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.

ARTICLE INFO

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}.
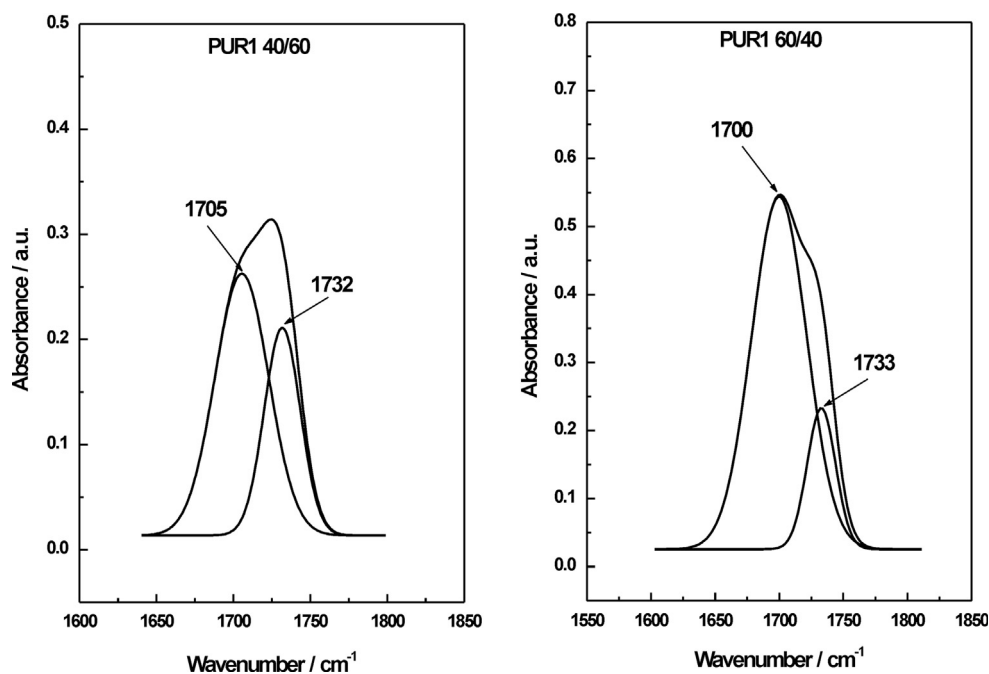

Fig. 1. Representative deconvoluted C=O region in poly(ester-urethane)s.

The peak placed at lower wavenumbers corresponds to the hydrogen bonded C=O groups. The carbonyl groups uninvolved in hydrogen bonding have a peak shifted to 1730 cm^{-1}. On the basis of these results, the degree of phase separation (DPS) was calculated according to equation (Chen et al., 2000):

$$DPS = \frac{A_{C=O\ bonded}}{A_{C=O\ bonded} + A_{C=O\ free}}$$

where: $A_{C=O\ bonded}$, $A_{C=O\ free}$ are the absorbance of bonded and free C=O groups respectively.

As was expected, the microphase separation is higher for PURs containing larger amount of hard segments. For PUR1 60/40 the DPS value reaches about 70% while for PUR1 40/60 is almost 15% smaller. Similar tendency was observed for PUR2 containing 60 wt% and 40 wt% HS. It was estimated that the degree of phase separation for these samples is about 64% and 54%, respectively.

Analyzing the influence of the soft segment chain length on microphase separation it was found that molecular weight of applied oligo(ethylene-butylene adipate)diol has significant impact on DPS only if its participation is smaller than HS. We observed that for PUR2 60/40 constructed from OAD of MW=2000 Da the degree of microphase separation is around 64% i.e. noticeably lower as compared to DPS=70% determined for PUR1 60/40 (OAD of MW=1000 Da).

These results confirmed that

1. The vast majority of N–H groups participate in the creation of hydrogen bonds as there is no peak situated at 3495 cm^{-1} related to the nonbonded (free) amino groups (Szycher, 2012).
2. Extent of the interurethane hydrogen bond network decreases with increasing content of SS as seen from diminishing microphase separation for PURs containing 60% and 40% soft segments.
3. The phase separation decreases when the length of aliphatic chains increases, both for PURs 40/60 and for PURs 60/40.

3.2. Mechanical analysis

The tensile stress–strain properties of poly(ester-urethane)s are presented in Fig. 2. It was observed that the hard/soft segment ratio has significant influence on the mechanical properties of non-irradiated and irradiated samples. With increasing HS content the tensile strength increases while ultimate elongation decreases considerably demonstrating progress in the microphase separation. PURs 40/60 exhibit high elasticity and weak mechanical strength whereas PURs 60/40 demonstrate behavior characteristic for semi-brittle materials.

There is a distinct difference in the mechanical properties of non-irradiated PURs constructed from SS of various molecular lengths as elongation at break is about 150% longer for PUR2 40/60 than for PUR1 40/60 and 100% longer for PUR2 60/40 than for PUR1 60/40. Additionally, exposure of the polyurethanes to an e-beam reveals further discrepancies concerning their radiation stability. It was found that upon irradiation the tensile strength of PUR1 40/60 decreased from 18 to 16 MPa whereas the ultimate elongation at break increased from around 880% up to 1250%. As given in Fig. 2, the ultimate tensile strength of PUR2 40/60 decreased from around 20 to 10 MPa for irradiated sample whereas elongation at break increased of ca. 150%. PUR1 60/40 shows significant radiation resistance contrary to PUR2 60/40 whose mechanical properties deteriorate upon irradiation.

Summarizing, the mechanical tests confirmed that

1. Contribution of particular segments in PUR determines its mechanical characteristic making the material either flexible or rigid and semi-brittle.
2. Longer SS in PURs enhances elongation at break preserving a similar level of tensile strength at break both for PURs 40/60 and PURs 60/40.
3. Radiation induced effects depend on the proportion between HS and SS. The poly(ester-urethane)s synthesized from short oligodiol (1000 Da) are more radiation resistant as, when irradiated to 112 kGy, either remain unchanged (PUR1 60/40) or gain additional flexibility (PUR1 40/60). PURs containing SS two times longer (2000 Da) are more susceptible to ionizing radiation since upon irradiation tensile stress distinctly decreases whereas elongation at break for PUR2 60/40 declines and for PUR2 40/60 grows but far less than for PUR1 40/60.

3.3. Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical measurements of PURs containing various amounts of soft and hard segments and diverse lengths of soft segments are presented in Fig. 3. In the temperature range from −100 to −25 °C the poly(ester urethane)s are in the glassy state. Above −25 °C loss modulus (E'') declines due to the glass transition of soft segments (T_{gSS}). The new distinct rubbery state is reached only by PURs 40/60 as, contrary to this behavior, loss modulus of PURs 60/40 exhibits small broad variations at temperatures below 0 °C and a very intensive decrease just at about 50 °C assigned to the glass transition of hard segments (T_{gHS}).
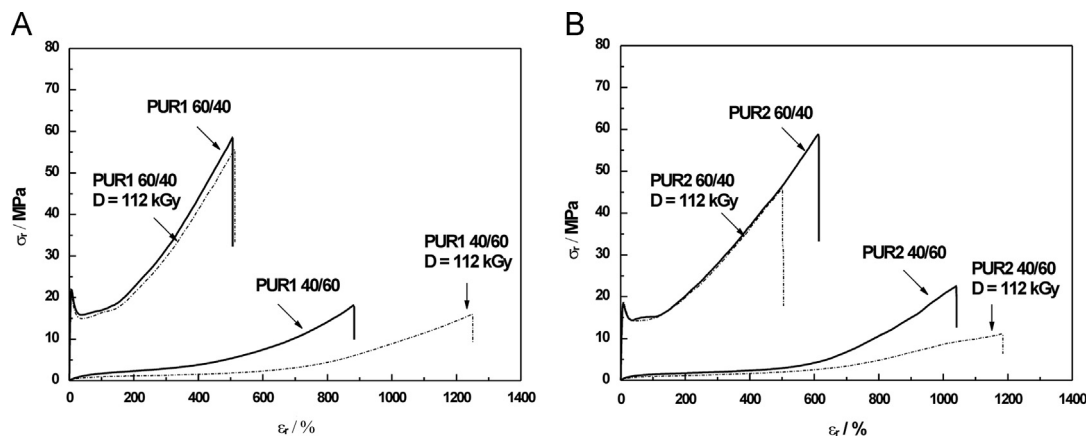

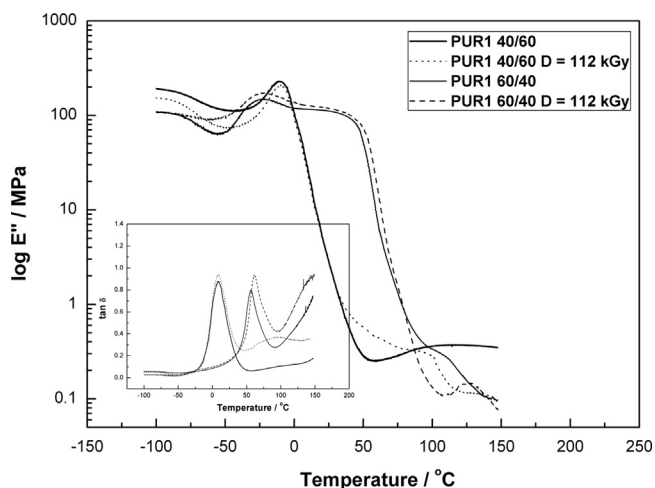**Fig. 2.** Stress–strain curves for poly(ester-urethane)s: (A) PUR1 and (B) PUR2.

Fig. 3. Representative DMTA profiles for PUR1.

Table 1

Glass transition temperature evaluated from $E'' = f(T)$ curves.

Sample abbreviation	Dose, kGy	T_{gSS}, °C	T_{gHS}, °C	T_{HS}, °C
PUR 1 40/60	**0**	−10.1	–	–
	112	−9.7	–	–
PUR 1 60/40	**0**	−25.7	44.3	110.0
	112	−25.3	47.0	127.4
PUR 2 40/60	**0**	−24.7	–	–
	112	−24.4	–	–
PUR 2 60/40	**0**	−24.1	43.9	99.0
	112	−26.0	47.0	108.7

The changes in the region 50–55 °C are attributed to the destruction of short-range order created during cooling and further annealing at room temperature. Minor changes in the log E'' curves in the region above 100 °C are due to the dissociation of hard domains with long range order (T_{HS}) (Lamba et al., 1998). A relationship loss tangent versus temperature shows the dominant transitions in the poly(ester urethane)s – low temperature peak of T_{gSS} characteristic for PURs 40/60 and high temperature peak of T_{gHS} distinctive for PURs 60/40. The interval between main transitions of PURs 40/60 and PURs 60/40 exceeds 50 °C. At ambient temperature the first group of materials is in the rubbery plateau region and as mechanical test showed, exhibits elastic, rubbery-like features. The character of PURs 60/40 are predominantly defined by the hard segment glass transition at about 50 °C therefore under stretching at room temperature they elongate continuously till fracture like a brittle solid.

In the reported work the glass transition temperatures were determined on the basis of E'' loss modulus changes. The obtained results are collected in Table 1.

The phase transition temperatures confirm the extensive segmental separation in PURs 60/40 as in these cases the distinct transitions assigned to the soft and hard regions were found. On the other hand, in the case of PURs 40/60 the HS phase transition effects are negligible revealing mixed, complex, undefined nature of the soft segments. The SS glass transition temperatures of PURs are almost the same before and after irradiation, while the temperatures associated with HS transitions are shifted towards higher temperatures upon radiation treatment.

4. Conclusions

Poly(ester-urethane)s morphology is complex and results from various contributions of two different types of phases of various order arising from hydrogen bond systems created between amino group of urethane unit and carbonyl group located either in urethane or in ester functional group. Increasing participation of

SS in PURs facilitates generation of N–H···O═C (ester) linkages simultaneously reducing intraurethane bonding network forming well-defined hard segment domains.

Assuming that the SS has a dominant influence on PUR elasticity it seems that during irradiation the hydrogen bonds situated in this segment are ruptured as a consequence of radiation induced effects in ester group regions what results in a distinct increase in elongation at break observed for PURs 40/60. On the other hand, PURs 60/40 features are defined rather by hard segments. It is generally known that urethane groups of HS are relatively resistant to radiation effects (Maxwell et al., 2003) thus hydrogen bonding system of these domains is less affected by an e-beam treatment. Therefore, mechanical properties of PUR 1 60/40 remain unchanged. When the chain lengths of SS increase, availability of ester groups grows due to an overall enhancement of flexibility which was confirmed by strain–stress measurements revealing that elongation at break of PUR2 60/40 is higher than PUR1 60/40. These structural changes result in the development of additional hydrogen bonds involving ester carbonyl groups, which as was mentioned previously, are radiation susceptible. Thus, observed for PUR2 60/40 radiation induced deterioration of mechanical properties is related to the reduction of the degree of phase separation.

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