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# Characterization of volatile compounds, structural, thermal and physico-mechanical properties of cross-linked polyethylene foams degraded thermo-mechanically at variable times

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ABSTRACT

Waste cross-linked polyethylene foam (wXLPE) was thermo-mechanically degraded at variable time using internal batch mixer. The progress of wXLPE degradation has been investigated by using a simultaneous thermogravimetric/differential scanning calorimetry analyzer coupled with Fourier transform infrared spectroscopy, swelling measurements, tensile tests and scanning electron microscopy. Volatile organic compounds generated during wXLPE degradation were determined using static head-space and gas chromatography-mass spectrometry. It was observed that duration of thermo-mechanical processing of wXLPE has significant impact on content of low molecular degradation products, chemical structure, swelling, thermal and morphological properties of degraded wXLPE, while its impact on physico-mechanical properties was negligible. This indicates complex structural and chemical changes in wXLPE during its thermo-mechanical degradation, which is related to two opposite factors: (i) decrosslinking efficiency during thermo-mechanical processing of wXLPE and (ii) partial plasticization of polyethylene matrix by volatile degradation products.



## 1. Introduction

Plastics are commonly used in a wide range of industrial applications, which is related to their specific properties such as durability, light-weight, easy processing and low-cost production. As a consequence, dynamic development of plastics production is observed each year. Estimated data showed that global production of plastics in 2014 increased to 311 million tonnes with approximate growth of 3.9% annually. Therefore, waste management of plastics became a huge environmental, economical and social problem [1].

In Europe, the current level of plastic production is 59 million tonnes annually. Simultaneously, 25.8 million tonnes of post-production and post-consumer waste plastics are generated to multiple solid waste stream. Although 69.2% of waste plastics in Europe are recovered through material recycling (29.7%) or energy recovery (39.5%), almost 30.8% are still accumulated in the landfill [2]. Therefore, searching for new solutions and forms in material recycling of waste plastics, being eco-friendly alternative for landfill disposal or energy recovery, is currently a subject of interest of many academic and industrial research centers around the world [3–5].

Among various plastic wastes, recycling of cross-linked polymers is a major problem requiring solution. Three-dimensional network present in cross-linked polymers improves their performance properties, including mechanical properties, chemical resistance or thermal and dimensional stability. However, these features cause significant difficulties during the recycling of cross-linked polymeric materials, such as polyurethane foams [6,7], vulcanized rubber [8,9], thermosetting resin based composites [10,11] or cross-linked polyethylenes [12,13], due to their poor fluidity and processability.

*Abbreviations:* ATR-FTIR, attenuated total reflectance mode Fourier transform infrared spectroscopy; DHS-GC-MS, dynamic headspace and gas chromatography-mass spectrometry; DSC, differential scanning calorimetry; DTG, derivative thermogravimetry; wXLPE, waste of cross-linked polyethylene foam; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; TGA/DSC-FTIR, simultaneous thermogravimetric/differential scanning calorimetry analyzer coupled with Fourier transform infrared spectroscopy; VOCs, volatile organic compounds.

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Recently, several research groups reported that reactive extrusion could be used to convert cross-linked polymers into decrosslinked and processable ones. Goto et al. [14,15] proved that single- and a co-rotating twin screw extrusion combined with supercritical alcohols (1-propanol, methanol) allow for selective decomposition of the cross-linking in cross-linked polyethylene (XLPE). The continuous process was performed at temperatures in range of 310–335 °C and in reaction time between 20 and 30 min. It was observed that final properties of the decrosslinked XLPE were similar to the virgin polyethylene. Baek et al. [16,17] performed decrosslinking of XLPE using a single screw extruder and supercritical methanol. The reaction was conducted at temperatures in the range of 360–390 °C and in time around 0.5–2 min. The obtained results indicated that efficiency of XLPE decrosslinking increased with increasing of temperature, supercritical methanol content and reaction time. Isayev research group proposed application of ultrasonically aided extrusion to decrosslinking of cross-linked polyethylene, which was previously successfully used for waste rubber [18–20]. Ultrasonic decrosslinking of cross-linked polyethylene was performed at a barrel temperature of 200 °C, while the mean residence time in the ultrasonic treatment zone at various flow rates was varying from 7.7 to 25.9 s. The authors evaluated ultrasonic decrosslinking of XLPE progress as function of ultrasonic amplitude [21–24], throughput [21], screw design [22], polyethylene type and its degree of cross-linking [23,24]. It should be noticed that the above mentioned variables affect (more or less) the residence time distribution of XLPE during extrusion, which has significant impact on the final performance properties of recycled XLPE and emission of volatile organic compounds (VOCs) formed during thermo-mechanical processing of material.

In the literature, only few works describe the application of headspace analysis technique for investigation of the gas phase of polyethylene thermo-mechanically processed with extruders [25–28]. However, according to our best knowledge, there is no information about the correlations between volatile organic compounds (VOCs) emitted during degradation and structure-properties of the decrosslinked XLPE as a function of processing time. It is well known that VOCs have negative impact on the environment, which could be a serious problem during implementation of laboratory results into industrial scale due to environmental regulations. Therefore, their detailed analysis is particularly important in the case of new and innovative technologies, such as decrosslinking of XLPE via thermo-mechanical processing.

In this work, post-production waste of cross-linked polyethylene foam (wXLPE) was thermo-mechanically degraded at variable time (in range: 0–20 min) using internal batch mixer. Thermogravimetric analysis/differential scanning calorimetry analysis coupled with Fourier transform infrared spectroscopy (TGA/DSC-FTIR) and attenuated total reflectance mode Fourier transform infrared spectroscopy (ATR-FTIR) were applied for the determination of change in chemical structure of recycled cross-linked polyethylene foams. VOCs generated from wXLPE degraded at variable time were investigated using static headspace analysis techniques. Furthermore, swelling properties (cross-link density, sol fraction), physico-mechanical properties (tensile strength, elongation at break, hardness, density) and morphology (scanning electron microscopy) were determined to evaluate the structure-property relationships of thermo-mechanically degraded wXLPE.

## 2. Experimental

### 2.1. Materials

Post-production waste of cross-linked polyethylene foam (wXLPE) generated during manufacturing of foamed panels was obtained from Joongpol Ltd. Polish-Korean Production and Trade Enterprise (Poland). The density of waste XLPE foam was $76.8 \pm 0.2$ kg/m$^3$.

### 2.2. Sample preparation

Waste cross-linked polyethylene foam (wXLPE) at ambient temperature was passed through a small gap (high shear forces) of two-roll mills from Buzuluk (Czech Republic). This operation reduces the volume of wXLPE and improves its further processing. Subsequently, wXLPE was thermo-mechanically degraded at 180 °C using a Brabender batch mixer model GMF 106/2 (Germany). The rotational speed of rotors was 100 rpm. The mixing time during thermo-mechanical degradation of wXLPE was selected as 5, 10, 15 and 20 min, respectively. The obtained materials were formed into sheets of the 2 mm the thickness by compression molding, for 2 min at 180 °C and under the pressure of 4.9 MPa, and then cooled for 6 min at room temperature, under the same pressure. The samples were coded as wXLPE – Z, where Z means the time of thermo-mechanical degradation. For example, wXLPE – 5 min is a sample of wXPLE thermo-mechanically degraded for 5 min The wXLPE without prior thermo-mechanical treatment formed in the same conditions was used as a reference sample, and coded as sample obtained at 0 min (wXLPE – 0 min). The appearance of wXLPE at different processing stages is shown in Fig. 1.

### 2.3. Measurements

Chemical structure of thermo-mechanically degraded wXLPE was determined using Fourier transform infrared spectroscopy (FTIR) analysis by means of a Nicolet iS10 spectrometer from Thermo Scientific (USA) equipped with a diamond crystal. Measurements were performed in a reflective absorbance mode (ATR-FTIR), at 1 cm$^{-1}$ resolution in the range 650–4000 cm$^{-1}$.

The thermal analysis of samples was performed using the simultaneous TGA/DSC model Q600 from TA Instruments (USA). Samples weighing approx. 10 mg were placed in a corundum dish. The study was conducted in an inert gas atmosphere - nitrogen (flow rate of 100 mL/min) in the temperature range from 25 to 700 °C with a temperature increase rate of 20 °C/min. Volatile products from thermal degradation of samples were also evaluated using a Fourier transform infrared spectroscopy (FTIR). During TGA/DSC measurements volatile degradation products were directed (using heated transfer line with the temperature of 220 °C) to Nicolet iS10 spectrometer from Thermo Scientific (USA). Presented solution allows "on-line" characteristics of volatile products during TGA/DSC measurements. The timing offset of FTIR spectra comparing to TGA curves is related to a volume of thermogravimetric apparatus chamber.

Identification of volatile organic compounds generated from wXLPE samples was performed using a static headspace and gas chromatography-mass spectrometry (SHS-GC-MS). All experiments were conducted using a Shimadzu GC2010 PLUS GC-MS equipped with a split/splitless inlet. The GC-MS system was equipped with an AOC5000 Headspace Auto-Sampler. During analysis, the vial was transported by the injection unit from the tray to the agitator; when the sample achieved the equilibrium, the headspace sample of 2.5 mL volume was drawn from the vial and injected into the GC injector. The sampled vial was then returned by the injection unit to the tray. Detailed information about the conditions and parameters of SHS-GC-MS analysis is presented in Table 1.

Tensile strength and elongation at break of the obtained samples were tested according to the standard ISO 527 using a Zwick