^{17}O NMR INVESTIGATION OF NYLON HYDROLYSIS

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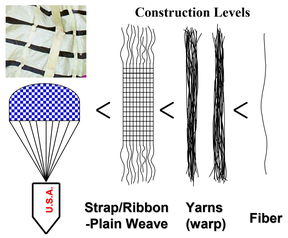
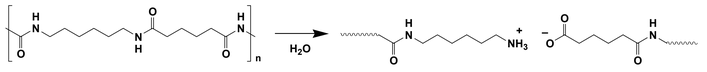
Abstract

Selective use of the ^{17}O isotope has proven to be a powerful tool to study polymer degradation using Nuclear Magnetic Resonance (NMR) spectroscopy. Due to the low natural abundance of ^{17}O (0.037%), the use of an ^{17}O-enriched source during hydrolysis ($H_2{}^{17}O$) and/or oxidation ($^{17}O_2$) of materials allows the selective observation of the resulting degradation species by NMR, without interfering signal from "native" or unaged material. This poster will report the recent use of ^{17}O NMR to study the oxidative hydrolysis of nylon 6.6. It has been demonstrated that the hydrolysis of nylon is strongly dependent on the chemical composition of the hydrated atmosphere. A series of experiments involving a matrix of conditions with ^{17}O-labeled H_2O, ^{17}O-labeled O_2, Ar and various combinations were studied by ^{17}O NMR allow the distribution of different degradation species to be determined.



Nylon Aging

Hydrolysis of Nylon 6.6



Nylon 6.6

• A series of aged nylon samples were prepared using ^{17}O labeled H_2O and O_2 as detailed in the Aging Matrix Table below.

• The aged nylon samples were removed from aging containers and immediately dissolved in trifluoroethanol (TFE) to retain both non-volatile and semi-volatile degradation species. Previous studies have shown that drying prior to NMR analysis of the aged sample removes many of the semi-volatile aged species.

Aging Matrix Table

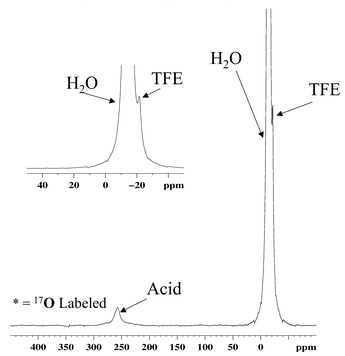
Sample Type	Nylon Weight (mg)	H_2O^* (µl)	H_2O (µl)	O_2^* (torr)	O_2 (torr)	Time (days)
$O_2 + H_2O^*$	30.398	200			107.0	3
$O_2 + H_2O^*$	30.787	200			129.9	10
$O_2 + H_2O^*$	29.536	200			137.0	22
$O_2^* + H_2O$	31.509		200	107.0		3
$O_2^* + H_2O$	30.891		200	123.9		10
$O_2^* + H_2O$	30.619		200	135.1		30
$O_2^* + H_2O^*$	30.814	200		106.4		3
$O_2^* + H_2O^*$	29.607	200		125.0		10
$O_2^* + H_2O^*$	30.625	200		138.0		22

Note: All samples aged at 125°C

* = ^{17}O Labeled

^{17}O NMR

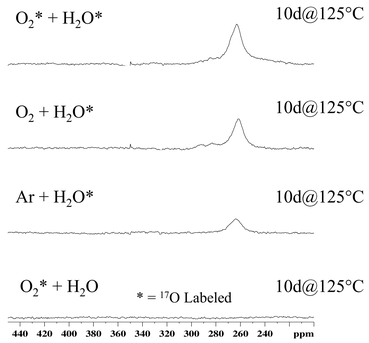
$H_2O^* + O_2^* +$ Nylon



• The ^{17}O NMR spectra for ***all*** nylon samples aged under ^{17}O-labeled H_2O show a strong resonance from surface adsorbed water (-14.2 ppm), along with a resonance from carboxylic acids (258.8ppm) produced during aging.

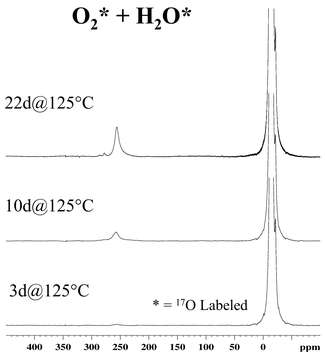
• No ^{17}O resonances are observed for aldehydes, ketones (+800 to 550 ppm), esters (+375 to 325 ppm and +175 and 100 ppm) or amides (+350 to 300 ppm) demonstrating that these degradation species are not produced under the aging conditions investigated.

Carboxylic Acid Region

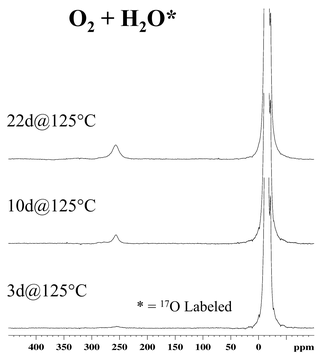


• Different concentrations of ^{17}O-labeled carboxylic acid are produced depending on which hydrolysis occurs.

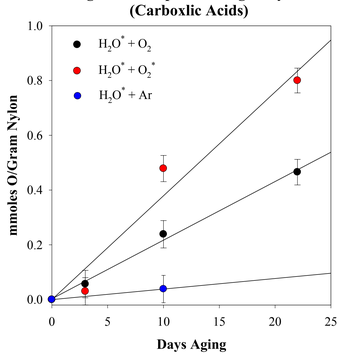
$O_2^* + H_2O^*$



$O_2 + H_2O^*$



Concentration of Oxygen Containing Degradation Species in Aged Nylon (Carboxlic Acids)



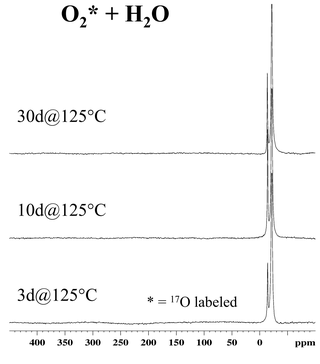
• Even though no new ^{17}O-labeled degradation species are observed, the presence of O_2 during aging at 125 °C clearly increases the rate of nylon hydrolysis.

• For samples containing ^{17}O labeled H_2O the concentration of the carboxylic acid increases with exposure time, consistent with the hydrolytic cleavage of the nylon as described in Eqn. 1.

• The lack of any observable amide ^{17}O NMR resonance shows that the reverse reaction of Eqn 1 does not occur.

• The strong resonance from adsorbed H_2O may obscure any weak resonances from alcohol or ether species (+50 to 0 ppm).

$O_2^* + H_2O$



• In the ^{17}O NMR spectra for the H_2O + ^{17}O aged samples the strong resonance from adsorbed water is not present (since the H_2O was not labeled). For these samples no other ^{17}O-labeled degradation species are observed, < 30µmole O/gram polymer (***even alcohols and ethers***) demonstrating that O_2 is not directly involved in the production of oxygen containing degradation species. This experiment also demonstrates that back exchange between the $^{17}O_2$ gas and acids produced during hydrolysis does not occur.

Conclusions

• The use of ^{17}O NMR to follow aging in polymer systems is a powerful tool.

•There appears to be a synergism between hydrolysis and the presence of oxygen during the aging of nylon 6.6.

•The discrepancy between the acid concentration produced under $H_2{}^{17}O + O_2$ versus $H_2{}^{17}O + {}^{17}O_2$ has not been explained. Replication of these experiments under identical conditions are now in progress

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.