

**Environmentally advantageous thermooxidative
transformation of poly(vinyl chloride)**

PhD thesis

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I. Introduction and aims

Nowadays, polymer industry is the biggest chemical section in our homeland. The products made from polymers with extremely broad variety of structures cause considerable problem as high amounts of waste. Significant research efforts are going on worldwide to find new ways as environmentally advantageous alternatives to the routine waste treatment procedures, such as incineration and disposing them to the landfill. The biggest problems are related to chlorinated polymers, because during incineration toxic gases disengage from them. Among chlorinated polymers, poly(vinyl chloride) (PVC) is produced in the largest amount in the world. PVC is broadly applicable for many purposes, but as a waste it does not break down in the environment. During its incineration, less energy can be earned than in the case of polyolefins and the arising harmful materials need additional handling. Because of all these aspects, my aim was to carry out fundamental research on thermooxidative degradation processes which have been seldom investigated despite their significance, but which can be potentially useful for waste management or recycling of PVC.

During my work, the mild thermooxidative degradation of PVC was investigated because PVC normally processed in the presence of air at about 200 °C. However, it is interesting to note that in spite of the significance of thermooxidation of PVC, remarkable research results on this process only occasionally can be found in the literature.

Scientists nowadays start to realize that the degradation of plastic products is a complex process, and every additive can affect the arising products of degradation. This significantly encumbers revealing and investigating the details of single elementary processes. In order to avoid these difficulties in the course of my investigations, the degradation experiments were made in solution because this way the single reactions can be better studied than in the case of solid samples. As a solvent, dioctyl phthalate (DOP, bis-2-ethyl-hexyl

phthalate), the plasticizer of PVC used in the largest amounts was used. To determine the degree of degradation, the amount of the eliminating HCl from PVC was monitored, and for the degraded PVC the average molecular weights, the molecular weight distribution and the structure of the degraded polymers were also examined. The thermal properties of the thermooxidatively degraded PVCs were investigated as well.

The effect of the 2,6-di-tert-butyl-4-methyl-phenol (BHT) antioxidant on the thermooxidative degradation of PVC in dioctyl phthalate was also investigated in order to determine whether the mild thermooxidative degradation of PVC in the case of products containing BHT can be also utilized.

Investigations were carried out to determine the effect of the relative amount of dioctyl phthalate by carrying out the thermooxidative procedure in dioctyl phthalate/1,2,4-trichlorobenzene solvent mixtures.

The recycling ability of the thermooxidatively pretreated PVC was attempted in a model experiment, in which polymer blends were made with poly(lactic acid) a biodegradable polymer. The thermal properties of the blends were also investigated.

II. Applied methods

The amount of the evolved HCl gas during the thermooxidative degradation process was monitored by conductometry via a Metrohm PVC Thermomat 763 equipment. The molecular weight distribution, number and weight average molecular weights and polydispersity values were determined with gelpermeation chromatography. The structure of the predegraded PVCs was investigated with Fourier-transformed infrared spectroscopy (FTIR), and different kinds of magnetic resonance spectroscopy such as ^1H NMR, ^{13}C NMR,

DOSY NMR, HSQC and HMQC two dimensional NMR spectroscopies. The thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA).

III. New scientific results

1. The primary and secondary processes of the thermooxidative degradation of PVC were investigated in solutions made with its industrially most widely applied plasticizer, dioctyl phthalate. It was surprisingly found that significant chain scission of PVC occurs under the mild conditions applied by me. Such results have not been reported in the literature yet. The molecular weight data indicate that this chain scission process proceeds with constant rate during the starting period of the degradation (up to ~2 hours) independently of the degree of degradation. At longer degradation times (~4 hours), oily products were formed.
2. Structural investigations of the degraded PVCs showed that the polymer was oxidized, and some extent of degradation of the dioctyl phthalate took also place under these circumstances. The products from this reaction are partially connected to the PVC. DSC investigations revealed that the partial oxidation of PVC and the connection of dioctyl phthalate to the polymer backbone decreased the glass transition temperatures, that is this process results in internal plasticization.

3. It was proved that the concentration of dioctyl phthalate has also an effect during degradation. The effect of the amount of the dioctyl phthalate on the thermooxidative degradation of PVC was investigated in dioctyl phthalate/1,2,4-trichlorobenzene (DOP/TCB) solvent mixtures. It was found that the amount of dioctyl phthalate can be reduced to 10% without the significant decrease of the rate of the degradation processes.

4. Beside the oxidation sensitive plasticizers, antioxidant is added to polymers to avoid undesired effects. Therefore, the effect of the most commonly used antioxidant, 2,6-di-tert-butyl-4-methylphenol (BHT) was investigated on the thermooxidative degradation of PVC in order to explore whether it is able to inhibit the changes during thermooxidative degradation. According to my results, BHT is not able to prevent the chain scission of PVC during thermooxidative degradation. It has some initial stabilizing effect from the point of dehydrochlorination, and as a consequence chain scission occurs with lower extents than that in the case of unstabilized PVC in this initial stage. From these findings, it can be concluded that our process is applicable for the high extent break down of PVC wastes with BHT content under mild thermooxidative conditions.

5. The mixing of PVC, degraded under thermooxidative circumstances, with poly(lactic acid) (PLA) a biodegradable polymer was investigated. It was found that in contrast to the unsuccessful blending of the starting, untreated PVC, the thermooxidized PVCs are miscible with poly(lactic acid) in a wide range of composition. This may create unique opportunities to manufacturing of new kinds of blends made from waste PVC and biodegradable poly(lactic acid).

IV. The importance of the new scientific results

During my work, the thermooxidative degradation of poly(vinyl chloride) was investigated, because in spite of the fact that the processing of this polymer takes place under these circumstances, beyond inert thermal degradation studies, data can hardly be found on the details of this process in the literature. I obtained the surprising result, unprecedented in the literature, that the thermooxidative degradation of PVC in dioctyl phthalate leads to significant scission of the polymer chains, and longer reaction times (~4 hours) produce oily product. This result may create the opportunity for a new environmentally advantageous modification and breakdown of PVC. The structure of the thermooxidatively degraded PVC was investigated in details, and it was found that the oxidation products of dioctyl phthalate and PVC was connected during this process. This way, a partially oxidized, internally plasticized product with unique structure was obtained. The effect of the relative amount of the applied plasticizer was also investigated, because polymer products can contain plasticizers in different amounts. An optimal concentration range was observed, in which the degradation took place without rate decrease. Since it was found that the BHT antioxidant cannot prevent the chain scission of PVC under thermooxidative circumstances, the stabilized PVCs can be also decomposed or modified by the mild thermooxidative treatment developed in the course of my research. The successful blending of the the thermooxidatively predegraded PVC and poly(lactic acid), a biodegradable polymer may open new routes in the field of waste management.

V. List of publications and presentations

V. 1. Publications

1. Szarka Gy., Iván B.: „Environmentally benign mild degradative transformation of poly(vinyl chloride) into useful products”, *Polym. Prep.*, **2007**, *48*, 584-585.
2. Szakács T., Szarka Gy., Pollreisz F., Szesztay A., Iván B.: „A PVC termooxidatív láncszakadása oldatban”, *Műanyag és Gumi*, **2007**, *44*, 89-93.
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4. Szarka Gy., Iván B.: „Degradative transformation of poly(vinyl chloride) under mild oxidative conditions” In: Celina MC, Wiggins JS, Billingham NC (szerk.) *Polymer Degradation and Performance*, Washington: American Chemical Society, **2009**, pp. 219-226. (ISBN: 978-0-8412-6978-1)
5. Iván B., Pálfi V., Szarka Gy.: „Novel functional polymers by terminal and pendant functionalizations via thiol-ene and thiol-polyene click reactions”, *Polym. Prepr.*, **2010**, *51*, 715-716.
6. Szarka Gy., Iván B.: „Environmentally Advantageous Utilization of Degraded Poly(vinyl chloride)”, *Polym. Prepr.*, **2010**, *51*, 681-682.
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V. 2. Presentations and posters

1. Szarka Gy., Iván B.: Environmentally benign mild degradative transformation of poly(vinyl chloride) into useful products, American Chemical Society Meeting, Chicago, March 25-30, 2007
2. Szarka Gy., Szesztay A., Iván B.: A poli(vinil-klorid) környezetileg előnyös lebontása, termékeinek analízise infravörös spektroszkópiával és gélpermeációs kromatográfiával, Centenárium Vegyészkonferencia, Sopron, 2007. május 29.-június 1.
3. Szarka Gy., Szesztay M., Iván B.: Environmentally advantageous thermooxidative transformation of poly(vinyl chloride), European Polymer Congress, Portoroz, 2-6 July 2007
4. Szarka Gy., Iván B.: A poli(vinil-klorid) környezetileg előnyös termooxidatív átalakítása, XIII. Nemzetközi Vegyészkonferencia, Kolozsvár, 2007. november 8-11.
5. Erdődi G., Fodor Cs., Groh Werner P., Haraszi M., Iván B., Kali G., Mezey P., Pálfi V., Soltész A., Szabó L. S., Szanka I., Szarka Gy., Verebélyi K.: Új nanoszerkezetű polimer rendszerek, mint új nanohibrid anyagok platformja, A Magyar Tudomány Ünnepe 2007, Budapest, 2007. november 14.
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 11. Szarka Gy., Szesztay M., Iván B.: Environmentally advantageous degradative transformations of poly(vinyl chloride) under conditions, European Polymer Congress, Graz, Austria, 12-17 July, 2009 (poster)
 12. Szarka Gy., Iván B.: New ways for blending biodegradable polymers with poly(vinyl chloride), 2nd International Conference on Biodegradable Polymers and Sustainable Composites (BIOPOL-2009), Alicante, Spain, 30 September-2 October, 2009
 13. Szarka Gy., Iván B.: Environmentally Advantageous Utilization of Degraded Poly(vinyl chloride), 39th American Chemical Society National Meeting & Exposition, March 21-25, 2010, San Francisco

14. Szarka Gy., Iván B.: A PVC újrahasznosítási lehetőségei enyhe termooxidációval és a kapott anyagok blendjei politejsavval, Műanyagok Körforgása II., Magyar Kémikusok Egyesülete Szakosztályi Ülés, Tiszaújváros, 2010. május 11.
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16. Iván B., Pálfi V., Szarka Gy.: Novel functional polymers by terminal and pendant functionalizations via thiol-ene and thiol-polyene click reactions , 240th ACS National Meeting & Exposition, Boston, USA, August 22-26, 2010
17. Iván B., Galát M., Illés G., Lórántfy L., Pálfi V., Szabó Á., Szanka I., Szarka Gy.: Novel Functional Polymers by High Efficiency Reactions: From Environmentally Benign Ozonolysis to Thiol-Polyene and Other Click Reactions, 3rd EuCheMS European Chemistry Congress, Nürnberg, August 29 - September 2, 2010
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22. Németh B., Verebélyi K., Kasza Gy., Szarka Gy., Iván B.: Hiperelágazásos polisztirol szintézise stzirol és divinil-benzol karbokationos kopolimerizációjánval környezetileg előnyös reakciókörülmények között, MKE I. Nemzeti Konferencia, Sopron, 2011. május 22-25.
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