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Review

Thermal degradation of PVC: A review

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ABSTRACT

This review summarized various chemical recycling methods for PVC, such as pyrolysis, catalytic dechlorination and hydrothermal treatment, with a view to solving the problem of energy crisis and the impact of environmental degradation of PVC. Emphasis was paid on the recent progress on the pyrolysis of PVC, including co-pyrolysis of PVC with biomass/coal and other plastics, catalytic dechlorination of raw PVC or Cl-containing oil and hydrothermal treatment using subcritical and supercritical water. Understanding the advantage and disadvantage of these treatment methods can be beneficial for treating PVC properly. The dehydrochlorination of PVC mainly happed at low temperature of 250–320 °C. The process of PVC dehydrochlorination can catalyze and accelerate the biomass pyrolysis. The intermediates from dehydrochlorination stage of PVC can increase char yield of co-pyrolysis of PVC with PP/PE/PS. For the catalytic degradation and dechlorination of PVC, metal oxides catalysts mainly acted as adsorbents for the evolved HCl or as inhibitors of HCl formation depending on their basicity, while zeolites and noble metal catalysts can produce lighter oil, depending the total number of acid sites and the number of accessible acidic sites. For hydrothermal treatment, PVC decomposed through three stages. In the first region ($T < 250$ °C), PVC went through dehydrochlorination to form polyene; in the second region (250 °C $< T < 350$ °C), polyene decomposed to low-molecular weight compounds; in the third region (350 °C $< T$), polyene further decomposed into a large amount of low-molecular weight compounds.

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1. Introduction

Plastics play an important role in our life as many objects of daily use are made of different kinds of plastics: from packaging, films, covers, bags and containers, to construction, electrical and electronic applications. Of plastics, low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) account for 74.2% of the European plastic demand in 2012 (Fig. 1). Among these six major types of plastics, the consumption of PVC contributes to 12% of total demand. Global plastics production capacity for PVC was about 61 million tons in 2013. Of this, China accounted for a half (Fig. 2). The consumption of PVC in 2013 reached 38.5 million tons. It is estimated that global demand will rise by about 3.2%/year to 2021 (Ceresana Research, 2014). The various applications of PVC are listed in Table 1. The biggest markets are pipes and window profiles, followed by rigid films and cables as shown in Fig. 3. A wide range of additives are incorporated during PVC production which can improve mechanical properties of PVC products and make applications of PVC extensive. Even though the durable PVC products can sustain long service life compared with other plastics, they will eventually become solid waste (Sadat-Shojai and Bakhshandeh, 2011).

In Europe, up to 30.8% of waste plastic was landfilled, where plastic waste incineration with purpose of energy recovery represented the principal alternative being 39.5%. Unfortunately, only 29.7% of total plastic waste was recycled (PlasticsEurope, 2015). Diminishing viable landfill capacity, environmental persistence and loss of chemical/calorific value of plastics makes the landfilling of plastic an undesirable, unsustainable option which poses a considerable problem to future generations. A more suitable route is recycling. There are mainly four types of plastic recycling and reuse, categorised as primary (re-extrusion), secondary (mechanical), tertiary (chemical recycling) as well as quaternary recycling (energy recovery) as shown in Fig. 4 (Goodman, 2014). The type of recycling used is dependent upon a number of factors, varying from location, to physical and chemical requirements. Primary recycling is the technique whereby waste plastic polymers of a single type or origin, are reintroduced into the extrusion cycle to produce similar materials or products. Plastics found in municipal solid waste are often not suitable for use in the primary recycling process due to contamination. Energy recovery, mainly incineration, is highly controversial due to the formation of toxic pollutants such as SO_2, NO_x, heavy metals and particulates in both flue gas and solid residues even though it can reduce the volume and produce energy. Secondary recycling, also known as mechanical recycling, is a preferable way only if sufficient quantities of homogeneous and source-separated waste can be prepared. The inhomogeneity of municipal solid waste makes it very difficult to be recycled (Sadat-Shojai and Bakhshandeh, 2011). Among all the four methods of recycling, only chemical recycling conforms to the principles of sustainable development because it leads to the formation of the raw materials from which the plastics are originally made. Therefore, chemical recycling is increasingly gaining the attention of more researchers. Chemical recycling refers to the use of advanced technologies to convert plastic materials by depolymerisation to smaller units either in the form of monomers or partial degradation to secondary valuable materials. Chemical recycling can be classified as cracking/pyrolysis, gasification and chemical depolymerisation. One usual approach for chemical recycling of PVC wastes is cracking/pyrolysis including hydrocracking, thermal cracking and catalytic cracking (Goodman, 2014). Gasification is also used to produce a mixture of hydrocarbons and synthesis gas (CO and H_2), which has advantages over the normal process of combustion due to some of the calorific value being derived

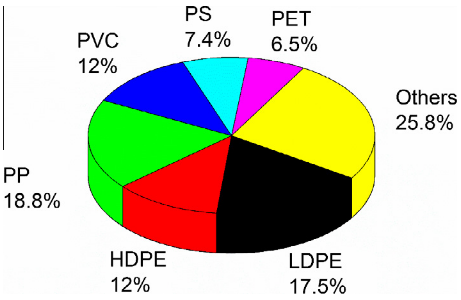

Fig. 1. European plastic demand by category (PlasticsEurope, 2013) (date: 2012).

Table 1
Overview of the major applications of PVC (Keane, 2007).

General application	Specific examples
Construction	Window frames and doors; Potable and gravity pipes; Gutterings; Cables ducting and conduits; Flooring; Wall coverings; Reservoir linings; Sheets and panels; Roller shutters; Sports stadium seats
Medical	Pharmaceutical blisters; Blood bags; Plasma bags; Tubing; Infusion kits
Electrical	Keyboards; Computers; Power tools; Electrical cords; Phone systems; Cellular phones; Component housings
Automobile	Interior trims (sun visors handbrake and gearbox lever parts carpets etc.); Window encapsulation; Dashboard skins; Coated fabrics (seat coatings door panels etc.); Wire harness systems (cable sheaths grommets etc.); Sealant (underbody insulation etc.)
Packaging	Food packaging (thermoformed cups); Mineral water bottles; Cling films; Non-food packaging (trays cosmetics and detergents containers etc.); Bottle caps
Cards	Credit cards; Smart cards; Identity cards; Telephone cards
Leisure and sports	Toys; Footballs; Swimming rings; Garden hoses; Liferafts; Ship construction
Office	Office supplies (folders ring binders rulers etc.); Computer cases; Computer keyboards; Printing applications
Clothing	Raincoats; Lifevests; Shoe soles; Rubber boots; Imitation leather

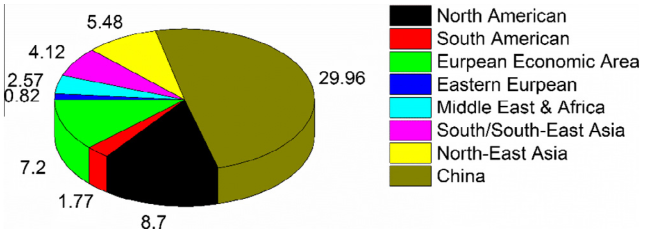

Fig. 2. Distribution of global PVC production, by region (Attenberger et al., 2014) (date 2013: 61 million tons).

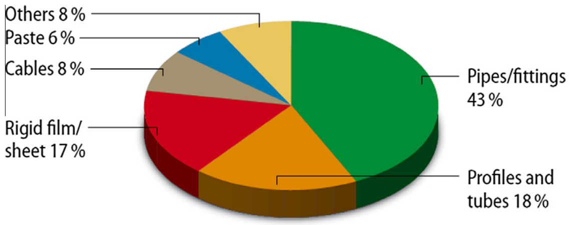

Fig. 3. PVC application worldwide (Attenberger et al., 2014) (date 2013: 38.5 million tons).

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