SAND2000-3032C

OXIDATIVE DEGRADATION ANALYSIS OF HTPB/IPDI POLYURETHANE USING ^{17}O AND ^{13}C NMR

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Introduction

Hydroxyl-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) polyurethane rubbers are used as polymeric binders in solid propellant grain. Accelerated aging at elevated temperatures has been used to predict the lifetime of this material.[1] One critical assumption in the extrapolation of the higher temperature data to ambient temperature is that the degradation mechanism and products are temperature invariant. Temperature dependence of oxidation products will result in non-Arrhenius temperature behavior.

Degradation products of HTPB and polybutadiene have been studied previously. FT-IR studies of the oxidation of polybutadiene[2] has suggested that the oxidation results mainly in hydroperoxides and/or alcohols, and ketones. HTPB binder has also been studied by FT-IR[3] and the spectra revealed the presence of alcohol degradation products. An IR peak with a frequency of 1698 cm^{-1} was also present in the spectrum and was assigned to be unspecified types of carbonyl groups. Finally, the authors reported the loss of *trans*-1,4 and *vinyl*-1,2 unsaturation.

The objective of this research is to quantitatively determine the aging temperature dependence of oxidation products for unstabilized and antioxidant (AO) stabilized HTPB binder. Degradation products were quantitatively analyzed with ^{17}O and ^{13}C NMR spectroscopy.

Experimental

Materials The polyurethane rubber is composed of HTPB cured with IPDI. The resins were supplied by Elf Atochem and Hüls America Inc. The approximate functionality of the HTPB is 2.1 and the average molecular weight is $M \approx 2800$ g/mol. A ratio of HTPB to IPDI of 12.1:1 wt:wt was used to obtain a one molar reactivity ratio. To determine the effects of antioxidant and to facilitate investigations of a wider aging temperature range, some samples for the ^{17}O aging study contained 1% Vanox MBPC antioxidant (2,2'-methylene-bis (4-methyl-6-*t*-butylphenol)) while other samples contained no antioxidant. All samples for the ^{13}C aging study contained 1% antioxidant. Resins were thermally cured in Teflon coated molds for 1 week at 65 °C to obtain sheets of 2 mm thickness.

Thermal Aging and Oxygen Consumption (Uptake) Rubber shreds (approximately 1 mm thick) were cut from the sheets and sealed in steel ampoules of known volume. The thinness of the samples was optimal for homogeneous degradation: diffusion-limited oxygen effects and loss of antioxidant were both minimal. The ampoules were evacuated and filled with 81% enriched $^{17}O_2$ (Isotec) (or unlabeled O_2 gas for the ^{13}C NMR experiments) to a pressure calculated to result in a 150 mmHg pressure at the relevant aging temperature. The containers were then placed in temperature-controlled (±1 °C stability) commercial air-circulating aging ovens. The aging time was calculated to allow for approximately 30% of the O_2 to be consumed, thus resulting in an average partial pressure of $^{17}O_2$ during each aging exposure of 130 mmHg: the ambient air conditions in Albuquerque. Varying the aging time and the ratio of sample to gas volume in the sealed ampoule allowed a sensitivity range of $\phi \approx 10^{-13}$ – 10^{-8} mol/gs.[4,5] Gas chromatography analyzed the loss of O_2 and generation of CO_2. A summary of samples used for the ^{17}O oxidation studies is listed in Table 1.

Table 1. $^{17}O_2$ oxygen uptake on HTPB/IPDI binder samples. The amount of CO_2 is calculated as the percentage of consumed O_2.

Sample	Exposure	O_2 in sample	CO_2
HTPB + 1% AO	10 d at 110 °C	1.89 wt%	18%
HTPB + 1% AO	256 d at 80 °C	1.98 wt%	3%
HTPB + 1% AO	575 d at 65 °C	0.60 wt%	19%
HTPB, no AO	2.25 d at 80 °C	3.27 wt%	19%
HTPB, no AO	14 d at 50 °C	3.87 wt%	14%
HTPB, no AO	145 d at 23 °C	3.68 wt%	6%

NMR Spectroscopy The ^{17}O NMR solution spectra were obtained on a Bruker DRX400 NMR at a resonant frequency of 54.3 MHz using a 5-mm broadband probe. The oxidized samples were swollen by hot 1,2,4 trichlorobenzene (Aldrich) to decrease the molecular correlation time and thus reduce the observed linewidths in the NMR spectra.[6] Approximately 100 mg of each sample and 500 mL of solvent were placed in 5-mm NMR tubes. The spectra were run at 75 °C with a spin-echo and proton decoupling. The following parameters were used: 90° pulse length = 11 μs; recycle delay = 0.2 s; dwell time = 7.7 μs; acquisition time = 15 ms; number of scans = 200 k; total experiment time = 12 hours. The spectra were calibrated to an external H_2O standard which has a sharp peak assigned to be $\delta = 0$ ppm.

The solid-state ^{13}C NMR spectra were obtained on a Bruker AMX400 spectrometer with a ^{1}H frequency of 400.2 MHz and a ^{13}C frequency of 100.6 MHz. Binder samples were placed in 4-mm diameter zirconia rotors and spectra were obtained under 10 kHz magic-angle spinning. Typical 90° pulse lengths for ^{13}C were 4.0 μs and the ^{1}H decoupling strength was 60 kHz. Hahn-echoes were used in all experiments to minimize baseline distortions. Quantitative ^{13}C spectra were obtained with single-pulse excitation and a 10 s recycle delay. The chemical shifts were calibrated to the carbonyl of an external glycine reference ($\delta = 176.0$ ppm).

Results and Discussion

The ^{17}O spectra of aged HTPB binders without antioxidant are shown in Figure 1. The observed peaks in the spectra are assigned to degradation products based on ^{17}O chemical shifts of small molecules[7] and oxidized polymers.[8,9] In all spectra, the main peak is observed at $\delta = 11$ ppm and is assigned to be alcohols. Primary, secondary, and tertiary alcohols have ^{17}O chemical shifts of $\delta \approx 0$, 35, and 60 ppm, respectively. There is a shoulder on the downfield side that is attributed to secondary, tertiary, and/or unsaturated alcohols.

The other major degradation products detected in the ^{17}O spectra are esters and carboxylic acids. The ^{17}O peak at 260 ppm is present in all spectra and is assigned to be carboxylic acid functional groups. The ester functional groups result in two observed peak regions at 350 and 195 ppm which correspond to the C=O and C-OR oxygens, respectively. There are two observed types of esters, but no assignment is made. The peak at –9.2 ppm is attributed to H_2O, and the peak at 77.3 ppm is an unidentified small molecule.

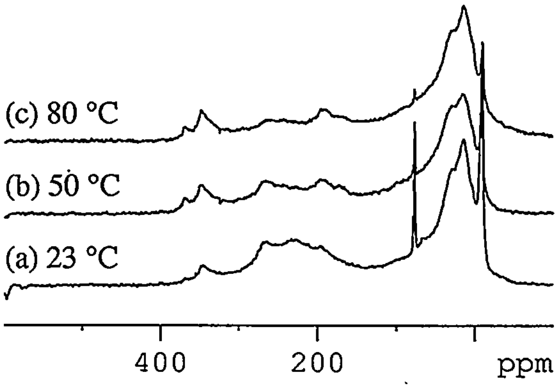

Figure 1. The solution ^{17}O spectrum of HTPB/IPDI polyurethane with no antioxidant aged for (a) 145 days at 23 °C, (b) 14 days at 50 °C and (c) 2.25 days at 80 °C.

A bar graph, calculated from the ^{17}O peak integrals, is shown in Figure 2. The integrated areas of the acid and ester peaks are divided by 2 to compensate for the two oxygens per functional group, and the CO_2 is calculated from gas chromatography. For samples with no antioxidant, higher temperature aging results in greater loss of CO_2 and thus less carboxylic acid remaining in the polymer. The total quantity of acid and released CO_2 is constant.

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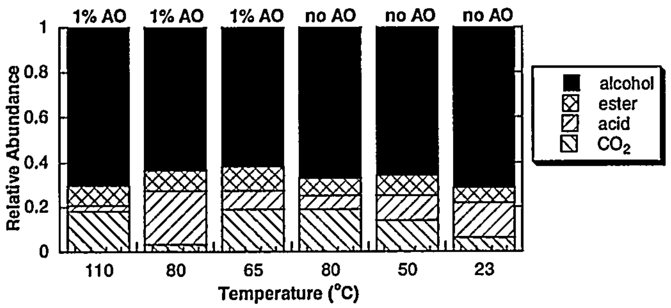

Figure 2. Temperature and antioxidant dependence of degradation products of HTPB/IPDI polyurethane with 1% antioxidant (left) and without (right).

The ^{13}C spectra provide complimentary information about the chemical environment of the carbons in aged HTPB/IPDI polyurethanes. The spectrum of unaged binder shows that initially half of the carbons, as expected, are unsaturated hydrocarbons. The distribution of this unsaturation is: 22% 1,2 unsaturation, 55% *trans* 1,4 unsaturation, and 23% *cis* 1,4 unsaturation. After aging the polyurethane at 80 °C, Figures 3b-f, the peaks broaden, a lower percentage of carbons are unsaturated, and both alcohol and carbonyl degradation products appear. The peak arising from the alcohols is broad, ranging from 85 to 65 ppm. This breadth may be the result of secondary and tertiary functional groups. Diols might also be responsible for the high chemical shift of some alcohol carbons.

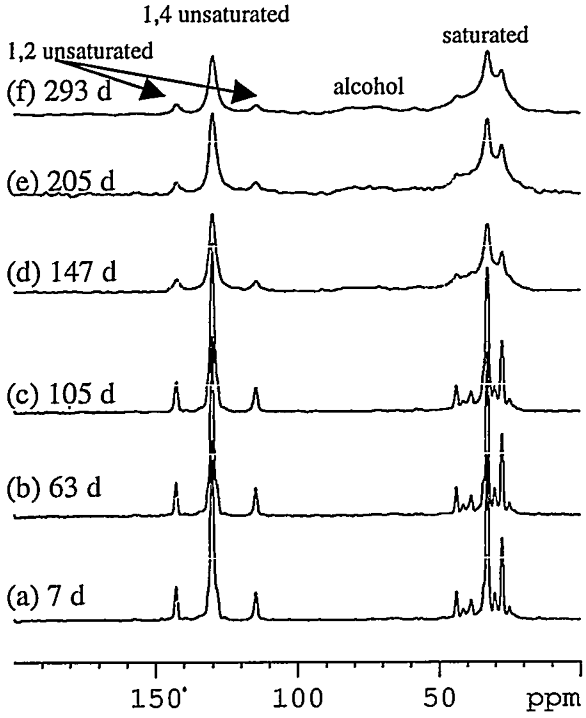

Figure 3. Solid-state ^{13}C single-pulse excitation spectra of HTPB/IPDI polyurethane aged at 80 °C for (a) 7 days, (b) 63 days, (c) 105 days, (d) 147d, (e) 210 days, and (f) 293 days.

Integration of the regions yields the relative abundance of the functional groups. A graph of the results, Figure 4, shows that oxidative degradation of the unsaturated carbons results in an approximately equal increase in both saturated hydrocarbons and alcohols.

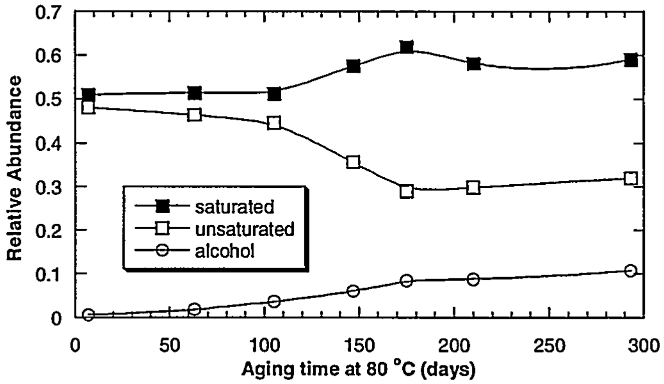

Figure 4. Relative abundance of degradation products as determined from ^{13}C single-pulse excitation spectra. Lines are guides for the eye.

Conclusions

The ^{17}O NMR spectra showed that the relative abundance of degradation products in aged HTPB/IPDI polyurethane is relatively independent of aging temperature. Oxidation results primarily in alcohols. Esters and carboxylic acids were also present at all studied temperatures but higher temperature results in production of CO_2 gas and thus less carboxylic acid. Ketones and aldehydes are not detectable. Loss of unsaturation was detected by the ^{13}C spectra. The ^{13}C spectra also confirmed the presence of alcohol and carbonyl functional groups.

Acknowledgement We thank Leanna Minier for advice and support. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL8500.

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