

Modification and investigation of waste low-density polyethylene with functional group containing compounds

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Abstract: Composite materials are utilized across a broad range of applications, including automotive, aerospace, shipbuilding, wind turbine blades for wind energy production, oil and gas exploration, and the renewable energy industry. One of the challenges in recycling composite materials, particularly thermoset-based polymer composites, is their inherent heterogeneity. The management of current and future waste necessitates the proper recovery and recycling of products at the end of their life cycle, which would result in resource and energy savings. Various technologies focused on reinforcing fibers have been developed to facilitate the recycling of composite materials. This includes mechanical recycling methods, where polymers are separated from contaminants and can be transformed into granules through melting and extrusion. Mechanical recycling involves operations such as separation, melting filtration, and size reduction. A downside of mechanical recycling is the potential alteration of the product's properties at each stage. Chemically, recycling can be based on the depolymerization of polymers into monomers, which can then be repolymerized to restore the polymer. Considering composite materials as a viable energy source, their energy content can be recovered, though the synthesis process may produce environmentally harmful substances. The high cost of recycling and low quality of the recycled materials are significant barriers for composite material recycling. Identifying well-processed composites and implementing efficient separation methods are crucial for their recycling. New processing technologies will be developed for the recycling of composite materials, leading to more easily recyclable materials in the near future.

Keywords: Polyethylene, Oligomer, Modification, Processing, Composition.

1. INTRODUCTION

Composite materials, composed of two or more components with various physical and chemical properties, have been used since ancient times, such as the natural fibrous straws used in wall construction in Egypt 3000 years ago. Recycling of composite materials in sectors like wind energy, marine, oil, and automotive will reduce environmental impacts. Various processing methods have been proposed for recycling different types of fiber-reinforced composite materials, which has become a subject of scientific interest.

The recycling of high molecular weight compounds, including elastomers and other materials, is not keeping pace with increasing production. The disposal of

polymer waste in landfills or incineration poses serious environmental problems due to their low biodegradability. Researchers have reviewed recycling strategies for waste thermoplastic and thermoset materials, highlighting that recycling can mitigate the problems associated with discarded or incinerated plastic waste. Choosing the correct recycling method can effectively solve the recycling problem without compromising the mechanical properties of the construction material. The importance of initial cleaning of waste polymer materials to ensure compatibility with construction materials has often been overlooked. Research is needed to facilitate the recycling of thermosets and thermoplastics, aiming for resource conservation and sustainability.

2. EXPERIMENTAL DETAILS

Challenges in recycling plastic waste include its disposal in landfills, the poor biodegradability of commonly used polymers, rising costs, and legislative pressures. Additionally, incinerating plastic waste creates ecological problems. Mechanical and chemical recycling are among the most effective methods for managing plastic waste. Polyolefins, widely used thermoplastics globally, primarily include polyethylene (LDPE, HDPE) and polypropylene (PP). Approximately 22 million tons of these polymers are produced and consumed annually in Western Europe, accounting for over half of the processed thermoplastics. This study investigates the recycling of LDPE, HDPE, and PP using dissolution/precipitation and pyrolysis methods. Dissolution/precipitation is part of mechanical recycling, while pyrolysis belongs to chemical recycling. The process involves separating and recycling polymers in a solvent environment, using various solvents and waste plastics under different weight percentages and temperatures. Most samples showed a recovery rate of over 90%. Additionally, the pyrolysis of LDPE, HDPE, and PP was conducted with or without an acid catalyst, analyzing the resulting gases and oils. It was determined that pyrolysis products, comprising a range of alkanes and alkenes, could serve as raw materials for producing new plastics or purified fuels in the petrochemical industry.

The import of materials with high usage rates, particularly in the iron-steel and plastic industries, leads to significant waste production during manufacturing and consumption. The most challenging wastes include the dust from the furnaces of the iron and steel industry. The increasing use of plastic materials, which do not decompose quickly once their service life ends, allows them to persist in the environment as waste for extended periods. The majority of the world's plastic materials are made from low-density polyethylene (LDPE), and their recycling can reduce environmental problems and contribute to the national economy. Studies have shown that LDPE and high furnace dust can be combined through extrusion to produce composite granules. These granules, once molded, have their mechanical, physical, and chemical properties studied and have been found suitable for use as flooring materials in the construction industry.

The consumption of thermoplastics like polyethylene and polypropylene is on the rise, causing difficulties in managing solid household waste. Plastic waste is considered a serious pollutant for water systems and the lithosphere. Mechanical recycling is a viable alternative to reduce the volume of plastic waste.

Research has shown that assessing the post-industrial waste recycling process through thermomechanical and thermochemical treatments is possible. Experiments with up to 30% PP in LDPE waste and polypropylene (PP) blends have been conducted under controlled temperature and nitrogen flow, incorporating zeolite and Ziegler-Natta catalysts. Results indicate that the zeolite catalyst, during the thermomechanical processing phase, acts as a modifier of the polymer structure, leading to significant changes in the properties of the LDPE/PP blends depending on the experimental conditions. The catalytic purification of polymer wastes offers a potential method for recycling polymer materials with high contamination and improves the properties of the recycled materials.

Reducing the consumption of single-use plastic bags, identifying the best recycling methods, and managing roadside waste collection are important tasks. In terms of waste management costs and energy usage, two key aspects are the production and recycling of polyethylene (PE) waste. Studies suggest that implementing best practices can achieve economical and environmental benefits, with potential reductions in unrecycled PE waste by approximately 4.4 million tons. This reduction could decrease CO₂-equivalent emissions by about 1.46 million tons and increase net energy demand by 16.5 million due to the energy produced from waste.

Among polyolefins, polyethylene and polypropylene are the most used and are difficult to degrade, accumulating in the environment and causing ecological problems. Various bacterial and fungal organisms are utilized to facilitate their biological degradation. Polyethylene, being the most commonly used polymer, has packaging materials with a short lifespan. One of the main methods of recycling PE is the production of plastic bottles that can be used up to 50 times. LDPE is applied to these bottles under specific conditions, and the bottles should be recyclable. The essential properties of the recycled bottles have been determined through testing.

Packaging materials used for product packaging are mainly made from low-density polyethylene (LDPE). Recycling LDPE-based plastic materials poses challenges as they are not easily decomposable and can harm the environment. The most effective approach for safely recycling plastic waste is converting it into simpler compounds. Biodegradation is the most common method used for this purpose, being cost-effective and efficiently conducted in specific aqueous environments. Studies on the biodegradation of LDPE have used various combinations of LDPE and starch, observing that degradation increases with higher starch content over 150 days.

Research in biotechnology primarily focuses on exploring the catabolic repertoire of natural bacteria for the biodegradation of plastic waste. LDPE is difficult to degrade and poses serious environmental risks. The biodegradation potential of LDPE using enriched aerobic bacteria from municipal waste has been studied, along with challenges like the high molecular weight preventing microbial cell penetration, chemical stability, the absence of functional groups for microbial enzymes, and crystallinity. Plastic waste, especially accumulating on roads, streets, and in water, is used in various industries like automotive, medical, and oil, posing environmental and aesthetic concerns. Studies have examined the activity of microbes and organisms in using the substrate as an energy source, indicating that low-density polyethylene can be used as a sole carbon source, confirming their ability to degrade polymers. Using various methods, waste polyethylene has been modified with bitumen, a complex mixture of hydrocarbons and elements like oxygen, nitrogen, and sulfur. Bitumen can exist in semi-liquid, semi-solid, and solid forms. Waste polyethylene, sourced from commercial packaging bags, has been found to enhance the high-temperature stability of modified bitumen. Modified bitumens with waste polyethylene were prepared using different processing parameters and a high-speed cutting mixer. The thermal stability of the modified bitumen was analyzed using differential scanning calorimetry and thermogravimetric analysis, revealing that the modified bitumen exhibits better heat resistance than the base bitumen, independent of the preparation parameters.

Bitumen is a fundamental component of asphalt binders, used to combine gravel, sand, and mineral powder in monolithic forms, with its adhesiveness and ability to become liquid when heated and solid when cooled, also demonstrating thermoplastic properties. Lower strength properties make bitumen sensitive to transportation loads and climatic factors, softening at high temperatures and cracking at low temperatures. Modifying bitumen with polymers like elastomers and latex improves its properties and the durability of asphalt concrete, increasing adhesion strength, heat resistance, and enhancing low-temperature characteristics.

The high cost of polymer modifiers limits their use

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shown that recycled polyethylene from agricultural films and packaging materials meets these requirements. The effect of electrical discharge on the copolymerization process of linear low-density polyethylene has been analyzed, showing changes in the physical and mechanical properties due to the

energetic atoms, molecules, and ions produced, affecting chemical reactions.

Surface modification of polyethylene, assessed using various nitrogen-containing plasmas, introduces nitrogen functional groups, affecting surface tension. Plasma treatment, using N₂ and Ar + NH₃ mixtures, analyzed by X-ray photoelectron spectroscopy, enriched surface oxygen content, with Ar + NH₃ plasma found to be effective for nitrogen and amine functionalization.

3. CONCLUSION

Studies have indicated that composites of recycled thermoplastics with natural fibers offer an appealing alternative, conserving natural resources, reducing waste, and providing economical materials. The interfacial adhesion between low-density polyethylene (LDPE) and aluminum (Al) foil is weak, posing challenges in multilayer packaging design. Various methods have been proposed to improve LDPE's adhesive properties, with comparative studies showing enhanced adhesion in LDPE-modified samples, particularly when using small concentrations of sulfur-containing compounds, improving the bonding strength for multilayer lamination applications.

Ziegler-Natta catalysts have enhanced the mechanical and conductivity properties of cross-linked low-density polyethylene (XLDPE), highlighting the superior activity of metallocene-based catalysts and the high performance of XLDPE produced directly by late transition metals. The use of these catalysts has improved resistance, flexibility, transparency, and productivity. XLDPE products are increasingly used in electrical, medical, and surgical fields and have the potential for industrial-scale application.

The properties of polyethylene produced at the Shurtan gas chemical complex were studied, and its suitability for use in road bitumen was assessed. The impact of the heavy fraction components of furnace oil on the properties of the diesel fraction was determined, and the technology for separating low-density polyethylene from local waste was developed.

The addition of various polymers to bitumen, a common practice, reduces its temperature sensitivity. Recycled materials are increasingly reused in road construction to improve overall performance and durability. Local governments and road agencies are

implementing waste management initiatives.

Post-consumer low-density polyethylene (LDPE) has been used to address significant environmental problems and improve bitumen's performance characteristics. The study created modified bitumen by adding different percentages of LDPE (1%, 2%, 3%,

and 4%), and tests on penetration, softening point, and ductility were conducted at two different temperatures (135°C and 165°C). LDPE additions improved the softening point and ductility compared to pure binder, with one LDPE type outperforming another in enhancing bitumen properties.

Worldwide, plastic waste constitutes a significant part of solid waste, impacting the environment and public health. Research has explored the use of recycled high-impact polystyrene (HIPS) and LDPE in producing durable lightweight concrete for cement-based composites. The inclusion of recycled plastic granules reduced workability, density, and compressive strength, demonstrating feasibility for concrete production up to 10% plastic content.

The disposal of plastic waste, given its low biodegradability and large volume, poses a major problem. Research mixing high-density polyethylene waste with Portland cement explored the production of plastic cement, assessing the impact of replacing various percentages of sand with polyethylene waste. Recycled LDPE and waste rubber have been used to modify asphalt binder, with rheological properties measured using dynamic shear rheometry and binder beam rheometry. Mixing LDPE and waste rubber in asphalt resulted in decreased phase angle, increased ductility, and higher softening point.

Finally, recycled LDPE from agricultural films and packaging materials is used in creating asphalt surfacing, showing the practical reuse of plastic waste in construction and road building.

REFERENCES:

- 1.Y.Yang, R.Boom, B.Irion, D.Jan van Heerden, P.Kuiper, H. de Wit, Recycling of composite materials, Chemical Engineering and Processing: Process Intensification, №51, pp.53-68, 2012.
- 2.A.E. Krauklis, Christian W. Karl, Abedin I. Gagan, Jens K. Jorgensen, Composite Material Recycling Technology—State-of-the-Art and Sustainable Development for the 2020s Journal of Composites Science, №5, pp.1-33, 2021.
- 3.M.Kazemi, Sk Faisal Kabir, Elham H. Fini, "State of the art in recycling waste thermoplastics and thermosets and their applications in construction"

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- 4.Bryan D.Vogt, Kristoffer K.Stokes, Sanat K.Kumar, Why is Recycling of Postconsumer Plastics so Challenging?, Applied Polymer Materials, №3, pp.4288-4745, 2021.

5. N.Singh, D.Hui, R. Singh, I.P.S. Ahuja, L. Feo, F. Fraternali, Recycling of plastic solid waste: A state of art review and future applications, Composites Part B: Engineering, №115, pp. 409-422, 2017.

- 6.D.S.Achilias, E.Antonakou, C.Roupakias, P.Megalokononimos, A. Lappas, "Recycling techniques of polyolefins from plastic wastes", Global Nest Journal, vol.10, №1, pp.14-122, 2008.

- 7.M.T.Kayıtlı, G.Çelebi, A.Güldaş, Sustainable building material target with the recovery of iron steel and plastic industry wastes, Çukurova University Engineering and Architecture Faculty Journal, №33(2), pp.33-44, 2018.

- 8.R.Veloso de Camargo, C.Saron, Mechanical-chemical recycling of low-density polyethylene waste with polypropylene, Journal of Polymers and the Environment, №28, pp.794-802, 2019.

- 9.V.Andreoni, Hans GM Saveyn, P.Eder, Polyethylene recycling: Waste policy scenario analysis for the EU-27, Journal of Environmental Management, №158, pp.103-110, 2018.

- 10.J.Arutchelvi, M.Sudhakar, A.Arkatar, M.Doble, S.Bhaduri, P.V.Uppara, Biodegradation of polyethylene and polypropylene, Indian Journal of Biotechnology, №7, pp.9-22, 2008.

- 11.L.Markovicova, V.Zatkalikova, T.Kojnokova, D. Gana, T. Liptakova, The physical-mechanical properties of low-density polyethylene films, IOP Conference Series: Materials Science and Engineering, pp.1-5, 2020.

- 12.K.S.Veethahavya, B.S.Rajath, S.Noobia, B.Manraj Kumar, Biodegradation of Low-Density Polyethylene in Aqueous Media, Procedia Environmental Sciences, №35, pp.709-713, 2016.

- 13.A.Sundar De, H.Bose, B.Mohapatra, P.Sar, Biodegradation of Unpretreated Low-Density Polyethylene (LDPE) by Stenotrophomonas sp. and Achromobacter sp., Isolated From Waste Dumpsite and Drilling Fluid, Frontiers in Microbiology, №11, pp.1-15, 2020.

- 14.F.E.Uwakwe, T.N.Ezejiolor, T.E.Ogubulie, E.A.Anyalogbu, S.A.Okafor, Investigation of biodegradation of low-density polyethylene by Proteus and Serratia spp, Engineering and Technology Journal, №8, pp.2052-2055, 2023.

- 15.S.Ghatge, Y.Yang, Jae-Hyung Ahn, Hor-Gil Hur, Biodegradation of polyethylene: a brief review, Journal of Environmental Science and Technology, 2020.

- product distribution and process mechanism analysis, Chemical Engineering Journal, №385, pp.1-11, 2020.

- 17.U.M.Memmedli, F.E.Amirov, X.V.Allahverdiyeva, I.H.Movlayev, N.T.Gahramanov, Modified polyolefins, Scientific Journals, №2, pp.65-70, 2019.

- 18.A.Graziano, S.Jaffer, M.Sain, Review on modification strategies of polyethylene/polypropylene immiscible thermoplastic polymer blends for enhancing their mechanical behavior, *Journal of Elastomers and Plastics*, №4, pp.1-46, 2018.
- 19.G.T.Nuraliev, P.J.Tojiev, H.H.Turaev, A.T.Djalilov, Modification of polyethylene with nitrogen-, phosphorus-, and metal-containing oligomers, *Universom Chemistry and Biology*, №10, pp.68-71, 2022.
- 20.K.Shixaliyev, Methods of modification of used polyolefins, *Indian Journal of Advanced Chemistry*, №2, pp. 14-18, 2021.
- 21.Felipe W.Fabris, Fernanda C.Stedile, Raquel S.Mauler, Sonia M.B.Nachtigall, Free radical modification of LDPE with vinyltriethoxysilane, *European Polymer Journal*, №40, pp.1119-1126, 2004.
- 22.M.Iqbal, Ch.Chuai, Y.Huang, Ch.Che, Modification of low-density polyethylene by Graft Copolymerization with Maleic Anhydride and Blends with Polyamide 6, *Applied Polymer Science*, 2010, No. 3, pp. 1558-1565,2010.
- 23.J.Mosnacek, M.Bertoldo, C.Kosa, C.Cappelli, G.Ruggeri, I.Lukac, F.Ciardelli, Modification and photostabilization of low-density polyethylene film by photodecomposition of various diazo-compounds and methyl azidocarboxylate, *Polymer Degradation and Stability*, №92, pp.849-858, 2007.
- 24.U.M.Ahmedova, Modification of used low-density polyethylene, *Azerbaijan Chemical Journal*, №4, pp.140-142, 2011.
- 25.C.Fang, P.Liu, R.Yu, X.Liu, Preparation process to affect stability in waste polyethylene-modified bitumen, *Construction and Building Materials*, №54, pp.320-325, 2014.
- 26.S.Kishchynskiy, V.Nagaychuk, A.Bezuglyi, Improving Quality and Durability of Bitumen and Asphalt Concrete by modification Using recycled polyethylene-based polymer composition, *Procedia Engineering*, №143, pp.119-127, 2016.
- 27.E.Ahmedov, N.Mammadov, S.Rzayeva, The mechanism of electric discharge effect on the modification process of linear low-density polyethylene, *Academic Journal*, №6, pp.208-211, 2023.
- 28.C.Lopez-Santos, F.Yubero, J.Cotrino, A.R.Gonzalez-Elipse, Nitrogen plasma functionalization of low-density polyethylene, *Surface and Coatings Technology*, №205, pp.3356-3364, 2011.
- 29.M.R.Kazimi, T.Shah, S.S.Binti Jamari, I.Ahmed, C.K.M. Faizal, Sulfonation of low-density polyethylene and its impact on polymer properties, *Polymer Engineering and Science*, №11, pp.2522-2530, 2014.
- 30.J.M.Goddard, J.H.Hotchkiss, Tailored functionalization of low-density polyethylene surfaces, *Journal of Applied Polymer Science*, №5, pp.2940-2948, 2008.
- 31.P.A.Dilara, D.Briassoulis, Degradation and stabilization of low-density polyethylene films used as greenhouse covering materials, *Agricultural Engineering Research*, №4, pp.309-321, 2000.
- 32.D.D.Pinzon Moreno, C.Saron, Low-density polyethylene waste/recycled wood composites, *Composite Structures*, №176, pp. 1152-1157, 2017.
- 33.M.Nassr, I.Krupa, M.Ouederni, S.K.Krishnamoorthy, A.Popelka, An adhesion improvement of low-density polyethylene to aluminum through modification with functionalized polymers, *Polymer Metal-Hybrid Materials*, №15, pp.1-14, 2023.
- 34.M.An, B.Cui, X.Duan, Preparation and applications of linear low-density polyethylene, *Journal of Physics Conference Series*, №2229, pp.1-9, 2022.
- 35.P.V.Shchodrodsko, Features of polyethylene products processing, *Science Bulletin*, №5, pp.327-332, 2022.
- 36.S.Nizamuddin, M.Jamal, R.Gravina, F.Giustozzi, Recycled plastic as bitumen modifier: The role of recycled linear low-density polyethylene in the modification of physical, chemical, and rheological properties of bitumen, *Journal of Cleaner Production*, №266, pp.1-12, 2020.
- 37.I.Bektas, E.Yalçın, O.E.Yamac, M.Yılmaz, Use of two different low-density polyethylene plastic wastes in bitumen modification, *Firat University Journal of Languages*, №33, pp.339-346, 2021.
- 38.O.Olifinnade, S.Chandra, P.Chakraborty, Recycling of high impact polystyrene and low-density polyethylene plastic wastes in lightweight concrete for sustainable construction, *Materials Today Proceedings*, №5, pp.2151-2156, 2021.
- 39.Ahmad K.Jassim, Recycling of polyethylene waste to produce plastic cement, *Procedia Manufacturing*, №8, pp.635-642, 2017.
- 40.K.Yan, H.Xu, L.You, Rheological properties of asphalts modified by waste tire rubber and reclaimed low-density polyethylene, *Construction and Building Materials*, №83, pp.143-149, 2020.
- 41.T.M.Naibova, T.T.Şirinov, G.S.Akberova, P.M.Hasanlı, Modified epoxy-dian and phenol-formaldehyde sooligomer based composite with acrylamide, *European Journal Covering Top Themes and Problems in Various Fields of Science*, №31, pp.33-37, 2022.
- 42.T.M.Naibova, T.T.Şirinov, Modified high-density polyethylene based composite, *Journal of Science, Lyon*, №30, pp.9-13, 2022.