MICROBIAL DEGRADATION OF POLYURETHANE FOAMS 
AND ISOCYANATE BASED POLYUREAS IN DIFFERENT 
MEDIA

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Abstract. To assess the possibilities of the liberation of toxic aromatic amines under different conditions of disposal, the degradation of different 14C-labelled polyurethane foams was investigated in the leachate of a refuse tip, in composted municipal waste and in an agricultural soil. With unlabelled foam cubes experiments were run under the environmental conditions of a refuse tip. The degradation of 14C-labelled polyureas was studied in different agricultural soils. In the laboratory tests the criteria of degradation were the liberation of aromatic amines and the production of 14CO2. The degradation in the refuse tip was estimated on the basis of weight loss.

From the results it can be assumed that the polyether based polyurethane foams are largely resistant to microbial as well as chemical attack under all practical conditions of disposal. Polyester based polyurethane foams are susceptible to chemical hydrolysis favored by extreme environmental conditions such as high temperature and/or low or high pH values. Under these circumstances an accumulation of aromatic amines can occur if their further microbial degradation is impeded by the lack of suitable conditions for the growth of microorganisms. No indication of any degradation of the isocyanate based polyureas was found.

1. Introduction

The microbial degradation of synthetic polymers has been studied in the past from two points of view. The first concerns the destruction of plastic materials by microbial degradation which could affect the intended use of the polymers. The second concerns the important necessity of incorporating waste polymers into the biocycle by the action of microorganisms. Information from these extensive studies indicates that the majority of plastics produced, the thermoplastic such as the polyolefins, polyvinylchloride and polystyrenes, are largely resistant to microbial attack and hence cannot be recycled into the environment. Some of remaining polymers such as polyamides, phenolic resins, polyacrylic esters can be attacked by microorganisms, but the degradation is slow and superficial. Definite and fast degradation occurs only in the case of various cellulose derivatives (Wallhäuser, 1972; Potts et al., 1973).

Despite the fact that the plastic products in use are harmless from a toxicological point of view, there are strong objections to the use of some of the monomers. The question arises as to whether these toxic substances are released into the environment when the polymer structure is degraded. As a result of the high recalcitrance of most polymers, it follows that there should be no risk of liberation of toxic monomers or metabolites into the environment, but in this respect no information is available on the fate of polyurethane (PUR) foams under the influence of microorganisms. Degradation experiments carried out in the past by several authors (Kaplan et al.,
1968; Darby and Kaplan, 1968; Hendrick and Crum, 1968; Filip, 1978) led only to the general conclusion that polyester-based PUR-foams are susceptible to microbial attack whereas the polyethers are completely or almost completely resistant. In all these experiments, no attempts were made to analyse the formation of metabolites.

The object of this research was to find out by using $^{14}$C-labelled PUR-foams whether the microbial activity of different media could lead to the release of aromatic amines. The detection of $^{14}$CO$_2$ during the test period should give an indication of the breakdown of any liberated toluene-diamine (TDA) or diphenylmethane-diamine (MDA). As an additional test, the degradation of unlabelled foam cubes in a sanitary fill was followed by macroscopic and gravimetric analyses.

A further problem concerning environmental pollution by the aromatic amines mentioned above is the transport of the corresponding isocyanates, 2,4- and 2,6-toluenediisocyanates (TDI) and diphenyl-methane-diisocyanate (MDI). In the event of spillage during an accident the highly reactive liquid of the isocyanates will react immediately with the water of a contaminated soil to form polyurea compounds. By simulating this situation with the use of $^{14}$C-polyureas, the possibility of degrading these polymers with the liberation of aromatic amines was investigated in different soils.

2. Material and Methods

2.1. PUR-foams and Polyureas

The following polymeric compounds were under investigation:

(a) Soft PUR-foams on polyester or polyether base, both prepared with the isomeric mixture of 2,4- and 2,6-TDI (2,4- and 2,6-toluenediisocyanates), $^{14}$C-labelled in the methyl groups of the TDIs with a radioactivity of 7.22 µCi g$^{-1}$ (ester based) and 5.04 µCi g$^{-1}$ (ether based).

(b) Rigid PUR-foam on polyether base, prepared with MDI (diphenylmethane-4,4'-diisocyanate), $^{14}$C-labelled in the methylene group of the MDI, with a radioactivity of 13.87 µCi g$^{-1}$.

(c) Polyurea formed by the reaction of an isomeric mixture of 2,4- and 2,6-TDI with water, $^{14}$C-labelled in the methyl group of the TDIs with a radioactivity of 0.15 µCi g$^{-1}$.

(d) Polyurea formed by the reaction of MDI with water, $^{14}$C-labelled in the methylene group of the MDI with a radioactivity of 3.01 µCi g$^{-1}$.

The radioactive materials were supplied by the International Isocyanate Institute Inc., New York. The corresponding unlabelled materials were supplied by Bayer AG, Leverkusen.

2.2 Studies on PUR-foams under laboratory conditions

The degradation of the labelled foams was investigated in three different media: Leachate from a refuse tip near Braunschweig (pH 7.5); composted municipal waste from the city of Duisburg (water content 49%; pH 7.2); and soil (Para brown earth,