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Ref. No.

**Electron-Spin-Resonance Study of Oxidation in
X-irradiated Poly(ester urethane) Containing Nitroplasticizer**

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Abstract

The effect of oxidation on x-irradiated Estane[®]5703 containing nitroplasticizer (NP) has been examined by electron-spin-resonance spectroscopy, and the results are compared to similar data previously obtained on pristine Estane[®]5703. Although both specimens exhibit similar spectra immediately following x irradiation, their decay upon exposure to air is quite different. The free-radical concentration of the pristine specimen continuously decreases with time whereas the NP sample exhibits an initial *decrease* followed by a significant *increase* due to the growth of a newly-formed radical. Terminal species of the pristine and NP- Estane[®]5703 samples are identified as peroxy and nitroxy radicals, respectively. Hyperfine coupling constants and *g*-values are extracted for the nitroxy radical and a tentative model is proposed to explain the reaction pathway leading to its production.

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Keywords: ESR; Polyurethane; Polymer; Free Radicals; BDNPA/BDNPF

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1. Introduction

Plasticized polyurethane elastomers are used as hot melt curatives [1], polymer electrolytes [2,3], and binders for energetic materials [4-9]. The role of polymeric binders in energetic materials is to impart structural integrity to the composite, desensitize the material to external stimuli, and enhance the maximum extracted energy [5]. Understanding the physical and chemical mechanisms that contribute to time-dependent degradation of these polymers is necessary for predicting their useful lifetime.

In recent work we have examined optical and magnetic resonance properties of Estane[®]5703, a poly(ester urethane) copolymer, and found that x irradiation at room temperature (RT) induced a complex electron-spin-resonance (ESR) spectrum that decayed upon exposure to air [10]. A relatively stable end product of this decay was the well-known peroxy radical. In the present work we examine the RT ESR spectrum of Estane[®]5703 containing nitroplasticizer, observe its time-dependent decay upon exposure to air, and compare the results with the non-plasticized material. Previous work on the plasticized polymer includes dichroic response [11] and transient impact measurements [9].

2. Experimental

Estane[®]5703 was obtained from B. F. Goodrich in pellet form and were compression molded into appropriate specimens for ESR experiments.

Polyurethane (MDI) hard segment

Polyester soft segment

The nitroplasticizer (NP) was prepared by Los Alamos National Laboratory and consists of a 50/50 wt. % mixture of bis(2,2 dinitropropyl)formal and bis(2,2 dinitropropyl)acetal.

Estane[®]5703 with NP is comprised of a 50/50 blend of the two materials.

BDNPF

BDNPA

Although sample irradiation and measurements were done at RT, the sample was mounted in a cryostat and evacuated to 10^{-6} Torr to simulate the experimental arrangement employed in the previous work on nonplasticized Estane[®]5703 [10]. This allows comparison of their time-dependent ESR spectral decay following exposure to air. A molybdenum target x-ray tube operating at 50 kV and 40 mA was used to irradiate the samples to a dose (in air) of 18 kGy. ESR spectra were obtained with an X-band spectrometer operating at 100 kHz modulation/detection frequency with microwave power between 0.5 and 2.0 mW. Modulation amplitude varied between 0.1 and 0.5 mT as needed to produce optimum signal-to-noise or spectral resolution.

3. Results and discussion

Figure 1 shows ESR spectra of NP- Estane[®]5703 recorded as a function of time in air following *in-vacuo* x irradiation at RT. The initial spectrum consists of four broad lines ($\Delta H_{pp} \sim 1$ mT) and a poorly resolved central line. Exposure of the sample to air causes a change in the complex resonance, thus suggesting lack of stability of one or more of the initial radicals. After four hours exposure to air it is evident that at least two groups (A and B) of overlapping resonances exist. The ESR lines associated with each group are given by arrows in Fig. 1. We make the tacit assumption that these two groups of resonances correspond to two free radicals denoted A and B. Radical A consists of four lines characterized by major and minor splittings of approx. 5 and 2 mT, respectively. These resonances are very similar to those observed in pristine Estane[®]5703 (compare with the topmost spectrum of Fig. 2). After 24 hours exposure to air, radical A in NP- Estane[®]5703 has significantly decayed and the lines attributed to radical B become very prominent. This latter spectrum has characteristic asymmetric features of a peroxy radical and is similar to the spectrum observed in pristine Estane[®]5703 following approx. one hour exposure to air (see Fig. 2); however, there is a distinct difference between these two spectra. In pristine Estane[®]5703 the primary radicals A and B decay in the presence of air without yielding any measurable secondary radicals. In contrast, exposure to air of NP- Estane[®]5703 produces an apparent new species, denoted radical C, that begins to evolve well in advance of the complete decay of radicals A and B. Figure 3 shows the total free-radical concentration as a function of exposure time in air for pristine Estane[®]5703. To emphasize the exponential decay at early times this plot shows data for only the first 3 hrs., but it is evident from Fig. 2 that no increase in free-radical concentration occurs by 15 hrs. Conversely, the time evolution of free-radical concentration in NP- Estane[®]5703 upon exposure to air shows a significant increase for times exceeding approx. 4 hrs, as illustrated in Fig. 4.

Although the spectrum of radical C is very similar to that of radical B, which has been previously attributed to a peroxy radical [10], its spectral features are more consistent

with a polycrystalline nitroxy radical ($-\dot{\text{N}}\text{O}$). This well-known species exhibits hyperfine coupling parameters and g -value relationships as shown in Fig. 5 [12]. Extracted parameters for the putative nitroxy radical in NP- Estane[®]5703 are $A_{||} = 2.89$ mT, $A_{\perp} = 0.45$ mT, $g_{||} = 2.0094$ and $g_{\perp} = 2.0122$. It must be noted that similarity between the peroxy and nitroxy radicals observed in pristine and NP- Estane[®]5703 currently precludes their unambiguous assignment. Additional experiments designed to confirm this assignment and to elucidate the reaction mechanisms in NP- Estane[®]5703 are underway. Nevertheless, based on current data we propose a tentative model to explain the ESR observations. The nitro group (P-NO_2) present in NP- Estane[®]5703 may react with polyurethane (PU) radicals $\dot{\text{U}}$ to yield $-\dot{\text{N}}\text{O}$

The formation of nitroxy radicals thereby prevents propagation of the PU peroxy radicals $\dot{\text{U}}\text{O}_2$. Peroxy radical decay with concomitant accumulation of nitroxy radicals has been demonstrated in γ -initiated oxidation of polypropylene [13]. Also, effective prevention of oxidative degradation in polymers by the introduction of stable nitroxy radicals has been previously reported [14].

4. Conclusions

Room temperature x irradiation of NP- Estane[®]5703 produces a complex ESR spectrum that is similar to one observed in pristine Estane[®]5703. However, free-radical decay upon exposure to air is quite different in the two samples. Pristine Estane[®]5703 exhibits an exponential decrease in free-radical concentration with increasing time, whereas NP- Estane[®]5703 exhibits an initial *decrease* followed by a significant *increase* due to the formation of a new radical species. The terminal species in pristine and NP-Estane[®]5703

resulting from oxidation are tentatively identified as peroxy and nitroxy radicals, respectively.

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Figure Captions

Figure 1. Temporal evolution of the NP-Estane[®]5703 ESR spectrum obtained by x irradiating the sample at room temperature *in vacuo* and subsequently exposing it to air.

Figure 2. Temporal evolution of the pristine Estane[®]5703 ESR spectrum obtained by x irradiating the sample at room temperature *in vacuo* and subsequently exposing it to air.

Figure 3. Total free-radical concentration of pristine Estane[®]5703 as a function of time in air. The relatively stable terminal species is identified as the peroxy radical.

Figure 4. Total free-radical concentration of NP-Estane[®]5703 as a function of time in air. The relatively stable terminal species is identified as the nitroxy radical.

Figure 5. ESR spectrum of the nitroxy radical with hyperfine coupling and g-value relationships shown by arrows.

FIG. 2

FIG. 3

FIG. 4

FIG. 5