OPTIMIZATION AND CHARACTERIZATION OF FACILE SYNTHESIS OF PENTAETHYLENEHEXAMINE-TERMINATED POLYISOBUTYLENE

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ABSTRACT

Polyisobutylene plays a significant role as the long oil-soluble tail that can produce excellent oil solubility and prevent the engine's aggregation of deposit particles. We have demonstrated an easy work-up synthesis of pentaethylenehexamine-terminated polyisobutylene (PIB-PEHA) using BF₃ as a co-initiator. Fourier transform-infrared (FT-IR) spectroscopy, UV-vis spectrophotometer, thermogravimetric analysis and liquid chromatography-electrospray ionization-quadrupole time-of-flight-tandem mass spectrometry (LC-ESI-QTOF-MS/MS) were performed to analyze the chemical properties of the prepared product. The results showed that a reaction time of 4 h and co-initiator loading of 0.023 M is the best condition for synthesizing PIB-PEHA. This study shows that the methodology has potential for industrial application as an alternative option to manufacture dispersants with economic benefits.

Keywords: Combustion, Deposit, Dispersant, Gasoline Additives, Polyisobutylene.

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INTRODUCTION

Dispersant additives in gasoline play a significant role in keeping engines wall clean, preventing the generation of gum and sludge in the combustion process and decreasing the release of the contaminants into the environment^{1,2}. However, the accumulation of these solid materials consisting of organic and inorganic components is harmful to engines through wear and oil filter³. Several dispersants are widely used in the oil additive industry, including polyalphaolefins, polyisobutylene (PIB) and polypropylene, and acrylate-based polymers⁴.

Polyisobutylene (PIB) is a fully saturated hydrocarbon polymer with widespread commercial applications as an additive for an internal combustion engine in lubricating oil. Due to its essential features, including remarkable flexibility on low-temperature, low glass transition temperature (T_g), excellent stability under chemical, thermal, and oxidative changes, and capability of chemical transformations^{5,6,7}. PIB can be obtained by the cationic polymerization mechanism of isobutylene in inert solvents, and Lewis acids such as AlCl₃, TiCl₄, BCl₃, and BF₃ function as co-initiator and secondary aliphatic alcohol and ether as initiating system⁸. The amount of double-bound end groups is one of the fundamental properties for commercially synthesized PIB⁹. Moreover, exo-olefin-terminated PIB is a critical intermediate for prior chemical modification to hydroxyl, phenol, epoxide, and sulfonic acid-terminated PIB⁶.

Several studies have been performed on the mechanism of PIB as a dispersant which is affected by its structure^{1,10,11}. The polar groups of dispersant structures that can adsorb the tiny particles of deposit consist of amine, hydroxyl, or ether. PIB has a long oil-soluble carbon tail that can produce excellent oil solubility and prevent the aggregation of deposit particles¹². The average molecular weight of PIB and the amine's chemical structure may impact the PIB-type dispersants¹³. Forbes et al. reported that PIBs with an average molecular weight of 900–1000 showed a better detergency performance than PIBs with higher molecular weight. Further, the polarity of the head group of the dispersant may act on stabilization of the small particles in which the less polar amine exhibits lower detergent adsorption on the low polarity carbon particle than more polar head group¹⁰.

In recent years, various methods have been applied to synthesize functionalized PIB using different reaction conditions.¹⁴⁻¹⁷ Herein, we report simple protocols of synthesis and characterization of pentaethylenehexamine-terminated polyisobutylene (PEHA-PIB) using BF_3 as a co-initiator. The reaction optimization was employed to determine a method that improves reaction rate, shorter reaction time, and more straightforward procedure with satisfying yield. If so, this may become an alternative option to manufacture dispersants in the industry with economic benefits.

EXPERIMENTAL

Material and Methods

Chemicals used in this study were used without purification and were acquired from Merck-Sigma Chemical Company, including boron trifluoride (99%) as co-initiator. Polyisobutylene (PIB) with an average molecular weight of 1000 kDa was purchased from Sigma Aldrich. Pentaethylenehexamine (PEHA) as the source of the polar head with an alkylamine group was also obtained from Sigma-Aldrich. Mixture *O*-xylene (99%) and dichloromethane (99%) were employed as a solvent in reaction, while acetone (99 %) was used for the precipitation of the product. *n*-Hexane ($\geq 99\%$) was employed as a solvent in thin layer chromatography and UV-Vis spectrophotometer analyses. The evaluation of the reaction's progress and the targeted product's formation was carried out by thin-layer chromatography using silica gel plate 60 F254 (Merck) visualized by UV light. All substance was formulated by mass applying a Mettler Toledo analytical balance with 0.0001 g precision.

General Procedure

The dispersant of PIB-PEHA was synthesized by reacting 62.5 mM polyisobutylene (PIB) (average molecular weight of 1000 g mol⁻¹) with 62.5 mM pentaethylenehexamine (PEHA) as polar head and 0.046 M boron trifluoride as co-initiator, and 125 mL of solvents (*O*-xylene : dichloromethane, 9 : 1 v/v) based on nucleophilic acyl substitution mechanism in a 500 mL, two-necked round-bottom flask equipped with a thermometer, magnetic stirrer, heating mantle and reflux condenser. The reaction was carried out at a temperature of 110 °C for 4 h and the progress of the synthesis was observed using thin-layer chromatography (TLC). The polymer was then separated by precipitation from solutions into acetone upon cooling to ambient temperature. The reaction is shown in Fig.-1.

Fig.-1: Chemical Reaction of Synthesis of PIB-PEHA

Detection Method

The synthesized compounds were characterized using Fourier transform infrared spectroscopy (FTIR) spectra within the 4000–400 cm⁻¹ region (Thermo Scientific). The thermal alteration of PIB-PEHA products during the heating rate of 20 °C/min was evaluated by a thermogravimetric analyzer (TA Instrument). The UV–Vis spectra of the product were observed using a spectrophotometer (Shimadzu). The molecular weights of the prepared compounds were evaluated using liquid chromatography-mass spectrometry (LC–ESI-QTOF-MS/MS) by Agilent.

RESULTS AND DISCUSSION

Synthesis and Characterization of PIB-PEHA

The absorption of FT-IR spectra acquired at a wavelength from 400 to 4000 cm⁻¹ for PIB and PIB-PEHA are shown in Fig.-2. Primary and secondary amine peaks in the prepared dispersant were discovered by peaks at 3000–3500 cm⁻¹. In addition, the peak of C–N stretching obtained at the region of 1250–1020 cm⁻¹ was related to the formation of new chemical bonds between PIB molecule and pentaethylenehexamine molecule. The observation of N–H bending vibration from pentaethylenehexamine indicates that desired product was successfully synthesized. The stretching vibration of C–H bonds of polyisobutylene chain did not alter during the reaction discovered at the strong peak around 2800–3000 cm⁻¹ and was regarded as a reference.

Fig.-2: FT-IR Spectra of the PIB and PIB-PEHA

The prepared PIB-PEHA was then analyzed using a UV-vis spectrophotometer after solubilization in hexane. A blank solution comprised of the same solvent was employed each recording time, as shown in Fig.-3. There is a noticeable absorption band shift and several new peaks in PIB-PEHA compared to the PIB spectrum. This optical observation showed that polyisobutylene and pentaethylenehexamine have reacted, producing the desired product of PIB-PEHA with different chemical properties.

Fig.-3: UV-vis Spectra of the PIB and PIB-PEHA

Thermogravimetric analysis (TGA) was used to study the thermal decomposition of the synthesized PIB-PEHA and to determine its component by monitoring the change of its weight that takes place during heating in the temperature range from 25 to 800 °C at a constant temperature rate of 20 °C/min, as shown in Fig.-4. Thermal decomposition of synthesized PIB-PEHA started at a temperature of 214.40 °C and finished at 487.47 °C with significant loss of its weight took place at a temperature of 449.11 °C. A small peak was observed at a lower temperature of 69.12 °C due to the volatilization of acetone used in separating the polymer after the reaction. Polyisobutylene used as starting material showed thermal decomposition that began at the temperature of 156.30 °C and ended at 486.18 °C with substantial weight loss peaked at 486.18 °C. It can be observed from these results that PIB-PEHA exhibited higher molecular weight than polyisobutylene itself, as confirmed by comparing thermal decomposition peaks between them. These results also agree with UV-vis spectroscopy results that polyisobutylene and pentaethylenehexamine have

joined chemically by forming new bonds and producing compounds with a more considerable molecular weight that had greater decomposition temperature.

Fig.-4: TGA Curves for PIB, PEHA and PIB-PEHA

The molecular weight of synthesized PIB-PEHA was evaluated using a liquid chromatography-mass spectrometry (LC-ESI-QTOF-MS/MS) system in negative ionization modes¹⁸. The TOF-MS system in LC-QTOF instrumentation allowed screening and quantification of both unknown and targeted organic compounds. Working in MS/MS mode confirmed compounds identification with no fragment ions or low intensity/relative abundance fragments from in-source CID fragmentation system¹⁹. The compounds were first separated from a mixture in an HPLC system and then injected separately into the quadrupole-time-of-flight mass spectrometer generating different spectra of each component. The results showed that the isolated PIB-PEHA correspond to the desired dispersant with estimated molecular mass, as shown in Fig.-5. By comparing mass spectra of PIB and PIB-PEHA, it can be observed that the synthesized PIB-PEHA had higher molecular weight and different fragmentation patterns than polyisobutylene as starting material. These results also demonstrated that the desired product of PIB-PEHA has been formed with other chemical properties. The LC chromatogram showed that this facile method could produce the desired outcome with satisfied purity.

Optimization of Reaction Condition

An efficient method with less time, energy and material for the preparation of PIB-PEHA as dispersant through the reaction of polyisobutylene (PIB) and pentaethylenehexamine (PEHA) in the presence of BF_3 as co-initiator has been described. Fig.-6 shows the effect of varying reaction times from 1–4 h on isolated yield of synthesized PIB-PEHA while maintaining the co-initiator loading (0.046 M), reactant ratio (1:1) and reaction temperature (105 °C). Longer reaction time promoted an increase in yield of the desired product as it exhibited more time to proceed, as seen in the reaction time of 1 h to 4 h. Reaction time for 4 h was able to generate an excellent yield of 83.94% compared to other reaction times. On the other hand, there was no significant rise in percentage yield of the product when comparing 2 to 4 h reaction time. Thus, 4 h was selected to the best reaction time for the synthesis of PIB-PEHA.

Fig.-5: LC Chromatogram and M/z spectra of the PIB and PIB-PEHA

Fig.-6: Effect of varying reaction times on isolated yield of PIB-PEHA

Figure-7a shows Fourier transform-infrared (FT-IR) spectra of PIB-PEHA products synthesized at reaction times of 1, 2 and 4 h. A reduction in peak intensity around 1600-1700 cm^{-1} indicates the presence of a double bond originating from polyisobutylene molecule with increasing reaction time. The reaction time for 4 h possessed the lowest intensity of the peak compared to other reaction times. These results showed that more polyisobutylene molecules reacted with pentaethylenehexamine molecules to form PIB-PEHA products in 4 h reaction time. In addition, the results of the TGA analysis also provided a similar trend for reaction times for 1, 2 and 4 h (Fig.-7b). The decomposition temperature with significant loss of weight

occurred at 445.47, 443.61 and 449.11 °C for reaction times of 1, 2 and 4 h, respectively. Although there is no significant improvement, reaction time for 4 h generated a higher decomposition temperature than other reaction times. These results confirmed that more product PIB-PEHA that possessed higher molecular weight than initial PIB were synthesized in 4 h reaction time than others. The TGA results also showed that the synthesized dispersant is stable at a high temperature which is necessary for its application on engine operation up to 200–300 °C ^{9,20}.

Fig.-7: FT-IR Spectra (a) and TGA Curves (b) of PIB-PEHA by varying reaction times

The next series of experiments were carried out with a varied loading of BF_3 as co-initiator, from 0.012 to 0.046 M, while maintaining the reaction time (4 h), reactant ratio (1:1) and the reaction temperature (105 °C). The yield data described in Fig.-8 shows a noticeable improvement of the isolated yield of prepared PIB-PEHA with the increase of co-initiator loading. Furthermore, reaction conditions with co-initiator loading of 0.023 M generated a product of PIB-PEHA with a higher yield than other amounts. These results indicated that satisfactory isolated yield with co-initiator catalyst loading would positively impact synthesizing PIB-PEHA on an industrial scale. However, simultaneous thermal analysis (STA) results appeared with no significantly different decomposition temperatures between 0.023 and 0.046 M co-initiator loading, as shown in Fig-3b.

Fig.-8: The effect of co-initiator loading on isolated yield of PIB-PEHA (a) and its STA analysis (b)

CONCLUSION

Polyisobutylene plays a significant role as the long oil-soluble tail that can produce excellent oil solubility and prevent deposit particles' aggregation. The molecular weight of polyisobutylene and the chemical structure of the amine as polar functional groups may impact the performance of the PIB-type dispersants. We have demonstrated an easy work-up synthesis of pentaethylenehexamine-terminated polyisobutylene (PIB-PEHA) using BF_3 as a co-initiator. The results showed that a reaction time of 4 h and co-initiator

loading of 0.023 M was the most optimum conditions for the synthesis of PIB-PEHA. Fourier transform-infrared (FT-IR) spectroscopy, UV-vis spectrophotometer, thermogravimetric analysis and LC-ESI-QTOF-MS/MS were performed to analyze the chemical properties of the prepared product. We believe this methodology has potential for industrial application as an alternative to manufacturing dispersants with economic benefits.

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REFERENCES

1. Y. Chevalier, M.-C. Dubois-Clochard, J.-P. Durand, B. Delfort, P. Gateau, L. Barre, D. Frot, Y. Briolant, I. Blanchard, R. Gallo, *Progress in Colloid and Polymer Science*, **118**, 110(2001), https://doi.org/10.1007/3-540-45725-9_25
2. APF dos Santos, K.K. da Silva, L.A. d'Avila, J. Dweck, *Journal of Thermal Analysis and Calorimetry*, **131**, 783(2018), <https://doi.org/10.1007/s10973-016-6035-0>
3. A.M. Nassar, N.S. Ahmed, H.S. Abdel-Hameed, A.F. El-Kafrawy, *Applied Petrochemical Research* **6**, 49(2016), <https://doi.org/10.1007/s13203-015-0110-5>
4. T. Rajasekhar, G. Singh, G.S. Kapur, S.S.V. Ramakumar, *RSC Advances*, **10**, 18180(2020), <https://doi.org/10.1039/d0ra01945c>
5. T.P. Holbrook, R.F. Storey, *Journal of Polymer Science*, **58**, 280(2020), <https://doi.org/10.1002/pol.20190017>
6. S. Ummadisetty, D.L. Morgan, C.D. Stokes, J.J. Harrison, C.G. Campbell, R.F. Storey, *Macromolecular Symposia*, **323**, 6(2013), <https://doi.org/10.1002/masy.201200017>
7. B. Yang, R.F. Storey, *Reactive and Functional Polymer*, **150**, 104563(2020), <https://doi.org/10.1016/j.reactfunctpolym.2020.104563>
8. J.E. Puskas, Y. Chen, Y. Dahman, D. Padavan, *Journal of Polymer Science*, **42(13)**, 3091(2014), <https://doi.org/10.1002/pola.20114>
9. L.B. Zhang, Y.X. Wu, P. Zhou, R.W. Xu, *Polymer for Advanced Technologies*, **23(3)**, 522(2012), <https://doi.org/10.1002/pat.1908>
10. E.S. Forbes, E.L. Neustadter, *Tribology*, **5(2)**, 72(1972), [https://doi.org/10.1016/0041-2678\(72\)90121-2](https://doi.org/10.1016/0041-2678(72)90121-2)
11. A.R. Cox, R. Mogford, B. Vincent, S. Harley, *Colloids and Surface A: Physicochemical and Engineering Aspects*, **181**, 205(2001), [https://doi.org/10.1016/S0927-7757\(00\)00778-0](https://doi.org/10.1016/S0927-7757(00)00778-0)
12. Z. Qin, Z. Liu, L. Wang, X. Zhang, Y. Fu, G. Xu, G. Liu, *Energy & Fuels*, **34(5)**, 5634(2020), <https://doi.org/10.1021/acs.energyfuels.0c00230>
13. Y. Kim, J. Kim, D.H. Hyeon, J.S. Han, B.H. Chun, B.H. Jeong, S.H. Kim, *Fuel*, **158**, 91(2015), <https://doi.org/10.1016/j.fuel.2015.05.008>
14. T. Rajashekar, U. Haldar, J. Emert, P. Dimitrov, R. Severt, R. Faust, *Journal of Polymer Science Part A Polymer Chemistry*, **55(22)**, 3697(2017), <https://doi.org/10.1002/pola.28751>
15. F. Balzano, A. Pucci, R. Rausa, G. Uccello-Barreta, *Polymer International*, **61(8)**, 1256(2012), <https://doi.org/10.1002/pi.4228>
16. MY Sen, J.E. Puskas, D.E. Dabney, C. Wesdemiotis, C. Absalon, *Journal of Polymer Science Part A Polymer Chemistry*, **48(16)**, 3501(2010), <https://doi.org/10.1002/pola.24058>
17. I. Kulai, A. Karpus, D.E. Bergbreiter, M. Al-Hashimi, H.S. Bazzi, *Macromolecular Rapid Communications*, **41(17)**, 2000382 (2020), <https://doi.org/10.1002/marc.202000382>
18. A.H. Cahyana, A.R. Liandi, Y. Safitri, R.T. Yunarti, *Rasayan J.Chem*, **13(3)**, 1491(2020), <https://doi.org/10.31788/RJC.2020.1335700>
19. M.J. Gómez, M.M. Gómez-Ramos, O. Malato, M. Mezcuca, A.R. Fernández-Alba, *Journal of Chromatography A*, **1217**, 7038(2010), <https://doi.org/10.1016/j.chroma.2010.08.070>
20. A.M. Danilov, *Petroleum Chemistry*, **55(3)**, 169(2015), <https://doi.org/10.1134/S0965544115030020>

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