

Crosslinking and Decomposition of Epoxy Resins Induced by Contamination with Water – Assessment of an Industrial Scale Scenario

Pietro Tanasini^{*a}, Gregory Widmer^b, Romain Raballand^b

^aHuntsman Process Safety Centre of Excellence, c/o Huntsman Advance Materials UK Ltd., Ickleton Rd, Cambridge CB22 4XQ, United Kingdom

^bHuntsman Advanced Materials (Switzerland) Sàrl, route de l'Île-au-Bois, 1870 Monthey, Switzerland
pietro_tanasini@huntsman.com

During the down-stream processing of an undiluted epoxy resin, water contamination, *e.g.* due to the failure of a tube of a heat exchanger, can introduce the risk of an unwanted hydrolysis reaction, followed by a crosslinking reaction. The latter, despite not being inherently dangerous, can lead to a dramatic increase of viscosity and the subsequent loss of agitation, bringing the resin in pseudo-adiabatic conditions and limiting the possibilities of intervention. Depending on the type of resin, the heat released by these reactions and the opening of epoxy rings can remain confined in the core of the mass and accumulate, triggering product decomposition: this may represent a significant hazard, potentially leading to high temperature carbonisation, gas release, overpressure with potential for vessel burst and/or release of toxic substances.

Thermal Safety investigations were carried out to characterise the hydrolysis, crosslinking and decomposition reactions after water contamination, assessing different types of remediation actions that the plant may take to solve the situation. In particular, vacuum distillation of water has been identified as the most straightforward method to remove instability and normalise the situation.

However, the reactive behaviour of the mass can be significantly different depending on the conditions in which the distillation is carried out, and it is found that early cross-linking may happen during the distillation if no solvent is added, before the water is actually removed.

In the undesirable situation where contaminated resin waste is generated on site, product characterisation and aging testing can determine how to safely manage it during storage and transportation to a third party for destruction.

1. Introduction

1.1 Undesired reactions initiated by water contamination

Under certain conditions, epoxy resin are prone to be hydrolysed, causing the conversion of the epoxy ring into a glycol (Lee and Neville, 1967). This reaction opens the way to a series of unwanted, exothermic reactions as detailed in Figure 1. Indeed, the hydroxyl moieties that are generated by hydrolysis can react with epoxy rings (crosslinking), increasing its viscosity. Since the crosslinking reaction does not cause a reduction of the hydroxyl moieties in the mass, the cross-linking can propagate further, *i.e.* until the gel point is reached. Even after that, the mobility of the dangling epoxy groups can be sufficient to allow further reaction in the solidified mass, particularly at high temperatures (Lee and Neville, 1967).

If this happens in an industrial-scale production unit, the resin mass can be practically confined (pseudo-adiabatic conditions) as soon as the viscosity is too high to allow sufficient heat exchange. In such case, the reaction enthalpy released by the opening of the tensioned epoxy rings is accumulated inside the mass, leading to a significant self-heating.

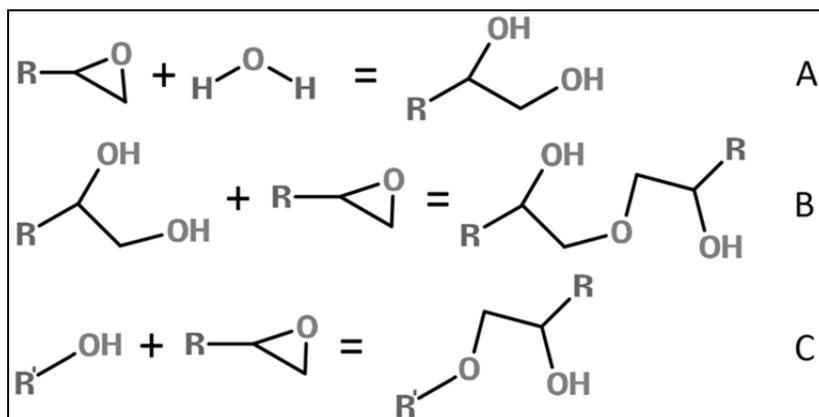


Figure 1: Scheme of undesired exothermic reactions of epoxy resins in presence of water. A) Hydrolysis. B) Cross-linking, initiation. C) Cross-linking, propagation.

Ultimately, decomposition reactions can be initiated, depending on the type of resin, if the self-heating brings the mass to a sufficient temperature. The term “decomposition” refers to a complex chain of exothermic reactions in the mass, including the opening of the residual epoxy rings, bond breaking and molecular rearrangements, leading to the carbonisation of the thermoset material and the release of gaseous by-products. This issue is particularly significant for highly functionalized resins, *i.e.* containing high concentration of epoxy groups and therefore presenting high potential of self-heating.

This paper describes the thermal safety study of the contamination of an epoxy resin with water, with the objective of providing guidance on how to avoid crosslinking in an industrial-scale vessel, thereby eliminating a critical step towards decomposition.

Furthermore, the characterisation of contaminated and cross-linked resin allows identifying the hazards related to its disposal as an unstable waste, and to provide guidance on how to safely manage its storage until safe transportation off site becomes possible.

1.2 Root-cause of water contamination

Depending on the synthesis process, water is often present in the production of epoxy resins, *e.g.* as a cleaning agent to dissolve and wash out the salt generated by the conversion of chlorohydrin into an epoxy ring in presence of caustic soda (Lee and Neville, 1967). However, this normally happens in presence of an organic solvent, allowing to physically segregate the epoxy moieties from the water. Furthermore, a lower viscosity of the organic phase allows the washing and decantation steps to be done at low temperature, decreasing the rate of the hydrolysis reaction.

Process Hazard Analysis (PHA) can identify the potential for water contamination of pure epoxy resins during processing, after the solvent medium has been distilled. Typically, this can be the result of the failure of a heat-exchanger, leading to the ingress of water or steam into the process side.

Generic failure rates of tubes in heat exchangers leading to a significant water contamination are fairly low: Heirman (2009) indicates an order of 10^{-5} /y for a large leak or rupture; however, recent internal findings show that pyrolysis treatment, a widespread method used to clean heat exchangers, can weaken the tubes, thereby significantly increasing the likelihood of failure in service. Metallurgic investigations of a pre-heater that had undergone this type of treatment determined that the pyrolysis of product plugs inside the tubes (process side) resulted in bloating due to the formation of pyrolysis gases and pressure increase, causing deformation and resulting in severe weakening of the tubes.

Therefore, PHA Leaders should carefully review the history of heat exchange failures of the plant in order to estimate the likelihood of tube failure related to the local cleaning and maintenance practices.

1.3 Remediation measures

Knowing the hazard represented by water contamination, the most obvious remediation action that can be taken is to remove the water, *e.g.* by vacuum distillation, in order to restore the product stability and allow a safe discharge. Dumping of the contaminated resin is not advised if there is the potential of decomposition during storage or transportation to the final disposal location.

However, great care must be taken in assessing the correct conditions to carry out the vacuum distillation operation, as it may allow sufficient time for the crosslinking reaction to proceed before the hazard has been removed, increasing the resin viscosity to the point of leading to pseudo-adiabatic conditions.

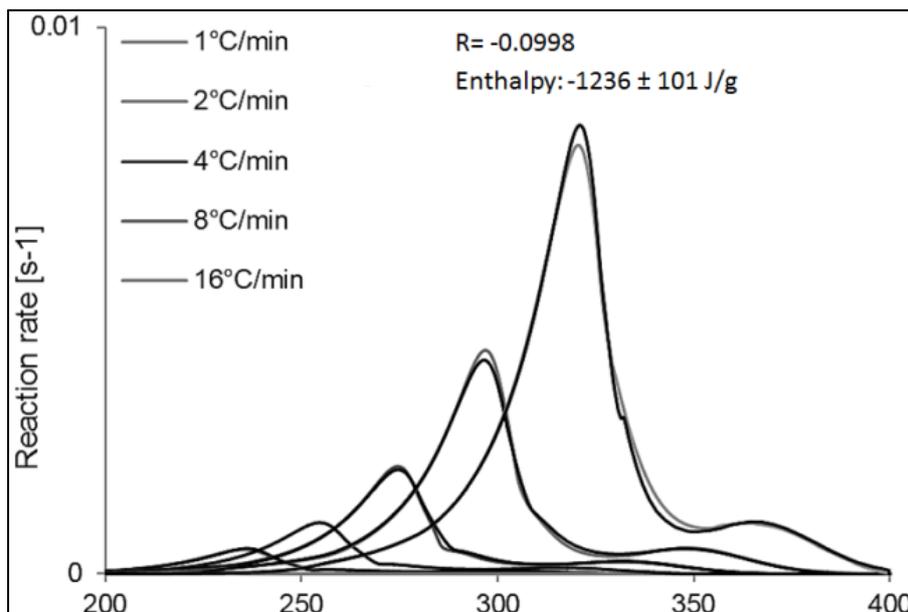


Figure 2: Dynamic DSC performed on resin containing 5 % water, fitted by isoconversional model.

A critical decision at this point is whether to perform the remediation action directly on the contaminated resin, or to introduce a solvent in order to carry out the distillation. It is worth noting that the use of solvents can introduce a flammable/toxic hazard, and their introduction in a vessel where they are normally not used can lead to contamination issues or be practically difficult, requiring flexible/temporary connections. These factors can increase the complexity of the modification to be assessed through Management of Change (MoC).

The present paper presents the results of lab-scale simulation of water distillation from a contaminated resin both with and without added solvent and thermal safety investigation of the undesired reactions related to water contamination during the corrective operation.

Also, thermal safety investigations were carried out to characterise the product stability in storage and transportation conditions, in order to determine a safe way to manage unstable waste material.

2. Thermal safety investigations

2.1 Reactive behaviour of the water-contaminated resin without added solvent

The contamination of a highly functionalised resin with 5 % water was reproduced at lab scale. After dispersion of the water in the medium at room temperature, macroscopically homogeneous samples were taken and analysed with DSC at different scan rates (Figure 2). The measured specific reaction enthalpy was 1236 ± 101 J/g, corresponding to approximately 600 ± 50 °C of adiabatic self-heating when considering a typical heat capacity for organic materials of 2 J/g·K.

The commercial software “AKTS Thermokinetics”, using an extension of Friedman’s isoconversional method, was used to fit the DSC results (see Figure 2) in order to determine the activation energy and pre-exponential factor as a function of the reaction progress and to describe the reaction kinetics (Roduit, 2000). It is worth noting that all the exothermic reactions happening in that range of temperature, regardless of their nature (hydrolysis, cross-linking, decomposition reactions), are fitted and described by this same model.

The model was used to simulate the reaction rate and reaction progress in isothermal conditions (Figure 3, Left). The simulation revealed the presence of three main groups of reactions: a first, minor peak appears in a relatively short time and corresponds to less than 5 % of the total reaction progress (*i.e.* less than 60 J/g of specific enthalpy), practically invisible at naked eye on the DSC thermographs due to the overlap with the left tail of the main reaction peaks. This seemingly innocuous reaction was followed by the two main exothermic phenomena. The main signals were identified as the exothermic opening of the epoxy rings and the decomposition reactions.

The Time to Maximum Rate in adiabatic conditions (TMR_{ad}) at 70 °C, a typical temperature that could be used to carry out the vacuum distillation, was calculated from the isoconversional model and was found to be about 100 h. With such a long TMR_{ad} , well above the threshold of 24 h that is usually considered as indicating a low probability of event happening (Stoessel, 2008), one may consider that the corrective operation on the pure

resin does not represent a significant risk. Conversely, the temperature corresponding to a TMR_{ad} of 24 h was estimated to be 97 °C.

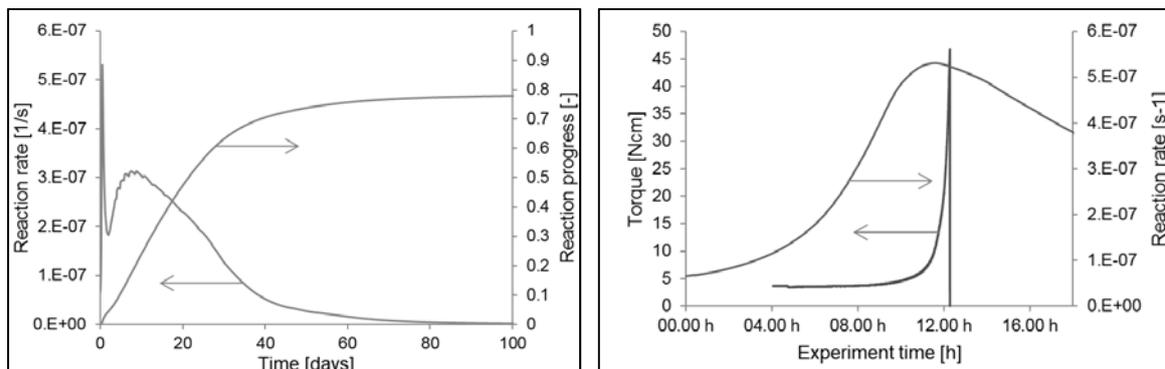


Figure 3: (Left) Simulated reaction rate and reaction progress of resin containing 5 % water in isothermal conditions at 95 °C. (Right) Comparison of torque measured during lab aging done in the same condition with the first reaction peak shown on the left, on expanded time scale.

Viscosity evolution of the same water-contaminated resin was evaluated at lab scale. The following experiment was prepared: 1 kg of resin containing 5 % water was agitated at 95 °C, with viscosity measurements carried out periodically, while the stirrer torque was continuously registered. It was planned to continue the experiment for up to 10 days but, after 12 hours from the start of the experiment, the reaction medium cross-linked and solidified: the stirrer torque rose to very high values, showing a viscosity tending to infinity as it is expected for fluid materials reaching their gel point.

The registered torque was superimposed to the simulation of the reaction rate reproducing lab conditions (95 °C, isothermal) from the isoconversional model. It was found a very good match of the time scale of the gel-point time (indicated by the torque spike) with the peak of the first reaction group (Figure 3, Right). It was then concluded that the first, "minor" reaction group, which had been overlooked because of its low potential, is directly related to a dramatic increase of viscosity, potentially causing loss of agitation and cooling thus leading to pseudo-adiabatic conditions.

It is worth noting that having a TMR_{ad} of 24 hours or higher is usually considered a safe situation, as it should allow adequate remediation and enable to prevent a decomposition reaction in most cases. However, this reference value needs to be used with care, as it can be completely inappropriate in certain cases (Stoessel, 2008). In the particular case treated, if several cubic meters of solidified resin undergoing decomposition are blocked in a vessel, this time scale is probably inadequate to allow an adequate intervention, and even the 100 h that have been found in the present study could be insufficient and transmit a false sense of security. This is a critical point, as decision-making based on misleading information can lead, for this scenario, to high temperature carbonisation, gas release, overpressure with potential for vessel burst and/or release of toxic substances, a high severity event with important economic consequences for the plant, even if all the personnel had been evacuated and is unharmed.

2.2 Reactive behaviour of the water-contaminated resin after solvent addition

Two solvents (Toluene and Xylene) were introduced to dilute a mixture of resin with 5 % water. As it is shown in Figure 4, this allows to immediately decrease the water content of the resin allowing easy and rapid phase decantation. In order to quantitatively measure this effect, the mixture was agitated vigorously and was then left decanting for one minute before sampling the organic phase.

By physically separating the epoxy moieties from the water, it is expected to observe an increase of the stability of the medium, as the hydrolysis reaction would be hindered.

In order to validate this hypothesis, a sample of organic solution obtained after introducing 15 % toluene was measured by DSC at different scan rates. As it could be expected, the total enthalpy averaged over five thermograms was 1003 ± 94 J/g, *i.e.* approximately 15 % lower than the value found on the undiluted resin. The isoconversional model obtained for this case was used to calculate the TMR_{ad} at 70 °C, obtaining a value of the order of 10^5 h, three orders of magnitude higher than in absence of solvent. Conversely, the temperature corresponding to a TMR_{ad} of 24 h was estimated to be 155 °C, higher than the boiling point of xylene. Moreover, it was not possible to identify the crosslinking reactions as an early peak, and it was found that all the exothermic reactions happen on the same time scale.

These results validate the proposed hypothesis, and demonstrate that the presence of solvent has a strongly stabilising effect by hindering effectively the undesired reactions.

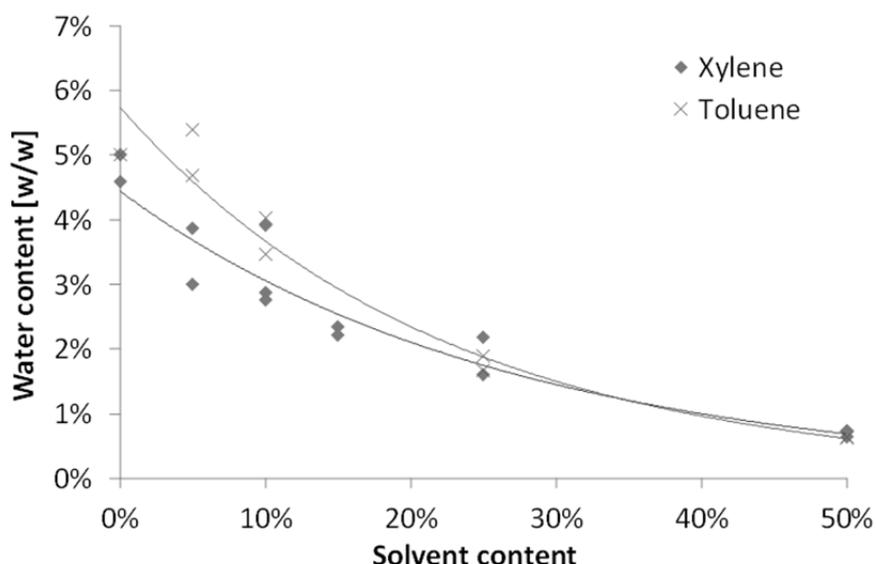


Figure 4: Water content determination by Karl-Fischer titration in a water-contaminated resin as a function of solvent introduction.

2.3 Management of contaminated resin wastes

The dumping of contaminated resin is not advisable if there is a significant risk of decomposition, since the exothermic reactions could happen during storage or transportation.

However, in certain cases it may be necessary, e.g. when the viscosity is already too high to allow anything but an emergency discharge. In this case, the risk of vessel overpressure is eliminated, but each single container may be origin of a decomposition event, with the potential release of toxic and/or upsetting emissions, or even smaller burst events depending on the container nature.

The use of small, open packaging is preferred, since the higher specific area would allow a more efficient heat exchange to evacuate the reaction enthalpy and would minimize the chances of creating hotspots in the core of the containers. However, this will still cause the accumulation of unstable material on site, a situation that needs to be managed and resolved safely.

It is important to underline that, if happening at a controlled rate, the reactions initiated by the presence of water will end up exhausting the exothermic potential of the resin, eventually eliminating or at least decreasing the instability. To validate this hypothesis, a sample of water-contaminated resin was left aging at room temperature for a few months. Despite the fact that the resin was solid due to crosslinking, DSC screening determined that the specific enthalpy had decreased from 1236 J/g to 545 J/g in five months (-56 % reduction).

The United Nations guidelines for transportation of dangerous good (also known as the “Orange Book”), test H.1 (United Nations, 2009) defines a threshold of 300 J/g over which the SADT (Self Accelerating Decomposition Temperature) has to be determined in order to verify if the substance needs to be classified as self-reactive. This has been performed by carrying out DSC measurements on the aged resin at different scan rates and by fitting the DSC results to obtain an isoconversional model of the reaction kinetics, in the same way described previously. However, in this case the model was imported by the commercial software “AKTS Thermal Safety” to determine the SADT based on finite elements simulations coupling the reaction kinetics with heat transfer in the geometry of the container of choice (Roduit et al., 2008; Dellavedova et al., 2012).

The SADT obtained was 96 °C, thereby excluding the substance from the classifications according to self-reacting substances of the Orange Book.

3. Conclusions

The water contamination of an undiluted epoxy resin in a downstream step of the production process, typically initiated by a mechanical failure of a heat exchanger, valve leakage or by residual water present at start-up, may represent a significant hazard due to the series of exothermic reactions that are triggered by the presence of water.

The results shown in the present paper are used to provide guidance on how to face such an event, and the following conclusions are extracted:

- A) The pyrolysis cleaning of heat-exchangers may be a source of weakening and increase the likelihood of this particular initiating cause. If possible, plants should consider a mechanical pre-cleaning of the tubes to remove plugs and avoid bloating of the tubes. Pressure testing procedures are particularly important for the heat exchangers whose rupture has been identified as an initiating cause for such type of events, particularly after a pyrolysis cleaning and re-installation.
- B) Attention has been drawn on the fact that minor, often overlooked reaction peaks may be related to early cross-linking of the resins; those need to be carefully evaluated and the impact of a solidification analysed. Stability screenings done in laboratory to guide decision making should be designed to monitor the viscosity; DSC screening or test tube stability essays, typically used to detect exothermic behaviour of a sample, would fail to do so as they provide little or no data on the cross-linking reaction, potentially misleading the decision-makers.
- C) The TMR_{ad} of the decomposition reaction needs to be put in perspective if a solidification is likely to occur: values above the typical reference of 24 hours could transmit a false sense of security, as such time scale could be insufficient to prevent the decomposition of several cubic meters of resin solidified in a vessel. Although it may still be sufficient time to evacuate the unit and avoid harming the personnel, the damage of the assets could be significant.
- D) The use of an apolar solvent is extremely effective in stabilising the contaminated resin and facilitate the water removal by vacuum distillation. If at all possible, this option should be preferred to manage such type of event, as the drawbacks related to solvent flammability or toxicity and the practical complications of the operation are offset by significantly decreasing the risk of cross-linking and decomposition.
- E) In the undesirable situation where unstable, water-contaminated resin waste was generated on site, provided that sufficient heat exchange is ensured by splitting the product in small containers to avoid the creation of hot-spots, a few months aging at room temperature may suffice to bring stability to the waste material, thus allowing safe transportation off site for destruction.

References

- Dellavedova M., Pasturenzi C., Gigante L. and Lunghi A., 2012, Kinetic evaluations for the transportation of dangerous chemical compounds, *Chemical Engineering Transactions*, 26, 585-590
- Heirman, J.P., 2009. Handbook failure frequencies, Environment, Nature and Energy Department of the Flemish Government.
- Neville, H.L. and K., 1967. Handbook of epoxy resins., McGraw-Hill.
- Roduit B., Folly P., Berger B., Methieu J., Sarbach A., Andres H., Ramin M., Vogelsanger B., 2008, Evaluating SADT by advanced kinetic-based simulation approach, *Journal of Thermal Analysis and Calorimetry*, 93, 153-161
- Roduit B., 2000, Computational aspects of kinetic analysis. The ICTAC Kinetics Project - numerical techniques and kinetics of solid state processes. *Thermochim. Acta*, 355, 171
- Stoessel, F., 2008. Thermal Safety of Chemical Processes: Risk Assessment and Process Design, WILEY-VCH Verlag.
- UN (United Nations), 2009, Recommendations on the Transport of Dangerous Goods, Manual of tests and criteria, 5th revised ed., New York and Geneva, United States/Switzerland, 28.3.7