Serbian Tribology Society

SERBIATRIB '25

19th International Conference on Tribology

Faculty of Engineering University of Kragujevac

Kragujevac, Serbia, 14 – 16 May 2025

Research paper DOI:10.24874/ST.25.162

CASTOR OIL BASED TERPOLYMER WITH STYRENE AND A-OLEFIN AS BIODEGRADABLE ADDITIVE IN LUBE OIL

Sayak P GHOSH[1], Pranab GHOSH[1,*]

[1]Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

*Corresponding author: pizy12@yahoo.com

ABSTRACT: *Development and characterisation of biodegradable multifunctional lube oil additives is a vast and advanced field of research area. Polymers with high molecular weight, long alkyl chain are preferred in this field as better pour point depressants (PPD) and viscosity index improvers (VII). Free radical polymerisation using either BZP or AIBN is one of the mostly used methods for the preparation of these polymers. In the present context, we have prepared homopolymer of castor oil, its copolymers with styrene and α-olefin like 1-decene and also a terpolymer of these three. Characterization of theses prepared polymers were carried out by molecular weight determination and spectroscopic methods. Further they were evaluated as PPD and VII in lube oil.*

KEYWORDS: *Lube oil additives, PPDs, VIIs, free radical polymerisation, α-olefin, terpolymer*

1. INTRODUCTION

High performance lubricating oil is a major exploring area in automotive industry. It is the lubricant which keeps the moving surfaces away from each other and protects them from corrosion and rust and thus enhances engine's durability and performance [1]. Modern lubricants are formulated from wide variety of mineral base oils blended together with some appropriate chemical additives [2]. The additives play very important role to optimize the properties of lubricants such as pour point depressants [3, 4], viscosity index improvers [5,6], extreme pressure additives [7] etc. Polymers have conquered a special and major place in this aspect to be explored as additives. A number of research groups have been engaged in this field to synthesize multifunctional polymeric additive. But still there is a quest to find out the most suitable cost effective yet biodegradable additive with minimum dosage but maximum effect.

The vegetable oils surpass the mineral base oils mainly because of their biodegradability, renewability less toxicity, high viscosity index, better thermal stability and better tribological properties [8,9,10]. Although these properties sought for the vegetable oils as the potential replacement of mineral base oils, still some limitations have been big barrier against raw application of these vegetable oils in automotive industry. These are poor oxidative stability, low flow property at low temperature, high coefficient of friction at elevated temperature and poor hydrolytic stability [11-13] etc. Recent studies have

shown that chemical modification can suppress these drawbacks and rather enhance some of the existing properties [14, 15]. But still solo application of vegetable oils either in raw form or modified form is below the mark mainly due to high cost of production and evaluation. Hence another criterion is getting much attention to have at least partially biodegradable additive from these vegetable oils.

One of the most well known vegetable oils in this field is castor oil which consists of high percentage of triacylglycerols of ricinoleic acid (85-95%), a C-18 fatty acid. It has a double bond at C-9 and a nonconjugated hydroxyl group at C-12 (Figure 1). Presence of trifunctional groups makes castor oil highly rigid and thermally stable as well whereas the long fatty acid chain accounts its flexibility [16]. Free hydroxyl group on ricinoleic acid can interact with metal surfaces of engine parts and hence castor oil is known to exhibit excellent lubricity. Besides high flash point and presence of polar functional groups accounts for its potential application of automotive engine and gear box as lubricant [17, 18]. In a comparative study by Quinchia et al., it has been reported that castor oil based copolymers ethylene – vinyl acetate exhibited better tribological properties than sunflower or soybean based copolymers [19]. In another study by Madankar et al., methyl ester of castor oil has been established as bio lubricant due to its high viscosity, low pour point, and good lubricity [20]. In the present context we have prepared castor oil based homopolymer, copolymer and terpolymer as well with styrene and 1-decene. Their performances as PPD and VII have been evaluated in mineral base oil.

2. EXPERIMENTAL SECTION

2.1 Materials

Refined castor oil (~85% unsaturation) was collected from local market. 1-Decene (95%, Acros organics) and styrene (99%, Sigma–Aldrich) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), hexane (99.5%, S. d Fine Cheme Ltd.) and methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) was purified by re-crystallization before use. AIBN (GC 98%), obtained from Spectrochem Pvt. Ltd. Mumbai (India) was recrystallized from $CHCl_3$–MeOH before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. Properties of the mineral base oils used are tabulated in Table 1 (BO1, BO2 collected from IOCL, Dhakuria, West Bengal).

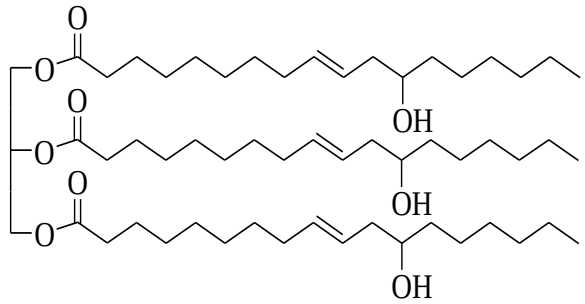

Figure 1. Triricinolein, the major component of castor oil

Table 1. Base Oil (BO) Properties

Physical Property	BO1	BO2
Density (gcm-3 at 40 °C)	0.83	0.95
Viscosity at 40 °C in cSt	6.698	24.211
Viscosity at 100 °C in cSt	2.02	4.47
Viscosity Index (VI)	81.13	89.87
Pour Point (PP in °C)	-3	-6
Cloud Point (°C)	-10	-8

2.2 Preparation and purification of polymers

The homo polymer of castor oil (P_1), its copolymer with styrene (P_2), 1- decene (P_3) and finally the terpoymer (P_4) were prepared via free radical polymerisation using AIBN initiator. The detailed process of preparation and purification of the polymers was same as was reported in our previous publication [2]. The specifications of the prepared polymers are given in Table 2.

Table2. Molecular weight data of the prepared polymers

Polymer	Weight percentage of castor oil	Weight percentage of styrene	Weight percentage of 1-decene	M_n	M_w	PDI
P_1	100	-	-	8235	10035	1.22
P_2	90	10	-	42033	60948	1.45
P_3	90	-	10	18424	25056	1.36
P_4	90	5	5	45081	59958	1.33

P_1 represents homopolymer of castor oil, P_2 represents copolymer of castor oil and styrene, P_3 represents copolymer of castor oil and 1-decene, P_4 represents terpolymer of castor oil, styrene and 1-decene.

3. MEASUREMENTS

3.1 Molecular weight determination

The average molecular weights of the prepared polymers were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 308 K temperature at a flow rate of 1mL/min. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) data are given in Table 2.

3.2 Spectroscopic Measurements

IR spectra of the prepared polymers were recorded on a Shimadzu FT–IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range (400 to 4000 cm^{-1}). NMR spectra were also recorded for the polymers in Bruker Avance 300 MHz FT–NMR spectrometer using a 5 mm BBO probe in $CDCl_3$ solvent and tetramethylsilane (TMS) as reference material.

3.3 Performance evaluation as pour point depressants in lube oil

The lowest temperature at which movement of the oil sample can be noticed when the sample container is tilted, is called pour point of that oil [21]. To achieve high performance lube oil its pour point must be lowered with perfect dosage of perfect additives called pour point depressants. The performance of our prepared polymers as ppds in the mineral base oils (BO1 and BO2) was tested according to the ASTM D 97–09 method. Solutions were prepared using different doping concentrations ranging from 1% to 5% (w/w) for each of the prepared polymer and the pour points of the prepared solutions were measured using cloud and pour point tester model WIL–471 (India). The values are given in Table 3.

Table 3. Pour point (PP) data (^oC) with respect to the different concentrations (% w/w) of the additives in BO

Conc^n	PP data in BO1					PP data in BO2				
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%
P_1	–5.8	–6.1	–6.6	–7.1	–7.0	–8.9	–9.1	–9.6	–10.1	–10.2
P_2	–7.9	–8.2	–8.1	–7.8	–7.5	–10.6	–11.0	–11.7	–12.2	–12.1
P_3	–8.8	–9.0	–9.3	–9.5	–9.7	–12.0	–12.8	–13.6	–14.0	–14.0
P_4	–8.9	–9.6	–10.1	–10,6	–10.5	–12.9	–13.8	–14.4	–14.8	–14.8

Conc^n represents concentrations (% w/w) of the additives in base oil (BO)

3.4 Performance evaluation as viscosity index improver (VII)

Viscometric properties of the prepared polymers were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer. For each polymer five solutions were prepared from 1% to 5% (w/w) concentration in both the base oils. The time of flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was

chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. Viscosity index (VI) data in BO1 and BO2 are given in Table 4.

4. RESULTS AND DISCUSSION

4.1 Molecular Weight Analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity index data (PDI) of the prepared polymers (P_1 to P_4) are given in Table 2. It is evident from the molecular weight data that the homopolymers have lower molecular weight than the copolymers. It is evident from the data that the terpolymer ha highest molecular weight both number average and weight average. But PDI values are more or less near about one which suggested quite better uniformity in all. The values indicated successful polymerization in all cases.

4.2 Spectroscopic analysis

In IR spectra for all the polymers, peaks around 1733cm $^{-1}$ clearly indicate the presence of ester carbonyl group. No peak is obtained above 3000 cm^{-1} which indicates absence of C=C unsaturation and supports complete polymerisation in all the cases.

^{1}H–NMR and ^{13}C–NMR data also support the above result. Here again the absence of peaks around 6 ppm supported total polymerisation. In ^{13}C–NMR the peak around 176 ppm indicated the presence of ester carbonyl carbon. Again absence of peak in the range of 120–150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization.

Table 4: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO

Conc^n	VI data in BO1					VI data in BO2				
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%
P_1	98	111	118	121	126	93	97	109	114	120
P_2	105	114	124	136	140	103	110	121	130	141
P_3	98	110	116	122	128	98	105	110	113	121
P_4	108	116	126	137	149	115	123	134	143	152

Conc^n represents concentration in % w/w

4.3 Performance evaluation as pour point depressant

When the temperature decreases and reaches towards pour point wax crystals come out of the base oil and gradually gets bigger in shape and finally form a 3D network of wax crystal which entraps the liquid and at some point immobilises the oil. Pour point depressants do not in any way affect the temperature at which the wax crystals grow or the amount of wax precipitates out, rather they modify the growing pattern of the waxes [22]. With decreasing temperature PPDs also come out of the solution as crystals along with the wax crystals and form a PPD backbone on the wax crystals. Due to this PPD backbone there plays a steric hindrance which keeps the wax crystals far apart and prevents the formation of 3D network of wax crystal. Thus PPDs improve the flow property of base oil. Generally polymers with long alkyl chain, high molecular weight are good enough in this field [23].

Analysing the pour point data given in Table 3, it may be said that all the prepared polymers acted as good flow improvers. But the copolymers are proved to be better PPDs than the homopolymer. Styrene or α-olefin incorporation in additive is well known to form an effective pour point depressant. This is also supported by our results. The most interesting part is that the terpolymer has

outweighed all other polymers as the most effective PPD here in both the base oils.

4.4 Performance evaluation as viscosity index improver

Solubility of the polymer, its molecular weight and composition play important role on its performance as viscosity index improver [24]. It is said that polymers exist as random coils in base oil solutions. As the temperature increases solubility of the polymer increases and it unfolds itself to an open configuration of higher volume and hence overall higher viscosity is exhibited at higher temperature by polymer-doped base oil. This activity offsets the normal trend of decrease in viscosity with increase in temperature [25].

It is seen from the table 4 that the terpolymer exhibited higher VI values at all concentrations compared to the homopolymer and other copolymers. Higher molecular weight of the terpolymer may be the reason behind it since higher the molecular weight of the polymer higher is the volume it exposed in the solution and hence higher viscosity is observed [26]. With increasing concentration of the polymer in the bas oil, total volume of the polymer micelle increases and hence the viscosity index data also increases with increasing concentration of the polymer in base oil [27].

5. CONCLUSION

This comparative study reveals that the terpolymer or castor oil exhibited better performance as viscosity index improver and pour point depressant compared to the homopolymer and other copolymer as well. The oxy-rich property of castor oil molecules and the olefinic part are the key reasons for such observation. The higher cross link density in case of castor oil-styrene copolymer is responsible for showing higher viscosity index values in this case also. Moreover the reported polymers are biodegradable and hence environment-friendly as well. Therefore, the above study is definitely a potential approach towards development of cost effective and sustainable lubricant composition.

ACKNOWLEDGEMENT

The authors thank IOCL, Dhakuria, West Bengal for providing base oil and UGC, New Delhi for providing financial support.

ORCID iDs

Sayak P GHOSH
Pranab GHOSH 0000-0002-9388-3820

REFERENCES

[1] M. R. Mortier and T. S. Qrszulik, *Chemistry and Technology of Lubricants*, London, U.K.: Blackie Academic and Professional, 1997, doi: 10.1007/978-1-4615-3554-6.

[2] P. Ghosh and T. Das, “Copolymer of decyl acrylate and styrene: synthesis, characterization and viscometric studies in different base stock,” *Advances in Applied Science Research*, vol. 2, pp. 272, 2011.

[3] K. M. Jung, B. H. Chun, S. H. Park, C. H. Lee, and S. H. Kim, “Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricating oil,” *Journal of Applied Polymer Science*, vol. 120, pp. 2579, 2011.

[4] P. Ghosh, T. Das, D. Nandi, G. Karmakar, and A. Mandal, “Synthesis and characterization of biodegradable polymer–used as a pour point depressant for lubricating oil,” *International Journal of Polymeric Materials*, vol. 59, pp. 1008, 2010.

[5] A. I. Akhmedov, “Copolymer of alkyl methacrylates with styrene as VI improvers for lubricating oils,” *Chemistry and Technology of Fuels and Oils*, vol. 30, pp. 34, 1994.

[6] I. S. Jerbic, J. P. Vukovic, and A. Jukic, “Production and application properties of dispersive viscosity index improvers,” *Industrial & Engineering Chemistry Research*, vol. 5, pp. 11914, 2012.

[7] T. K. Miwa, J. A. Rothfus, and E. Dimitroff, “Extreme-pressure lubricant tests on jojoba and sperm whale oils,” *Journal of the

American Oil Chemists' Society*, vol. 56, pp. 765, 1979.

[8] S. Boyde, “Green lubricants: Environmental benefits and impacts of lubrication,” *Green Chemistry*, vol. 4, pp. 293–307, 2002.

[9] H. M. Mobarak *et al.*, “The prospects of biolubricants as alternatives in automotive applications,” *Renewable and Sustainable Energy Reviews*, vol. 33, pp. 34–43, 2014.

[10] A. Adhvaryu, S. Z. Erhan, and J. M. Perez, “Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants,” *Wear*, vol. 257, pp. 359–367, 2004.

[11] N. B. Samarth and P. A. Mahanwar, “Modified vegetable oil based additives as a future polymeric material—review,” *Open Journal of Organic Polymer Materials*, vol. 5, pp. 1–22, 2015.

[12] Z. Liu, B. K. Sharma, S. Z. Erhan, A. Biswas, R. Wang, and T. P. Schuman, “Oxidation and low temperature stability of polymerized soybean oil-based lubricants,” *Thermochimica Acta*, vol. 601, pp. 9–16, 2015.

[13] A. Adhvaryu, S. Z. Erhan, Z. S. Liu, and J. M. Perez, “Oxidation kinetic studies of unmodified and genetically modified vegetable oils using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy,” *Thermochimica Acta*, vol. 364, no. 1–2, pp. 87–97, 2000.

[14] B. K. Sharma, A. Adhvaryu, Z. Liu, and S. Z. Erhan, “Chemical modification of vegetable oils for lubricant applications,” *Journal of the American Oil Chemists' Society*, vol. 83, pp. 129–136, 2006.

[15] Y. Xia and R. C. Larock, “Vegetable oil-based polymeric materials: Synthesis, properties, and applications,” *Green Chemistry*, vol. 12, pp. 1893–1909, 2010.

[16] K. R. Kunduru, A. Basu, M. H. Zada, and A. J. Domb, “Castor oil based biodegradable polyesters,” *Biomacromolecules*, vol. 16, pp. 2572–2587, 2015.

[17] A. K. Singh, “Castor oil based lubricants reduces smoke emission in two stroke engines,” *Industrial Crops and Products*, vol. 33, pp. 287–295, 2011.

[18] R. Sánchez, M. Fiedler, E. Kuhn, and J. M. Franco, “Tribological characterization of green lubricating greases formulated with castor oil and different biogenic thickener agents: a comparative experimental study,” *Industrial Lubrication and Tribology*, vol. 63, pp. 446–452, 2011.

[19] L. A. Quinchia, L. A. Delgado, T. Reddyhoff, C. Gallegos, and H. A. Spikes, “Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers,” *Tribology International*, vol. 69, pp. 110–117, 2014.

[20] C. S. Madankar, S. Pradhan, and S. N. Naik, “Parametric study of reactive extraction of castor seed (Ricinus communis L.) for methyl ester production and its potential use as bio lubricant,” *Industrial Crops and Products*, vol. 43, pp. 283–290, 2013.

[21] Y. J. Zuo, D. D. Zhang, and J. H. Ng, “An improved thermodynamic model for wax precipitation from petroleum fluids,” *Chemical Engineering Science*, vol. 56, pp. 6941, 2001.

[22] L. C. A. Machado, F. E. Lucas, and G. Gonzalez, “Poly(ethylene-co-vinyl acetate) as wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and phase behaviour of organic solutions,” *Journal of Petroleum Science and Engineering*, vol. 32, pp. 159, 2001.

[23] J. K. Liao and C. Y. Zhai, “A study on alcohols mixture esterified copolymer of maleic anhydride with mixed olefins, acrylic alkyl ester and styrene as pour-point depressant for diesels,” *Petroleum Science and Technology*, vol. 17, pp. 51, 1999.

[24] N. M. Amal *et al.*, “Preparation and evaluation of acrylate polymers as viscosity index improvers for lube oil,” *Petroleum Science and Technology*, vol. 23, pp. 537, 2005.

[25] C. J. Hipeaux, M. Born, P. J. Durand, P. Claudy, and M. J. Letoffe, “Physico-chemical characterization of base stocks and thermal analysis by differential scanning calorimetry and thermomicroscopy at low temperature,” *Thermochimica Acta*, vol. 348, pp. 147, 2000.

[26] A. A. Abdel-Azim, M. A. Nassar, S. N. Ahmed, and S. R. Kamal, “Multifunctional additives as viscosity index improvers and pour point depressants for lube oils,” *Petroleum Science and Technology*, vol. 27, pp. 20, 2009.

[27] A. M. Nassar, “The behaviour of polymers as viscosity index improvers,” *Petroleum Science and Technology*, vol. 26, pp. 514, 2008.