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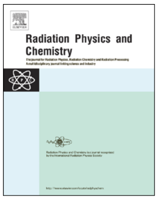

The effect of hard/soft segment composition on radiation stability of poly(ester-urethane)s

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HIGHLIGHTS

- Hard/soft segment composition affects radiation stability of poly(ester-urethane)s.
- Degree of phase separation increased with increasing content of hard segments.
- Ionizing radiation modifies thermal and mechanical properties of polyurethanes.

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ABSTRACT

In this paper studies on the structures and radiation stability of four poly(ester-urethane)s (PUR)s synthesized from oligo(ethylene-butylene adipate)diol of various molecular weights and isophorone diisocyanate/1,4-butanediol are reported. PURs with 40 and 60 wt% soft segments were irradiated at ambient temperature with a high energy electron beam to a dose of 112 kGy. The effect of different segmental compositions on thermal and mechanical properties of polyurethanes, both before and after irradiation, were investigated using mechanical testing and dynamic mechanical thermal analysis. ATR-FTIR spectroscopy was used to study the progress of polycondensation, structure of synthesized polymers and extent of phase separation were determined on a basis of the contribution of hydrogen bonding in poly(ester-urethane)s. Correlation between degree of phase separation and mechanical and thermal properties of poly(ester-urethane)s was found.

1. Introduction

Physical and chemical effects of ionizing radiation on polymeric systems are of interest in many researchers continuously for 60 years. It is commonly known that the final effect of radiation is affected by many factors, starting from the molecular structure, the presence of various additives such as stabilizers, plasticizers and antioxidants to the irradiation conditions. However, for newly synthesized materials such as composites, nanocomposites and for materials of the unique segmental structure, predicting the direction of these changes is very difficult. Therefore, it requires an insightful analysis of the effects of ionizing radiation on the diverse properties of such materials.

Among polymers, polyurethanes (PUR)s are one of the most interesting materials. They are used in many applications, such as textiles, adhesives, modern materials for electronics and biomaterials (Krol, 2007). Polyurethanes exhibit a broad range of physicochemical and mechanical properties, due to their structural diversity. PURs are known as phase-separated polymers but the extent of this separation depends on many factors, e.g. type and molecular weight of the oligodiol, the chemical structure and symmetry of diisocyanate, the hard/soft segment weight ratio, and the synthesis method (Mishra et al., 2006). Formation of hydrogen bonding between urethane linkages also strongly influences PURs phase separation (D'Arlas et al., 2008).

The physicochemical properties of aromatic polyurethanes have been studied extensively for a few last decades. In contrast, the influence of ionizing radiation on aliphatic PURs has been conducted relatively rarely. Moreover, many researches examine radiation modified polyurethanes without paying attention to the impact of hard/soft segment contribution on the final effect of irradiation. It is well-known that polyurethanes are qualified as materials possessing excellent radiation stability (ISO:11137:2006). However, depending on the molecular architecture and segments composition, radiation resistance of polyurethanes differs significantly.

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In the reported work we focused on the relationships between chemical composition and radiation sensitivity of poly(ester-urethane)s. To the best of our knowledge this is the first report describing the effect of soft and hard segment weight contribution on radiation stability of aliphatic PURs.

2. Experimental

2.1. Sample preparation

Isophorone diisocynate and 1,4-butanediol used for polyurethane synthesis were purchased from Sigma-Aldrich and were vacuum distilled. Oligo(ethylene-butylene adipate)diols (OAD) with molecular weight of 1000 and 2000 Da were purchased from Purinova (Poland) and were dried under vacuum for 2 h at 120 °C before using. The polyurethanes were synthesized by a two-step polycondensation without any catalyst and solvents. The reaction progress was followed by measuring disappear of isocyante stretching band at 2260 cm^{-1} and its conversion into N–H group with a band at around 3350 cm^{-1}.

Polyurethanes denoted PUR1 40/60 contained 40 and 60 wt% of hard segment (HS) and soft segment (SS) with $MW=1000$ Da, respectively. Analogically, PUR1 60/40 was constructed from 60 and 40 wt% of HS and SS. PUR2 40/60 and PUR2 60/40 had the same segmental composition like PUR1 except molecular weight which was $MW=2000$ Da.

2.2. Irradiation

Polyurethane films were irradiated in the presence of air at ambient temperature with a 10 MeV electron beam generated in a linear electron accelerator Elektronika 10/10 to a dose of 112 kGy by the multipass exposure (28 kGy per one pass).

2.3. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra were recorded with a Bruker Equinox 55 FTIR spectrometer. The spectra were collected in the range of 4000–650 cm^{-1} at a resolution of 4 cm^{-1} by means of an accessory equipped with ZnSe crystal designed for single reflection ATR technique. Curve-fitting simulations of the ATR-FTIR carbonyl region were performed using Origin 6.1 program. A flat baseline was chosen in the range of 1600 to 1850 cm^{-1}. The second derivatives of the spectra in $C{=}O$ region were used to determine the number of Gaussian peaks.

2.4. Mechanical testing

Mechanical testing was made at ambient temperature and at a crosshead speed 100 mm/min using Instron 5565 apparatus. Five measurements were performed for each sample.

2.5. Dynamical mechanical thermal analysis (DMTA)

The dynamical mechanical thermal analysis was performed on a DMA Q-800 modulus (TA Instruments) in the temperature range from -100 to 150 °C at 1 Hz.

3. Results and discussion

3.1. ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was used to determine the microphase separation in polyurethanes by examining the relative contents of hydrogen bonds participating in the formation of separated segments. Hydrogen bonding in poly(ester-urethane)s involves N–H groups in urethane units as a proton donor, and ester and urethane carbonyl groups as proton acceptors (Lamba et al., 1998). For all PURs it was found that almost all N–H groups (peaks located between 3200 and 3450 cm^{-1}) were involved in the hydrogen bonding system. Other bands located above 1700 cm^{-1} also reveal hydrogen bonding and are assigned to the urethane and ester carbonyl groups. In order to identify free and hydrogen bonded $C{=}O$ groups in the polymer, spectrum deconvolution was employed (Kumari et al., 2007). As seen in Fig. 1 the carbonyl absorption band is split distinctly into two peaks; the first is located at around 1700 cm^{-1} and the second one at 1730 cm^{-1}.

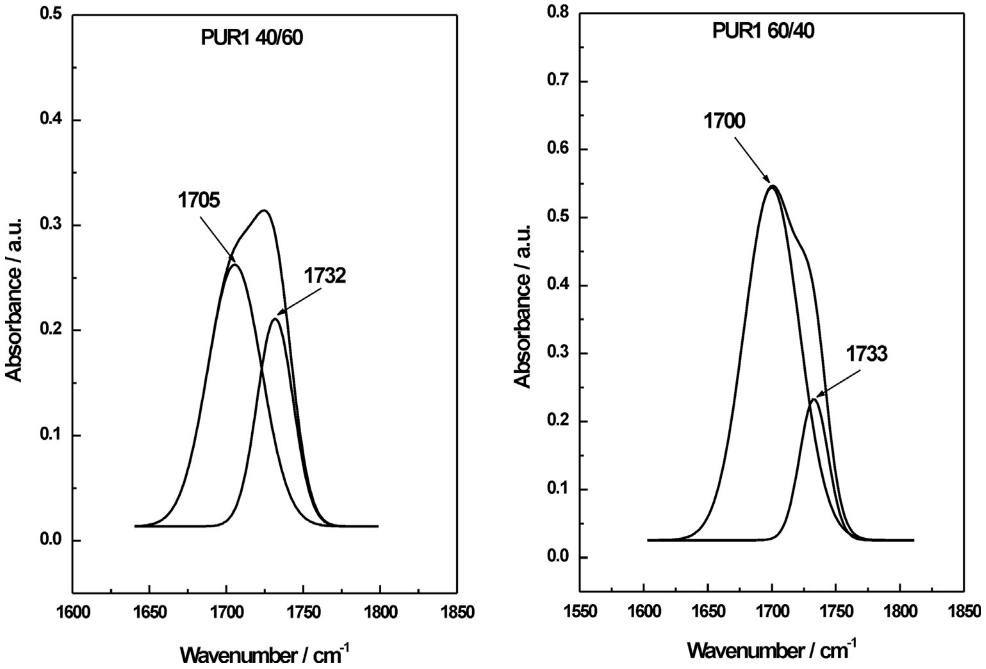

Fig. 1. Representative deconvoluted $C{=}O$ region in poly(ester-urethane)s.