Research & Trends in Castor Oil-based Biopolymers

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Introduction

Environmental concerns and soaring oil prices create renewed interest in bioplastics.

While, in the past, plastics from alternate sources were significantly more expensive as well as less efficient than those derived using petroleum technology, higher oil prices have rendered these alternatives cheaper in comparison. Moreover, mounting environmental concerns and legislative incentives, particularly in the European Union (EU), are stimulating keen interest in the adoption of biodegradable plastics. This is in turn spurring research to improve bioplastic technology, and developments in plant breeding and processing are expected to further narrow the cost differential between bioplastics and synthetic ones.

Bioplastics fast market growth of more than 8-10% per year. Bioplastics cover approximately 10-15% of the total plastics market and will increase its market share to 25-30% by 2020. The market itself is huge, it reached over 1bn US$ in 2007 and will be over 10 billion by 2020. More and more companies are entering and investing in this market. New applications and innovations in the Automotive and Electronics Industry lead to market boom. Over 500 bioplastics processing companies are already available, more than 5000 is expected by 2020.

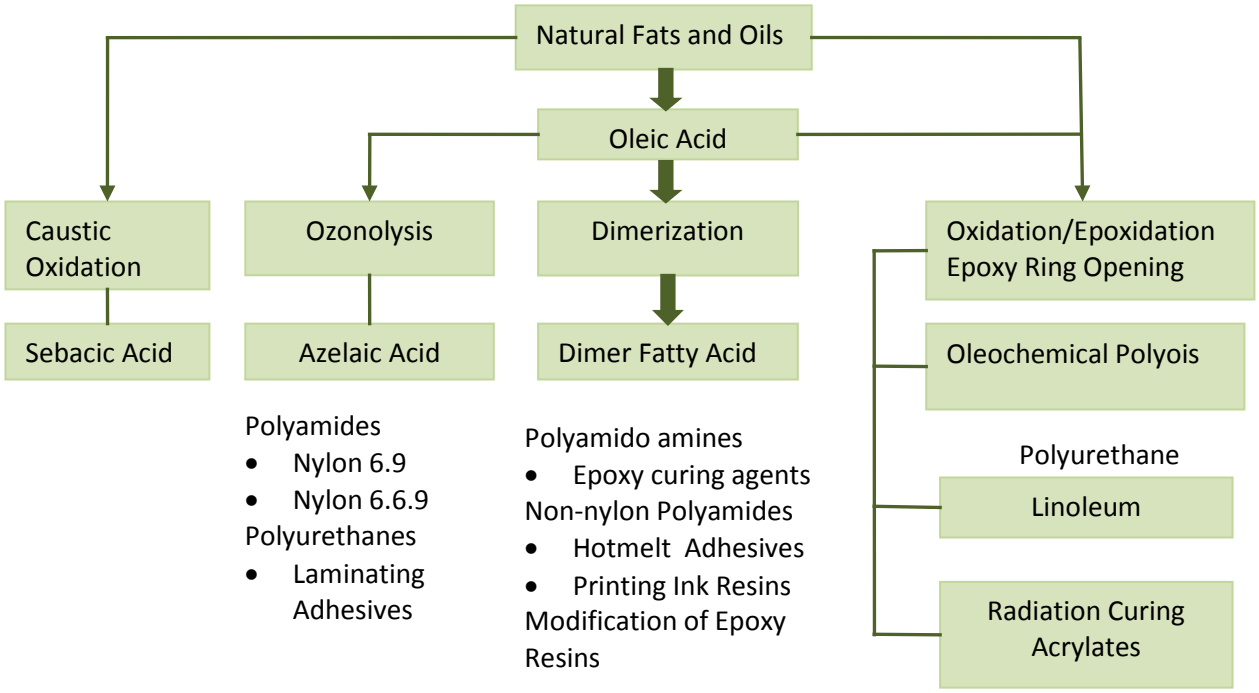
Biopolymers have taken a place of large potential source of feedstock for biodegradable plastics because of their plentiful presence, variety of their chemical structure, the biodegradability and their non toxicity. One or more biopolymers combine to form Bioplastics.

In this white paper, we have provided industry insights on biopolymers from castor oil. We have summarized industry's performance and research trends in the last 5 years.

Biopolymers and Castor Oil

The use of oleochemicals in polymers has a long tradition. One can differentiate between the use as polymer materials, such as linseed oil and soybean oil as drying oils, polymer additives, such as epoxidized soybean oil as plasticizer, and building blocks for polymer, such as dicarboxylic acids for polyesters or polyamides. Considering the large market for polymers, the share of oleochemically based products is relatively small - or, in other terms - the potential for these products is very high.

Building Blocks for Polymers-based on Natural Oils



Karlheinz Hill, Pure Appl. Chem., Vol. 72, No. 7, pp. 1255–1264, 2000

Development of new bio-materials and applications continues at a strong pace despite practical obstacles such as high prices, limited production capacity, and the lack of an infrastructure for effective composting. New materials and modifying agents are expanding biopolymers' reach, particularly in the case of polylactic acid (PLA). Efforts are focused on boosting mechanical and thermal properties so biopolymers can be effective alternatives to less costly commodity materials. The good news is that more biopolymers are approaching commercial viability for a long list of familiar and unfamiliar objects.

A McKinsey & Co. 2006 survey provides the following data for the potential for bio-based materials.

Market segment	Market size in 2010 ($billion)	Growth % 2005-10	CAGR 2005-10
Biofuels	42	100	**15%**
Plant extracts	23	20	**3.7%**
Pharma ingredients	20	100	**15%**
Bulk chemicals and polymers	15	50	**8.5%**
Food ingredients	11	35	**6.1%**
Oleochemicals	8	6	**1.1%**
Enzymes	**4**	**100**	**15%**

An analysis of the above table shows that there are some market segments that have much higher growth potential and in which castor oil could play a significant role.

Among the segments in the table above, it is doubtful whether castor oil can have a significant role in the biofuels industry, given castor oil's relatively high cost as well as the small quantities of castor oil produced when compared to the massive volumes required for transportation fuel. However, in high growth segments such as pharma ingredients, biopolymers and food ingredients castor oil could have a considerable role to play.

The quest for bio-sourcing of plastics has also brought back a castor oil-sourced polyamide. For instance, BASF produced a nylon 6.10 about 50 years ago but the product was discontinued. Now, with growing interest in producing plastics from renewable resources, the company has reintroduced the material. It contains about 60 per cent sebacic acid - derived from castor oil. It has a relatively low density for a polyamide, good low temperature impact strength and good dimensional stability because of its low water absorption and BASF says it is suitable for typical nylon 6 applications.

Biopolymers in Durables

While biodegradable plastics such as PLA have made strong penetration so far in disposable consumer packaging, durable applications may not be that far behind.

Mitsubishi Motors Corp. and the Aichi Industrial Technology Institute have developed a biopolymer of polybutylene succinate (PBS) and bamboo fiber for auto interiors. PBS is made

from 1, 4-butanediol (a petrochemical) and succinic acid (a product of fermenting sugar cane or corn). The fiber-reinforced material is said to provide greater rigidity and strength.

Meanwhile, Fujitsu Ltd. and Fujitsu Laboratories Ltd., Tokyo, have chosen Rilsan nylon 11 from Arkema for notebook PCs and cell phones. Based on castor oil, nylon 11 is typically used in automotive tubing and air-brake hose. Formulations contain 60% to 80% nylon 11 with high-density fillers for increased strength. Previously, the Fujitsu companies developed a notebook PC housing based on PLA and PLA/polycarbonate blends (the latter in cooperation with Toray Industries). This was its FMV BIBLO notebook PC series, which it had manufactured using a material called Ecodear.

(Reference URL from Fujitsu - http://www.fujitsu.com/global/news/pr/archives/month/2006/20061207-01.html & based on a July 2007 news report)

In Dec 2008, Toyota announced plans to use plant-derived plastic in more vehicle models, starting with hybrids next years. The company said that it will use a variety of materials (polylactic acid, plant-derived polyester, castor oil derivatives and more) to make seat cushions, sun visors, trunk liners, door trim, scuff plates and other interior parts.

In Dec 2008, solar cells manufacturer BioSolar announced that it planned to use biomass in solar panel components in an effort to reduce the costs of solar cells, thus replacing petroleum-based solar panel components with durable biomass-based plastic materials. According to BioSolar, one of its first product offerings, a BioBacksheet, is in the pre-production phase. The product forms the bottom layer of most crystalline silicon (c-Si) solar cells—a layer traditionally comprised of petroleum-based plastics. BioSolar will use primarily recycled cotton in combination with natural polymers derived from castor bean oil in its BioBacksheet product, according to the company.

In Jan 2009, Icynene Inc. (www.icynene.com), a manufacturer of opencell foam insulation products introduced castor-based spray foam insulation. ICYNENE LD-R-50™ is a renewable-based foam insulation and air barrier material that reduces the need for petroleum-based polyols. The product was made using castor oil and exceeds United States Department of Agriculture (USDA) requirements for a rapidly renewable product.

In Feb 2009, Keetsa, a San Francisco retailer that calls itself "the eco-friendly mattress store," announced it was selling mattresses made from a material it enthusiastically promotes as "BioFoam". This contains a polyurethane foam that partially utilized castor oil (The other 88 percent, though, is still petroleum-based)

After two years of research and development, French nylon yarn specialist SOFILA announced in March 2010 that it had developed a new commercially available range of high performance nylon yarns, produced using bio-polymers derived from the castor oil plant. The new 'Greenfil' yarns have been developed by Sofila in partnership with chemical company Arkema which has supplied its 'Rilsan' polyamide 11 polymer to produce the yarns. These yarns have been presented at Premiere Vision in Paris last year and were under trial (as of March 2010) by major French and European textile brands, for instance in hosiery and socks.

With the growth in the biopolymers industry, it is expected that there will be a simultaneous demand for the suitable grades of castor oil.

Castor Oil Polyurethane

Castor oil is increasingly finding application in the manufacture of polyurethane foams. The polyurethane is produced from polyols based on castor oil. Polyols can be reacted with diisocyanates to make polyurethanes.

Polyurethane is ultimately used to make elastomeric shoe soles, fibers, foam insulation for appliances, adhesives, mattresses, automotive seats and so on.

There are a limited number of naturally occurring vegetable oils (triglycerides) which contain the unreacted hydroxyl groups that account for both the name and important reactivity of these polyols. Castor oil is the only commercially-available natural oil polyol that is produced directly from a plant source: all other natural oil polyols require chemical modification of the oils directly available from plants.

The hope is that using renewable resources feedstocks such as castor oil for polyols and subsequently polyurethane production will reduce the demand on non-renewable fossil fuels currently used in the chemical industry and reduce the overall production of carbon dioxide, the most notable greenhouse gas.

Features of Castor Oil-based Polyurethane

- Superior to PPG (Polypropylene Glycol) or polyester in water and hydrolysis resistance
- Superior to PPG or polyester in insulation
- Lower viscosity than Polybutadiene or Polyester
- One of the most challenging issues of polyurethane flooring is heat and humidity. The urethane produced from castor oil is stable under high heat and humidity.

Nylon

Nylon 11

The world's largest single use of castor oil in one product, outside the lubricants markets, is in the manufacture of polyamide 11 (Nylon 11). The commercially available polyamide made from castor oil is Arkema's (earlier Atofina) Rilsan Nylon 11.

The world's only producer of polyamide 11 using amino-undecanoic acid, Arkema controls the entire production chain for Rilsan ® A and B thanks to the resources of TotalFinaElf, its parent company, and Costacem, its subsidiary specialising in the production of seeds for castor plants. With its extensive and wide-ranging properties, Rilsan ® has become a pioneer in many diverse areas, and remains the choice polymer of high tech industries for the manufacture of parts requiring optimum reliability.

Wide-ranging powders and application processes accommodating various types of support have made Rilsan ® the choice material for coating. Uses of Rilsan ® include:

- Polyamides 11 and 12 (Rilsan ®): automotive parts (fuel lines, pneumatic brake lines for heavy goods vehicles, sheathing for control cable, air-conditioning ducts); components for precision mechanical and electrical industries; flexible tubing for compressed air, hydraulics and oil industry (offshore extraction); aviation parts (alkaline battery trays).
- Thermoplastic polyamide coating powders (Rilsan ®): protection of automotive parts (clutch controls, bumpers, brake lines), protection of materials for construction and public works (cladding, aluminium profiles, heating pipes and fittings, soundproofing walls, stadium seating, etc.), printing components (press rollers), water pipes, pipelines and various equipment (dishwasher baskets, refrigerator shelves, garden furniture, screws, nuts and bolts, haberdashery (hooks, buckles), etc.

Arkema has now extended the technology into TPEs (thermo plastic elastomers) by producing a grade of its Pebax polyether block amide with the nylon block using the nylon 11 chemistry. The new grade is being sold as Pebax RNew in 25 to 72D hardness.

Polyamide from BASF

The quest for bio-sourcing of plastics has brought back a castor oil-sourced polyamide from BASF's old chemistry notebooks. Produced from Sebacic acid, this has a relatively low density for a polyamide, with good low temperature impact strength and good dimensional stability

because of its low water absorption, and BASF says it is suitable for typical Nylon 6 applications and those where nylon 6 has shown limitations.

Nylon 6/10

At the end of 2009, the company announced that it was introducing a new nylon 6/10 range of materials made in part from castor oil.

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- Belgium-based Solvay had announced its partnership with Mitsubishi Gas Chemical (MGC) on the development of high performance castor oil-based polyamides. The plastic is expected to be among the highest temperature bio-based polyamides in the industry with a heat deflection temperature of approximately 270°C for glass-filled compounds, according to Solvay. Solvay and MGC are currently working together to develop an optimized manufacturing process for the new polymer. MGC said it has filed numerous patents to cover its extensive development work in resin composition, production, and applications. (Nov 2010)
- DSM (http://www.dsm.com) introduced 5 new grades of its bio-based Ecopaxx resin. Ecopaxx was launched on 2009, and is said to contain 70% bio-based materials derived from castor oil.
- In Oct 2010, Toyota announced its plans to introduce a model in the year 2011 that will use renewable plastic-based compounds that cover 80 percent of the interior. One of the new applications in 2011 will be a fiber that backs vinyl in sheets used to cover seats, dashes and door interiors. The fabric layer under the vinyl is made 55 percent from recycled PET bottles. A plasticizer made from soybean oil and castor bean oil makes up 10 to 35 percent of the main layer. They planned to replace 100 per cent of the phthalates with soy oil and castor bean oil in the next iteration.
- Ford Motor Company is also a leader in using bioplastics in cars. Ford engineers have pioneered developments leading to large-sale use of castor-oil as a feedstock in polyurethane foams.
- Castor oil based polyurethane adhesives for wood-to-wood bonding - Most adhesives are polymeric adhesives, and if made from renewable sources they will have low cost and biodegradability which are of importance. In view of these properties research is being done on polyurethane (PU) adhesives from different polyester polyols obtained from castor oil.

- Lactic Acid and Ricinoleic Acid Based Copolyesters - Copolyesters based on purified ricinoleic (RA) and lactic (LA) acids with different RA: LA ratios have been synthesized by thermal polycondensation and by transesterification of high molecular weight poly(lactic acid) (PLA) with ricinoleic acid and repolyesterification. Transesterification of high molecular weight PLA with pure ricinoleic acid and repolymerization of those oligomers by condensation resulted in multiblock P (PLA-RA) copolyesters of molecular weights between 6000 and 14000.
- Ricinoleic acid-based biopolymers as drug carriers - Polyanhydrides synthesized from pure ricinoleic acid half-esters with maleic and succinic anhydrides have been shown to possess desired physicochemical and mechanical properties for use as drug carriers. Biocompatibility studies have demonstrated their toxicological inertness and biodegradability.
- Millable polyurethane elastomers based on difunctional castor oil and poly (propylene glycol), 2,4-toluene diisocyanate and 1,4-butane diol were prepared and cured using toluene diisocyanate dimer as crosslinking agent. All elastomers were characterized by conventional methods. Physical, thermal and mechanical properties of elastomers were studied. Investigation of these properties showed that the elastomers could be tailor made in order to fulfill industrial needs.
- Modification of the biopolymer castor oil with free isocyanate groups to be applied as bioadhesive - Surgical adhesives have been used for several applications, including haemostasis, sealing air leakages and tissue adhesion. Recently, efforts have been made to develop a biodegradable urethane-based bioadhesive based on castor oil containing free isocyanate groups. This material presents the advantage of being biodegradable, biocompatible and having the capacity of reacting with amino groups present in the biological molecules.
- Polyesteramide resins from dehydrated castor oil and various dibasic acids - Attempt has been made in this study, to utilize castor oil in the preparation of polyesteramide resins. Castor oil was first converted into dehydrated castor oils (DCO) to improve drying characteristics. DCO was then converted into diethanolamide {(N, N- bis hydroxethyl) castor oil amide} of mixed fatty acids using 0.5 per cent sodium methoxide as a catalyst and converted to polyesteramide resins after reacting with various dibasic acids such as phthalic anhydride, sebacic, succinic and adipic acids in presence of xylene as azeotropic solvent. The resins obtained were then analysed for its physico-chemical, film performance properties and resistance to various chemicals.
- Electrical characterization of castor-oil resins - Several Brazilian research works have shown that new materials, based on polyurethane resins derived from castor oil, have

had great success in the medical field. This could in fact be expected because of their stable physical and chemical properties. In this work, using the same fabrication techniques, thin films and circular plates of 1-2 mm thickness, of these resins were made and electrically characterized. Tests for a.c. electrical breakdown, permittivity, d.c. insulation resistance and dissipation factor show that these materials are very good insulators. Internal insulators and conductor covers are among their main applications. Their mechanical properties are also presented and discussed.

Conclusion

The recent research and trends in the castor oil biopolymer industry imply the potential of castor oil for bioplastics production. For most of these applications, the market is still developing. Hence, there is a need for research and development to ensure the sustainable mass production of castor oil biopolymers and improving its suitability for a wide range of applications.