, were present in aldehyde, the product yield was excellent (Table 4, entry 3b, k, m, h, l respectively). But it was also observed that, when an aldehyde contained electron withdrawing group i.e. fluoro at meta position, the yield was medium (Table 4, entry 3i). When an aldehyde contained heterocyclic moieties

Table 4 Synthesis of functionalised benzo[*d*]thiazole derivatives (Scheme 2)





Reaction of aldehydes (1 mmol), 2-amino-thiophenol (1 mmol) and humic acid (15 mg) under solvent-free condition for 1 h

like thiophene and furan, the product yield was medium to good (Table 4, entry 3d, f, respectively). Aldehyde, containing electron donating N, N dimethyl and methoxy groups, at para position, produced medium to good yield (Table 4, entry 3e, o, respectively). Vaniline and Salicylaldehyde gave very good yield (Table 4, entry 3c, j, respectively). Also, 2 naphthaldehyde produced a very good yield (Table 4, entry 3n).

Reusability experiment

Renewability of humic acid was confirmed through a model reaction, with benzaldehyde (5 mmol) and 2-aminothiophenol (5 mmol) in presence of 75 mg humic acid, under optimized reaction condition. After finishing of the first run, ethyl acetate (4 ml) was added to the reaction mixture. Catalyst was taken back smoothly from the reaction mixture by easy filtration procedure. Then, the

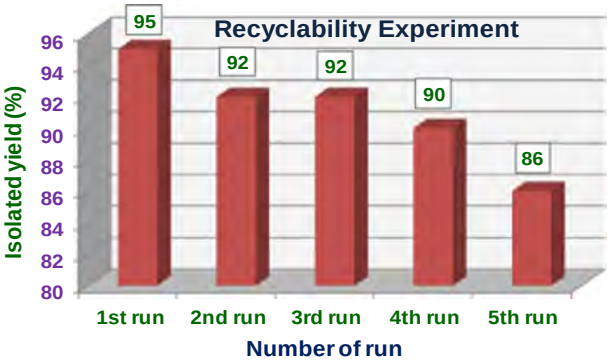


Fig. 3 Reusability of humic acid catalyst

recovered catalyst was washed with ethyl acetate (3 × 4 ml) and next it was dried before being handed down for the next run. The filtrate of reaction mixture was shifted to another container and this method was done for two times repetitively. The catalyst was then washed with ethyl acetate again and after that, it was dried for affording the black coloured humic acid, which was used in the next run, with its dryness. Recuperation of humic acid was slightly lower than the amount used in the first run. However, the recuperated catalyst was used continuously for four runs with almost similar affinity and there was no noteworthy degradation in the transformation. This recyclability test of humic acid catalyst has been shown in Fig. 3, below, through bar diagram. It signifies that, humic acid can expose its catalytic activity up to five successive runs without any considerable reduction in it and in lowering of the yield of the product.

Gram—scale reaction

The application of this methodology was examined in large scale, through carrying out the reactions in **gram-scale** (10 mmol scale) procedure. These also produced good yield, like the yield obtained in small scale reaction techniques. This Gram – Scale Reaction technique has been shown below, schematically, through Fig. 4.

Scale-up experiments

See Fig. 4**.**

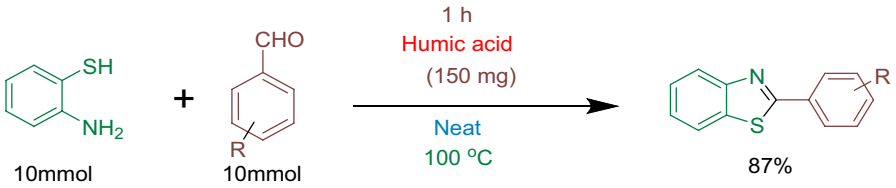
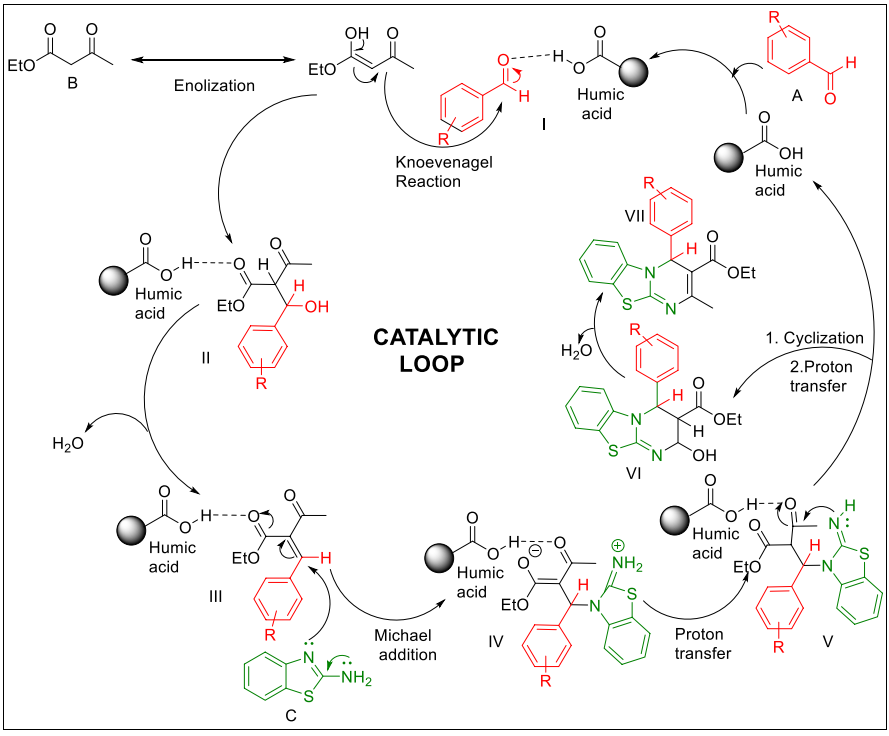


Fig. 4 Gram—scale reaction

Plausible mechanism for the synthesis of 4H-benzo[4,5] thiazolo[3,2-a]pyridine-3-carboxylate and benzo[d]thiazole

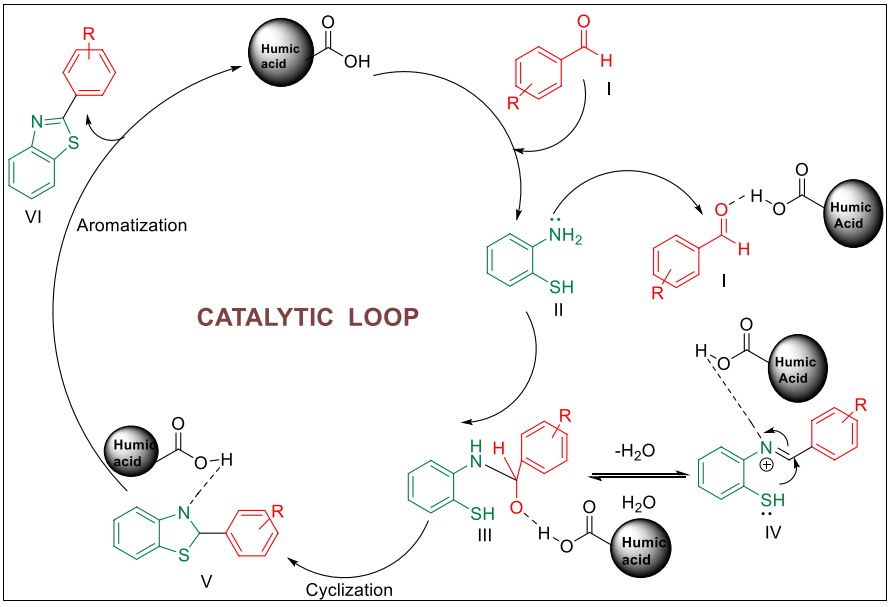
From the literature survey we have prepared the plausible mechanism for the synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate, which is shown in scheme 3. At first, the catalyst activates the aldehyde (A), through its acidic part (–COOH) to enhance the electrophilicity of the carbonyl group so that it can help the nucleophilic attack by enolised form ofethyl acetoacetate (B), by simple nucleophilic addition pathway and the intermediate (II) is formed. Humic acid activates further, the carbonyl carbon of –COOEt in intermediate (II). Then, after water elimination we



Scheme 3 Plausible mechanistic pathway for synthesis of 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

get the intermediate (III), into which, the nucleophilic centre of 2-aminobenzohiazole (C) attacks through Michael addition pathway i.e. at the four position. Thus we get the intermediate (IV) in which carbonyl carbon is activated again by humic acid catalyst. After that, through proton transfer, we get the intermediate (V), which then undergoes cyclization, followed by proton transfer process. Thus, we get the compound (VI), which forms the final product 4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (VII), by elimination of water and after that, the humic acid catalyst is restored. This reaction mechanism and pathway have been diagrammatically shown through the following Scheme 3.

From the surveying of literature, we have designed the plausible mechanism for the synthesis of benzo[*d*]thiazole, which is shown in scheme 4. At first, the catalyst activates the aldehyde (I) through its acidic part (–COOH), to increase the electrophilic nature of carbonyl group and so, it helps the nucleophilic attack by $–NH_2$ group of 2-aminothiophenol (II) by simple nucleophilic addition pathway and intermediate (III) is formed. This is transformed into intermediate (IV), by the loss of a water molecule. The enamine intermediate (IV) is activated again by the catalyst. Then, nucleophilic attack occurs by –SH group of the same compound, followed by cyclization and aromatization. Through the formation of intermediate (V), the expected product benzo[*d*]thiazole (VI) is formed. After that the humic acid catalyst is restored. This reaction mechanism and pathway have been diagrammatically shown through the following Scheme 4.



Scheme 4 Plausible mechanistic pathway for synthesis of benzo[*d*]thiazole

Conclusion

In conclusion, we have represented an environment friendly and feasible technique for synthesizing a number of functionalised 4*H*-benzo[4,5]thiazolo[3,2-*a*] pyrimidine-3-carboxylate and benzo[*d*]thiazole derivatives under the absence of any solvent, taking humic acid as catalyst to activate carbonyl oxygen of respective aldehydes and ester for enhancing the electrophilicity of carbonyl carbon, followed by nucleophilic addition onto that position. The overall mechanism proceeds through Cascade reaction, involving a well known Knoevenagel and Michael Addition pathway. Since, no metal was used here, so, the overall method was maintained as greener synthetic one. Again, the solvent-free condition, contributes a huge environmental sustainability to the protocol. Humic acid catalyst can be regained through easy filtration procedure and its recovery factor can proceed up to fifth run in devoid of any characteristic deviation of its extent of activity. So, the basic uniqueness and creativity manifestation of this methodology, is, the utilization of environmentally benign, easily accessible and low priced humic acid catalyst, instead of any toxic, fatal, dangerous, exhaustive, hazardous and expensive metal catalyst. This methodology proposed in the present study can be considered as a part of the consistent effort of the scientists and researchers by creating a significant evolution within the chemical world of medicines, synthetic pathways of natural products and drug industries, in future endeavours.

Supporting information summary

Supporting Information contains the experimental analysis, spectroscopy data and scanned copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of some of the synthesized compounds.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11164-024-05237-1.

Acknowledgements M. N. is grateful to CSIR, New Delhi for financial support.

Authors contribution MN has completed the whole experimental work, preparation of manuscript and contributed equally to these methodologies. BM helped her in the generation of idea of work, reviewing and editing of the whole procedure, under the supervision of PG.

Declarations

Conflict of interests The authors declare no competing interests.

Ethical approval Hereby, I consciously assure that, for this manuscript, entitled here, the following items are fulfilled. At present, this paper is not being contemplated for publication, elsewhere. All authors have been involved, actively and personally, in all the considerable work, leading to the paper and will take public accountability for this content.

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Asian Journal of Green Chemistry 7 (2023) 269-282

Asian Journal of Green Chemistry

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Synthesis and Performance Evaluation of Castor Oil-Styrene Co-Polymer: An Outstanding Multipurpose Directional Lubricant Additive

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ARTICLE INFORMATION

Submitted: 20 May 2023
Revised: 26 June 2023
Accepted: 3 July 2023
Available online: 11 July 2023

Manuscript ID: AJGC-2305-1392
Checked for Plagiarism: Yes
Language Editor:
Dr. Fatimah Ramezani
Editor who approved publication:
Dr. Abdolkarim Zare

DOI: 10.22034/ajgc.2023.396588.1392

KEYWORDS

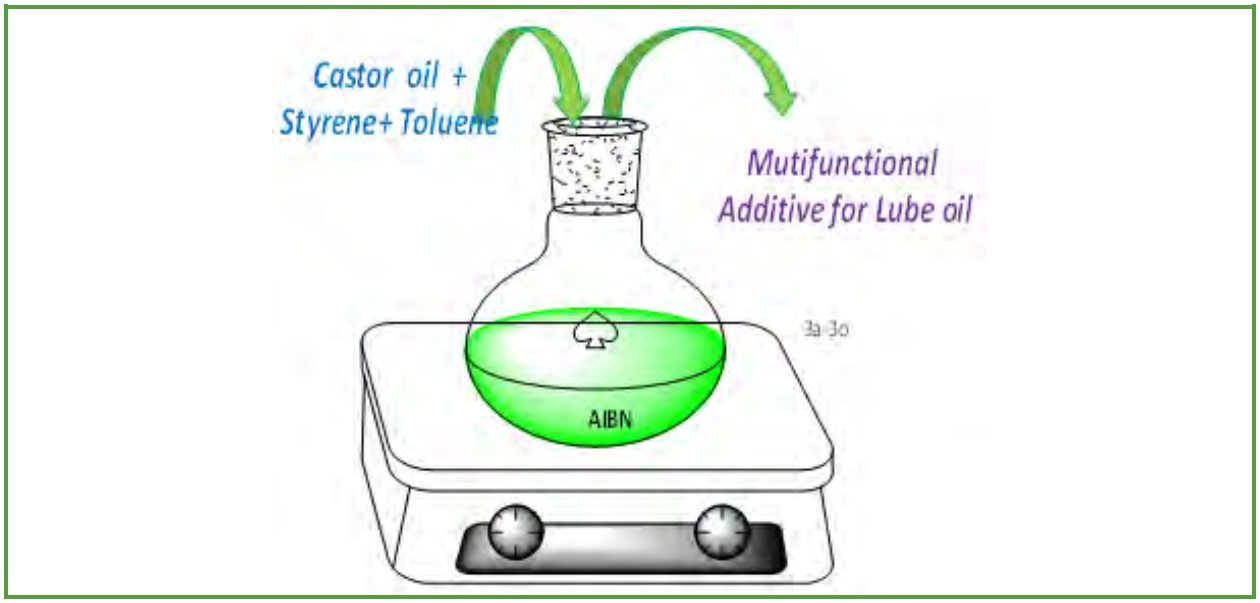
Additives
Pour Point Depressant
Viscosity Modifier
Castor oil
Styrene

ABSTRACT

Polymer and chemical industries are actively concentrating on the discovery and application of vegetable oils for polymer composites. In this work, castor oil homopolymers and their copolymers with styrene were made, as well as their assessment was done by spectroscopic methodology, thermo gravimetric analysis (TGA), and gel permeation chromatographic (GPC) strategy. The ASTM standard approach was employed to determine these polymers' efficiency in base oil. Photo-micrographic imaging was utilized to assess the efficacy of additives as pour point depressants by examining their impact on the microstructure. The biodegradability experiment for polymers was also conducted and outcomes are quite promising. Their performance comparisons have been further assessed and reported.
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Graphical Abstract



Introduction

There are many different base fluids and chemical additives used in the formulation of sophisticated lubricants.

The moving surfaces are kept separated from one another by the basal liquid, which creates a fluid zone between them to reduce friction. It reduces the amount of heat generated during operating condition and gets rid of the wear particles. Without sophisticated lubrication, additive chemistry and lubricant conceptualization, it would have been difficult to develop advanced engine and gearbox technologies. Contemporary engine oils are made up of various additives combined with base oils to create a comprehensive product that can meet even the most rigorous performance standards.The compounds, known as additives, satisfy the desired properties of lubricating and repelling the same.

In most cases, they are chemical compounds with a non-polar hydrocarbon chain and a polar head group. Numerous lubricating oil additives are employed, including detergent-dispersants, corrosion inhibitors and substances for usage under extremely high pressures, viscosity index improvers (VIIs), antioxidants (AOs), and pour point depressants (PPDs).

The least temperature at which lubricating oil flows without interruption when refrigerated within defined parameters is known as the pour point. Paraffinic wax, a component of petroleum oils, crystallizes into stiff lattice-like frameworks at lower temperatures, obstructing flow. Hindering the production of wax crystal formations that would block passage of oil at low temperatures is how some high molecular weight polymers work. These chemical additives are also known as pour point depressants, flow improvers, paraffin antagonists, or wax moderators. Pour point depressants have no impact on the temperature or quantity of developed crystals.

The adsorption, co-crystallization, aggregation, and enhanced wax dissolution rate of these compounds are among their most generally acknowledged modes of action. Pour point depressants allow flowing at

temperatures underneath the pour point of unaltered lubricant, because they co-crystallize along with paraffinic wax; alter the development of the lattice-like organization.

Chlorinated polymers, wax alkylated phenol polymers, wax alkylated naphthalene polymers and polymethacrylates are examples of popular pour point depressants.

Another crucial lubricant property, viscosity is assessed using the arbitrary Viscosity Index (VI), which is derived through the measured viscosities within two different temperatures. This change in viscosity with temperature should be kept to a minimum for a lubricant to be effective. Thus, the lubricant performance is improved by a greater VI. Viscosity Index Improvers (VIIs) additives were incorporated into lubricating oils to regulate the rate at which viscosity changes in response to temperature fluctuations.

The behavior of polymer molecules in the oil affects how well VIIs work. The most crucial characteristics of these VIIs are their molecular weight, durability to strain breakdown, and polymer solubility. The lubricant causes the polymer molecule in solution, which is a randomized coil, to enlarge. As the polymer molecules shift from a tightly wound shape to an exposed framework, which has a larger volume, polymer solubility often rises with rising temperature. This volume addition makes the oil more viscous, counteracting the natural decline in viscosity with rising temperature.

The polymer capacity in an oil solution rises along with the polymer molecular weight. As a result, a polymer with a greater molecular weight will have a greater viscosity index than one with reduced molecular weight of similar kind. Acrylate-based polymers have been proved to be very good VIIs.

Some additives are antioxidants in nature. They can enhance the life span of a lubricant through the raising of oxidative constrains of base oils. This is known as anti-wear (AW) property of lubricant, with which they can lower the friction extent in between the movable portions of those oils, by absorbing shock, reducing noise and minimization of the corrosion towards the portions. With decreasing the friction, decreases the extent of heat generation and thus reduction of most of the wear and tear portions occurs. Such additives are known as the anti-wear additives. They are known as extensive pressure additive and able to make a film or barrier or a protective layer on the wear surfaces.

Castor oil is one of the most popular vegetable oils, obtained from the seeds of the castor bean (Figure 1).

It has a wide range of industrial prospects and can be used medicinally as a purgative and an adhesive. Because of their low virulence, bio-absorbability, and outstanding wrangling qualities, such as excellent lubricity, minimal effervescence, great viscosity index [1], and cost effectiveness, this is one of the most commonly used recycled assets for manufacturing chemicals and polymers. Automotive technology [2, 3], medicine, the coatings industry [4], cosmetics, surface-active agents, nutrition, the food and beverage industry, inks [5], pesticides, and plasticizers [6] are just a few industries that use bio-dependent compositions extensively.

This oil is basically made up of triglycerides entity of fatty acids with long chain. These fatty acids consist of various triglyceride kinds, most of which are unsaturated. The fatty acid (FA) chain of this oil has a significant extent of unsaturation (-C=C-), which results in low thermal and oxidative stability and restricts such significance like lubricants into a moderate temperature [7].

To enhance the convenient rigidness and technical features, the synthetic modification of

triglyceride entity is necessary before its application to the field. For this accomplishment, polymerization of the oil is mandatory to enhance its molecular weight and extent of cross linking. Once more, copolymerization of this substance with the proper monomers can provide further benefits, such as ecological phenomenon of the currently prepared copolymer.

Polyacrylates and methacrylates are popular effective execution additives for lube oil. Methacrylates are frequently used as pour point depressant (PPD) and viscosity modifier (VM) of lube oil [8, 9].

However, in modern trend, the use of greener lubricants has brought some limitations to their vast application in automobile industries. In last few decades, to maintain the environmental sustainability and greener approach, the researchers have mainly focused to initiate production of environmentally benign lubricants or greener additives for inventing better fuel wealth, multi utilitarian skill development, and remove chemical threats [10, 11].

Castor oil was taken as a prospective element of copolymerization as it is promotionally accessible for trading, cost effective, and contains satisfactory unsaturation. The current research performs an intense scanning onto the additive efficiency of produced polymeric ones with styrene and castor oil. Four varieties of copolymers of castor oil-styrene were constructed by different styrene concentrations in the mass (8%, 6%, 4%, and 2%).

The paper performs the polymers synthesis followed by their characterization, performance evaluation, and ecological explanation of all polymers.

With this framework, present study is governed to the copolymer production of castor oil-styrene succeed by their characterization (by thermogravimetric analysis to measure thermal stability of polymer and gel permeation chromatographic analysis [GPC] to determine their molecular weight and spectroscopic analysis [IR and NMR] for structural analysis) and estimation of their additive performance (as PPDs, AW, and VMs) in lubricating oil. Moreover, the extent of biodegradability was determined by GPC [12].

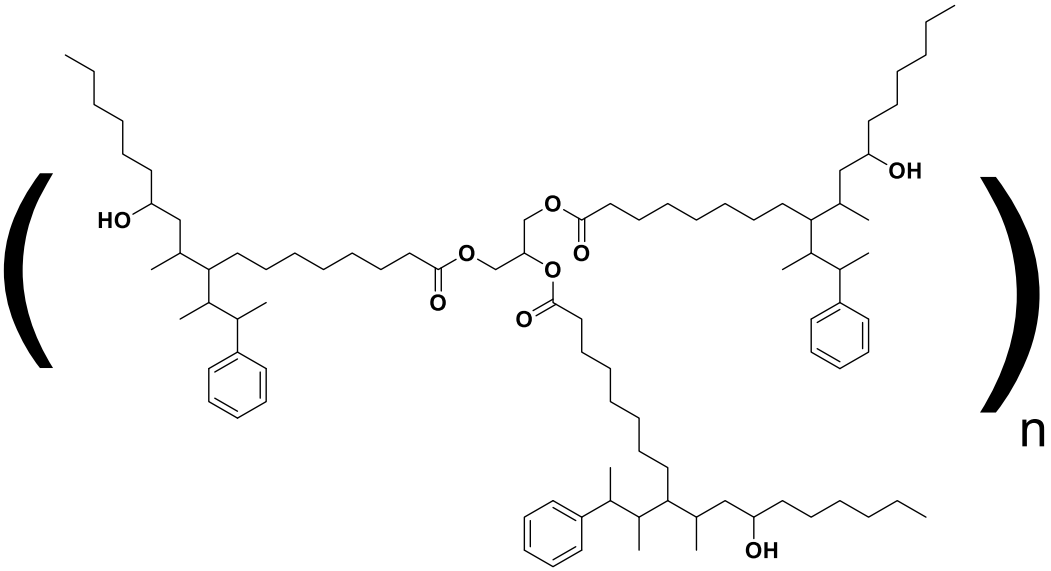


Figure 1. Structure of castor oil-styrene co-polymer

The outcomes of conducted biodegradability experiment for polymers are quite promising. Their performance comparisons have been also assessed and reported. The castor oil and styrene co-polymer demonstrated biodegradability in combination to the effectiveness of multipurpose additives (PPD and VM), and as a result, is thought to be more beneficial in field activities than the current additives.

This study represents a challenging approach for constructing a novel lubricant composition with enhanced flexible additive properties. By increasing the polymer composition in the lubricating oil, the overall volume of polymer micelles is increased, leading to improved viscosity index (VI) properties and reduced wear scar diameter (WSD).

Experimental

Materials and Methods

Sigma-Aldrich, an Indian company, supplied the hydroquinone (> 99%) whereas Conc. H_2SO_4 (98%) and Toluene (GC 99.5%) was supplied by Merck Specialties Pvt. Ltd. The castor oil (CO) (see Table 1 for its fatty acid composition) was obtained from local suppliers whereas Styrene (GC 99.8%)) and Methanol (GC 99.8%) was received from Thomas Baker Chemicals Pvt., Ltd., India. Azobisisobutyronitrile (AIBN, GC 98%,) was obtained from Spectrochem Pvt. Ltd. in Mumbai, India, and was recrystallized from $CHCl_3$-MeOH. All other chemicals were utilized in its original form as received from the supplier without any additional purification. The fungal samples were cultured and obtained from the Microbiology Department of the affiliated organization and the Mineral base oils (BO_1 and BO_2) (see Table 2 for properties) used in the present study was provided by Indian Oil Corporation Ltd. (IOCL), India.

Table 1. Fatty acid components present in castor oil

Fatty acid	Percent composition in castor oil
	Castor oil
Palmitic(16:0)	3
Stearic(18:0)	3
Oleic acid(18:1)	9
Ricinoleic acid(18:1)	75
Linoleic acid(18:2)	10

Table 2. Physical properties of base oils

Properties	Method	BO_1	BO_2
Viscosity at 40 °C in cSt	ASTM D445	7.229	23.472
Viscosity at 100 °C in cSt	ASTM D445	1.874	3.938
Viscosity Index	ASTM D2270	81	86
Pour Point, °C	ASTM D97	-3	-6
Density ($g.cm^{-3}$) at 40 °C	ASTM D4052	0.83689	0.85514

**BO collected from IOCL, Dhakuria, West Bengal.*

Preparation of castor oil homo polymer

Following the same process outlined in the literature [13], homopolymer of castor oil was created at 90 ^{o}C by polymerization reaction in a three necked circularbase flask for 6 h.

Preparation of copolymers

The castor oil- styrene copolymer was constructed using various concentrations of styrene with castor oil. Four varieties of copolymers of castor oil-styrene were constructed with different castor oil concentrations in the mass (8%, 6%, 4%, and 2%). The radical polymerization was performed using the technique that has been previously reported [14].

Results and Discussion

Spectroscopic measurements

FT-IR and NMR techniques were used to characterize the polymers' and composites' spectrum properties. IR spectra in the 400-4000 cm^{-1} wave number region were captured using 0.1 mm KBr cells at room temperature on a Shimadzu FT-IR 8300 spectrometer. Using a 5 mm BBO probe and $CDCl_3$ solvent, NMR spectra were captured through a Bruker Advance NEO 400 MHz FT-NMR spectrometer. TMS was employed as a source of standard information.

Analysis of the spectroscopic data

The analysis of spectroscopic data for the prepared polymers confirmed the predicted structure of the additives.

For copolymers, the presence of ester carbonyl group of castor oil was verified by the characteristic IR absorption peak at 1743 cm^{-1}. In addition, peaks in the range of 2857-2931 cm^{-1} indicated the presence of other components. The peaks at 695 cm^{-1},724 cm^{-1}, 756 cm^{-1}, and 810 cm^{-1}were indicative of the aromatic part of styrene (Figure S1, supporting information).

The ^{1}H-NMR spectra analysis revealed specific chemical shift ranges corresponding to different proton groups in the polymers. Protons in the methyl group were observed between 0.88-0.90 ppm. Protons in the methylene group were assigned peaks ranging from 1.28-1.63 ppm. The methine protons were observed within 2.04-2.30 ppm. The proton associated with -OCH_2 group appeared at 4.08 ppm. Protons from the -$COOCH_2$ group of castor oil peaks are represented by the peaks in the range of 4.10-4.15 ppm. The aromatic ring protons of styrene exhibited a broad peak spanning from 6.80-7.64 ppm (Figure S2, supporting information).

In ^{13}C-NMR spectra, different carbon groups in the copolymer exhibited specific chemical shift ranges, allowing for their identification. Carbon atoms in the CH_3 and CH_2 groups appeared within the range of 14.1-41.0 ppm. Peaks at 58.1 ppm testify the existence of methine carbons in the -CH- of the -COCH group. Peaks ranging from 60.0 to 62.1 ppm and 64.6-68.9 ppm represents carbon atoms in the -OCH_2 groups and -CH_2 carbons in the -$OCOCH_2$- group respectively. The peaks in the range of 127.9-130.8 ppm and 165.6-173.0 ppm represent the aromatic carbons and ester carbonyl carbon (Figure S3, supporting information). The homopolymer of castor oil, showed IR absorption band at 1741 cm^{-1} (Figure S4, supporting information file).

The ^{1}H-NMR spectra of castor oil is presented in Figure S5 (supporting information). The peaks observed within 4.12-4.33 ppm, 0.86-0.90 ppm, 1.26-1.62 ppm and 2.29-2.34 ppm.

Figure S6 (supporting information), indicated the presence of protons from the -

COOCH2 group in castor oil, methyl protons, the methylene protons, and methine protons specific to the alkyl chains.

The Figure S7 of supporting data represents the ^{13}C-NMR spectra for the homopolymer of castor oil, where peak at 173.9 ppm represents ester carbonyl group and the peaks in the range 62.1-68.9 ppm represent the carbons of –OOCH$_2$ group.

Thermo gravimetric analysis (TGA)

Alumina crucible in air was used to measure the thermal stabilities of the synthesized co-polymer and homo polymer using a thermo gravimetric evaluator (Shimadzu TGA-50). A 10 °C/min heating rate was used to operate the system. Calculations were made to determine the samples' percentage weight loss (PWL) as the temperature rose.

Thermo gravimetric analysis (TGA) study

The TGA (Thermo gravimetric Analysis) values of the five polymers are presented in Table 3 and Figure 2. Based on the provided information, several conclusions can be drawn. Polymer P-1 exhibits higher thermal degradation compared to the other polymers, indicating that it is less thermally stable. It begins significant decomposition at 180 °C, resulting in approximately 28% weight loss. For Polymer P-2, major decomposition starting at around 220 °C, leading to approximately 25% weight loss. On the other hand, the thermal decomposition of polymers P-5, P-4, and P-3 is nearly similar, with major decomposition initiating at approximately 255 °C. Therefore, it can be concluded that the copolymerization process has enhanced the thermal stability of the castor oil-based polymers.

Determination of average molecular weights of the copolymer

The number average molecular weight (Mn) and weight average molecular weight (Mw) of the polymers were determined using the Gel Permeation Chromatography (GPC) method. The GPC system used was Water 2414 and polystyrene calibration was employed. The measurements were conducted in HPLC grade THF (Tetrahydrofuran) at room temperature, with a flow rate of 1 mL/min.

The experimental data in Table 4 presents the weight average molecular weights (Mw) and number average molecular weights (Mn) of the prepared polymers (P-1 to P-5). Among all the polymers, P-5 exhibits the highest molecular weight, indicating a larger average molecular size. Enhancing styrene percentage of the castor oil skeleton, correlates with an increase in molecular weight.

Table 3. Percentage composition and TGA values of the prepared polymers

Polymer code	% Composition of monomer (w/w) in the feed		TGA values	
	Castor oil	Styrene	Decom. Temp	PWL
P1	100	0	180/350	28/85
P2	98	2	220/360	25/90
P3	96	4	245/385	20/82
P4	94	6	260/396	17/79
P5	92	8	270/402	16/75

**Decom. Temp.= Decomposition temperature and PWL=Percentage Weight Loss*

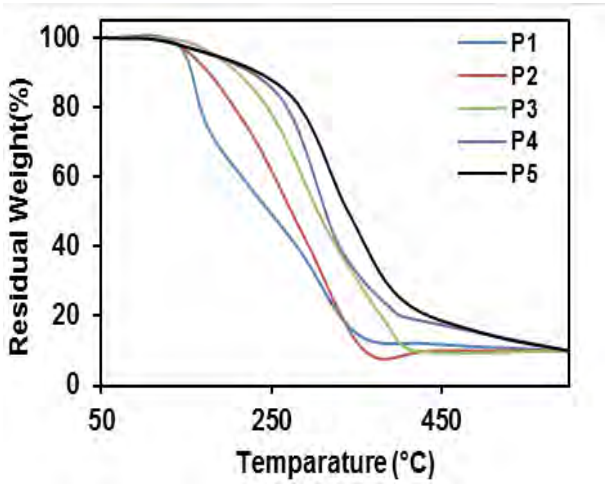


Figure 2. Plausible Schematic diagram of Thermo Gravimetric Analysis (TGA) values

Table 4. Molecular weight of the prepared polymers

Polymer code	Average Molecular weight (before biodegradation)			Average Molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P1	7911	10663	1.21	4561	5023	1.11
P2	16723	24792	1.11	13221	21325	1.63
P3	18563	30768	1.26	15342	26756	1.77
P4	20279	34908	1.35	16765	30289	1.79
P5	27068	40346	1.41	22390	33435	1.51

This suggests that the styrene proportion significantly influences the polymerization process. The observed trend highlights the significance of styrene percentage in determining the resulting molecular weight of the polymers.

Therefore, it can be concluded that the presence and proportion of styrene in the polymer backbone has a crucial impact on the molecular weight characteristics of prepared polymers.

Determination of viscosity index

To assess the effectiveness of the manufactured polymeric additives as viscosity modifiers, the viscosity index (VI) of the additives in a paraffinic base oil (VM) was determined (Table 5). The VI calculations were performed using the formulae provided by Tanveer and Prasad, following the ASTM D2270 method. VI values were calculated for various concentrations of additives in the base oil, ranging from 1% to 5% (w/w). The experimental VI values are presented in Table 5. VI values enhance as the polymers concentration in the base oil increases.

This suggests that higher polymer concentrations have a positive impact on viscosity index. The viscosity of lubricating oil typically represents an inversely proportional relationship with temperature. However, with increasing temperature, polymer molecules expand, resulting in the enlargement of micelles. The increased micelle size hinders the viscosity reduction of the lubricant.

When the polymer concentration in lubricating oil is increased, it results in an augmentation of the volume of polymer

micelles. Consequently, this enhances the viscosity index (VI) property of the lubricating oil. Incorporating styrene in the homo-polymer skeleton of castor oil, leads to an increase in VI values which results in higher crosslink density of the copolymers. Among the copolymers, P-5 demonstrates the maximum impact on VI enhancement, followed by P-4, P-3, P-2, and P-1. Grater VI values observed in P-5 can be attributed to its larger solvated additive molecule (micelle) volume. This characteristic can be linked with greater average molecular weight and lower PDI (Polydispersity Index) value.

Determination of pour point

The pour points of the lubricants used in the present study was determined (in accordance with ASTM D97 standard) using a Cloud and Pour Point Tester model WIL-471 (India). The instrument can also be used for the measurement of pour point depressant characteristic of base oils with polymeric additives. In addition, five distinct additive concentrations were applied for every sample in this instance.

Table 6 displays the pour point values of the lubricants obtained by blending the polymers at different concentration levels ranging from 1% to 5% (w/w). All the polymers exhibit effectiveness as pour point depressants (PPD). This means that they are capable of reducing the pour point temperature of the lubricants. The efficiency of the polymers as pour point depressants increases with an increase in the concentration of polymers, up to limit 4% concentration.

Beyond this concentration, further increases do not significantly enhance the pour point performance. The effective interaction between the polymer and the paraffinic wax present in the base oil is believed to be responsible for the improved pour point performance. At the optimal concentration (4%), the polymer effectively interacts with the paraffinic wax, leading to a reduction in the crystal size of the wax [17].

P-4 demonstrates the best efficiency as a pour point depressant. It exhibits superior efficiency in lowering the pour point temperature compared to the other polymers. To sum up, the experimental data suggests that all the polymers can be utilized as pour point depressants, till a certain threshold level. Furthermore, among the prepared polymers, P-4 stands out as the most effective pour point depressant.

Analysis of anti-wear properties

Table 7 lists the values of wear scar diameter (WSD) obtained through the FBWT (Four Ball Wear Test) apparatus, using a 392 N load, for the lubricant compositions. Blending the polymers with the lubricant leads to a significant improvement in the anti-wear performance, as represented by the lower WSD values of the lubricant compositions.

Table 5. Viscosity index (VI) values of polymer blended base oil

Polymer code	VI of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P1	85/-6	92/-9	99/-12	108/-18	116/-24	125/-23
P2	85/-6	95/-12	105/-15	115/-15	121/-24	131/-22
P3	85/-6	102/-12	112/-15	122/-18	128/-25	138/-25
P4	85/-6	115/-15	122/-22	131/-25	135/-28	146/-28
P5	85/-6	118/-15	127/-18	139/-27	146/-30	147/-29

Table 6. Pour point (PPt) values of polymer blended base oil

Polymer code	PPt of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P1	85/-6	92/-9	99/-12	108/-18	116/-24	125/-23
P2	85/-6	95/-12	105/-15	115/-15	121/-24	131/-22
P3	85/-6	102/-12	112/-15	122/-18	128/-25	138/-25
P4	85/-6	115/-15	122/-22	131/-25	135/-28	146/-28
P5	85/-6	118/-15	127/-18	139/-27	146/-30	147/-29

Table 7. Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition

Polymer code	Anti-wear property in terms of wear scar diameter (WSD in mm) of polymer blended base oil at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P1	1.107	1.045	1.025	1.016	1.009	1.001
P2	1.107	1.039	1.017	1.008	1.005	0.995
P3	1.107	1.034	1.011	1.002	0.994	0.983
P4	1.107	1.028	1.004	0.995	0.988	0.978
P5	1.107	1.022	0.998	0.986	0.981	0.969

This indicates that the addition of polymers enhances the lubricant's capability to reduce wear between moving metal surfaces.The copolymers exhibit better anti-wear performance compared to the homopolymer. This suggests that the presence of multiple monomers in the copolymers contributes to their improved tribological properties.

Among the polymers, P-5 at a concentration of 5% demonstrates the highest reduction in WSD values. The lubricant composition with P-5 forms a strong film amid the two moving metal surfaces; effectively reducing wear. The observed improvement in anti-wear performance is due to several factors. Initially, the higher molecular weight of the polymers, especially in the case of P-5, contributes to a greater number of polar side chains from ester carbonyl groups and hydroxyl groups present in rapeseed oil.

These polar groups enhance the lubricant's film-forming properties. Moreover, the higher percentage of styrene in the polymer feed, with its aromatic ring structure, likely plays a substantialpart in enhancing the tribological properties of lubricant composition.

Photo micrograph and wax modification

To investigate the impact of an additive on wax crystallization, the wax modification of the base fluid was examined using a Banbros polarizing microscope (BPL-400B, India) equipped with a cooling thermostat (Figure 3). The microscope provided a magnification of 200X, enabling detailed observation of the base fluid.

The temperature was controlled at 0 °C during the study to ensure consistent conditions for the examination of wax crystallization.

By capturing photo micrographic images of the base fluid under these controlled settings, the effectiveness of the additive in controlling wax crystallization could be evaluated.

Analysis of the photo micrographic image

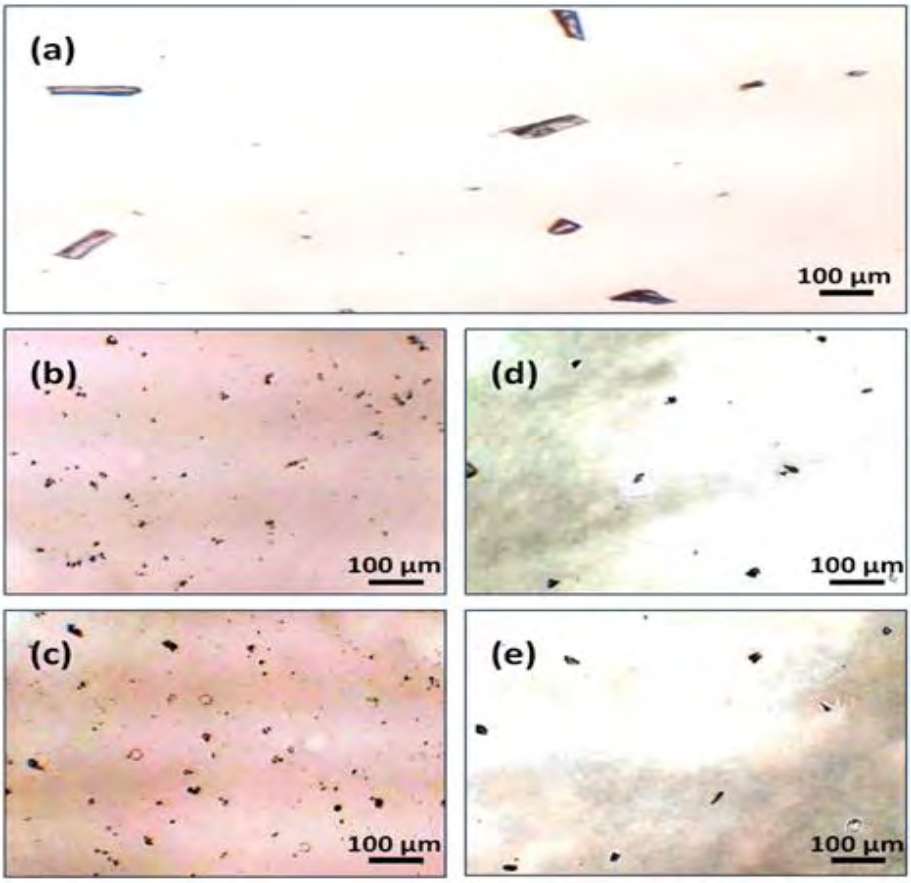


Figure 3. Photomicrograph of: (a) pure base fluid, (b) base fluid + additive P-1 (4%, w/w), (c) base fluid + additive P-3 (4%, w/w), (d) base fluid + additive P-4 (4%, w/w), and (e) base fluid + additive P-5 (4%, w/w)

Table 8. Result of biodegradability test by disc diffusion method and soil burial degradation

Sample	Weight loss in disc diffusion method in gm					Weight loss in soil burial degradation method in gm
	Pathogens used					
	[CC]	[FE]	[AA]	[CG]	[CE]	
P-1	0.56	0	0.59	0	0	0.55
P-2	0.44	0	0.51	0	0	0.48
P-3	0.35	0	0.46	0	0	0.39
P-4	0.31	0	0.34	0	0	0.33
P-5	0.27	0	0.26	0	0	0.28

**CC=Calletotricheme camellia, FE= Fussariumequisitae, AA=Alterneria alternate*
**CG=Colletrichumgleosproides, and CE=Curvulariaeragrostidies.*

The photomicrographs of the pure base fluid and the pure base fluid with added additives are presented in Figure 3. The photo micrograph (Figure 3a) of the original base fluid (pour point =-6 °C) reveals the presence of large rod-shaped wax crystals. These crystals contribute to the high pour point of the base fluid. Upon adding additive P-2 (pour point = -24 °C, Figure 3b) and additive P-3 (pour point = -25 °C) (Figure 3c) to the base fluid at a concentration of 4% (w/w), a significant decrease in the volume and shape of the wax crystals is observed. The obtained crystals appear to be more dispersed

compared to the original base fluid. Similarly, additive P-4 (Figure 3d) (pour point = -28 °C) and additive P-5 (pour point = -30 °C, Figure 3e) also result in a substantiallessening in the size of the wax crystals. The crystals appear highly dispersed in the base fluid.

Biodegradability analysis

The extent of biodegradability was assessed using the ISO 846:1997 method for soil burial testing and the disc diffusion method against fungi. After the experiments, weight loss in the polymer samples was evaluated, and IR spectra were collected to look for any noticeable shifts in IR frequencies [18, 19]. With the recovered polymers, further GPC examination was underwent in expectation of changes in Mn and Mw following biodegradation [12].

Disc diffusion method

In Petri dishes, culture media for fungi strains were made using the necessary quantity of agar, dextrose and potato extract mixture. Before usage, all the glass equipments underwent autoclaving. The test involved the use of five different fungal pathogens: Curvulariaeragrostidis (CE), Colletotrichum gloeosporioides (CG), Alternaria alternata (AA), Fusarium equiseti (FE), and Colletotrichumcamelliae (CC). The culture media's transformation from yellow to black confirmed the fungus growth. One gram of specific polymer samples was placed to Petri dishes, where they were then cultured at 310 K for 30 days. After 30 days, rescued polymer samples were purified, chloroformed-cleaned, and dried in an open tank [18]. Dry sample masses were determined, and then FT-IR and GPC analyses were performed.

Soil burial degradation test

The ISO 846:1997 method was used to conduct the soil burial test. We buried polymer films in soil that was dug up from the university campus. In a humidity chamber, a thermostat was used to maintain a temperature of 303 K while adjusting the soil's humidity to between 50% and 60% prior to usage. After 60 days, the films that had been buried were found. Polymer samples were purified, dried, and chloroform washed [20]. After the dried samples were examined, FT-IR and GPC analyses were performed.

Analysis of biodegradability test

The results of the biodegradability tests, as presented in Table 8, indicate significant biodegradability for both the homopolymer (P-1) and copolymers (P-2 to P-5) when exposed to fungal pathogens, specifically Calletotricheme camellia and Alternaria alternata. As expected, the homopolymer of castor oil (P-1) exhibited better biodegradability compared to the copolymers. Detailed analysis of the experimental data revealed noticeable biodegradation for all the samples. The results obtained from the Sequential Biodegradation (SBD) study indicate a progressively increasing trend for the degradation of polymeric additives with test duration. Moreover, both the homopolymer and copolymers exhibited substantial weight losses when exposed to the fungal pathogens, particularly Alternaria alternata, in the Direct Degradation (DD) test.

As anticipated, the homopolymer (P-1) with zero styrene content and the presence of natural monomer units displayed the highest level of biodegradability among all the additives, as observed in both tests. In the Fourier Transform Infrared (FT-IR) analysis, the peaks corresponding to the polymer P-1 exhibited shifts in their positions and a significant reduction in the height of peak and

its intensity after DD test. This confirms biodegradable nature of prepared polymers, as indicated by the changes in the IR peak positions, peak intensities, and the Polymer Weight Loss (PWL) values before and after the biodegradation tests.

Conclusion

Copolymers of castor oil and styrene have higher thermal stability than castor oil alone. Again, when styrene concentration in the copolymers rises, so does thermal stability. However, the shear stability of castor oil homopolymer is higher than that of their styrene copolymers, and shear stability declines as styrene concentrations in the copolymers rises. The castor oil-styrene copolymer functions as a much better PPD and viscosity modifier than the castor oil homopolymer, according to performance assessment of the additives. In addition, research shows that while castor oil homopolymer is significantly biodegradable, but very poor solubility in lube oil and showed low thermal stability and middling performances as a PPD and VM. In contrast, the castor oil and styrene copolymer demonstrated biodegradability in combination to the effectiveness of multipurpose additives (PPD and VM), and as a result, is thought to be more beneficial in field activities than the current additives. Indeed, the study mentioned above presents a promising approach for formulating a novel lubricant composition with enhanced flexible additive properties. By increasing the polymer composition in the lubricating oil, the overall volume of polymer micelles is increased, leading to improved viscosity index (VI) properties and reduced wear scar diameter (WSD). This approach can contribute to the development of environmentally friendly lubricants that offer enhanced performance and functional capabilities, making them an attractive option for various applications.

Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Funding

This research received grant from CSIR, New Delhi, India.

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Supporting Information

Supporting information contains the experimental analysis, spectroscopic data, and scanned copies of ^{1}H-, ^{13}C-NMR and FT-IR spectra of some synthesized homopolymers and co-polymers.

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How to cite this manuscript: Manishita Nandi, Passang Tshering Lepcha, Pranab Ghosh*. Synthesis and Performance Evaluation of Castor Oil-Styrene Co-polymer: An Outstanding Multipurpose Directional Lubricant Additive. *Asian Journal of Green Chemistry*, 7(4) 2023, 269-282.
DOI: 10.22034/ajgc.2023.396588.1392



Asian Journal of Chemical Sciences

Volume 14, Issue 1, Page 42-49, 2024; Article no.AJOCS.111909
ISSN: 2456-7795

Evaluation and Synthesis of Environmentally Benign Multifunctional Additives for Lube Oil

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJOCS/2024/v14i1284

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/111909

Original Research Article

Received: 22/11/2023
Accepted: 27/01/2024
Published: 03/02/2024

ABSTRACT

Behenyl acrylate (BA) homo-polymer and its copolymers with citral were synthesized with varying percentage compositions (w/w) and subjected to thorough characterization through GPC (gel permeation chromatography) analysis and spectroscopic techniques (FT-IR, NMR). The polymers' capability was assessed through viscosity index improvers/viscosity modifiers (VII or VM), anti wear (AW) additives and pour point depressants (PPD) for base oils (lubricating oil). The action mechanism of the PPD properties was investigated through photomicrographic analysis. Additionally, the thermal stability of the polymers was measured using TGA or thermo gravimetric analysis. Biodegradability tests on copolymers were conducted using soil burial test (SBT) and the Disc Diffusion (DD) method. The copolymers exhibited exceptional PPD, VII, and AW performance when incorporated into lubricating oil.

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Keywords: Citral; copolymer; biodegradable; lube oil; viscosity index improver; pour point depressant; anti wear; photo micrographic analysis.

1. INTRODUCTION

Lubricants consist of a combination of a base fluid and additives designed to enhance performance. The additive content typically ranges from 1% to 30% or even higher. While mineral oils of petroleum origin are commonly used as base fluids, vegetable and synthetic oils also find application. Polymeric additives are introduced to the base fluid to improve the operational efficiency of engine oil and extend the engine's lifespan.

Additives typically serve various functions, such as ameliorating the pour point (PP) [1] of base oils through the dissolution of wax crystal deposits [2] at lower temperatures, boosting the viscosity index (VI) [3] to maintain viscosity stability amidst temperature fluctuations, minimizing wear, and effectively transporting contaminants away. These components are commonly labeled as viscosity index improvers (VII) [4], pour point depressants (PPD) [5], detergent-dispersants [6] and antiwear agents [7].

Commercially available synthetic acrylate-based additives, although effective, are non-biodegradable, prompting environmental concerns. The increasing desire for environmentally friendly technology has spurred researchers to create lubricant additives that are ecologically benign. Vegetable oils [8-11], recognized for their natural occurrence, biodegradability, non-toxicity, and high viscosity index, present a promising alternative [12]. They exhibit excellent tribological properties, acting as antiwear and friction modifiers in lubricant formulations [13,14].

Modified vegetable oils have been utilized as additives in lubricating oils in numerous cases, with patents describing their application as extreme pressure additives, friction modifiers, and viscosity index improvers [15-17]. In line with these considerations and as part of our ongoing efforts to develop chemical additives for lubricating oil, our present investigation focuses on synthesizing copolymers of acrylate ester based citral through copolymerization. The aim is achieving an optimal balance between performance and environmentally friendly chemistry. The study encompasses the synthesis and characterization of behenyl acrylate (BA) homopolymer and BA copolymer with citral, followed by biodegradability testing and evaluation of their effectiveness as pour point depressants, viscosity modifiers, and antiwear additives.

2. MATERIALS AND METHODS

2.1 Materials

Hydroquinone, sulfuric acid and Toluene, were sourced from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilized with 0.02% Hydroquinone monomethylether), Behenyl alcohol and n-Hexane were procured from SRL Pvt. Ltd. Methanol and Benzoyl Peroxide (BZP) wereobtained from Thomas Baker (Chemicals) Pvt. Ltd. andLOBA chemicals respectively.They underwent recrystallization using a $CHCl_3$-MeOH mixture before application. Citral was sourced from a nearby grocery store, and the base oils were acquired from IOCL (Indian Oil Corporation Ltd.), Kolkata, India. Remaining substances were utilized in their pristine condition without extra purification. All specimens were subjected to testing before reaching their designated expiration dates.

2.2 Methods

The thermal radical polymerization of behenyl acrylate and its subsequent copolymerization with citral at varying concentrations (5%, 10%, and 15% w/w) were carried out employing benzoyl peroxide (BZP) as the initiator following the method as reported elsewhere [16]. The resulting additives were subjected to thorough characterization using spectral analysis techniques, including Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The determination of the average molecular weight of the polymeric additives, both number average (Mn) and weight average (Mw), was accomplished using gel permeation chroma-tography (GPC). Tetrahydrofuran (THF) of high-performance liquid chromatography (HPLC) grade served as the mobile phase in the water GPC system, calibrated with polystyrene, and the analysis was conducted at room temperature.

The thermal stability of the additives was evaluated using the Mettler TA-3000 system,

employing a heating rate of 10 K min^{-1}. The multifunctional performance of the base oil treated with additives, encompassing improvements in viscosity index, pour point depression, and antiwear properties, was assessed in accordance with ASTM methods. The antiwear (AW) characteristics were determined utilizing a Four-ball wear test apparatus, following the ASTM D 4172-94 method [18], with a weld load of 392 N at 75°C for 30 minutes and a rotational speed of 1200 rpm.

The biodegradability of the polymeric additives underwent testing through the disc diffusion method [19], evaluating their effectiveness against fungal pathogens, and the soil burial test as per ISO 846:1997 [20,21]. Microbial degradation was confirmed by measuring the shift in the infrared (IR) frequency of the ester carbonyl after the biodegradability test.

3. RESULTS AND DISCUSSION

3.1 Spectroscopic Description

In FT-IR spectrum, homopolymer of behenyl acrylate (P-1) demonstrated an absorption peak at 1732 cm^{-1}, corresponding to ester carbonyl, attached with distinctive peaks at 1467, 1271, 1190, and 1060 cm^{-1}. The ^{1}H NMR spectra of P-1 revealed a broad singlet centered at 4.02 ppm, associated with the $–OCH_2$ protons. Methyl protons from the behenyl chain were evident between 0.81 ppm and 0.86 ppm, and the lack of a singlet in the 5-6 ppm range indicated the absence of vinylic protons in the polymer. The ^{13}C NMR spectrum of P-1 disclosed the carbonyl carbon at 174.4 ppm, along with other SP^3 carbons ranging from 65.03 to 10.66 ppm.

In FT-IR spectrum of the copolymers, the ester carbonyl peak appeared at 1731 cm^{-1}, containing a peak at 1714 cm^{-1} corresponding to the citral's aldehydic group. The ^{1}H NMR of copolymers exhibited a multiplet in the span of 4.119-4.402 ppm, indicating $–OCH_2$ protons. SP^3 protons were observed within 1.259-1.989 ppm, while peaks at 5.343 ppm and 5.360 ppm were attributed to ethylenic unsatura-tionfrom-citralportion of copolymer. One peak around 10 ppm indicated presence of the aldehydic hydrogen of citral in that copolymer. In ^{13}C NMR of the copolymer, peaks within 167.70-173.36 ppm indicated the ester carbonyl carbon. Peaks at 190.81 ppm were due to the aldehydic carbonyl group of citral. The $–OCH_2$ carbon peak appeared at 68.93 ppm. Peaks within 14.09-34.05 ppm represented all SP^3 carbons of the copolymer.

3.2 Performance of the Prepared Additives in the Form of Pour Point Depressant

The results of pour point depressant (PPD) properties of the prepared samples, covering a range of additive concentrations within 1 wt% to 5 wt%, are outlined in Fig. 1. The figure vividly demonstrates the efficacy of the prepared additives as pour point depressants, showcasing a consistent reduction in pour point with increasing additive concentration. Notably, the pour point magnitudes of copolymers (P-2, P-3, and P-4) exhibit a remarkable similarity and consistently register lower values compared to the homopolymer (P-1). Consequently, all copolymers demonstrate significant pour point depressant properties.

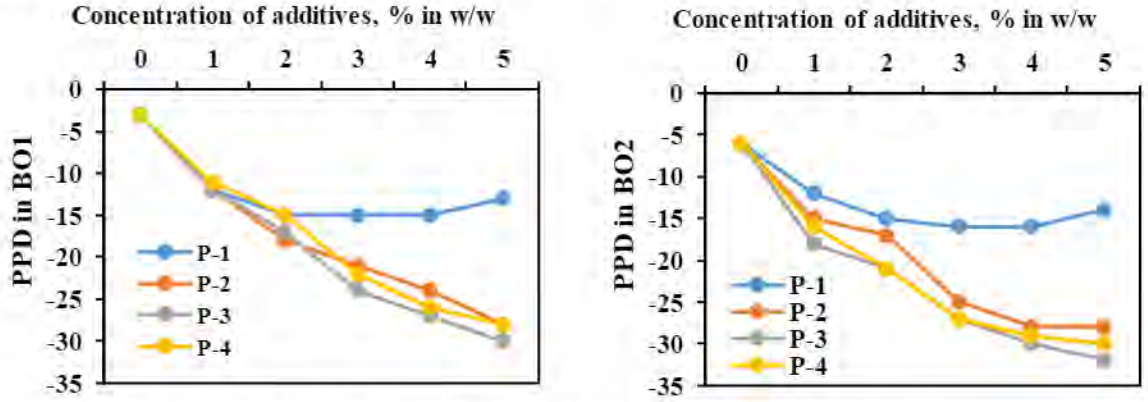


Fig. 1. Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

The efficacy of the polymers as potent pour point depressants was evaluated through photomicrographic experimentation. The wax crystal size exhibited a notable reduction, transitioning from a large crystal structure in the base oil to very small dots dispersed in the oil phase of the lubricating oil [22].

3.3 Performance of the prepared additives as viscosity index improver (VII)

Fig. 3 presents the viscosity indexes for base oils treated with additives derived from polymers (P-1, P-2, P-3, and P-4). The data reveals a steady increase in VI magnitudes as the polymer concentration rises in both base oil types (BO1 and BO2), reaching a peak at 4%. The elevated polymer concentration corresponds to an increased volume of polymer micelles within the oil solutions. Consequently, a higher concentration of the polymer contributes to a higher VI, in contrast to a lower concentration of the same polymer.

3.4 Performance of the Prepared Additives as Anti Wear Additive

A reduction in wear scar diameter (WSD in mm) was observed with increasing additive concentration in the case of studied base stocks with varying load conditions (Table 1). The most distinct drop was observed at 20 kg load condition, as illustrated in Figs. 2 and 3. This suggests that the additives exhibited comparatively lesser effectiveness at higher load conditions. However, there was no noteworthy enhancement in the performance beyond a 5% additive concentration.

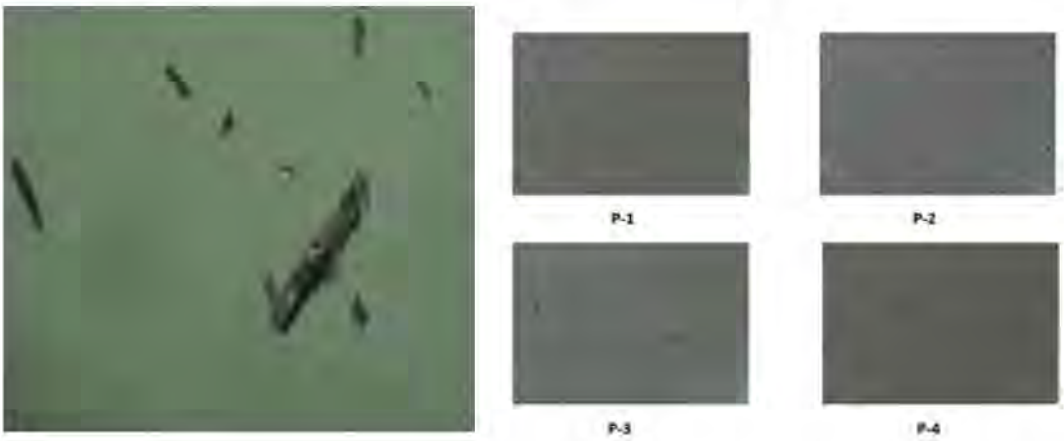


Fig. 2. Photomicrographic images of base oil (left side) and additive (P-1, P-2, P-3 and P-4) Doped base oil (right side)

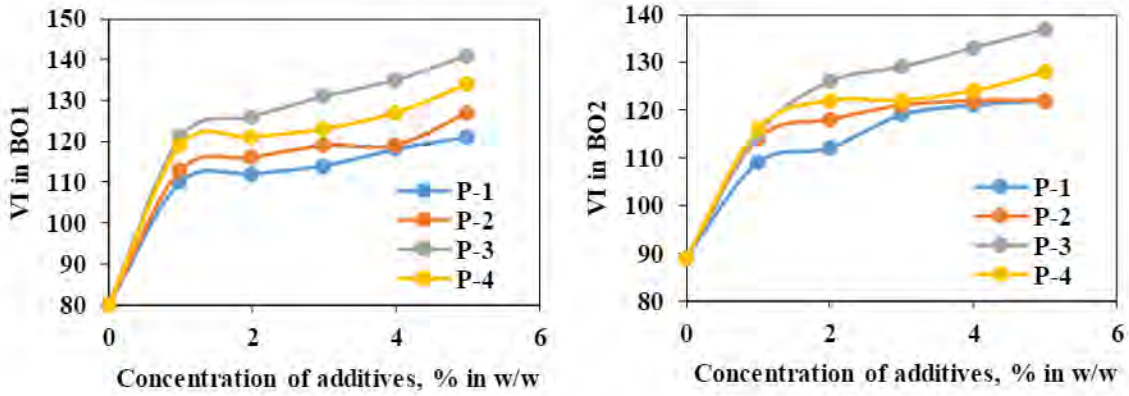


Fig. 3. The VIs corresponding to additive-doped base oils

Table 1. Anti wear values in terms of WSD in mm of polymers P-1, P-2, P-3 and P-4 in the base oils (BO1 and BO2) at 40 kg load

	WSD in mm. in BO1 Concentration of the additives, % in w/w						WSD in mm. in BO2 Concentration of the additives, % in w/w					
Sample	0	1	2	3	4	5	0	1	2	3	4	5
P-1	1.067	0.991	0.887	0.718	0.713	0.665	1.110	0.984	0.907	0.865	0.844	0.823
P-2	1.067	0.954	0.861	0.711	0.688	0.645	1.110	0.971	0.891	0.843	0.821	0.812
P-3	1.067	0.901	0.813	0.703	0.641	0.633	1.110	0.898	0.822	0.804	0.791	0.776
P-4	1.067	0.903	0.811	0.710	0.632	0.635	1.110	0.846	0.798	0.806	0.793	0.781

It was observed that the studied copolymers exhibited superior antiwear properties compared to the homopolymer (P-1). The presence of aldehydic functionality and ester functionality can be attributed to such observation [23,24]. As a result, copolymer (P-4), with larger fraction of citral units, demonstrated enhanced antiwear performance.

3.5 Analysis of Biodegradability Test Result

The biodegradability test results obtained from disc diffusion method and soil burial test (Table 2) indicates notable biodegradability for fungal pathogen Alternaria alternata, compared to the homopolymers. This observation was subst-antiated by the shift in the IR frequency of the ester carbonyl. As anticipated, the copolymer exhibited superior biodegradability in comparison to the homopolymer.

Table 2. Results of biodegradability test by disc diffusion method and soil burial test for polymeric additives

Disc diffusion method		*Soil burial test*
Polymers	***Alternariaalternata* Wt. loss(%)**	**Microorganism Wt. loss(%)**
P-1	00	00
P-2	31.60	16.30
P-3	37.70	23.20
P-4	40.30	25.70

3.6 Determination of Molecular Weight of the Polymers

The molecular weight data obtained from the GPC analysis method (Fig. 4) indicates the drop in molecular weight, both Mw and Mn compared to the homopolymers. The GPC data also suggested that the gradual increase in citral concentration in the feed of polymerization resulted in a gradual decrease in the Mol wt and the drop is directly related to the increase in performance of the additive doped base oil upto a certain limit. The poly dispersity index values indicated the linear nature of the polymer chain which is a very significant parameter to yield the best performance of the polymeric additives.

3.7 TGA Data of all the Polymer Samples

Table-3 displays the Thermogravimetric Analysis (TGA) data for both the homopolymer and copolymer of dodecyl acrylate. The data reveals that the copolymers (P-2, P-3, and P-4) exhibit greater thermal stability compared to the homopolymer (P-1). Furthermore, there is a discernible trend indicating that as the concentration of citral in the feed increases, the thermal stability of the copolymers also increases.

Table 3. TGA data for homo and copolymer of behenylacrylate

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
P-1	513	84
	541	77
	562	16
	589	4
P-2	523	86
	551	80
	577	21
	611	5
P-3	561	85
	584	79

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
	605	23
	627	8
P-4	566	85
	589	80
	617	7
	640	5

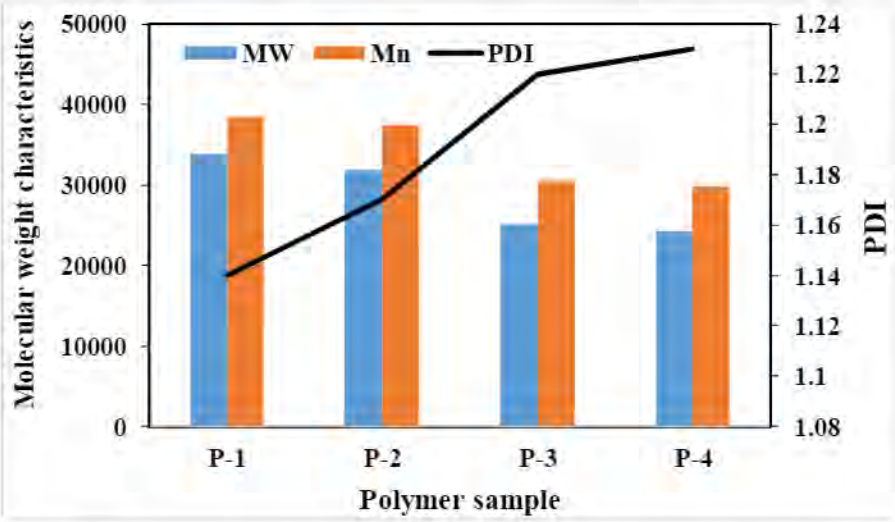


Fig. 4. Molecular weight characteristics of the polymers

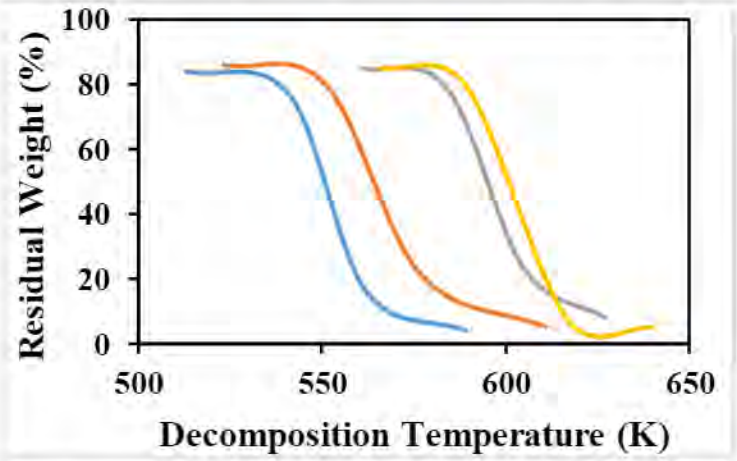


Fig. 5. TGA data for homo and copolymer of behenylacrylate

3.8 Physical Properties of Base Oils

Table 4. Physical properties of Base oils

Properties	*BO1*	*BO2*
Density(kg.m^{-3}) at 313K	839.98	918.68
Viscosity at 313K	5.97×10^{-6}	20.31×10^{-6}
Viscosity at 373K	1.48×10^{-6}	3.25×10^{-6}
Viscosity index	80.05	89.02
Cloud point (°C)	-10	-8
Pour point (°C)	-3	-6

4. CONCLUSIONS

All the copolymers (P-2, P-3, and P-4) along with the homopolymer (P-1) demonstrated excellent viscosity index improver (VII), pour point depressant (PPD) and antiwear (AW) properties. Additionally, the copolymer also exhibited significant biodegradability. Therefore, the copolymer, derived from castor oil and behenyl acrylate, holds promise as a potential environmentally friendly multifunctional additive for lubricating oil.

ACKNOWLEDGEMENTS

The authors express gratitude to CSIR, New Delhi, for the financial support provided, and extend their thanks to Indian Oil Corporation Limited (IOCL) for the supply of base oil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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