Conversion of Polymer and Resin Wastes into the Valuable Products

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Abstract

Progress in materials science, which took place more than a century ago, has change the life of mankind cardinally. Starting from the moment of their invention, plastics and a variety of materials made from them have filled up almost all areas of the industrial and household activities. The dark side of the picture is that the plastics wastes being hardly self-degraded constitute a menace to the environmental and the health of all living forms. Nowadays, the most part of the plastic wastes are disposal in landfills. Development of new efficient approaches to conversion of such wastes into the valuable products is of great importance. The present research is devoted to analysis of possibility of the polymer and resin wastes processing into nanostructured carbon materials in a closed reaction volume.

Keywords: Plastic wastes; Polymers; Resins; Disposal; Incineration; Recycling

World of Plastics

The first man-made plastic material was invented in England by Alexander Parkes in 1856 [1]. Almost 80 years after the invention, in 1940s, mass production of the plastics has begun along with the improvements in chemical technology taking place after World War I. Since 1964, the production volume has increased twenty-fold and exceeded 300 million tonnes in 2011 (Figure 1), and in the coming 30 years, it is expected to treble [2]. Plastic materials possess a combination of low cost and unique properties that makes them to be of great popularity and wide usage [3,4]. No doubt that today it is completely impossible to envisage the modern world without plastics.
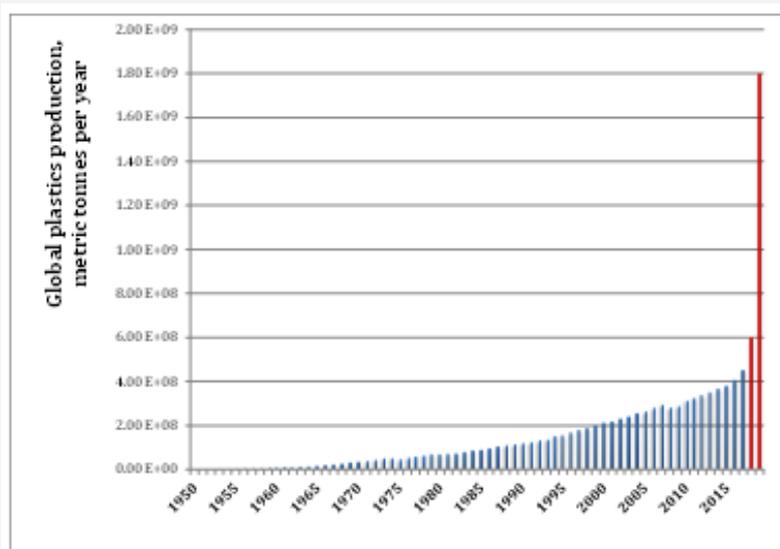

Figure 1: Global plastics production for 1950-2017 and projected levels of production for 2025 and 2050.

Table 1: Main types of plastic resins.

| No	Polymer (resin)	Abbreviation	Areas of application
1	Polyethylene terephthalate	PET	Water and soft drink bottles, salad domes, biscuit trays, salad dressing and peanut butter containers, carriers for magnetic tape and backing for pressure-sensitive adhesive tapes
2	High density polyethylene	HDPE	Milk bottles, freezer bags, dip tubs, crinkly shopping bags, ice cream containers, juice bottles, shampoo, chemical and detergent bottles, bottle caps, coax cable inner insulator, banners, boats, ballistic plates, fuel tanks for vehicles, swimming pool installation, backpacking frames, corrosion protection for steel pipelines, electrical and plumbing boxes, far-IR lenses, folding chairs and tables, microwave telescope windows, chemical-resistant piping, natural gas distribution pipe systems, water pipes for domestic water supply and agricultural processes
3	Low density polyethylene	LDPE	Cosmetic containers, commercial cling wrap, corrosion-resistant work surfaces, packaging for computer hardware and optical disc drives, playground slides
4	Polyvinyl chloride	PVC	Squeeze bottles, cling wrap, shrink wrap, rubbish bags, urine containers, blood containers, blood taking and blood giving sets, catheters, heart-lung bypass sets, hemodialysis sets, commercial signage products, flooring, pipes for municipal and industrial applications, insulation on electrical cables, skiing equipment, shoes, jackets, aprons, and sports bags, wire rope and aircraft cable
5	Polypropylene	PP	Microwave dishes, ice cream tubs, potato chip bags, dip tubs, piping systems, insulation for electrical cables, nonwoven diapers and sanitary products, filters for air, gas, and liquids, cold-weather base layers, warm-weather clothing, carpets, rugs and mats
6	Polystyrene	PS	CD cases, water station cups, plastic cutlery and dinnerware, imitation 'crystal glassware', video cases, smoke detector housings, license plate frames, plastic model assembly kits, Petri dishes, laboratory containers (test tubes and microplates), film capacitors, thermal insulators
7	Expanded polystyrene	EPS	Foamed polystyrene hot drink cups, hamburger take-away clamshells, foamed meat trays, protective packaging for fragile items, molded sheets for building insulation, solid blocks
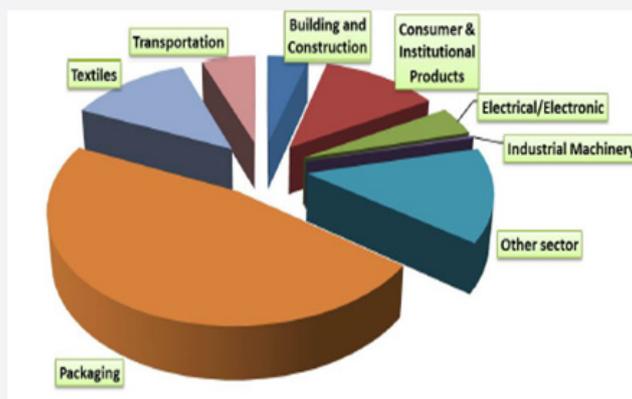
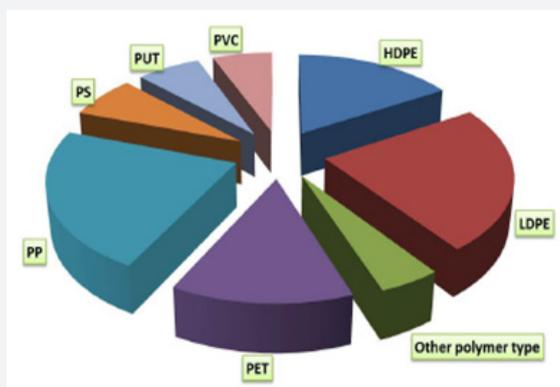**Figure 2:** Share of global plastic waste generation by industrial sector.

Figure 3: Share of global plastic waste generation by type of plastics.

Plastic materials penetrated mankind's everyday life, and everyone is being in the contact with them every day. The main types of plastic resins and areas of their application are summarized in (Table 1). As it follows from Table 1 and (Figure 2), almost a half of produced plastics are used for packaging purposes. As packaging materials, they are especially inexpensive, lightweight and high performing. Other benefits of their usage are that low weight of plastic packaging materials reduces fuel consumption in transportation, and its barrier properties keep food fresh longer, reducing food waste. All these result in the replacing of other packaging materials by plastics. In terms of plastic type, polyethylene terephthalate, polyethylene (high and low density), and polypropylene are mostly applied (Figure 3). Besides the packaging, the last two types play a major role in various piping systems. At the same time, chlorinated polymers (for instance, polyvinylchloride), due to their specific application areas such as medicine (blood containers, blood taking and blood giving sets, catheters, heart-lung bypass sets, hemodialysis sets), building (flooring, pipes for municipal and industrial applications, insulation on electrical cables) and sport (skiing equipment, shoes, jackets, aprons, sports bags), are also of great importance. It should be noted that production of polyvinylchloride is considered nowadays as an important part of the world chlorine industry [5-7].
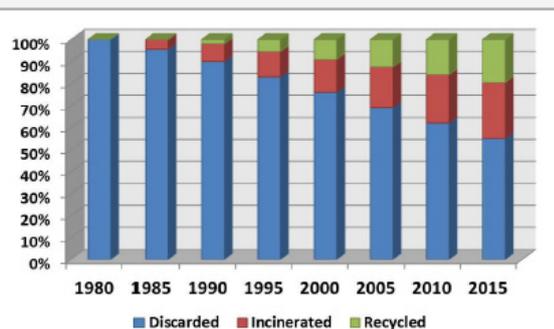

Figure 4: Estimated share of global plastic waste by disposal method.

Despite the attractiveness of the plastics, there are two negative environmental aspects that should be emphasized. First of all, a question of toxicity of such materials is still under open discussion [8-10]. This problem is connected with the facts that polymeric items can contain molecules of unreacted monomers or some additives used to improve both the physical properties of the plastics and their usability. All these components can be slowly extracted from the items and affect the health of the users. Moreover, the polymers are stable only within relatively narrow temperature range, and, thus, they can undergo decomposition being under the action of thermal or physical stress. It results in additional emission of harmful and hazardous contaminants. In the case of halogen-substituted plastics, this situation becomes even more deteriorated [9]. The second "dark side" of the coin deals with growing "mountains" and "oceans" of plastic wastes. As it is evident from Figure 4, until 1980 almost

100 % of plastic wastes were discarded. Nowadays, the portion of discarded wastes does not exceed 60%. Taking into account global production values (Figure 4), it can be estimated that the absolute value of throwaway plastics was doubled during the last 35 years.

Global Plastic Waste Management

In general, utilization of plastic wastes proceeds via one of five main directions shown in (Figure 5) [11-16]. As it was already mentioned, disposal in landfills remains the biggest in volume direction facing the global environmental problem [11]. Then follow incineration, recycling, degradation and composing. Incineration (combustion) process was the first approach for plastics processing [17-19]. In this case, plastics are considered as a solid burnable fuel, and used mostly for heat recovery. It gives the second name for this direction – waste-to-energy. However, depending on the type of plastic, combustion of wastes leads to formation of huge amount of toxic substances [17,20,21]. First of all, it concerns polyvinylchloride and other halogen-substituted polymers. Thereby, from ecological point of view, incineration of such materials should be prohibited. The next direction of the plastic waste disposal, which is under the intensive developing, is recycling [16,21-32]. Depending on the type of exposure, the process can be divided on mechanical and chemical recycling [32]. Chemical recycling, in its turn, combines such sub-processes as chemolysis, pyrolysis, fluid catalytic cracking, hydrogen techniques and gasification. In some cases, the recycling process can be merged with processing of biomass and renewables [27,31]. In general, the present direction is aimed to have at the end of the line production of gaseous and liquid fuels [18,19,21,29,30].

Figure 5: Main directions of the plastic waste disposal.

Degradation and composing are the particular cases of the polymer recycling technologies. Within the composing approach, spent plastic items are considered as additives or fillers for various building and composite materials [25]. Degradation can be abiotic or biological [33]. A concern of efficient biodegradation of non-degradable synthetic polymers using microorganisms and enzymes attracts a growing interest [20,34-39]. Additionally, a new class of bioplastics with shortened biodegradation period

becomes more and more popular, especially for the packaging application [40-43]. Another example of easy degradable polymers is plastics with photocatalysts embedded into polymer matrix [44,45]. Such composite materials could be degraded effectively in ambient air under sunlight exposure. Among the photocatalysts used, titania, zinc oxide, α-FeOOH and $H_3PW_{12}O_{40}$ are the most studied. Kinetics of polymer degradation can be improved by combining the process with chemical exposure. Regarding with it, such processes as hydrolysis, acidolysis, alcoholysis, aminolysis, alcoholysis and glycolysis should be mentioned [46]. Application of supercritical fluids is also reported to contribute to the recycling process efficiency [47-49]. Taking into account all mentioned above, the plastic wastes recycling concept can be schematically presented as shown in Figure 6. Spent plastic items (bottles, containers, bags, pipes, etc.) after the appropriate classification could be recycled into fuel, chemicals, new carbonaceous or composite materials, or incinerated with energy recovery.

Figure 6: Scheme of the plastic wastes recycling.

Nanostructured Carbon Derived from Plastic Wastes

Transformation of polymers into carbon materials is a well-developed process. It underlies the industrial technology for production of carbon fibers via pyrolysis of polyacrylonitrile [50,51]. The temperatures of this process quite often exceed 1000 °C. On the other hand, Prof. Gedanken and co-workers have reported recently in their numerous research papers the efficiency of relatively new approach called reaction under autogenic pressure at elevated temperatures (RAPET) [52-55]. Reactions within this concept are performed in a closed reaction volume. As a result, various nanostructured materials (metal oxides; carbides of silicon, tungsten, and molybdenum; carbons) of unique morphology and properties can be produced. It should be noted that this approach is applicable for the fabrication of carbon-related materials via decomposition of organic precursors [52,54]. In our recent publications it was shown that decomposition of various organic precursors can be successfully performed in a closed reaction volume in the presence of bulk nickel-containing alloys [56-60]. In this case, presence of halogen atoms in the precursor's molecule is strictly necessary to realize the mechanism of metal dusting – self-disintegration of bulk
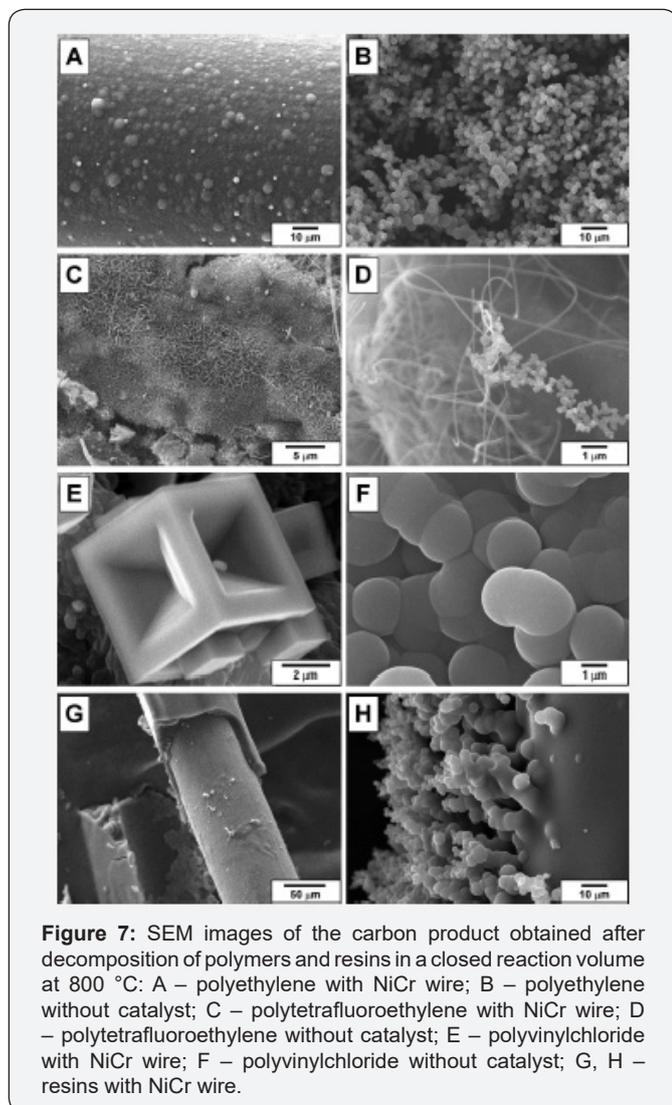
metals under the action of aggressive reaction media [61-63]. If molecule of organic precursor contains some other heteroatoms (for example, nitrogen) then the carbon nanostructures being formed will be doped with these heteroatoms [57].

Up to now, the RAPET approach was applied for recycling of polymer and resin wastes to nanostructured carbon. Similarly, to the recent studies, the RAPET experiments were performed in a quartz ampoule (d = 4-5 mm, V ~ 0.2 ml) used as a reactor. A piece of nichrome wire (commercial Ni-Cr alloy consisting of 80 wt.% Ni and 20 wt.% Cr; 0.2-0.3 mg) was placed in the ampoule together with 2-3 mg of polymer (polyethylene, polytetrafluorethylene, polyvinylchloride) or resin waste. The ampoule with reaction mixture was sealed and brought to thermal treatment at certain temperature for 2 h. After the reaction procedure, the ampoule was carefully opened, and the contents were studied by scanning electron microscopy (SEM) on a JSM-6460 (Jeol, Japan) electron microscope with a resolution of 4 nm in the range of magnifications from 5× to 300,000×. Similar reference experiments were carried out using the same plastics but without adding the catalyst (nichrome wire). Thus, two modes of plastics pyrolysis, thermal and catalytic, were realized.

The resulting SEM data are shown in (Figure 7). Since polyethylene does not contain any halogen atoms, initiation of metal dusting mechanism was not observed. The final material after the RAPET experiment at 800 °C is represented by initial piece of wire covered with spherical carbon deposits (Figure 7A). It should be noted that polyethylene undergoes pyrolysis at the same temperature without catalyst. In this case, the product is also spherical carbon of 1-2 μm in size agglomerated into the secondary mesoporous particles (Figure 7B). Oppositely, polytetrafluorethylene contains a lot of fluorine but no hydrogen, which presence is also important for metal dusting by halogenated organics [64]. At the same time, as it is seen from (Figure 7C), the process of metal dusting takes place and leads to formation of a thick carbon covering around the nichrome wire. The obtained carbon deposits are represented mostly by twisted nanofibers.

Thermal pyrolysis of polytetrafluorethylene at 800 °C results in formation of two types of carbon deposits (Figure 7D): prolonged nanofibers and agglomerated nanospheres of about 100 nm in diameter. The most unique carbon nanostructures were observed after the catalytic pyrolysis of polyvinylchloride (Figure 7E). Note that this organic compound contains both hydrogen and halogen in its composition. The formed deposits are shaped as microcubes with pyramidal cavities. These cubes are 4-5 μm in size. According to data of local energy-dispersion X-ray microanalysis, they contain 70-85 at % of carbon and 15-30 at % of nickel with traces of chlorine. Non-catalytic thermal decomposition of PVC proceeds through trivial route leading to deposition of spherical carbon of 1-2 μm in size, similarly as described above (Figure 7F). The resin wastes can also be decomposed using the RAPET approach. SEM images in Figures 7G and 7H demonstrate result of resin pyrolysis in the presence of nichrome wire at 800 °C. It is seen that carbon deposits

remind fibrous carbon. The thickness of the formed carbon layer is 15-20 μm. Close examination of the product (Figure 7D) has revealed that these fibers are comprised by carbon spheres of 1-2 μm in size.

Figure 7: SEM images of the carbon product obtained after decomposition of polymers and resins in a closed reaction volume at 800 °C: A – polyethylene with NiCr wire; B – polyethylene without catalyst; C – polytetrafluoroethylene with NiCr wire; D – polytetrafluoroethylene without catalyst; E – polyvinylchloride with NiCr wire; F – polyvinylchloride without catalyst; G, H – resins with NiCr wire.

Conclusion

The volume of global plastic production grows year by year with exponential rate. Low self-degradability of the plastic materials leads to accumulation of huge amount of solid plastic wastes, the most part of which is discarded. All these cause appearance of so-called plastic "mountains" and "oceans" having strong negative effect on the environmental, in general, and on human health, in particular. In the present study, application of the RAPET concept for recycling of the plastic wastes into valuable products (nanostructured carbon materials) was examined.

Acnowledgement

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