

KURZFASSUNG

Die Polyurethane stellen eine extrem vielgestaltige Kunststoffklasse dar, außerdem zählen sie, von den Produktionskosten her, zu den höherwertigen Kunststoffen. Ersteres erschwert die Entwicklung von Recyclingverfahren, letzteres ist der Grund, weshalb trotzdem seit längerem an Wiederverwertungsmethoden für Polyurethane gearbeitet wird. Eine ganze Reihe von Verfahren existieren bereits und werden mit Erfolg angewendet. Da es aber immer noch PUR-Typen gibt, die bisher nicht erfolgreich wiederverwertet werden können, besteht weiterhin Bedarf an zusätzlichen Verfahren.

Bei der Hydrolyse von Polyurethan-Abfällen wird das Material unter Zugabe von Wasser weitgehend in seine Ausgangsbestandteile zerlegt. Aufgrund einiger schwierig zu bewältigender Verfahrensschritte wird die Hydrolyse bisher nur im Labor- und Technikumsmaßstab angewendet. In dieser Arbeit wurde nun ein Hydrolyseverfahren entwickelt, bei dem die Auftrennung in die Bestandteile nur bis zu einem bestimmten Grad durchgeführt wird, also ein partieller Abbau stattfindet.

Der partielle hydrolytische Abbau wurde in einem Doppelschneckenextruder ausgeführt. Die Produkte („hydrothermisch abgebautes Polyurethan“; HA-PUR) wurden durch Bestimmung des unlöslichen Rückstands und der Viskosität, mittels Infrarotspektroskopie sowie mit Hilfe der Thermogravimetrie mit angeschlossener Massenspektrometrie charakterisiert.

Ausgehend von den Eigenschaften des Zwischenproduktes HA-PUR wurde nach Anwendungsmöglichkeiten gesucht.

HA-PUR lässt sich hervorragend mit Duromeren mischen. Diese Tatsache wurde genutzt, um die heute als Zähmodifikator für Duromere gebräuchlichen, aber teuren funktionalisierten Flüssigkautschuke durch ein preisgünstiges Recyclingprodukt zu ersetzen. Tatsächlich wirkte sich ein Zusatz von HA-PUR zu Duromeren günstig auf deren mechanische Eigenschaften, wie Bruchzähigkeit, Bruchenergie und Schlagzähigkeit aus. Weiterhin konnte HA-PUR auch als Härter für Epoxidharze eingesetzt werden.

Die kautschukähnlichen Eigenschaften von HA-PUR legten dessen Verwendung als Füllstoff in Kautschukrezepturen nahe. In Anteilen von 10-20 Gew.-% bewirkte HA-PUR bei einigen Kautschuksorten eine beschleunigte Vulkanisation sowie eine Verbesserung der mechanischen Eigenschaften. Im Falle einer Verschlechterung des Eigenschaftsprofils war es möglich, diese durch geringfügige Variationen der Rezeptur auszugleichen.

HA-PUR besitzt gewisse thermoplastische Eigenschaften. Daher wurde auch die Möglichkeit erprobt, es als Zähmodifikator für Polyoxymethylen (POM) einzusetzen. (Die Verwendung von thermoplastischem Polyurethan für diese Zwecke ist heute bereits Stand der Technik.) Bei Zusatz von 5 Gew.-% HA-PUR wurde eine leichte Erhöhung der Schlagzähigkeit festgestellt.

ABSTRACT

This work was aimed at studying the hygrothermal decomposition of polyester urethanes and the usability of the products in thermosets, rubbers and thermoplastics.

Polyurethanes (PUR) are one of the most versatile groups of plastic materials. The variety of PUR types reaches from flexible foams and rigid foams over thermoplastic elastomers to adhesives, paints and varnishes. This variety is one of the reasons, why the development of cost-efficient recycling methods is very difficult. On the other hand, the production of PUR is rather expensive - compared to the mass-produced plastic materials like the polyolefins. This fact was the reason for the development of recycling methods for PUR since the 60s. The recycling routes for PUR can be divided in mechanical and chemical methods. Mechanical methods cover e.g. grinding of PUR waste, compression moulding, adhesive pressing, bonding. Chemical methods (also called feedstock recycling) change the chemistry of the material. A third group of recycling methods is the recovery of energy. This can mean simple incineration of the PUR waste or the decomposition by pyrolysis or hydrogenation and the combustion of the products.

Chemical methods are e.g. glycolysis and hydrolysis. Glycolysis, which is already used on a commercial scale, means the decomposition of PUR by diols (e.g. glycol) at elevated temperatures through a transesterification reaction. The reaction products are polyols which are similar to the virgin components and can be directly used for the manufacture of new PUR. Amines can be products of side reactions of the glycolysis.

Hydrolysis of polyurethane waste means decomposition of the material to its virgin components by treatment with water at elevated temperatures. The products are polyols and amines which are related to the virgin isocyanates. After purification, the polyols can be used for the production of new PUR, as well as the amines - after conversion into isocyanates by phosgenation. Since there are still some problems with the processing (e.g. the separation of the amines), the hydrolysis of PUR waste has not yet been used on a commercial scale.

In this work, a process of hydrolysis has been worked out which does not lead to the virgin components. The formation of these virgin components can be avoided by stopping the process before reaching the state of complete decomposition.

This partial hygrothermally decomposition was carried out in a twin-screw extruder at temperatures between 150 and 250 °C and addition of 10 wt.-% of water. The material used for this process was polyester-PUR waste from the footwear industry and was ground into

particles of 1-3 mm size. The products („hygrothermally decomposed polyurethane“; HD-PUR) were characterized by determination of the insoluble residue and melt viscosity. The hygrothermal decomposition was traced by infrared spectroscopy and by thermogravimetry combined with mass spectrometry. These examinations allowed a monitoring of the decomposition degree. Further, some information about the chemical processes during decomposition could be obtained.

Based on the specific properties (consistency upon decomposition stage, compound containing primary and secondary amines) of HD-PUR attempts were made to check its use in selected thermoset, rubber and thermoplastic combinations.

HD-PUR is quite well miscible with thermosets such as epoxy resins (EP) phenolic resins (PF), and unsaturated polyester resins (UP). This fact was utilized for replacing the expensive functionalized liquid rubbers, which are used for toughening of thermosets, by this cost-efficient recycling product. The mixing of HD-PUR, especially with EP, leads to a clear improvement of the mechanical properties like fracture toughness, fracture energy, and impact toughness. Due to this promising results, the emphasis for further investigations was placed on experiments with HD-PUR in EP. Two EPs (one trifunctional and one tetrafunctional) of Ciba were used. Examinations of fracture surfaces by scanning electron microscopy gave some information about the phase structure and the toughening mechanism. Dynamic-mechanical thermoanalysis made it possible - apart from the investigation of other mechanical properties - to determine the crosslink density which was then correlated with the fracture mechanical data. The addition of HD-PUR in small amounts (up to 20 wt.-%) led to improved toughness along with only slightly reduced stiffness. It should be noted, that even mixtures with 80 wt.-% HD-PUR gave a curable resin yet with reduced stiffness and temperature resistance. HD-PUR alone could act as hardener for epoxy resins. Further, one phenolic resin, one unsaturated polyester resin, and one vinylester-urethane hybrid resin were examined. The results were, compared to the experiments with EP, less promising.

Due to its rubber-like properties, especially when extruded at lower temperatures, HD-PUR seemed to be qualified for using as polymeric filler and extender in rubber recipes. Five sorts of rubbers (natural rubber, nitrile-butadiene-rubber, styrene-butadiene-rubber, epoxidized rubber and fluoro rubber) were mixed with HD-PUR in ratios of 10-20 wt.-%. If possible, standard recipes without further additives were used. The changes of the rheological properties and the vulcanization behaviour were checked. The results showed, that HD-PUR not only could be regarded as neutral filler, but also as a kind of reactive plasticizer which could influence the

vulcanization behaviour and the mechanical properties. Indeed, the vulcanization rate and the tear strength of natural rubber was increased. If there was any deterioration of the performance, this could be compensated by small variations of the related recipes. Some experiments were conducted with regard to the comparison of two different vulcanization systems and two different grades of carbon black.

The applicability of HD-PUR as modifier for thermoplastics has been checked by adding HD-PUR to poly(oxymethylene) (POM). The modification of POM with thermoplastic PUR is already the state of the art. Due to its thermoplastic properties, HD-PUR should be suitable for this application. Mixing of HD-PUR with POM was possible in amounts from 5 - 40 wt.-%. If 5 wt.-% of HD-PUR was added, the impact toughness of POM was slightly increased. Higher amounts of HD-PUR led to a decrease of impact toughness, tensile strength and Young's modulus.

Future works could provide the complete clarification of the chemical reactions during the hygrothermal decomposition. The related information could serve for improved process control and for extending the decomposition on PURs of polyether type. Further, the applicability of HD-PUR as toughening agent for other (brittle) materials should be checked. The modification of thermoplastics still offers a wide field of applications. Also the use of HD-PUR as reactive filler in rubber recipes could be worked out. Finally, some other applications for HD-PUR, e.g. as pressure sensitive adhesive, as sealing material or for sound and vibration damping could be tested.