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Title: Thermal Degradation Studies of Nitroplasticized Estane® 5703 Utilizing 13C Enriched Model Polymers

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Thermal Degradation Studies of Nitroplasticized Estane® 5703 Utilizing ^{13}C Enriched Model Polymers

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ABSTRACT

Predicting the lifetime of PBX 9501 is critical to assurance of the reliability of the nuclear weapons stockpile. In support of the Lifetime Prediction Model, we have been investigating the physical and chemical aging processes that can potentially affect the lifetime of PBX 9501. Surveillance data of stockpile PBX 9501 binder have shown a decrease in Estane molecular weight as a function of age. Estane is a poly(ester urethane) consisting of poly(butylene adipate) as the flexible soft segment and 4,4'-methylenediphenyl-1,1'-diisocyanate (MDI) chain extended with 1,4-butanediol (BDO) as the rigid hard segment efforts have focused on chemical reactions that may cause chain scission of Estane through hydrolytic degradation of the polyester soft segments. Thermal aging of Estane in the absence of water shows no signs of hydrolytic degradation, whereas, appearance of high molecular weight species has been observed for Estane aged at elevated temperatures in the presence of nitroplasticizer. These high molecular weight species are most likely due to branching reactions that eventually leads to formation of an insoluble, cross-linked gel.

While the mechanisms of hydrolytic degradation of polyesters has been addressed, the degradations reactions of poly(ester urethane) (PESU) in the presence of NP are not well understood. We have prepared a series of isotopically enriched PESU model compounds chemically similar to Estane for aging experiments in order to understand possible cross-linking mechanisms. Changes in physical properties are observed with less than 1 % chemical cross-linking. Isotopic enrichment of 13C from 1.1% natural abundance to 100% improves the sensitivity of spectroscopic techniques so that small quantities of degradation products can be observed. Because degradation reaction mechanisms of importance may occur at the hard segment portion of the polymer, we have prepared 13C PESU with 13C labeled at the methylene carbon. These model polymers have been formulated into a polymer-rich binder without stabilizer, thermally aged under different environments, and examined using NMR and FTIR spectroscopy to identify degradation products and possible degradation pathways. Results of these preliminary aging studies on unstabilized polymer rich binder are presented herein.

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Background and Purpose of Study

Determine possible oxidative degradation mechanisms for nitroplasticized Estane binder using Estane 5703, low molecular weight model compounds, and model polymers.

Experimental method

Polymer models (preliminary experiments)
- Synthesis of isotopically labeled MDI PESU Polymers
- Aging studies of 10%NP/Polymer (polymer rich) aged 120°C, 70°C & 50°C
  - NMR, FTIR & GPC analyses

Small molecule model
- Aging studies of compounds in the presence of NP
- Spectroscopic analysis

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Isotopically Labeled Materials for Polymers

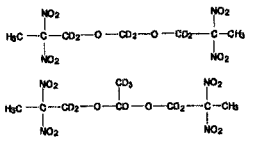
Isotopically Labeled BDO

BDO $HOCH_2CH_2CH_2CH_2OH$

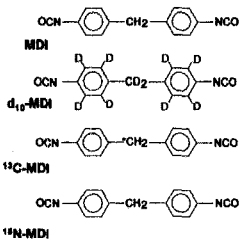
d_8-BDO $HOCD_2CD_2CD_2CD_2OH$

^{13}C-BDO $HO^*CH_2CH_2CH_2{}^*CH_2OH$

Isotopically Labeled NP



Isotopically Labeled MDI



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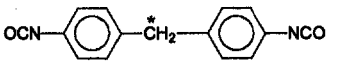
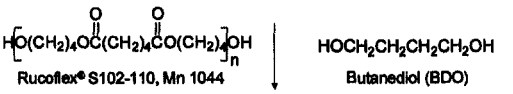
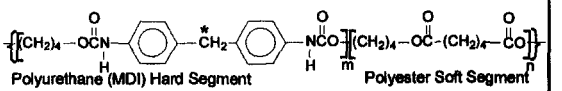


Methylene diphenyldiisocyanate (MDI)



Rucoflex® S102-110, Mn 1044

Butanediol (BDO)



Polyurethane (MDI) Hard Segment

Polyester Soft Segment

m = 1-3, n = 4-6

* Site of ^{13}C Enrichment

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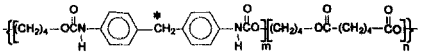
Aging Experiments with Isotopically Labeled Polymer



m = 1-3, n = 4-6

Poly(ester urethane) (PESU) prepared from ^{13}C labeled MDI

Experimental Method
- Cast and dry films of Binder sample of 10% NP in ^{13}C PESU or Estane from MEK
- Prepare samples under air, argon or desiccated argon
- Place samples in oven at 70°C or 120°C
- Analyze by NMR, GPC and IR

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^{13}C Labeled PESU / NP (10%)

Aged at 70°C
1 month

Aged 120°C
12 days

Samples in Air (vial), under dry Argon (ampule with silica) and under Argon (sealed ampule).
Note: Samples aged at 120°C have darkened in color.

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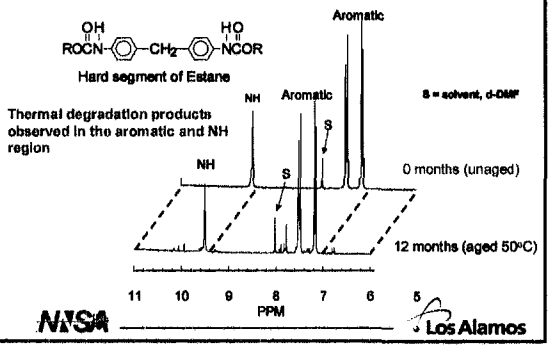
^{1}H NMR of 15%Nitroplasticizer in Estane® 5703



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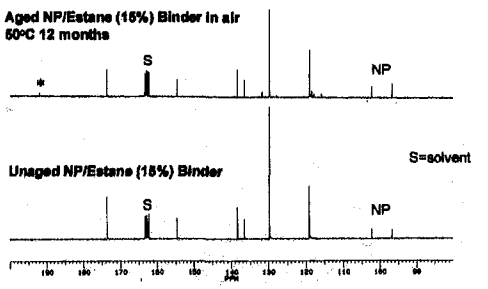
^{13}C NMR Spectra in d-DMF



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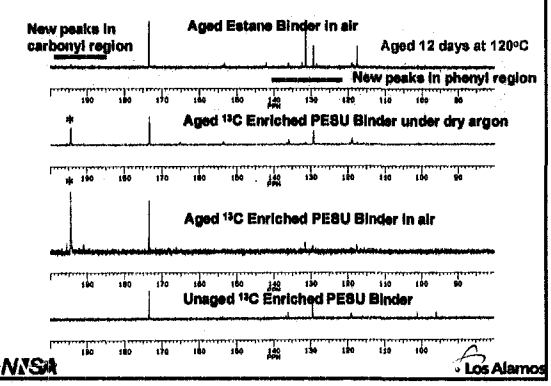
^{13}C NMR Spectra of Binder (10% NP) in $CDCl_3$



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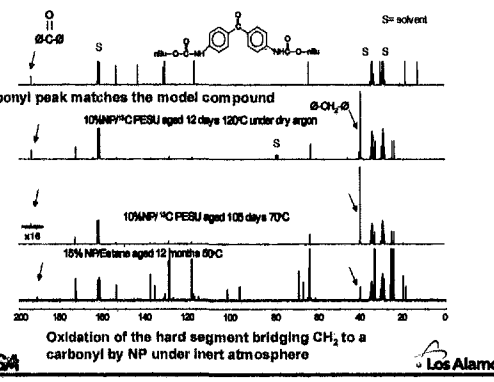
^{13}C NMR Spectra of Binder (10% NP) in d-DMF



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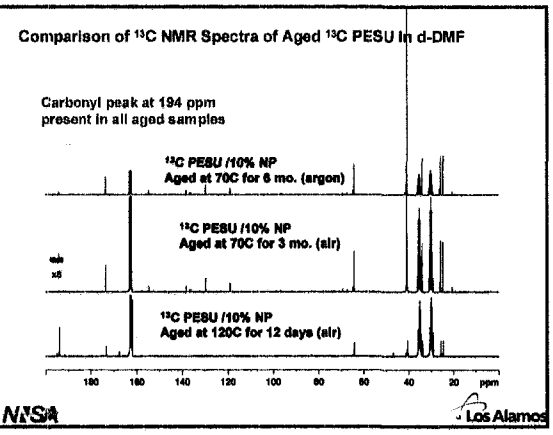
Comparison of ^{13}C NMR Spectra of Aged ^{13}C PESU in d-DMF



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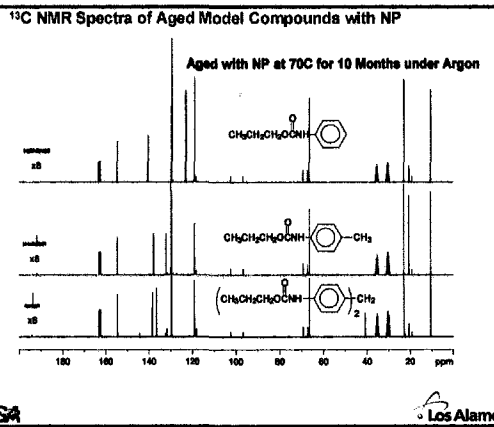
^{13}C NMR Spectra of Aged Model Compounds with NP



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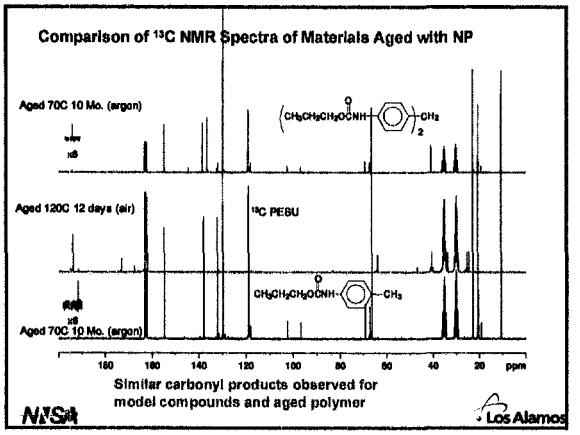
Comparison of ^{13}C NMR Spectra of Materials Aged with NP
Aged 70C 10 Mo. (argon)
Aged 120C 12 days (air)
^{13}C PESU
Aged 70C 10 Mo. (argon)
160 140 120 100 80 60 40 20 ppm
Similar carbonyl products observed for model compounds and aged polymer
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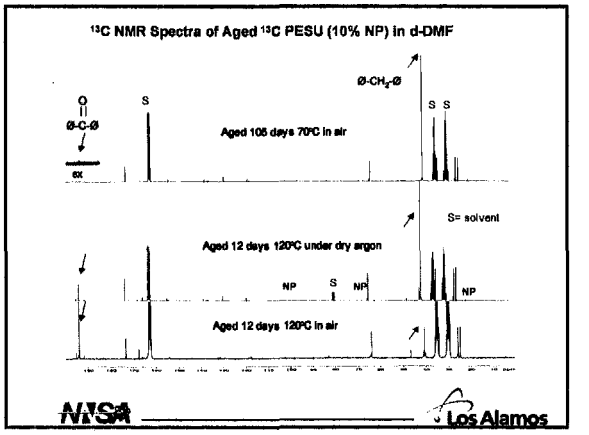
^{13}C NMR Spectra of Aged ^{13}C PESU (10% NP) in d-DMF
Aged 105 days 70ºC in air
S= solvent
Aged 12 days 120ºC under dry argon
NP
Aged 12 days 120ºC in air
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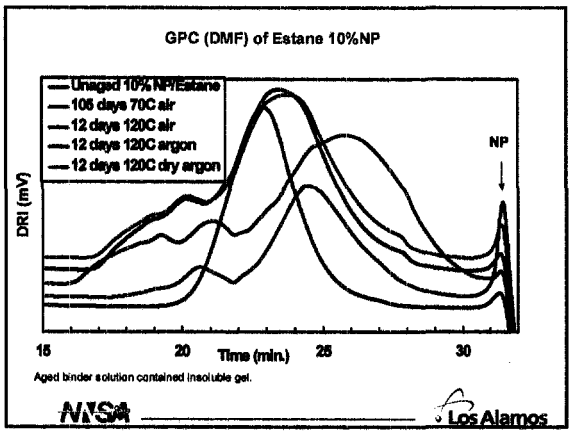
GPC (DMF) of Estane 10%NP
Unaged 10% NP/Estane
105 days 70C air
12 days 120C air
12 days 120C argon
12 days 120C dry argon
NP
DRI (mV)
15 20 Time (min.) 25 30
Aged binder solution contained insoluble gel.
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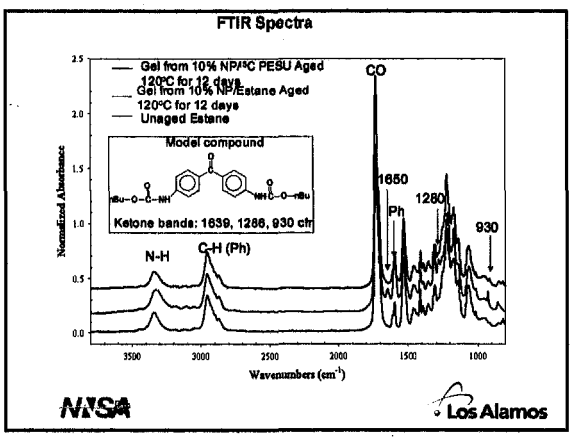
FTIR Spectra
Gel from 10% NP/^{13}C PESU Aged 120ºC for 12 days
Gel from 10% NP/Estane Aged 120ºC for 12 days
Unaged Estane
Model compound
Ketone bands: 1639, 1286, 930 cm
CO
1650
Ph
1280
930
N-H
C-H (Ph)
Normalized Absorbance
Wavenumbers (cm^{-1})
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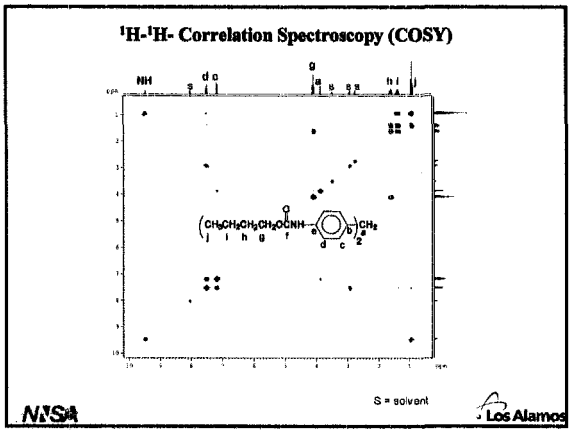
^{1}H-^{1}H- Correlation Spectroscopy (COSY)
NH
S = solvent
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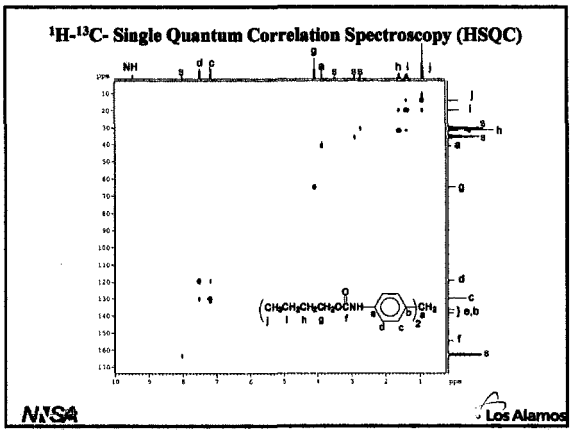
^{1}H-^{13}C- Single Quantum Correlation Spectroscopy (HSQC)
NH
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Conclusions

Preliminary results of thermal degradation with NP

- Isotopic enrichment (^{13}C PESU) allows observation of degradation products that *otherwise* are undetectable by ^{13}C NMR spectra
- Aging in the presence of O_2 – greater degradation;similar products under inert atmosphere
- Effect of temperature
  - All temperatures show similar products; gelation and signs of cabonyl degradation product
- Model molecules
  - Observation of degradation products similar to PESU by ^{13}C NMR
- Possible Mechanism – Oxidative – Carbonyl Product
  - Oxidation of bridging CH_2 to ketone
  - GPC shows signs bimodal MW distribution and signs of possible branching along with cross-linking as well as low MW species
  - FTIR of extracted gels show changes in carbonyl and phenyl regions
  - Good agreement of ^{13}C NMR and FTIR with bridging carbonyl model compound

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Future Studies

Chemical degradation studies

- Aging studies with isotopic labeled polymers with NP
  - Probe lower aging temperature – kinetics information
  - Probe effect of stabilizer content
  - Determine radical induced mechanism (ESR)
  - Examine insoluble gel with solid state NMR (^2H, ^{13}C, ^{15}N)
  - Spectroscopic characterization i.e. ^{13}C and ^{15}N solution NMR, multidimensional NMR, FTIR, ESR, Optical Absorbance / Luminescence Studies,
  - Identify the degradation products of small molecules and polymers
- NO_2 Polymer Studies of isotopic labeled polymer
- Determine initial NP degradation mechanism

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Acknowledgments

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