

TRENDS AND PERSPECTIVES IN FEEDSTOCK RECYCLING OF POLYMERIC MATERIALS

J.M.N. van Kasteren and Q.Zhou

Eindhoven University of Technology, Eindhoven Energy Institute, PO Box 513, 5600 MB Eindhoven, The Netherlands e-mail: j.m.n.v.kasteren@tue.nl

Abstract

This paper provides up-to-date information on the technological trends regarding polymer feedstock recycling, paying special attention to materials such as biomass, biodegradable polymers and thermosets, and the development and application of new processes for feedstock recycling of polymeric materials.

Keywords: Feedstock recycling; Waste polymers; Recycling

1. Introduction

The plastic production increased from 1.5 million tonnes in 1950 to 230 million tonnes in 2009 with the growth rate of around 9% a year on average [1]. As plastics are synthesized from non-renewable resources and are generally non-biodegradable, plastics should be properly managed in order to prevent serious environmental waste issues. For a sustainable use of polymers a necessary requisite is closing the material loop by either reuse or recycling. An attractive potential technology in this case, which can provide beside environmental also economical benefits is feedstock recycling.

Also known as chemical recycling, feedstock recycling refers to techniques used to break down plastic polymers into their constituent monomers, which in turn can be used again in refineries, or petrochemical and chemical production. A variety of treatments may be included under this category including chemical depolymerisation, gasification, thermal cracking and catalytic conversion [2].

Some lifecycle assessments show that feedstock recycling from mixed plastic waste has good environmental performance [3]. However, the rate of feedstock recycling for post-consumer plastic waste in the EU in 2008 is only 0.3% (0.07 Mt), and it shows no or little growth from 1995 to 2008 compared with mechanical recycling and energy recovery due to a combination of technological and economic reasons (Fig.1) [4].



Fig.1 Plastic recovery options in EU-15, 1996-2008[4]

In order to compete with other recycling methods, the key success factor for feedstock of recycling will be lowering processing cost in combination with producing high value-added products.

2. New Trends on Feedstock Recycling

- 2.1 Emerging sectors
- 2.1.1 Biomass

Recently natural polymers such as lignocellulosic biomass, which is the most abundant and inexpensive sustainable source of carbon, have been considered as a feedstock for the production of renewable fuels and commodity chemical feedstocks. One typical example is by combining fast pyrolysis with zeolite catalyzed hydroprocessing, lignocellulosic biomass can be converted into high value chemicals like light olefins and aromatic hydrocarbons (Fig.2) [5].



Fig. 2. Production of olefins, aromatic hydrocarbons, diols, and gasoline range alcohols from the integrated catalytic processing of pyrolysis oil [5].

2.1.2 Biodegradable polymers

Biodegradable plastics are supposed to be completely broken down by micro-organisms in the environment into non-toxic compounds. However, the microbial degradation of some biodegradable polymers such as PLA is limited to a few species of microorganisms [6]. Large-scale consumption of PLA products will lead to an excess of PLA waste, which will be difficult to be treated by biodegradation either in composting plants or in the natural environment. Moreover, recyclers complain that PLA is often indiscernible from the polyethylene terephthalate (PET), and even small amounts of PLA contamination in a PET recycling stream can affect the polyester's properties. Therefore, it is necessary to find efficient recycling methods for biodegradable polymers. If you can recover the polymer pure it is possible to convert PLA back to lactic acid/lactide (Fig.3) I71.



Fig.3 Cradle-to-cradle concept for PLA [7].

For mixtures of polymer feedstock recycling can deliver a good alternative.

2.1.3 Thermosetting polymers

Recycling of thermosets has been an important point on the agenda for the composite industry for a long period. Due to the crosslinked state, composites are neither fusible nor soluble and cannot be treated by simple methods. New technology that can make the recycling structurally possible is to bring reversible crosslinking decrosslinking functions to the thermosets (Fig.4) [8]. This function can be activated as function of certain process parameters: e.g. temperature and/or light.



Fig.4. Scheme of the Diels-Alder (DA) and Retro-Diels-Alder (RDA) reactions between PK-furan and bismaleimide [8].

2.2 New processes

2.2.1 Solar driven gasification

Solar-driven gasification uses concentrated solar radiation as the energy source to produce syngas, which offers an attractive alternative to conventional auto thermal processes. The advantages of this process include [9]:

- Produce high-quality synthesis gas with higher output per unit of feedstock and lower specific CO₂ emissions
- Elimination of an air separation unit
- Storing intermittent solar energy in transportable and dispatchable chemical form.

The prototype solar reactors have been experimentally demonstrated, yielding high carbon conversions and reasonable solar-to-fuel energy conversion efficiencies (Fig.5) [9].





2.2.2 Combination processes

Combinations of feedstock recycling methods are needed to produce high-value products with lower content of impurities instead of single methods. E.g. a pyrolysis-gasification process has been used to produce hydrogen [10]; ABS has been treated using a tandem hydrolysis-pyrolysis method, which has the advantage of high denitrogenation efficiency under mild reaction conditions and decrease of the probability of forming pyrolysis (Fig.6) [11]; Another example is polystyrene and PET which can be converted to biodegradable polymer polyhydroxyalkanoate (PHA) using a two-step pyrolysis-biosynthesis method [12,13]. In the frst step the polymers are converted into oil which can then be used as feedstock for the bio synthesis method.



Fig.6 A two-step process for thermochemical recycling of ABS [11].



2.2.3 Environmental-friendly process

When treating waste plastics, the environmental impact of the process should be considered. The development of environment-friendly methods for feedstock recycling is an area of considerable importance. The use of volatile and toxic solvents should be avoided, and the process should not produce other pollutions. New trend is to use so-called green solvents such as poly (ethylene glycol) (PEG) [14] and ionic liquids for chemical recycling. They have been shown to be effective for efficient dechlorination of PVC at atmospheric pressure (Figure 7) [15].



Figure 7. Plausible mechanism for [BMIM]Cl-enhanced dehydrochlorination of PVC [15].

3. Conclusions

In summary, this paper provides latest developments in the area of feedstock recycling of polymers, paying special attention to materials such as biomass, biodegradable polymers and thermosets.

Feedstock recycling of polymeric materials is still in its infancy. New combinations of both existing and promising technologies can meet the challenge and competition with existing mechanical recycling and energy recovery. The key factor to this is to both improve the cost efficiency of the processes and the production of high value end products.

References

[1] Plasticeurope, Plastics-the Facts 2010: An analysis of European plastics production, demand and recovery for 2009; Available at: www.plasticseurope.org., (2010).

[2] J.Scheirs and W.Kaminsky, Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels, Wiley & Sons., Hoboken, NJ., 2006, p.

[3] Waste & Resources Action Programme (WRAP), Environmental benefits of recycling – 2010 update., (2010). Jean-Charles Michaud, Laura Farrant and Olivier Jan, Birgitte Kjær and Ioannis Bakas, Available at: http://www.wrap.org.uk/wrap_corporate/publications/ben efitsrecycling.html

[4] Plasticeurope, The Compelling Facts About Plastics 2009: An analysis of European plastics production, demand and recovery for 2008; Available at: www.plasticseurope.org., (2009).

[5] T.P. Vispute, H. Zhang, A. Sanna, R. Xiao and G.W. Huber, Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils, Science 330 (2010) 1222-1227.

[6] Y. Tokiwa and B.P. Calabia, Biodegradability and biodegradation of poly (lactide), Applied microbiology and biotechnology 72 (2006) 244-251.

 [7] http://www.stonyfield.com/healthy-planet/ourpractices-farm-table/sustainable-packaging/multipackcups-made-plants/it-composta.

[8] Y. Zhang, A.A. Broekhuis and F. Picchioni, Thermally Self-Healing Polymeric Materials: The Next Step to Recycling Thermoset Polymers?, Macromolecules 42 (2009) 1906-1912.

[9] N. Piatkowski, C. Wieckert, A.W. Weimer and A. Steinfeld, Solar-driven gasification of carbonaceous feedstock—a review, Energy & Environmental Science (2011) 73-82.

[10] I.F. Elbaba, C. Wu and P.T. Williams, Hydrogen production from the pyrolysis-gasification of waste tyres with a nickel/cerium catalyst, International Journal of Hydrogen Energy 36 (2011) 6628-6637.

[11] Q. Zhou, J.W. Yang, A.K. Du, Y.Z. Wang and J.M.N. Van Kasteren, Fuel Oil from Acrylonitrile-Butadiene-Styrene Copolymers Using a Tandem PEG-Enhanced Denitrogenation-Pyrolysis. Method, AICHE Journal 55 (2009) 3294-3297.

[12] P.G. Ward, M. Goff, M. Donner, W. Kaminsky and E.O.C. Kevin, A two step chemo-biotechnological conversion of polystyrene to a biodegradable thermoplastic, Environmental Science & Technology 40 (2006) 2433-2437.

[13] S.T. Kenny, J.N. Runic, W. Kaminsky, T. Woods, R.P. Babu, C.M. Keely, W. Blau and K.E. O'Connor, Up-Cycling of PET (Polyethylene Terephthalate) to the Biodegradable Plastic PHA (Polyhydroxyalkanoate), Environmental Science & Technology 42 (2008) 7696-7701.

[14] Y.H. Wu, Q. Zhou, T. Zhao, M.L. Deng, J. Zhang and Y.Z. Wang, Poly(ethylene glycol) enhanced dehydrochlorination of poly(vinyl chloride), J. Hazard. Mater. 163 (2009) 1408-1411.

[15] T. Zhao, Q. Zhou, X.L. He, S.D. Wei, L. Wang, J.M.N. van Kasteren and Y.Z. Wang, A highly efficient approach for dehydrochlorinating polyvinyl chloride: catalysis by 1-butyl-3-methylimidazolium chloride, Green Chemistry 12 (2010) 1062-1065.