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## ECOENERGETICS

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**Abstract:** This article covers the synthesis of new poly(ester amide)s from renewable resources and their properties, together with a view on their potential applications in sustainable polymer development. The synthetic strategy involves regioselective polymerizations using diol-diamide monomers and the diacid diacyl chloride (Z)-octadec-9-enedioyl dichloride (D18:1), allowing hydrogen-bonding functionalities to be appended to the polymer backbone. These materials have enhanced thermal stability, improved crystallinity, and controlled dispersity, finding applications in advanced engineering areas. This work also investigates higher-order alcohol additives on diesel-biodiesel blends to present effects on fuel properties, engine performance, and emission parameters. These blends are a little promising for renewable fuel innovations with the optimization of cold flow characteristics along with reduced NO<sub>x</sub> emissions. Graphene-based nanomaterials are also integrated into the polymer matrix to further enhance mechanical, electrical, and thermal properties, adding an extra functionality for advanced engineering and energy applications.

**Keywords:** Poly(ester amide)s, renewable resources, polymerization, (Z)-octadec-9-enedioyl dichloride, hydrogen bonding, thermal stability, crystallinity, diesel-biodiesel blends, engine performance, NO<sub>x</sub> emissions, graphene nanomaterials, mechanical properties, energy applications.

## 1. INTRODUCTION

The work bridges advanced polymer synthesis with sustainable fuel development; thus, it has a dual focus: renewable materials and energy solutions. The PEAs synthesized from the bio-based monomers exhibited excellent thermal stability and crystallinity, representing an advance in sustainable polymer design. [1-5]

Simultaneously, higher alcohol additives in diesel-biodiesel blends improve fuel properties and reduce NO<sub>x</sub> emissions, offering a promising pathway for renewable energy optimization. Besides, the material properties are improved by incorporating graphene into the polymer matrix, which has been a modern way of enhancing the performance both for the polymers and the fuels. [6,12,30]. Altogether, these findings form a basis for synergistic collaboration between materials science and energy sustainability in innovative engineering applications for environmental conservation.

## 2. EXPERIMENTAL DETAIL

The synthesis was initiated by adding 7.02 g (22.47 mmol) of D18:1 and 105 mL of CH<sub>2</sub>Cl<sub>2</sub> to a 250 mL two-neck round-bottom flask equipped with a reflux condenser. After complete dissolution of the starting material, cooling to 0 °C was performed. Then, 5.76

mL (67.16 mmol, 3 equivalents) of oxalyl chloride was slowly added under intense stirring. [7-11, 13-17] The reaction mixture was then maintained at room temperature under constant stirring for 4 h. During the reaction, the HCl vapors produced were effectively trapped in a 15% w/v NaOH solution. (Figure 1)



*Fig.1. Laboratory Setup Illustrating Diacid Chloride Synthesis*

The solvent and excess oxalyl chloride were removed on a rotary evaporator to afford 7.81 g of diacid chloride with purity 99.5. [18-2

### Synthesis of diol diamide monomers

Synthesis of N,N'-bis(2-hydroxyethyl) butanediamide (HEBDA) is representative. The synthesis protocol was then modified to suit the dioldiamide synthesized. All syntheses are described in detail in Supporting Information, S1. In a typical synthesis, 9.784 g of succinic acid, mp 188°C (82.9 mmol) was added along with 100 mL, 1.657 mol, 20 equivalents of ethanolamine to a 250 mL reaction apparatus. [22-29] The mixture was heated to 160°C with constant stirring until the solution clarified in a few minutes. After a reaction period of 5 hours, the process reached completion. The reaction mixture was allowed to cool before being precipitated into 1 L of chloroform. The resulting insoluble product was filtered, thoroughly washed with 500 mL of fresh chloroform, and subsequently dried. The expected product was obtained in a 78.5% yield (13.29 g) with exceptional purity (100%). Structural and purity analyses were conducted using <sup>1</sup>H, <sup>13</sup>C.[31-35] C, HSQC NMR, and HRMS techniques. The product was a white crystalline solid that exhibited thermal stability up to 205°C (which corresponds to a 5% weight loss, T<sub>5%</sub>5%) and melted at 144°C.

### Synthesis of polymerizations from 2,2'-bis(2-oxazoline)

The polymerization of D18:1 with 2,2'-bis(2-oxazoline) was conducted in a cylindrical flask fitted with a mechanical stirrer under a nitrogen atmosphere, maintaining an equimolar ratio between the two monomers. In polycondensation, the insertion of amino alcohol is able to take place in various orientations, as observed from the directional regularity represented by dotted arrows. The reaction medium was subjected to temperatures between 140 °C and 190 °C for 5 to 98 hours, depending on the experimental run.[36-39] The bath salt for heating contained NaNO<sub>3</sub> 7%, NaNO<sub>2</sub> 40%, and KNO<sub>3</sub> 53% by weight. The obtained polymer after the reaction was over and cooled was dissolved in 2 mL NMP and then precipitated in methanol. The precipitated polymer was filtered and dried under vacuum at 30 °C for 24 hours to obtain the final product.

### Polymerizations based on diacid and diol diamide

Typical synthesis of PEA using D18:1 and (Z)-N,N'-bis(2-hydroxyethyl)octadec-9-enediamide [42] (HED18:1DA) is representative. The procedure was further optimized for each diacid, dioldiamide, and catalyst combination used. Experimental methodologies for each case are given in the Supporting Information. In each case, polymerization was carried out in two stages from an equimolar mixture of D18:1 and HED18:1DA using titanium tetra-butoxide (Ti(OBu)<sub>4</sub>) as catalyst.

In a typical procedure, 1.99 g of D18:1 (6.4 mmol) and 2.55 g of HED18:1DA (6.4 mmol) were charged into a two-necked Schlenk reactor. The system was heated up to 160 °C, at which temperature the mixture turned into a clear liquid within a few minutes. Under a nitrogen atmosphere and stirring, a solution of Ti(OBu)<sub>4</sub> in toluene was added at a concentration corresponding to 0.1 mol% with respect to the diacid component.[44] Further on, the polycondensation stage was realized by heating the mixture in a dynamic vacuum and with a temperature of 170 °C over the course of 4 h, affording efficient removal conditions of water byproduct. After postreaction, the product dissolved into 40 mL THF- which was subsequently precipitated onto 1 L methanol- allows one to realize subsequent treatment. The solid filtered then dried, affording a brown product of polymer (yield, 82%) equaled to 3.56 g. The structural characterization of the polymer was made by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy using CDCl<sub>3</sub>. Moreover, size exclusion chromatography, calibrated against polystyrene standards, has determined an M<sub>n</sub> value for the polymer of 12,000 g/mol with Đ of 1.97. Thermal analysis showed T<sub>5%</sub> = 299 °C, T<sub>9</sub> = -31 °C, T<sub>a</sub> = 43.5 °C, and T<sub>m</sub> = 73.5 °C.

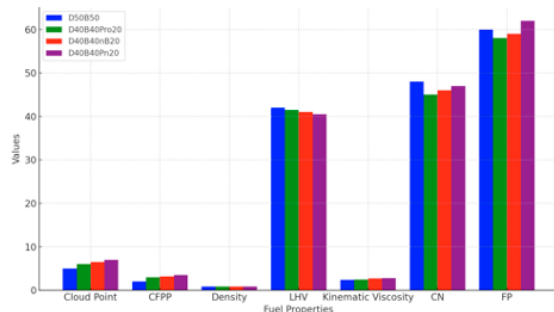
In the present work, a novel family of PEAs synthesized from monomers derived from renewable resources- succinic acid and D18:1- with controlled regioselectivity has been the focus. For the purpose of controlling the insertion of such monomers, diacids were reacted with ethanolamine, affording the corresponding intermediates bearing both dual alcohol and amide functionalities. By contrast, the first step of selectively forming an amide function to give a monomer terminated by alcohol groups has been confirmed in detail by <sup>1</sup>H, <sup>13</sup>C, and HSQC NMR. The subsequent polycondensation of diacid and dioldiamides obtained the polymers with dispersity values under 2, as demonstrated in SEC, which indicates little side reaction.

The corresponding PEA library exhibits superior thermal stability compared to the conventional aliphatic polyesters because of hydrogen bonding in an amid groups pair within the polymer. Most polymers demonstrated high melting points and a narrow temperature range between crystallization and melting—a critical feature for polymer melt processing, suggesting these materials could replace standard engineering polymers with similar thermal properties. Additionally, regioselective control and the incorporation of ester linkages in the polymer backbone enhance its biodegradability, aligning with contemporary goals for sustainable polymer development. This streamlined synthetic approach is also scalable, facilitating broader material production.

### **Comparative analyses of diesel–waste oil biodiesel and propanol, n-butanol or 1-pentanol blends in a diesel engine**

Higher alcohols have recently been regarded as potential alternative fuels for internal combustion engines on the grounds of economic and ecological interests. These alcohols present excellent blendability, hydrophobicity, and higher cetane numbers and calorific values compared to the lower alcohols. In this work, several key fuel properties are investigated and compared for three-phase mixtures of diesel, waste oil methyl ester-biodiesel (B), and higher alcohols-propanol, n-butanol, and 1-pentanol. The formed fuel blends contain 50% Diesel -50% Biodiesel; 40% Diesel-40 % Biodiesel-20%propanol(Pro); 20% n-butanol( nB); and 20% 1-pentanol( Pn) in volumetric proportions.[45-47]

Higher alcohol blending improved the cloud point and cold filter plugging point CFPP while it worsened the set properties of density, LHV, kinematic viscosity, CN and FP of the diesel biodiesel blend. Further, in furtherance to that, various blend effects were further tested for engine performance and exhaust emission at four different engine loads of 1, 3, 6, and 9 kW at constant engine speed of 1800 rpm. Among D40B40Pro20 blends tested under all operating conditions, the results have shown higher BSFCs compared to the ternary blends of D40B40nB20 and D40B40Pn20. EGT values of D40B40Pro20, D40B40nB20, and D40B40Pn20 were higher compared to that of diesel-biodiesel blend.(Figure 2)



**Fig.2. Comparison of fuel properties for different blend**

NO<sub>x</sub> emissions for all higher alcohol blends reduced; 1-pentanol blends showed the best performance while propanol blends gave the least performance. However, CO emissions increased upon the addition of alcohols in the blend. Among the hydrocarbon emissions, the best performance was found with D40B40Pn20 blend, followed by D40B40PnB20.

### **Effect of higher alcohol additive on basic fuel properties**

The addition of higher-order alcohols into fuel blends affects a wide range of fuel properties; of most interest, however, is the small yet identifiable reduction in both the density and viscosity of such higher-order alcohol-based blends. Indeed, this trend of such physical property variations corroborates some previous reports too about the nature of alcohol-based mixtures. That reduces viscosity and can further improve the characteristics of fuel flow, especially fuel atomization and combustion efficiency.

Furthermore, there is great concern about diesel-biodiesel cold flow characteristics with higher alcohol additives. Among various cold flow properties, generally speaking, pour point and cloud point bear major importance while assessing fuel performance in cold temperature conditions. Diesel-biodiesel blends, especially with higher alcohols, may result in better low-temperature flow property enhancements due to viscosity reduction and possible changes in the crystalline structure of the fuel. It may well have improved cold start conditions and increase reliability for the engine during the cold period when most problems are encountered with the fuel.[32,46]

Their role in modifying these properties bodes well for the overall improvement in performance of biodiesel blends, hence a potential pathway for optimization in renewable fuel formulation.

The tests for different parameters of engine performance and emission—which included changes in BSFC, brake thermal efficiency, EGT, HC, CO, and NO<sub>x</sub> with respect to 1, 3, 6, and 9 kW of engine load at a constant speed of 1800 rpm—were conducted for diesel–biodiesel–higher alcohols blends and compared with D50B50. Test results obtained in the current study for diesel-biodiesel–higher alcohols blends were compared with literatures related to the lower alcohol blends and discussed in terms of both engine performance and emission characteristics.

#### **a) CO emission**

After the addition of methanol in waste cooking oil biodiesel, CO emissions increased, while reported that the emission of CO was lower with the methanol blend as compared to karanji biodiesel due to more complete combustion because of a higher oxygen content of the chemical structure of methanol. Besides, it was reported that ternary blends such as biodiesel (20%)–ethanol (10%)–diesel (70%) and biodiesel (20%)–methanol (10%)–diesel (70%) emitted less CO compared to biodiesel–diesel blends.

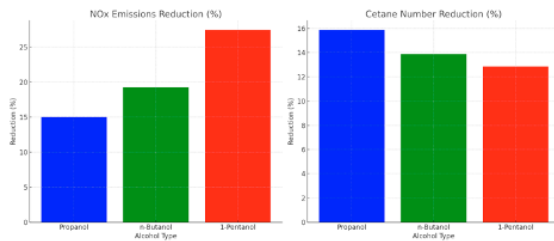
#### **b) emission**

NO<sub>x</sub> emissions are formed due to higher in-cylinder temperatures. With increasing engine load, the in-cylinder temperature also increases, and hence NO<sub>x</sub> with respect to higher engine loads 11.6. NO<sub>x</sub> emissions of

B100 and D50B50 were 1.68% and 9.74% lower than diesel. This is due to the lower cetane number and ignition delay, which cause the hot gases to remain in the combustion chamber less under high temperature, leading to form less NO<sub>x</sub>. Besides, temperature distribution is an important factor toward the formation of in-cylinder NO<sub>x</sub>, as there exist various reports in literature regarding these reasons.

### c) NO<sub>x</sub> emission

Higher alcohols added to diesel-biodiesel blend showed reduced NO<sub>x</sub> emissions for all higher alcohols within the range of 15.05% propanol, 19.27% n-butanol, and 27.44% 1-pentanol. The cetane number of a higher alcohol blend was 15.86, 13.89, and 12.86% lower, respectively, than D50B50. An increase in ignition delay, caused due to lower cetane number in general, affects the quantum of fuel in premixed combustion and an increase in post-combustion temperature for higher NO<sub>x</sub> emissions. However, oxygen amount and latent heat of evaporation of fuel act positively towards NO<sub>x</sub> reduction during combustion.



**Fig.3. Effect of Higher Alcohol Additives on NO<sub>x</sub> Emissions and Cetane Number Reduction in Diesel-Biodiesel Blends**

Results in this work showed that those two factors dominated the reduction of NO<sub>x</sub> caused by the effect of lower cetane number. Results obtained from this work were consistent with those obtained by Intendant et al., for the 10% n-butanol in diesel-biodiesel blend (Figure 3) [42-45].

### Bioeconomy

This article is proposing a framework of anticipatory governance to analyze and prepare for the possible implications that might come with emerging technologies, focusing on the fast-growing area of synthetic biology. Essentially, the core of the assessment dwells on the end-to-end analysis of biosynthetic menthol along several dimensions of production and use. Based on documentary analysis, available data, and interviews, our approach is developed according to a three-step procedure: We first outline the sociotechnical transition in menthol production by comparing present agricultural and chemical modes of production with the emergent biosynthetic methods—the so-called "biological

turn." Second, we examine the logics, promises, and expectations of menthol's bio-transition, focusing on the drivers of change to shed light on which goals and values this innovation aims to and could serve. We finally reflect on the opportunities and challenges of this transition to propose an agenda for responsible innovation and anticipatory governance that may inform governance mechanisms and deepen the understanding of distributed responsibilities among all the actors involved, as well as those that may be impacted by potential consequences.[25-27]

While CE, GE, and BE rest on different assumptions and differ in their strategy of implementation, all three ambition the reconciliation of economic, environmental, and social objectives. Despite their increasingly important role in scientific research and policy-making as strategies toward sustainability, comparative analyses are scant. This research aims at an in-depth investigation of these concepts, studying the diversity both within and between them. The aim is not to imply that these concepts are synonymous but rather to explain how they should be combined. The session sets out synergies and constraints to direct further research and policy-making. Over the past decade, CE, GE, and BE have also received heightened political attention, working their way into various aspects of society, including industries, academia, NGOs, and policy makers. This would suggest that the conceptualization of those models involves a number of actors, making them internally heterogeneous. Besides, different actors may embrace or reject particular concepts of the guideline, depending on whether they facilitate or obstruct certain interests and activities. A much-needed critical research of the potentials and limitations of CE, GE, and BE would be very useful to inform research and policy implementation.[33]

The aim of this part is to 1) explore heterogeneity within and between CE, GE, and BE through analysis of temporal and geographical trends, as well as content analysis of relevant literature, and 2) present the positions of CE, GE, and BE in regard to six sustainability narratives, with an emphasis on environmental and social perspectives. Our part covers nearly two thousand scientific research on CE, GE, and BE through machine learning-based analysis, focusing on English language publications. The results show that these concepts differ geographically: CE research is predominantly concentrated in China, BE is mainly centered in Europe, and GE has a more global presence. While CE focuses on the decoupling of resource use from economic output by industrial processes, BE focuses on biological resource-based innovation and land use practices for rural development. GE, in turn, provides a broad framework for balanced social-environmental development at a global level. We find GE to be the most inclusive concept, covering elements

of both CE and BE. None of them focuses on degrowth, which is a gap in the debate about the limits to growth. Although our research provides a rather static perspective on the CE, GE, and BE concepts and their contributions to sustainability transitions, we are aware that these concepts are multi-dimensional, flexible, and dynamic. Especially for GE and BE, considerable internal diversity can be observed. Nevertheless, paradigmatic clarity issues have not yet been adequately discussed in the literature. In other words, up to now, the conceptual development is not mature, and RRI and CE both carry many meanings for many people. [48]. Graphene, a single-layer carbon material with exceptional mechanical strength, electrical conductivity, and thermal stability, is revolutionizing biomaterials and renewable energy. Its incorporation into biopolymers, such as graphene oxide (GO)-functionalized systems, enhances thermal resistance, crystallinity, and processability, enabling sustainable applications with biodegradable materials. In renewable fuels, graphene's high surface area and functional groups accelerate catalytic reactions, such as biodiesel synthesis, improving efficiency and sustainability. These versatile properties position graphene as a key material in advancing environmentally friendly technologies.

### 3. CONCLUSION

The article connects advanced polymer synthesis with the development of sustainable fuel feedstocks, underlining the focus on renewable materials and energetic solutions. These bio-based polys synthesized in the paper indicate excellent thermal stability and crystallinity, making the breakthrough in sustainable polymer design, while higher alcohol additives present an improvement in the fuel properties and a decrease in NO<sub>x</sub> emissions when combined in diesel-biodiesel fuels, offering promising prospects towards renewable energy optimization. These enhanced properties of the material with added graphene to the polymer matrix create a new perspective on improving both the characteristics of polymers and fuels. Collectively, these highlight synergy in material science to energy sustainability and are now opening completely new avenues to possible novel applications in engineering for the conservation of the environment.

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