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# Crosslinking of polyamide-6 initiated by proton beam irradiation

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ABSTRACT

Initiation of crosslinking of polyamide-6 (PA6) by proton beam irradiation was investigated for a virgin material as well as for PA6 containing up to 5 wt% of triallyl cyanurate (TAC) as a crosslinking coagent. The gel point was found to be 144 and 40 kGy for virgin PA6 and for PA6 with 1 wt% of TAC, while for higher TAC content gel content was determined to be around zero absorbed dose. The ratio between crosslinking and scission of macroradicals formed by irradiation was found to be around 0.65 regardless on presence or absence of TAC and its concentration. The more detailed discussion on chemical processes as well as on final structure formation after irradiation is based on data from differential scanning calorimetry, detecting a decrease of both lamellar thickness and crystalline portion, but an increase of glass transition temperature.

## 1. Introduction

Utilization of radiation energy belongs to important procedures for modification of polymers. At the beginning, the study of related processes was focused on polymers with simpler structure for which the mechanism of crosslinking is well understood if initiated by thermal decomposition of organic peroxides (Lazar et al., 1990; Chodák, 1995). Investigation of radiation effect, in particular electron beam, started already in the fifties of the last century; later the concern has broadened involving besides polyolefins also number of other polymers. The initiating radiation was mainly gamma irradiation (Hua et al., 2005; Lu et al., 2005; Chytiri et al., 2005), later electron beam (Dadbin et al., 2005; Sengupta et al., 2005, 2006a, 2006b; Porubská et al., 2014).

Interesting but different effects were reported if crosslinking was initiated by application of UV irradiation in the presence of UV sensitizers (Teixeira et al., 2013; Pan et al., 2015).

Recently another source of high energy radiation, namely accelerated protons, is applied for various purposes such as preparation of radio-medical products and direct-writing methods utilizing focused proton beam. Martinez-Pardo et al. (1998) investigated irradiation of polystyrene (PS) and low density polyethylene (LDPE) films by proton beam under vacuum or in air. Crosslinking and scission, along oxidation when exposed in air, were reported as the main radiation induced processes and the ratio between them depended on the dose. Scission became dominant at high irradiation doses. Another paper (Tripathy et al., 2002a) describes irradiation of polypropylene (PP) in air by proton beam applying 10–80 kGy doses. An increase in lamellar thickness demonstrated by melting temperature growth was observed as a result of restoration and increase in regularity of the original lamellar structure of PP due to partial scission of PP macromolecules in solid state.

The same authors (Tripathy et al., 2002b) examined also polytetrafluoroethylene (PTFE) degradation under identical conditions. The thermal stability and the melting temperature were observed to decrease with the increase of proton dose due to certain degree of disordering the original crystal structure and simultaneously radiation-induced formation of new crystalline structures was observed, however, the latter was of marginal abundance.

Irradiation of polycarbonate films with different doses of protons (Abdel-Salam et al., 2011) showed that the carbonyl group (C=O) is the most sensitive group towards proton irradiation. Besides a decrease in the average molecular mass and increase in the degree of ordering in the degraded samples also crosslinking was reported leading to more compact structure.

Arai et al. (2013) examined proton beam irradiation of fluorinated polyimide film. It was found that the depth of the penetration increases with dose. Crosslinking of polydimethylsiloxane (PDMS) pre-polymer by proton beam irradiation is described by Huszank et al. (2015). The rate of the solidification strongly depends on the deposited ion dose. Szilasi et al. (2011) investigated chemical changes in poly(methyl methacrylate) (PMMA) due to proton beam irradiation in the depth profile of the sample. Higher doses affected chemical structure in whole irradiated volume while zone of maximal modification was restricted

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only to the Bragg peak for samples irradiated by lower doses. Several papers are devoted to research of proton beam impact on electrical properties of polymers. Abdel-Hamid et al. (2002) investigated the dependence of specific electrical resistance of non-plasticized polyvinyl chloride films on dose; the resistance was found to drop substantially. On the other hand, perfluoro sulphone polymer membrane showed an increase of electrical conductivity of direct current independent on the ions penetration depth as described by Nagata et al. (2007). Under irradiation of polyethylene terephthalate by proton beam (Singh et al., 2005), the radiation induced the changes of both electrical conductivity and thermal properties and bond breaking at higher doses was found. Shah et al. (2008) reported higher alternating current conductivity and hardness for PMMA filled with organometallic compound after being irradiated with 3 MeV proton beam.

Mazzei et al. (2003) reported the application of proton beam to initiation of grafting reactions on PP films immersed in aqueous solutions of styrene, acrylic acid or methyl methacrylate. In several papers proton beam has been examined also to be used for proton beam writing system (Simcic et al., 2005; Kamila et al., 2006).

As evident from the literature outline, information about proton beam effect on polyamides is absent, if not mentioning our paper on FTIR effects of PA6 irradiated by various sources (Porubská et al. 2012). Therefore this work is aimed to the investigation of the impact of proton beam on the structure and properties of virgin polyamide-6 in absence or presence of the co-agent of crosslinking. We investigated influence of absorbed dose and the co-agent concentration on gel generation and thermal characteristics of the exposed polyamide samples. A practical aspect of this work may consist in a fact that the processing temperature of polyamides is well above temperature of thermal decomposition of organic peroxides which are considered to be the simplest initiators of crosslinking reactions in a number of polymers. Thus, proton irradiation may be an alternative for polyamide crosslinking initiation.

## 2. Experimental

### 2.1. Materials

Polyamide-6 (Belamid PA-6, Jelínek Trading spol. s r.o., Zlín, Czech Republic; hereafter PA6) was used as the polymeric matrix without antioxidant additives. Following data on properties were provided by the supplier:

- density/(g $cm^{-3}$): 1.13;
- melt flow index/g per 10 min; 230 °C; load 2.16 kg: 21.1;
- melting temperature/°C: 220;
- strength at yield/MPa: 71;
- elongation at yield/%: 4;
- Young's modulus/MPa: 2367;
- Charpy notched impact strength/(kJ $m^{-2}$); 23 °C: 2.4;
- Vicat thermal resistance/°C: 186.

Triallyl cyanurate (hereafter TAC, formula $C_{12}H_{15}N_3O_3$) with melting temperature of 26 °C as crosslinking co-agent and 90% formic acid for the gel determination were supplied by Merck Slovakia.

### 2.2. Sample preparation

Blends of PA6 with TAC in concentrations 0-1-3-5 wt% were prepared as follows: molten TAC was added to dried PA6-pellets (drying 24 h at 80 °C). and the mixture was mechanically thoroughly mixed at 40 °C and then homogenized in twin-screw kneading line Werner-Pfleiderer ZSK 30 under the following conditions: screw revolutions 200 $min^{-1}$, output 12 kg/h, temperature of heating zones 215-238-244-242-250 °C, melt temperature at die 242 °C. The dried pellets (drying 24 h at 80 °C) were compression-moulded at 270 °C into 1.7 mm thick slabs of dimensions 150×150 mm. From the plates, specimens - bars were cut with dimension 150×10×1.7 mm. During the period between preparation and irradiation, the specimens were kept in a desiccator containing dry silica gel.

### 2.3. Irradiation

Irradiation by accelerated proton beam $^1H^+$ was performed in equipment Cyclone 18/9, in a company Biont, Bratislava. The specimens were exposed in air at outlet of external line by scanning defocused collimated proton beam with energy of $E_p$~17.8 MeV and current of approximately 300 nA. The samples in a shape of 1.7 mm thick slabs with length and width 150 and 10 mm, respectively were used. Irradiation of the polyamide samples was performed by the proton collimated beam using carbon collimator. Since during irradiation it is impossible to measure the homogeneity of irradiation, stability of irradiation was estimated before the irradiation of the PA samples according to change of colour of testing paper irradiated for various times. The stability determined by such a way was found to be very good.

The defocused beam was collimated on the area on the sample where homogeneous irradiation intensity was possible to be maintained. Since the area of the whole specimen was larger than the irradiated area, the specimen was slowly moving under the beam so that each part of the specimen was irradiated several times until total desired dose was applied. The energy loss of the beam was changing during passing through the sample by approximately 15%, therefore, to keep the radiation dose to be homogeneous through the cross-section of the slab, one side of the sample was irradiated for a half of irradiation time, and after that the sample was turned over and irradiated from the other side for the same time. Then the real dose can be considered as homogeneous through the whole cross-section of the specimen.

For the determination the irradiation dose the current was measured and the applied dose in the range of (200-300-500-700-1000) kGy was calculated form the value of integrated current consumed by the equipment. The irradiation intensity was kept at low level to prevent excessive heating of the sample.

### 2.4. Gel content

The gel content in the samples was determined according to the previously described methods (Porubská et al., 2010) taking sample for analysis from the whole specimen cross-section. Samples of approximately 0.2 g were packed in glass fabric and extracted in 90% formic acid using an orbital shaker at room temperature. The extraction for PA6 took 48 h with exchange of the solvent after 24 h. The insoluble portion was dried and weighed. The relative standard deviation was below 3%, as calculated from three measurements for each sample, including reference sample.

### 2.5. Differential scanning microcalorimetry (DSC)

Thermal analysis was performed on cut-offs taken from the whole specimen profile using a DSC Mettler $821^e$ instrument under nitrogen atmosphere according to ISO 11357-1:2000. The heating and cooling rates were 10 °C/min within the interval from 0 to 260 °C. Both the first and the second runs were performed. The corresponding melting/remelting temperatures and enthalpies of crystallization as well as glass transition temperatures were determined from the thermograms.

## 3. Results and discussion

As said in the Introduction part, no paper on proton beam irradiation focused to polyamide was found in literature up to now. Therefore no data are available for comparison of our results with