Optimization of Curing Conditions for a Chemical Resistant Tank Coating with the Help of Dynamic Mechanical Analysis

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Tank Fast

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Abstract

The glass transition temperature (T_g), storage modulus and loss modulus has been investigated for an amine cured Novolac epoxy based tank coating, over a range of different curing conditions, using dynamic mechanical analysis (DMA). Correlations were found between curing time, curing temperature and T_g. Correlations between T_g and chemical resistance of the tank coating were investigated. Also, the effect different curing media have on the coating properties were investigated. The use of DMA proved to be an effective way of establishing necessary curing/post-curing time and temperature for this particular tank coating.

Keywords

Tank coating, DMA, curing conditions, glass transition.

Introduction

Currently, when the necessary curing conditions for a coating are to be found, the coating is applied to test panels which are then cured at different temperatures and for different periods of time. The different panels are then immersed in water and other chemicals of interest, at different temperatures. These experiments are time consuming to say the least, as one might have to wait up to a year to get adequate results. By using DMA to investigate the glass transition temperature (T_g) of the coating one can, with reasonable certainty, decide the needed curing conditions for a coating to be used at a given working temperature.

In addition to the pure temperature factor, it is widely known that post-curing of epoxy coatings at elevated temperatures most often will improve their chemical resistance. This can be explained theoretically, as elevated temperatures increase the reaction rate of curing. The molecules 'trapped' at low temperatures can move more freely and therefore react more easily. This will result in a 'tighter' polymer matrix and a tighter polymer matrix means less diffusion through the film. Diffusion of molecules through the film is often a problem, especially with small molecules like methanol and water. A tighter net will for epoxy films often result in a harder, and less flexible, film. This 'tightening' of the polymer network can be measured by calculating the cross-link density using results from DMA.

It is also important to know how low we can go on initial curing temperature. Is curing the film for two weeks at 5°C tantamount to curing for two weeks 23°C as long as one post-cures the coating at a given elevated temperature? To know this would save one a lot of time required for testing.

Dynamic Mechanical Analysis Theory

Dynamic Mechanical Analysis (DMA) is a method involving application of an oscillating force to a sample and analysis of the material's response to that force.[1] Figure 1 shows how one by applying stress to a film observe a material response (strain) and a phase lag between the applied stress and resulting strain.
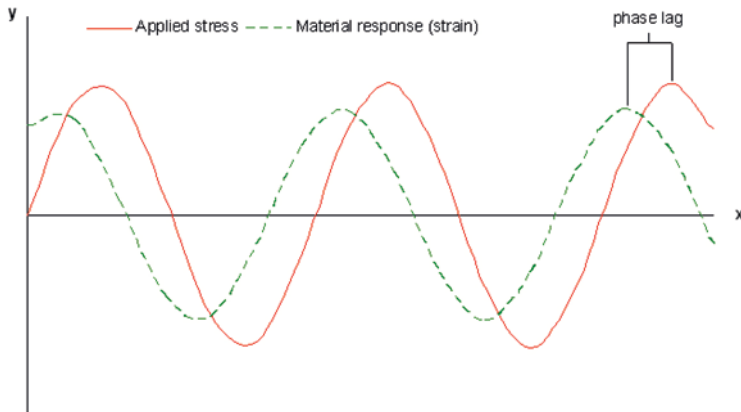

Figure 1: The oscillating force applied to the sample is most commonly sinusoidal as shown here. By measuring the amplitude of the deformation (material response) curve and the phase difference between applied stress and material response (strain), quantities like modulus, damping and T_g can be measured.

Definitions of dynamic properties are given below in terms of maximum oscillatory strain ($\varepsilon 0$), maximum resulting stress ($\sigma 0$) and phase lag (δ) between strain and stress.

$$\text{Storage modulus} = \frac{\sigma 0 \cos \delta}{\varepsilon 0} = E'$$

$$\text{Loss modulus} = \frac{\sigma 0 \sin \delta}{\varepsilon 0} = E''$$

$$\text{Loss tangent} = \frac{E'}{E''} = \tan \delta$$

where E' is the storage modulus, E'' is the loss modulus and $\tan \delta$ is the loss tangent.
Increase in this ratio relates to a harder and (often) more brittle polymer.

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The cross-link density (M_c) is usually calculated from the minimum value of storage modulus E' (also called the rubber modulus) in the rubbery plateau. The theoretical relation between molecular weight between two cross-linking points (M_c) and the tensile storage modulus (E') can be expressed as follows:[2]

$$E' = \frac{3\rho RT}{M_c}$$

where E' is the storage modulus, ρ is the materials specific gravity, R is the ideal gas constant, T is temperature and M_c is the molecular cross-link density. The density of the material increases as the molecular cross-link density value, M_c, decreases (shorter molecular chains between cross-link points in the polymer network).

The glass transition temperature (T_g) can be found from the storage modulus curve, the loss modulus curve or the tan δ curve. This is shown in Figure 2.
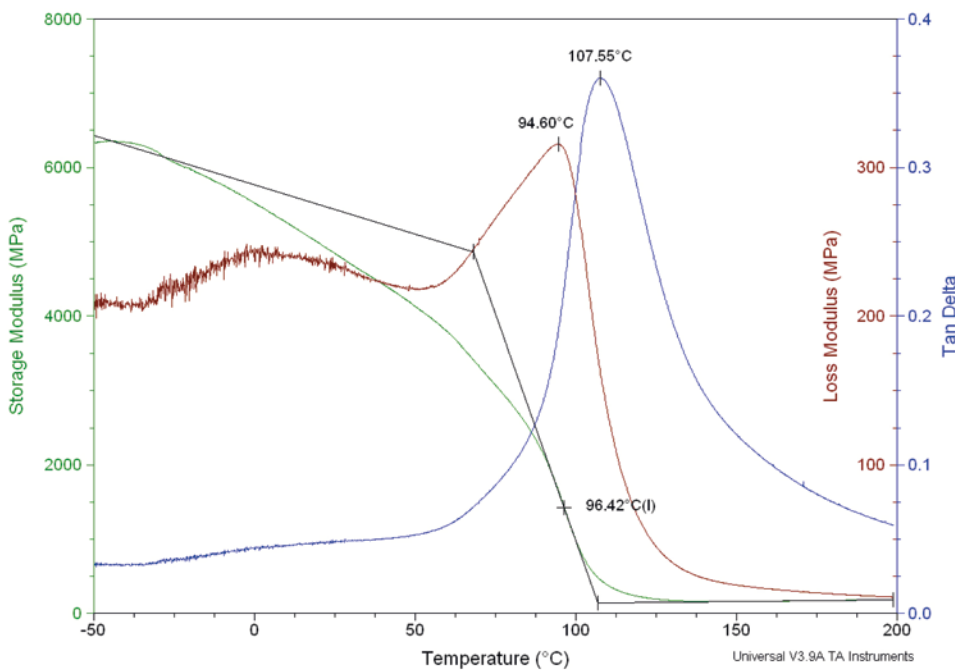

*Figure 2: This figure shows how T_g can be found from any of the curves storage modulus (~97°C),
loss modulus (~98°C) or tan δ (~108°C).*

As seen from Figure 2 the T_g can vary quite a bit (up to 11°C in this case) depending on which function is used to decide T_g. One should therefore always keep in mind the degree of uncertainty when it comes to deciding Tg and always decide T_g from the same function within a set of experiments. Also, one should take into account that the glass transition for a polymer blend is never a set temperature but rather a temperature distribution, where T_g is the maximum.

Experimental part

Materials

The tank coating investigated here is based on a Novolac epoxy binder with an amine adduct as the main curing agent. The recipe also contains different additives, extenders and pigments picked specifically to improve the barrier effects of this coating.

Preparation of the Coating

The two component coating was applied to smooth plastic polyester films using a 250µm applicator. The panels were cured at different temperatures in climatic air chambers or in hot water/hot oil baths.

Dynamic Mechanical Analysis

A DMA 2980 analyser from TA Instruments was used to determinate storage modulus, loss modulus and tan δ. The T_g was determined from the peak of the tan δ curve. The samples were heated from -50°C to 200°C with a heating rate of 4°C/min. The pre-load force was set to 0.020 N and the amplitude to 5µm. The graphs were plotted in TA Universal Analysis Version 3.9A and Microsoft Excel 2002.

Results and Discussion

Calculated results from the primary experiments are given in Table 1. All coated plates were cured at a given temperature for 14 days and then post-cured at an elevated temperature for a variable number of days (1–5 days).

Table 1: T_g is the glass transition temperature maximum found from the tan δ curve. E'_m is the minimum storage modulus while. TE'_m is the temperature at minimum storage modulus. $M_{c,min}$ is the cross-link density at E'_m. The 'curing conditions' column gives the curing temperatures with number of days given brackets.

Curing conditions	T_g [°C]	E'_m [MPa]	TE'_m [°C]	$M_{c,min}$ [g/mol]
5°C(14 d)+23°C(5 d)	73	63.6	105.1	296.5
5°C(14 d)+50°C(5 d)	91	170.5	116.2	113.9
5°C(14 d)+60°C(2 d)	101	114.1	134.6	178.3
5°C(14 d)+60°C(5 d)	108	157.4	146.7	133.1
5°C(14 d)+80°C(1 d)	103	111.6	148.3	188.4
5°C(14 d)+80°C(5 d)	121	165.6	162.6	131.3
10°C(14 d)+23°C(5 d)	69	91.4	109.3	208.8
10°C(14 d)+50°C(5 d)	85	113.1	120.4	173.6
10°C(14 d)+60°C(2 d)	99	126.0	133.0	160.8
10°C(14 d)+60°C(5 d)	106	214.4	147.9	98.0
10°C(14 d)+80°C(1 d)	117	60.3	198.3	390.0
10°C(14 d)+80°C(5 d)	122	208.5	175.0	107.2
23°C(19 d)	72	86.6	109.8	220.6
23°C(14 d)+50°C(5 d)	89	124.5	124.8	159.4
23°C(14 d)+60°C(2 d)	98	113.7	124.7	174.6
23°C(14 d)+60°C(5 d)	109	186.0	141.4	111.2
23°C(14 d)+80°C(1 d)	117	127.5	154.2	167.2
23°C(14 d)+80°C(5 d)	132	85.7	165.1	255.1
40°C(14 d)+23°C(5 d)	98	119.7	134.5	169.9
40°C(14 d)+50°C(5 d)	101	154.2	140.2	133.7
40°C(14 d)+60°C(2 d)	106	108.2	141.2	191.0
40°C(14 d)+60°C(5 d)	108	203.2	139.4	101.3
40°C(14 d)+80°C(1 d)	111	144.3	146.1	144.9
40°C(14 d)+80°C(5 d)	130	176.2	171.5	125.9

Effect of Curing Temperature on Glass Transition Temperature

As expected, the glass transition temperature (T_g) increases with increasing post-cure temperature. Figure 3 shows how varying the post-cure temperature affects the tan δ curve and the T_g of the coating film.
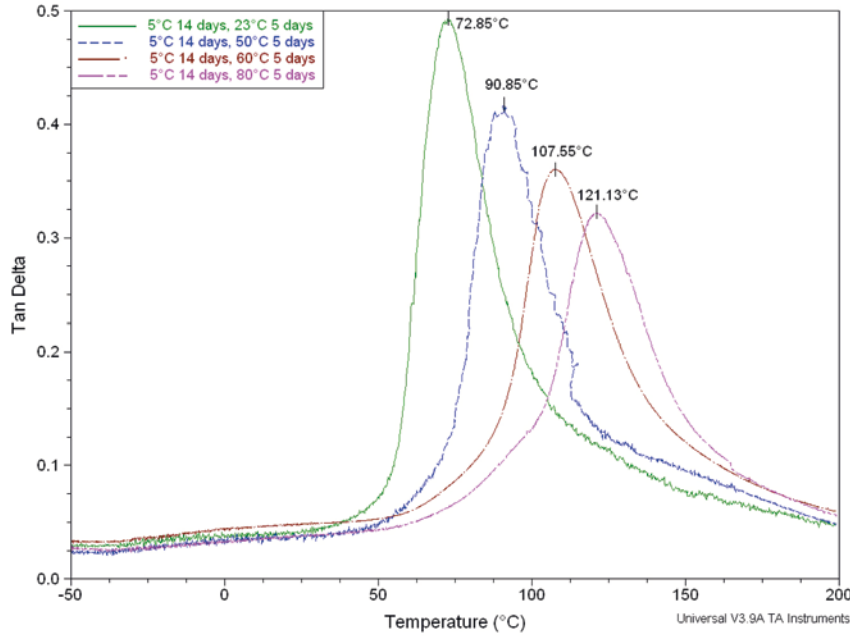

Figure 3: This graph shows tan δ of coating films cured at 5°C for 14 days and post-cured in hot air at different temperatures for five days.

The obvious trend seen from Figure 3 is the increase in glass transition temperature with increasing post-cure temperature. As mentioned earlier on, tan δ is the relationship between storage modulus and loss modulus (see Equation [3] on page 3). As post-cure temperature is increased the film becomes less flexible and the value of storage modulus increases relative to the value of loss modulus. Consequently, the absolute value of tan δ decreases with increasing post-cure temperature.

Figure 4 shows how varying initial cure temperature (using a fixed post-cure temperature) affects the tan δ curves and the T_g of the coating film.

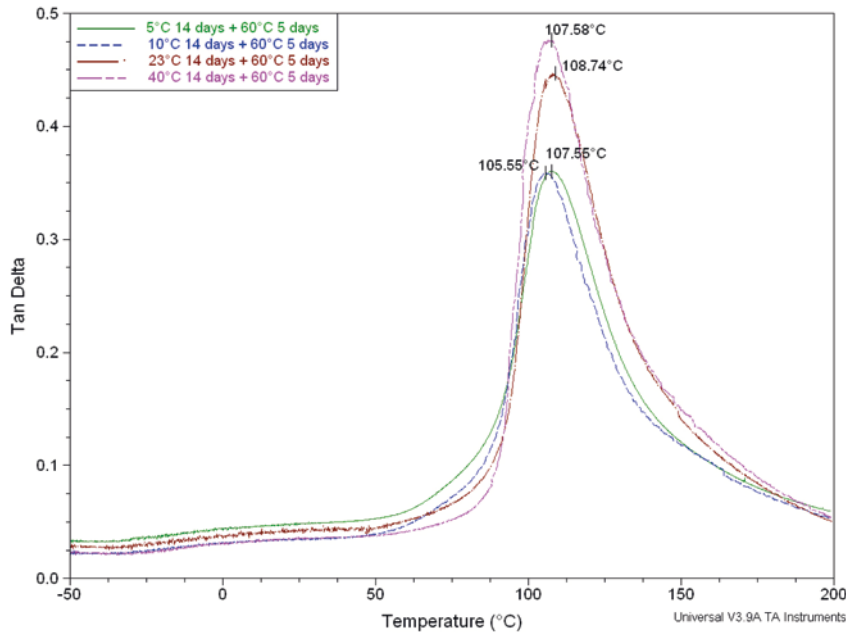*Figure 4: This figure shows how tan δ and T_g are affected by varying the initial cure temperatures
(5°C, 10°C, 23° and 40°C) using a fixed post-cure temperature (60°C).*

From Figure 4 one can see that as long as the sample is post-cured at an elevated temperature the initial cure temperature is close to insignificant when it comes to influencing T_g. Even cross-link density changes little within the different initial cure temperatures (see Table 1 on page 5). This tells us that we can cure this coating over the interval 5°C–40°C as long as we post-cure at a fixed elevated temperature. This is valuable information indeed, as seasonal changes in air temperature at application sites are substantial, and the coating can also be used at several different locations worldwide. One should note that these results are based on films that are post-cured only a few weeks after application. There is a time lag here that has to be taken into account. The desirable reaction is, of course, the curing of epoxy with the amine hardener. The competing reaction, between the amine hardener, carbon dioxide and water will cause problems over time, at least in poorly controlled humid environments. The product of this reaction is amine carbonates (amine blush). Amine blushing is described in detail by Rinker et al. [3]. Due to this one has to make sure the coating is post-cured within a reasonable time limit (and at least within three months of application).

Effect of Curing Temperature on Storage Modulus

The general observed trend is an increase in storage modulus as the post-cure temperature is increased, as shown in Figure 5. This is as expected since a higher cure temperature gives a higher cross-link density and, consequently, a less flexible film.
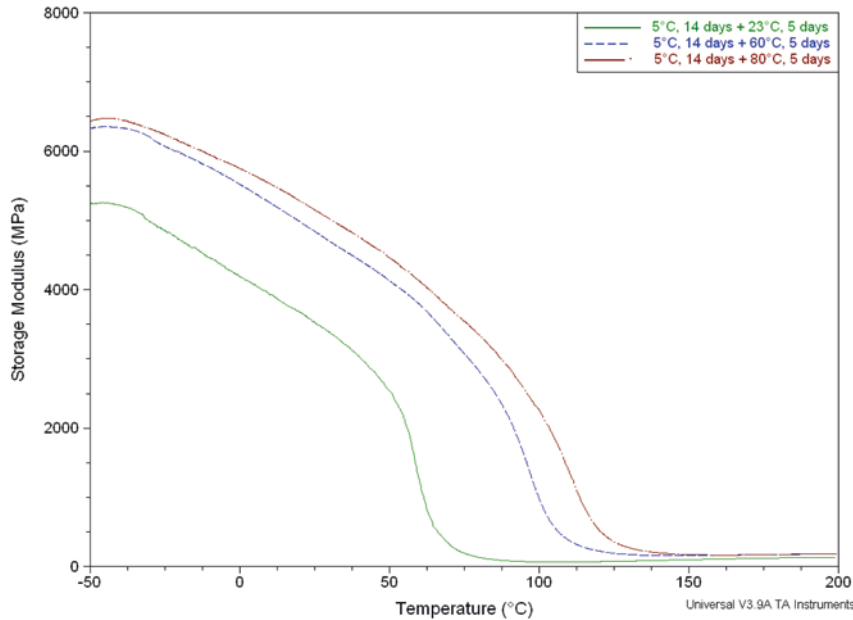

Figure 5: This graph shows storage modulus (E') of coating films pre-cured at 5°C for 14 days and post-cured at different temperatures for 5 days.

From Figure 5, looking at the interval between 0°C and 50°C, we clearly see that the film gets less flexible and more brittle with increasing post-cure temperature (the storage modulus curves are shifted upwards). There is little difference in flexibility, however, between the coating post-cured at 60°C and the coating post-cured at 80°C. This tells us that we can safely increase the post-cure temperature without having to worry to much about brittleness and cracking of the film. Even though the coating films post-cured at 60°C and 80°C are less flexible than the film post-cured at 23°C, neither are what one would call a brittle coating. Especially at working temperatures above 50°C all the films can be considered quite flexible.

Glass Transition Temperature as Function of Post Cure Temperature

A plot of T_g versus post-cure temperature gives some very interesting curves as seen in Figure 6.
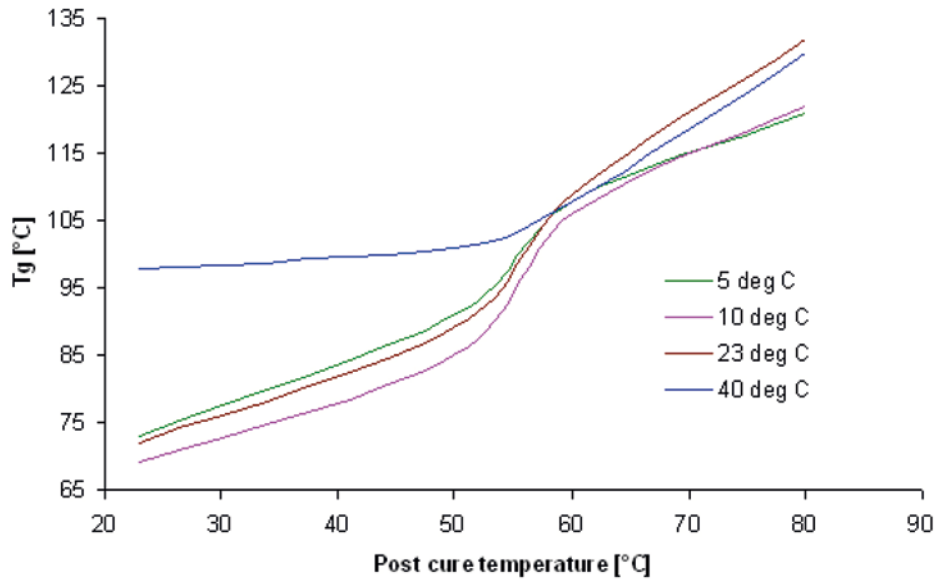

Figure 6: This graph shows the effect of post-curing temperature on the glass transition temperature, T_g. The coating film was first cured for two weeks at 5°C, 10°C, 23°C and 40°C, respectively. This was followed by a five-day post-cure at 23°C, 50°C, 60°C and 80°C, respectively. Each curve represents an initial cure temperature.

As seen from Figure 6 the range between 50°C and 60°C is critical with a leap in the nearly linear T_g curve. Although hard to prove, a critical chemical change is probably the reason for this break in linearity. One hypothesis is that at temperatures above 60°C we start to see the effects of some homopolymerisation between epoxy groups, causing a jump in T_g values. But then again, this is a hypothesis that needs to be studied further before any conclusion is drawn. We can, however, use what is seen here to argue that increasing post-cure temperature from 50°C to 60°C or above will make the coating more chemical resistant.

Effect of Curing Time on Glass Transition Temperature

Figure 7 shows how variation in post-curing time affects T_g. It is of great value to know how long one has to post-cure for the film to reach an optimal condition. For this specific coating a T_g of around 100°C is a satisfactory result.
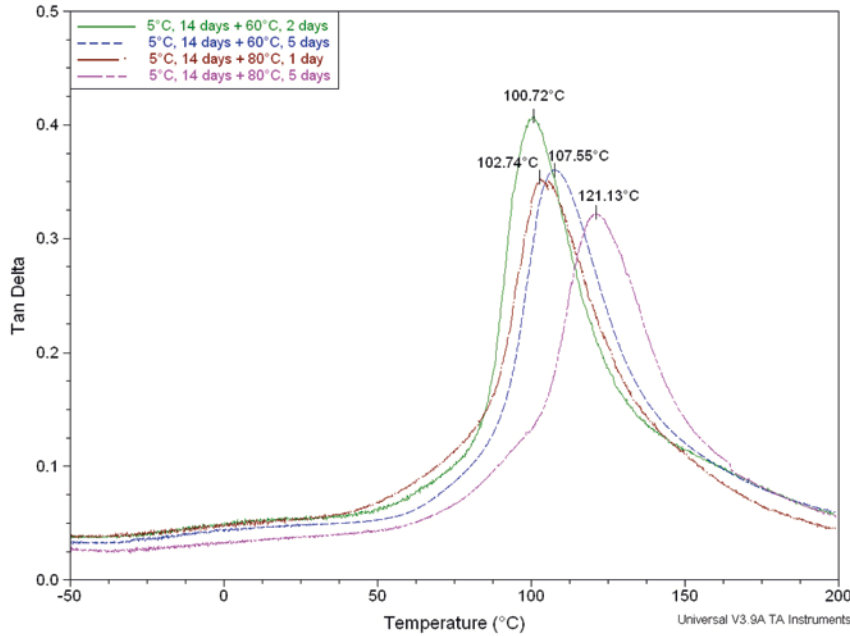

Figure 7: This figure shows how T_g and tan δ are affected by varying post-cure times and temperatures.

As the desired T_g for this coating is around 100°C we see from Figure 7 that post-curing for as long as 5 days is hardly necessary, neither at 60°C nor at 80°C. For a 60°C post-cure two days is sufficient and for an 80°C post-cure no more than one day is necessary to reach the desired T_g. The results are the same independent of the initial cure temperatures tested (5°C, 10°C, 23°C and 40°C).

Cross-link Density

The molecular cross-link density (M_c) can be calculated using Equation (4) on page 3. This method can be used to compare results within the same set relative to each other.

Looking at the results (see Table 1 on page 5), one can see that the molecular cross-link density of the polymer film, M^0_c, decreases when the post-curing *temperature is increased from 23°C to 50°C. Increasing the curing temperature above this, however, does not seem to affect M^0_c radically.*

Glass Transition Temperature and Chemical/Corrosive Resistance

As mentioned in the introduction tank coatings needs to be thoroughly tested in different chemicals and corrosive environments before a real-life product can be launched. Some of these tests are summarised in Table 2.

Table 2: Chemical and corrosive resistance linked to T_g. The degree of blistering, discolouration and/or rust is considered. The curing condition is given together with T_g in the top row. The results recorded here are after six months of exposure for chemical tests, 250 days for the rest (or until failure).

	23°C, 21 days T_g = 72°C	23°C, 14 days + 60°C (air), 5 days T_g = 109°C
Acetone	OK	OK
Acetic acid	failed (one day)	failed (three weeks)
Benzene	OK	OK
Ethanol diamine	failed (one day)	failed (three weeks)
Ethyl Acetate w/5% H_2O	OK	OK
Ethylene Dichloride	OK	OK
Methyl Acetate	OK	OK
Methanol	OK	OK
Methanol w/0.1% H_2O	OK	OK
Methanol w/1% H_2O	OK	OK
Monoethylene glycol	OK	OK
Tetrahydrofuran	blistering	OK
Crude oil[a]	OK	OK
Bioethanol (E85)	OK	OK
Methanol fatigue test[b]	OK	OK
80°C water	some blistering	OK
Salt spray[c]	rust creep = 2.7mm	rust creep = 3.3mm
Prohesion[d]	rust creep = 6.0mm	rust creep = 4.6mm
Cathodic disbondment[e]	some blistering	OK
Continuous condensation[f]	some blistering	OK
Sea water[g]	rust creep = 0.9mm	rust creep = 0.7mm

[a] Crude oil from the North sea (the Balder field).
[b] Cyclic testing involving 5 days immersion in methanol, 12 hour drying and then 2 days immersion in water. Cycle repeated ten times.
[c] ASTM B 117, continuously exposure to humidity and salt spray.
[d] ASTM G85, cycling between salt spray and dry periods.
[e] ASTM G8, coated steel plate with an artificial damage coupled with an anode, immersed into an electrolyte.
[f] ISO 6270.
[g] Temperature varies between 4C – 20C depending on season.

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In addition to chemical testing the coated panels were also subjected to accelerated corrosion tests including hot water testing, salt spray (ASTM B 117), prohesion (ASTM G 85), continuous condensation (ISO 6270), cathodic disbondment (ASTM G8, ASTM G42) and sea water immersion. The panels tested in salt spray, prohesion and sea water were scribed to see how well the coating system could handle a damage in the film (by measuring length of rust creep).

As seen from Table 2 the 60°C post-cured coating does not differ much from the coating cured at 23°C. A few exceptions are seen with acetic acid, ethanol diamine, tetrahydrofuran, cathodic disbondment and condensation, in which the 23°C cured coating shows some blistering while the post-cured coating is performing well. It should be noted that the panels in these tests were post-cured using hot air and that one might get completely different results with a hot water or hot oil cure.

Hot Air Post Curing Versus Hot Liquid Post Curing

In practice a tank coating is often post-cured using a hot cargo instead of (or in addition to) hot air. It was therefore of interest to use DMA to study coated panels cured using hot liquid instead of hot air. The results are given in Table 3.

Table 3: T_g is the glass transition temperature maximum found from the tan δ curve. E'_m is the minimum storage modulus while. TE'_m is the temperature at minimum storage modulus. $M_{c,min}$ is the cross-link density at E'_m. The 'curing conditions' column gives the curing temperatures with number of days in brackets.

Curing conditions	T_g [°C]	E'_m [MPa]	TE'_m [°C]	$M_{c,min}$ [g/mol]
Hot air				
23(14)+60(2)	98	113.7	124.7	174.6
23(14)+60(5)	109	186.0	141.4	111.2
23(14)+80(1)	117	127.5	154.2	167.2
23(14)+80(5)	132	85.7	165.1	255.1
Hot water				
23(14)+60(2)	112	66.6	156.3	321.7
23(14)+60(5)	116	69.1	162.5	314.5
23(14)+80(1)	128	75.5	172.8	294.6
23(14)+80(5)	145	69.1	162.5	314.5
Hot oil				
23(14)+60(2)	109	118.5	137.8	173.0
23(14)+60(5)	114	98.9	147.5	212.2
23(14)+80(1)	123	114.6	161.7	189.3
23(14)+80(5)	131	184.4	163.3	118.1

The results given in Table 3 are very interesting, but their interpretation is not straight-forward. The T_g is about a factor of 7°C – 14°C higher for hot water post-cure than for hot air post-cure. And the cross-link density roughly double.

One explanation to these phenomena might be that the small water molecules migrate somewhat into the coating film which in turn causes the film to soften to some degree. This temporary swelling, in addition to the higher temperature, might increase the molecular movements of the unreacted polymer side chains and/or the amine hardeners enough to make for a better cure than the one achieves using just hot air (resulting in a higher T_g). When the water is removed and the coating ventilated most of the trapped water evaporates, leaving behind a fully cured coating film.

One might argue that not all the water leaves the film, but some molecules remain, acting as an softening agent. This is why we see an increase in the molecular cross-link density, calculated from storage modulus (see Equation [1] on page 2).

Of course, these are only a mere hypotheses, which needs further study to accept or reject. However, if one assumes these hypotheses to be valid, further study is needed to see if the coated steel is affected by the uptake of water into the coating film.

In actual application oil is often used for post-curing and as seen from Table 3 this differed to some extent from post-curing with hot water. The molecular cross-link density, $M0_c$, is almost half that seen for the water immersed panels.

One possible explanation for this effect is that both water and oil work as a softening agent, but oil to a lesser degree than water due to the obvious difference in molecular size.

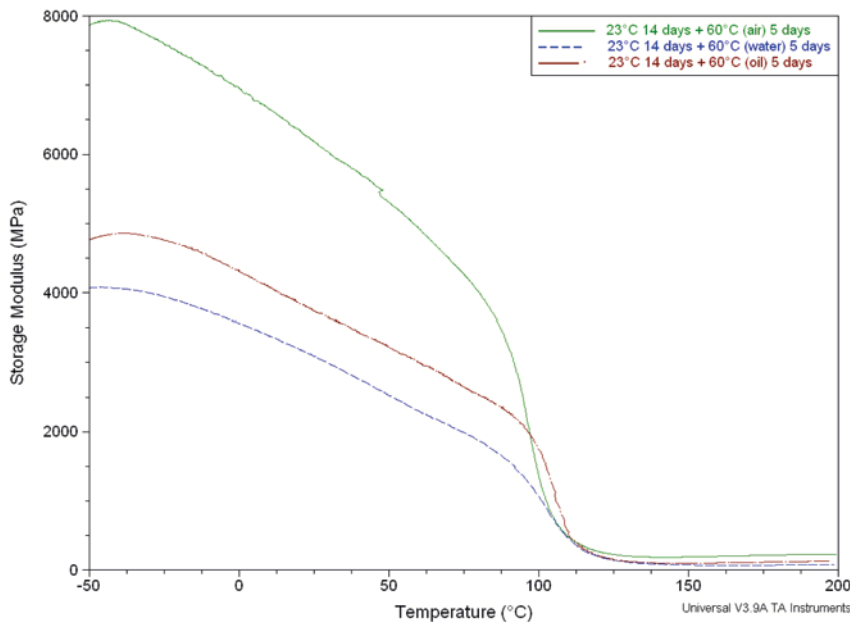The storage modulus curves of the coating post-cured in different media are shown in Figure 8.

Figure 8: This figure shows how storage modulus is affected by varying the post-cure medium.

From Figure 8 it can be seen that post-curing the coating in hot water or hot oil gives a softer/less brittle film than curing the coating in hot air at the same temperature. Indeed, the storage modulus is more than double up to 50°C. This confirms the hypothesis that both water and oil is taken up to by the coating, to some extent, working as a softening agent. The danger of this, however, is that depending on what chemicals are transported, this higher flexibility might only be temporary. If one were to load a hot water cured tank with for example hydroxide slurry (which is very hygroscopic in nature) all the remaining water could possibly be drawn out of the coating leaving behind a highly stressed coating full of 'gaps'. This could in turn leave to cracking and, consequently, corrosion of the underlying steel structure.

Conclusion

A Novolac epoxy-based tank coating was analysed using dynamic mechanical analysis resulting in a greater understanding of the coating system and how it is affected by varying post-curing time, temperature and medium. As expected, T_g was found to increase with post-curing time and/or post-curing temperature. A sufficiently good T_g value (~100°C) was achieved by curing at 60°C for two days or 80°C for one day, regardless of cure medium. T_g was also found to be nearly independent of initial cure temperature (5°C – 40°C) as long as the coating was post-cured at an elevated temperature.

Good correlations were found between mechanical properties of the coating and real life testing. The post-cured film was more dense and its glass transition occurred at a higher temperature, which resulted in a more protective coating that could withstand higher working temperatures and more corrosive chemicals.

Research into the effect of different post-curing media showed that post-curing in either hot water or hot oil resulted in a more flexible coating with a higher glass transition temperature compared to the coating post-cured in hot air. This heightened flexibility might however only be temporary and so this needs to be studied further.

Acknowledgements

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Bibliography

[1] Menard, Kevin P. Dynamic Mechanical Analysis : A practical introduction; 1st ed.,
     CRC Press LLC, Florida 1999.

[2] Hill, Loren W. J. Coat. Tech., **64**, 1992, 29-40.

[3] Rinker, E. B., Ashour, S.S. and Sandall, O.C. Ind. Eng. Chem. Res., **39**, 2000, 4346-4356.

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