Absorption-desorption in tank linings

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Abstract

The absorption-desorption of different cargoes in two different Novolac epoxy tank linings has been investigated. It was shown that the degree of absorption is highly dependent on the specific cargo and its chemical functionality. It was also seen that absorption-desorption testing alone cannot help one differentiate between the quality of different coatings.

Introduction

Investigations show that the degree of absorption is highly dependent on the specific cargo and its chemical functionality. It was also seen that absorption/desorption testing alone cannot help differentiate between the quality of different coatings. Chemical tankers are built to carry a wide range of chemicals worldwide, including petroleum products, specialised chemicals and foodstuffs. Some of the more specialist vessels switch from one type of cargo to another in each port. It is important to try and understand the absorption mechanisms in order to avoid cross-contamination and/or premature paint failure. It is also important to know if absorption testing alone can tell us anything about the overall quality of a coating system.

Experimental procedures

Two different, two-component, Novolac epoxy tank linings were investigated; Novolac 1 and Novolac 2.[2] They were applied on Mylar polyester film for easy removal. After application the coating was cured for seven days at 23°C and for 3 days at 60°C. The coating was removed in squares of approximately 2 x 2 inches and each square was weighed before liquid immersion. During the absorption period the coating squares were immersed in water[3] or different organic solvents in closed containers. The samples were removed at intervals for weighing. All surface liquid was removed and samples wiped off with a dry paper towel. Weighing was performed using an analytical balance to ~0.1 mg.

During the desorption period the coating was left to ventilate in 23°C and weighed periodically until equilibrium was reached.

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[2] In contrast to 'standard' epoxies which are diglycidyl ethers of either bisphenol-A or bisphenol-F, Novolac epoxy resins are glycidyl ethers of phenolic Novolac resins. Novolac epoxy resins generally have higher functionality and give more cross-linking and subsequently a better chemical resistance.

[3] Artificial sea water was made in according to ASTM D 1141. Brackish water was made mixing the artificial sea water with distilled water in the ratio 1:1.

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For chemical exposure testing 150x75x1.5 mm steel panels, with a surface profile of µm and a cleanliness of Sa 2.5 (ISO 8501-1:2007), were coated with Novolac 1 and Novolac 2, respectively. The dry film thicknesses averaged around 300 µm. Several panels were tested to ensure authenticity.

Definitions

Sorption describes the combined processes of adsorption and absorption.(1) Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another phase. Absorption is the incorporation of a substance in one state into another of a different state. For the sake of this article we will assume that the migratory process is purely absorptional and all the molecules contributing to weight gain are incorporated in the free volume of the coating film.

Desorption is a phenomenon whereby a substance is released from or through a volume. The process is the opposite of sorption (that is, either adsorption and absorption). This occurs in a system being in the state of sorption equilibrium between the bulk phase and an absorbing volume (coating film). When the concentration (or pressure) of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state.

Some of the most important factors contributing to the degree of absorption into a coating (and following desorption) are: temperature, functional groups and molecular size of the absorbed substance (2).

In high temperature conditions the absorption rate most often increases, and so does also the desorption rate, due to increased molecular movements at higher temperatures.

The absorption and diffusion of water in polymeric materials such as epoxy systems is related to the free volume (3,4) and the polymer-water affinity (4, 5). It is natural to assume that this is also true for other chemical species than water. Methanol and ethanol are related to water in that they are both polar protic molecules (can donate a hydrogen to form a relatively strong hydrogen bond with the hydroxy and amine groups in the polymer network). (6) 1,2-Dichloroethane (EDC) and tetrahydrofuran (THF) are slightly polar but they are aprotic and cannot form hydrogen bonds. When the coating is immersed in these chemicals they fill the free volume. Even though they cannot form hydrogen bonds they can still disrupt the polymer chains as they show more affinity towards the largest part of the polymer network, the parts not containing hydrogen-bonding sites. These non-polar link sites consists of alifatic chains and aromatic rings. They have affinity towards dipoles of the polymer chain through relatively weak dipole-dipole forces or induced-dipole forces. These forces are often called London dispersion forces or van der Waal's forces. (7) An example of how the structure of an amine cured Novolac epoxy polymer network might look like is shown in Figure 1.
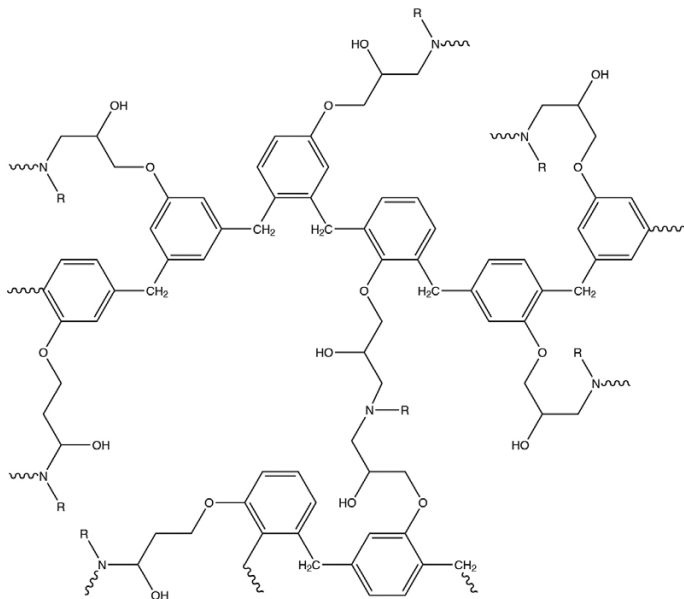

Figure 1: A two dimensional cross cut, showing what an amine cured Novolac epoxy polymer network might look like. The polymer network contains both polar hydrogen-bonding sites and non-polar alifatic chains and aromatic rings.

The amount of free volume depends on the molecular packing and is affected by both the cross-link density (and therefore the extent of curing) and physical aging (8). The polymer-water affinity is significantly influenced by the presence of hydrogen-bonding sites within the polymer (9). Water can sometimes be absorbed without causing swelling; when this happens, it is suggested that it remains unbound to the polymer and is effectively accommodated within the free volume (5). On the other hand, bound water molecules that attach to the polymer through hydrogen bonds disrupt the inter-chain hydrogen bonds and induce swelling (9, 10) and plasticize the polymer. In a Novolac epoxy binder network the hydroxyl (-OH) groups shows good affinity with chemicals containing -OH groups.

Other than functional group effects, molecular size plays an important role in the process of absorption. Molecules that are larger than the 'mesh' of the polymer network will not absorb into the volume at all. Some molecules might adhere to the surface structure, but the weight increase caused by this will, in the case of thick coatings, be negligible compared to the weight of the non-absorbing volume.

Results

In the absorption-desorption experiment with water, Novolac 1 was immersed in water with different levels of salinity. The results are given in Figure 2.
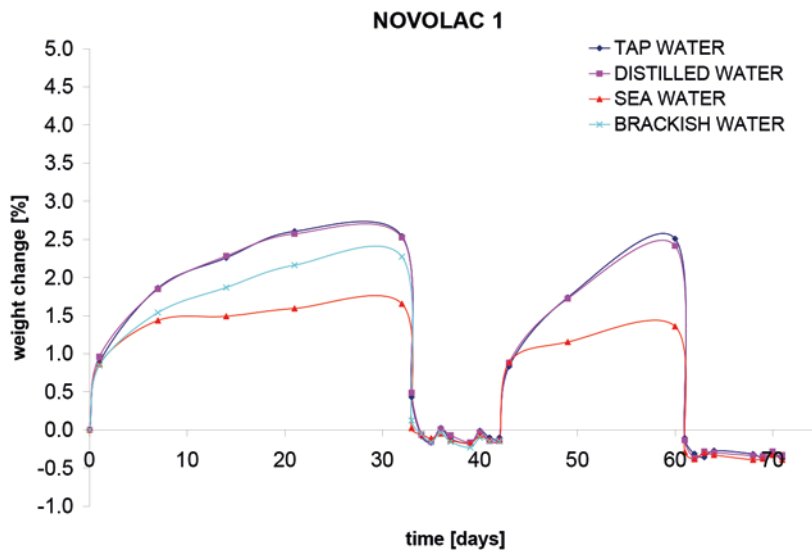
Figure 2: The two cycles of absorption-desorption of water solutions with varying degree of salinity in coating Novolac 1.

From Figure 2 we see a clear link between water absorption and level of salinity. Tap water and distilled water are quite similar and give the highest weight change. Sea water shows the lowest absorption and brackish water ends up right in-between.

During the second absorption cycle we see the same trend with sea water giving the least weight increase, but the overall rate of absorption has slowed down a little, using longer time to 'saturate' the coating. No data was obtained for brackish water during the second absorption-desorption cycle as a damage in the coating caused rust to form, making the weight measurements unreliable.

Interestingly enough, the desorption rate is quite fast and most all the water has left the coating within 24 hours of ventilation. In other words, by using Novolac 1, a tank can be put into service quite fast after sea trial or after water washing.[4] Absorption-desorption of water was not tested for Novolac 2, but one could probably expect similar results.

When it comes to the absorption-desorption of organic solvents, the different molecules will have different size and different affinity to the epoxy-amine polymer network, and will subsequently absorb differently. In Figures 3 and 4 this effect can be seen easily. Both EDC (1,2-dichloroethane) and THF (tetrahydrofuran) show a large absorption relative to methanol and ethanol for both coatings.
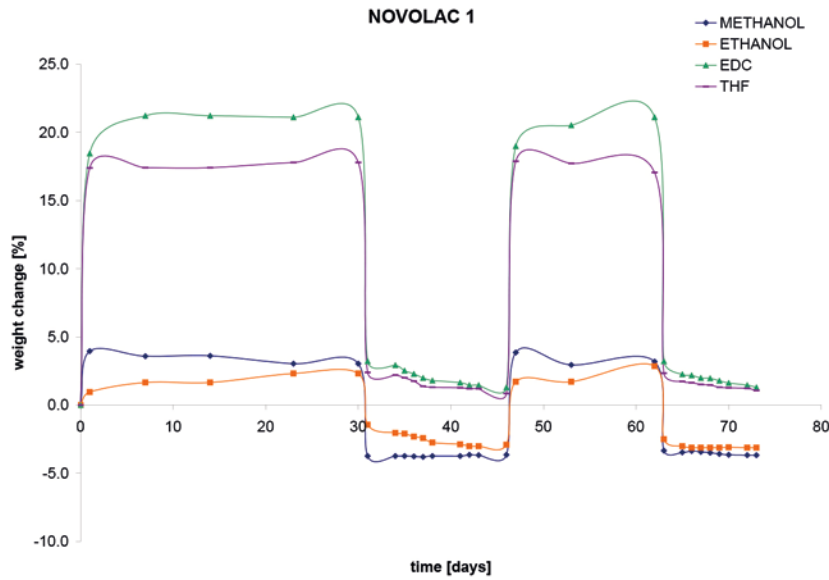

Figure 3: The absorption-desorption curves of various organic solvents in coating Novolac 1.
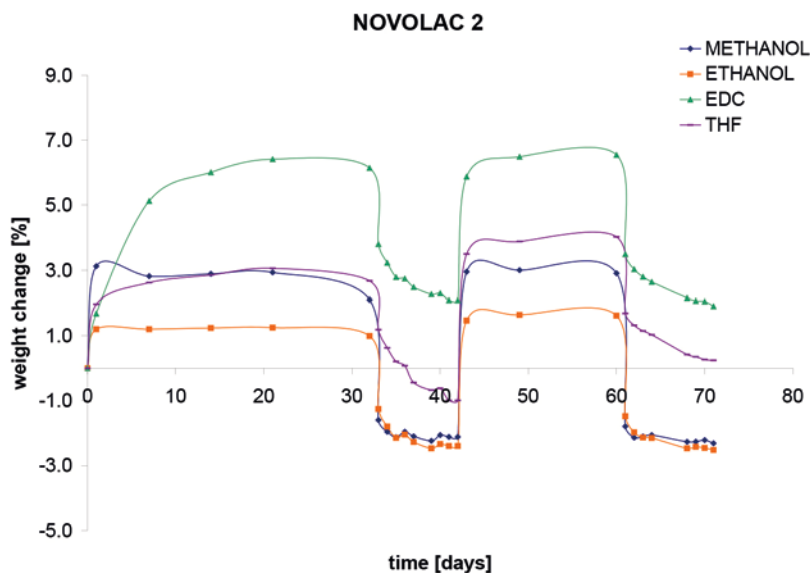

Figure 4: The absorption-desorption curves of various organic solvents in coating Novolac 2.

For methanol and ethanol a negative weight change was observed during the desorption phase. It was important to test if this net negative desorption increased further during a second absorption-desorption cycle as this would suggest a systematic breakdown of the coating (or to be more exact, the coating's organic polymer network).

From the two absorption-desorption cycles for methanol and ethanol for Novolac 1 it can be seen that the net negative desorption does not increase further, suggesting that a systematic breakdown is not taking place, but rather that some rest solvents and/or monomers are extracted from the coating during the liquid immersion of the first absorption cycle. This can be seen even more clearly by splitting up the two cycles and shifting down the abscissa of the 2nd absorption-desorption cycle; see Figure 6. A GC-MS analysis actually confirmed that the negative weight change was due mostly to trapped solvents, extracted by the polar medium.

Comparing Figure 5 and Figure 6 it can be seen that net weight gain during the absorption phase is larger in the second cycle. This is as expected, seeing that unreacted components were extracted during the first absorption-desorption cycle, leaving more free volume in the polymer network available for absorption. A promising result is that most all the methanol has left the coating after only one day in air.

The fact that the net negative weight is quite substantial during the first absorption-desorption cycle, but not the second cycle, indicates that it might be recommendable to wash down a tank lining thoroughly with a polar solvent before it goes into service, especially if foodstuffs are part of the freighted cargo. It is reasonable to assume that water will have the same washing effect as a low molecular polar solvent like methanol.

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[4] The panels in this experiment were left to ventilate in a, relative to area, infinite volume of air. The desorption rate will depend on the access to 'fresh' air and so the results might be different for a more poorly ventilated storage tank.

For both 1,2-dichlorethane and tetrahydrofuran the net weight gain during absorption is quite substantial for both Novolac 1 and Novolac 2. The absorption curves seemingly reach equilibrium after one-to-two weeks of immersion. During the desorption phase however, Novolac 1 differs from Novolac 2. Interestingly enough, it seems that Novolac 1 reaches equilibrium faster than Novolac 2 during desorption. While Novolac 1 seems to reach equilibrium after just one to three days depending on the chemical, Novolac 2 has not reached equilibrium after 10 days; After 10 days, solvent is still trapped in the network. While Novolac 1 seems to show a higher degree of absorption, the desorption is correspondingly fast meaning that Novolac 1 probably has a slightly more open network.
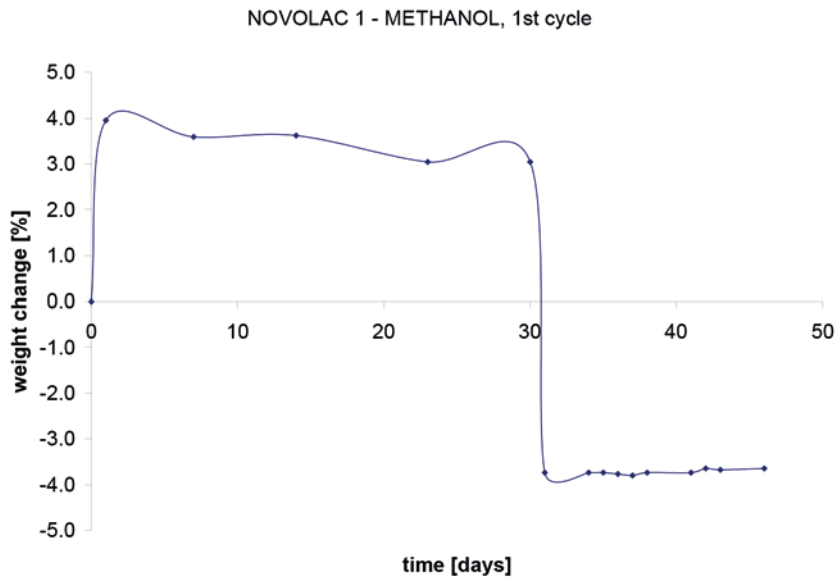
NOVOLAC 1 - METHANOL, 1st cycle

Figure 5: Novolac 1, methanol, 1st cycle
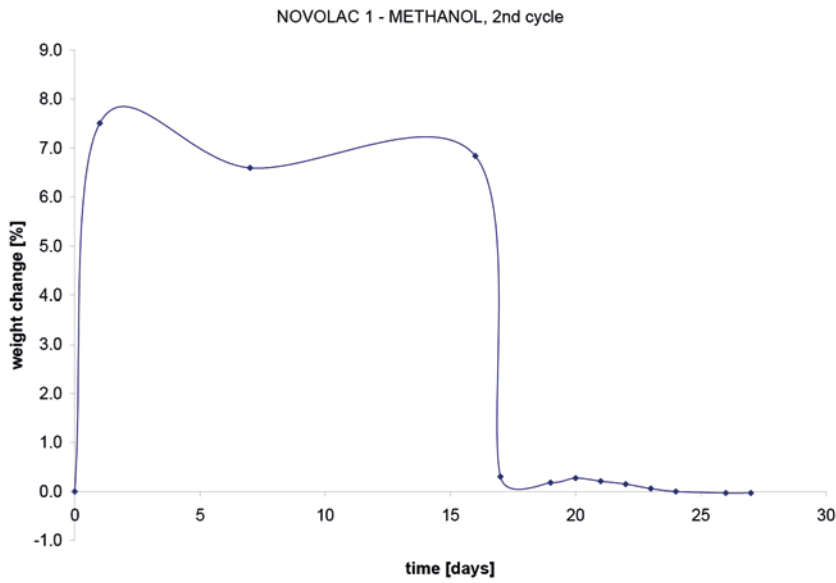
NOVOLAC 1 - METHANOL, 2nd cycle

Figure 6: Novolac 1, methanol, 1st cycle

Long-term chemical immersion testing

Based on the absorption-desorption of organic solvents one would perhaps think that Novolac 2 is a better coating material, seeing that the net weight gain during absorption is lower for Novolac 2 than for Novolac 1 for all chemicals. To further test this assumption steel panels coated with Novolac 1 and Novolac 2 were exposed to different chemicals (fully immersed), including a cyclic methanol fatigue test (five days in methanol – eight hours ventilation – two days in water – eight hours ventilation; repeated for up to 10 cycles). The results are given in Table 1.

Table 1: Long-term chemical exposure testing.

	Novolac 1	**Novolac 2**
Methanol	OK, 180 days	OK, 180 days
Ethanol	OK, 180 days	OK, 180 days
EDC	OK, 180 days	OK, 180 days
THF	OK, 180 days	OK, 180 days
Distilled water	OK, 180 days	OK, 180 days
Methanol fatigue	OK, 10 cycles	Fail, 2 cycles

It can be seen from these results that there is not much difference between the two coatings. They both withstand aggressive chemicals, quite impressively, for 180 days. However, for methanol fatigue, which is a maximum stress test, Novolac 1 showed no sign of failure while Novolac 2 blistered and rusted severely after only two cycles.

So even though Novolac 1 shows a significantly higher absorption than Novlac 2 (compare Figure 3 and Figure 4) this alone cannot tell us that Novolac 2 is the better coating. Quite the opposite, the methanol fatigue test shows that Novolac 1 is probably a better coating. One explanation for this is that Novolac 1 has perhaps a slightly more open polymer network allowing for fast desorption, but is still tightly cross-linked enough to ensure a good chemical resistance. Novolac 2 might suffer from being too tightly cross-linked, and subsequently more brittle, and can therefore not handle the same degree of chemical stress.

Conclusions

This work raised a lot of new questions, but it answered some as well. First of all it is evident that absorption-desorption testing alone is not enough to differentiate on quality between different tank coatings. It was found that even though the relative absorption of Novolac 1 was high compared to Novolac 2, Novolac 1 was the overall better performer in that it had a faster desorption rate (faster return to service) and a better overall chemical resistance.

It was also shown that the degree of absorption is highly dependent on the specific cargo and its chemical nature.

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