

Conversion of long chain alpha olefins present in refinery streams to value added products via polymerization

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR-Harnessing Appropriate Rural Interventions and Technologies (CSIR-HARIT) for the award of Degree of PhD



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Declaration – I, Bhawna Sharma, hereby certify that the work presented in this Report entitled “**Conversion of long chain alpha olefins present in refinery streams to value added products via polymerization**” in partial fulfillment of the course requirement for award of the Degree of PhD, being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at CSIR-IIP, Dehradun during the period of November, 2019 to March, 2020 under the supervision of Dr Umesh Kumar.

Date *29th Sep, 2020.*

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1. Introduction

Nowadays due to the scarcity of crude oil reserves, the demand for lubricating oil is increasing at an alarming rate. The demand has increased exponentially over the last decade.^[1] Generally, lubricants are composed of base oil and various additives such as viscosity index improvers (VII), pour point depressants (PPDs), anti-wear agents, detergents, and antioxidants which are added to enhance their properties. Since at low climatic regions lubes or base oils containing waxes starts to solidify in the form of wax crystals by forming 3-dimensional network structure. PPDs work by forming small isotropic crystals which improves the property of lubes by modifying or stopping the growth of 3-dimensional network structure so that lube oils can flow easily even at low temperature.^[2,3] Therefore, undoubtedly, the progress in the development of additives to lower the pour point is a captivating research area in both academics and petroleum industry which not only save energy but also help in reducing the chemical waste which is a major concern these days.

Poly(acrylates) and poly(methyl methacrylates), due to their structural properties are broadly used as VII and PPDs, and continuous improvement is still needed for their better performance for the industrial applications.^[3-8] Recently, the researchers have drawn attention towards the development of n-alkyl paraffin's and n-alkyl acrylates based copolymeric additives. They exhibit remarkable lubricating properties and at the same time depress the pour point due to their comb shapes.^[9] The comb shapes copolymers have the ability to reduce the size of the wax crystal, thereby allowing the crude oil to flow at even low-temperature areas. Some researchers have also developed eco-friendly and bio-based lubricating additives as cost-effective lubricants.^[10-13] However the utilization of LCAO (Long Chain Alpha Olefins) for the development of multifunctional additives for lubricating oils is still less explored. The earlier methods which are known up to date either utilized ethylene-propylene or ethylene along with alpha-olefin (C₈ to C₁₀) derived copolymers which work as viscosity improvers for lubricating oils. However, the main disadvantage of using pure alpha-olefins is that it makes the known processes/ additives less attractive to economic viewpoints. Therefore, by keeping in mind the economic standpoint the proposed work is targeted to polymerize LCAO with alkyl acrylates for the synthesis of multifunctional polymeric additives, which works as VII and PPDs for lubricants.

Here we report the design and synthesis of three copolymeric additives namely poly(alkyl acrylate-co-linear α -olefins) (P1, P2, and P3) based on LCAO and different alkyl acrylates using free radical polymerization route under solvent-free conditions. The synthesized polymeric materials are characterized by proton and carbon NMR, and molecular weights of the polymers were determined using gel permeation chromatography (GPC). The synthesized polymeric additives are tested for their physical properties such as viscosity, pour point by mixing with three different base oils (BO-1, BO-2, and BO-3).

2. Material and Methods

2.1. Materials: Acrylic acid, toluene sulfonic acid (p-TSA), benzoyl peroxide (BPO), 1-hexanol, 1-decanol, 1-hexadecanol, toluene, hydroquinone (HQ), methanol, diethyl ether, and chloroform were purchased from Merck, India. MAK-150 (also known as N-150) was obtained from the BPCL, Mumbai, India, BO-2, and BO-3 were obtained from UAE.

2.2. Preparation of simulated coker feed (SCF) mixture: The simulated feed is prepared as follows: 1-octene (12.5 g), 1-decene (17.5 g), 1-dodecene (12.5 g), n-decane (23 g), n-dodecane (30 g), n-hexadecane (30 g) were taken together to simulate similar like Coker feed. The total olefin content is 33 % with the composition of C₈ olefin (10 %), C₁₀ (13 %), C₁₂ olefin (10 %) and the remaining paraffin is (67 %).

2.3. Synthesis of different acrylate monomers: All the synthesis procedure were carried out in 500 mL round bottom flask which is further equipped with dean stark assembly to remove the azeotropic water formed during the reaction. For the synthesis of different alkyl acrylates (C₆Ac, C₁₀Ac, and C₁₆Ac), 0.5 M of acrylic acid was reacted with 0.5 M alkyl alcohol in which 0.5 wt % p-toluene sulfonic acid (p-TSA), 0.05 wt % hydroquinone in toluene were added. The reaction was initiated by heating the reaction mixture to reflux at 120 °C for 12 h. After completion of reaction, the mixture was washed with de-ionized water for 4-5 times to remove the unreacted acid and p-TSA impurities. ¹H and ¹³C NMR confirmed the successful synthesis of acrylate monomers. The inhibitors present along with the monomer acrylates were removed by passing through a neutral alumina column.

2.4. Polymerization: The copolymerization of alkyl acrylates (C₆Ac, C₁₀Ac, and C₁₆Ac) with LCAO present in simulated coker feed in 1:1 molar ratio is carried out in 500 mL round bottom flask having a magnetic stirrer and a purging system for the continuous supply of nitrogen to

create an inert atmosphere. The polymerization has been carried out in a solvent-free medium by using benzoyl peroxide (BPO) as a free radical initiator at a reaction temperature 80 °C under constant stirring for 24 h under nitrogen atmosphere (Table 1). The reaction was terminated by precipitating the copolymers in methanol as per the usual procedure. The resulting solid products were dried at 40 °C in a vacuum oven overnight. ¹H and ¹³C NMR spectral analysis confirmed the successful synthesis of the copolymers.

2.5. Spectroscopic characterizations: The ¹H and ¹³C NMR spectra of all the synthesized copolymeric additives were recorded on a Bruker Avance 500 spectrometer. Tetramethylsilane (TMS) is used as an internal standard and CDCl₃ is used as a deuterated solvent. All the FT-IR spectra of the copolymeric additives were recorded by KBr pellet method with a Perkin Elmer Spectrometer between 650 to 4,000 cm⁻¹.

2.6. Molecular weight determination: The number-average (M_n), weight-average molecular weight (M_w), and poly dispersity index (PDI) were calculated using Agilent Technologies HPLC system (Model Series 1260 Infinity) having column of Plgel MinMIX-E, 3 μm (250 × 4.6 mm) and evaporative light scattering detector (ELSD). HPLC grade tetrahydrofuran (THF) is used as an eluting solvent whereas for calibration of instrument polystyrene standards (Polymer Laboratory/Varian) were used.

2.7. Evaluation of synthesized copolymeric additives as pour point depressants (PPDs): The ASTM D-97-15 test method^[14] is followed for the determination of pour point of the synthesized copolymeric additives/base oil blends.

2.8. Evaluation of prepared copolymeric additives as viscosity index improvers (VIIs): The viscosity index of the synthesized copolymeric additives/base oil blends were evaluated according to ASTM D2270-93.^[15] The viscosity of the synthesized copolymeric additives at different concentration (0, 2000, 4000, and 6000 ppm) were calculated at 40 °C and 100 °C temperature.

3. Results and Discussion

3.1. Synthesis and Structural Characterization of Copolymeric Additives.

Table 1 tabulates the ratio between the monomers being used for polymerization, polymerization time, the yield of the polymers, molecular weight details (M_n and M_w) and PDI of the polymers. All the three polymerizations were performed using an equimolar ratio of alkyl acrylate monomers and SCF monomers at 80 °C under N_2 atmosphere in a solvent-free medium for 48 hours. The resulting polymers were white solid with a yield above 60 %. The molecular weights of the polymers were determined via GPC and indicated high molecular weight for the polymers with M_n above 7000 molecular weight.

Table 1. Polymer designation, mole ratio of monomers, polymerization time, yield, molecular weight, and poly dispersity index (PDI) of polymers

| Sample | Ac:SCF (mole ratio) | Time (h) | Yield % | M_n | M_w | PDI |
|-------------------------|---------------------------|-------------|------------|-------|-------|-----|
| polymeric additive (P1) | 1 : 1 | 48 | 89.6 | 7109 | 20543 | 2.9 |
| polymeric additive (P2) | 1 : 1 | 48 | 60.0 | 7731 | 58912 | 7.6 |
| polymeric additive (P3) | 1 : 1 | 48 | 70.6 | 10070 | 56569 | 5.6 |

Polymerization temperature 80 °C, initiator: BPO (0.7 wt % with respect to monomer)

Figure 1 illustrates the FT-IR spectra of polymeric additives (P1, P2, and P3). The peak corresponding to 1738 cm^{-1} is due to carbonyl stretching whereas the stretching band at 2854 and 2923 cm^{-1} corresponds to aliphatic C–H symmetric and asymmetric respectively.

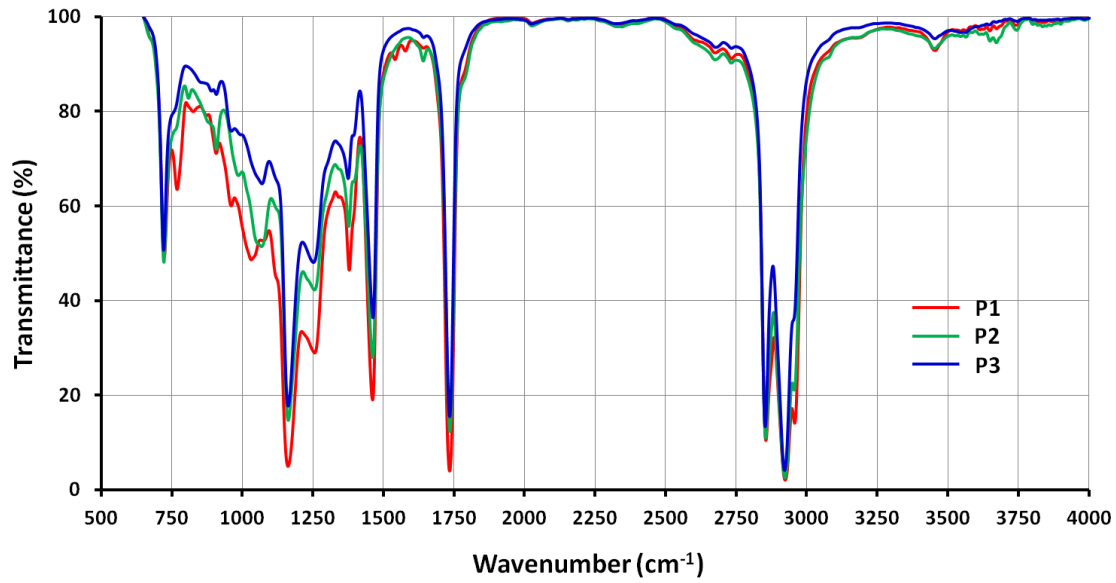


Figure 1. FT-IR spectra of polymeric additives

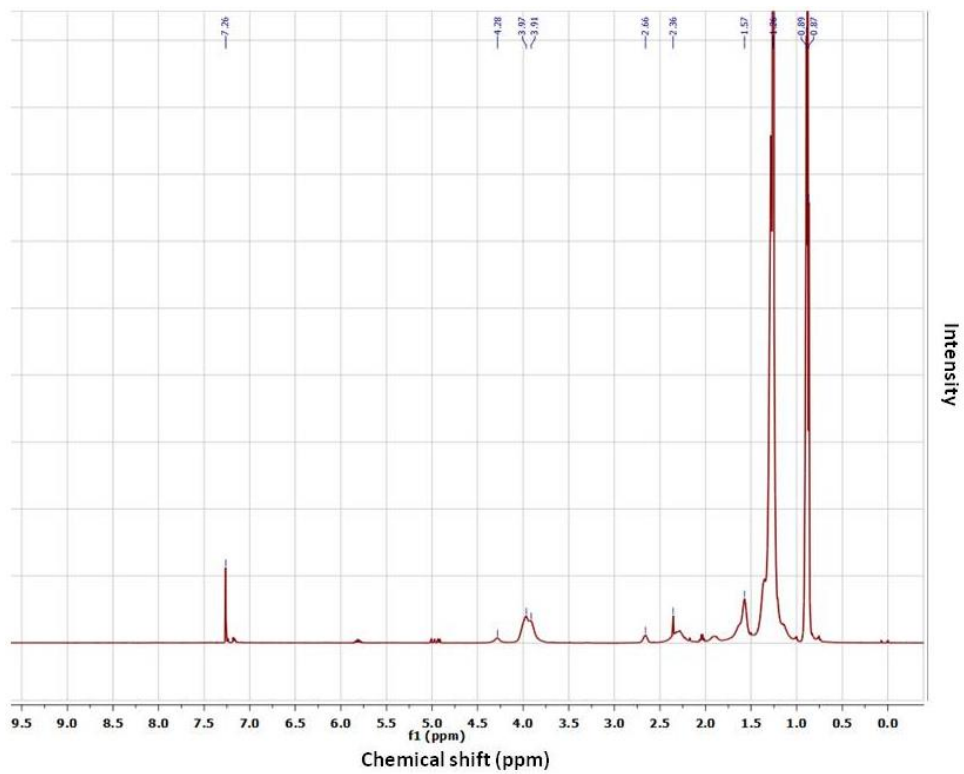


Figure 2. ^1H NMR spectrum of polymeric additive P1

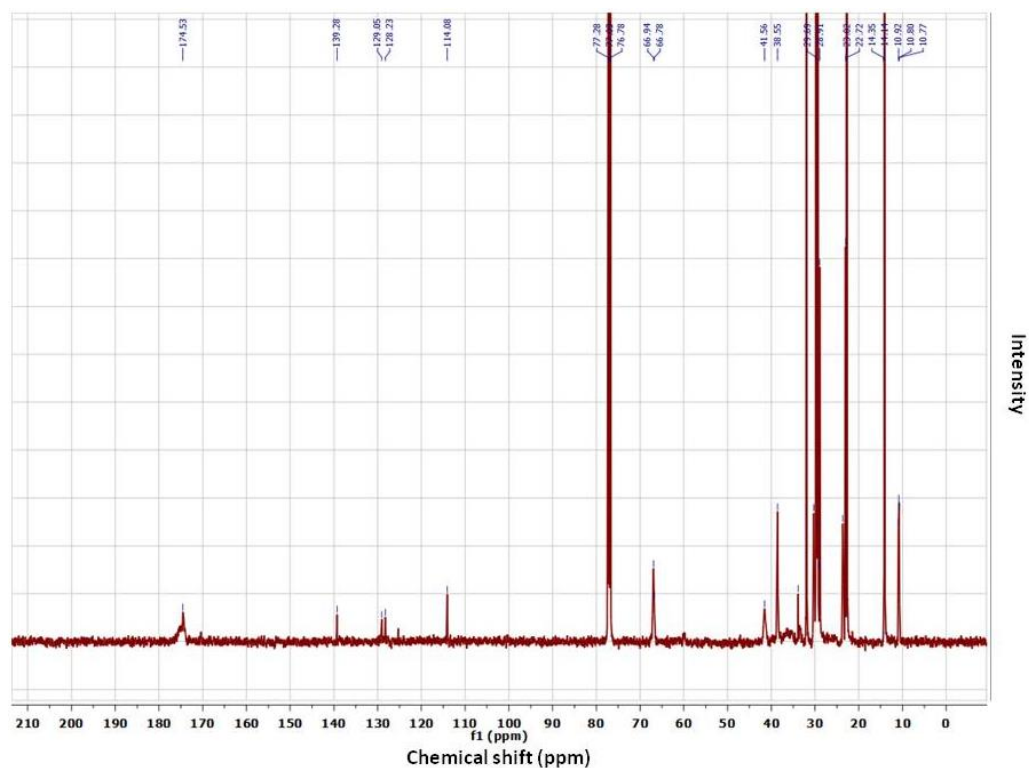


Figure3. ^{13}C NMR spectrum of polymeric additive P1

Figures 2 & 3 represents the ^1H and ^{13}C NMR of the synthesized polymer P1.

The ^1H NMR spectra of the polymer P1 showed a broad singlet at 4.28 ppm which is attributed to $-\text{OCH}_2$ protons. The absence of signal in between 5-5.5 ppm ruled out the possibility of vinylic protons in the copolymer (Figure 2) and the absence of monomeric double bond peaks.

Figure3. (^{13}C NMR) spectra of the polymer P1, the peak at 174 ppm which is assigned to carbonyl ester further confirmed the successful synthesis of the desired copolymer. The two consecutive peaks at 38 and 41 ppm due to $-\text{CH}$ protons confirmed the incorporation of both the monomers in the polymeric backbone (Figure 3).

3.2. Performance Evaluation of the Polymeric Additives Blended Base Oils

Figure 4 reveals the blending of polymeric additives (P1, P2, P3) with three different base oils, namely BO-1 (base oil MAK-150 obtained from BPCL), BO-2, and BO-3 (base oils from UAE). The process of blending does not make any changes in terms of color, miscibility, and appearance of the base oils. The base oils were blended with all the three polymeric additives at different concentrations (0, 2000, 4000, and 6000 ppm and were evaluated for the properties such as viscosity index, density, and pour point and summarized in **Table 2, 3, and 4**

respectively. There is no change in density of the blended base oil which is indicative of similar structure and property of additives. It is observed that in case of base oil which are blended with P1 and P3 polymeric additives, there is an appreciable increase in viscosity index with increasing concentration, whereas base oil which is blended with P2, there is decrease in viscosity index with increasing concentration.

The pour point of the base oils blended with P1 decreases with increasing concentration of P1 and the pour point of base oils blended with P2 slighter decrease for BO-1 and BO-2 and more decrease with increasing concentration of P2. In the case of P3 blended base oils, the pour point did not change with increasing concentration of P3. A critical observation of pour point value decrease at 4000 ppm suggests the optimum concentration of polymeric additive required in the base oil, but all the same additives showed marginal improvement in base oil BO-2 irrespective of the additive concentration. Whereas in base oil BO-3 polymeric additive (I and II) performed better at 6000 ppm while polymeric additive III worked better at lesser concentration, i.e., 4000 ppm. Therefore in a nutshell it is observed that P1 acts as a better additive in comparison to P2 and P3 by increasing the viscosity index and lowering the pour point. Since the composition of all the base oils are different; therefore to improve the properties of base oil in terms of VII and PPDs polymeric additives of a specific design are required.

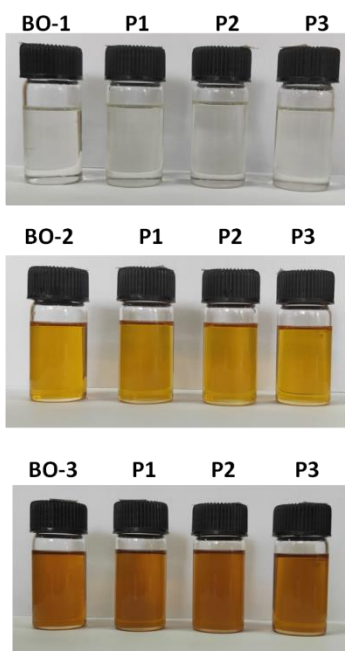


Figure4. Represents the base oils and three copolymeric additives blended base oils

Table 2: Performance of the copolymeric additives in BO-1 as PPD and VII

| Sample | Additive concentration in base oil (ppm) | Viscosity index | Density (g/cm³) | Pour point (°C) |
|-------------------------|---|------------------------|-----------------------------------|------------------------|
| BO-1(Base Oil) | 0 | 108.166 | 0.8164 | -21 |
| polymeric additive (P1) | 2000 | 115.834 | 0.8165 | -21 |
| | 4000 | 121.983 | 0.8164 | < -27 |
| | 6000 | 123.264 | 0.8165 | -24 |
| polymeric additive (P2) | 2000 | 121.419 | 0.8164 | -24 |
| | 4000 | 116.279 | 0.8164 | -21 |
| | 6000 | 115.045 | 0.8167 | -21 |
| Polymeric additive (P3) | 2000 | 122.434 | 0.8164 | -18 |
| | 4000 | 117.83 | 0.8165 | < -27 |
| | 6000 | 110.77 | 0.8169 | -15 |

Table 3: Performance of the copolymeric additives in BO-2 as PPD and VII

| Sample | Additive concentration in base oil (ppm) | Viscosity index | Density (g/cm³) | Pour point (°C) |
|-------------------------|---|------------------------|-----------------------------------|------------------------|
| BO-2 (Base oil) | 0 | 94.53 | 0.8554 | 3 |
| polymeric additive (P1) | 2000 | 95.557 | 0.8555 | 0 |
| | 4000 | 98.915 | 0.8553 | 0 |
| | 6000 | 96.608 | 0.8556 | -3 |
| polymeric additive (P2) | 2000 | 95.892 | 0.8553 | -3 |
| | 4000 | 99.271 | 0.8552 | -6 |
| | 6000 | 96.54 | 0.8551 | -3 |
| Polymeric additive (P3) | 2000 | 92.158 | 0.8556 | -9 |
| | 4000 | 99.316 | 0.8556 | -9 |
| | 6000 | 102.811 | 0.8554 | -9 |

Table 4: Performance of the copolymeric additives in BO-3 as PPD and VII

| Sample | Additive concentration in base oil (ppm) | Viscosity index | Density (g/cm ³) | Pour point(°C) |
|-------------------------|--|-----------------|------------------------------|----------------|
| BO-3 (Base oil) | 0 | 103.72 | 0.8352 | 0 |
| polymeric additive (P1) | 2000 | 100.307 | 0.8348 | -3 |
| | 4000 | 106.272 | 0.8347 | -6 |
| | 6000 | 102.321 | 0.8349 | -12 |
| polymeric additive (P2) | 2000 | 100.93 | 0.8347 | -6 |
| | 4000 | 110.346 | 0.8346 | -9 |
| | 6000 | 102.201 | 0.8346 | -12 |
| polymeric additive (P3) | 2000 | 107.537 | 0.8347 | -15 |
| | 4000 | 107.516 | 0.8349 | -15 |
| | 6000 | 108.488 | 0.8350 | -12 |

4. Conclusion

In summary, three copolymeric additives (P1, P2, and P3) were synthesized successfully in the solvent-free medium by free-radical polymerization route using BPO as initiator. All the synthesized copolymers exhibits better PPD performance. Further to check their multifunctional nature, other properties and performances were measured in base oils. Marginal improvement in VI characteristics was observed. The PPD's characteristics of the copolymeric additives show excellent performance with the order as follows BO-1>BO-3 >BO-2.

5. Acknowledgement

The author would like to acknowledge the Director CSIR-IIP for his kind permission to publish these results. The author is thankful to Analytical Science Division of CSIR-IIP for their analytical support. The author is also highly grateful to Dr Umesh Kumar, Dr T Senthil Kumar and Dr Aruna Kukrety for their constant support and motivation. The author is also thankful to CSIR-New Delhi for financial support through junior research fellowship (JRF).

6. References

1. M. Fuchs, The world lubricants market, current situation and outlook. In *12th international colloquium on Tribology*, **2000**.
2. K. M. Jung, B. H. Chun, S. H. Park, C. H. Lee, S. H. Kim, *J. Appl. Polym. Sci.* **2011**, *120*, 2579–2586.
3. P. Ghosh, T. Das, D. Nandi, G. Karmaka, A. Mandal, *Int. J. Polym. Mater.* **2010**, *59*, 1008.
4. P. Ghosh, T. Das, *Adv. Appl. Sci. Res.* **2011**, *2*, 272.
5. A. I. Akhmedov, *Chem. Tech. Fuels Oil.* **1994**, *30*, 34.
6. I. S. Jerbic, J. P. Vukovic, A. Jukic, *Ind. Eng. Chem. Res.* **2012**, *5*, 11914.
7. A. A. A. Abdel-Azim, R. M. Abdel-Aziem, *J. Polym. Res.* **2001**, *8*, 111.
8. A. M. Nassar, *Pet. Sci. Technol.* **2008**, *26*, 514.
9. R. K. Singh, A. Kukrety, A. Kumar, A. Chouhan, R. C. Saxena, S. S. Ray, S. L. Jain, *Adv. Polym. Technol.* **2018**, *37*, 1695.
10. R. K. Singh, A. Kukrety, A. K. Chatterjee, G. D. Thakre, G. M. Bahuguna, S. Saran, D. K. Adhikari, N. Atray. *Ind. Eng. Chem. Res.* **2014**, *53*, 18370.
11. R. Sánchez, G. B. Stringari, J. M. Franco, C. Valencia, C. Gallegos, *Carbohydr. Polym.* **2011**, *85*, 705.
12. P. Nagendramma, S. Kaul, *Renewable Sustainable Energy Rev.* **2012**, *16*, 764.
13. G. Karmakar, P. Ghosh, *ACS Sustainable Chem. Eng.* **2013**, *1*, 1364.
14. ASTM D97–15, In: Annual Book of ASTM Standards (Eds: N. C. Baldini, E. I. Barkley, L. M. Brecht, C. M. Leinweber, V. A. Mayer, K. A. Peters, E. A. Whealen, R. F. Wilhelm), ASTM International, West Conshohocken, PA, **2015**.
15. ASTM D2270-93, In: Annual Book of ASTM Standards (Eds: N. C. Baldini, E. I. Barkley, L. M. Brecht, C. M. Leinweber, V. A. Mayer, K. A. Peters, E. A. Whealen, R. F. Wilhelm), ASTM International, West Conshohocken, PA, **1998**.
16. ASTM D130-12, Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test. In Annual Book of ASTM Standards; ASTM International: West Conshohocken, PA, **2012**.