

Recycling of High-Molecular-Weight Organosilicon Compounds in Supercritical Fluids

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The main known patterns of thermal and/or catalytic destruction of high-molecular-weight organosilicon compounds are considered from the viewpoint of the prospects for processing their wastes. The advantages of using supercritical fluids in plastic recycling are outlined in this entry. They are related to a high diffusion rate, efficient extraction of degradation products, the dependence of solvent properties on pressure and temperature, etc. A promising area for further research is described concerning the application of supercritical fluids for processing the wastes of organosilicon macromolecular compounds.

Keywords: polydimethylsiloxane ; silicone rubber ; supercritical fluids ; recycling

1. Introduction

The accumulation of huge amounts of plastic waste is one of the global challenges that the world is currently facing. Indeed, the serious environmental risks of landfills or the incineration of plastic waste are a growing global concern. Under these conditions, the inevitability of the transition of the polymer industry in the foreseeable future towards the production of either biodegradable or easily recyclable polymers is obvious. Therefore, the biodegradable or easily recyclable polymers can be called the “polymers of the future”. However, in the case of biodegradable materials, one may fear deterioration of consumer properties as a result of preliminary storage for too long or the artificial induction of premature degradation. On the other hand, chemical recycling seems promising, allowing the plastic waste to be disassembled into initial monomers or other useful compounds. The search for new recycling strategies is constantly intensified. The polymers to be disassembled to small building blocks are conceptually reminiscent of KiddyCraft or Lego building bricks: after the end of the usage of the product, it is subject to disassembly into elementary bricks, which, after a simple cleaning procedure for monomers, are again used to build new products.

Unlike most commonly used organic polymers, high-molecular-weight organosilicon compounds (polysiloxanes, silicones) fit well with this strategy. Indeed, not only can they be obtained using waste-free green technologies, but they can also be recycled to initial monomers, oligomers, or derivatives.

In particular, currently there are several strategies for solving the increasingly pressing problem of efficient disposal of plastic waste: (1) mechanical recycling, (2) disposal in specially equipped landfills, (3) incineration with energy release, and (4) chemical recycling. Mechanical recycling ideally does not lead to changes in the chemical structure of the polymer (or these changes are minor) and is certainly an attractive method for the recycling of plastics. However, the widespread use of the mechanical recycling of polymers is fundamentally limited due to high requirements for the purity of feedstock materials, the accumulation of defects in the chemical structure of macromolecules, and the gradual decrease in performance with each processing cycle. Concerning environmental risks, as compared to hydrocarbon polymers, polysiloxanes seem to be relatively safe for landfilling since they are bioinert and readily decompose in soil into hydroxyl derivatives of silicon and low-molecular-weight organosilicon oligomers [1][2][3]. However, the consumption of silicones is growing rapidly, since they are widely used in cosmetics, pharmaceuticals, personal care products, cleaning products, and other everyday goods. Moreover, the degradation products of polysiloxanes are volatile [4], and their possible impact on the environment and living organisms is still not fully understood (indeed, even inert inorganic silica in a highly dispersed state is not completely safe) [5][6][7][8]. All the mentioned factors are of growing concern to the scientific community and promote the search for new strategies for the recycling of polysiloxanes.

2. Recycling of Polysiloxanes in Supercritical Media

2.1. Plastic Waste Recycling in Supercritical Media

There are hundreds of original research papers and a significant number of reviews that are dedicated to the topic of plastic recycling in supercritical media [9][10][11][12]. Most of the research is focused on the study of polymer degradation processes in sc water (SCW) and sc alcohols; however, there are examples of works in which chemical recycling of plastic is carried out in sc acetone, sc ammonia, and a number of other sc media.

Among all the listed sc fluids, the majority of scientific research is dedicated to the study of plastic recycling in SCW. This is not surprising, given that SCW is extremely reactive, the properties of SCW can be controlled by adjusting solvent pressure or temperature, and SCW is absolutely compatible with the environment. Hydrolysis in sub- and supercritical water of polymers obtained in the polycondensation process, such as poly(ethylene terephthalate) (PET), polyamides, or polycarbonates, can lead to the formation of the corresponding monomers in high yields [13][14][15][16]. The situation is more complicated with the most common vinyl polymers obtained in the polymerization process, e.g., with polyolefins, poly(vinyl chloride) and polystyrene. The thermal destruction of polystyrene and polyolefins in SCW leads to the formation of a multicomponent product composed of solid, liquid, and gaseous phases [17]. Although both oligomers in the solid phase and low-molecular-weight compounds in the liquid and gaseous phases may be of interest to the chemical industry or energy industry, the development of an efficient industrial chemical recycling process in this case is associated with obvious difficulties. It should be noted, however, that the isolation of certain products can be facilitated by separating the liquid reaction product into a polar aqueous phase and a non-polar phase containing aliphatic and aromatic hydrocarbons. A separate niche for the use of SCW can be the chemical recycling of polymers containing chlorine or fluorine atoms, since in this case potentially environmentally hazardous elements are “locked” in the water phase, without harmful emissions into the atmosphere. For example, when poly(vinyl chloride) is recycled in SCW, although the composition of the product turns out to be multi-phase and multi-component, due to the dehydrohalogenation reaction, chlorine atoms quantitatively participate in the formation of hydrochloric acid in the aqueous phase [18]. Similarly, if fluoroplastics are recycled in SCW, fluoride ions are localized in the aqueous phase [19][20].

The motivation for the transition from SCW to sc alcohols is a decrease in operating temperatures and pressures (for comparison, the critical point of water is 374 °C and 217 bar, the critical point of methanol is 240 °C and 78 bar, the critical point of ethanol is 241 °C and 63 bar) as well as reduction of the corrosion load on high-pressure reactor equipment (it is well-known that sub- and sc water in the presence of ions is an extremely corrosive medium). The general trends in the chemical recycling of the common types of plastics remain unchanged during this transition: in the case of recycling of PET, polycarbonates, and polyamides, monomers or chemical derivatives of monomers can be obtained in high yields; for the vinyl polymers the recycling products have complex phase and component composition. The processing of PET in sc methanol is one of the most scientifically and technologically developed processes of this kind. The products of PET methanolysis are dimethyl terephthalate and ethylene glycol, which can be used as monomers for further synthesis of PET [21].

Both mechanical and chemical recycling strategies for PET are currently implemented on industrial level; the obtained recycled PET (rPET) is used in various applications [22]. It is important to note that chemical recycling of PET in sc methanol is a rare example of a supercritical fluid recycling process for which industrial implementation has been carried out: a pilot plant for PET methanolysis was launched by Mitsubishi Heavy Industries, Ltd. (Japan).

From a practical point of view, one of the most interesting areas of the application of sc media in the processes of plastic recycling is the chemical recycling of materials of complex composition and structure: crosslinked polymers, resins and vulcanized rubbers [23][24], thermosetting materials [25][26][27][28], carbon-fiber-reinforced polymers (CFRPs), and fiberglass-reinforced plastic materials. For example, the processing of CFRPs in sc water and sc alcohols leads to chemical destruction of the polymer component of the composite while retaining the reinforcing carbon fiber. It is important to note that in this process carbon fiber is not subjected to destruction or deformation, completely retains its mechanical properties, and is ready for reuse.

2.2. Recycling of Silane-Crosslinked Polyethylene in SCW and sc Alcohols

Crosslinked polyethylene (XLPE) is a chemically resistant, durable material that can be used, for example, as an insulator for high voltage cables or as a material for water pipes or heating systems. One of the options for chemical crosslinking of polyethylene chains is “silane crosslinking”, in which the crosslinking agent is a silane with various functional chemical groups. Typically, such silanes contain one vinyl group and two or three hydroxyl groups. Then, at the first stage, the silane is grafted to the PE polymer chain (alternatively, ethylene can be copolymerized with vinyl-silane), and at the

second stage, the condensation of hydroxyl groups occurs with the formation of siloxane chemical links (--Si--O--Si--) between the PE chains. This process for making silane-crosslinked PE (silane-XLPE) is chemically flexible and economically viable, while the resulting silane-XLPE is a robust high-performance material. At the same time, due to the presence of chemical links between PE chains, this material is particularly difficult for mechanical recycling. The optimal recycling strategy for silane-XLPE seems to be selective de-crosslinking, followed by re-molding and re-setting of the material. Although the siloxane bond in silane-XLPE can undergo selective hydrolysis or alcoholysis, the strong hydrophobicity of silane-XLPE makes it difficult for polar solvents such as water or alcohols to dissolve in the material and participate in the reaction. In this regard, the tunable properties of supercritical fluids, and in particular the decrease in polarity of sc water and sc alcohols with increasing temperature, arguably make them an ideal solvent for the silane-XLPE recycling process.

The chemical recycling of silane-XLPE in sc media was first proposed by T. Goto et al. [29]. To obtain silane-XLPE, the authors used vinyltrimethoxysilane as a crosslinker and dibutyltin dilaurate as a catalyst; after the crosslinking procedure, the gel fraction of the obtained silane-XLPE was 60%. Then silane-XLPE was decomposed in sc water and sc methanol, and the molecular weight and gel fraction were determined for the product after this treatment. The results show that when silane-XLPE is processed in sc methanol, the gel fraction is 0 at a treatment temperature above 300 °C, while for the treatment in SCW, the gel fraction is absent only at treatment temperatures above 370 °C. At the same time, during the destruction of silane-XLPE in SCW, the molecular weight of the product decreases compared to the molecular weight of the initial non-crosslinked PE, which indicates the destruction of the PE backbone as well. In sc methanol, the cleavage of crosslinking elements proceeds selectively, without degradation of the PE backbone. Analysis of the degradation products by NMR spectroscopy showed that a small amount of dimers was present in the product, but most of the siloxane crosslinks decomposed to alkoxysilane after exposure to sc methanol. In conclusion, the authors demonstrate that the product of chemical recycling of silane-XPE in sc methanol can be crosslinked again after re-molding, albeit with some loss of performance. In Ref. [30] the authors continue the study of the process of selective cleavage of crosslink elements in silane-XLPE, in which the results are compared when the process is carried out in various sc alcohols. It is shown that the efficiency of crosslink breaking decreases in the series: methanol, ethanol, 1-propanol, isopropanol.

After the first works demonstrated the high potential of the process under consideration, a number of further studies were focused on its technological implementation. The authors of Refs. [31][32][33] present various options for implementing a continuous process using extrusion technologies. The study [32] shows the possibility of efficient processing of silane-XLPE in sc 1-propanol on a pilot industrial plant, consisting of two extruders and providing a processing volume of 20 kg/h. In Ref. [31], processing was carried out on a model single-screw extruder in order to increase the economic efficiency of the process.

Baek and co-workers studied the kinetics of the selective de-crosslinking of silane-XLPE in sc alcohols in a batch process [34] and in a continuous process [33][35][36]. For example, in their Ref. [34], the authors described the study on the rate of de-crosslinking of silane-XLPE in a batch process in an excess of sc methanol in the temperature range of 300–400 °C. The results show that the kinetics of the process correspond to a first-order reaction with respect to the content of the gel fraction. As the temperature increases, the rate constant increases from 0.02 min⁻¹ at 300 °C to 5.3 min⁻¹ at 400 °C. At the same time, at temperatures above 360 °C, a decrease in the molecular weight of PE occurs. These results are of undoubted interest for an adequate choice of the optimal process parameters for the chemical recycling of silane-XLPE. The work also shows that the de-crosslinking of XLPE in sc methanol occurs more efficiently for silane crosslinks than for peroxide ones. The reaction kinetics does not undergo significant changes upon transition from a batch process to a continuous process [35], indeed, the experimental data still indicates a first-order reaction. In addition, it was confirmed that the rate constant increases with increasing temperature according to the Arrhenius law. Finally, in Ref. [36], a comparison of the kinetics of the de-crosslinking of silane-XLPE in various sc alcohols and in SCW is given. It is shown that at 380 °C the reaction rate constants for sc methanol, ethanol, 2-propanol, and water are, respectively, 2.8 min⁻¹, 2.6 min⁻¹, 2.4 min⁻¹ and 2.1 min⁻¹. The authors conclude that sc ethanol, which exhibits a reaction rate similar to sc methanol, but is not toxic, may be the optimal choice of sc alcohol for the industrial implementation of chemical recycling of silane-XLPE.

Thus, selective de-crosslinking of silane-XLPE in SCW and sc alcohols is an important example of a process, where the areas of plastic recycling in supercritical fluids and chemical recycling of silicones overlap. It should be highlighted that the efficiency of the process under consideration is directly linked to unique properties of the mentioned supercritical media. More specifically, the decrease in the polarity of water and alcohols in the sc state allows for higher affinity of the fluids towards the PE backbone, while high reactivity promotes selective de-crosslinking.

3. The Prospect of Chemical Recycling of Polysiloxanes in sc CO₂

The critical pressure of sc CO₂ is ≈74 bar, which is much lower than the critical pressure of water but comparable to the values for ethanol or propanol. The critical temperature of CO₂ (≈31 °C) is significantly lower than that of all the sc fluids considered above, which makes it possible to carry out various chemical or technological processes in sc CO₂ under “softer” conditions, as compared to sc water and even to sc alcohols. Supercritical CO₂ also compares favorably with sc alcohols in that it is a non-flammable and non-toxic solvent. In addition, the fundamental difference between sc CO₂ and SCW or sc alcohols is that under normal conditions CO₂ is a gas: this greatly facilitates the process of its purification and reuse in industrial processes.

For the process of chemical recycling of plastics, sc CO₂ is considered mostly as a solvent and not as an active medium, unlike SCW and sc alcohols; this is due to the high chemical inertness of CO₂ molecules. For example, the extraction processes in sc CO₂ are well developed from a technological point of view, which makes it possible to use sc CO₂ to extract various functional additives from PE and PP [37][38]. Such extractions can be used for pre-treatment of plastic before its mechanical or chemical processing or for the extraction and reuse of the functional additives themselves, i.e., flame retardants, antioxidants, and others. As applied to chemical recycling, extraction with sc CO₂ can be used to purify and separate the products of thermal oxidation of polyolefins [39]. Finally, the authors of Refs. [40][41] show that the thermochemical degradation of polyolefins in oxygen-enriched sc CO₂ leads to the formation of paraffins and low-molecular-weight acids in high yields. The papers compare thermochemical degradation in pure oxygen under pressure and sc CO₂ with the same amount of oxygen and show that sc CO₂ facilitates the formation of oligomers from high-molecular-weight polyolefin molecules. The detected increase in the reaction rate of thermochemical degradation of polyolefins in sc CO₂ can be associated with the plasticization of the polymers, which facilitates the access of oxygen molecules to polymer chains.

The foaming of plastics in sc CO₂ can also be considered promising as part of the recycling strategy. In Refs. [42][43], the authors describe the process to obtain a polymer composite based on microcellular PP foamed in sc CO₂ and rubber waste. Note that plastic waste can be used both as a filler, as in Refs. [42][43], and as a matrix. For example, the production of foamed PET can be a cost-effective alternative to the standard process of its mechanical or chemical recycling [44].

Polysiloxanes are a rare example of macromolecular compounds with relatively high solubility in sc CO₂. The authors of Ref. [45] provide data on the phase behavior of PDMS of various molecular weights in sc CO₂: at a polymer concentration of 5 wt.%, PDMS with $M_w = 38,900$ g/mol showed the minimum cloud point pressure at 270 bar and 47 °C; as M_w increases these values also increase and for PDMS with a molecular weight of 273,500 g/mol they were 380 bar and 62 °C. The authors report that further increase in M_w had no significant effect on the phase behavior of the system. The solubility of PDMS increases significantly with the decrease in molecular weight, and oligomers with molecular weight around 400 g/mol are soluble even in the liquid phase of two-phase CO₂ at room temperature; at 40 °C, the minimum cloud point pressure for these oligomers in sc CO₂ is below 100 bar in the concentration range of 1–4 wt.% [46]. The authors note that for PDMS oligomers, the structure of the end groups has a significant effect on the solubility in sc CO₂. Low-molecular-weight organosilicon compounds, such as alkoxysilanes of various structures [47][48], chlorosilanes [49], allylsilanes, etc., are also readily soluble in sc CO₂.

The variety of functional properties of organosilicon compounds and the unique features of sc CO₂ as a solvent make their combination in various chemical processes highly promising. In the review paper [50], the examples of such processes are given, namely, the synthesis of polymers and polymer composites, the design of polymer membranes, including composite membranes with organosilicon or silica inclusions [51][52], as well as the modification of various surfaces with functional organosilicon compounds. The process of one-step synthesis of porous organosilicon matrices is of particular interest. This concept was first presented in Ref. [53], where it was shown that during the polycondensation of alkoxysilanes in sc CO₂ with the addition of anhydrous formic acid, a porous monolithic material (aerogel) is formed in a simple one-step process that does not require time-consuming and resource-intensive stages of solvent replacement and drying. Another option for the one-step preparation of organosilicon aerogel directly in sc CO₂ is the hydrosilylation reaction involving polymethylhydrosiloxane and PDMS oligomers with vinyl end groups [54][55]. By varying the composition and structure of macromonomers in the described process, one can effectively control the morphology and mechanical properties of the resulting porous materials [56]. The resulting aerogels are superhydrophobic, while they adsorb hydrocarbon compounds well, and thus they can be used in the field of environmental protection, namely for water purification during oil spills.

There are no direct examples of the use of sc CO₂ in the chemical or mechanical recycling of polysiloxanes in the scientific literature, though the concept is very promising. Indeed, low-molecular-weight organosilicon compounds

demonstrate high solubility in sc CO₂. This fluid efficiently extracts low-molecular-weight products from polymer matrices. The polymerization reaction of silicones is an equilibrium one. Efficient extraction of low-molecular-weight cycles should pronouncedly shift the reaction towards the breakdown of polymer chains. The only problem is to find proper conditions (i.e., catalysts) for accelerating the slow reaction kinetics.

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