A perspective approach on the amine reactivity and the hydrogen bonds effect on epoxy-amine systems

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A perspective approach of the influence of H bonds in epoxy networks, from synthesis to final properties

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Abbreviations: 3-cyclohexanedimethanamine (**1,3-BAC**), 2,5-bis[(2-oxiranylmethoxy)methyl]-benzene (**BOB**), 2,5-bis[(2-oxiranylmethoxy)-methyl]-furan (**BOF**), bisphenol A (**BPA**), 1,3-cyclohexanediamine (**1,3-CHDA**), carcinogenic, mutagenic and reprotoxic (**CMR**), 4,4'-diaminodiphenylmethane (**DDM**), density functional theory (**DFT**), diglycidyl ether of bisphenol A (**DGEBA**), dynamic mechanical analysis (**DMA**), differential scanning calorimetry (**DSC**), Fourier transform infrared spectroscopy (**FTIR**), high performance liquid chromatography (**HPLC**), isophoronediamine (**IPDA**), kinetic substitution effect (**KSE**), *m*-phenylenediamine (***m*PDA**), *m*-xylylenediamine (**MXDA**), non-isocyanate polyurethane (**NIPU**), nuclear magnetic resonance (**NMR**), polyamide (**PA**), poly(ε-caprolactone) (**PCL**), poly(diglycidyl ether of bisphenol A) (**poly(DGEBA)**), poly(ethylene oxide) (**PEO**), poly(methyl methacrylate) (**PMMA**), polyurethane (**PU**) size-exclusion (**SEC**), tetrafurane (**THF**), volatile organic compound (**VOC**).

Abstract

The observation and influence of hydrogen bonds in epoxy-system curing and material properties is also discussed through a state of the art of literature. Epoxy-amine systems are widely used polymers for various industrial applications, such as composites, adhesives, paints and coatings due to their high thermal and mechanical properties. The reactivity of epoxy-amine system is crucial for both academic and industrial communities and is dramatically influenced by H bonds. In addition, the ring opening reaction of epoxy system yields hydroxyl groups, which can form hydrogen bonds and thus influence the curing kinetic and the material properties. Those formed hydroxyl groups have also an influence on the properties of cured materials due to their H bond sites. Hence, this article focuses on the description of an amine reactivity scale and on the gathering of literature data mentioning the hydrogen bond observation and study in epoxy-amine system. First, this article presents an amine reactivity scale clarification due to our team expertise and knowledge. Then, all external factors influencing the hydrogen bond formation are described based on several studies. Finally, the influence of hydrogen bond in epoxy-amine system was summarized.

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1. Introduction and motivation

It is often necessary and desirable to alter an epoxy-amine formulation to adapt it to industrial applications.[1] Due to its aromatic structure and availability, diglycidyl ether of bisphenol A (DGEBA) is most often used as epoxy part and represents at least 75% of all epoxy thermoset precursors.[2] Thus, amine hardener part is varied in order to modify epoxy-amine properties and some diluents can be added to the formulation in the same view. However, the amine structures could widely influence the reaction because of the large range of their different reactivities. Nucleophilic character, steric hindrance and reaction kinetic are indeed related. Moreover, they can form hydrogen bonds (H bonds) with the initial epoxy reactant or with the hydroxyl (annotated –OH) moieties, impacting also the curing reaction. Amine reactivity and H bonds are indeed two closely related factors, but unfortunately only a few studies linked them. Each publication is often independent and focuses on one element, such as the impact of the solvent, the epoxy-amine ratio, curing temperature influence, change in amine hardener or epoxy prepolymer structure. Therefore, many clarifications concern the epoxy material advances but, so far, none of them described accurately the amine reactivity scale, while it is nevertheless a key point of the chemical industry.[3–7] Depending on the targeted application, scientists search for amines, which are reactive at room temperature or not, leading to a long or short gel point formulation, with various functionalization and functionalities, *etc.* Moreover, the physical aspect is also important, as well as the viscosity, because of their influence on the reactant homogenization and thus curing reaction. However, all of this is complex to predict because of the lack of knowledge on amine reactivity and properties.

In our previous works,[8,9] we noted that the presence of H bonds increased drastically the viscosity and the reactivity of hardener, and they also reduced the macroscopic deformations of the final materials. The observation of H bonds are described in polymer chemistry, such as in polyamide (PA),[10] polyurethane (PU) and non-isocyanate polyurethane (NIPU),[11,12] benzoxazine,[13,14] and epoxy-amine thermosets.[15] Some studies even used H bonds in a beneficial way to design high-performance materials through non covalent cross-linking.[16–19] However, even if the H bond interactions are known to be present in cross-linked thermosets and to influence the material properties[17] and the reaction,[20] so far, no clarification was performed on H bond interactions in epoxy-amine system.

Many reviews and books on epoxy materials or on new bio-based epoxy materials exist,[5–7,21] but there is no global contribution on the observation and influence of H bonds and the elaboration and properties of epoxy materials. Hence, in order to provide a global point of view to the scientist community, this article proposes to gather and discuss some works focusing on the amine reactivity depending on their structure and the impact of H bond formations in epoxy-amine system, from reactants to materials.

2. Hydrogen bonds, brief definition

Hydrogen bonds are found in the nature and play integral role in biological structure, such as in the DNA repair process through their efficient reformation.[22] Another famous example of the H bond presence in the nature is illustrated by the water and its ice form.[23] However, the understanding of these interactions remains incomplete, despite the numerous studies on this topic.[24] Basically, H bond refers to an electrostatic interaction between a donor (D) – requiring the presence of H atom on the donor group - and an acceptor (A) site, which could be intra or inter molecular phenomena.[25] H bonds are usually described as non-covalent forces, as well as halogen bonds, π–π interactions, cation/anion–π interactions and van der Waals forces.[26] H bond energy, and thus its effectiveness, is known to depend on the D and A nature, remaining weaker than covalent bonds.[27] A and D sites must be electronegative atoms of the first row of the periodic table (*i.e.* N, O, F or Cl),[28] and the environment (steric hindrance, substituent, angle of H bonds, …) has also an impact on the H bond force.[29] For instance, the H bond linkage geometry is known to be flexible, but should approach linear profile to reach a minimum energy. Thus, the closer the D-H---A angle to 180°, the stronger the H bond and the shorter the H---A distance.[30] More recently, H bonds were analyzed from FTIR and a summarization of the different signals found in all articles described in this clarification were reported in the Table 1. These values show that molecular environment influence the shift of the band values, such as the difference between intra and inter molecular H bonds or between hydroxyl and amine or another hydroxyl moieties. In addition, the H bond length difference between two hydroxyl groups or one hydroxyl and one amine functions results in the peak wavenumber shift. The higher the H bond length, the lower the H bond energy and therefore its strength, the lower the peak wavenumber value. This phenomenon will be further discussed in this article.

Table 1: H bonds stretching band in FTIR analysis

	Networks	Molecules and prepolymers
bonds	cm-1	cm-1
Free		
–OH	3 650	3 570-3 600
intermolecular		
OH---NH	3 400	3 070-3 350
OH---OH	3 430-3 490	3 410-3 459
C=O---NH	1 720	
C=O---OH	1 712	
intramolecular		
OH---OH	3 550-3 581	

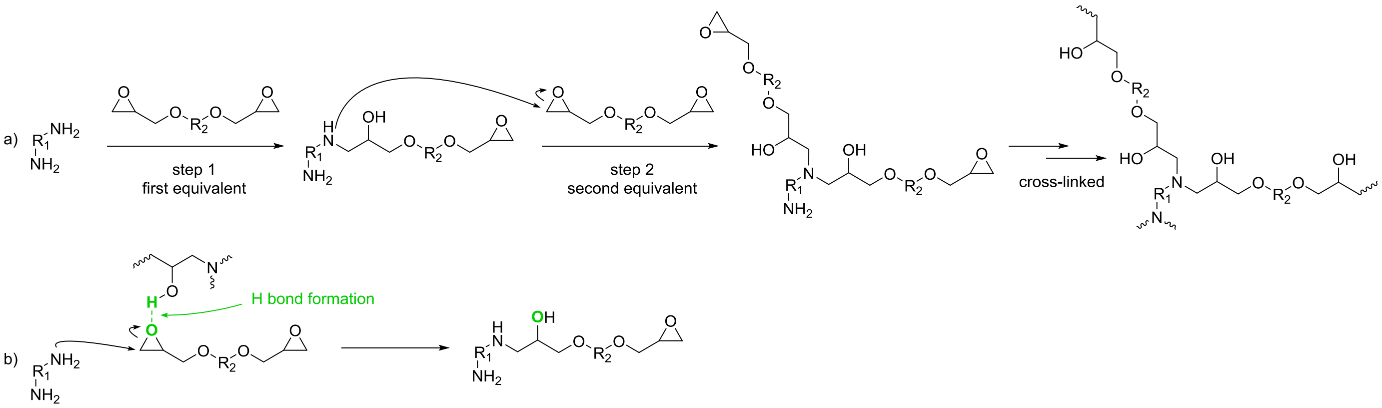
3. Epoxy-amine thermosets, widely used materials for various industrial applications

3.1. Brief history of epoxy-amine thermosets

The first discovery of the synthesis of epoxy compounds was described in the literature as early as the late 1890s.[4] However, their commercial production only started in the late 1940s, with the publication of two successive patents by P. Castan of DeTrey Fréres Co. in Switzerland and by S. Greenlee of DeVoe and Raynolds Co. in the United States.[31,32] Since the date, epoxy based thermosetting polymers have largely evolved and now represent approximately 70% of the market of thermosetting polymers (except polyurethanes). Due to their high thermo-mechanical performance and their great chemical resistance, epoxy materials find their application in broad range of industrial fields, such as coatings, composites, adhesives, and electronics/electrical components.[7] Epoxy materials have important environmental impact because of their cross-linked polymer nature, which prevents their recycling. Moreover, 90% of the worldwide epoxy polymers are derived from bisphenol A (BPA), which is a carcinogenic, mutagenic and reprotoxic (CMR) and an endocrine disruptor substance. Therefore, researches recently focused on the development of non-toxic and/or bio-based epoxy as substituent to BPA.[7,21] In the same view, the interest for bio-based amines is also increasing in the last few years, with the synthesis of eco-friendly amines. Our team has recently developed new efficient bio-based amine hardeners, by a direct amination method of epoxy monomers using aqueous ammonia solution.[8,9] These new hardeners showed high reactivity but also high viscosity due to the presence of many H bond sites in their structures. During these works, we realized that there was a lack of knowledge concerning the amine reactivity and the influence of H bonds in the epoxy-amine reaction.

3.2. Epoxy thermoset synthesis

Epoxy monomers or prepolymers may be reacted either with themselves through chain grow the homopolymerization reaction, or by polyaddition with the addition of polyfunctional nucleophiles, named hardeners, such as amines, anhydrides, acids, thiols, alcohols and phenols.[7] The most common type of hardeners used to synthesize epoxy thermosets is amines, which can react with one epoxy per –N*H* active function (*i.e.* primary amine can react twice, whereas secondary amine once. Scheme 1, a). Epoxy-amine polyaddition yields the formation of hydroxyl groups by epoxy ring opening reaction. These –OH groups can form H bonds, which will have multiple interactions with reactants (Scheme 1, b), solvents, reaction intermediates or catalysts.[33]



Scheme 1: a) epoxy-amine mechanism with a standard diglycidyl as DGEBA, b) interactions between hydroxyl group of a reaction intermediate and epoxy moieties.

In spite of the simplicity of the polyaddition mechanism, many factors are also known to have an impact on the reaction, increasing the complexity of the reaction understanding. These factors will be related and discussed throughout this article, such as the steric hindrance effect, the presence of catalyst or the reactant structures, which can interact with each other by the formation of H bonds. Some authors indeed studied H bond as a whole,[34] however, the H bonds in epoxy thermosets were only reported in a handful of studies, in spite of the importance of their role for determining the mechanical properties and curing behavior of epoxy materials. H bonds may interact with the reactants during the reaction or with the tridimensional final networks and impact their properties. Moreover, amines widely influence the reaction due to the range of factors applicable to them, which can modify their properties and reactivity. There is many scattered information on amine reactivity in the literature, but no general scale of amine reactivity. The present article proposes to gather some works concerning the amine reactivity and the impact of H bonds in epoxy-amine reactants, reaction and materials.

3.3. Epoxy or amine equivalent weight and stoichiometry calculation

First of all, the epoxy equivalent weight (EEW) of epoxy prepolymer and the amine hydrogen equivalent weight (AEW or AHEW) of the amine hardener are theoretically determined by the following equations:

$$EEW = \frac{M_{epoxy}}{n_{fonction}} \tag{1}$$

$$A(H)EW = \frac{M_{amine}}{n_{fonction\ NH}} \tag{2}$$

These equations can be adapted in the case of reactant is mixed with reactive diluent, as follows:

$$EEW\ of\ mix = \frac{Total\ Wt}{\sum_i \frac{Wt_{\ epoxy\ i}}{EEW_{epoxy\ i}}} \tag{3}$$

$$A(H)EW\ of\ mix = \frac{Total\ Wt}{\sum_j \frac{Wt_{\ hardener\ j}}{EEW_{hardener\ j}}} \tag{4}$$

Then, to synthesize epoxy thermosets, a theoretical molar ratio of 1:2 between amine and epoxy functions is usually used (also described as ratio of 1:1 –N*H* active and epoxy functions). The amount of hardener required for $\mathcal{X}$ weight of epoxy is calculated according to equation (5):

$$m_{hardener} = \frac{\mathcal{X}\ weight\ of\ epoxy\ \times\ A(H)EW}{EEW} \tag{5}$$

However, several factors can impact the theoretical ratio, such as the –OH moieties induced by the ring opening reaction, which could react with epoxy, the steric hindrance induced by the curing reaction, the viscosity or the H bond formation, which can prevent the end of the cross-link process. Thus, optimal molar ratio can be determined with the adjustment of equation (5) by multiplying the $m_{hardener}$ by various ratio of amine-epoxy. Then, differential scanning calorimetry (DSC) analysis allows to determine the highest glass temperature transition (T_g) value, corresponding to the optimal ratio.

4. Epoxy-amine reactivity and H bond influence

Epoxy and amine moieties can be impacted by their structure and substituent or by the H bond formation during the reaction, which can impact the curing reaction and the material properties. Moreover, there is a lack of knowledge on the amine reactivity and the influence of H bonds on the epoxy-amine reaction, in spite of their important role on the reaction kinetic and material properties. This part focuses on the reactant reactivity, especially on amine reactivity scale and the influence of H bond on epoxy-amine reaction.

4.1. Influence of epoxy structure and H bonds on the reaction

The structure of epoxy and its substituents have an influence on the reactivity between epoxy and amine moieties.[35] Generally, end epoxy groups are more reactive than internal epoxy groups due to the steric hindrance and the inductive effect. Substituents in α-position of epoxy have indeed a positive or negative inductive effect on the electrophilic site of epoxy moieties, and thus modifying the reactivity of epoxy ring (Figure 1). Thus, the higher the inductive or mesomer effect on the α-carbon of epoxy ring, the higher the reactivity towards amines. In this view, an alkyl epoxy is less reactive than an allyl epoxy, then vinyl epoxy and aromatic epoxy.[36] *N*- and *O*- glycidyl also exhibit a high reactivity due to the presence of heteroatom in their backbone,[3] which has two impacts on the reactivity towards amines. The oxygen of the epoxy ring indeed induces an inductive effect and can form H bonds with amine reactant, favoring the molecular positioning between two reactants and thus the epoxy-amine reaction.[4]

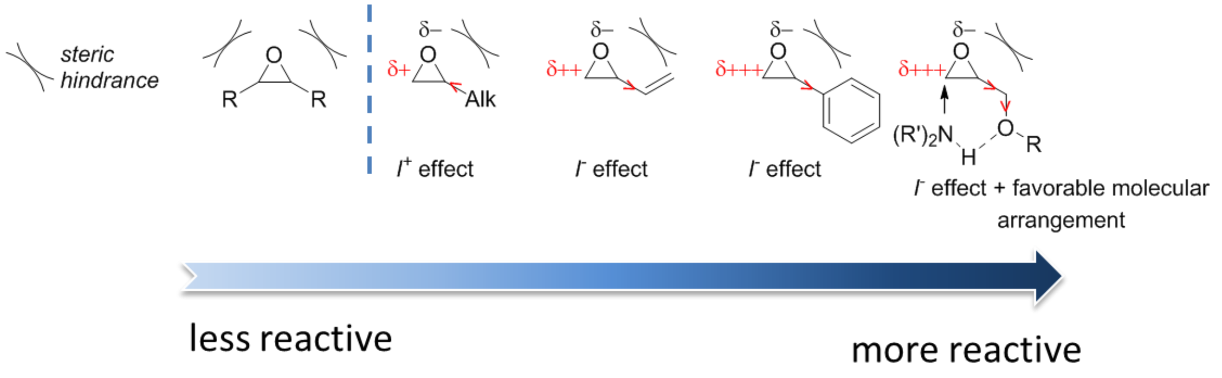


Figure 1: illustration of the positive electron-withdrawing inductive effect induced by substituents on the epoxy ring.

4.2. Influence of amine nature on the reaction

The structure of amines has a great influence on their properties and thus on the epoxy-amine reaction. First, their backbone weight and then their substituent could impact the intra or intermolecular H bond formation and change their properties, such as the boiling point, the physical aspect, the miscibility degree in the solvent or with other reactant and the reactivity. For instance, regarding methanamine (T_b = -6 °C), ethanamine (T_b = 17 °C), and propylamine (T_b = 49 °C), the simple enlargement of the carbon chain gives higher boiling point, allowing to perform reactions at higher temperature. By comparing methanamine with dimethylamine (T_b = 7 °C) and trimethylamine (T_b = 3 °C), the methyl addition to the nitrogen atom leads to a slight shift of boiling point, but a modification the reactivity and the AHEW of the molecule (this fact will be explained in the following part). Many other examples concerning the impact of added substituents or heteroatoms on the amine structure could be cited, such as the impact of the aromatic ring on the properties. However, the following part focuses on the reactivity of the three amine states observed during epoxy-amine reaction (primary amine, β-hydroxylamine as secondary amine, and tertiary amine) and the changes induced by general backbones of amines, such as aromatic, cycloaliphatic or alkyl amines.

4.2.1. *Reactivity of primary amines towards epoxy moieties*

Amine structure has an effect on the kinetic of epoxy-amine reaction, indeed, the basicity, nucleophilicity and the steric hindrance of amine are related. The amine reactivity is complex and no accurate scale was described so far in the literature. Therefore, we propose a *summary of amine reactivity scale established from related data literature* in Figure 2. First, the most reactive class of amine hardeners are aliphatic amines containing heteroatoms. The reactivity of amine hardeners could be indeed enhanced by the introduction of heteroatom in the amine backbone, in spite of the electron-withdrawing inductive effect of heteroatom. This can be explained by the formation of H bonds with amine reactant and/or epoxy moiety, which then catalyzes the epoxy-amine reaction by favoring molecular positioning. For instance, the polyethyleneamine hardeners, such as diethylenetriamine (DETA) and triethylenetetramine (TETA), are considered as the most reactive polyamines exhibiting two primary amines at the aliphatic chain end and secondary intern amines, depending on the backbone length. However, our team recently proved that primary β-hydroxylamines exhibit a really high reactivity towards epoxy due to the formation of H bonds between the –OH of β-hydroxylamine and the oxygen atom of glycidyl epoxy reactant.[8] Polyetheramines (*e.g.* EDR-148) are also aliphatic amine containing heteroatoms currently used in the industry, that seem to exhibit a reactivity close to standard aliphatic amines (except β-methylated polyetheramines, which will be mentioned in following lines), despite the presence of oxygen atom in β-position.[37] This one should indeed decrease the reactivity due to its I^- effect, however, no one studied this phenomenon.

Then, conventional aliphatic amines can easily react at room temperature due to their low steric hindrance environment (*e.g.* hexamethylenediamine,[38] trimethylhexane-1,6-diamine[39]) and are more reactive than comparable cycloaliphatic ones, and much more reactive than aromatic amines.[4] Moreover, the steric hindrance has a strong impact on the reactivity. Arylyl compounds are therefore more reactive than their aryl analogous. For instance, the usual hardener 3-cyclohexanedimethanamine (1,3-BAC) is more reactive than isophoronediamine (IPDA), due to the presence of two methylene groups in the 1,3-BAC structure against one in IPDA. In this sense, 1,3-cyclohexanediamine (1,3-CHDA), is even less reactive due to the absence of methylene group, increasing the steric hindrance and thus decreasing the reactivity.[43]

Next, previously mentioned polyetheramines can be functionalized by a methyl group in β position, inducing highly reduced reactivity due to the I^+ effect and mainly the steric hindrance. There are various commercialized hardeners with different chain lengths, which overcame the lower reactivity by pluri-functionality. For instance, the

Jeffamine T403 hardener is a β-methylated polyetheramine with a reactivity between aliphatic and aromatic amines.[44] Moreover, the addition of ethyl instead of methyl group allows to increase the steric hindrance around amine, reducing again the reactivity.[45]

Furthermore, aromatic amines belong to low reactive hardeners class, requiring high temperatures to start the reaction. The attractiveness of the lone pair is indeed lessened because of the conjugated system with the delocalized ring electrons, decreasing the nucleophilic character. However, as in the case of cycloaliphatic ones, arylyl compounds show higher reactivity, such as *m*-xylylenediamine (MXDA),[46] having close reactivity to similar IPDA for example.[42,47]

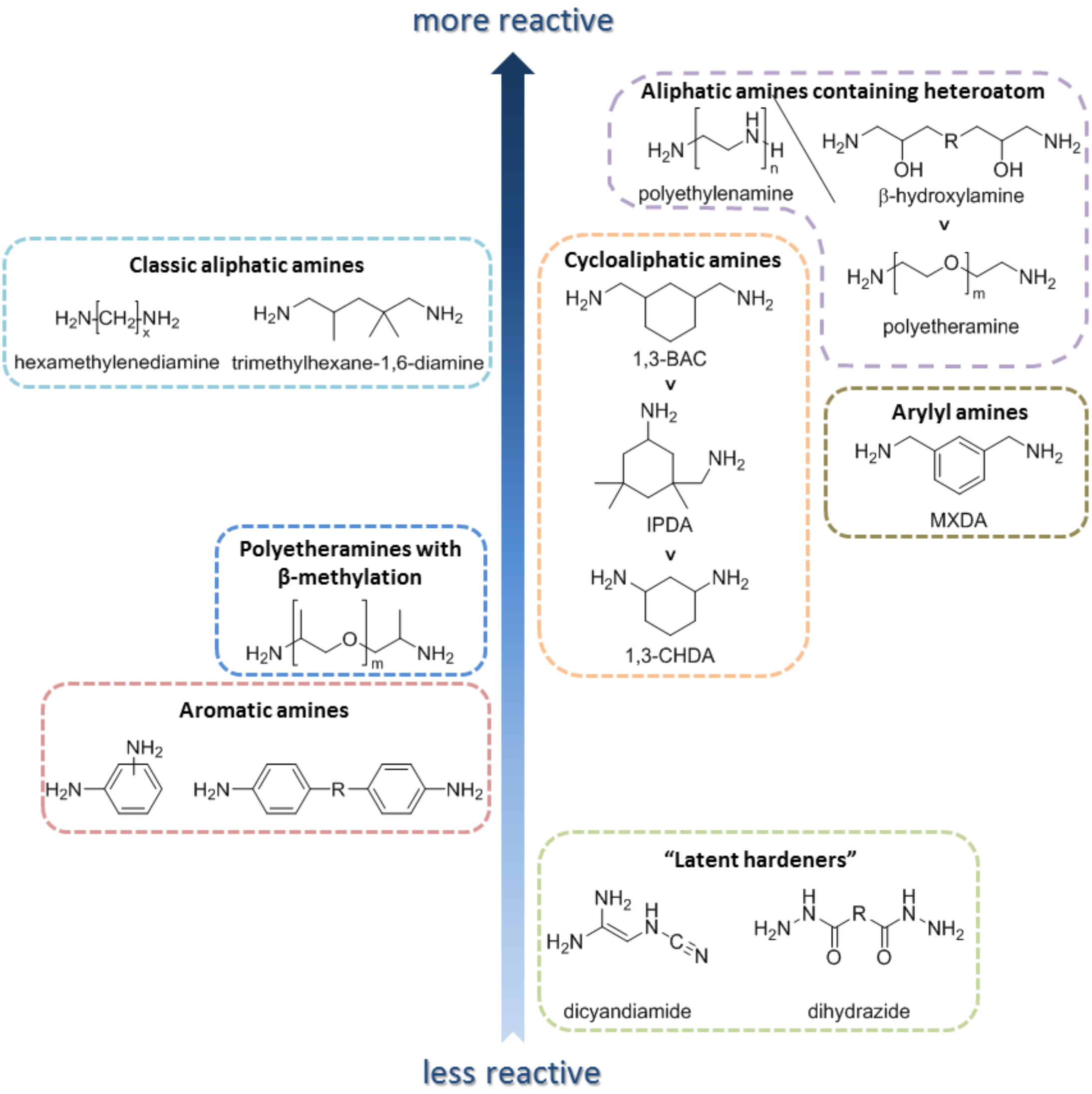


Figure 2: summary of amine reactivity scale established from related data literature.

Finally, latent curing agents are a particular class of solid hardeners for epoxy materials, such as dicyandiamide and dihydrazide, which cannot react with epoxy prepolymers at room temperature and do not increase the resin viscosity. They indeed form strong internal H bonds and are insoluble in epoxy prepolymers, preventing the reaction at low temperature. Dicyandiamides do not react with epoxy moieties at moderate temperatures but react very fast at their melting point (>180 °C), while dihydrazide can cure at lower temperature than dicyandiamide.[49] Accelerators are usually used for latent hardeners to reduce the curing temperature.[50]

However, this *summary of amine reactivity is an overall vision and* the reality is more complexe by considering H bonds and inductive or mesomer effects induced by amine substituents. Some factors allow to modify the reactivity, such as the presence of heteroatom in the chain, allowing to form H bonds, or by adding moieties inducing inductive of mesomer effect.[51,52] Mayr's group has besides created an online database concerning the reactivity parameters of various electrophile and nucleophile molecules, including some aliphatic and aromatic amines.[53] The reaction kinetics of various amines were performed and their nucleophilic degrees (*N* parameters) were evaluated according to the linear free energy relationship as described by the eqn 6,[54] allowing to empirically predict their reactivity towards electrophiles.

$$\log k_2\ (20\ °C) = s_{\mathrm{N}}(N + E) \qquad (6)$$

where:

k = second-order rate constant in $M^{-1}.s^{-1}$
s_{N}= nucleophile specific slope parameter
N = nucleophilicity parameter
E = the electrophilicity parameter

For instance, they compared the nucleophilic character of three different hydroxylamines (Figure 3). They observed that γ-methylation slightly impacts the amine reactivity, while *β*-ethylation decreases a lot the reactivity, due to the higher steric hindrance.

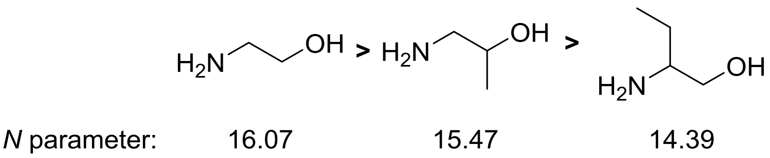


Figure 3: May's group empirical scale between three different ethanolamine, no substituted, γ-methyl substituted and β-ethyl substituted (solvent: DMSO).

4.2.2. *Reactivity of secondary amines towards epoxy moieties*

In the same way, primary amines are generally considered as higher reactive molecules than secondary ones towards electrophilic compounds, such as epoxy reactants because of the steric hindrance effect.[6] Moreover, the steric hindrance limits the H bond formation by preventing the molecules from getting closer. However, as previously explained, various functionalization are known to influence the amine reactivity, such as the amine methylation, the amidification or even the hydroxylation induced by the ring opening during the epoxy-amine reaction (Figure 4). These functionalization could lead to secondary amines more reactive than primary ones.

4.2.2.1. Functionalized secondary amines

The direct amine methylation allows to increase the reactivity, such as the mono methylation of ammonia, which induces a positive inductive effect (I^+ effect) to the newly formed methylamine, increasing its nucleophilicity (named α-effect).[52] In the same view, the α-methylation of methylamine increases the nucleophilicity, inducing a higher reactivity to the obtained dimethylamine compared to methylamine. Nevertheless, literature assumes that methylamine is a primary amine which theoretically should be more reactive than secondary one due to the steric hindrance.[55] This contradiction illustrates the lack of knowledge concerning amine reactivity scale. Moreover, as a reminder, the β-alkylation logically decreases the amine reactivity, by increasing the I^+ effect and mainly the steric hindrance, while α-methylation increases reactivity with similar effects. This difference could be explained by the fact that β-methylation induces a steric hindrance dominating the polarity, whereas it is not the case for the α-methylation.

Other functionalization increase the amine reactivity, such as the incorporation of –OH groups on the backbone, allowing to form H bonds with epoxy moieties, which thus catalyze the reaction.[4,8] In the same way, Mannich bases, which are adducted from the reaction between amine, phenol and formaldehyde, are well known for their high reactivity due to the presence of phenol moieties, which can catalyze the epoxy amine reaction.[56–58] On the contrary, the reactivity can be decreased with functionalization, such as amidification, leading to an inactive –N*H* function,[59] or some Michael addition cases, such as the addition of maleate esters as substituents with an electron-withdrawing inductive effect.[60] However, the functionalization effect on the secondary amine reactivity compared to primary one could be predicted but not compared, because of the lack of information about their respective impact on the amine nucleophilic character.

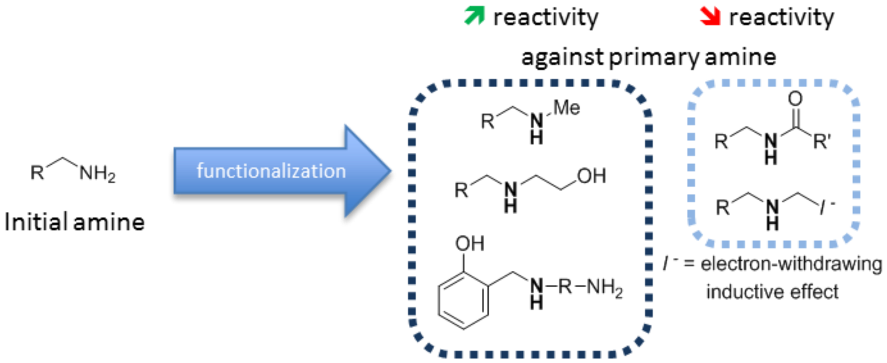
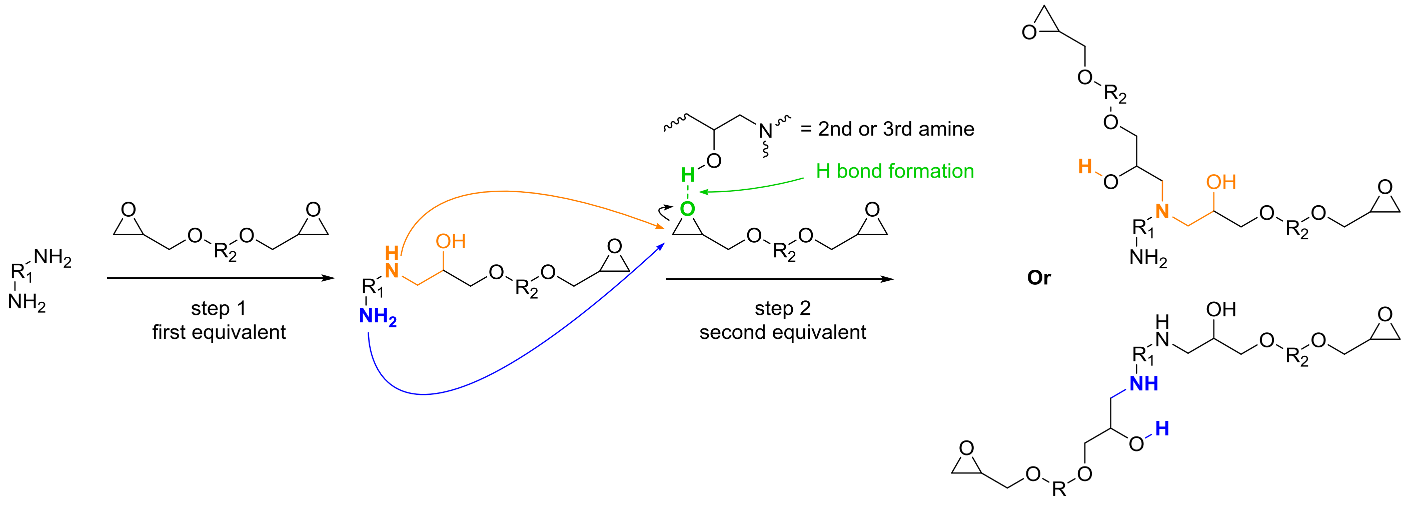


Figure 4: example of amine functionalization changing the nucleophilic character in comparison with initial amine.

4.2.2.2. Autocatalytic effect of the β-hydroxylamine, as newly amine formed during the reaction

In epoxy-amine reaction for thermosets, a primary amine reacts with another epoxy moiety, resulting in a secondary amine, which will also react with epoxy ring. Theoretically, by considering primary amines more reactive than secondary ones due to the steric hindrance, polyaddition of primary amines is faster than the reaction of secondary amines which are formed during the reaction. However, as was previously explained, the presence of –OH in β-position of secondary amine increases the reactivity towards epoxy due to the possibilities of H bond formation, favoring a new ring opening reaction. Thus, one of the most debated questions of the epoxy-amine reaction is: which amine is the most reactive between the initial primary amine and the secondary β-hydroxylamine formed during the reaction (Scheme 2)?[61–65]



Scheme 2: representation of the competition between the primary amine and the secondary β-hydroxylamine formed during the epoxy-amine reaction.

Some early publications assume that primary amines react faster than secondary amines.[4,66–68] However, last years, other accurate works concerning the competition between primary and secondary amines were aroused. For instance, in order to study the mechanism of epoxy-amine curing reaction, Ehlers *et al.* examined the competitiveness of the primary and secondary amine towards epoxy moieties, using density functional theory (DFT) methods.[69] They explained that secondary amines would react faster than primary amines, while opposite results are discussed in the literature. However, they did not consider the auto-catalytic effect and they chosed dimethylamine as secondary amine model, which is described, as a reminder, as more reactive than methylamine (as the primary amine model in this study) due to the α-effect..[52]

In 2002, Zvetkov studied the kinetics of reaction between *m*-phenylenediamine (*m*PDA) and DGEBA, by considering the autocatalytic parameters.[70] He listed a range of calculation methods to determine the kinetic substitution effect (KSE) of epoxy-amine reactions since the beginning of epoxy-amine kinetic study. A positive KSE is obtained if the primary amine is less reactive than the secondary one, otherwise, KSE is negative. Two groups of experimental techniques were identified to obtain kinetic data: techniques using solubility parameters, such as sol/gel fraction chemical analysis, size-exclusion (SEC) or high-performance liquid chromatography (HPLC), and real time *in situ* monitoring, such as DSC and Fourier transform infrared spectroscopy (FTIR). It was highlighted that negative KSE was more often observed when solubility techniques were applied, while real team monitoring techniques exhibited positive KSE. Zvetkov assumed that the inconsistent results found in the literature might be explained by the solubility of the reaction components. Thus, only DSC is considered as a highly accurate method for determining the reaction rate, the degree of conversion and the KSE. However, some other parameters are required to be considered, such as the viscosity of the reactants and miscibility of each other in epoxy-amine mixture,[71] or the measurement bias caused by thermal inertia of the studied material (*i.e.* heating-up bias) which was more recently described.[72]

To conclude, according to Zvetkov clarification, it could be considered that the β-hydroxylamines formed during the reaction are generally more reactive than the initial primary amines. However, due to the range of external factors, which will be a topic of discussion in the following part, this development remains theoretical and each system required to be studied to determine the reactivity. For instance, in the case of thermoset syntheses, the degree of curing has also an influence on the kinetic reaction due to the increasing of viscosity mixture and the steric hindrance, decreasing the probability of molecule meeting.

4.2.3. *Catalytic effect of the tertiary amine*

As previously explained, the reaction of primary amine with an epoxy leads to the formation of secondary amine, which can react with another epoxy moiety to form tertiary amine. Due the absence of active hydrogen on tertiary amine structure, this latter cannot take part to the epoxy-amine polyaddition but can act as catalyst, resulting in the acceleration of the epoxy-amine curing.[73] Tertiary amines are indeed a really important class of accelerators or co-curing agents for phenol, acid anhydride, polyamide and polyamine curing agents.[7,74] Due to an anionic mechanism, tertiary amine formed during the epoxy-amine curing could also catalyze the homopolymerization reaction between the secondary alcohols with epoxy groups, which is actually a really slow reaction.[75] However, due to steric hindrance, the tertiary amine formed during the reaction cannot act as catalyst. The homopolymerization is usually insignificant in the final thermoset, unless there is an excess of epoxy groups, a catalyst or high curing temperature.[76–78]

4.3. Conclusion

To conclude, a *summary of amine reactivity scale was established without considering functionalized secondary amines. The* epoxy-amine kinetic depends on some factors, such as the structure of the reactants, the steric hindrance and the H bond formation. H bonds have indeed an important role on the reaction due to the ability of the reactants and their substituents to form H bonds, changing the electronic environment and weakening the C-O bond of epoxy ring. Moreover, the molecule positioning in space is also influenced, favoring the attack of amine towards the epoxy ring. However, there is still a lack of information in the literature and some examples are very difficult to class, such as lysinol,[79] which exhibits alkyl substituent in β position, decreasing largely the amine reactivity, but also an –OH group, increasing highly the amine reactivity. It would be interesting to study the reactivity of polyethylenamine and β-hydroxylamine towards an epoxy moiety. It is indeed possible that β-hydroxylamines are the most reactive amines due to the presence of –OH group, which is more efficient to form strongest H bonds. This part also highlighted contradiction concerning the competition between primary and newly formed secondary amine during the reaction and studies remain to be done concerning this competition.

5. Influence of external factors on epoxy-amine system through H bonds

External factors, such as the presence of solvent, miscibility or the temperature, could influence the amount of H bonds, the kinetics of curing reaction, and even the material properties. This part focuses on the literature data concerning the observation of the external factor influences in the epoxy-amine system and the H bond behaviors.

5.1. *Miscibility between reactants*

5.1.1. *Reactants affinity*

The effective choice of the reactant structure is the basis of the epoxy-amine chemistry. First, the physical state of the reactant is important: formulation with two solid reactants would be complex, requiring effective mixing and similar boiling point to obtain homogeneous thermoset at the end of the cross-linking reaction. In the same view, a solid reactant insoluble in the other part of the system will encounter similar difficulties (*e.g.* the insoluble latent curing agents). The choice of two reactants possessing similar nature (*e.g.* two aromatics or two aliphatics), allows to favor the achievement of homogeneous system. For instance, two aromatic monomers are more miscible than one aromatic and one aliphatic monomers. Moreover, complementary functions could be selected as H bond acceptor and donor sites to improve the miscibility between reactants.

5.1.2. *Addition of modifier prepolymer*

Epoxy-amine thermosets are known to be highly cross-linked but often brittle. Therefore, in order to improve the material properties, some modifiers or diluents can be added to epoxy-amine mixture, which reduces the viscosity by weakening the interaction between reactants.[80,81] However, the majority of polymer-polymer blends from different natures are not miscible and induce a phase separation if they are mixed together. In the case of the polymers which can form H bonds between them (*e.g.* hydrogen atoms of hydroxyl or amine group with oxygen atoms of carbonyl group),[82] the mixture miscibility is increased, delaying or preventing the phase separation phenomenum. For instance, Blanco *et al*. studied the influence of poly(methyl methacrylate) (PMMA, Figure 5) content, as thermoplastic modifier.[83] They observed that PMMA is initially miscible in DGEBA as epoxy prepolymer. However, the addition of the amine hardener (4,4'-diaminodiphenylmethane, DDM), allows to observe a phase separation appearance during the reaction. This could be explained by the increase of the molecular mass of the system, which is induced by the polyaddition reaction. It should be noted that this study does not mention the amidification reaction between amine and PMMA. Anyway, Blanco *et al.* observed that the phase separation appearance was faster with the amount of modifier (0 to 40 w%). On the other hand, when they added *p*-toluidine as amine extender, they observed a delay in appareance, or no phase separation. This fact could be explained by the decrease of the hindrance induced by the system mobility provided by extender.

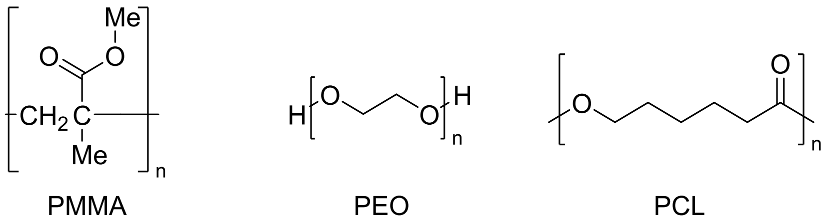


Figure 5: some examples of modifiers used for epoxy-amine mixtures.

Larrañaga *et al.* performed similar study than Blanco *et al.*,[84] using the same epoxy-amine system, with poly(ethylene oxide) (PEO) as modifier due to its ability to accept H bonds from donor sites, such as –OH group formed during epoxy-amine polyaddition. They added PEO up to 30 w% in the stoichiometric epoxy-amine system. They concluded than the amount of H bonds increases with a higher PEO content. They also observed that, in the case of a higher PEO content, H bonds can change the free volume of system and modify completely the properties. Moreover, they mentioned that some amines with higher nucleophilic character could favor OH---N interactions, preventing the H bonds formation with PEO. Another example of modifiers is the poly(ε-caprolactone) (PCL) blend. H bonds may occur due to oxygen atoms of ester groups which increase its miscibility with the epoxy-amine materials.[85] Some researches studied the influence of H bonds on the miscibility of PCL in epoxy materials.[86,87] Results showed that PCL is partially miscible in epoxy amine mixture due to the H bond formation between ester oxygen atoms and hydroxyl or amine moieties of epoxy-amine system. However, depending on the mixture nature, phase separation can start at a certain content of PCL, while a fully homogeneous PCL/epoxy blends can be obtained with a reasonable amount of PCL, as showed Zheng et *al*.[88]

Some other examples of modifiers exist as poly(vinyl acetate),[89] poly(etherimide),[90] more complex structures, such as poly(phthalazinone ether nitrile ketone),[91] and even poly(styrene),[92] which cannot form H bonds but can interact with π-bonds with aromatic epoxy and amine reactants, allowing initial miscibility.

5.2. Temperature and viscosity relationship for reactants and mixture analysis

5.2.1. *Nature of reactants and H bonds*

The physical state and viscosity of the reactant are directly determined by their structure.[93] For instance, DGEBA viscosity depends on the number of repeating units and thus the molecular weight. Moreover, the nature of the reactant functions could also affect the viscosity, such as the presence of hydroxyl functions in the DGEBA oligomer. For instance, our team recently highlighted the high viscosity of β-hydroxylamine obtained by amination of epoxy ring using aqueous ammonia solution.[8,9] The –OH group in β-position of amine allows indeed to form a lot of inter and intramolecular H bonds, increasing the viscosity compared to usual hardeners without hydroxyl function. The group position has also an influence on the product aspect and viscosity. For instance, the usual amine hardener 1,6-hexanediamine is solid while its isomer 2-methylpentane-1,5-diamine is liquid due to the presence of one branched methyl in amine β-position. This branched methyl group allows to reduce the viscosity of the amine monomer due to the steric hindrance, making the reactant liquid (2-methylpentane-1,5-diamine, T_m = -60 °C against

45 °C for 1,6-hexanediamine). Moreover, epoxy and amine reactants interact each other by H bond formation between oxygen atom of epoxy ring and hydrogen atom of amine moiety. Then, the ring opening reaction induces the formation of –OH group, which can also interact with reactant due to its oxygen and H atoms, also impacting the viscosity.

Sangroniz *et al.* recently studied the effect of H bonds on rheological properties of phenoxy materials as homopolymer of DGEBA.[94] This prepolymer allows to study only the effect of same –OH moieties as epoxy-amine thermoset, without the presence of epoxy and amine moieties. This prepolymer possesses indeed hydroxyl and ether groups, resulting from the ring opening reaction. In this view, they modified original prepolymer by acetylation or benzoylation of the hydroxyl group to prevent H bond formation. Then, original prepolymer and modified prepolymers were analyzed by rheological measurements, which were performed in the linear regime, in order to study the variation of the elastic and the viscous moduli. Results showed that the higher the amount of H bonds, the higher the viscosity. Then, the glass transition temperature were measured by DSC for original and modified prepolymers in order to define if the H bonds have an influence on the T_g. They concluded that the T_g decreased when reducing H bond amount, which can be explained by the increasing in chain mobility. On the other hand, the addition of bulky groups like benzoyl to functionalize hydroxyl groups increases the T_g.

5.2.2. *Viscosity and temperature relationship*

In order to adjust the viscosity, reaction temperature could be modified and some previously mentioned diluents or modifiers can be added in epoxy-amine mixture.[95–97] Viscosity and temperature are two indivisible concepts. Obviously, the temperature increase has a great impact on the average speed of the molecules and the average intermolecular forces, allowing to reduce a lot the viscosity,[98] the reaction exotherm and thus the curing kinetic.[99] Moreover, due to the evolution of the cross-linking process, the molar mass of the system rises, increasing the viscosity.[100] Because of the steric hindrance increase induced by the high viscosity, the diffusion of low molecular weight species decreases, reducing the reaction rate after passing through a maximum.[101] Only a few articles focused on the viscosity change during the curing kinetic of epoxy-amine system. Lee and Wei studied the viscosity change of epoxy-amine system during cross-linking step by rheological measurements, using bisphenol A based epoxy and 3,3’-dimethyl-4,4’-diaminodicyclohexyl methane as hardener.[102] They compared the viscosity of several samples, at different temperatures. First, by using DSC analysis, they highlighted the evolution of the diffusion process by changing the temperature from 50 to 80 °C, observing the increase of reaction exotherm with the increase of temperature (Figure 6). Then, by comparing the rheological measurements, they observed that at higher temperature, the viscosity of the mixture is initially lower, but increased earlier due to the faster curing (Figure 7). In fact, the higher the temperature, the faster the curing.

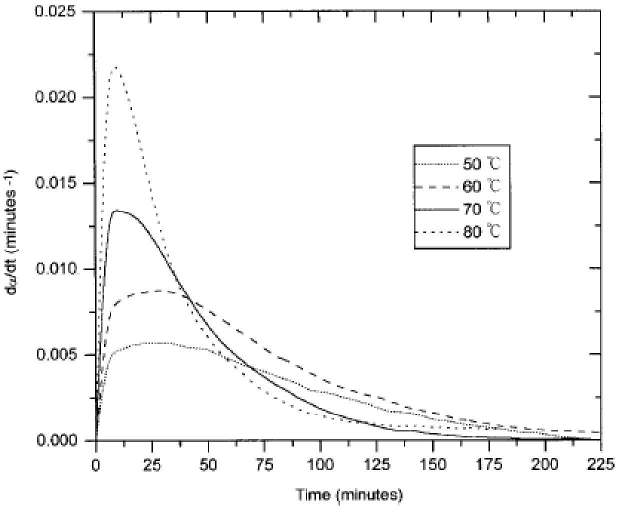


Figure 6: reaction rate in function of time for different curing temperatures.

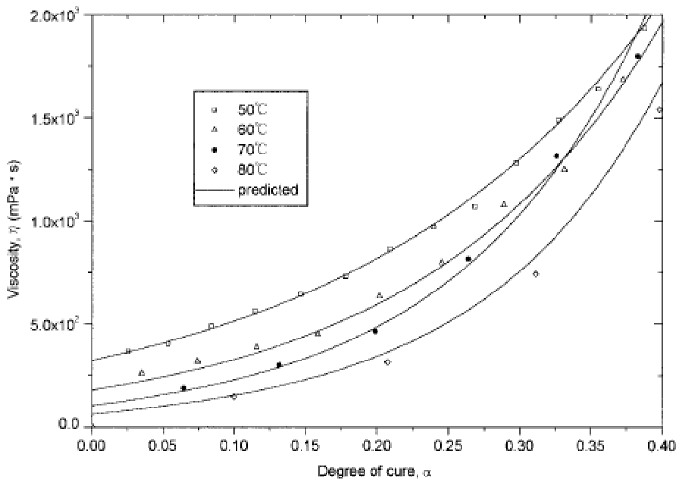


Figure 7: comparison of experimental data with model predictions; viscosity in function of degree cure.

In 2018, Ozgul and Ozkul studied the viscosity of epoxy-diluent-amine sand mortars in function of the selected diluent, and then their properties.[103] They chose three diluents: monofunctional C12-C14 glycidyl ether, difunctional hexane diol diglycidylether and trifunctional trimethylolpropane triglycidylether. They observed that the monofunctional is the most efficient diluent while trifunctional is the less reactive one. However, they could expect these results due to the extender role of monofunctional compound. In fact, the system required more than two average functions to cross-link (*e.g.* classically 2 primary amine and 2 epoxy ring functions), and the higher the number of functional groups, the higher the cross-link density. Thus, first results of this study are logical. They also described that the addition of 5% of the diluent caused a significant reduction of viscosity, while the increase of diluent content further has lower impact on the viscosity.

5.2.3. *Temperature and H bonds*

In the same way, H bonds could interact during the cross-linking process, improving the reactivity at the beginning of reaction, as previously explained (*0. However, several factors can impact* the theoretical ratio, such as the –OH moieties induced by the ring opening reaction, which could react with epoxy, the steric hindrance induced by the curing reaction, the viscosity or the H bond formation, which can prevent the end of the cross-link process. Thus, optimal molar ratio can be determined with the adjustment of equation (5) by multiplying the $m_{hardener}$ by various ratio of amine-epoxy. Then, differential scanning calorimetry (DSC) analysis allows to determine the highest glass temperature transition (T_g) value, corresponding to the optimal ratio.

Epoxy-amine reactivity and H bond influence). Conversely, they might slow down the curing kinetic at the end of reaction because of a stabilization of the system, decreasing the probability of the encounter of the reactive moieties. That is why, it is important to understand the H bond behaviors.

The H bonds have an influence on the IR spectra of monomer containing heteroatom as acceptor of H bonds and some scientists used FTIR analyses to highlight the presence of H bonds.[104–106] Moreover, external factors have also an influence on the H bond shift in IR spectra. For instance, the temperature has a great impact on H bonds, indeed the higher the temperature, the lower the amount of H bonds. Coleman and Moskala studied the effect of the temperature up to 150 °C on the hydroxyl stretching band region of poly(diglycidyl ether of bisphenol A) (poly(DGEBA)) by FTIR (Figure 8).[107] They highlighted that the H bond signal corresponds to a broad band centered at 3 410 cm^{-1} at room temperature, which was gradually shifted towards higher wavenumber values and developed a shoulder at 3 570 cm^{-1} with an increase of the temperature. This shoulder corresponds to free –OH group stretching.

Previously mentioned study of Sangroniz *et al*. also explained the influence of higher temperature on the amount of H bonds, using phenoxy prepolymer as homopolymer of DGEBA, by FTIR analyses.[94] They followed the disappearance of –OH signal with the increase of temperature up to 240 °C (Figure 9). IR spectra allow to observe the presence of free and associated –OH groups. At room temperature, a dominant broad signal is observed around 3 400 cm^{-1}, corresponding to the associated –OH groups, while the slight shoulder at 3 600 cm^{-1} corresponds to the free –OH groups. By increasing the temperature up to 170 °C, the absorbance of the free –OH signal becomes higher than that of the associated –OH, keeping quite intense associated –OH signal. However, if the temperature is increased up to 240 °C, the absorbance of the associated –OH groups is considerably reduced.

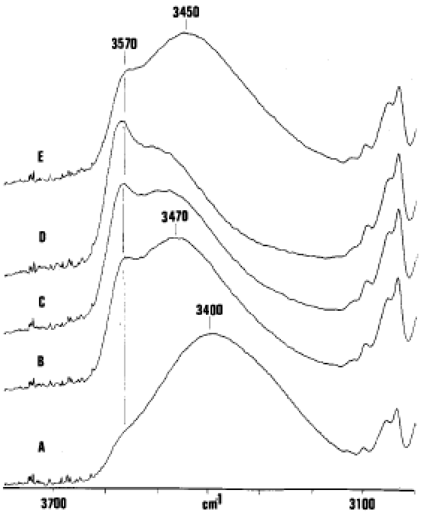


Figure 8: FTIR spectra of poly(DGEBA) from 3 000 to 3 800 cm^{-1} recorded at (A) 35 °C, (B) 100 °C, (C) 120 °C, (D) 150 °C and (E) 35 °C after two days.

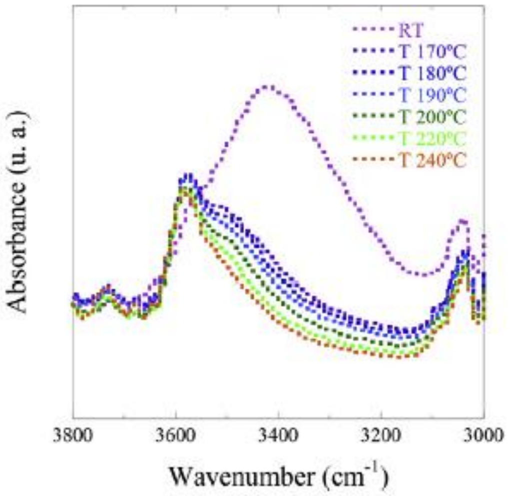


Figure 9: infrared spectra of phenoxy prepolymer at the indicated temperatures zoom in on the –OH stretching vibration.

5.3. Solvent effect

Coating industry requires most often free-solvent formulations in order to reduce volatile organic compound (VOC) emissions. Moreover, solvents interact with epoxy-amine reactants due to H bonds, π-bonds or steric hindrance, and thus could impact the extent of reaction and coating properties. Generally, only few studies in the literature reported the influence of solvent on the epoxy or amine reactants, curing behavior, and material properties. Solvent interactions could be undesirable to the final product, or instead used in order to take advantage of them. For instance, formulations are sometimes additivated with compatible unreactive (*e.g.* xylene, which then evaporates) or reactive solvent (*e.g*. acetone, furfural) in order to decrease the viscosity, to favor reactant homogenization or to change the final coating aspect (shining, smoothing…).[108] On the contrary, undesirable traces of solvent could be found in the formulations, even in the case of free solvent formulations. These solvents could indeed originate from reactant synthesis and purification. Water could also be found due to the hygroscopic character of amine hardeners, thus acting as plasticizer and changing material properties,[109,110] as well as solvent or catalyst entities.[111]

5.3.1. *Interactions with reactants*

Before the reaction occurs, the solvent has an impact on each reactant, which can change its properties or reactivity. Any traces of solvent, originating from the reactant synthesis or water (natural solvent trapped by hygroscopic character of amines) may alter the epoxy-amine reaction.[112] The amount of H bond formation between solvent and reactants changes depending on the solvent (polarity, protic character). Janarthanan and Thyagarajan highlighted the solvent interactions on poly(DGEBA) as epoxy prepolymer, using FTIR analysis.[113] Poly(DGEBA) contains –OH groups as H bond donors, and ether and epoxy as acceptors. Chloroform, benzene, and carbon tetrachloride were used as solvents in different concentrations. They observed that the band shift is not significantly dependent on concentration but depends on the solvent with broad peak centered at 3 460 cm^{-1} in chloroform, at 3 490 cm^{-1} in benzene and at 3 475 cm^{-1} in carbon tetrachloride. These shifts were explained by the formation of H bonds and/or other interactions (such as π-bonds) between solvent and -OH group of the poly(DGEBA). Here, the solvent choice was not ideal due to the chloroform, benzene and carbon tetrachloride natures. Carbon tetrachloride and benzene prevent to form H bonds due to their aprotic character. The use of benzene only allows the highlight of π-bonds. Chloroform can form H bonds with donor sites but the hydrogen electron density is weak. The presence of three chlorine atoms in α-position of hydrogen have indeed an important negative inductive effect. Some protic solvents with higher hydrogen electron density would be selected as H bond donors, such as water or alcohol. Some aprotic solvents, such as dimethylformamide and dimethyl sulfoxide could be chosen to study the influence of H bond acceptors.

5.3.2. *Interactions during the reaction*

The selected solvent can influence the epoxy-amine reaction by the formation of H bonds with reactants. Shechter *et al.* compared the reaction of diethylamine with phenyl glycidyl ether in free solvent conditions to concentrated solutions.[114] They showed that benzene and acetone slowed similarly the reaction, while isopropanol and water accelerated the ring opening reaction due to the H bond formation. So far, this old article is one of the few studies allowing to prove the influence of solvent on the epoxy-amine reaction. Then, Smith reported that the cross-linking of epoxy-amine systems can also be accelerated by entities having H bond donor groups or retarded by molecules able to act as hydrogen-bond acceptors.[33] Hong *et al*. studied accurately the influence of the presence of solvent on the curing behaviors, using DGEBA as prepolymer and dicyandiamide as curing agent in presence of 2-methylimidazole as accelerator.[99] They selected toluene as aprotic and apolar solvent (π-bonds effect), THF as aprotic and slightly polar solvent (H bond acceptor) and acetone as aprotic and polar solvent (H bond acceptor). Proportionally to their boiling point, induced by their volatility and polarity, the curing enthalpy decreased as function of selected solvent (toluene > THF > acetone). They explained that heat absorbed during the solvent evaporation consumed the curing enthalpy and influenced the temperature dependent curing mechanisms, inducing an increase of the curing rate time. By comparing the reaction heats obtained from formulations containing solvents to free solvent formulations, they concluded that the solvent evaporation effect corresponded to the decrease of the curing temperature by more than 10 °C.

More recently, Ehlers *et al.* studied the mechanism of epoxy-amine curing reaction with benzene (aprotic and nonpolar), THF (aprotic and slightly polar) or methanol (protic and polar) as solvent, using density functional theory methods.[69] They observed that alcohol dominates the kinetics of the overall reaction over the autocatalytic reaction by β-hydroxylamine species formed during the ring opening reaction.

5.3.3. *Indirect solvent effect on material properties*

In 2014, Jang *et al*. performed a molecular simulation study of the cross-linking network rearrangement of a stoichiometric epoxy-amine mixture (DGEBA as epoxy and polyetheramine Jeffamine T400 as curing agent), with a varied amount of solvent (dichloromethane), as inert solvent.[115] Results suggested that solvent medium changes the network topology, without modifying cross-linking density, glass transition temperature or Young's modulus value. These results indicated that unreactive solvent addition or traces of solvents have no impact on the material properties. However, Jang *et al*. considered an ideal system with a fully cross-linking yield, without unreacted epoxy or amine moieties and without any trace of solvent after drying. However, experimentally, these results would be difficult to obtain because of the solvent medium, which prevent a fully cross-linking yield. Moreover, in the case of fully cross-linking system, some solvent entities would be trapped in the network because of the high cross-linking density of epoxy-amine networks. In order to prevent the influence of residual solvent, reactive solvent could be used.

Zhang *et al*. experimentally described the use of reactive carbonyl solvent in epoxy-amine formulations for concrete in order to reduce viscosity of the system.[108] They obtained epoxy coatings exhibiting great wettability and permeability and they described the increase of concrete strength, due to the incorporation of carbonyl solvent. Conversely, Yi *et al*. recently performed a complete study concerning the negative influence of added solvent on the properties of epoxy-amine thermosets.[116] They described that the presence of solvent decreases the curing degree, affecting the cross-linked structure and its properties. In this study, the higher the solvent content added to uncured system, the higher the number of uncured epoxy groups at the end of the curing. Thus, the lower the tensile strength, the higher the flexibility and the T_g. Moreover, in this case, the addition of solvent decreased the adhesive strength, even leading to an adhesive failure of the system. This study allowed to conclude that the use of 3 to 13% of xylene as aprotic and apolar solvent particularly reduced the thermoset properties. Loos *et al*. had already found similar results with the presence of residual acetone solvent in epoxy-amine system, leading to altered cross-linking reaction and changing its thermo-mechanical properties, such as the Young modulus and the thermal degradation.[117]

5.4. Amine blush, also named carbonation

A regular problem with epoxy-amine formulation is the « amine blush » effect observed during the cross-linking reaction and favored by a long gel time. In other words, the « amine blush » is the carbonation reaction between amine functions with water and CO_2 of air atmosphere, leading to unreactive carbamate and ammonium ions (Figure 10).[118] Due to the H bond formation and thus the hygroscopic character of amines, water molecules are absorbed by the epoxy-amine system during cross-linking reaction. Then, the reaction with CO_2 induces the carbonation. In this case, sticky film appears on the surface of the cured epoxy material, stopping the curing degree and decreasing the adhesion properties. Blain *et al*. performed a clarification about the carbonation in epoxy-amine system.[119] They explained that there are several methods to prevent carbonation, such as the use of inert atmosphere, the use of catalyst in order to reduce the reaction gel time and the use of amine adduct to reduce the H bond formation with CO_2 and water of air. Finally, they highlighted that the carbonation reaction is reversible at 90 °C.

$$\mathrm{R\text{-}NH_2 + CO_2} \xrightarrow{\mathrm{H_2O}} \longrightarrow \mathrm{R\text{-}NHCOO^- + NH_3^+}$$

Figure 10: reaction of amine carbonation

Thus, looking at the different points discussed in this article, to perform the curing reaction with a temperature of at least 90 °C could be the solution to simultaneously prevent carbonation, reduce the gel time of the reaction and decrease the H bond formation.

5.5. Conclusion

This part allowed to highlight various parameters which influence the epoxy-amine cure degree and/or the material properties through H bonds (Figure 11). In some cases, H bonds favor the unwanted interactions. For instance, the literature allows to assume that entities trapped in the epoxy-amine cross-linking system could have a great impact on the epoxy-amine mechanism, preventing the end of cross-linking reaction, and even solvent traces could have an influence on the reaction curing or on the material properties. However, only a few studies reported the influence of H bonds on the material properties. Sometimes even no relationship with H bond is mentioned, as shown by the example of solvent presence in final material without any characterization of H bond presence. In the other hand, some studies showed that H bonds could be used in a beneficial way to improve epoxy-amine system during the reaction. Hence, the following part focuses on the H bond observation in cross-linked materials and their impacts on the properties.

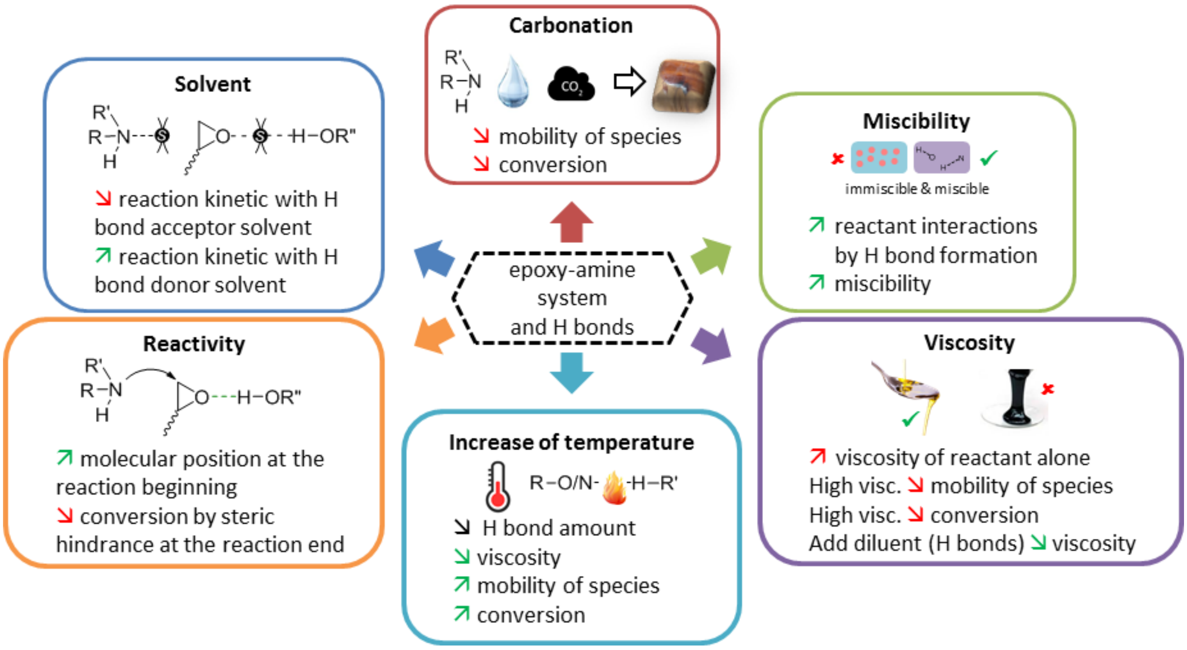


Figure 11: global scheme of H bond influence in epoxy-amine system

6. Observation and influence of H bonds in epoxy-amine materials

Polymers are usually described by their structural, thermo-mechanic and physico-chemical properties. Many studies concern the epoxy-amine thermoset properties,[120–123] but only a few mentioned H bonds and their influence on the mechanical properties and material curing behavior. That is why, this literature data clarification focuses on the H bond observation in epoxy-amine system and their influence.

6.1. Observation of hydrogen bonds in the final materials

The hydrogen bonds formed into the final material are classically observed by FTIR analyses and spectrum aspect depends on the structure of the final materials and the analysis temperature. As in the case of molecules and prepolymers (*5.2.3 Temperature and H bonds*), there is a difference between free –OH functions, inter and intramolecular H bonds in a cured system. Moreover, FTIR analysis aspect depends on the temperature. Williams and Delatycki indeed observed in 1970 that absorption frequency of –OH group present in epoxy-amine materials showed a temperature dependence with the shift to higher wavenumber with the temperature increase.[124] They used DGEBA as epoxy and C2 to C12 aliphatic α,ω-diamines as curing agents. They explained that –OH band moved of 40 to 55 cm^{-1} to higher wavenumber with the increase of the temperature from 50 to 150 °C.

Then, Lee and Jang described this effect in 1997 with the study of FTIR analyses of ester-epoxy-amine system (Figure 12), focusing on the study of the carbonyl and hydroxyl zones.[125] The first observation is that the amount of H bonds increased with the curing time and the content of curing agent. They differentiated two type of intermolecular H bonds present in the material (Figure 13). The first type corresponds to H bonds formed between –OH group and amine function, corresponding to the peak at 3 400 cm^{-1}, and the H bonds formed between two –OH groups, which corresponds to the peak at 3 490 cm^{-1}. The shifting to higher values of the peak wavenumber could be explained by the higher electronegativity of oxygen atom compared to nitrogen atom, which induces the decrease of the bond length. Curiously, Lee and Jand assumed that the higher wavenumber is explained by the lower bond dissociation energy of the OH---O hydrogen bond compared to OH---N one (lower than 2 kcal.mol^{-1}). However, it seems that they compared water-water interaction (5.0 kcal.mol^{-1}) with water-ammonia one (6.9 kcal.mol^{-1}),[126] which are not influenced by inductive effect induced by substituents. Thus, in the case of secondary or tertiary amines, the electronegativity decreases by inductive effect, which seems to be more a relevant explanation. Moreover, the Cambridge Structural database shows that C-OH---O and NH---O hydrogen bond lengths are respectively equal to 2.00 and 2.29 Å, indicating a weaker NH---O hydrogen bond.[127]

Lee and Jang also highlighted the intramolecular H bonds between two –OH groups, appearing as a shoulder at 3 550 cm^{-1}. They explained that the amount of the intramolecular H bonds is directly proportional to the amount of tertiary amine during the curing reaction. Lastly, they identified free –OH group at 3 650 cm^{-1}.

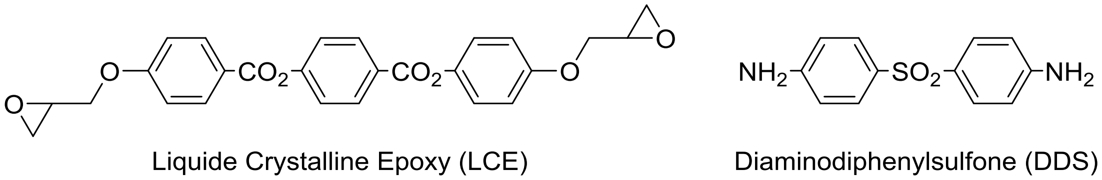


Figure 12: chemical structures of reagents using in the Lee and Jang study.

They also studied the influence of H bonds in IR spectra by following the shift of the carbonyl peak of ester moiety: free carbonyl peak is found at 1 732 cm^{-1}, carbonyl-amine peak H bonds is at 1 720 cm^{-1} and carbonyl-hydroxyl H bond peak is at 1 712 cm^{-1}.

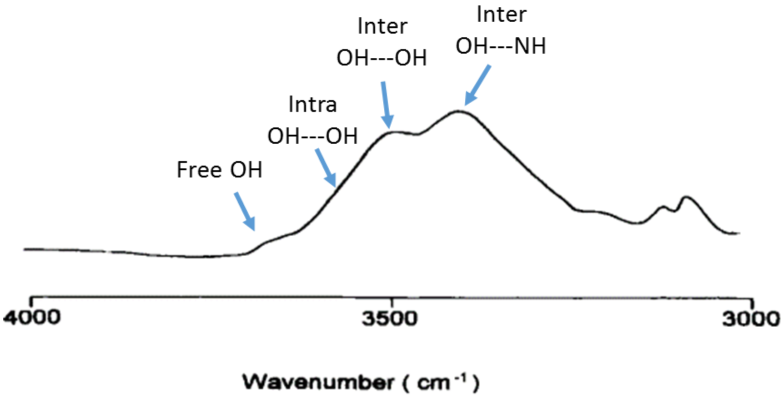


Figure 13: IR absorption spectrum of hydroxyl region of cured epoxy-amine system.

During the same period, Dyakonov *et al.* performed a complex study on epoxy-amine system and its corresponding models. In this view, they used X-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy in order to study H bonds in epoxy-amine thermosets.[128] By using X-ray crystallography, they showed that the di-β-hydroxyl tertiary amine is able to form intramolecular H bond with –OH group present in the network.

They explained that the spatial arrangement is important for the H bond formation. Then, they confirmed by NMR that the β-hydroxyl secondary amine is also able to form intramolecular H bonds. They explained that H bonds change the cross-linking density of epoxy systems, influencing the cure kinetics.

6.2. Influence of hydrogen bonds on physico-chemistry properties

The chemical composition of materials influences their final properties because of the proportion of free volume or the reacted or unreacted functions present in the networks.[129] For instance, Wang *et al*. recently studied the effect of the epoxy-amine ratio change on the material properties.[130] They explained that the increase of stoichiometric ratio (defined as the ratio of -N*H* active functions to the number of epoxy groups) induces the trapping of free amine entities in the network, which could further restrain the mobility chain at low temperature (-180 °C) due to the H bond formation between hydroxyl and residual amine groups. The presence of these strong H bonds impacts the elongation at break and the toughness of the material.

Thermo-mechanical properties are determined by various parameters, such as Young modulus or thermal transition temperature that depend on the material and network deformations. The deformation corresponds to the response of intra and intermolecular movements of polymer chains at the microscopic scale and to the response of the global material structure at the macroscopic scale.[131] For instance, a traction force on the bulk material allows to repulse atoms each other, while strength bonds oppose it (microscopic scale). Thus, the final slight movement of bonds between atoms allows to cause macroscopic deformations.

Recently, some publications discussed the impact of H bonds on the thermo-mechanical properties of epoxy thermosets. For instance, Hu *et al*. studied in 2014 the formation of H bonds between the oxygen atoms of furan rings and the –OH groups in epoxy-amine thermoset. They used a system composed from DGEBA as epoxy prepolymer and 2,5-bis[(2-oxiranylmethoxy)-methyl]-furan (BOF) as furan-based hardener and 2,5-bis[(2-oxiranylmethoxy)methyl]-benzene (BOB) as aromatic-based reference (Figure 14).[132] A higher T_α (gap of 8 °C, determined by DMA, Figure 15) was observed by changing the aromatic moiety by the furan ring. They supposed that this difference was induced by the hindered rotation of the furan ring and the H bond formation possibility between the oxygen atoms of the furan rings and -OH groups present in the epoxy-amine network.

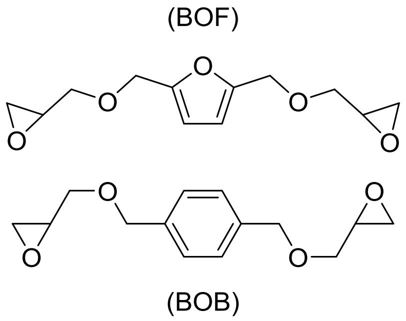


Figure 14: chemical structures of hardeners used by Hu *et al.*

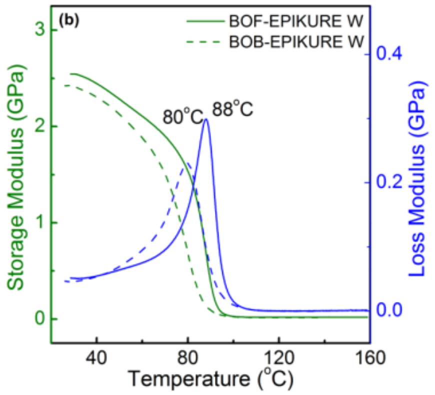


Figure 15: DMA thermograms of BOF- and BOB-based materials, cured with

DGEBA (EPIKURE W).

In 2018, Ramsdale-Capper and Foreman explained that the little-known omega transition, which is a barely or no discernible transition present in the temperature range of 30 to 150 °C, is also influenced by the network structure because of the combined effect of phenylene ring rotation and H bond formation between hydroxyl propyl ether groups.[133] They compared four networks from triglycidyl *p*- or *m*-aminophenol (TGPAP and TGMAP) as epoxy and *para* or *meta* diaminodiphenylsulphone (4,4'-DDS and 3,3'-DDS) as curing agents (Figure 16). In the case of triglycidyl *meta* substituted aminophenol, no discernible transition was observed by DMA, because of the restricted phenylene ring rotation compared to *para* substituted equivalent (Figure 17). Then, the use of *meta* substituted curing agent with triglycidyl *p*-aminophenol as epoxy allowed to increase the intensity of the omega transition, indicating more H bond formation in this case.

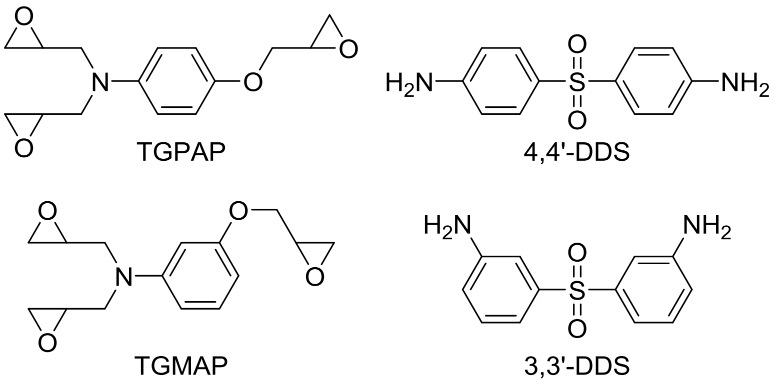


Figure 16: chemical structures of epoxy and amine reactants used in the study of Ramsdale-Capper and Foreman.

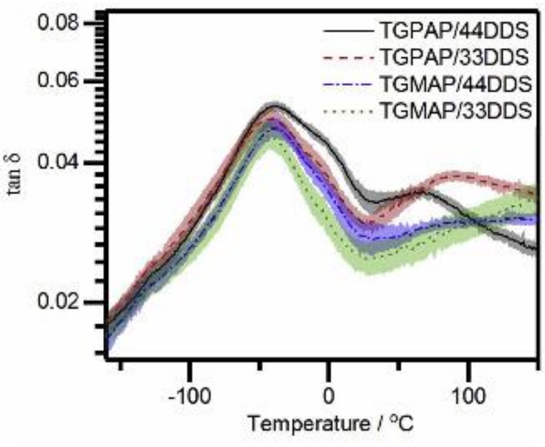


Figure 17: β- (left) and ω- (right) transition of the four studied materials.

In the same way, Hernandez *et al*. compared two epoxy-amine thermosets from DGEVA or DGEGD as epoxy prepolymers (Figure 18).[134] Using DMA analyses (Figure 19), they observed that the methoxy moiety increased the flexibility (T_g) at the microscopic scale due to their spacer role, which induced the repulsion of the polymeric chains for each other. In the other hand, they observed a higher storage modulus *E'*, indicating a lower macroscopic deformation. This could be explained by the H bond formation ability of methoxy function with –OH groups,[135] allowing to increase the mechanical strength.

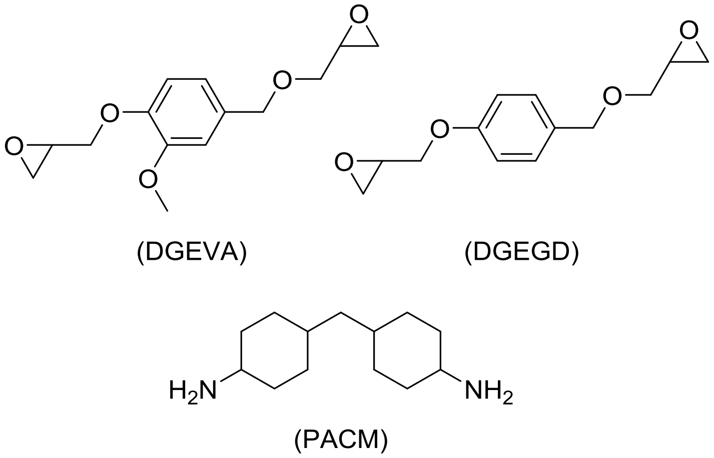


Figure 18: chemical structures of reactants used by Hernandez *et al.*

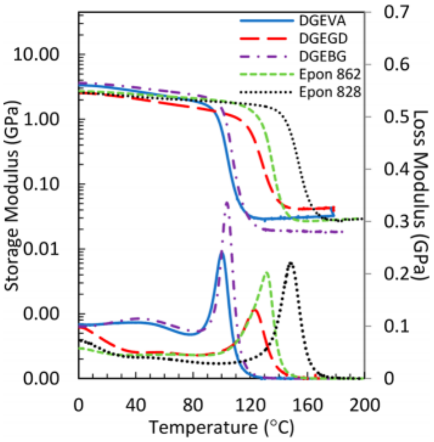


Figure 19: DMA thermograms of epoxy materials cured with PACM as hardener.

Finally, Lefebvre *et al*. reported that H bonds have an influence on the thermoset adhesion through hygroscopic effect.[136] They observed that high relative humidity value tended to decrease the adhesion because of the formation of H bonds between –OH groups of the epoxy thermoset and the water present in the atmosphere. The H bonds of the epoxy-amine network were displaced by water-mediated "bridges" between polar groups, and thus formed ring structures, which decreased the adhesion to the substrate.

6.3. Conclusion

In the literature, the observation of H bonds and their influence in epoxy-amine system are only reported in a handful of studies and poorly described, in spite of their great role on the thermosets cure and properties. H bonds can influence micro and macroscopic deformations in the epoxy-amine thermosets with temperature dependence. In fact, H bonds depend on temperature and steric hindrance and the higher the H bond amount, the lower the deformations. Thus, some parameters are directly impacted as T_g, Young modulus, adhesion and elasticity properties. The interest of the H bond impact study could be really important for industrial field to understand and control the H bond formation in order to change the epoxy-amine system properties.

7. General conclusion

Despite the large range of applications of epoxy-amine systems, only a few industrial hardeners are available and are often a mixture of several amines and adducts in unknown proportions, with different reactivity. Moreover, only a few information are available concerning the reactivity induced by the amine structures and their functionalization. In addition, to change the reactivity of amine with functionalization or adduction can also drastically change the physical state and the viscosity of hardeners. To finish, the presence of H bond acceptor or donor sites in the reactant structures impacts widely the reactant properties and reactivity, the curing reaction and the material properties. Since the number of epoxy monomers is also very limited, the amines have the main influence on the creation of H bonds in epoxy-amine systems, owing to these structures and functionalities.

Therefore, the choice of amine reactants is of crucial importance. That is why we established an amine reactivity scale clarification and described the observation and influence of H bonds in epoxy-system curing through a state of the art of literature. This article highlighted a lack of knowledge concerning essentially the H bond influence on the curing reaction and material properties. Many works remain to be done to study the influence of H bonds in the epoxy-amine system, such as the comparison of the influence of different functions incorporated in the system towards H bond amount, the study of the H bond increase on the material deformation and adhesion.

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