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UTILIZATION OF POLYMERIC WASTES

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Abstract. A method for pyrolysis of polyolefinic wastes at 350–550 °C has been developed using a film-type bubble reactor of original construction. The mixture of alkanes and alkenes obtained can be used as a raw material for organic synthesis. Alkylsulphonates synthesized from alkenes obtained were used as air-entrainment agents and plasticizers to improve the properties of cement mortars.

Key words: polyehtylene, polypropylene, wastes, pyrolysis, alkanes, alkenes, alkylsylphonates, additives for concrete mixtures.

Polyolefinic wastes, which cannot be used as a secondary raw material, can be utilized by thermal degradation, as the studies performed at the Tallinn Technical University have shown [1, 2]. For that, a film-type bubble reactor has been developed in which a hot gaseous heat carrier is bubbled through the melt layer of polymer [3]. If air is used as the heat carrier, the rate of thermo-oxidizing destruction is sufficient at 350 °C, in the oxygen atmosphere, beginning from 250 °C. The higher the temperature, the higher is the production of gaseous compounds (up to 25–30%). The yield of gaseous products can reach 50% level if oxygen is used. Oxygen also promotes the formation of polynuclear arenes. With thermo-oxidizing destruction in the presence of air in the temperature range 350–450 °C, the primary products tend to condense and the mixture of molecular weights in the range of 450–500 is formed with the yield of 75–80%. The content of functional groups per 1000 C atoms is: double bonds 22.0–28.0; carbonyl groups 18.0–21.0; hydroxyl groups 8.0–9.0. The drop-falling temperature of the product mixture is 50–70 °C. The process of thermo-oxidation would enable a high-rate utilization of polyethylene wastes. However, using the product as oxidized wax involves difficulties because of its low molecular weight.

If an inert gas is used as the heat carrier, the thermal destruction (pyrolysis) will proceed at a sufficient rate in the temperature range of 450–550 °C in case of polyethylene, and at 350–450 °C for polypropylene. The addition of polypropylene to polyethylene increases the rate of pyrolysis. Pyrolysis of polyolefins gives a mixture of alkanes and alkenes as the product. At that, the higher the temperature, the shorter is the chain length of the hydrocarbons formed. Polypropylene gives generally substantially shorter chain-length compounds (C_2–C_{16}) than polyethylene (C_7–C_{32}). The temperature dependence of polyethylene pyrolysis parameters is presented in the Table.

Temperature dependence of polyethylene (PE) pyrolysis parameters

Temperature, °C	Productivity, $g \cdot cm^{-2} \cdot h^{-1}$	Yield of wax-like product, $g \cdot cm^{-2} \cdot h^{-1}$	Yield from PE, %
450	5.18	5.09	98.3
475	9.26	8.93	96.4
500	15.50	14.70	95.4
525	26.04	24.68	94.8
550	34.54	31.78	92.0

Infrared (IR) spectrometric analysis of the product mixture and distilled fractions shows functional groups typical of alkanes and alkenes only: vinyl (—CH=CH_2—) and vinylidene groups (—CH=CH—) are characterized by $\nu(=CH_2)$ at 3085 cm^{-1}; $\nu(=CH)$ at 3010 cm^{-1}; $\nu(C=C)$ at 1650 cm^{-1}; $\gamma(=CH)$ at 910, 965, and 990 cm^{-1}. According to IR analysis no arenes and no oxidation products are formed. These results were also confirmed by ^1H and ^{13}C NMR analysis of the product mixture, which showed the compounds formed to be 1-alkenes and *n*-alkanes [4]. It was not possible to determine whether the mixture contained dienes with double bonds at both ends of a molecule. Polypropylene destruction differs in the formation of branched structures, but alkenes have a double bond at C_1 like in case of polyethylene.

A possible application of pyrolysis products is the synthesis of alkylsulphonates and modification of cement mortars with them. The hydrocarbon mixture obtained by polyethylene pyrolysis was vacuum-fractionated according to the chain length of alkanes–alkenes: C_7; C_8–C_{10}; C_9–C_{11}; C_{10}–C_{13}; C_{13}–C_{15}; C_{15}–C_{17}; C_{18}–C_{20}. These fractions were used for alkylsulphonate synthesis [5]. To study the effect on the strength properties of cement mortars, alkylsulphonates were added in amounts from 0.02 to 0.2% of cement to 1/3 and 1/6 cement/sand mixtures [6]. The effects determined were the rate of air-entrainment, changes in volume mass and bending strength.

The experiments showed that long-chain alkylsulphonates in mortars and concrete behave generally as air-entrainment promoting agents. The effect is the strongest with C_{15}–C_{17} fraction. Alkylsulphonates with up to

10 carbons in alkyl chain act as plasticizers. Longer-chain alkylsulphonates increase the mechanical strength of mortar and concrete mixtures by 10–15% at concentrations 0.02–0.07% of cement amount. At higher concentrations the strength decreases sharply. An optimum concentration for shorter-chain alkylsulphonates is 0.07%. At higher concentrations a slow reduction of mechanical strength values begins. However, even at 0.2% concentration the strength values stay higher than those of original unmodified mixtures.

In alkylsulphonate-containing mortars a homogeneously porous structure is formed containing series of small closed thin-walled caves which do not admit water into the interior of the material.

Alkylsulphonate additives do not show any negative effect on the normal consistency, setting times, and smoothness of the volume change in cement compositions.

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POLÜMEERSETE JÄÄTMETE UTILISEERIMINE

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On välja töötatud meetod polüolefiinsete jäätmete utiliseerimiseks pürolüüsi teel temperatuuripiirkonnas 350–550 °C, kasutades originaalse konstruktsiooniga reaktorit. Saadav alkaanide ja alkeenide segu sobib orgaanilise sünteesi tooraineks. Alkeenidest sünteesitud alküülsulfonaate on kasutatud betoonisegude õhusisalduse tõstmiseks, plastifitseerimiseks ja tugevusomaduste parandamiseks.

УТИЛИЗАЦИЯ ПОЛИМЕРНЫХ ОТХОДОВ

Эдуард ПИЙРОЯ

Разработан способ утилизации полиолефиновых отходов путем их пиролиза при температурах 350–550 °C на реакторе оригинальной конструкции. Получаемая смесь алканов-алкенов пригодна в качестве сырья для органического синтеза. Синтезированные из ненасыщенных компонентов смеси алкилсульфонаты можно использовать для пластификации, повышения содержания воздуха в бетонных смесях и их прочностных свойств.