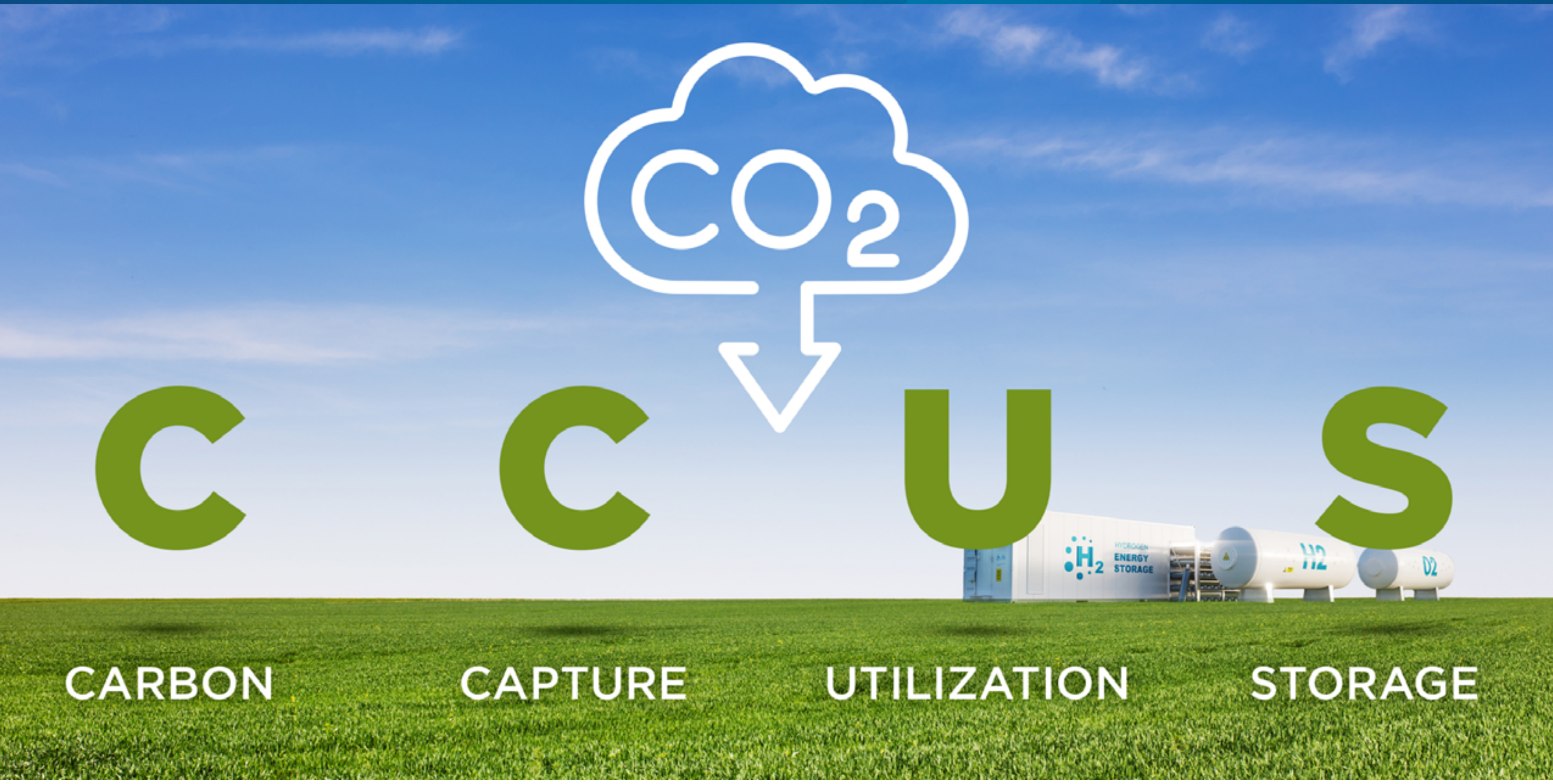
WHITE PAPER



MATERIALS THAT DEFY THE ODDS

IN CARBON CAPTURE APPLICATION

Not all FFKMs and PEEKs are compounded the same – **formulation matters!**

AUTHORS:
Seema Gangatirkar, MBA | Ferdinand Gonzaga, PhD | Kerry Drake, PhD

MATERIALS THAT DEFY THE ODDS IN CARBON CAPTURE APPLICATION

Not all FFKMs and PEEKs are compounded the same – **formulation matters!**

Introduction

Concerns over climate change have increased the urgency to reduce the global carbon footprint. Regulatory bodies around the world are setting ambitious objectives, bold deadlines, and strict measures to tackle this pressing issue. In response, leading companies in the energy, industrial and transport industries are considering hydrogen fuel to significantly lower emissions and pave the way for a more sustainable future.

Hydrogen offers tremendous promise as a clean energy solution, yet current production methods are carbon dioxide (CO_2)-intensive. Natural gas is converted to hydrogen, producing CO_2 as a byproduct. CCUS technologies are integrated to capture, compress, and store the CO_2 emissions underground, significantly reducing the carbon footprint of hydrogen production.

Amine-based CO_2 capture systems are highly effective in reducing carbon emissions in hydrogen production. Chemical absorption-desorption using amine-based solvents, such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and diglycolamine (DGA), are highly effective at removing CO_2. However, these solvents are also inherently corrosive and can pose challenges to the process equipment, which generally operates at up to 150°C and up to 10 bars pressure. Selecting appropriate materials for process equipment is critical to mitigating corrosion-related issues, ensuring operational reliability, and minimizing downtime.

In this paper, we will explore challenges posed by amines to elastomers and plastics, and present new innovative formulations developed to overcome amine resistance.

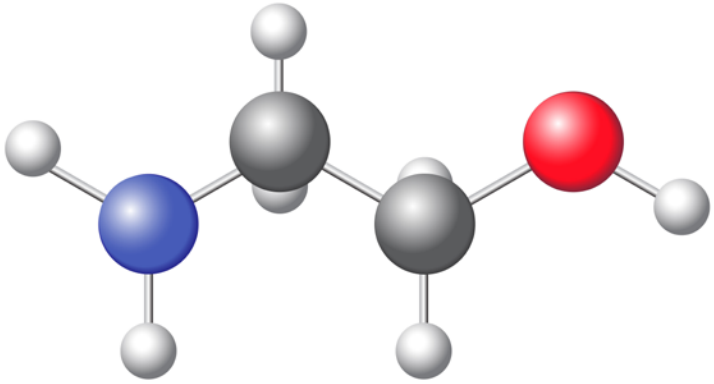
1. Amines: A Challenging Environment for Elastomers & Plastics

Amines are used to capture CO_2 and due to their interactive chemistry, these chemicals can have an aggressive effect on materials used for sealing or wear applications. We'll also share key testing data that highlights these challenges and how they can be mitigated.

2. Advancing Formulation Techniques for Amine Resistance

Operating in chemically harsh conditions requires robust material solutions. This is why advanced approaches, such as compounding FFKM for chemical resistance and applying cross-linking technologies for materials like advanced grades of PEEK, are crucial for improving performance.

This information will guide you in selecting the best materials for your carbon capture process.



monoethanolamine

Amines: A Challenging Environment for Elastomers & Plastics

Materials used in carbon capture can experience chemical degradation due to the wide use of amines, which are particularly aggressive due to their interactive chemistry. The risk can be mitigated by selecting materials with excellent resistance to chemicals, such as perfluoroelastomers (FFKM) and polymers like PTFE, PEEK, and PEI. Amines combine three detrimental properties:

They are good solvents for several polymers, which lead to swelling and/or dissolution.

They are basic compounds, and thus reactive towards any acidic hydrogen or moiety present in the elastomer or polymer.

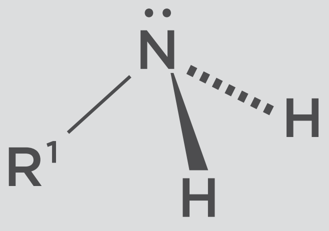
They are strong nucleophiles, and able to react with several functional groups present in polymers such as ketones, esters, and halogens.

These properties make amines a challenging environment for common elastomers and plastics.

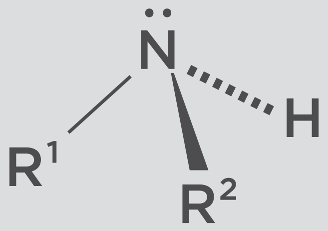
Amine structure diversity —ranging from primary to tertiary classes **(see call out box)**—makes it difficult to label any material as generally “amine-resistant,” as a material’s resistance to one class of amine may not translate to another class. Greene Tweed’s research emphasizes rigorous testing as minor structural differences can lead to very different behaviors, reinforcing that each material needs to be tested in conditions as close as possible to the application.

Amines are categorized in three main classes, following the number of chemicals groups attached to the Nitrogen atom versus the ammonia parent structure (NH3): primary amines have one substituent R1, secondary amines have two substituents R1 and R2, and tertiary amines have three substituents R1, R2 and R3, as shown below:

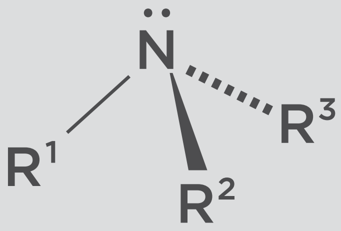
Primary (1°) amine



Secondary (2°) amine



Tertiary (3°) amine



The substituents can be identical, like in triethylamine (three identical ethyl groups as R1, R2 and R3), or different. Additionally, the substituents can be alkyl groups (saturated hydrocarbons) or unsaturated (like in allylamine) or aromatic (containing aromatic rings such as phenyl rings, like in aniline).

Finally, these substituents can also be functional and contain other reactive groups. One type of especially relevant functional amines to CCUS would be hydroxylated amines, which contain a hydroxyl group in one or more of the substituents.

Glycol amines are a type of hydroxylated amines, where the hydroxyl group is attached to a two carbons group (by analogy with glycol ethers). The most common amines include ethanolamine (MEA, a primary amine), diethanolamine (DEA, a secondary amine), diglycolamine (DGA) and methyldiethanolamine (or MDEA, a tertiary amine).

The richness of structural variations found in amines leads to a wide range of physico-chemical properties, in terms of solvency power, basicity and reactivity.

In the case of carbon capture, the risks of either chemical attack and/or solvent interactions can be significant. Amines are highly basic and, under certain conditions, can react with polymer functional groups present in common high-performance polymers, including PEEK and polyamides (aka “nylons”) and C-H containing groups in partially fluorinated elastomers (FFKMs).

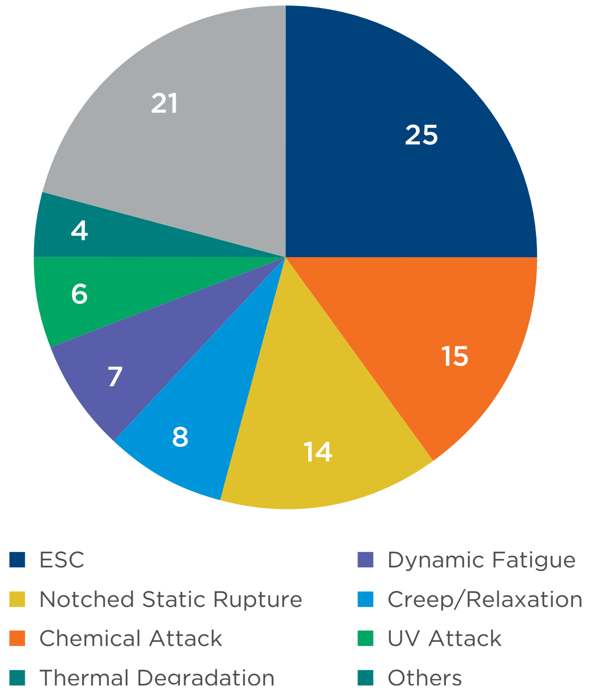
Chemical effects can account for up to 30 % of all field failures observed across multiple industries.

Plastics and Amines

For many plastic applications, chemical attack is the key failure mode attributed to amines. Chemical attack encompasses failures resulting from the material interacting with the chemical environment.

These are broadly categorized as chemical reactions resulting in chemical changes (often irreversible) or chemically induced changes in the polymer (solvation/swelling or solvent induced stress cracking-ESC **(See Figure 1)**. Chemical effects can account for up to 30 percent of all field failures observed across multiple industries, and in the case of aggressive chemistries at elevated temperatures, that failure rate may increase significantly.

Figure 1. Failure of Plastics and Rubber Products: Causes, Effects and Case Studies, Involving Degradation[iii]



Greene Tweed has more than 35 years of experience developing amine-resistant perfluoroelastomers (FFKMs), sold under the Chemraz® brand name. The high fluorine content in FFKMs offers better chemical resistance to harsh amine environments than other elastomers.

When designing seals for challenging applications, the cure chemistry of elastomers plays a pivotal role. For example, seals exposed to heat perform better with triazine-cured compounds, while peroxide-cured materials offer enhanced steam and acid resistance. However, improvements in one property, such as extending operational temperature limits, often require trade-offs in chemical resistance.

Greene Tweed developed a peroxide cured FFKM, Chemraz 555, that boasts superior compression set resistance compared to legacy FFKM 505 and 605 and thus earning a market-leading high operating temperature rating for a peroxide cured compound. Despite these enhancements, testing revealed that Chemraz 555 exhibited significant variability in performance depending on the specific amine exposure. For instance:

- **Similar Performance:** Chemraz 555 and 505 showed comparable hardness and volume changes in dipropyl amine and tributyl amine.
- **Weakened Performance:** Chemraz 555 demonstrated excessive hardness loss (over 30 durometer points) and significant swelling (>100%) when exposed to diglycolamine.

These results underscore the importance of understanding that FFKMS compounded with different polymers, fillers and curatives can have disparate outcomes under specific chemical conditions.

Advancing Formulation Techniques for Amine Resistance

Selecting the right material in chemically aggressive environments requires a deep understanding of the operational conditions and the intricacies of material behavior. Formulation is what matters here: Greene Tweed's innovative FFKM and cross-linked PEEK materials offer performance attributes such as heat and chemical resistance.

Introducing Chemraz® 541: Enhanced Chemical Resistance

Furthering its innovation, Greene Tweed introduced Chemraz® 541, optimized for chemical resistance in harsh environments using a proprietary formulation that included a next-generation polymer, fillers and cure system. While maintaining the operational temperature comparable to legacy materials, Chemraz® 541 demonstrated a marked improvement in performance when exposed to aggressive chemicals, including various amines used in carbon capture and storage (CCUS) applications.

Testing of Chemraz® 541 showed superior performance over FFKM 505 in **(see Table 1)**:

- **Diglycolamine Resistance:** Chemraz 541 exhibited only 4 durometer points of hardness change compared to the 12-point change in FFKM 505.
- **Reduced Swelling:** Volume change for Chemraz 541 was just 6%, a striking improvement from FFKM 505's 29%.

GREENE TWEED
Chemraz®
541

Table 1. Comparison of legacy FFKM 505 and new FFKM 541 in steam, acid and amines.

Fluid Aging		Chemraz® 541	Chemraz® 505	Fluid Aging		Chemraz® 541	Chemraz® 505
70 hrs @ 347°F in Stauffer 7700				**70 hrs @ 250°F in Steam**			
Hardness Change, Type M	Points	0.37	2	Hardness Change, Type M	Points	0.2	-4
Tensile Strength	%	5.83	-2	Tensile Strength	%	-6.8	-8
Elongation	%	6.23	-2.8	Elongation	%	2.5	-8
Volume Change	%	0	1	Volume Change	%	1.0	1.2
70 hrs @ Room Temp in ASTM Ref. Fuel				**168 hrs @ 250°F in Reagent Grade Sulfuric Acid**			
Hardness Change, Type M	Points	0.2	1	Hardness Change, Type M	Points	-3.5	-9
Tensile Strength	%	4.5	-16	Tensile Strength	%	2.5	-4
Elongation	%	3.1	-11	Elongation	%	-0.2	-6
Volume Change	%	0	1.9	Volume Change	%	9.3	19
70 hrs @ 250°F in Distilled Water				**168 hrs @ 302°F in Diglycolamine**			
Hardness Change, Type M	Points	1.3	-4	Hardness Change, Type M	%	-4	-12
Tensile Strength	%	-2.9	-11	Tensile Strength	%	-1	-16
Elongation	%	5.1	-3.5	Elongation	%	31	-30
Volume Change	%	1.3	1.45	Volume Change	%	6	29

Amine Compatibility for Carbon Capture and Storage (CCS)

Knowing that the class of amine could affect how a material behaves in application, Greene Tweed tested Chemraz 541 in DEA, MEA, MDEA, and TEA. Independent labs were engaged to evaluate Chemraz® 541's resistance to these chemicals under rigorous ISO 1817 and ISO 23936-2 guidelines.

Results confirmed Chemraz® 541's exceptional chemical robustness. Across 7- and 14-day tests at 150°C, Chemraz® 541 exhibited minimal volume and hardness changes, highlighting its suitability for CCUS applications **(See Figure 2 and 3)** for most chemicals tested. The biggest changes came during the immersion testing for TEA, where 541 showed a relatively higher amount of change in hardness and swell.

These findings stress the importance of matching FFKM elastomer formulations to the specific operational environment. Proper testing in application-specific conditions, including temperature and fluid exposure, is critical to ensuring long-term seal reliability.

Figure 2. Chemraz® 541 Hardness Change in Amines 7 and 14 days at 150°C/302°F

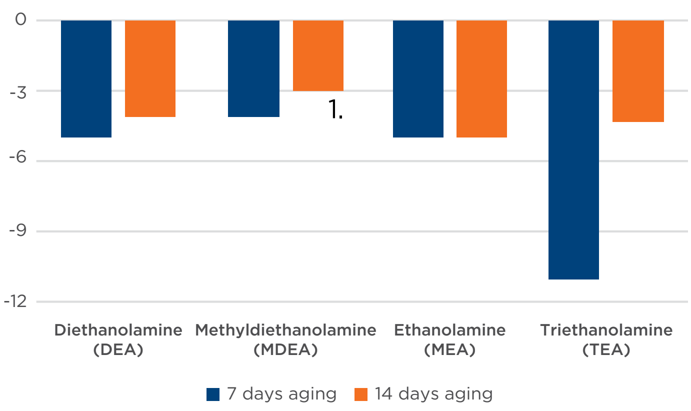
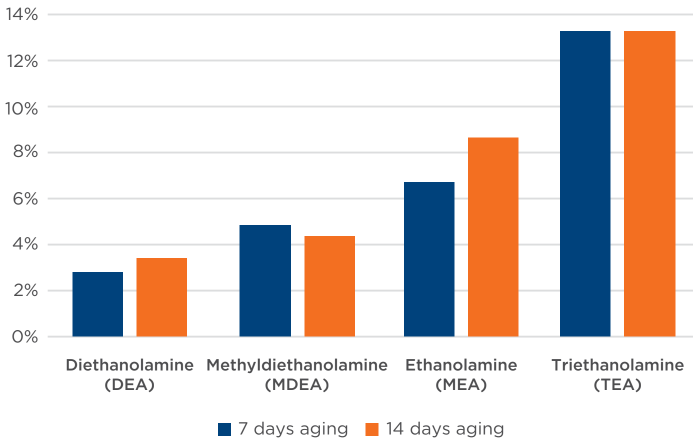


Figure 3. Chemraz® 541 Volume Change in Amines 7 and 14 days at 150°C/302°F



Cross-linking for Arlon 3000XT® over filled grades of PEEK

Several advanced applications rely on thermoplastics such as PEEK for its resilience, but the presence of amines introduces a significant challenge. Advanced chemical enhancement techniques, such as Greene Tweed's patented Arlon 3000XT® cross-linking technology, have redefined PEEK's performance in chemically aggressive settings. Unlike filled grades of PEEK, which rely on physical fillers for enhanced properties, Greene Tweed's cross-linked Arlon 3000XT® offers superior resistance to chemical degradation.

Advantages of Cross-Linking in Arlon 3000XT®

The cross-linking process creates covalent bonds between polymer chains, significantly improving thermal stability and mechanical strength. For applications requiring chemical robustness, Arlon 3000XT®'s cross-linked structure:

1. **Prevents Chemical Degradation:** Acts as a molecular shield against aggressive chemicals like amines.
2. **Minimizes Permeation:** Cross-linked polymers resist swelling and permeation, which can compromise material integrity.
3. **Enhances Longevity:** Improved durability ensures consistent performance under extreme operating conditions.

Compared to filled PEEK grades, Arlon 3000XT® demonstrates unmatched performance in environments where strength and chemical resistance are critical – when it can't fail.

Enhanced Resistance with Arlon 3000XT®:

Amongst performance plastics, PEEK shows enhanced resistance to amines; in particular, PEEK exhibits great resistance to ammonia and hydrazine, but also to organic amines such as aniline, diethylamine and pyridine.

Greene Tweed's proprietary cross-linked PEEK polymer, Arlon 3000XT®, demonstrates outstanding amine resistance compared to conventional plastics like PEEK.

- **Crosslinking technology** improves resistance to solvents and ensures minimal swelling in amine environments.
- **Higher glass transition temperatures** (Tg) bolster mechanical properties above operational ranges.

Arlon 3000XT®

Immersion Testing Results:

Testing under ISO 1817 and ISO 23936-2 guidelines revealed Arlon 3000XT retains its exceptional physical and mechanical properties after exposure to amines at 150°C for up to 14 days.

The 4 amines selected were MEA (Ethanolamine), DEA (Diethanolamine), MDEA (Methyldiethanolamine) and TEA (Triethylamine).

KEY FINDINGS

Minimal mass, volume, and density changes were observed, confirming outstanding physical stability. Immersion tests showed that Arlon 3000XT® was virtually unchanged, even after 14 days at 150C, in the 4 amines tested. These results can be attributed to the combination of cross-linking and crystallinity, which prevent diffusion of the amines inside the material **(See Figure 4-6 on page 8)**.

Mechanical properties like tensile strength and modulus showed less than 10% variation, even after prolonged exposure. The mechanical properties of Arlon 3000XT® remain strong after immersion for 7 days in 4 different amines at 150°C. Even after 14 days, the variation in Tensile strength remains inferior to 10%, and the Young's Modulus shows very minor variation. The only property showing a significant effect would be the elongation at break, especially for ethanolamine after 14 days. **(See Figure 7-10 on page 9)**.

Figure 4. Arlon 3000XT® Volume Change (%) at 150°C

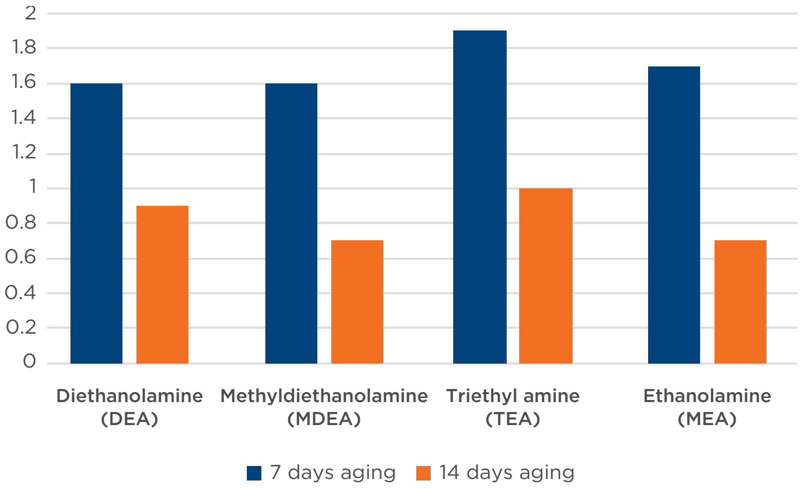


Figure 5. Arlon 3000XT® Density Change (%) at 150°C

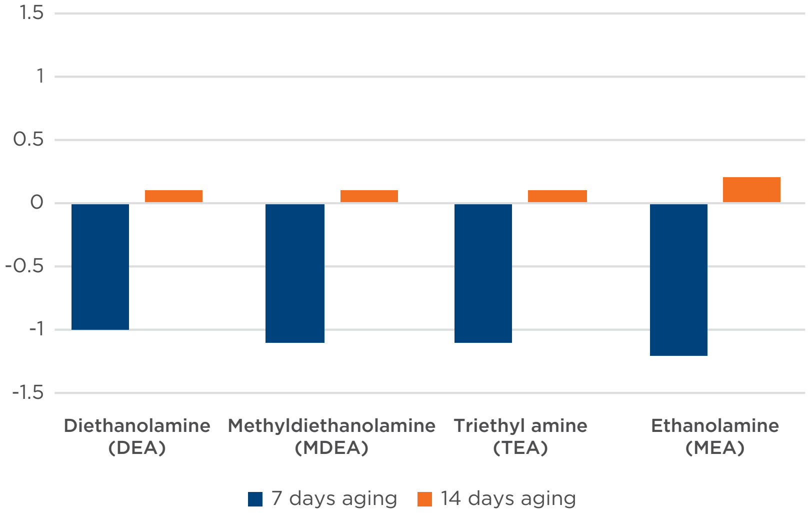


Figure 6. Arlon 3000XT® Mass Change (%) at 150°C

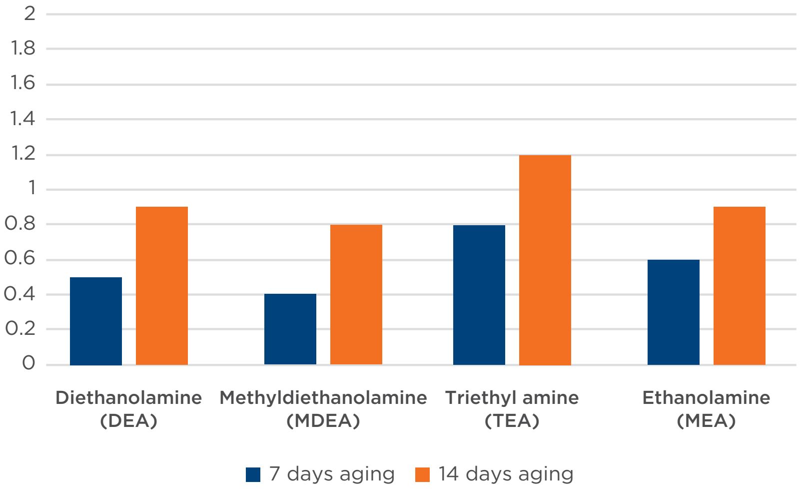


Figure 7. Arlon 3000XT® Tensile Strength Variation (%) at 150°C

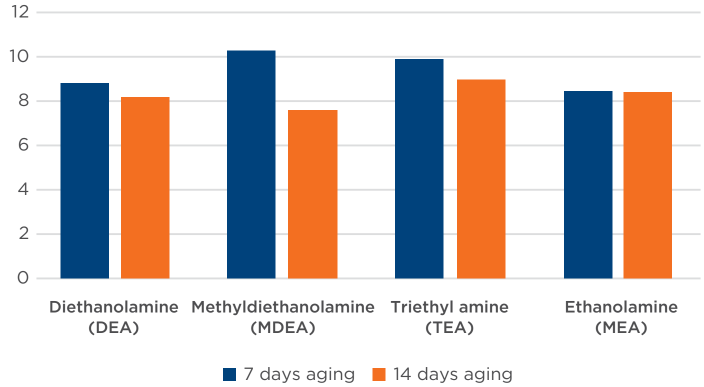


Figure 8. Arlon 3000XT® Tensile Stress at Yield Variation (%) at 150°C

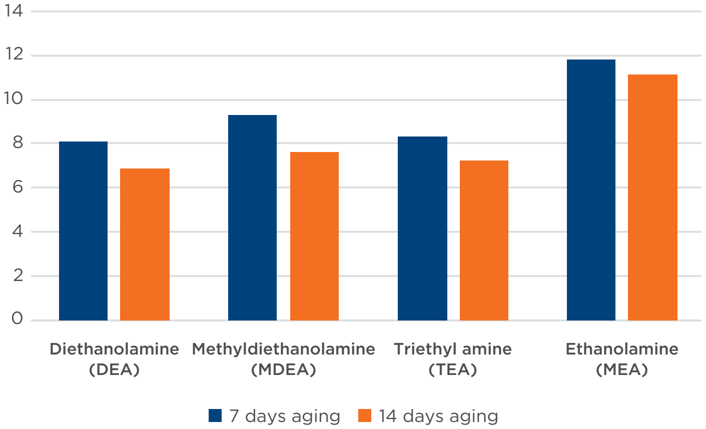


Figure 9. Arlon 3000XT® Elongation at Break Variation (%) at 150°C

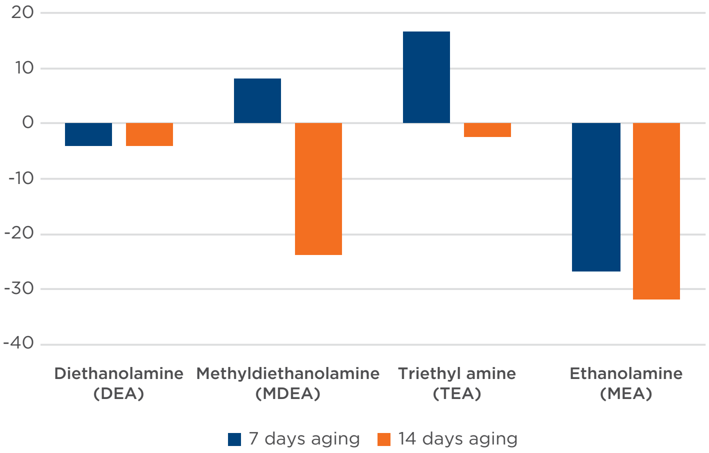
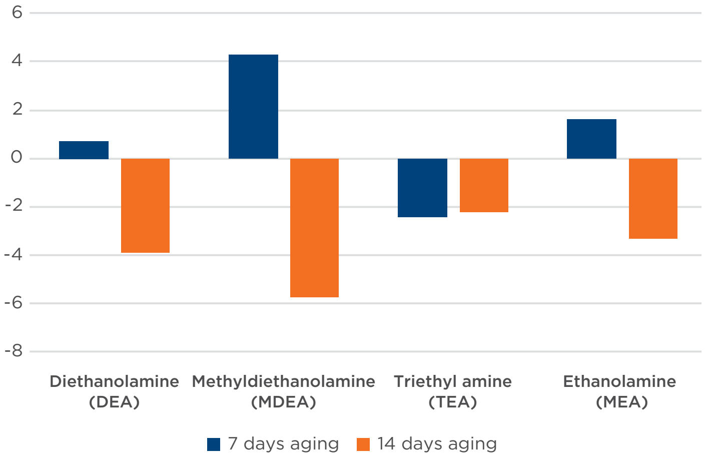


Figure 10. Arlon 3000XT® Young's Modulus Variation (%) at 150°C



Taken together, the immersion testing clearly shows the enhanced resistance of Arlon 3000XT® to amines even in the most stringent conditions. The results would grant this material a rating grade of 'A' by the most common standards (the Compass guide for the chemical resistance of Plastics rates materials with an A if they exhibit swelling below 10% and a less than 15% loss of tensile strength, corresponding to little or no chemical attack).

Conclusion

For, selecting the right material for elastomeric or thermoplastic seals, as well as other components such as valve seats, couplings, bushings/bearings, for use in CCUS applications is crucial. Precise material selection ensures optimal performance and reliability in these demanding environments.

Greene Tweed's test regime for amines found that the materials best likely to resist chemical attack in amines depended greatly on formulation and the class of amine used in application. In addition, advanced technologies such as using cross-linked PEEK or improved filler and polymer packages, may be necessary to avoid premature failure due to chemical attack. Extensive testing shows that Chemraz® 541 and Arlon 3000XT® can offer enhanced resistance to amines when compared to similar materials.

As technology for reducing emissions continues to advance, new application requirements will emerge, driving the need for materials, along with increased testing, that can survive in those harsh applications.

Extensive testing shows that Chemraz® 541 and Arlon 3000XT® can offer enhanced resistance to amines when compared to similar materials.

References

[i] CNBC News, 2024. Spencer Kimball. *Big oil is racing to scale up carbon capture to slash emissions but the challenges are immense* https://www.cnbc.com/2024/04/06/big-oil-is-racing-to-scale-up-carbon-capture-to-slash-emissions.html

[ii] Scientific World Journal, 2014: https://onlinelibrary.wiley.com/doi/10.1155/2014/828131; https://pmc.ncbi.nlm.nih.gov/articles/PMC3947793/

[iii] Wright, David. 2001. *Failure of Plastics and Rubber Products Causes, Effects and Case Studies Involving Degradation* [textbook] Rapra Technology.

Greene Tweed Unpublished data, collected by ISO certified lab