GREEN CHEMISTRY IN REPLACEMENT OF CONVENTIONAL POLYMERS

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Abstract: Given the difficult problems facing traditional petroleum-based polymers, a replacement that is sustainable, biodegradable, comparable, and economical is desired. There is mounting evidence and considerable research in favor of adopting polyhydroxyalkanoates, PHAs, as the biopolymer of choice. Recent advances in this technology support the argument in favor of a transition away from conventional plastics. Taken together, the sustainable production, biodegradability, compatibility, and non-toxicity of PHAs makes for a compelling case toward their adoption. In the near future, improvements in economic competitiveness will further enhance the long-term relevance of PHAs.

Index Terms- Conventional Polymers, Green Chemistry, PHA, Biopolymers

I. INTRODUCTION

Plastics and polymers are everywhere on the earth today. From simple bottles to biologic stents, universally we find applications of these materials. These synthetic compounds are preferred because they can be structurally customized to have assorted physical properties (Madison, L.L. and Huisman, G.W., 1999). Unfortunately, most of these materials are synthesized from contaminating petroleum sources such as polyethylene and polypropylene reveal insignificant biodegradation when they achieve their end. Plastics production exceeds 75 billion pounds every year, of which no less than 40% ends up in landfills, causing an imperative accumulation of waste globally (Reddy, C.S.K. et al., 2003). Regardless of whether much exertion is put resources into recycling those materials, the challenges of categorization the used material and structural weakening limits its feasibility while there is considerable research in the field of remediation, significant exertion is important to restrict the negative outcomes of these petroleum-based polymers (Johnstone, B., 1990). The principles of green chemistry can be applied to this venture, and a standout amongst the most advantaged solutions is the advancement of polymers. These should be made from inexhaustible resources and biodegrade in surrounding conditions while maintaining the most yearning characteristics of conventional polymers, such as Polyhydroxyalkanoates (PHAs) (Keshavarz, T. and Roy, I., 2010). These biopolymers have diverse and easily variable physical properties that enable them to contend with synthetic plastics (Akaraonye, E. et al., 2010). The most popular is poly (3-hydroxybutyrate), or PHB discovered by Maurice Lemoigne, was itself a first member of a class of PHAs called short chain length PHAs (or scl-PHAs), which contain up to five carbon atoms per unit monomer (Keshavarz, T. and Roy, I., 2010). Larger examples are called medium chain length PHAs (or mcl-PHAs), and contain up to fourteen carbon atoms (Keshavarz, T. and Roy, I., 2010).
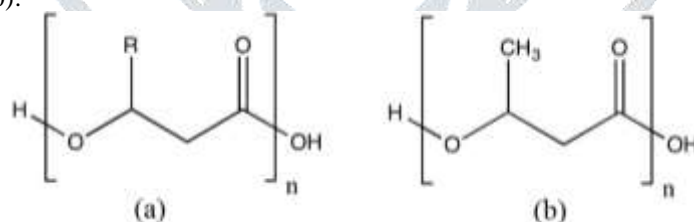

Figure: Structure of polyhydroxyalkanoates: (a) General structure of PHAs, (b) Structure of PHB

Despite their size, PHAs are synthesized by self-sufficient organisms, among which are over 300 types of microscopic organisms (Keshavarz, T. and Roy, I., 2010). They are made by means of biosynthetic pathways involving a chain of enzymatic reactions; however, the pathway varies for each producer and polymer (Huisman, G.W. et al., 1989). For instance, PHB is synthesized in following three steps (Huisman, G.W. et al., 1989)-

   (i)   Condensation of acetyl co-enzyme A (acetyl-CoA) molecules

   (ii) Reduction of acetyl-CoA, and (iii) Polymerization.

In another route, PHAs can be synthesized by metabolism of fatty acids (Steinbuchel, A. and Lutke-Eversloh, T., 2003). All of these naturally occurring syntheses involve aqueous processing conditions and generate only nontoxic wastes (Akaraonye, E. et al., 2010). When this procedure is meant to commercial scale, PHA production requires just two stages (Tsuge, T., 2002).

In recent years, PHAs have turned into the subject of extensive exploration and improvement. Clear favorable circumstances have been explained, among which are ways to sustainable sourcing and generation, apparent biodegradability and non-toxicity, likely physical properties, and financial viability. Given these astral properties, there is incredible motivation to move to these biopolymers in the future prospect. Consumers and industry alike ought to in this manner intently look at such a progress.

II. SUSTAINABLE RESOURCE AND PRODUCTION

The sketch of better and greener polymers, such as PHAs, begins at the support. Similarly as with other innovation, it is of great meaning to elude the consequence of shifting ecological problems somewhere else in the life cycle (Coats, E.R. et al.., 2007). To resolve the plastics issue, this plan must be of main concern. Subsequently, the best solution fabricates no material waste that nature can't deal with (Reddy, C.S.K. et al., 2003). PHAs satisfy this standard. They are produced from a variety of inexhaustible sources, for example, sucrose, starch, and even carbon dioxide (Reddy, C.S.K. et al., 2003). Moreover, it is feasible to produce PHA by exploiting antecedents found in existing waste streams. This moderates the effect of the waste. Dairy byproducts (Singh, P.K. et al., 2015), raw sewage (Coats, E.R. et al.., 2007), fermented paper mill wastewater (Jiang, Y. et al., 2012), and even discarded fruit (Suwannasing,W. et al., 2015) are among some of these sources. By utilizing these innovative sources, it is conceivable to sustainably source the materials expected to synthesize PHAs.

Sustainability concerns don't end at the sourcing of feedstocks. The production procedure itself should likewise endeavor to maintain the standards of green chemistry. Some present commercial PHA production techniques show higher non-renewable energy source involvements and carbon emanations than traditional plastics manufacturing. This is due to poor selections of feedstock (Coats, E.R. et al.., 2007). The use of exhaustible feedstock represents up to 33% of the total energy requirements of PHA production, and the use of incompetent bioreactors can include at least 30% on top of that proportion (Coats, E.R. et al.., 2007). By using inventive and inexpensive antecedent sources, for example, the ones previously mentioned, the feedstock cost can be considerably reduced (Kalia, V. C. et al., 2000).

As research advances, the objective of an altogether sustainable manufacturing process ends up conceivable. This is believed on the grounds that PHAs are synthesized as a store of energy and nutrients (Keshavarz, T. and Roy, I., 2010). Actually ordinary efforts of bacteria, for example, *A. eutrophus*, *A. latus*, or recombinant *E. coli* synthesize most varieties of PHAs (14). These bacteria naturally produce PHAs when exposed to an atmosphere plentiful in carbon, however restricted in another nutrient, for example, nitrogen or phosphorous (Keshavarz, T. and Roy, I., 2010). The competence to biologically synthesize PHAs isn't constrained to bacteria. Numerous other organisms can be genetically altered to produce polymers. Provided that a PHA synthase gene is transferred, a synthase protein is enacted, and substrates can be dependably given, many organisms can produce PHAs (Stubbe, J. et al., 2005). Since the genes required for PHA production are simply separated, plants might be tailored to produce huge amounts of these polymers (Nawrath, C. et al., 1994). This procedure is especially proficient with oil-producing plants (Reddy, C.S.K. et al., 2003). The concluding step of PHA manufacturing is seclusion and extraction of the polymer. Conventionally, this step utilizes organic solvents such as toluene and chloroform. These chemicals are toxic and harmful to the environment. Providentially, current developments have found out the reasonability of supplanting these solvents with milder ammonium hydroxide (NH_4OH) and sodium hydroxide ($NaOH$) solutions at 0.2 M concentrations (Choi, J. and Lee, S. Y., 1999). This substitution yields just a slightly impure product, not beneath 94 % purity (Choi, J. and Lee, S. Y., 1999). Reorganization of the whole procedure implies that PHA production will shortly be a sustainable and eco-friendly process.

III. BIODEGRADABILITY AND NON-TOXICITY

PHAs are highly biodegradable under encompassing conditions. The degradation process just reflects the natural object of PHA as a resource of nutrients for microorganisms. These organisms split the polymer to originate energy (Jendrossek, D. and Handrick, R. 2002). Studies reveal that these polymers entirely degrade in aerobic conditions after short timeframes (Volova, T. G. et al., 2006). Whereas, other biopolymers such as poly (lactic acid) has significant difficulty degrading outside controlled conditions (Nampoothiri, K. M. et al., 2010). This timescale is remarkable even compared to those of other biopolymers such as poly (lactic acid), which has significant difficulty degrading outside controlled conditions (Nampoothiri, K. M. et al., 2010). When disposed in aquatic conditions with ambient water temperatures below six degrees, PHAs degrade completely in time period of nine months (Johnstone, B., 1990). In freshwater lakes, the level of degradation achieves 100% within two months (Salim, Y. L. et al., 2012). In general, total biodegradability has been found under different conditions, a significant achievement for such useful materials (Choi, J. and Lee, S. Y., 1999).

The products the procedure yields are also important as the speed of biodegradation. Water and carbon dioxide are the only products under aerobic conditions (Akaraonye, E. et al., 2010). Under anaerobic conditions, the products are carbon dioxide (CO_2) and methane (CH_4) gas (Reddy, C.S.K. et al., 2003). None of these products are exceptionally hazardous, and all can be reused in various industrial and practical applications. When PHB is degraded, the main product is naturally occurring 3-hydroxybutyric acid, which is a harmless constituent of blood plasma (Akaraonye, E. et al., 2010). In this manner, PHB is especially appropriate to medicinal use. The inferences of these characteristics are noteworthy. With PHAs, it is feasible to practically visualize a world where carelessly littered bottles and bags can safely vanish into the ground, and where plastic rings never again cause a threat to marine ecology.

IV. COMPATIBILITY AND COMPETITIVENESS

Apart from their low environmental effect, PHAs are having almost same function as traditional petroleum-based polymers. Bacterial PHAs have adequate molecular mass to have polymer features like polypropylene and others (Madison, L.L. and Huisman, G.W., 1999). In view of the fact that many bacterial strains produce polymers of varying structures; PHAs can mostly match the range of synthetic polymers. Also, PHA reveals varied physical properties with alterations to the length of the chain and the occurrence of functional groups (Akaraonye, E. et al., 2010).

Therefore, for roughly all physical properties that differentiate synthetic polymers, there is a equivalent analogue in the PHA family. For instance, scl-PHAs are crystalline, brittle, and hardened with high melting points and low glass transition temperatures (Akaraonye, E. et al., 2010). PHB melts at 180 °C and breaks with less than 10% prolongation. Due to these

properties these are excellent choices for packaging applications (El-Hadi, A. et al., 2002). Conversely, mcl-PHAs are thermoplastic and having low melting points (Akaraonye, E. et al., 2010). They are competent for stretching long distances without breaking, which make them appropriate for making films and adhesives (Akaraonye, E. et al., 2010). Moreover, generally all PHAs have a high degree of polymerization, are insoluble in water, and are UV-resistant (Reddy, C.S.K. et al., 2003).

Also, PLAs are not preferable compared to PHAs in some aspects. PLAs lack structure variability and material properties PHAs possess, hence restricting their practical use (Keshavarz, T. and Roy, I., 2010). For example, most PLAs have softening points of around 60ºC, a temperature sufficiently low to cause their distortion under sunlight or while holding a hot beverage (Nampoothiri, K. M. et al., 2010). With immense diversity, varied PHAs can replace many traditional polymers for a wide range of uses (Akaraonye, E. et al., 2010).

V. MONEY MATTERS AND YIELD

Regardless of the advantages, the principal concern of adopting any new innovation or product is cost, and biopolymers are no exception. Providentially, the contest of PHAs with traditional petroleum-based polymers extends to cost. While earlier techniques produced PHAs at costs more than those of conventional plastics, recent developments and rational designs reduce the cost to significant levels (Akaraonye, E. et al., 2010). To accomplish this objective, following essential routes are important. To start with, advances to the production procedure improve the quality, quantity, and value of PHAs. Furthermore, the valorization of existing waste streams brings forth chances to produce PHAs at minimum cost, accordingly bringing down the cost.

For instance, upgrades in the productivity of PHA synthetic processes reduce the cost by escalating the yield. Earlier, bacterial PHA production was quite incompetent with yields below 25%. In recent times however, procedures using modest recombinant *E. coli* specimens have brought about yields more than 75%, and this is projected to rise (Choi, J. and Lee, S. Y., 1999). In the recombination process, a gene that encodes for a degradation enzyme can be inactivated, bringing about an increased yield (Miyake, M. et al., 2000). Furthermore, immediate cost reductions can be achieved by reducing the cost of feedstock, since that factor alone comprises half of the total cost (Kim, B. S. et al., 1992). Expenses can also be reduced at the recovery stage, where an extensive extent of aggregate cost starts (Li, R. et al., 2007). Undoubtedly, these innovative ways to deal with PHA production significantly reduce its cost.

Transforming waste streams into PHA production pathways can bring about a cost reduction around 50% and free from major capital investment (Kim, B. S. et al., 1992). The processes make use of fermented paper mill wastewater put up PHA yields up to 77% (Jiang, Y. et al., 2012). In like manner, municipal sewage has produced PHA approximate 25% by weight (Coats, E.R. et al.., 2007). In both cases, no investment was required outside the repurposing of existing amenities. Developments like these are basic to extending the scope of PHA. In fact, even with existing technologies, PHA is within reach of most manufactures. These dynamic changes have effectively affected the financial matters of PHA, and their cost has consistently declined. PHAs have superior physical properties, making them the best preference for companies looking for a sustainable polymer.

However, the cost is still declining. Here, the concentration shifts to green engineering, wherein the design of procedure becomes significant. PHA synthase enzymes at steady concentrations to appropriate substrates can bring about major economic upgrades (Stubbe, J. et al., 2005). Furthermore, as production increases, the fixed costs of machinery and overhead considerably decrease (Choi, J. and Lee, S. Y., 1999). As result, PHAs become viable with traditional polymers, and will probably have a large influence on their acceptance.

VI. CONCLUSION

Green chemistry is dedicated to improve the eco-system and to nurture sustainable development. It looks to give answers for the issues conventional chemistry confront. A standout amongst the most difficult issues confronting the present reality is that of polymer utilize and development. Since, PHAs have exposed, innovative development in Chemistry can have expansive impacts toward explaining this dilemma. Chemistry has made embracing these biopolymers a standout amongst the most determinedly sustainable preferences ordinary consumers can make. It is up to firms to enthusiastically commence the changeover from contaminating petrochemical polymers and welcome a new invention of sustainable, biodegradable, viable, and prudent ones. PHAs are fabricating the world more sustainable and less harmful. The monetary barrier to their adoption is being conquered, and consumers and industries alike are observing. Everyone can gain from this genuine example of green chemistry.

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