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Physical Aging in Anhydride-Cured DGEBA Epoxy

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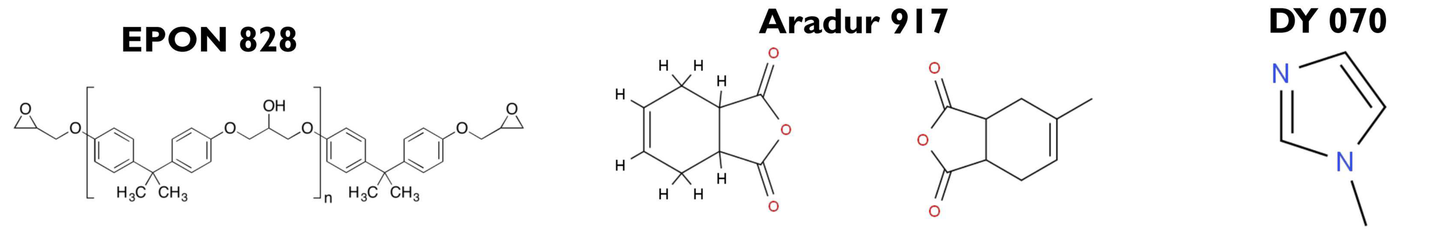
Introduction

Epoxy resins are a type of thermosetting polymer that are ideal for many applications because of their high specific strength and stiffness, and ease of manufacturing. Epoxies are commonly used as encapsulants and adhesives, as well as in many other applications. Because of their relatively high strength and given applications, epoxies may be exposed to elevated temperatures and harsh environments for long periods of time. Being held at these conditions can result in the aging of the material. When using epoxies for long-term applications, it is important to take into account the effects of aging because of the potential changes in reliability of the material.

In this work, the effects of aging were studied on an anhydride-epoxy system. This system was composed of a DGEBA epoxy resin (EPON 828, Hexion), an anhydride (Aradur 917, Huntsman), as well as an accelerator (DY 070, Huntsman) to increase the rate of reaction between the epoxide and the anhydride. This system (epoxy-rich, 1:0.9 molar ratio of epoxide:anhydride) will be referred to as 828/917.

EPON 828 | **Aradur 917** | **DY 070**



Diglycidyl Ether of Bisphenol A
100 pbw

Tetrahydrophthalic Anhydride | 4-Methyltetrahydrophthalic Anhydride
79 pbw

1-methylimidazole
0.895 pbw

The results are compared to those found for an amine-epoxy system, composed of the same DGEBA resin but mixed with Jeffamine T-403 (at a stoichiometric ratio), a polyetheramine.

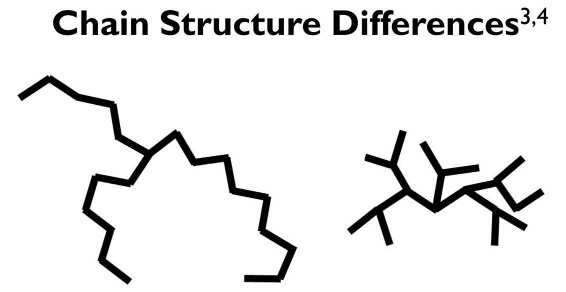
EPON 828 | **Jeffamine T-403**

Diglycidyl Ether of Bisphenol A
100 pbw

Polyoxypropylene Polyamine
43 pbw

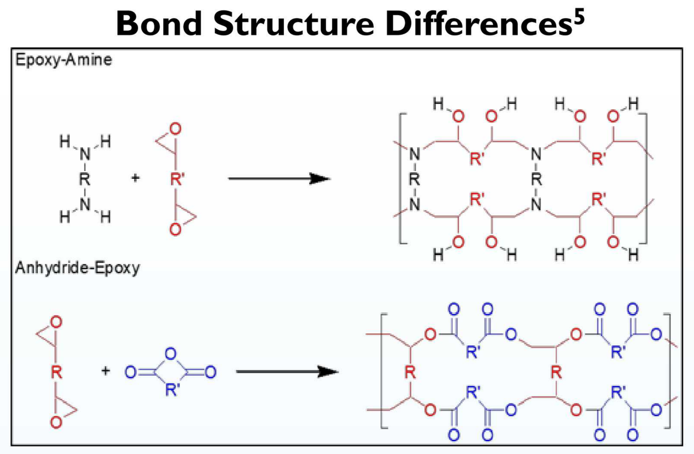
The network formation of these two thermosets is considerably different, due to the epoxy-amine reacting by a step-growth mechanism versus the epoxy-anhydride reacting by a chain growth mechanism. A comparison of these materials provides some insight into the dependence of aging on network structure.

Chain Structure Differences[3,4]



Chain-growth | Step-growth

Bond Structure Differences[5]

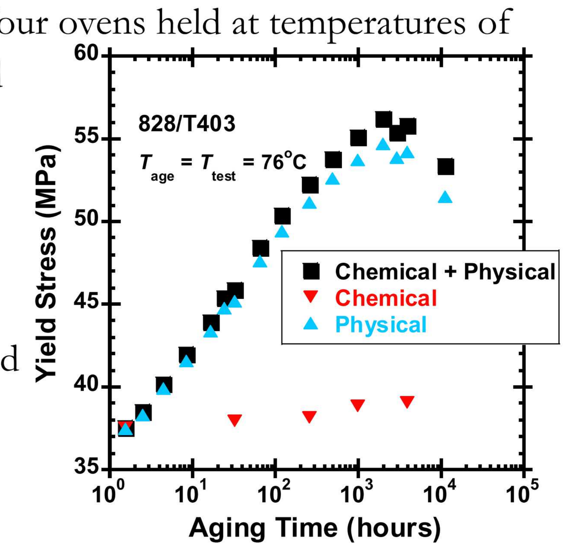


Experimental Methods

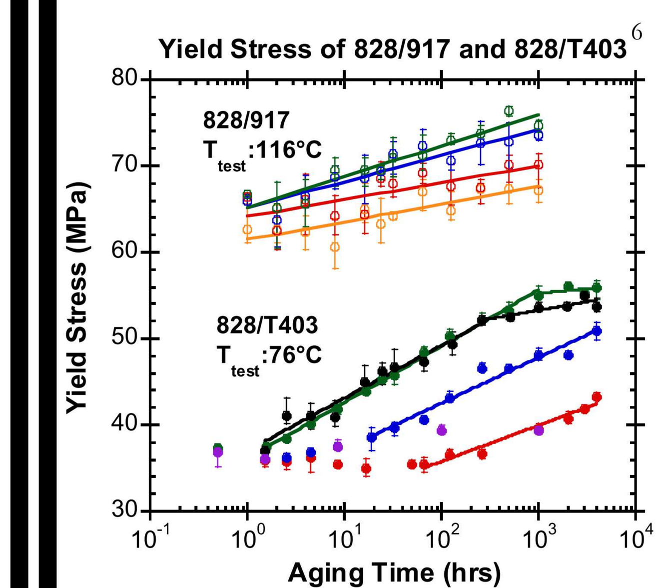
Compression samples of the 828/917 material were created by curing the material in cylindrical molds (D=0.56") for 5 hours at 80°C followed by 3 hours at 140°C. After the cure, the samples were cut to have a length of 1.12" to provide a 2-to-1 length to diameter ratio. Samples were annealed at ~30°C above the glass transition temperature, T_g, for 30 minutes and then cooled to room temperature at 1°C/minute to erase history associated with the manufacturing process and define a known history.

After samples were prepared, they were placed into one of four ovens held at temperatures of 96°C, 106°C, 116°C, and 124°C (corresponding to 19°, 27°, 37°, and 47° below T_g). The samples were allowed to remain in the ovens for up to 1000 hours. Compression samples were tested on an Instron load frame. The samples were allowed to equilibrate to test temperature for 1 hour and then compressed to a 12% strain at a strain rate of $0.1 min^{-1}$.

While current 828/917 experiments include any chemical and physical aging effects on the compressive stress-strain response, previous work on other materials suggest the dominant contribution to yield stress changes are associated with physical aging.[5]

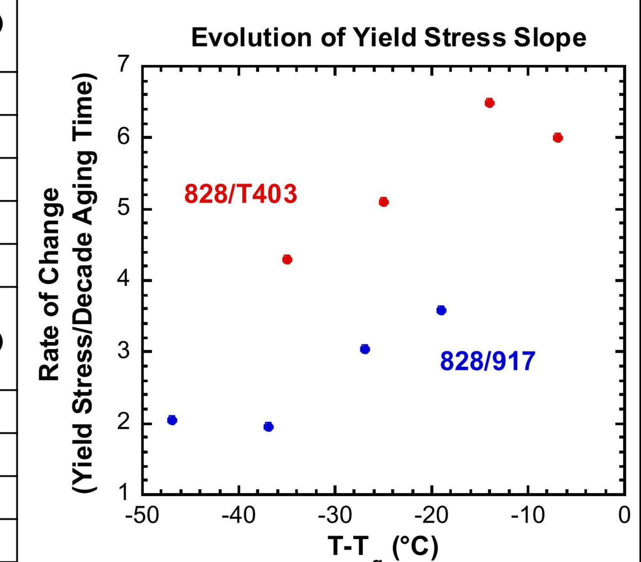


Comparison between 828/917 and 828/T403



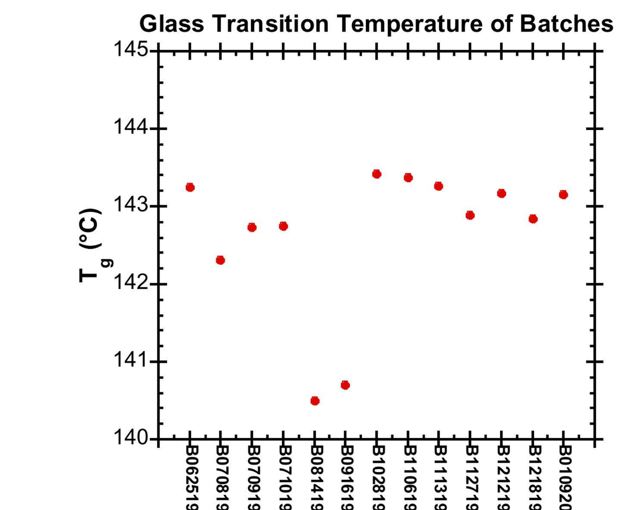
Aging Temperature	Rate of Change (MPa per decade) (828/917)
○ T_g – 47°C	2.0
○ T_g – 37°C	2.0
○ T_g – 27°C	3.1
○ T_g – 19°C	3.6

Aging Temperature	Rate of Change (MPa per decade) (828/T403)
• T_g -35°C	4.2
• T_g -25°C	5.3
• T_g -14°C	6.5
• T_g -7°C	6.1
• T_g + 15°C	-

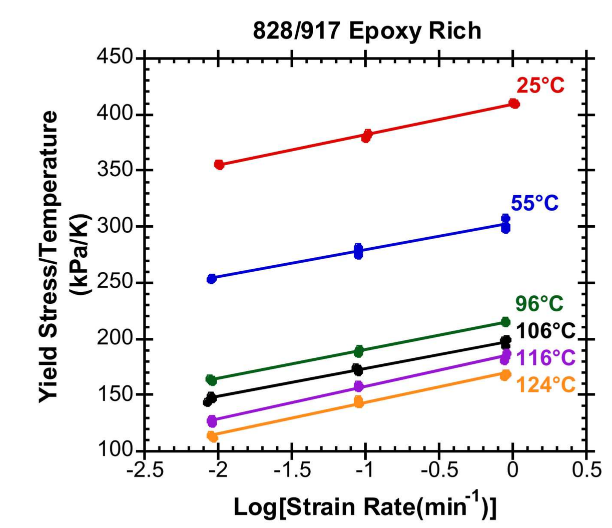


- At lower aging temperatures (≤ T_g-25°C), 828/T403 yield stress evolution appears to exhibit an "induction time"
- Discrimination of such an induction time for the 828/917 yield stress evolution is not clear at this point. Additional data at longer aging times may resolve this question.
- At equidistance from T_g, 828/T403 exhibits a faster evolution of yield stress than 828/917

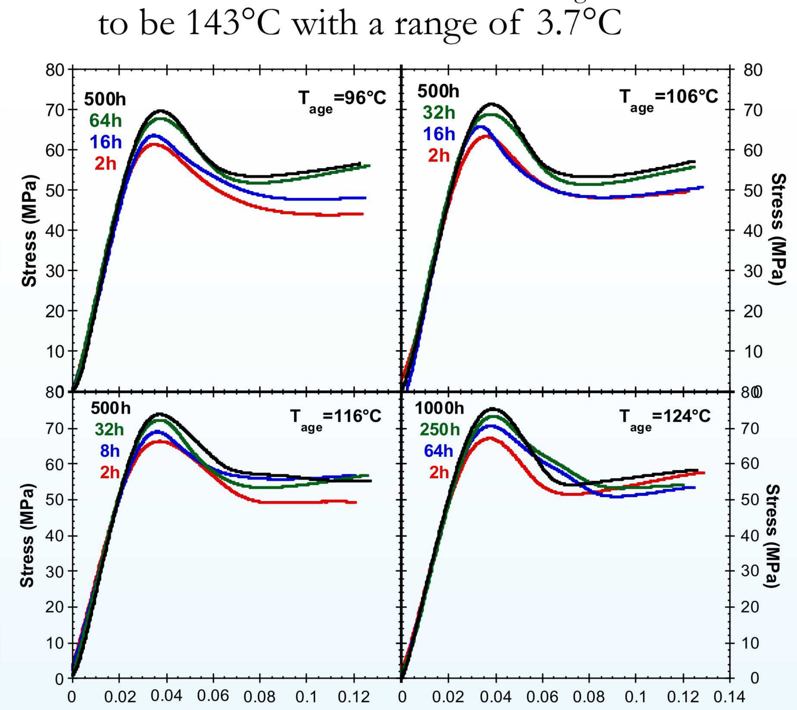
Epoxy-Anhydride Results



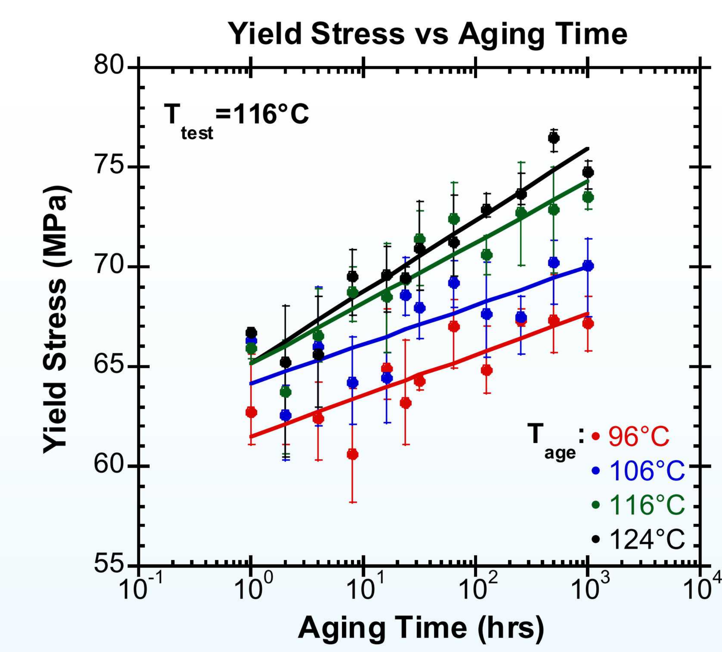
The glass transition temperature variation from batch to batch. The average T_g found to be 143°C with a range of 3.7°C



The 828/917 material exhibits a slope of 26.5 kPa/K per decade, implying an Eyring activation volume of 1.2 nm^3



The figure above displays the changes in the compressive stress-strain response due to thermal aging. All samples were tested at 116°C but aged at one of the four aging temperatures.



An increase of yield stress occurs faster at higher aging temperatures. At lower aging temperatures (96° and 106°C), an increase in yield stress is more difficult to discriminate.

Conclusions

An 828/917 epoxy-anhydride system was aged for up to 1000 hours at four different sub-T_g temperatures. The effects of aging on the compressive stress-strain response are assessed and compared to that of an 828/T403 epoxy-amine .

From the results:

- Yield stress increases with aging time for both materials
    - The effects of aging are not equivalent between the materials at the same distance from T_g; the 828/T403 yield stress evolution occurs faster
        - If physical aging is the dominant contribution to yield stress evolution, this suggests that the more rigid structure of the anhydride molecule (versus the amine) and the differences in network structure between the thermosets results is less ability of the epoxy-anhydride to physically rearrange below T_g and densify the material.
- Temperatures well below T_g (e.g., T_g-25°C and below) appear to exhibit an induction time before observing a significant change in the yield stress. This is particularly apparent in the 828/T403 data with the induction time increasing with distance below T_g. It is less distinct in the 828/917 data at this point due to the smaller total changes in yield stress, but may become more apparent as data at additional aging times is obtained.

Moving Forward

The current research focused on the effects aging has on the yield stress of the system. Future work will include the following:

- Add additional aging temperatures closer to T_g (136°C; T_g-7°C)
- Continue aging samples to examine effects of more long term aging
- Erasing the physical history of the samples after aging and before testing to discriminate any chemical effects of aging on the compressive stress-strain response
- Investigate effects of aging on the enthalpy of the system through Differential Scanning Calorimetry
- Explore differences in physical aging of the current 828/917 system and the 828/917 system with the addition of polypropylene glycol

References

[1] Roth and Baglay in *Polymer Glasses*. Ed. Roth, C. B. CRC Press, 2017.
[2] Odegard and Bandyopadhyay, (2011) *Journal of Polymer Science Part B: Polymer Physics*, 49(24), 1695-1716.
[3] Kropka et al., SAND2019-9512.
[4] McCoy et al., (2019) *Thermochemical Acta*, 671 149-160.
[5] Kropka et al., SAND2017-13680.
[6] Wilson, (2018) *Physical Aging in a Polyether-Amine Cured DGEBA Epoxy.* MS Thesis, New Mexico Tech.

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