APPLICATION OF ECO-PROFILE METHODOLOGY TO POLYAMIDE 11

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1. Introduction

Polyamide-11 (PA11) is a high performance, lightweight bioplastic (plastic produced with 100% of the carbons coming from plant based renewable resources) with a unique combination high performance properties. Compared to other high performance and engineering plastics, PA11 delivers an outstanding level of chemical, thermal and impact resistance over a wide range of flexibility. PA11 is widely used in applications where safety, durability and versatility are critical. Polyamide 11 is therefore frequently used as a cost effective replacement for metal or rubber in highly technical applications.

PA11 is produced from renewable castor seeds and is commercialized by ARKEMA under the Rilsan® brand[1].

The purpose of this article is to present new data regarding the environmental benefits of PA11 as compared to other high performance polymers.

2. Rilsan® Applications

PA11 exhibits superior high temperature and cold impact resistance, has a lower moisture pick-up and exhibits superior ageing resistance compared to conventional high performance polyamides. This unique combination of properties allows to use Rilsan® B in a wide variety of highly demanding applications, including packaging, automotive and truck (ex. air brake tubes and fuel lines), oil and gas (ex. Offshore flexible pipes), sporting equipment (ex. soles for sports shoes, ski top layers), medical devices, cable and electrical components.

Some recent applications examples:

Rotomolding applications

Rilsan® CC for ski top layers

Multi-Layer Technology: Rilperm®

Conductive Rilsan in tubes applications

3. PA11 history

The history of PA11 development began in 1938 when Joseph Zeltner and Michel Genas envisioned the possibility to prepare the monomer of PA11 from undecenoic acid, obtained from castor oil cracking. Development of this process progressed sporadically through the wartime years. A pilot production finally began in 1944. An industrial monomer plant started in 1955 in Marseille (France) and supplied a polymerisation plant in Serquigny (France).

Today Rilsan® PA11 is produced in France (Serquigny), USA (Birdsboro, PA) and in China (Changshu).

4. PA11 production technology

PA11 life cycle starts with the castor bean plant named Ricinus Communis. Castor oil, which is extracted from its seeds, is the raw material for further transformations into PA11.

All free energy consumed by this biological system arises from solar energy that is trapped by the process of photosynthesis. All the carbon atoms, that compose castor oil, as well as PA11 have their origin in the carbon dioxide that are absorbed by the castor plant.

After harvesting, the seeds are treated in a similar manner than most oil seeds. The seeds are transported to a castor mill, where the oil is separated from the meal by crushing and/or solvent extraction. Because of its high nitrogen content, castor meal is recycled as fertilizer. Crude castor oil is further refined and then transported to our Marseille (France) monomer plant.

Castor seed contains nearly 50% castor oil. Castor oil is a unique triacylglycerol, that is composed of 85 to 90% 12-hydroxyoleic acid, also known as ricinoleic acid.

At Marseille plant, castor oil undergoes five chemical steps that are represented on Figure 1.

Ricinoleate triglyceride is first transesterified with methanol to methyl ricinoleate (see Figure 1 - ①) along with glycerin co-product. Cracking of methyl ricinoleate leads to heptaldehyde and methyl undecylenate (②). After hydrolysis, undecylenic acid is obtained along with methanol, which is recycled to the first step (③). The following step is an addition on hydrogen bromide (④) followed by a nucleophilic substitution with ammonia to form 11-aminoundecanoic acid (⑤), which is PA11 monomer.

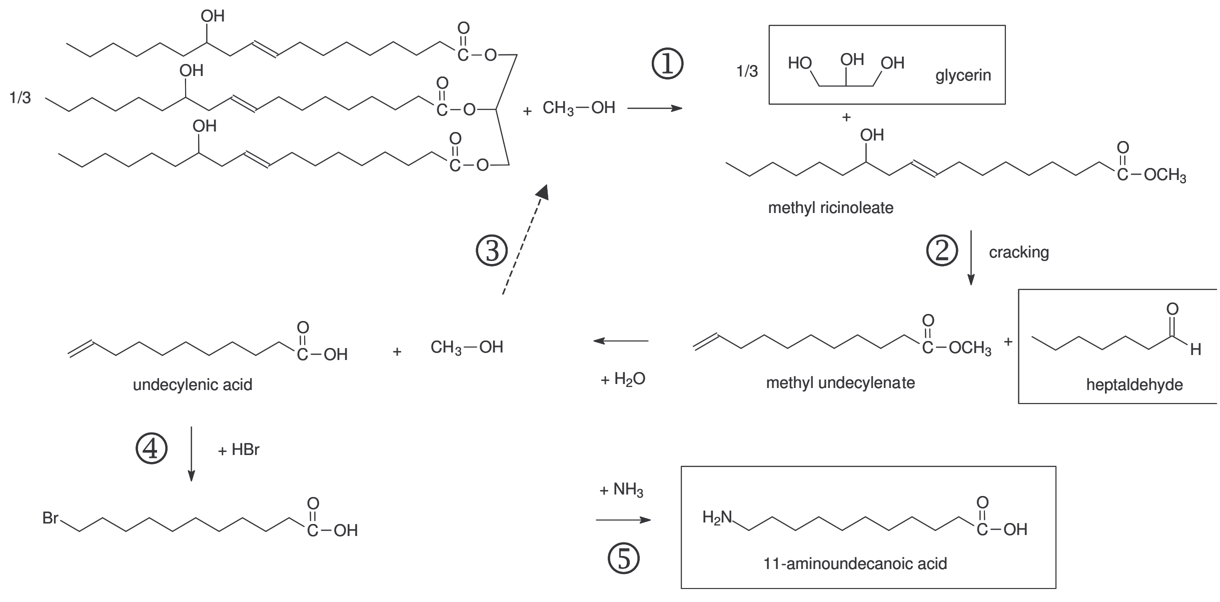


Figure 1

Aminoundecanoic acid is then sent to one of our polymerization plants where it is transformed into PA11 according to Figure 2.

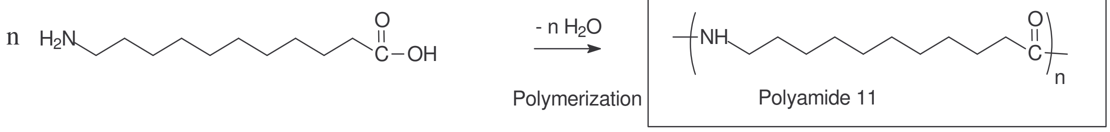


Figure 2

5. What is a Bioplastic?

The notion of "bioplastics"[2] is fairly recent and is applied to an innovative but relatively small range of plastic materials. The collective term "bioplastics" can be used to describe plastics with two different properties:

a) Those that are degraded in the biosphere. For these kinds of plastics, the term biodegradable plastic is used. Today, several certifications[3] exist in order to define the conditions where the tests have to be done in order to evaluate this property.

b) Those that are produced from renewable raw material resources (RRM). The terms biomass based or bio-based plastics describes this type of plastics.

Note: Bio-based plastics are not necessarily biodegradable and biodegradable plastics are not necessarily bio-based.

As a result of its vegetal origin, Rilsan® PA11 has received the "Biomass" based label from JORA[4] (Japan Organic Recycling Association) in April 2006.

Rilsan® PA11 is a unique high performance "bio-based" bioplastic produced from castor beans, a 100% renewable resource.

Biomass Based

Japan Organics Recycling Association (JORA)

6. Bioplastics environmental benefits

Sustainable development is the driving force for acting more responsibly to protect our world for future generations. It encompasses a combination of environmental, social and economic aspects. In this three aspects plastics play a vital role.

The plastics industry continues to innovate in order to advance its contribution to a more sustainable society. Among all the reasons for the success of plastics , the key reason they are used is that plastics are a better alternative for many applications in comparison of metal not only for the sustainable considerations but also in term of properties. For example, their advantages are : weight reduction, flexibility, resistance to corrosive attacks, better processability (less energy requirement), versatility…

During an eco-design approach for a similar function, generally, plastic is the best solution. A recent study[5] has estimated the effects on climate change if plastics were to be replaced by alternative materials wherever possible across the whole of Western Europe. The results indicate that there would be an additional energy requirement of around 10%, or about 25 million tons of crude oil, corresponding to 105 million tons of CO_2 greenhouse gas emissions per year.

Furthermore, the bioplastics (sub-family of plastics) at equivalent properties are generally more CO_2 neutral than their homologue based on fossil raw materials. To illustrate this last point, we have to consider the global carbon cycle during the whole life of a product[6].

When we consume fossil resources to make our polymers, chemicals & fuel, we release the carbon back into the atmosphere as CO_2 in a short time frame of 1-50 years, we disequilibrate the carbon cycle. The rate at which biomass is converted to fossil resources is in imbalance with the rate at which they are consumed and liberated

($>10^6$ years vs. 1-50 years). Thus, we release more CO_2 than we sequester as fossil resources – which results in a kinetics problem.

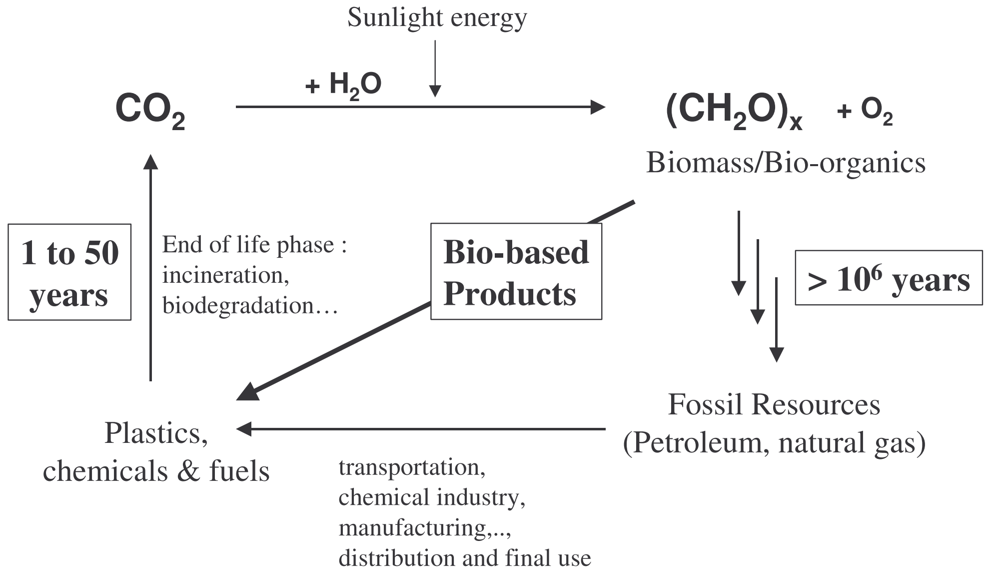


Figure 3

However, if we use annually renewable crops or biomass as the feedstocks for manufacturing our carbon based polymers, chemicals, and fuels, the rate at which CO_2 is fixed equals the rate at which it is consumed and liberated – this is sustainable and the use of annually renewable crops/biomass would allow us to manage carbon in a sustainable manner.

Thus, using annually renewable carbon feedstocks allows for:

• Sustainable development of carbon based polymer materials

• Control and even reduce CO2 emissions and help meet global CO_2 emissions standards – Kyoto protocol

• Provide for an improved environmental profile

In PA11, all the carbons are organic and renewable. That is unique since no others commercial performance polymers have 100% organic renewable carbons in their structure. This characteristic could be quantified and measured according to the standard ASTM D6866.

Finally, bioplastics do not only have ecological advantages (see chapter 7 for the quantification). They also help to conserve fossil raw materials and reduce our dependency on petroleum. , This opportunity should not be disgarded in times of constantly rising prices for fossil raw material even for economical reasons.

7. Eco-profiles, a tool for measuring environmental sustainability

7.1 Introduction

Eco-profile assessment is a method to account for the environmental impacts associated with a product. The term “Eco-profile” indicates that all stages from resource extraction to the product are taken into account (i.e. cradle to pellet).

Eco-profile differentiates from “life cycle assessment” (LCA), in that eco-profile does not deal with the use of the product and its disposal whereas LCA does (i.e. cradle to grave).

The four phases of an eco-profile study and its methodology are defined by international standard ISO 14040 to 14043:

- Description of the system that is studied
- Inventory phase – where the aim is to provide a detailed description of the inputs of energy and raw materials into the system and the outputs of solids, liquids and gaseous wastes from the system
- Evaluation of the potential environmental impacts associated with those inputs and outputs
- Interpretation of the results of the inventory analysis and impact assessment phases in relation to the objectives of the study.

The inventory and the impacts environmental evaluation (Steps 2 and 3) of PA11 eco-profile were performed by *Boustead Consulting* that have over 35 years experience in life cycle assessment and eco-profiles and is largest generator of public inventory data. Their database and software was used for the calculations.

In particular, *Boustead Consulting* has calculated and put in public arena a large number of eco-profile of the main polymers for the Association of Plastics Manufacturers of Europe[7]. The results of PA11 eco-profile were done with the same methodology and are presented in the same format, so that relevant comparison with the other polymers can be made.

7.2 System description and methodology

In this eco-profile, we evaluated the total amount of raw energy sources and primary raw material for 1 kg of polyamide 11 out of our Serquigny plant, as well as the total amount of air and water emission and solid wastes in this production from raw energy sources and primary raw materials.

Primary raw materials and raw energy sources are raw material and energy sources that are taken directly out of the nature. For example caustic, ammonia, diesel or electricity are not primary raw materials or primary energy sources, whereas sodium chloride, crude natural gas in the gas field, crude oil in the oil field, wind or coal are primary raw materials or primary energy sources.

The system boundary for polyamide 11 production is described in Figure 4.

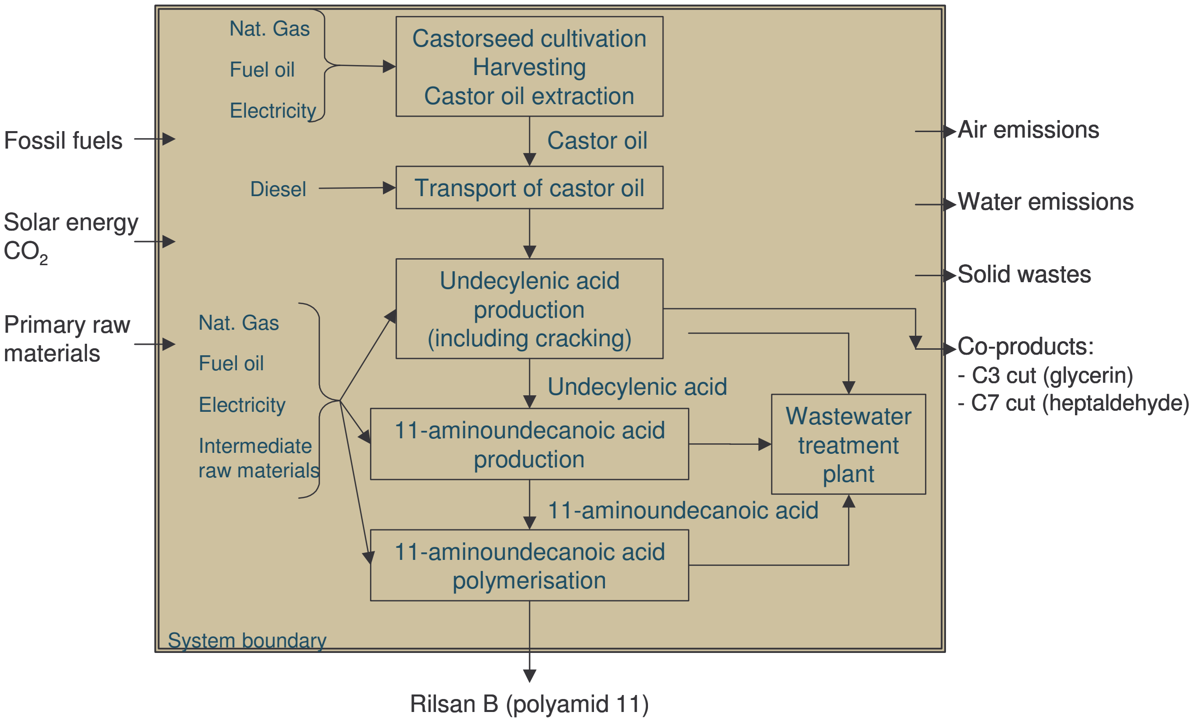


Figure 4

7.3 Inventory

As we saw it in the previous section (7.1), the inventory is the step where we globally quantify each input and output. We divided this system into elementary sub-systems. Each of this sub-system corresponds to an industrial step for which data are available. We collected the following data for 1 kg of the product of the step:

- Mass of fuels (natural gas, coke, fuel oil, diesel…) and amount of electricity and mass of intermediate raw materials (catalysts, caustic, ammonia, ….) and amount of energy that is recovered through incineration of co-products (if any) that were used for the production of these 1kg of product, including process and cooling water supply, steam production, compressed air supply, wastewater plant operations… Mass of each fuel is then converted into energy unit (megajoule).
- Amount of CO_2 and other emissions that are released in the atmosphere at this step (process, combustions…)
- All liquid and solid waste emissions of this step.

Data for producing and delivering intermediate energy sources (diesel, delivered natural gas, electricity…) or intermediate raw materials were taken from the *Boustead* Core database. Whenever relevant, country specific data were used (electricity, natural gas…).

Energy consumption and air emissions in transport of each input data have been taken into account with the real distances for the raw materials.

Concerning gas emissions, it is important to know that castor seeds cultivation corresponds to a CO_2 consumption. So it bears a negative CO_2 emission, obviously a major advantage of PA11.

7.4 Co-product allocation

As we saw earlier (7.1), the co-product allocation is the procedure in order to divide the environmental footprint to each product obtained during the same process. In the production of PA-11, we have for example two co-products: glycerin and heptaldehyde. With the co-product allocation procedure, they take on part of the burden of the inputs and outputs.

The allocation has been made on a mass basis at the stage of undecylenic acid plant.

More precisely:

- Let's consider that the undecylenic acid plant produces 1 kg of undecylenic acid, x kg of glycerin and y kg of heptaldehyde, and uses z kg of delivered castor oil + a certain amount of each other input data, and generates t kg of CO_2 + a certain amount of other air emissions, water emissions and solid wastes.
- We actually allocated to 1 kg of undecylenic acid: z / (1 + x + y) kg of delivered castor oil, t / (1 + x + y) kg of CO_2. We did the same allocation for all other inputs or outputs.

7.5 Impact assessment

One of the objectives of these eco-profile studies is to be able to compare different materials for a specific use on an environmental point of view.

This article focuses on two categories of impacts that have an increasing importance around the word today.

- <u>Energy consumption</u>

  The "*gross energy requirement*" represents the total amount of energy of primary fuels that is used to make the product It is expressed in MJ per kg of PA11. The gross energy requirement comprises feedstock energy (energy that is brought to the system as material rather than fuels – for example biomass has an energy content), fuels that are used / burned at the plants (delivered fuel), fuels that are used in transport, and energy that is used for fuel production and energy delivery.

  The gross energy requirement can be subdivided in:

  Fossil energy requirement: fossil energies are oil, natural gas, coal and lignite

  Non fossil energy that includes among others biomass and other renewable energy sources.

- <u>Global impact on the climate</u>

  We measure the amount of greenhouse gases. The work of the Intergovernmental Panel on Climate Change (IPCC) provides a framework for aggregating data on those air emissions that are thought to be significant contributors to global warming. These data are summarized as Global Warming Potential (GWP) or carbon dioxide equivalent. The following table gives the conversion factors for several gases.

  Because the different gases react chemically in the atmosphere as a result of sunlight, their effect will change with time as they are changed chemically. Therefore, three parameters are defined for each emission corresponding to a 20 year, 100 year and 500 year effect. The choice of the time horizon depends on the environmental impact considered. Generally, the 100 years horizon is a good compromise between short and long-term processes.

Species	20 years GWP in CO_2 equivalent	100 years GWP in CO_2 equivalent	500 years GWP in CO_2 equivalent
Carbon dioxide	1	1	1
Carbon monoxide	10	3	1
Methane	62	23	7
Nitrous oxide	275	296	5200

Carbon dioxide equivalents of selected chemicals

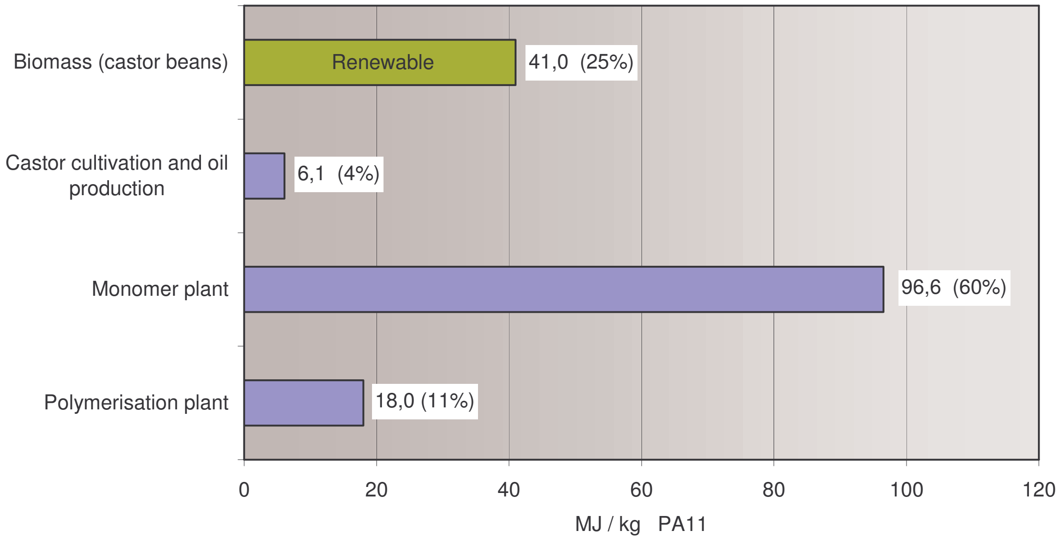
8. Eco-profile of polyamide-11

8.1 Results of polyamide-11 ecoprofile

Total gross energy to produce 1 kg of PA11 is 161.7 MJ/kg.

Out of this total amount, Fossil fuel energy requirement (oil, gas, coal and lignite) is 111.4 MJ/kg, 9.3 MJ/Kg is provided by nuclear supply, and 41 MJ/kg is the renewable biomass energy of castor beans feedstock.

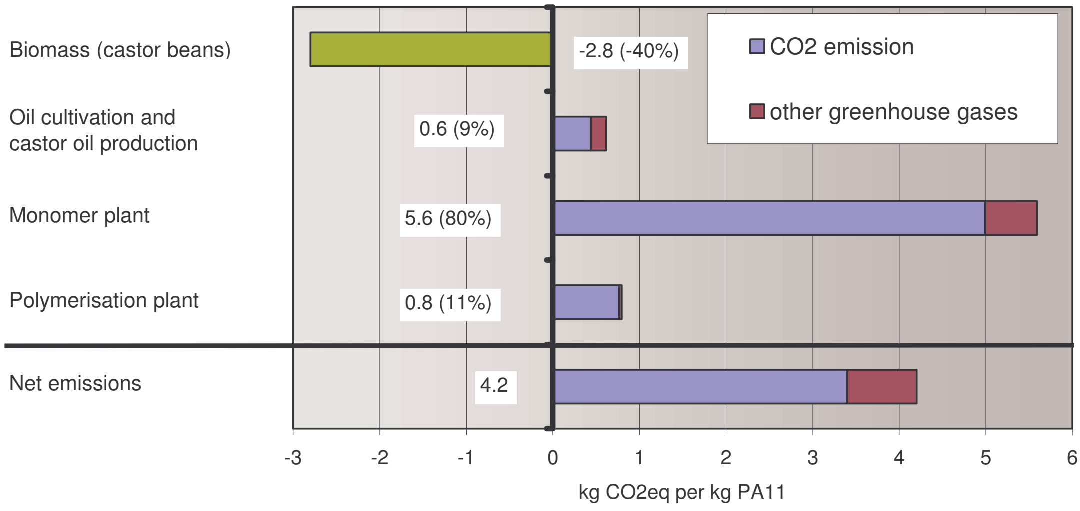
The following graph shows how much gross energy is required by each step of PA11 production.



Graph 1: gross energy breakdown by process step

Production of 1 kg of PA11 uses 2.8 kg of CO_2 (castor seed cultivation) and generates 6.2 kg of CO_2: net carbon dioxide air emission is 3.4 kg per kg of PA11. The global warming potential at 100 years horizon time of 1 kg PA11 is 4.2 kg CO_2 equivalents.

The following graph shows how much each step of the process emits.



Graph 2: breakdown by process step of CO2 and CO2 equivalents air emission for the production of 1 kg PA 11

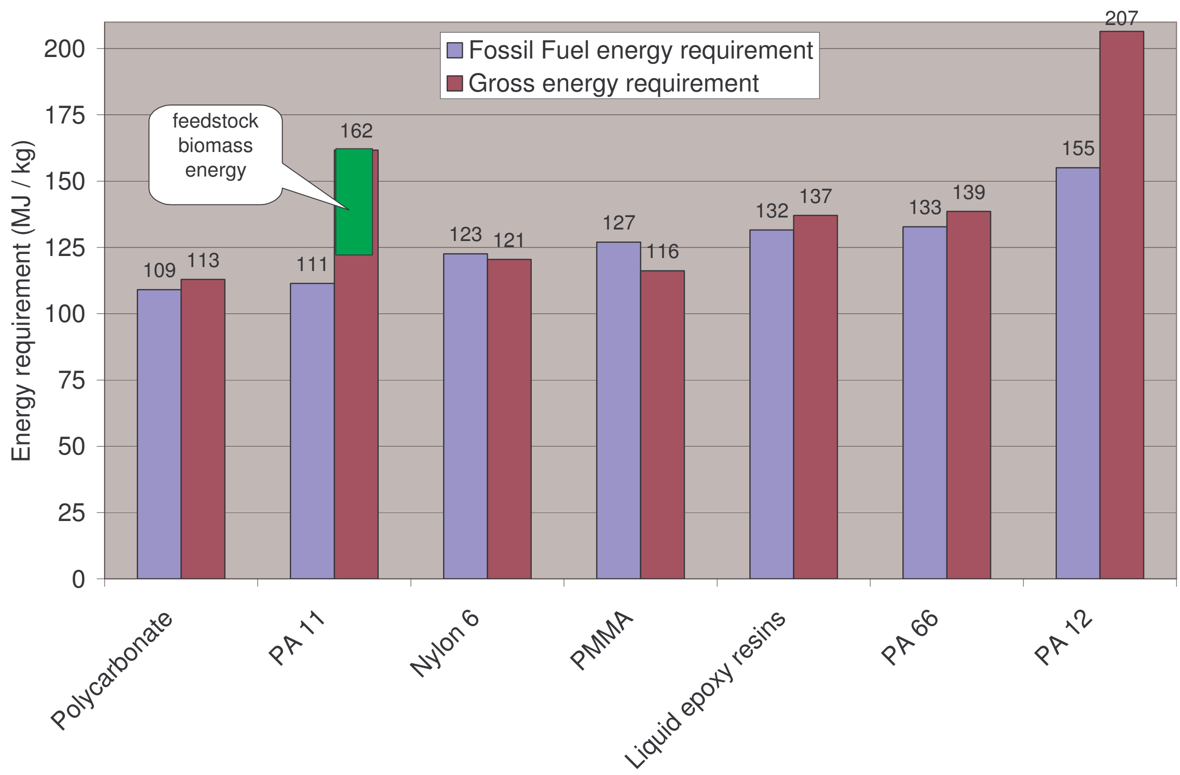
8.2 Eco-profile comparison with other polymers

Gross energy requirement and fossil fuel requirements of several performance polymers are represented on Graph 3 (all data calculated by Boustead Consulting are available in the website of Plastics*Europe*)

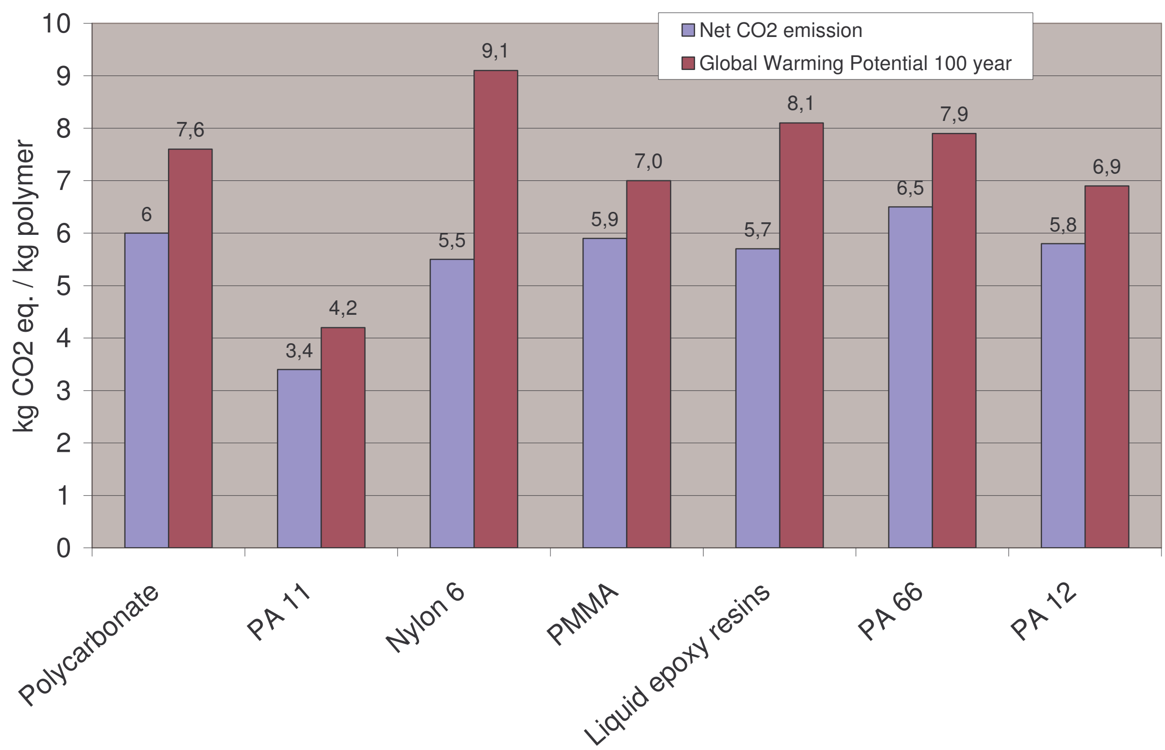
This comparison shows that PA11 requires less fossil energy as PA12 or PA66. The fossil fuel energy requirements of PA11 are in the range of high volume thermoplastics such as polycarbonate, nylon 6 or PMMA.

More strikingly, the analysis of graph 3 demonstrates that PA11 production enjoys a much lower contribution to global climate change: -40 to -55% GWP compared to other technical polymers.

Eco-profile assessment provides valuable insight into the way PA11 performs environmentally compared to competing performance plastics. Due to the fact that the starting feedstock is biomass, the consumption of fossil fuel is one of the lowest of performance polymers. Greenhouse gases emission for PA11 production are much lower than all other performance polymers. The explanation of this feature is that PA11 production starts with a big atmospheric CO_2 consumption (castor seed cultivation).



Graph 3 **:** comparison of total energy requirement



Graph 3: comparison of greenhouse gases emissions

9. Conclusions

Arkema endorses Responsible Care®, a voluntary undertaking by the chemical industry to improve safety and the protection of health and the environment, under the aegis of the International Council of Chemical Associations (ICCA) worldwide and of the European Chemical Industry Council (CEFIC) at European level.

Reducing greenhouse gas emissions is a priority. As a major energy consumer directly concerned about carbon dioxide emissions, Arkema is continuously improving the energy efficiency of its installations. Since 1990, the baseline year for the Kyoto Protocol establishing improvement targets for industrialized nations, Arkema has cut greenhouse gas emissions by a factor of three.

In this same spirit, ARKEMA is looking forward to developing and commercializing more products with improved environmental performance. Bio-based products development is one of the four-top priorities of ARKEMA Research and Development teams.

As described in this article, one of these products, Rilsan® (Polyamide-11) contributes to sustainable development in that:

- It is a bio-based, high performance bioplastic – all carbons in Polyamide-11 are organic and renewable (ASTM 6866)
- Its production from primary energy sources and primary raw materials requires less fossil energy than most performance polymers
- Its production from primary energy sources and primary raw materials generates much less CO_2 and other greenhouse gases emission than other performance polymers.

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[1] See PA11 and PA12 technical center in the OMNEXUS website : http://omnexus.com/tc/pa11-pa12/index.aspx

[2] German IK association position paper “Bioplastics, chances and opportunities” published in January 2006 – IK association regroups manufacturers of plastics packagings and films on the German market

[3] EN13432 , ASTM 6400 or GreenPla in Japan – See ADEME website for more information about biodegradable plastics : http://www2.ademe.fr/servlet/getDoc?id=11433&m=3cid=96

[4] JORA website : http://www.jora.jp/eng/

[5] David Cadogan, ECPI, Plasttekniske Dager, “The future belongs to plastics and plastics belong to the future”, Oslo, 8-9 November 2006

[6] Pr. Narayan, National ACS Symposium hed in San Diego, in june 2006

[7] Plastics*Europe* website : http://www.plasticseurope.org

The EcoProfile of PA11 described in this technical memo has been set up by Boustead Consulting Ltd on the basis of information collected by the authors. For any additional information plse contact: : info.rilsan@arkema.com

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