

Effect of ZnO nanoparticles on the thermal stability of a T-DDM benzoxazine resin

Dissertation presented by
Carl VAN TIEGHEM DE TEN BERGHE

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Supervisor
Christian BAILLY

Readers
Bonnaud LEILA, Delcorte ARNAUD, Horion JÉRÉMY

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Abstract

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by Carl VAN TIEGHEM DE TEN BERGHE

In this work, nanocomposites with a high thermal stability were developed using T-DDM, a benzoxazine resin based on 4,4'-diaminodiphenylmethane (DDM) and Tyrosol, and zinc oxide nanoparticles.

The neat T-DDM resin was investigated for its curing kinetics and its cure cycle was improved. Data from DSC experiments allowed to determine an activation energy of 90 kJ/mol and an overall order of reaction in the range of 2.2 to 2.5 for the autocatalytic curing reaction. A cure cycle was devised based on the criteria of a complete cure and a minimal cycle time. The resulting cycle is composed of three steps: (i) 60 minutes at 165°C, (ii) 90 minutes at 200°C, and (iii) 30 minutes at 220°C to achieve a complete cure. While this cycle worked well in DSC, it should be improved for curing of larger samples in a furnace.

Nanocomposite blends were produced at various concentrations of ZnO and with different sonication times. The dispersion of the nanoparticles within the blends was evaluated with SEM and TEM. Blends up to 5wt% ZnO were found to have an adequate dispersion for 90 seconds of sonication. In blends at 10wt% ZnO sonicated for 90 seconds, the particles formed some large aggregates. DSC experiments showed a synergic increase of the heat of reaction due to the addition of the nanoparticles with a maximum at 17wt% ZnO, associated with an increase of the expected value by 16%. TGA measurements showed an improved thermal stability for the blends compared to the neat T-DDM resin. A significant raise of the degradation temperatures was observed for only a small fraction of ZnO nanoparticles in the blends. Moreover, a synergy was observed for the char yield. At 11wt% ZnO, 27% of char yield is added, due to the ZnO and the synergy, to the char yield of the neat resin. Finally, the interactions between the T-DDM resin and ZnO were studied by FTIR. In cured nanocomposites a peak at 1678 cm^{-1} was observed and attributed to hydroxyl groups, originating from a condensation reaction in T-DDM, chemisorpted on the ZnO nanoparticles.

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Lists of Abbreviations and Symbols

Abbreviations

BA-a	Benzoxazine based on B isphenol- A and a niline
BA-m	Benzoxazine based on B isphenol- A and m ethylamine
BS-ZnO	Benzoxazine terminated silane functionalized ZnO
CRM	Certified Reference Materials
DDM	4,4'- d iaminodiphenyl m ethane
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared spectroscopy
IR	Infrared radiation
IUPAC	International Union of Pure and Applied Chemistry
MTDSC	Modulated Temperature Differential Scanning Calorimetry
NA	Numerical Aperture
P-DDM	Benzoxazine based on p henol and DDM
PAEK	Poly(a rylether k etone)
PBZ	Poly b enzoxazine
pHBA	p ara- h ydroxy b enzyl alcohol
pHBA-DDM	Benzoxazine based on pHBA and DDM
pPDA	p ara- p henylene d iamine
ROP	Ring Opening Polymerization
SEM	Scanning Electron Microscopy
T-DDM	Benzoxazine based on tyrosol and DDM
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
UV	Ultraviolet radiation
ZnO	Zinc oxide

Symbols

C_p	specific heat capacity	$[Jg^{-1}K^{-1}]$
CY	char yield	$[\%]$
E_a	activation energy	$[Jmol^{-1}]$
h	Planck constant, $6.62607 \cdot 10^{-34}$	$[m^2kgs^{-1}]$
H_r	heat of reaction	$[Jg^{-1}]$
H_r^{iso}	isothermal heat of reaction	$[Jg^{-1}]$
H_r^{max}	heat of reaction for complete conversion	$[Jg^{-1}]$
H_r^{res}	residual heat of reaction	$[Jg^{-1}]$
H_r^{tot}	total heat of reaction ($H_r^{iso} + H_r^{iso}$)	$[Jg^{-1}]$
H_{res}	residual heat of reaction	$[Jg^{-1}]$
k	kinetic rate constant	$[s^{-1}]$
m_0	mass of an electron, $9.109 \cdot 10^{-31}$	$[kg]$
R	ideal gas constant, 8.3145	$[Jmol^{-1}K^{-1}]$
t_{cure}	cure time	$[s]$
T_c	cure temperature	$[^{\circ}C]$
T_{c0}	critical reaction temperature	$[^{\circ}C]$
T_{cure}	isothermal cure temperature	$[^{\circ}C]$
T_d	degradation temperature	$[^{\circ}C]$
T_g	glass transition temperature	$[^{\circ}C]$
T_p	peak temperature	$[^{\circ}C]$
X_{ZnO}	weight fraction of ZnO nanoparticles	$[-]$
α	conversion	$[\%]$
$(d\alpha/dt)$	reaction rate	$[s^{-1}]$
β	heating rate	$[^{\circ}Cmin^{-1}]$
λ_e	wavelength of electrons	$[m]$
T_{β}	β -transition temperature	$[^{\circ}C]$

Introduction

General introduction

This master thesis was written in the context of Jérémy Horion's doctoral thesis, which is on turn part of the Flycoat project, a project subsidized by the Walloon region. The aim of this project is to develop bio-sourced nano-reinforced resins to serve as coatings on aluminum surfaces.

Aluminum alloys are widely used in aerospace applications due to their improved mechanical properties compared to pure aluminum. Nevertheless, these alloys are strongly sensitive to localized corrosion and, therefore, need to be protected [1]. Different kind of coatings have been developed to enhance their corrosion resistance, but these coatings often contain chromate. While having excellent anti-corrosive properties, chromate exhibits high levels of bio-toxicity and will, therefore, be banned from use in the aeronautic sector in 2017 [2].

In this context of increasingly strict regulations in the field of aerospace applications, the most commonly used resins also fail to meet the requirements in terms of properties. For example, epoxies have been used as organic coatings to prevent corrosion in aircrafts, but they suffer from major drawbacks such as water uptake or limited thermal stability. Furthermore, the release of by-products during polymerization and the use of acid and base as catalysts makes them unattractive [2].

This led to an increased focus on polybenzoxazines because they have highly attractive properties such as high glass transition temperatures, low absorption of water, near zero shrinkage, and good dielectric properties. Moreover, they show an increased thermal stability due to high char formation. Benzoxazine monomers are synthesized by the reaction of three basic compounds: a phenol, an amine, and formaldehyde. Based upon a careful selection of these compounds a large panel of properties can be obtained with several types of benzoxazines. For instance, in T-DDM, the DDM moiety is trapped between two benzoxazine rings, thus, limiting its cleavage during the cross-linking and the drawback of outgassing.

The benzoxazine precursors Flycoat develops are bio-sourced, and thus renewable. Moreover, the properties of these precursors and their resulting polymers are improved by the creation of composites with carefully selected nano-reinforcing particles dispersed within the polymer matrix. The unique properties of the materials developed within the Flycoat program include resistance to wear, anti-corrosion protection, anti-static properties, and improved resistance to thermo-oxidation and thermal cycling [3].

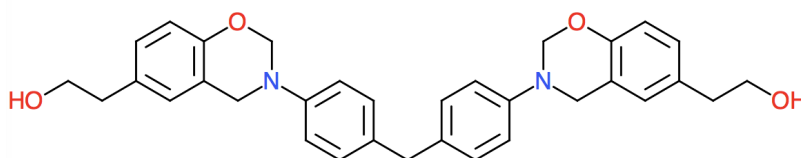
Aim of this work

Based on the general context provided in the first part of this introduction, multiple objectives were set for this master thesis. The main objective was to study the effect of the inclusion of zinc oxide nanoparticles into the benzoxazine matrix on the thermal stability of the resulting composite. However, as the benzoxazine resin in question, namely T-DDM (figure below), was recently developed, a first part of this work consisted in studying the cure kinetics of this resin and to optimize its cure cycle. Only then, the effect of ZnO nanoparticles was studied. The choice of ZnO nanoparticles resulted from a previous study by A. Raynaud [4], where it was found that ZnO did not only improve the UV resistance of a benzoxazine resin, but also its thermal stability.

The first part of this dissertation provides the theoretical background for the parts that follow. In this first chapter, a closer look is taken at the benzoxazine resins and their properties, with a focus on the ones based on DDM. Then, the curing of thermosetting resins is discussed both on basis of their kinetics as of the cure cycle. A third chapter presents zinc oxide nanoparticles and their uses in benzoxazines. Finally, the different techniques for analysis are discussed.

In the second part of this work, the materials used for the experiments are presented. Their origin and composition, as well as their blending into nanocomposite blends are detailed. Then, the different methods applied on these materials and blends are presented for each technique.

The third and final part of this master thesis is dedicated to the results of the multiple experiments. These results are presented and discussed in four distinct chapters. The first one briefly presents results on the neat T-DDM resin and on ZnO nanoparticles. The second one considers the curing kinetics of the neat T-DDM resin. The third one aims to optimize the cure cycle of the resin both for the pure resin as for blends with ZnO. Finally, the fourth, and most important one, discusses the improved thermal stability of nanocomposite blends composed of T-DDM and ZnO nanoparticles. This analysis is conducted with SEM and TEM, to study the dispersion of the particles into the nanocomposite blends; with DSC and TGA, to study the thermal properties of the blends; and with FTIR, to explain the interactions at the origin of the thermal properties for the T-DDM–ZnO blends.



Structure of the T-DDM benzoxazine monomer.

Part I

Theoretical background

Chapter 1

Benzoxazines

This first chapter focuses on benzoxazine resins; and more in detail on T-DDM, the benzoxazine resin used in the experimental part of this work. Therefore, this chapter will begin with a general overview of benzoxazine resins and their properties. Then, a greater emphasis will be placed on T-DDM and strongly resembling resins.

1.1 Benzoxazine resins

The name "benzoxazine" stems from a specific structure which can be found in the uncured monomer of the resin. This benzoxazine structure is composed of an oxazine ring, a heterocyclic six-membered ring with an oxygen and a nitrogen atom, coupled to a benzene ring [5]. Depending on the position of the heteroatoms within the oxazine ring, different benzoxazine structures can be obtained.

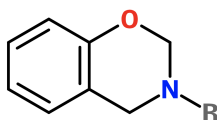


FIGURE 1.1: Monofunctional benzoxazine monomer (1,3-benzoxazine).

The position of the oxygen and nitrogen atom determines the name of the resulting benzoxazine. For example, the benzoxazine monomer presented in Figure 1.1 is a 1,3-benzoxazine, where the first number refers to the position of the oxygen atom and the second to the nitrogen atom. The naming of benzoxazines according to the IUPAC notation is very impractical for routine use. Therefore, the names of benzoxazines are often abbreviated following a certain convention that is based on the components of a benzoxazine. These components will be presented later in Subsection 1.1.2 on benzoxazine chemistry. The abbreviated phenolic component is referred to by a capital letter while a lower-case letter is used for the amine component and both are connected with a hyphen. The name of the aldehyde used in the synthesis is often omitted as formaldehyde is used in most cases. For example, a common commercial benzoxazine derived from bisphenol-A and aniline is noted as BA-a for the monomeric compound and as poly(BA-a) once polymerized [5]. Even this simplified notation is often not sufficient to differentiate benzoxazines due to their huge flexibility in molecular design. Thus, specific abbreviations are given for benzoxazines by researchers in their work. For instance, T-DDM refers to a bifunctional benzoxazine based on 4,4'-diaminodiphenylmethane (DDM), 4-(2-hydroxyethyl)phenol or

tyrosol (T) and formaldehyde; which yields the name T-DDM.

The first small molecular weight benzoxazine resins were developed a little over 70 years ago by Holy and Cope [6]. These small molecular weight molecules were extensively studied by Burke et al. in the 1950s and 1960s. A few years later, Schreiber, Higginbottom and Riess studied oligomer formation and polymer development of benzoxazine monomers, but they did not report on polybenzoxazine properties [5]. In 1994, Ning and Ishida were the first to publish a paper on the synthesis and properties of cross-linked polybenzoxazines [7]. Since then, through the contributions of many researchers, the properties, the chemistry and reaction kinetics of benzoxazines have been extensively studied and are now better known. Moreover, within those resins, new materials were developed based on bi- and multifunctional benzoxazine monomers.

Over the years, the applications of benzoxazines also expanded. Initially, they were considered as attractive candidates to replace traditional phenolic resins, such as phenolics, epoxies and bismaleimides; which are obtained through condensation polymerization. The reason why they were considered as a replacement is because their polymerization mechanism, ring-opening polymerization or ROP, overcomes almost all the shortcomings of condensation polymerization, more specifically ROP avoids the formation of by-products. Nowadays, benzoxazines are not only considered as a good replacement for condensation chemistry phenolic resins, but as a whole class of materials which goes much farther than those traditional resins. Benzoxazine resins display a wide range of mechanical and physical properties that can be adapted for various applications and needs. Thus, reflecting a rich flexibility in molecular design [5].

Benzoxazines exhibit good thermal, chemical, electrical, mechanical and physical properties, which makes these resins suitable alternatives for existing applications. Additionally, they show a near-zero shrinkage, a very high char yield and a fast development of the mechanical properties during curing. Also, they can have glass transitions occurring at temperatures much higher than the curing temperature, exhibit excellent electrical properties and, despite having many hydrophilic groups, show a low water uptake [5].

1.1.1 Thermosetting resins

The polybenzoxazines obtained from multifunctional benzoxazine monomers exhibit a cross-linked structure. This cross-linked macromolecular structure is typical for thermosetting resins. According to the IUPAC Compendium of Chemical Terminology, thermosetting polymers or resins are defined as polymers which change from a prepolymer, in a soft solid or viscous state, irreversibly to an infusible, insoluble polymer network by curing. The curing, also referred to as cross-linking or reticulation, is induced by the action of heat, suitable radiation, or both. The term thermoset refers to a cured thermosetting polymer [8].

The first thermoset was discovered by Goodyear in 1839 through the vulcanization of natural rubber. However, the first synthetic thermoset was produced in 1909 by Baekeland. His product, Bakelite, was a phenolic based thermoset [9].

The thermosets can be categorized in three groups, which are presented in Table 1.1 with some examples. These groups are general purpose, engineering, and specialty thermosets. The first category having average properties, the second one higher

properties and the final category one of more highly specific or unusual properties. The benzoxazines, depending on their structure, can be placed within the categories of engineering thermosets for the most basic ones, and specialty thermosets for more advanced benzoxazines.

TABLE 1.1: Classification of thermosets [9].

Category	Examples
General purpose	Phenolics, polyesters
Engineering	Epoxy, polyurethane
Specialty	Polyimides, cross-linked thermoplastics

Cross-linking and curing

Figure 1.2 illustrates several types of polymer configurations schematically. Linear polymers, on the left, form long continuous chains of C – C bonds with the two other valence bonds primarily attached to hydrogen or another hydrocarbon moiety. Network polymers, on the right, are the result of build-up from prepolymer thermosetting materials or chemical interactions between linear polymers. The process of interaction, which forms the network, is called cross-linking and is the main element defining thermosets.

The name thermoset implies, from the first part of the name, that the cross-linking proceeds under the influence of heat, although, this factor is not always required for curing. The second part refers to the irreversible character of the formation of the network.

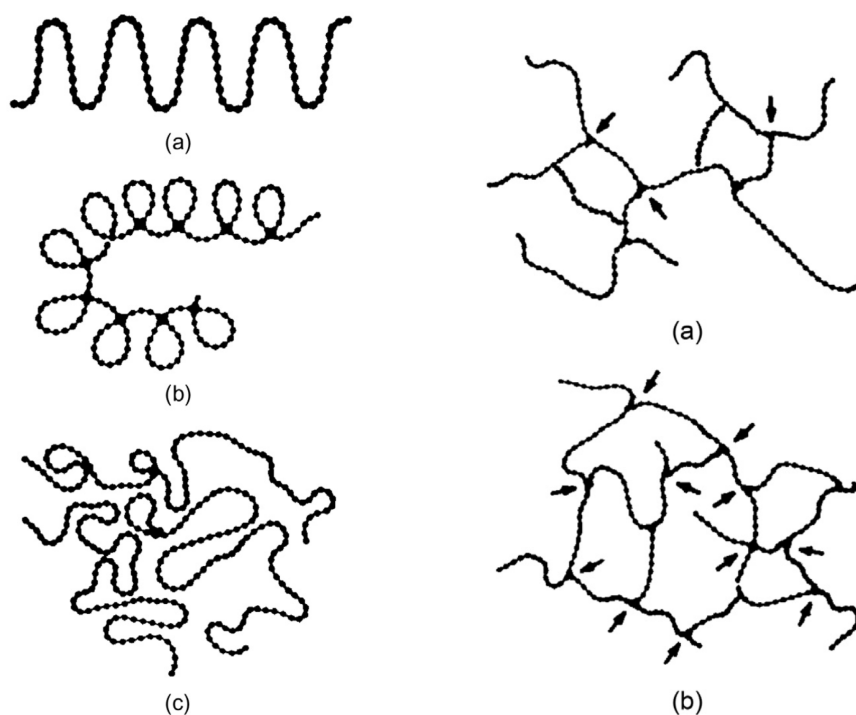


FIGURE 1.2: Simplified representation of several polymers. *Left:* linear polymer configurations. *Right:* (a) lightly and (b) highly cross-linked network polymer [9].

The curing reaction occurs via a cure cycle, which is a well-established sequence of time, temperature and pressure required to produce the thermoset according to the desired specifications. This cure schedule is derived by plotting the change in the materials properties of interest with respect to the time, temperature and pressure. In practice, the cure time is often set to the level where a specified fraction of the ultimate properties is reached. This is done because the evolution of the properties is in most cases logarithmic and a much longer time is needed to reach the value of the ultimate property. This logarithmic evolution stems from the cure behavior of the thermosetting polymers, which is similar for all of them. Upon heating the viscosity drops and passes through a region of maximal fluidity. Then, once the polymerization starts, the viscosity increases again as the length and the degree of cross-linking of the oligomers in the resin raises. Once a tri-dimensional network is created, the gelation stage is reached. Then, to achieve the desired qualities of the resin, it is often required to increase the process temperature to reach the vitrification of the resin. Finally, once vitrification is reached, even more time is needed to increase the curing degree as the evolution beyond vitrification is very slow and diffusion controlled. Therefore, at higher conversion, the evolution of the properties is bound to a very slow increase. If several properties are of interest, the cure schedule must try to reflect an optimized combination of these properties [9].

Properties

The properties of a thermoset depend on a large variety of factors. The cross-link density, however, is a critical parameter in the determination of these properties; especially for the mechanical properties.

This cross-link density is defined as the number of effective cross-links per unit volume of the thermoset, in inverse relation to the molecular weight between cross-links [9]. This parameter is affected by the number of functional sites on the monomers, the chain length between two cross-links, the actual number of functional sites that react, and the chain mobility between cross-links. A low cross-link density leads to a looser network, where more chain mobility is possible. Therefore, in general, a thermoset with a low cross-link density is more flexible, has better impact strength, and higher elongation. A thermoset with a high density is harder, but also more brittle [9].

Table 1.2 lists and compares the properties of four types of thermosetting polymers, where PBZ refers to polybenzoxazines. When comparing the properties of traditional resins, such as epoxy and phenolics, with polybenzoxazines, it can be confirmed that this class of thermosetting resins can be used to replace these traditional resins. Moreover, benzoxazines possess several unique properties that will be discussed in Subsection 1.1.5, some of which are already mentioned in the table.

1.1.2 Benzoxazine chemistry

Figure 1.3 illustrates the basic chemistry of benzoxazines: monofunctional benzoxazine monomer are synthesized from a phenolic derivative, an aldehyde (usually formaldehyde) and a primary amine. The figure shows the synthesis of a monofunctional benzoxazine. However, many benzoxazine resins are bifunctional or even multifunctional. In the case of bifunctional benzoxazines, they are either synthesized from a bifunctional phenol, such as bisphenol-A, with a monoamine or from a diamine with a monofunctional phenol [5]. Bifunctional benzoxazines synthesized

TABLE 1.2: Properties of thermosetting polymers [10].

Property	Epoxy	Phenolics	Cyanate ester	PBZ
T_{cure} [°C]	25-180	150-190	180-250	160-220
T_{max} use [°C]	180	200	150-200	130-280
Cure shrinkage	≥ 3	0.002	≈ 3	≈ 0
T_g [°C]	150-220	170	250-270	170-340
Tensile strength [MPa]	90-120	24-45	70-130	100-125
Tensile modulus [GPa]	3.1-3.8	3.0-5.0	3.1-3.4	3.8-4.5
Elongation [%]	3.0-4.3	0.3	2.0-4.0	2.3-2.9
T_{onset} degradation [°C]	260-340	300-360	400-420	380-400

from a bisphenol and a monoamine are called class A benzoxazines. The ones synthesized from a diamine and a phenol are called class B benzoxazines.

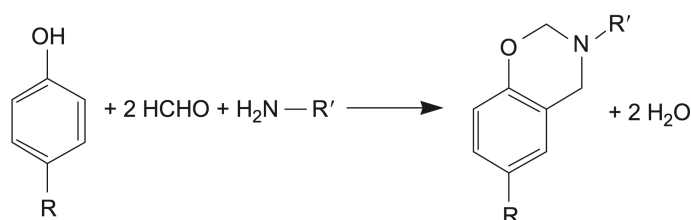


FIGURE 1.3: Synthesis of a monofunctional benzoxazine monomer [5].

The resulting monomers crystallize depending on its initial components and if a good purification took place, which can be difficult due to the tendency of benzoxazines to retain small amounts of solvents and impurities [5]. However, upon polymerization, an amorphous structure is generally obtained for the polybenzoxazines [11]. The cured benzoxazines have an excellent thermal stability, even though they are Mannich base polymers and that the Mannich bridge, $\text{CH}_2 - \text{NR} - \text{CH}_2$, of small molecules undergoes thermal degradation or a reverse Mannich reaction at moderate temperatures. Thermogravimetric analysis of cured bifunctional benzoxazines even shows that they only start degrading at 260°C with the degradation rate depending on phenol used in the resin [12]. This excellent thermal stability is the result of a stabilization of the Mannich bridges through intramolecular hydrogen bonding between the nitrogen atom in the bridge and the phenolic OH [13], as shown in Figure 1.4.

On the down side, the raw materials in the production of benzoxazines, such as phenolic derivatives, formaldehyde and amines, are often toxic. Yet, substantially less by-products are formed during polymerization than during the polymerization process of more traditional phenolic resins. Moreover, ROP does not produce water as opposed to condensation polymerization.

Finally, the selected components at the base of the benzoxazine monomer strongly influence the resulting mechanical and physical properties of the final resin. The more common benzoxazines, such as the commercial bisphenol-A based benzoxazine, have properties which favorably compare to those of traditional phenolic and epoxy resins. High performance polybenzoxazines are comparable to bismaleimides and polyimides, but can be produced at lower cost [15].

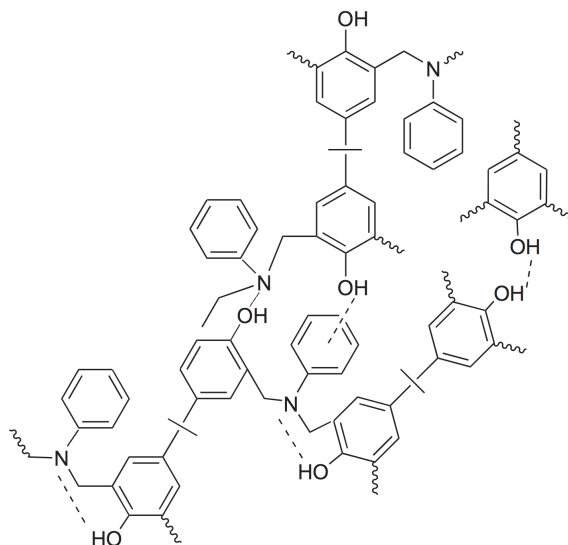


FIGURE 1.4: Structure of a polybenzoxazine with hydrogen bonding [14].

1.1.3 Polymerization mechanism of benzoxazines

Previously, ring-opening polymerization was mentioned as the global mechanism for the polymerization of benzoxazines. The benzoxazine structure is essential for this type of polymerization. ROP of benzoxazine resins occurs through the opening of the oxazine ring of the benzoxazine structure to form a linear or branched polymer in the case of monofunctional benzoxazines and a cross-linked polymer in the case of multifunctional ones. The formation of this macromolecular network during polymerization for multifunctional benzoxazines is called the curing, cross-linking or reticulation of the resin and is typical for thermosetting polymers, of which these benzoxazine resins are part of.

A thermally accelerated cationic ring-opening of the oxazine ring is at the origin of the ROP. However, while heat is needed for the polymerization it should not be confused with thermal polymerization as there is no thermal cleavage of a bond followed by free radical polymerization. Instead, the ROP is initiated due to small amounts of cationic initiator present into the monomer. Those cationic initiators are usually residual phenolic materials from the monomer synthesis present as impurities. The heating is simply required to accelerate the cross-linking of the resin [5]. Once the polymerization reaction is initiated, either with residual phenolic materials present in the monomer or by an initiator, the reaction is autocatalyzed [16]. The phenolic structure resulting from the ROP acts as an initiator and catalyst to the reaction. As mentioned before, depending on the type of monomer, either linear or cross-linked polymers are obtained, respectively for mono- and bifunctional benzoxazines.

According to studies, the precise mechanism of ROP is believed to be ionic in the case of benzoxazines [17]. One of the most popular proposed mechanisms is the iminium ion mechanism. But although it seems to explain many of the phenomena observed during the reaction, it is not completely consistent. Therefore, the exact polymerization mechanism is still to be found - with the extremely complex formation of by-products at the origin of this problem. For instance, with the same

monomer but a different initiation mode, either a phenolic-based Mannich polymer is obtained or a non-phenolic aryether-based Mannich base polymer is produced [18]. This aryether structure can then again be converted into the phenolic structure which is usually found in benzoxazines via a heat treatment.

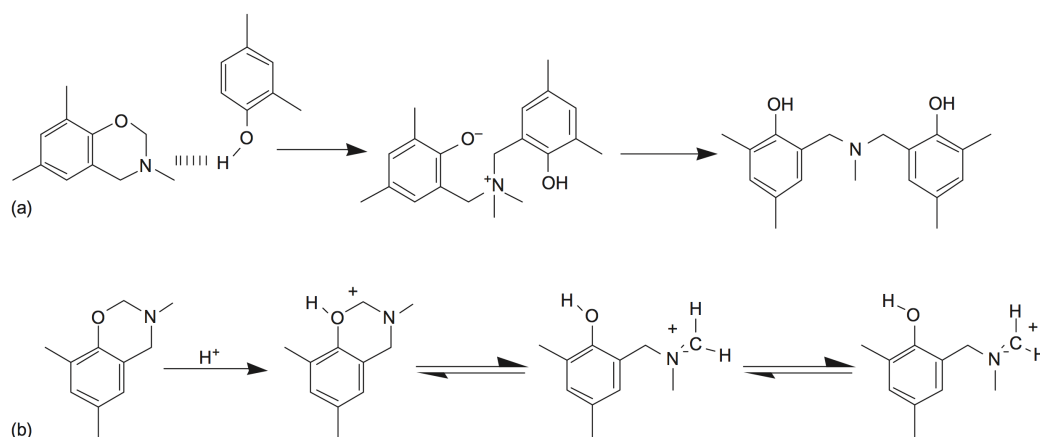


FIGURE 1.5: Polymerization mechanisms for benzoxazine resins proposed by: (a) Riess et al. and (b) Dunkers and Ishida [5].

Figure 1.5 illustrates two possible polymerization routes for benzoxazine resins. The first one was proposed by Riess et al. [19] and the second one by Dunkers and Ishida [20]. The mechanism developed in Riess paper, supposes the formation of an intermediary complex that results from the formation of an intermolecular hydrogen bond. From this complex, a hydrogen atom is then transferred from the positive nitrogen to the negative oxygen and a Mannich bridge is formed. In the second mechanism, the ring opening polymerization occurs by protonation of the oxygen atom. As a result, an iminium ion is formed and electrophilic aromatic substitution happens. A simplified scheme summarizing the thermal curing of benzoxazines with this iminium ion mechanism is shown in Figure 1.6. Several other reaction mechanisms have been proposed in papers, for example, by Wang [18], Sudo [21], and Chutayothin [22].

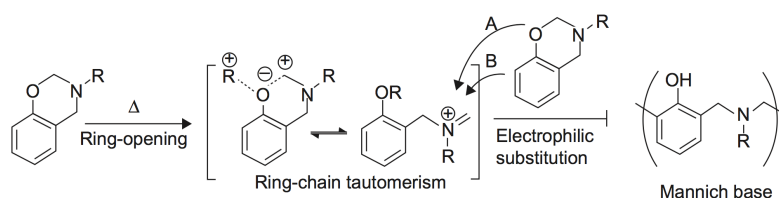


FIGURE 1.6: Simplified scheme of the thermal curing of benzoxazines with iminium ion mechanism [10].

Finally, an illustration of the typical structure of a cured benzoxazine is given by the phenolic Mannich bridge network obtained for the polymerized BA-a benzoxazine, depicted in Figure 1.7.

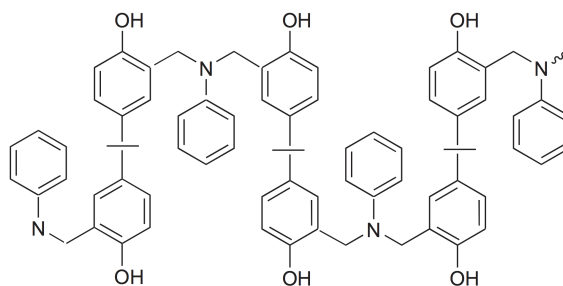


FIGURE 1.7: Phenolic Mannich bridge network formed in poly(BA-a) [14].

1.1.4 Degradation mechanism of benzoxazines

The decomposition of a material is initiated by thermal mechanisms or thermo-oxidative degradation. Then, small combustible fragments move to the material surface and thus to the flame front where oxygen burns the flammable gases. This process produces energy, which is then used to further degrade the material and the process goes on as long as the material burns. Char, the residue of the material after burning, forms an obstacle to this process by preventing combustible material to reach the surface. Thus, in order to reduce the burning, the use of high char-forming materials is needed for flame-resistant applications.

Polybenzoxazines are known for their excellent thermal stability, by their high degradation temperatures and char yield. The thermal degradation mechanisms of these materials are at the origin of these properties. However, the thermal degradation processes in polymers can be very complex and are influenced by a large variety of factors, but the study of the degradation mechanism in benzoxazines is crucial in the understanding of their properties, and, therefore, research is continuously initiated to get a grasp on these mechanisms [23].

In benzoxazines, the amine parts are thought to be easier to cleave due to the weaker C – N bond, 72.0 versus 82.6 kcal/mol for the C – C bond [23]. For instance, when comparing the degradation process of bisphenol-based BA-a and diamine-based P-DDM, a low temperature weight-loss phenomenon is observed for poly(BA-a) and not for poly(P-DDM). This weight-loss phenomenon can be associated with the loss of aniline compounds in poly(BA-a). It does not occur in poly(P-DDM) because the amine is incorporated into the cross-linked structure, while the aniline is dangling in poly(BA-a) [24]. This example shows that the diversity of structures has a significant effect on the degradation mechanism of polybenzoxazines.

An effective way to study the complex degradation process of benzoxazines is with the use of polybenzoxazine model dimers or oligomers with a Mannich bridge structure. Low and Ishida [25] used two benzoxazine dimers, methyl-dimer and amyl-dimer, to study the thermal degradation mechanism. Their research led to two types of degradation mechanisms in dimers associated with the cleavage of C – N and C – C. The schemes are shown in Figure 1.8. The first route (I), due to the scission of the C – N bond, is responsible for the majority of the weight loss and occurs at a lower temperature. The second route (II) is due to the more stable C – C bond and, therefore, only occurs at higher temperature. The main difference between both routes is the formation of the Schiff base structure in I and a secondary amine in II [23].

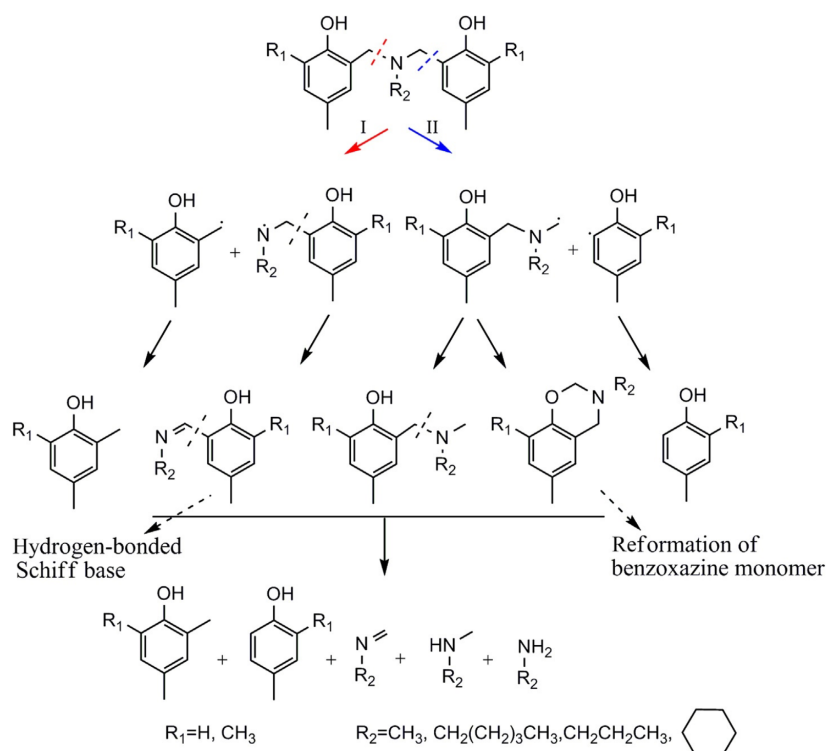


FIGURE 1.8: Proposed degradation process of Mannich base cleavage in benzoxazine dimer [23].

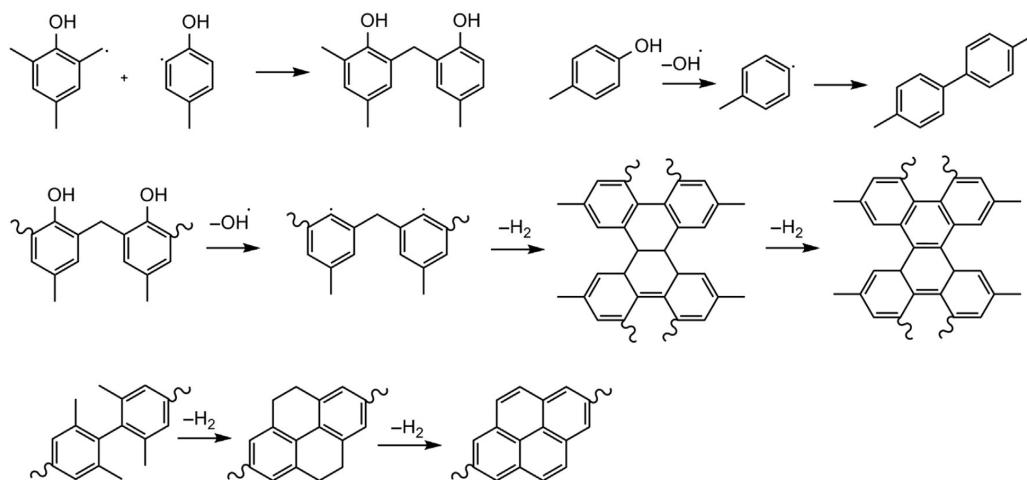


FIGURE 1.9: The couple reaction and char formation during the degradation of polybenzoxazine models [23].

Figure 1.9 depicts the couple reactions and the char formation in polybenzoxazines during their degradation process. As a result of the two degradation stages presented above in Figure 1.8, further degradation processes occur in the resin. During decomposition, if no substituents are present at the ortho position of phenols, the bisphenol compound is formed by coupling. Equally, the phenols can lose their hydroxyl group and cross-link to form biphenyl. In the last degradation steps, the char is formed by elimination reactions on the bisphenol and biphenyl compounds.

The elimination reactions include dehydrogenation, cross-linking, and aromatization [26].

From the study on polybenzoxazine dimer model, the cleavage of the C – N bond in the Mannich bridge was found to be the main factor for the degradation of polybenzoxazines. This degradation mechanism can easily be identified by the formation of a strong band in FTIR at 1670 cm^{-1} due to an aliphatic Schiff base in poly(BA-m) [25].

In a brief parenthesis, referring to the example comparing the thermal stability of poly(BA-a) and poly(P-DDM), the delayed degradation of poly(P-DDM) appears because the amines are incorporated into the cross-linked structure. Cleavage of the C – N bond occurs in both polybenzoxazines, but weight loss is only recorded for p(BA-a) because the amines are dangling and, thus, separated from the network upon cleavage. This can be prevented by the addition of functional groups to the polybenzoxazines to anchor these dangling amines into the cross-linked structures and delay the evaporation of the fragmented species [23].

To conclude, hydrogen bonding can strongly influence the cleavage of the Mannich base. The stabilization of intramolecular hydrogen bonding results in an easier cleavage of the C – N bond than of the C – C bond.

Also, the degradation products can be grouped in two categories: the ones from a primary decomposition processes, due to polymer chain scissions; and the ones from secondary decomposition processes, related to the formation of chars.

Finally, the addition of reactive functional groups into benzoxazines, retards the degradation, because of C – N bond scission, to a higher temperature.

1.1.5 Unique properties of benzoxazines

The aim of this subsection is to introduce the unique properties which derive from benzoxazines precursors and polybenzoxazines. This set of unique properties is what makes benzoxazines to be used for the development of specific applications as well as to replace other existing polymers.

Near-zero shrinkage

Thermosetting and thermoplastic polymers shrink during polymerization. While for thermosetting resins the shrinkage is between 2 and 15% in volume, it is even higher for thermoplastics [27]. Zero shrinkage or expanding polymers would be ideal as for high performance adhesives, sealants and coatings because of their superior mechanical interlocking. Also, polymerization shrinkage leads to residual stresses, which if they were reduced or eliminated would certainly profit to composite materials. In composite materials, the suppression of shrinkage removes optical distortion and warping of the composite [5].

Benzoxazines are especially interesting in this perspective as they show near-zero shrinkage while bearing high mechanical integrity [27]. Upon polymerization, most benzoxazine monomers experience a volumetric change within 1% [5]. This small shrinkage is the result of the ROP, which - as opposed to condensation polymerization - does not produce by-products and water. For some benzoxazines, a small expansion is even observed upon curing due to a change in the molecular packing [27].

It is this only slight shrinkage at high curing temperatures and the near-zero shrinkage at room temperature which make benzoxazines ideal in the perspective of a minimization of the residual stresses and demolding of pieces [5]. For example, the benzoxazines based on bisphenol-A with aniline and cyclohexylamine undergo respectively a shrinkage of 0.40% and an expansion of 0.43% upon polymerization [27].

Glass transition temperature T_g

The cured benzoxazines also develop a very high glass transition temperature T_g , which ranges from 160 to 400°C [5]. In the case of cured thermosetting resins, the apparent T_g approximately coincides with the cross-linking temperature, given that the reaction is carried out below the ultimate T_g of the material. Yet, some polymerization mechanisms allow further reactions or rearrangement of the polymer due to local motion. In this case, it is possible for the glass transition temperature to exceed the curing temperature T_{cure} [5].

In polybenzoxazines the presence of many active sites as well as the abundant benzene rings, to which the active sites react, allow the T_g to surpass the curing temperature. Thus, the β -transition temperature T_β provides enough mobility for these types of reactions. T_β is the temperature at which localized motions that involve the whole side chain and localized group movements are activated in the polymer. Another possible reason is the presence of a ring-opening polymerization mechanism instead of a condensation mechanism. Finally, a last possibility is the structural rearrangement at high temperatures [5].

Benzoxazines with a T_g higher than T_{cure} have a processing advantage over other high performance resins, since they require a lower cure temperature.

Low water absorption

A third notable property of benzoxazines is their low water absorption. Many thermosetting resins; such as polyesters, vinylester, phenolics, epoxies, bismaleimides and polyimides; have a high-water absorption at saturation due to the presence of polar groups in their structure. For example, both phenolic and epoxy resins take up 3 to as much as 20wt% upon saturation [28]. Polybenzoxazines also contain polar groups in the form of phenolic OH and the Mannich base, $\text{CH}_2 - \text{NR} - \text{CH}_2$, which are present in each repeating unit. However, much less water uptake is observed in those resins, probably because of intramolecular six-membered ring hydrogen bonding. In fact, for polybenzoxazines composed of bisphenol-A and aniline (BA-a) or methylamine (BA-m) the respective water absorption at saturation is only 1.9 and 1.3wt% [15]. Figure 1.10 illustrates the water absorption for those resins as a function of time. Once saturation was reached, no additional absorption was observed over more than 10 years. Finally, in benzoxazines, the use of amines and phenol with more hydrophobic radicals will decrease even more the water uptake.

The main advantage of this property is the ability to decrease the dielectric constant of the polymer. Because, just 1% of water absorbed, increments the dielectric constant by approximately 1 [5]. Also, a low water absorption reduces the difference between the dry and wet T_g , which is important from an industrial point of view to produce actual applications.

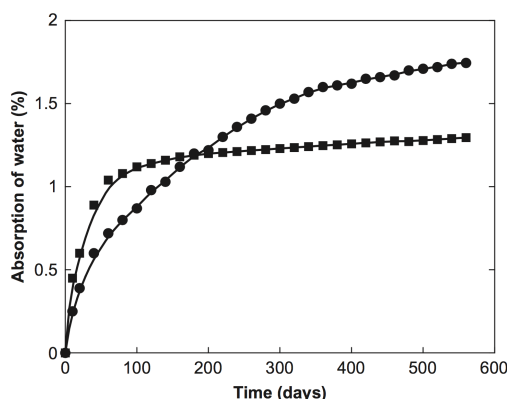


FIGURE 1.10: Water uptake of poly(BA-a) and poly(BA-m) at room temperature [15].

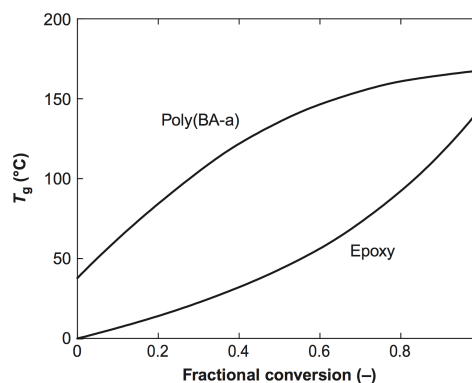


FIGURE 1.11: Evolution of T_g with the fractional conversion for poly(BA-a) and epoxy [5].

Fast property development

As depicted in Figure 1.11 condensation polymers such as epoxy resins require high degrees of curing to reach good physical and mechanical properties. At low degrees of conversion, the glass transition temperature increases slowly, whereas over the last few degrees of polymerization a significant increase of the T_g is observed.

For benzoxazines, the inverse is observed. At low degrees of conversion, a great rise of the T_g can be observed. This rise of T_g then slows down as the degree of conversion increases. A similar evolution can also be found for other physical and mechanical properties of benzoxazines. The origin of this difference with condensation resins lies within the polymerization mechanism, ring-opening polymerization is a type of addition polymerization, which results in a fast built-up of the molecular weight at low degrees of cure and thus a fast development of the properties of the material.

For instance, in the case of BA-a benzoxazine, 80% of the ultimate T_g is reached at 50% conversion as opposed to 25% for a bisphenol-A type epoxy resin at the same conversion [29]. This fast development of properties is advantageous to reduce the cure cycle time of benzoxazines. Because they develop their properties faster, a lower conversion needs to be reached to fulfill the requirements of certain applications.

Very high char yield

A fifth and final advantage of benzoxazines is their very high char yield, which is defined as the ratio between the residual mass and the initial mass of a sample after pyrolysis at high temperature. This property is especially interesting as the flammability of materials recently gained attention due to a strengthening of regulations on materials and the advent of new technologies.

For most polymers, the char yield after heating under a nitrogen atmosphere to 800°C is very low. Epoxies have char yields ranging between 5 and 15% and traditional phenolic resins reach 30 to 55% of char yield [5]. Although, there is no direct relation between benzene content and char yield, it has been experimentally found that when the amount of benzene groups increased within the material, a rise in char formation could be observed. This directly reflects into the char yield of benzoxazine resins, which despite a higher content in aliphatic groups, obtain a char

yield between 35 and 75% and thus higher than for traditional phenolic resins [5]. The char yield of bismaleimides, however, can also reach high levels up to 60% [30], but they lack other interesting properties benzoxazines have.

In order to theoretically compare the flammability of polymers, the heat release capacity of the material is an important property. This heat release capacity can be calculated theoretically from the contributions of the molar groups. Given the important contribution of hydroxyl groups, tertiary amines and benzene groups; polybenzoxazines can be considered as inherently good flame-retardant materials [31].

Molecular origin of unique properties

The five unique properties of benzoxazines can in part be explained by the complex hydrogen bond formation in polybenzoxazines. Polybenzoxazines exhibit almost all forms of hydrogen bonds, of which inter- and intramolecular $\text{OH} \cdots \text{OH}$, intramolecular $\text{OH} \cdots \text{N}$ six-membered hydrogen bonds (Figure 1.12), and $\text{OH} \cdots \pi$ interactions [5]. The formation of these intra- and intermolecular hydrogen bonds has been confirmed by many techniques, such as FTIR and H-NMR. Figure 1.12 depicts the six-membered hydrogen bond between OH and N, this very stable hydrogen bond is especially interesting as it explains the hydrophobicity, low dielectric constant, high char yield, and high modulus of benzoxazines.

While polybenzoxazines do not have a semi-crystalline structure due to their cross-linked nature, the presence of branched structures, and the complex hydrogen bonding, studies show that polybenzoxazines tend to form a helical structure locally. This structure, partially resulting from hydrogen bonding, is important with regard to the structure-property relationships of materials, especially for mechanical strength and thermal stability properties.

Finally, the ratio of intramolecular versus intermolecular bonds in benzoxazines depends on the nature of the raw materials used, in particular the amines. In general, most phenolic OH groups form intramolecular bonds with the nitrogen in the Mannich bridge, thus forming six-membered hydrogen bonds. The stability of this bond is exceptional: this hydrogen bond can remain stable over 300°C [13].

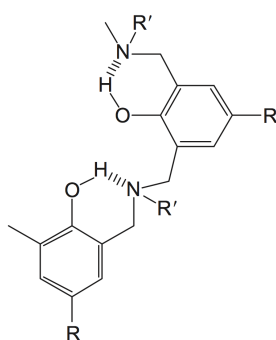


FIGURE 1.12: Intramolecular six-membered ring hydrogen bonding [5]

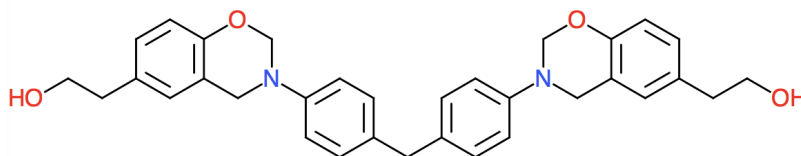


FIGURE 1.13: Structure of the T-DDM benzoxazine monomer.

1.2 T-DDM resin

T-DDM is the benzoxazine monomer that was used in the experimental part of this study. The T-DDM resin is synthesized from 4,4'-diaminodiphenylmethane or DDM, 4-(2-hydroxyethyl)phenol or tyrosol, for the amine and phenol components respectively, and paraformaldehyde. It is this combination of tyrosol and DDM that established the name T-DDM. The resin is yellowish and clear in its uncured form and turn red-orange upon curing. At room temperature and in both cured and uncured forms, the resin is already hard as the T_g of the uncured form is over room temperature.

This benzoxazine resin is bifunctional and has the structure shown in Figure 1.13. The central part of the structure is contributed by the DDM diamine and both extremities originate from the tyrosol. The central block is linked to each extremity by a benzoxazine structure.

The diamine component in T-DDM is 4,4'-diaminodiphenylmethane or DDM and is represented in Figure 1.14. DDM is a silvery, crystalline material which is formed by heating formaldehyde aniline with aniline hydrochloride and aniline. Its main uses are as curing agent for epoxy resins and as intermediate to synthesize diisocyanates for urethane elastomers and foams by reaction with phosgene [32]. The use of DDM as an epoxy resin hardener is not without risks as it possibly has carcinogenic, liver damaging effects and hepatotoxic on humans and animals [33].

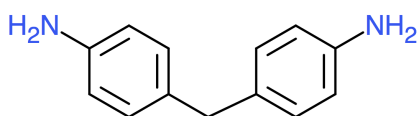


FIGURE 1.14: Structure of DDM.

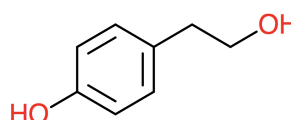


FIGURE 1.15: Structure of tyrosol.

Tyrosol, the common name for 4-(2-hydroxyethyl)phenol, is depicted in Figure 1.15. It is a derivative of phenethyl alcohol and this phenolic antioxidant can be found naturally in a variety of sources. For instance, it can be found in olive and argan oil [34]. Moreover, tyrosol appears to have cardio-protective effects [35]. Up to now, the majority of the research papers published on tyrosol and other multi-hydroxylated phenols have been related to their antioxidant properties and their effect on our health. However, polyphenolic molecules are also promising condensed phase flame retardants, which could be an alternative to halogenated flame retardants. Condensed phase flame retardants can control the spread of flames by two mechanisms. They decompose into gases, such as water vapor or carbon dioxide, thereby removing heat from the combustion source. The other mechanism, they are high char forming materials, which restricts the diffusion of oxygen and forms a heat insulation layer. Tyrosol is one of these phenolic monomers that are interesting

for their flame retardant properties once polymerized. Additionally, it is naturally occurring [36]. Thus, tyrosol is a good bio-sourced candidate for the phenolic part of a benzoxazine resin.

Although, a thorough search was conducted, no research papers published about benzoxazines with tyrosol and DDM combined were found. Moreover, it seems that tyrosol has never been used in benzoxazines at all from the results of an expanded search. However, many papers have already been published on benzoxazines with DDM and some even on a benzoxazine based on DDM and 4-hydroxybenzyl alcohol and looking very resembling to the T-DDM benzoxazine.

1.2.1 DDM in benzoxazines

Some papers on benzoxazines based on 4,4'-diaminodiphenylmethane and their conclusions will be briefly mentioned in this subsection. A focus will be placed on the benzoxazines which are the most like T-DDM.

A first study by Sini and Takeshi [37] developed di-, tri-, and tetrafunctional benzoxazine monomers solely containing benzoxazine moieties on their backbone to discover the role of an additional oxazine moiety on the thermal properties. The authors also synthesized tetrafunctional benzoxazines containing intermediate groups, namely pPDA and DDM, to understand the differences in thermal properties due to the distance created in between two benzoxazine moieties. The effects of an increasing number of oxazine rings include: (i) a reduction of the cure temperature, (ii) a slower curing rate, (iii) decreased weight loss during ROP, and (iv) an increase in T_g . However, the addition DDM as an intermediate group increased the cure temperature, but strongly reduced weight loss during curing and enhanced the thermal degradation temperature of the resulting polybenzoxazine. Therefore, adding DDM - or another intermediary - in between two benzoxazine moieties is desirable when the aim is to increase the thermal stability of a benzoxazine resin.

Another study by Men and Lu [38], which researched the synthesis and characterization of DDM-based benzoxazines, agrees with the previous observation. Their precursors were synthesized from DDM and different phenol derivatives, such as phenol, p-cresol and 2-naphtol. Their most important finding is that these DDM-based benzoxazines show higher glass transition temperatures and char yields than the corresponding bisphenol-A based benzoxazines. To illustrate this, the polybenzoxazine prepared from phenol reached 5 and 10% weight-loss at 346 and 432°C respectively, and a char yield of 65%.

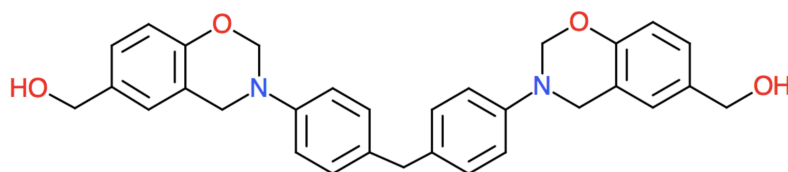


FIGURE 1.16: Structure of the pHBA-DDM benzoxazine monomer.

In his thesis, Baqar [7] studied methylol-functional benzoxazines. One of them, pHBA-DDM based on 4-hydroxybenzyl alcohol, pHBA, and DDM is of particular

interest due to its resemblance to T-DDM and is depicted in Figure 1.16.

Baqar studied the polymerization of pHBA-DDM and other methylol-functional benzoxazines with DSC and several differences between these functionalized benzoxazines and the unfunctionalized P-DDM, based on phenol and DDM, were observed. A first observation was a decrease in the heat of polymerization attributed to the endothermic nature of the methylol condensation, which is different from other cross-linking sites in the polybenzoxazine structure. A second observation is the broadness of the exothermic peak for the methylol-functional benzoxazines. This broadness was also attributed the condensation reaction of the methylol along with the polymerization of the benzoxazine resin.

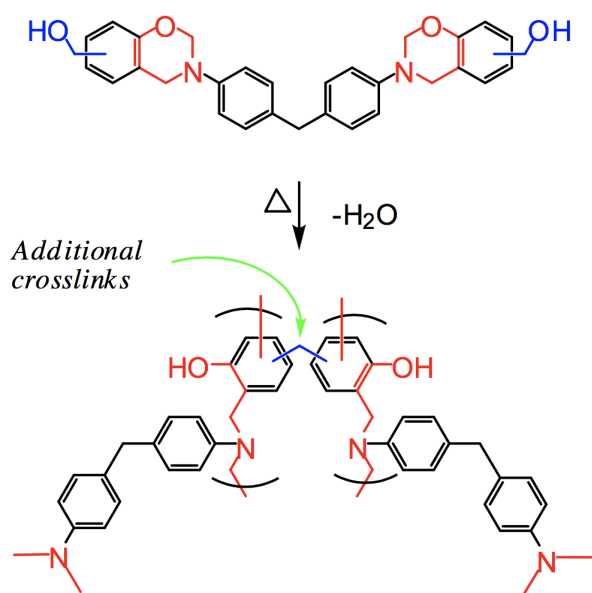


FIGURE 1.17: Proposed structure of methylol-functional benzoxazine monomers once cross-linked [7].

FTIR was also used to monitor the peaks related to the condensation reaction of the methylol along with the polymerization of the benzoxazine resin. The typical peak for methylol was observed at 1020 cm^{-1} due to C – O stretching. The condensation reaction could be seen at 1480 cm^{-1} through monitoring of the CH₂ bending of the methylene bridge. In pHBA-DDM, a decrease in the characteristic absorption bands at 950 and 1228 cm^{-1} , respectively for the benzene ring attached to the oxazine ring and the asymmetric stretching of the ether linkage, confirmed the ROP. Also, the appearance and increase of the signals at 1480 and 1104 cm^{-1} for the bending of the methylene bridge C – H band and the methylene ether bridge C – O – C were observed and confirmed the methylol condensation.

Furthermore, the characteristic bands associated with the benzoxazine ring at 952 and 1508 cm^{-1} due to the tri-substituted benzene ring, at 1328 cm^{-1} due to the CH₂ agitation in the benzoxazine ring, and at 1234 cm^{-1} due to the asymmetric stretching of the ether linkage all decreased. And an overlapped peak with the methylol methylene bridge due to the tetra-substituted benzene ring appeared at 1480 cm^{-1} ,

confirming the ROP reaction [7]. Thus, strongly backing the occurrence of both polymerization mechanisms upon thermal curing of the monomers. A resulting cross-linking structure is proposed in Figure 1.17.

Finally, Baqar found that, compared to P-DDM, pHBA-DDM showed increased thermal properties after curing. The T_g increased from 212 to 311°C, the temperatures at 5 and 10% degradation from 364 and 390 to 394 and 430°C, and the char yield from 46 to 56%.

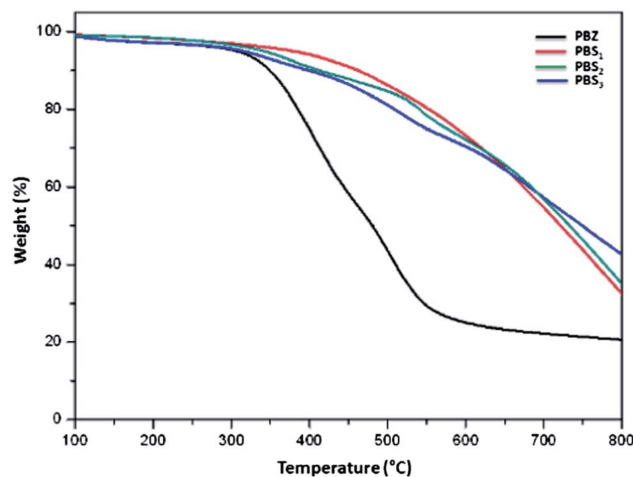


FIGURE 1.18: TGA curves of hybrids composed of pHBA-DDM and SiO_2 [39].

The use of pHBA-DDM was also found in two other papers written by Selvi et al. [39, 40]. In a first paper, silica reinforced polybenzoxazine hybrid materials, PBZ- SiO_2 , with a low surface free energy were developed. These hybrid materials displayed improved thermal stability, higher T_g , and higher char yield than the neat pHBA-DDM matrix. Moreover, Figure 1.18 shows an impressive improvement of the thermal stability on the TGA curves, thus a delay in the degradation of the PBZ- SiO_2 blends.

In the second paper, polybenzoxazine-silica-titania hybrid nanocomposites were produced. Again, the PBZ- SiO_2 - TiO_2 hybrid showed improved T_g , high char yield and improved thermal stability. Additionally, a similar shouldering as for the PBZ- SiO_2 hybrids was found in TGA.

These hybrids could be used for water repellent coatings in the case of PBZ- SiO_2 or thermal and self-cleaning coatings for PBZ- SiO_2 - TiO_2 ; both with enhanced performance and improved longevity.

To sum up, the use of DDM in benzoxazines increases their cure temperature, but improves their thermal stability, both in terms of char yield as of degradation temperature. In the specific case of pHBA-DDM, a second polymerization mechanism is detected besides the ROP: condensation polymerization occurs because of the methylol groups at the extremities of the precursor molecule.

Chapter 2

Curing of thermosetting resins

Two subjects will be addressed in this chapter: the cure kinetics, and the optimization of the curing cycle of a thermosetting resin.

2.1 Cure kinetics

Several methods to evaluate the kinetic cure parameters will be discussed in this section. These methods make use of isothermal and dynamic DSC methods.

2.1.1 Isothermal methods

In methods based on isothermal DSC experiments, it will be supposed that a single chemical process occurs during the curing. Nevertheless, a process combining several chemical reactions which are similar or simultaneous cannot be dismissed [16]. Moreover, the heat generated through the exothermic reaction is expected to result only from the curing reaction, which follows a ring-opening polymerization scheme. Therefore, it can be assumed that the measured exothermic heat corresponds to the heat of reaction [41]. Finally, it is supposed that no reaction takes place before the samples reached the isothermal cure temperature. The reaction rate ($d\alpha/dt$) and the conversion α can thus respectively be given by Equation (2.1) and (2.2), where H_r^{iso} is the heat of reaction measured in the isothermal experiment and H_r^{max} the maximal heat of reaction that can be reached practically while curing the material.

$$\frac{d\alpha}{dt} = \frac{dH_r^{iso}}{dt} \cdot \frac{1}{H_r^{max}} \quad (2.1)$$

$$\alpha = \int_0^t \frac{dH_r^{iso}}{dt} dt \cdot \frac{1}{H_r^{max}} = \frac{H_r^{iso}}{H_r^{max}} \quad (2.2)$$

Under the assumption that the reaction rate of the cross-linking reaction is proportional to the exothermic heat measured in the tests [41], Equations 2.1 and 2.2 presented above are valid. Moreover, with the value of H_r^{max} , the enthalpy for a maximum cure, the DSC curves can be converted to the reaction rate and the conversion using the equations.

Furthermore, for some thermosetting resins and for most benzoxazines, the reaction is autocatalytic. In DSC curves, this is verified by a single peak with a maximum reaction rate that does not occur at time zero [16]. Moreover, an inflection point is observed in the curves representing the conversion versus the cure time [42]. Usually,

the maximum reaction rate is found in the range between 20 and 40% conversion for autocatalytic reactions [43, 44]. However, it should be noted that the maximum reaction rate often does not occur at a similar conversion for the different isothermal cure temperatures. One explanation for maximum reaction rates occurring below 20%, would be that certain structural rearrangements, which lead to a higher conversion, only occur at the higher temperatures [16]. At lower temperatures, these rearrangements are never activated, thus reducing the overall extent of conversion of the resin and, consequently, the conversion at the maximal reaction rate. Finally, in the case of benzoxazines, the generation of free phenol groups, while the oxazine ring starts to open, is the reason for the autocatalytic nature of their curing kinetics. These free phenol groups, which serve as cationic initiators and accelerators, then further catalyze the ring opening process [16, 41].

Based on isothermal experiments, the critical temperature T_{c0} , below which no reaction occurs, can be determined using the method developed by Sourour and Kamal [45]. Over a certain range of cure temperatures, the residual extent of cure, $(1 - \alpha_{final})$, shows an exponential decrease. Therefore, when plotting the residual extent of cure versus the isothermal cure temperature on a semi-logarithmic plot, a linear correlation can be found for the data. And, assuming the extrapolation of the data is valid at lower temperatures, an estimate of T_{c0} can be determined when the conversion reaches zero - or the residual extent of cure reaches one. This extrapolation assumes the decrease in conversion, with a decrease in cure temperature, is exponential.

While most methods to establish the kinetic parameters require the knowledge of the reaction mechanism, some other methods do not need a mechanistic knowledge to determine them. This is especially useful for the class of benzoxazine resins, as their exact reaction mechanism is often unknown. These methods, based on non-isothermal experiments conducted at various heating rates, have as purpose to find the kinetic parameters, such as the activation energy, and are presented in the next subsection.

2.1.2 Non-isothermal methods

The simplest methods to evaluate kinetic parameters from dynamic DSC experiments are the methods of Ozawa [46] and Kissinger [47], which allow to compute the activation energy without considering the mechanistic aspects of the reaction. In both methods, the activation energy E_a is calculated from the slope of a line fitted on a set of data representing a logarithm function, which depends on the heating rate and often on the peak temperature, versus the reciprocal peak temperature.

The methods developed by Ozawa and Kissinger can be used in different ways: as maximum peak or as isoconversion methods. In both cases, the logarithm function, which is plotted against the reciprocal temperature, depends on the approximation of the temperature integral used. Therefore, this approximation is key to understand those methods. As a first point, all approximations for $p(y)$, the temperature integral, are only valid over a certain range of y -values ($y = E_a/RT$). Luckily, a clear majority of reactions occur for y -values in this range between 15 and 60 - for which the approximations are a good fit [48]. Senum and Yang [49] developed a series expansion for $p(y)$, which will serve as basis for simpler approximations. This

series expansion is presented in Equation (2.3).

$$p(y) = \frac{\exp(-y)}{y^2} \cdot \frac{y^4 + 18y^3 + 86y^2 + 96y}{y^4 + 20y^3 + 120y^2 + 240y + 120} \quad (2.3)$$

In the Ozawa method, the logarithm of the heating rate, $\log_{10}(\beta)$, is plotted versus the reciprocal peak temperature. The corresponding E_a can then be calculated using the Doyle approximation of the $p(y)$ -integral, $\log_{10}(p(y)) = -0.4567y - 2.315$ [49]:

$$\log_{10}(\beta) = -0.456 \cdot \frac{E_a}{RT_p} + Cst \quad (2.4)$$

On the other hand, the logarithm function used in the Kissinger method depends on the heating rate and the peak temperature: $(\ln(\beta)/T_p^2)$. Also, the approximation of the $p(y)$ -integral is the following:

$$p(y) = \frac{\exp(-y)}{y^2} \quad (2.5)$$

Which yields the following expression to determine the activation energy:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + Cst \quad (2.6)$$

Two other maximum peak methods are the Starink and the Flynn-Wall-Ozawa methods [48]. Depending on their specific approximations of the $p(y)$ -integral, their expressions for the measurement of E_a are given in Equation (2.7) for the Starink method and in Equation (2.8) for the Flynn-Wall-Ozawa method.

$$\ln\left(\frac{\beta}{T_p^{1.92}}\right) = -1.0008 \cdot \frac{E_a}{RT_p} + Cst \quad (2.7)$$

$$\ln\left(\frac{\beta}{T_p^{1.95}}\right) = -\frac{E_a}{RT_p} + Cst \quad (2.8)$$

The four methods presented above can also be used as isoconversion methods. When used as isoconversion methods, the temperature at a certain conversion is selected instead of the peak temperature.

The kinetic parameters can also be evaluated from the reaction rate equation by a multi-linear regression of experimental data. In Subsection 2.1.1 a certain emphasis was given on autocatalytic reactions as they often occur for benzoxazines. The general expression for autocatalytic systems is given by the following equation:

$$\frac{d\alpha}{dt} = k \cdot (1 - \alpha)^n \cdot \alpha^m \quad (2.9)$$

Where $\alpha(t)$ is the fractional conversion, k the kinetic rate constant and $n + m$ the overall order of reaction. With the assumption that the specific heat is constant or follows a linear variation with the heating rate of the DSC experiments and that the reaction rate follows an Arrhenius temperature dependence, Equation (2.9) can be rewritten:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - \alpha)^n \cdot \alpha^m \quad (2.10)$$

Then, using the definition of the heating rate, $\beta = dT/dt$, and by taking the natural logarithm of both sides of Equation (2.10), the following relation is obtained:

$$\ln\left(\beta \cdot \frac{d\alpha}{dT}\right) = \ln(A) - \left(\frac{E_a}{RT}\right) + n \cdot \ln(1 - \alpha) + m \cdot \ln(\alpha) \quad (2.11)$$

Equation (2.11) can be used to determine the values of the pre-exponential factor A , the activation energy E_a and the two exponents n and m with a multi-linear regression on the dynamic DSC data. Moreover, the resulting activation energies can be compared to the ones obtained by the maximum peak and isoconversion methods. However, the accuracy of the results strongly depends on how well the different hypotheses and assumptions are in line with the real data.

2.2 Cure cycle optimization

Before handling the aspect of the optimization of a cure cycle, it is important to recall the curing behavior of thermosetting resins. This behavior can be represented with a time-temperature-transformation or TTT diagram, as illustrated in Figure 2.1, which relates the properties the resin as a function of time and cure temperature. In the figure, constant degrees of cure are shown by lines: $C^* = C_g$ corresponds to the gel point, and $C^* = 1$ to the fully cured resin. Each degree of conversion is associated with a certain glass transition temperature. For instance, $T_{g,gel}$ for C_g , T_{g0} for the uncured resin, and T_{g1} for the fully cured resin. The evolution of T_g between T_{g0} and T_{g1} forms an S-shaped curve, called the vitrification line, in the time-temperature plane. This vitrification line represents the point at which T_g reaches the cure temperature T_{cure} .

Moreover, several regions are labeled in the diagram. The viscous liquid region is the region from the beginning of curing until the gel point has been reached. The char region occurs at high temperature and must be avoid because the resin is subjected to thermal degradation in this zone.

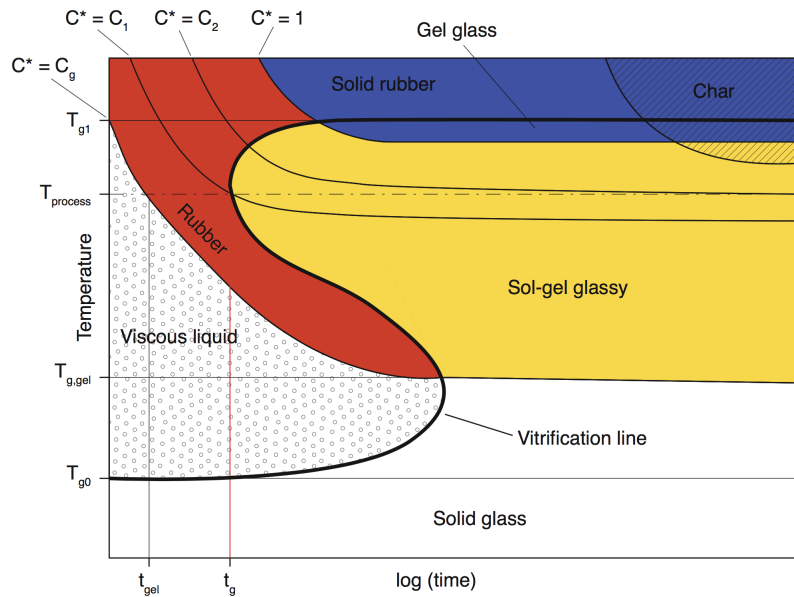


FIGURE 2.1: Time-temperature-transformation (TTT) diagram for a thermoset [50].

Finally, if an arbitrary cure temperature $T_{process}$ is considered, the polymer reaches the gel point after a time t_{gel} and the vitrification line at t_g . This leads to a degree of cure C_1 . Then, the material continues to cure in a diffusion controlled manner until it obtains a degree of cure of C_2 . This example shows the usefulness of selecting several cure temperatures. Once vitrification is reached, increasing the cure temperature raises the slow diffusion controlled reaction rate that occurs after vitrification and allows to obtain more rapidly an optimum conversion of the resin [50].

In the case of thermosets, the Di Benedetto equation can be used to describe the evolution of the glass transition temperature T_g with the conversion α [51]. This equation, expressed by Equation (2.12), uses the initial and final glass transition temperature of the thermoset, T_{g0} and $T_{g\infty}$, and the depends on the conversion. The factor λ is roughly approximated by $(T_{g0}/T_{g\infty})$ if experimental data lack.

$$\frac{T_g - T_{g\infty}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (2.12)$$

In the case of where λ is approximated, Equation 2.12 can be simplified to:

$$\frac{1}{T_g} = \frac{1 - \alpha}{T_{g0}} + \frac{\alpha}{T_{g\infty}} \quad (2.13)$$

Given this equation, this means that if a system is cured at an isothermal temperature T_{cure} below the final glass transition temperature $T_{g\infty}$, the maximum conversion that is reached is the one resulting from setting T_g equal to the T_{cure} [51]. This neglects the further curing in the glassy state, which is limited and evolves very slowly by diffusion controlled reactions.

With the previous observations in mind, the conception of the cure cycle of a thermosetting polymer can start. This conception starts with setting the conditions in the process control for a successful cure cycle [52].

First, it is crucial to determine which properties should be optimized by the cure cycle. When the aim is to get the highest possible T_g , the optimal conversion is the full conversion. However, in the case of epoxies, to reach the highest flexural and tensile strengths, optimum resistance towards compressive creep, and a low water uptake an optimum conversion, lower than the full conversion, is needed [51]. If a compromise is required between T_g and the mechanical and physical properties, a conversion between the full conversion and the optimum conversion for the mechanical and physical properties can be selected.

Another aspect to consider is the temperature. For thermosetting resins the curing reactions are usually exothermic. Therefore, during the curing, the temperature of the sample increases over the chosen cure temperature. For instance, if optimum mechanical and physical properties are the aim of the cure cycle, T_{cure} must be selected carefully to avoid a too high degree of cure in the middle of the material due to the additional heat from the exothermic reaction. T_{cure} must be chosen in agreement with the reaction rate at this temperature and the thermal conductivity of the material to keep the inner temperature of the material within boundaries and avoid a decrease of the properties. However, even when the aim of the cure cycle is to get the ultimate T_g , the cure temperature should be chosen wisely. If the reaction rate is too high at the chosen T_{cure} and the thermal conductivity of the material is not

sufficiently high to eliminate the heat of reaction, then there is a risk that the material will start degrading. Thus, the resin will lose both its mechanical and physical properties as well as its high T_g value. This can be avoided by curing the materials gradually with a cure program involving several steps of incrementally increasing cure temperatures.

Finally, and especially for industrial processes, the cure time is a critical factor. Short curing times allow the production of a higher volume of parts and dampens the high cost of the curing equipment [52]. Meeting all the properties requirements for the cured material with a time-optimal cure cycle should be strived for.

The cure cycle can then be determined either by an analytical or empirical method. The analytical methods are based on simulations of the heat transfer and the curing reaction. These methods analyze heat conduction and cure by calculating the numerical solutions to the coupled problem of both equations with certain initial and boundary conditions [53]. These equations are Equation (2.10) for the cure reaction and Equation (2.14) for the heat transfer. In Equation (2.14), ρ is the density of the resin, C_p the specific heat capacity, κ the thermal conductivity, H_r the heat of reaction, and z is the direction of the thickness of the resin.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right) + \rho H_r \frac{\partial \alpha}{\partial t} \quad (2.14)$$

However, empirical trial-and-error methods can also be used to develop the cure cycle of a thermosetting resin. For some well-known systems, these trial-and-error methods have even led to the development of rule-based heuristic expert systems to guide the cure cycle conception, such as the ones proposed by Choi and Lee [54] or Pillai et al. [55]. But these heuristic approaches are limited by the material, the geometry of the pieces and other practical restrictions.

The simplest empirical method consists in the evaluation of the properties of the specimens cured by a specific cycle. Based on the evaluation of the properties for the different cycles, an improved cure process is proposed. This method has several drawbacks such as the extensive experimental program needed to determine the proper cycle, the specificity of the cycle to a precise resin and certain conditions, and the probable loss of cure time compared to a cycle based on an analytical method [52]. Yet, this method is very practical for new materials which have not been extensively studied and for which the determination of a cure cycle with an analytical method requires a lot of work.

Chapter 3

Zinc oxide nanoparticles

The main characteristic for which ZnO was initially selected in blends with benzoxazine resins is because it is a broad-band UVA and UVB absorber. Figure 3.1 illustrates the UV/vis transmittance spectra of LDPE films with varying ZnO nanoparticles concentrations. In the figure, the UV absorption of the blends with ZnO covers almost the full UVA and UVB spectral range, between 280 and 400 nm. Thus, the ZnO possesses broad-band absorption characteristics of UV radiation. Yet, minimal absorption levels are detected in the visible light spectrum, which is very useful for potential applications which require transparency.

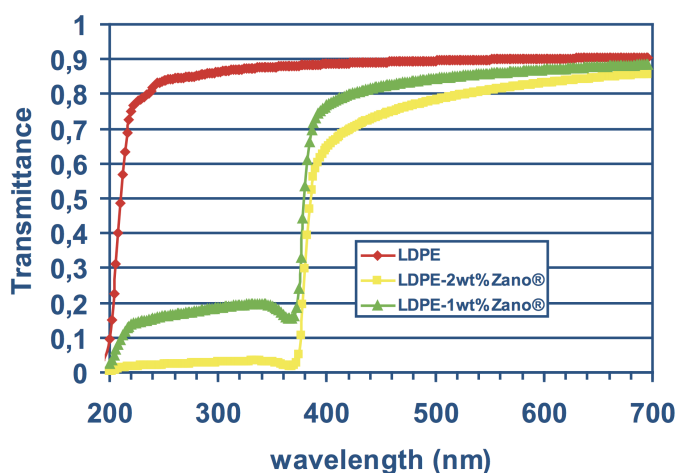


FIGURE 3.1: Transmittance spectra in the UV/vis range of LDPE films with varying ZnO nanoparticle loadings [56].

This chapter will deal with the synthesis and properties of zinc oxide and more specifically the ones related to ZnO nanoparticles. Then, their use in combination with benzoxazines will be discussed.

3.1 Synthesis and properties of ZnO nanoparticles

ZnO is composed of zinc and oxygen in stoichiometric proportions and has a molar mass of 81.40g/mol. Nanoparticles of zinc oxide melt at 1975°C [57]. Thus, given the temperature conditions that will be used in the experimental part of this work,

the particles can always be expected to be in the solid state.

TABLE 3.1: Conversion of ZnO precursor into ZnO nanopowder: volatilization temperatures, reactants, and intermediate compound [58].

Precursor	ZnO
Volatilization [K]	≥ 2200
First volatile reactant	CH_4
Volatile intermediate	Zn(g)
Volatilization [K]	1100
Second volatile reactant	air
Nanopowder	ZnO

ZnO nanoparticles can be manufactured following Umicore's patented production process [56]. This production process is a general process for the manufacture of nano-sized powders.

The manufacture of ZnO nanoparticles starts by grounding a solid ZnO precursor into a coarse powder. This compound is dispersed at low temperature into a hot gas stream ranging from 1000 to 3000K. Then, a first volatile reactant is injected and a gaseous metal intermediate compound is formed, which is volatile at a temperature lower than the volatilization temperature of the precursor. After the formation of this intermediate compound, a second volatile reactant is introduced into the gas stream, whereby the intermediate compound is converted into a nano-sized ZnO powder. Finally, this powder is separated from the gas stream [58]. A quench of the gas stream after the injection of the second volatile reactant and before separating the nano-sized powder from the gas stream, further enhances the production of the ZnO nanoparticles and narrows the resulting particle size distribution.

Table 3.1 summarizes the volatilization temperatures, the volatile reactants added to the gas stream, and the volatile intermediate during the process to produce nano-sized ZnO.

The resulting ZnO nanopowder is shown at 50,000 times magnification on the SEM micrograph in Figure 3.2. The average particle size of the particles varies between 27 and 37 nm depending on the experimental production conditions. A lower precursor ZnO feed results in a lower average particle size and the use of air instead of nitrogen increases the particle size [58].

Another technique for the synthesis of ZnO nanoparticles, which is more used on a laboratory scale, consists of adding a sodium hydroxide solution to an aqueous solution of zinc sulfate. Under vigorous stirring, a precipitate is formed that is filtered and washed thoroughly with distilled water. This precipitate is then dried in an oven and ground to a fine powder using an agate mortar. After grinding the ZnO to a powder, it is calcined at different temperatures depending on the desired morphology. A calcination temperature of 700°C for two hours is required for the formation of nanoparticles, at lower calcination temperatures nanoflakes are observed [59].

Finally, the FTIR spectrum for ZnO is shown in Figure 3.3. On the right of the figure, the characteristic peaks for zinc oxide are mentioned. The most significant peaks in the spectrum can be observed at 417, 440, 837, 1402 and 1512 cm^{-1} [60].

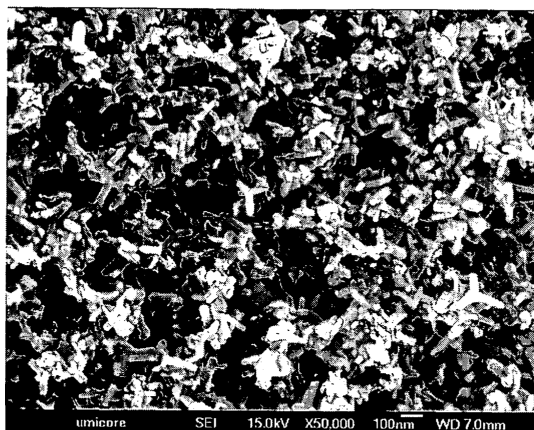


FIGURE 3.2: SEM micrograph at 50.000x magnification of ZnO nanopowder [58].

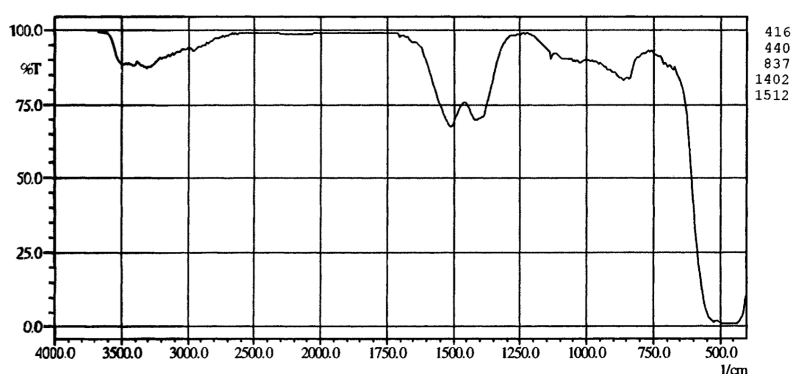


FIGURE 3.3: FTIR spectrum of zinc oxide in transmission [60].

3.2 ZnO nanoparticles as nanofillers in polymers

A fair amount of papers on the uses of ZnO nanoparticles in polymers have been published. This section will briefly present the overall effect of ZnO nanoparticles in polymers on their thermal properties, while the next section, Section 3.3, will focus on their specific use in benzoxazine matrices.

Liufu et al. [61] researched polyacrylate–ZnO nanocomposite blends. Thermal analysis and a study of the degradation mechanism were conducted. In TGA, the composites underwent some stabilizing/destabilizing interaction according to the temperature region. The authors found that in addition to the major weight-loss, associated with the polyacrylate, the nanocomposites showed two small losses; one before and one after the main peak.

The first weight loss in the blend was linked to the surface hydroxyl groups of the ZnO surface that can catalyze the thermal degradation of polyacrylate, as shown in Figure 3.4. However, as the ZnO particles have a higher thermal conductivity and a greater heat capacity than the polyacrylate, they can absorb the heat transmitted from the surroundings and retard the main degradation due to the scission of the polymer backbone. Thus, zinc oxide stabilizes the polymer molecules and delays the major degradation.

These aforementioned effects increase with the amount of ZnO nanoparticles and with a decreasing particle size.

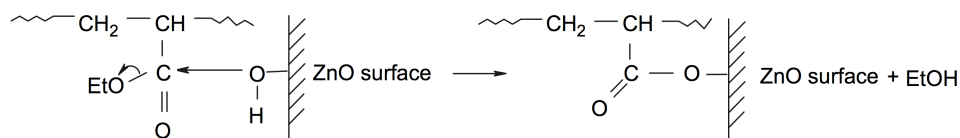


FIGURE 3.4: Catalytic decomposition of polyacrylate by the hydroxyl group on the ZnO surface [61].

In another study by Zabihi et al. [62], the effect of zinc oxide nanoparticles on the thermo-physical properties of an epoxy resin was studied. Their results showed that a relatively low concentration of ZnO was already sufficient for an impressive increment of the thermo-physical properties of the epoxy resin. In TGA, the char yield increased by 5% and T_{d5} , the temperature at 5% weight loss, by 60°C for a heating rate of 10°C/min. Moreover, the authors state that ZnO has anti-corrosion properties, which makes it especially attractive in high performance coating systems.

A third and last study presented here, by Vaishnav and Goyal [63], also researched the thermal properties of ZnO nanocomposite with polymers. In this case, the polymer was poly(aryletherketone) or PAEK, a semi-crystalline thermoplastic polymer.

In a similar fashion as in the two studies presented above, they found that the incorporation of ZnO in the PAEK matrix improved its thermal stability. This increase in thermal stability was assumed to result from a strong interaction and interfacial bonding between the matrix and the ZnO particles. Moreover, this increase grew with the amount of ZnO nanoparticles.

Based on the previous observations, it can be concluded that the use of zinc oxide particles in combination with polymers to form nanocomposites results in an increased thermal stability. This thermal stability is due to an interaction between the polymer matrix and ZnO, and increases with the amount of nanoparticles incorporated into the composite.

3.3 ZnO nanoparticles in benzoxazines

Up to this date, not many papers have been written on the uses of zinc oxide in benzoxazine materials. In an internship report from 2015, A. Raynaud [4] that studied the effect of ZnO nanoparticles on the properties of para-phenylenediamine or pPDA benzoxazine. Also, a paper by Rajamanikam et al. [64] investigated the optical and thermomechanical behavior of polybenzoxazine nanocomposites reinforced by benzoxazine functionalized ZnO.

Raynaud used ZnO in a pPDA benzoxazine matrix as he was initially looking to protect the pPDA resin from degradation due to UV radiation. Therefore, he selected ZnO because of its well known intensive UV absorption in order to create a UV barrier to prevent degradation. However, he found that the addition of zinc oxide nanoparticles also improved the thermal stability of the pPDA resin. In a first approach, Raynaud used TEM to analyze the dispersion of the ZnO nanoparticles into the benzoxazine matrix. He found that a sonication time of 60 seconds was already enough to obtain a good dispersion of the nanoparticles. Then, in the thermal analysis part of his report, DSC showed only a slight increase of the peak

temperature due to the addition of ZnO. However, a significant drop of the onset temperature was reported. Additionally, a shouldering was observed in the DSC curves and an increase of the enthalpy from 72 to 90 kJ/mol. Unexpectedly, those observations do not seem to be affected by the amount of zinc oxide or the sonication time.

The most interesting result, however, was obtained by TGA. The addition of ZnO nanoparticles increased the char yield and delayed the degradation temperature. Also, the only one degradation mechanism was found for the blend with 5wt% ZnO, while two were observed for the pure pPDA resin.

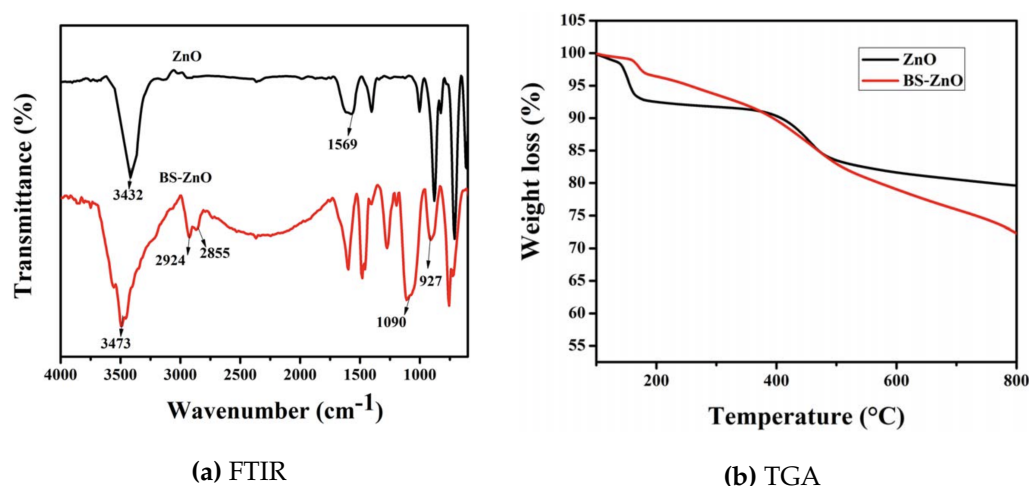


FIGURE 3.5: BS-ZnO compared to ZnO with FTIR and TGA [64].

Rajamanikam et al. functionalized ZnO nanoparticles with benzoxazine terminated silane to form BS-ZnO. The benzoxazine terminated silanes ended on a simple benzoxazine function (see Figure 1.1) and BA-a benzoxazine was selected for the matrix.

Figure 3.5 shows the FTIR spectra and TGA curves for ZnO and BS-ZnO. From these graphs they could confirm the functionalization of the zinc oxide. On the FTIR, the peak at 927 cm^{-1} corresponds to the N – C – O stretching mode and indicates the presence of the benzoxazine functionality. Other peaks that appeared are linked to the silane and its linkage to the benzoxazine and ZnO. The TGA curve shows a higher weight loss for the BS-ZnO than for the pure ZnO, this stems from the presence of an organo-silane framework on the surface of the ZnO, thus confirming its functionalization.

The authors produced several blends of neat polybenzoxazine, poly(BA-a), with different concentrations of BS-ZnO. These blends were characterized for their thermal and mechanical properties. FTIR was first applied to confirm that the polymerization occurred well. The absence of the peak at 927 cm^{-1} on the FTIR of the polymerized samples confirms the ROP. Moreover, the appearance of peaks at 873 and 1498 cm^{-1} was attributed to the tetra-substituted benzene ring, which further supports the ROP of the benzoxazine.

With DSC, they found evidence that the T_g increased with BS-ZnO concentration, probably because of a restriction of segmental motion or a nano-reinforcement effect because of the presence of ZnO and the interaction between BS-ZnO with the benzoxazine matrix. Figure 3.6a shows the resulting TGA curves for their blends. A

considerable increase in char yield was observed for the blend at 10wt% BS-ZnO.

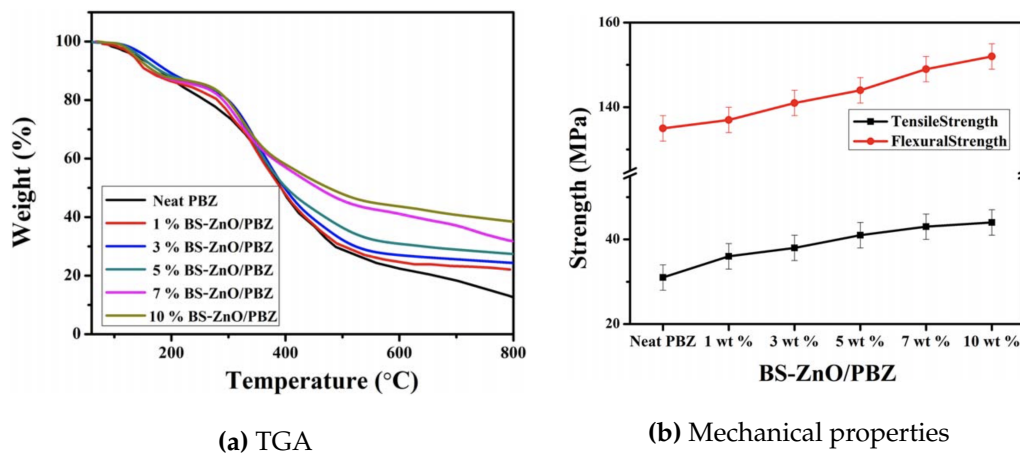


FIGURE 3.6: pBA-a with various loads of BS-ZnO: TGA curves and mechanical properties. [64].

Finally, as illustrated in Figure 3.6b, an increase of the tensile and flexural strength of the benzoxazine matrix occurred upon addition of BS-ZnO. The tensile strength improved from 31 to 44MPa and the flexural strength from 135 to 152 MPa. This improvement was linked to the ZnO nanoparticles, which added resistance to the applied stress and contributed to the stress transfer [64].

The results from both studies presented above may be very helpful for the experimental part of this work, especially for the part where the effect of ZnO nanoparticles on the T-DDM benzoxazine resin is studied.

Chapter 4

Analysis techniques

In Chapter 5 of this work, several techniques are used for the analysis of the samples. This chapter aim is to briefly discuss those techniques and the principles from which they derive.

Thermal analysis techniques are the most important to this work as they were required for all sections of the experimental part. In particular, Differential Scanning Calorimetry, DSC, and Thermogravimetric Analysis, TGA, were used in this study. Due to their importance in this study, those two techniques will be discussed in detail in this chapter.

The other techniques, were used in a smaller extent and will thus only briefly be introduced. Those techniques are Secondary Electron Microscopy or SEM; Transmission Electron Microscopy or TEM; and Fourier Transform Infrared Spectroscopy or FTIR.

4.1 Thermal analysis techniques

Thermal analysis and calorimetry refer to a wide range of techniques. Those techniques are measurement methods in which a change of temperature of the sample is investigated. Thus, these methods study some properties given a certain imposed variation of the sample temperature over time. For instance, in the case of DSC the heat received or generated by the sample is measured, while in TGA the mass variation of the sample is measured.

Usually, the thermo-analytical instruments and the calorimeters can also be used for isothermal experiments and as a result, methods allowing the experiment to be conducted at isothermal temperatures also belong to the field of thermal analysis and calorimetry [65].

One feature which is common to most thermo-analytical methods is that they are not equilibrium methods. In practice, it is not possible to change the sample temperature in a way that a thermal equilibrium is obtained between the sample and its surroundings and the inside of the sample. This lack of equilibrium, which is especially marked when working under dynamic temperature conditions, can be accounted for by the determination of the thermal lag. However, even with a correction factor, several effects should still be considered. For example, the sample is rarely homogeneous and therefore neither is the temperature within the sample. Also, upon heating, the sample often consumes or generates heat and undergoes variations in mass, volume, composition, and structure.

Thus, the results obtained by those methods depend both on the operation parameters, such as the heating rate, atmosphere or pressure, and on the sample parameters, such as mass, homogeneity and shape [65].

Because thermal analysis techniques involve temperature changes of the analyzed sample and its environment, precise sensors to measure the temperature are required. Temperature can be measured based on electrical conductivity, the pressure of a confined gas, black-body radiation laws or the Seebeck effect [66]. However, most TGA and DSC devices used for thermal analysis use thermocouples, which are based on the Seebeck effect.

This Seebeck effect, or thermoelectric effect, is based on the production of an electromotive force and the resulting electric current in a loop of material composed of two dissimilar conductors and when two junctions are maintained at different temperatures. Thus, if two semiconductors are linked together at the hot point in the furnace and a temperature difference ΔT is maintained between this hot point and a cold point outside the furnace, a voltage is generated at the semiconductor junction at the cold point [67]. In modern applications, an isothermal box is used to set the temperature of this cold point slightly above room temperature, due to the ease to maintain this temperature. However, this requires adjustments of the temperature versus voltage curves used to convert the signal into temperature, because they are calibrated for a cold point at 0°C.

Table 4.1 mentions some thermocouples which are often used. Their operation conditions, such as the applicable temperature range and the appropriate atmosphere, are also listed.

TABLE 4.1: Thermocouples used in TGA and their operation conditions [68].

Type	Thermocouple composition	Temperature range [°C]	Atmosphere
T	Cu/Cu-Ni	-250 to 850	air, inert
E	Ni-Cr/Cu-Ni	-250 to 850	inert
J	Fe/Cu-Ni	0 to 760	air, inert
K	Ni-Cr/Ni-Al	-270 to 1260	air, inert
S	Pt/Pt-10%Rh	0 to 1600	air, inert
R	Pt/Pt-13%Rh	0 to 1600	air, inert
-	W/W-26%Re	0 to 2700	inert, reducing

Another common sensor, which is mainly used in DSC, is the platinum resistance thermometer. This sensor determines the temperature by measuring the electrical resistance of a piece of pure platinum wire. Its temperature range and sensitivity are listed in Table 4.2.

TABLE 4.2: Platinum resistance thermometer properties [69].

Sensor composition	Temperature range [°C]	Sensitivity $d(R_\theta/R_0)/dT$ at 200°C
Platinum	0 to 1600	0.00374

Finally, for all types of temperature sensors, a calibration is required using fixed points on the international temperature scale. The choice of sensor depends on its sensitivity and the needs of the user, but also on its resistance to chemical attack, its temperature range, and its mechanical stability.

4.1.1 Thermogravimetric Analysis

Thermogravimetric Analysis or Thermogravimetry is a technique where the change in mass of a sample in a controlled atmosphere over a temperature range and at a certain heating rate is measured. Figure 4.1 illustrates the apparatus for TGA schematically. The basic principle of TGA is quite simple: the mass of a sample placed on a thermobalance in a furnace is measured. But instead of measuring it at a certain temperature, it is measured over time in the furnace, which follows a given temperature program.

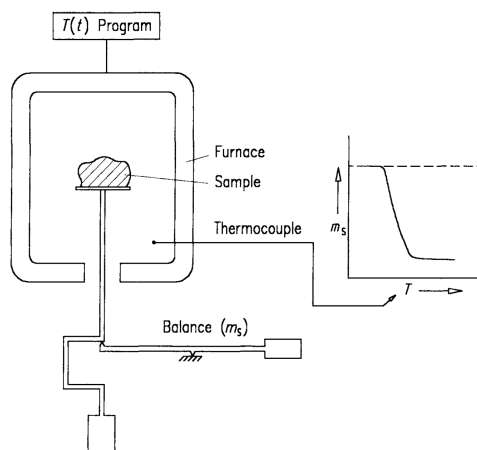


FIGURE 4.1: Schematic of the TGA apparatus [65].

The critical part of instrumentation within a TGA apparatus is the thermobalance. Thermobalances nowadays in use are based on electrobalances. In electrobalances, a taut ribbon suspension is connected to an electrical torque motor, which has a large linear range of torque versus electrical current, and placed in the fulcrum. Moreover, weights are placed on the tare pan to reach a weight which lies within the linear range of the motor. At the start of the measurement, the null position is determined through an arrangement using a lamp, mask, and a photodetector. This position is then fixed and maintained via a precise control of the current brought to the motor. If the change in weight occurs for the motor range in which a linear relationship between the torque and current is applicable, the variation in current required to keep the balance at the null position will be directly proportional to the weight change and according to the current flow reflect whether a gain or a loss of sample weight occurred.

Electrobalances are therefore especially useful for electronic data acquisition systems as the current can directly be translated into a voltage and read by a digital voltmeter. Additionally, they are very sensitive with a sensitivity approaching $0.1 \mu g$ in a static atmosphere and at room temperature [66].

Thermobalances differ from conventional balances because they can function, while allowing the sample to be heated or cooled in a controlled manner in the furnace. Moreover, the desired pressure and atmosphere must be maintained during the measurement. In the construction and operation of a thermobalance, three categories of factors are of importance: those associated with temperature, atmosphere, and the sample itself. Also, the various sources of errors must be considered.

Control of temperature

The control of the temperature in TGA involves the furnace, the temperature sensors, and their calibration. The furnaces used in TGA are either convective or radiative, because heat transfer by conduction would disturb the sample [66]. The temperature sensors and their placement with regard to the sample are essential in the control of the temperature. These sensors, usually thermocouples, can be placed either at the heating element, providing a better control and stability of the temperature environment, or at the sample point. While a thermocouple at the heating point has a quicker response and helps avoid overshooting, it ignores the changes of enthalpy and heat capacity of the sample during reactions. Also, changes in thermal conductivity within the atmosphere are essentially overlooked. Therefore, separate sensors are usually used for the control of the heating program and the sample temperature [66].

Finally, a precise calibration is needed to have accurate measurements. Two common calibration methods are the fusible link and the magnetic standard methods. The first is based on a thin wire of pure metal suspended from the sample support. Upon melting of the wire an abrupt loss in weight will be reported and the temperature can be calibrated with respect to the melting temperature of the selected metal. The latter approach is based on magnetic standards composed of pure metals or alloys possessing a sharp and well-defined value of the Curie temperature T_c .

Control of atmosphere

Experiments performed by TGA all rely on the atmosphere surrounding the sample. Next to an oxidizing atmosphere composed of air; helium, nitrogen, or argon can be used to obtain an inert atmosphere. These purge gases are used when purity is required but also to filter clean and deoxygenate the gas flow.

However, depending on the direction of the gas flow, the weight measured by the balance can be positively or negatively altered without real weight loss occurring in the sample. Additionally, if the sample is composed of a powder or other volatile materials, the gas flow must be adapted to avoid ejection of particles from the sample due to the incident gas flow, which leads to a false measure of weight loss.

Therefore, for a set of experiments it is important to use the same atmosphere for all tested samples. If a small error is generated by the atmosphere or the gas flow, it will be similar in all measurements. For non-volatile samples a purge gas flow of 100 ml/min is often used; and for powdered samples, which risk to be disturbed by the gas flow, a lower gas flow of 50 ml/min is common [38, 41].

Sources of error

Measurement errors can never be completely eliminated and those related to temperature can be assigned to three categories: the sensor, the rate of heating, and the heat of reaction [68]. The control of the atmosphere can also be at the origin of a certain range of errors. In this area, the most important source of error is due to the buoyancy effect. The differences in volumetric weight of gases must be accounted for, or the measurement of the sample weight will be biased. For instance, a cm^3 of air weights approximately 120 μg at room temperature and pressure of 1 atm. In the case of hydrogen this is below 9 μg and for carbon dioxide about 196 μg [66].

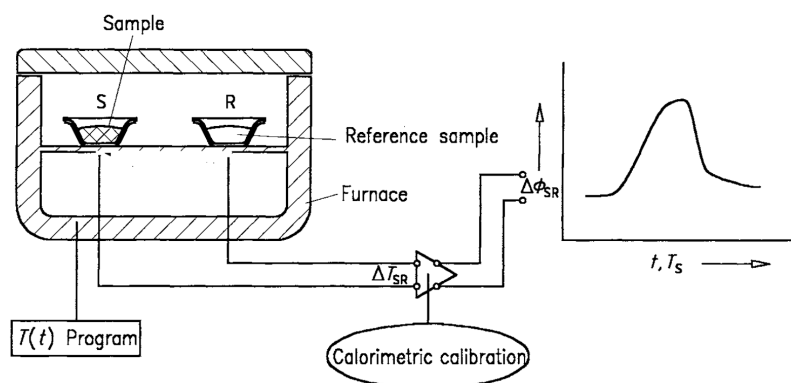


FIGURE 4.2: Schematic of a disk-type heat-flux DSC apparatus [65].

4.1.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry is - as indicated by its name - a technique in which the difference in heat flow to a sample and to a reference is measured by a calorimeter. The heat flow rate to and from the sample is analyzed while the sample is subjected to a temperature profile.

Two kinds of DSC exist: heat-flux and power compensation DSC. In the first kind, the difference in temperature between the sample and a reference is measured as a direct measure of the difference in heat flow rates to the sample and the reference. In this kind, a calorimetric calibration is required to assign the heat flow rates. Meanwhile, in power compensation DSC the difference in power supplied to the sample and the reference, to keep their temperatures as closely together as possible, is recorded.

Figure 4.2 depicts a heat-flux DSC of the disk-type. In disk-type DSC, the crucibles, which contain the sample and the reference, are placed on a disk. Temperature sensors, which are part of the disk or deposited on its surface, measure the temperature difference ΔT_{SR} between both crucibles [70]. Another type of heat-flux DSC is the cylinder-type, where the crucibles in the form of cylindrical cavities are part of the apparatus itself.

Additionally, specific DSC modes such as Modulated Temperature DSC or MTDSC exist. In MTDSC, the difference in heat flow rate or power to the sample and the reference are measured, as was normally done with classic DSC. In this case, however, this difference is recorded over time while the specimens are subjected to a modulated temperature program.

The derivatives of DSC curves can also be used. This is usually done to distinguish between transitions. For instance, the first derivative curve of a glass transition results in a peak with an area proportional to the value of ΔC_p , the change in heat capacity occurring at the glass transition. Another example with the second derivative concerns the onset of a DSC peak. The onset of a DSC peak is given by the maximum of the first peak obtained from this peak in the second derivative curve [70].

The instrumentation and the calibration of a DSC device as well as the interpretation of DSC curves will be covered in this subsection.

Instrumentation

A DSC device is composed of several parts. Figure 4.3 shows the major components of such a device. Globally, the parts of a DSC apparatus can be listed in four categories:

- The DSC sensors, their crucibles, and the signal amplifier.
- The furnace, its temperature sensor, and the atmosphere and cooling control components.
- The computer control unit.
- The recorder, plotter, and data processor.

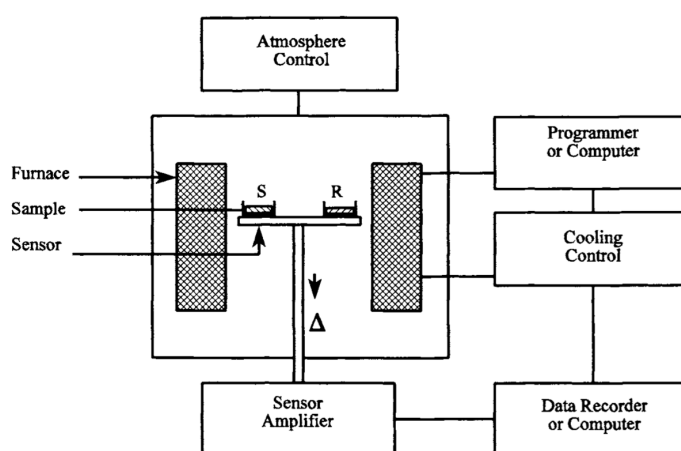


FIGURE 4.3: Schematic of DSC device and processing unit [70].

The sensors, the reference materials, and the crucibles and sample holders in DSC will be briefly considered.

As for all thermal analysis techniques, temperature sensors are required in DSC to measure temperature accurately. Thermocouples and platinum resistance thermometers are the ones which are the most often used in DSC. Also, if a reference material is used, it should be inert over the range of temperatures of the experiment, unreactive to the crucible and sensors, and ideally have thermal properties close to those of the sample [70]. However, as the signal should be independent of the thermal properties of the samples in DSC, an empty pan can also be used as reference. Finally, crucibles and sample holders in DSC were initially part of the DSC device, but nowadays the samples are put into an inert holder, which is then put in the sensor assembly. Many sorts of crucibles exist to accommodate all types of samples. The most common sample holders are made of aluminum and can be used over the range of -180 to 600°C [70]. Other more specific crucibles are made of silver, gold, stainless steel, etc. and are used in a specific context. For instance, stainless steel crucibles are used in DSC under high pressure. All these crucibles can then either be open or closed with a lid; which again can be loosely placed on the holder, cold welded in a press, pierced with a pin, etc.

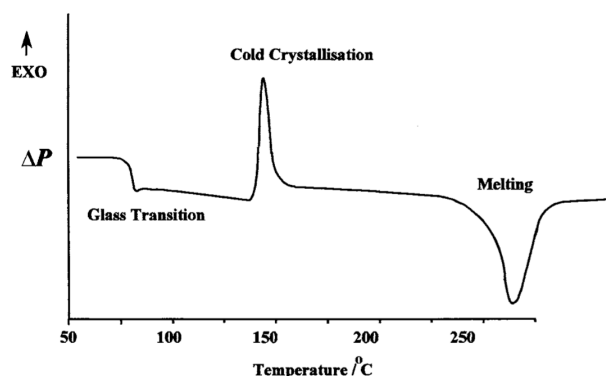


FIGURE 4.4: DSC curve of PET quenched from the melt [70].

Calibration

Before operating a DSC device, it must be checked for reliability and calibrated accordingly for accuracy. Three stages of calibration, with an increasing quantitative accuracy, can be distinguished.

Experimental runs of well-established samples are the first stage. This first stage allows to illustrate the capabilities of the equipment. One common material for these experimental runs is PET quenched from the melt. The resulting curve, illustrated in Figure 4.4, is characteristic with a glass transition in the range of 75 to 85°C, followed by cold crystallization between 130 and 180°C, and melting between 230 and 270°C [70]. While this experimental run cannot be used for temperature calibration, the temperatures of the transitions should lie within the ranges mentioned above. The sensitivity of the device can be tested using samples which are small, dilute or with small thermal changes. The resolution can be measured using samples with two transitions following each other closely in a temperature interval.

Temperature calibration forms the second stage of calibration. Calibration for temperature is done using certified reference materials or CRM, which must be pure, and stable to decomposition and oxidation [71]. Additionally, they should preferably have a low volatility and sharp reproducible transitions. Each calibrant should have been tested independently and be as invariant as possible in its properties. Depending on the source and the specifications, the properties for a same reference materials vary slightly.

Table 4.3 lists some of the reference materials used for calibration in DSC. Depending on the temperature range of the experiment, one calibrant may be preferred over another. In DSC, a widely-used reference material for temperatures between 0 and 300°C is indium with a melting point at 156.61°C.

Calorimetric calibration, the third stage of calibration, is necessary for the calorimetric measurements to match those of the experimental runs of the sample. This calibration can be executed based on the transition energies of reference materials, the specific heat capacity or through direct electrical calibration [70].

In the case of calibration with reference materials, the same materials as for temperature calibration can be used. Table 4.3 also lists the enthalpies of fusion of those reference materials. After a run has been completed with the calibrant, the enthalpy

of the fusion peak must be measured and corrected with respect to the enthalpy of fusion of the reference material.

TABLE 4.3: Materials for temperature and heat flow calibration in DSC [71].

Reference material	Melting point [°C]	$\Delta_{fus}h$ [Jg^{-1}]
Mercury	-38.86	11.469 ± 0.008
Indium	156.61	28.71 ± 0.08
Tin	231.92	60.55 ± 0.13
Zinc	419.53	108.6 ± 0.5
Aluminium	660.33	401.3 ± 1.6

Interpretation DSC curves

A first aspect to consider in the interpretation of DSC curves is their baseline. If the baseline is constant or shifts due to a variation in specific heat outside a peak, the interpretation of the DSC curves is easy, and the enthalpy corresponding to a peak is given by the integral of this peak with respect to its baseline. Because, baselines across a peak are easy to construct, if the baselines preceding and following the peak are collinear. However, problems arise when the sample properties change over the peak, especially the specific heat. In this case, the baselines can have different ordinates and even different slopes.

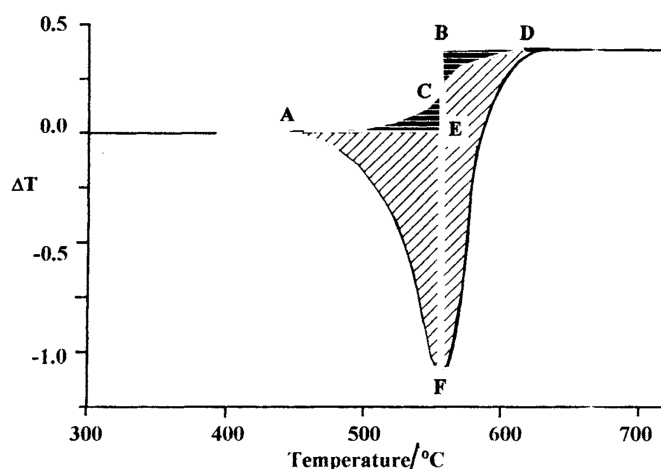


FIGURE 4.5: Area measurement with baseline shift [70].

With varying baselines across a peak, drawing a straight line between the onset and the endset of the peak results in a peak area which does not correspond to the heat of reaction. One way to measure the peak area is to compute a sigmoidal baseline as is done in Figure 4.5. Yet, this does give the exact heat of reaction, but an approximation much closer than the straight line. Other baselines, such as splines, can also be used in cases where a change in slope is observed.

Moreover, the interpretation of DSC curves can be difficult due to the possibility for many artefacts. These artefacts can have many origins such as the sample itself, the crucible in which the sample is contained, the sensors, or the atmosphere. For instance, the entry of cool air into the cell will lead to noise on the curve, and a movement of a sample into its pan results into a small fluctuation of the signal.

Figure 4.6 represents different types of possible artefacts on a DSC curve. The two examples given above are shown in *c* and *a* of the figure.

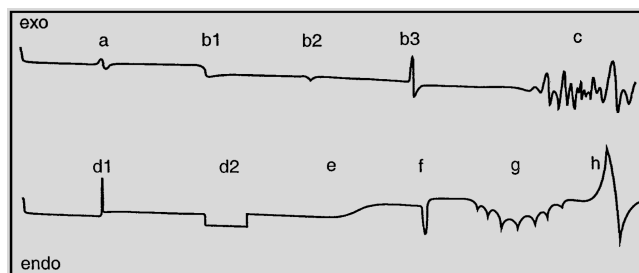


FIGURE 4.6: Types of artefacts observed in DSC curves [72].

However, apart from artefacts and supposing a correct calibration, the typical features of a DSC traces can be put in three categories of events [72]:

- Endothermic events: melting, sublimation, solid-solid transitions, desolvation, chemical reactions.
- Exothermic events: crystallization, solid-solid transition, decomposition, chemical reactions.
- Baseline shifts: glass transition.

DSC is widely used for the thermal characterization of polymers. For thermoplastic polymers, two thermal events are usually observed. These effects are the glass transition, which results in a baseline shift in the endothermic direction due to a change in the specific heat, and the melting endotherm. However, for semi-crystalline thermoplastic polymers, a third exothermic event appears due to the crystallization of the polymer. These events can be seen in Figure 4.4.

For thermosetting polymers, the observed events are T_g and the exothermic peak due to the curing reaction. The T_g is measured by the intersection of the slope of the shift and the original baseline; and the heat of reaction is proportional to the integral of the exothermic peak associated with the reaction. Yet, other physical effects can interfere with the reaction or secondary reactions can be present, which then complicates the evaluation of H_r [72]. Once cured, thermosets only show a T_g in DSC, which is generally much higher than the initial T_g of the uncured resin.

Thus, the main events which are of interest for bifunctional benzoxazines, which are thermosets, are the glass transition and the exothermic peak of the curing reaction, but if the benzoxazine resin is not well degassed endothermic desolvation also appears. Therefore, on a typical DSC curve for benzoxazine, a baseline shift due to the glass transition, followed by an exothermic peak for the reaction can be expected. Around the evaporation temperature of the solvent specific to the resin, an endothermic peak can also appear.

4.2 Other techniques

Next to thermal analysis techniques, three other techniques were used in the experimental part of this work. The first two, SEM and TEM, were mainly used to analyze the dispersion of zinc oxide particles within a benzoxazine matrix. In a lesser extent, SEM was also used to characterize the fracture surface of the samples. FTIR was also

employed on samples with zinc oxide particles but, in this case, to study the possible interactions of the particles with the benzoxazine matrix.

This section will briefly introduce each of these techniques and the main principle they are based on.

4.2.1 Transmission Electron Microscopy

Transmission Electron Microscopy or TEM is based on the transmission of a beam of electrons through a sample to form an image. Because the signal from the transmitted electrons must be strong enough, the specimen is usually an ultrathin section of less than 100 nm thick placed on a grid. From the interaction of the electron beam with the specimen, as it goes through it, an image is formed, which is then focused and magnified on an imaging device.

The very high resolution that can be achieved by TEM is due to "de Broglie" wavelength of electrons, which is much smaller than that of light. The resolution of TEM even allows to capture details as small as atoms.

The contrast of low magnification TEM images derives from the difference in absorption of electron by the specimen due to differences in thickness and composition. At higher magnifications, however, the intensity of the image stems from complex wave interactions and a high level of expertise is needed for the analysis of the images.

The maximum resolution d of a traditional light microscope is determined by the wavelength of the photons λ and the numerical aperture of the device, as shown in Equation (4.1).

$$d = \frac{\lambda}{2n \cdot \sin(\alpha)} \approx \frac{\lambda}{2 \cdot NA} \quad (4.1)$$

The wavelength λ of visible light ranges between 400 and 700 nm. Electrons, which have as all matter both wave and particle properties, have a wavelength λ_e that depends on their kinetic energy. Equation (4.2), also called the de Broglie equation, gives the expression of the wavelength.

$$\lambda_e = \frac{h}{\sqrt{2m_0E\left(1 + \frac{E}{2m_0c^2}\right)}} \quad (4.2)$$

where h is the Planck constant, m_0 the mass of an electron and E the energy of the accelerated electron. Given the high energy of the electron beam emitted from the electron gun, this wavelength λ_e is much smaller than the one of photons, and thus a very high resolution is obtained [73].

Figure 4.7 illustrates the general lay-out of the components in a TEM device. From top down, a TEM is composed of an electron gun, followed by condenser lenses to form the beam and a deflector coupling electromagnets and electrostatic fields to focus and shift the beam. Once the beam is transmitted through the sample, objective lenses focus the beam. Finally, projector lenses are used to expand the beam onto a fluorescent screen or another imaging component.

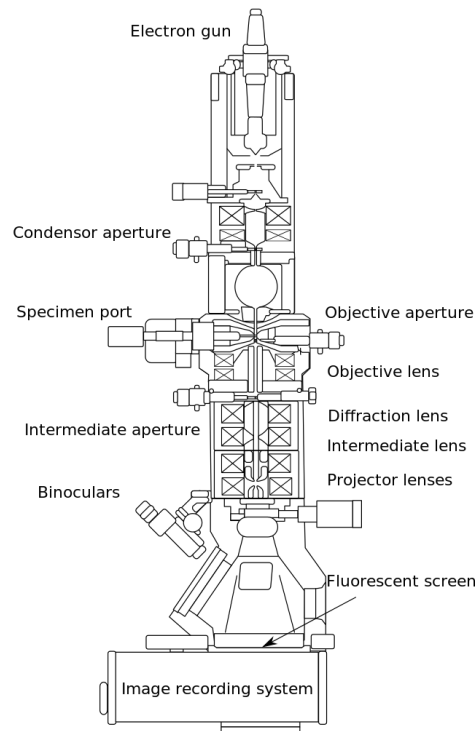


FIGURE 4.7: Schematic drawing of TEM apparatus [73].

4.2.2 Scanning Electron Microscopy

Scanning Electron Microscopy or SEM is a microscopy technique that uses an electron microscope to produce images of samples by scanning their surface with a focused beam of electrons. Due to interactions between the electrons of the beam with the atoms at the surface and first layers of the material, a signal is produced which contains information on the topography and the composition of the sample surface. Several types of signal can be produced. The most common SEM mode is to produce and detect secondary electrons, but, for instance, back-scattered electrons or characteristic X-rays can be used as well.

In secondary electron imaging, the detected secondary electrons originate from the top layers of the specimen, which yields very high resolution images of its surface. In the case of back-scattered electrons, they come from deeper within the sample as they are in fact electrons reflected from the primary electron beam through elastic scattering. Thus, a lower resolution is obtained in this mode.

The sample preparation is important in this technique, because the samples should be able to withstand vacuum conditions, the high-energy electron beam, and the build-up of electrical charge. When an overview of the bulk of the sample is wanted, the fracture surface of the specimen is studied by SEM. To produce an adequate fracture surface, soft samples need to be cooled down, sometimes to cryogenic temperatures. Also, to image in conventional SEM, the samples must be electrically conductive to prevent electrostatic charge accumulation due to the electron beam. Therefore, non-conducting samples are usually coated with an ultrathin layer of conducting material, usually gold, chromium or carbon, through high-vacuum evaporation or low-vacuum sputter coating.

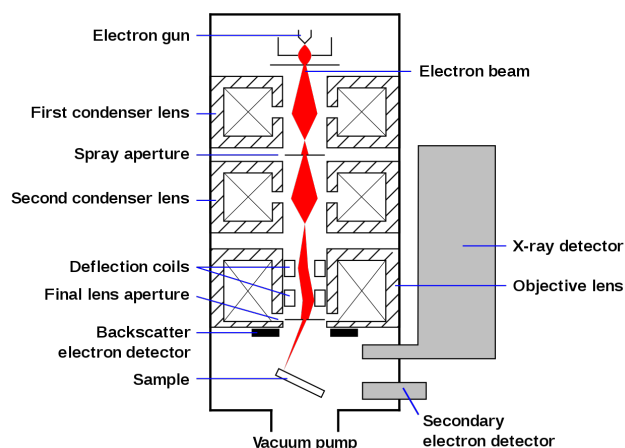


FIGURE 4.8: Schematic drawing of SEM apparatus [74] .

Figure 4.8 depicts a scanning electron microscope schematically. The electron beam is typically generated thermionically from an electron gun, fitted with a tungsten filament. This beam, of energy ranging from 0.2 to 40 keV, is then focused by condenser lenses and finally passes through a deflector, which is used to deflect the beam to raster scan the specimen surface. The incident electron then interacts with the sample in the so-called interaction volume, depicted in Figure 4.9, which size depends on various factors, such as the energy of the primary beam. Specific detectors then detect the emitted particles at each point from the scanned specimen surface (secondary electrons, back-scattered electrons, etc.) and amplify this signal to produce an image. This image is in fact a distribution map of the intensity of the emitted signal. Finally, images can be obtained with a magnification over a range of 6 orders of magnitude, from about 10 to 500000 times magnification and with a resolution under 1 nm [74].

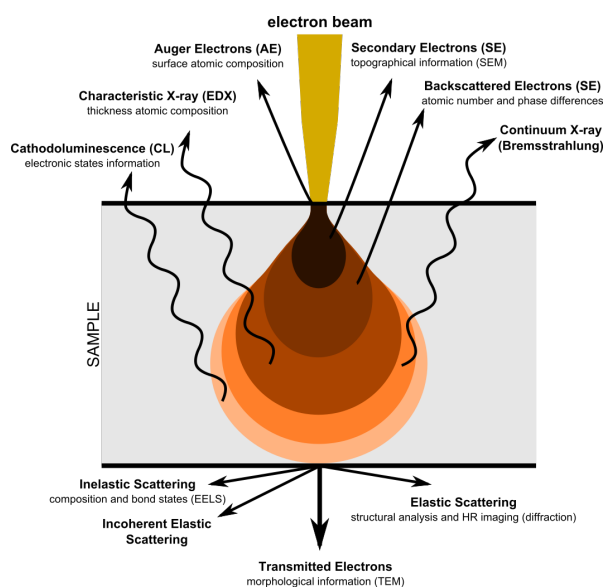


FIGURE 4.9: Signals emitted from the interaction volume [74].

4.2.3 Fourier Transform Infrared Spectroscopy

In Fourier Transform Infrared Spectroscopy, abbreviated as FTIR, the infrared spectrum of absorption or emission of a gas, liquid or solid is measured. The technique has been named FTIR because it works in the infrared spectrum and because a Fourier transform is necessary to convert the measured raw data into the spectrum. The main advantage of the spectrometer in FTIR over dispersive spectrometers is that it obtains high spectral resolution data over a wide spectral range.

The concept behind absorption spectroscopy is that spectrometers measure the absorption of light at each wavelength for a certain sample. In dispersive spectroscopy, this is done using a monochromatic beam on the sample. This beam is projected at each wavelength at the sample and the absorption is measured. In FTIR, however, the beam is constituted of an assembly of certain frequencies. Once the absorption is measured, the beam is modified to contain different set of frequencies and the absorption is measured again. This is repeated several times and processed by a computer that determines the absorption linked to each frequency. The beams containing a combination of frequencies start as a broadband light source and pass through a Michelson interferometer which forms those specific beams by blocking the undesired frequencies [75]. Figure 4.10 schematizes the working principle of FTIR as described above.

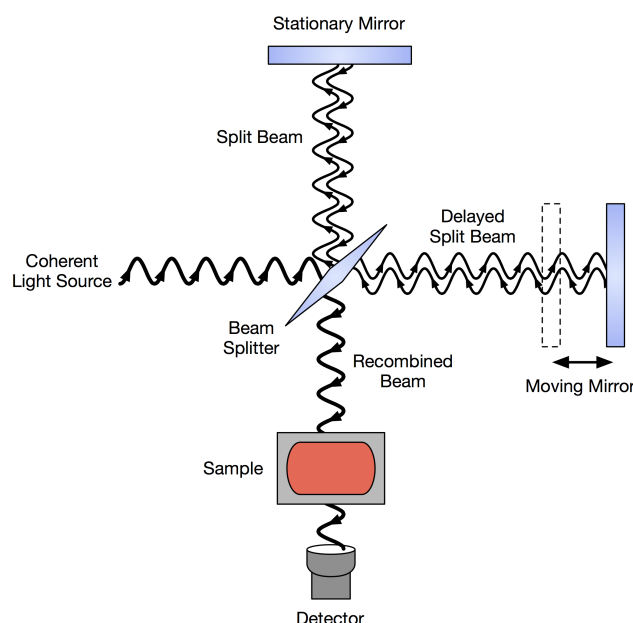


FIGURE 4.10: Schematic of the working principle of FTIR [75].

FTIR has three principal advantages over dispersive spectroscopy [76]. The first is the multiplex advantage. FTIR can collect information from all wavelengths simultaneously. This leads to a higher signal to noise ratio over the same scan time compared to dispersive spectroscopy. Also, a shorter scan time is needed for a given resolution. The throughput is the second benefit of FTIR. Again, a higher signal to noise ratio is obtained because the circular aperture used to restrict the convergence of the infrared beam allows more light through than a slit, which is used in dispersive spectroscopy. Finally, the third advantage of FTIR is its wavelength accuracy. In FTIR, the wavelength scale is calibrated by a laser beam of specified

wavelength that is passed through the interferometer. The accuracy is, in practice, limited to the divergence of the beam in the interferometer, which on turn depends on the resolution.

In a FTIR device, the infrared beam is generated by IR sources. In the mid-IR region, from 5000 to 400 cm^{-1} , silicon carbide heated to approximately 925°C is generally used as source. The beam is then either reflected on or transmitted through the specimen and usually pyroelectric detectors are used to recover the signal. These detectors are sensitive to changes in temperature as the intensity of the incident IR radiation on them varies. Another detector possibility in the mid-IR are MCT detectors. These are based on nitrogen cooled mercury cadmium telluride and provide higher sensitivity or a faster response [75].

Part II

Materials and methods

Chapter 5

Materials and methods

5.1 Materials

The materials used in this study are a T-DDM benzoxazine resin, ZnO nanoparticles, and blends of both components.

5.1.1 T-DDM resin

The benzoxazine selected for the experiments is a T-DDM precursor based on tyrosol and DDM, which was synthesized by Materia Nova in Mons, Belgium. This precursor was already introduced in Chapter 1 of this work and is shown in Figure 1.13.

The raw components to produce the bifunctional T-DDM are tyrosol for the phenol component, DDM for the diamine, and paraformaldehyde. The origin and purity of these components was not mentioned by Materia Nova. On one hand, DDM or 4,4'-diaminodiphenylmethane is known to be used as an epoxy hardener and has already been used in several benzoxazines. On the other hand, tyrosol or 4-(2-hydroxyethyl)phenol was never found in combined use with benzoxazines, but has the advantage to be bio-sourced.

This "home-made" resin produced by Materia Nova was provided in powdered form and has a yellow aspect when uncured that turns red-orange upon curing. Because the resin is produced on a laboratory scale, the batches can differ from each other. For example, the resin can still contain a certain amount of solvent or other impurities, and if the purity of the precursor varies it can affect its crystallization behavior from one batch to another. Moreover, small differences between two batches can result in variations of the heat of reaction, the degradation temperatures, and the char yield. The manufacturer, Materia Nova, specified a T_g of 167°C after curing of the T-DDM resin in DSC, and their value of T_g measured by DMA on a cured sample was 198°C.

5.1.2 ZnO nanoparticles

The zinc oxide used in this study is manufactured by the Zinc Chemicals division of Umicore and is in powdered form. This zinc oxide, with the commercial name *Zano®20*, is composed of nano-sized ZnO particles which can be used in plastics, fibers, and textiles [56]. Also, *Zano®20* has a controlled and narrow particle size distribution, which makes it a ideal additive for a wide range of applications. This particle size distribution is illustrated by Figure 5.1. The nano-sized ZnO particles

are of average 30 nm in diameter. The properties, synthesis and use in benzoxazines of ZnO nanoparticles were already discussed in Chapter 3.

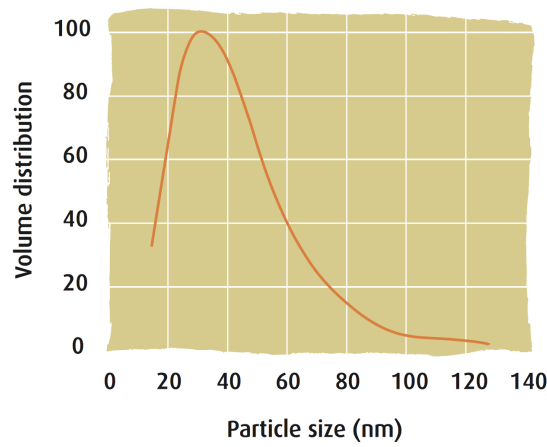


FIGURE 5.1: Particle size distribution of *Zano*® [77].

5.1.3 Blending of components

Blends of zinc oxide with TDDM were prepared at 0.5, 1.0, 2.5, 5.0, 10.0, 25.0 and 50.0wt% of ZnO. First, small doses of ZnO were weighed in a beaker. Then, the mass of T-DDM to be added was calculated according to the desired composition of the blend with the following formula:

$$m_{T-DDM} = \frac{m_{ZnO}}{wt\%_{ZnO}} \times 100 - m_{ZnO}. \quad (5.1)$$

Once the two components, which are both in powdered form, were put together, they were given a first mix with a spatula. The resulting mixture was then dissolved into chloroform. To obtain a good dispersion of the ZnO nanoparticles, further mixing of the components was done with an Omni-Ruptor 400 from OMNI International Inc. The mixture, dissolved in chloroform, underwent sonication pulses of 30 seconds broken up by pauses of 30 seconds between two pulses. The blends that were produced and their respective ZnO loadings and sonication times are listed in Table 5.1. The range of times for sonication was chosen accordingly to a previous study conducted by A. Raynaud on the effect of ZnO nanoparticles on a pPDA benzoxazine resin [4].

TABLE 5.1: List of the produced blends with their ZnO concentration and sonication times.

ZnO [wt%]	$t_{sonication}$ [s]				
	30	90	270	360	540
0.5	X	X	X		
1.0		X			
2.5		X			
5.0	X	X	X	X	X
10.0		X			
25.0		X			
50.0		X			

In a next step, the samples were degassed in a preheated oven at 150°C under vacuum. To ensure that all chloroform was degassed from the sample, the pressure in the oven was brought to 200 Torr and then put back to vacuum. This cycle was repeated several times, until no bubbles appeared on the sample surface anymore. Then, a part of the still uncured samples was collected, mainly to be used in DSC experiments. Finally, the rest of the samples were cured according to the following cycle: 2 hours at 150°C, 4 hours at 180°C and 2 hours at 200°C. In between those isothermal segments, dynamic segments in the form of ramps at 2°C/min were added.

5.2 Methods

Several techniques were used to study the samples and were discussed in Chapter 4. For each of these techniques the different methods applied to study the samples are discussed in this section.

5.2.1 DSC methods

DSC experiments were conducted on a robotic *DSC 821e* from Mettler Toledo in 40 μ L aluminum pans. Samples of approximately 3 to 5 mg were collected for the isothermal experiments, while samples between 4 and 10 mg were used for the dynamic measurements. The smaller sample weight required for isothermal experiments allows the sample to adjust rapidly to temperature changes in the oven and, thus, to obtain a more homogeneous temperature over the specimen. Also, prior to large series of experiments, an Indium check was used to calibrate the DSC device in temperature and heat flow. All experiments by DSC were executed in nitrogen atmosphere under a flow of 50 mL/min. The working principle of DSC was explained in Chapter 4, where the analysis techniques used in this work were presented. The methods used in DSC are subdivided according to their objective: (i) determining the curing kinetics, (ii) optimize the cure cycle of the resin, and (iii) study the effect of ZnO on T-DDM.

As a first series of experiments by DSC, the heat of reaction and the peak temperature of the neat resin were evaluated on three samples in a dynamic heating from 30 to 300°C at a rate of 10°C/min. The pure ZnO nanoparticles were also tested by DSC with the same method.

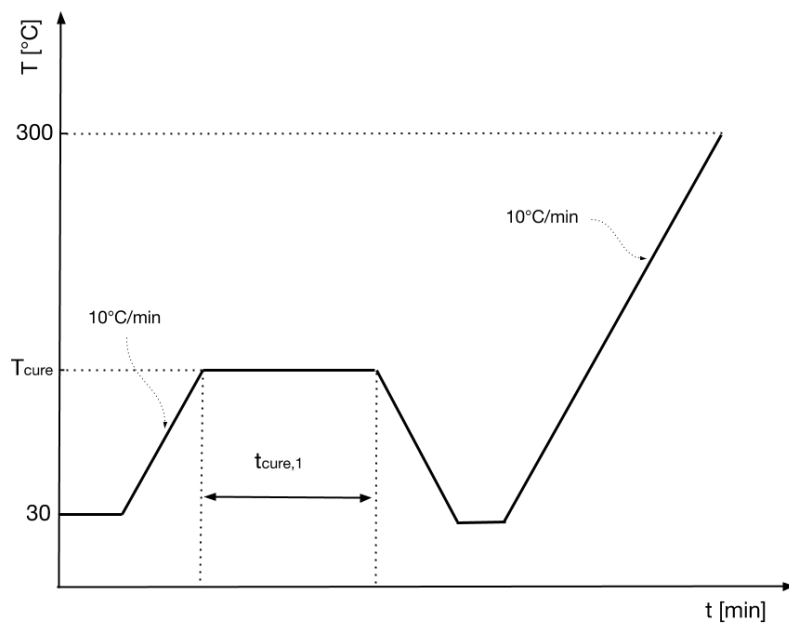
Curing kinetics

Both isothermal and dynamic DSC experiments were conducted to establish the curing kinetics. The isothermal measurements were conducted at 160, 170, 180, 190, 200 and 220°C with a certain protocol. After a stabilization time of 2 minutes at 30°C, the samples were heated at 10°C/min to a first level at 120°C. Then, after 2 minutes at 120°C, they were again heated with a ramp of 10°C/min until they reached the desired isothermal temperature. Such a heating procedure for the isothermal experiments was proposed by Ishida and Rodriguez [16]. Once this temperature was reached, the samples were cured isothermally for 60 minutes.

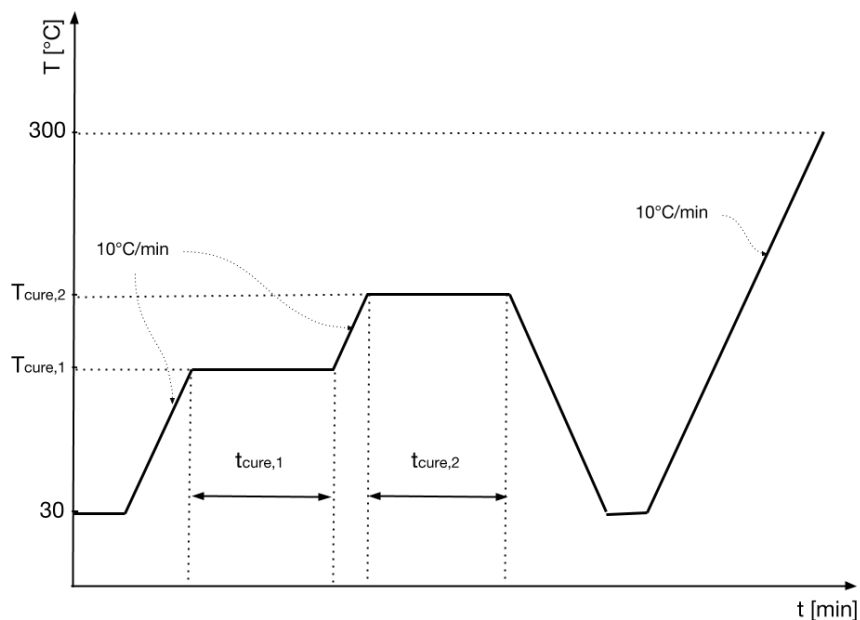
The non-isothermal experiments followed another method. First, the temperature of the sample was stabilized at 30°C. Then, the samples were dynamically heated till 300°C at a certain rate. This heating rate varied between 5, 10 and 15°C/min.

Cure cycle optimization

For the optimization of the cure cycle, the experiments conducted by DSC required an isothermal run followed by a dynamic run to measure the residual enthalpy. Several sets of experiments were performed both on neat T-DDM and on a blend with 10wt% ZnO sonicated for 90 seconds.



(a)



(b)

FIGURE 5.2: Temperature versus time cure profiles with dynamic heating: (a) single T_{cure} (b) different T_{cure} .

The various series of cure cycles applies to the neat T-DDM resin are listed in Table 5.2. In a first set of experiments with only one stage of cure, cure cycle series (1), the residual enthalpy was measured for curing temperatures T_{cure} of 150, 165, 180, and 200°C each with curing times t_{cure} of 15, 30, 60, 90 and 120 minutes. The isothermal experiments were constructed such that after a stabilization period at 30°C, the samples were heated at 10°C/min to T_{cure} and kept at this temperature for the selected time. After cooling to 30°C, the samples were subjected to a dynamic heating at 10°C/min to 300°C. This cure profile is depicted in Figure 5.2a. The other series of experiments on neat T-DDM, cure cycle series (2) and (3), involved two isothermal curing temperatures and Figure 5.2b shows the cure profile for these series.

TABLE 5.2: List of the cure cycles applied to the neat resin.

Cure cycle series	$T_{cure,1}$ [°C]	$t_{cure,1}$ [min]	$T_{cure,2}$ [°C]	$t_{cure,2}$ [min]
1a	150	15, 30, 60, 90, 120	X	X
1b	165	15, 30, 60, 90, 120	X	X
1c	180	15, 30, 60, 90, 120	X	X
1d	200	15, 30, 60, 90, 120	X	X
2a	150	120	180	30, 60, 90, 120
2b	150	30, 60, 90, 120	180	120
3a	150	60	200	30, 60, 90, 120
3b	165	60	200	30, 60, 90
3c	180	60	200	30, 60, 90

Regarding the experiments conducted on the blend, they were similar to those for the neat resin. The residual enthalpy was measured for curing temperatures T_{cure} of 150, 165, 180 and 200°C each with various cure times t_{cure} . In cure cycle series (2), only (a) was tested, and in series (3) not all $t_{cure,2}$ were executed.

Once the results of these DSC experiments on the neat resin and the blends were analyzed, a last series of experiments was conducted to verify the effectiveness of the proposed cure cycle. For the neat T-DDM, dynamic DSC experiments to measure the residual enthalpy were conducted on samples which had been cured for 60 minutes at 165°C followed by 90 minutes at 200°C. Some samples were also further cured for 30 minutes at 220°C. The cure cycles were applied both in a DSC device and in a furnace to evaluate whether this cure cycle also works for a sample cured in a furnace.

Regarding the blend, the dynamic DSC experiments were applied on samples which had followed the same cure cycles as mentioned above, but solely by DSC.

Effect of ZnO

The dynamic method described previously was employed for the curing or cross-linking of the samples.

DSC experiments to determine the effect of ZnO on the T-DDM benzoxazine matrix were conducted on all blends which are mentioned in Table 5.1. From each of these blends, three samples were taken to be analyzed with DSC. The resulting data were then treated using the *Star^e* evaluation software developed by Mettler Toledo and for each measured property, the mean value was selected and 95% confidence intervals (CI) were constructed.

5.2.2 Dispersion of ZnO nanoparticles by TEM and SEM

The dispersion of the ZnO nanoparticles within the T-DDM matrix was studied by TEM and SEM.

TEM

Nanocomposite blends at 0.5 and 5.0wt% ZnO and at different sonication times were cut to obtain ultrathin 95 nm sections. The sections were cut with a Zeiss microtome using a Diatome histo diamond knife at a cutting angle of 35° under ambient conditions and then collected and placed on a 200 mesh carbonated copper grid. A LEO 922 transmission electron microscope operating at 120 kV was used for the imaging of the sections.

The different samples investigated by TEM are listed in Table 5.3. Samples with a sonication time of 90 seconds containing 0.5 and 5.0wt% ZnO were analyzed with TEM to investigate the effect of an increasing proportion of ZnO particles. Then, TEM images were taken on another sample at 5.0wt% ZnO, but with an increased sonication time of 270 seconds, to show the effect of an increasing sonication time on the dispersion of the particles.

SEM

Samples were studied with SEM on a LEO 982 device at 15.0 kV. The samples had been cut into small sections and metallized beforehand to avoid charge accumulation.

SEM was used on the same blends as TEM, except for the sample at 0.5wt% ZnO which had a sonication time of 30 seconds instead of 90. Later, two additional samples were imaged with SEM, one composed of pure T-DDM and one sonicated for 90 seconds and containing 10.0wt% ZnO to verify whether aggregates become more visible at higher ZnO concentrations. Table 5.3 summarizes the different samples imaged with SEM.

TABLE 5.3: Samples analyzed with TEM and SEM.

ZnO [wt%]	$t_{\text{sonication}}$ [s]	TEM	SEM
0.0	0		X
0.5	30		X
0.5	90	X	
5.0	90	X	X
5.0	270	X	X
10.0	90		X

5.2.3 Thermal stability of the cured blends by TGA

The thermal stability of the nanocomposite blends was obtained by thermogravimetric experiments using a TGA 851e from Mettler Toledo. Those measurements were performed on all blends mentioned in Table 5.1 with the following method under a nitrogen flow of 100 mL/min: after a stabilization time of 2 minutes at 30°C, samples weighing approximately 10 mg were dynamically heated till 800°C at a rate of 10°C/min. Over this whole temperature range, the weight loss of the samples was recorded by the TGA apparatus. Before applying this method to the samples, a

blank curve was run to correct the TGA curve. This method was then used on three specimens of each blend, the neat T-DDM resin, and pure ZnO nanoparticles. The resulting data were then treated using the *Star^e* evaluation software developed by Mettler Toledo and for each measured property, the mean value was calculated and 95% CI were constructed.

5.2.4 T-DDM–ZnO interactions by FTIR

FTIR was used in transmission mode on samples of neat T-DDM and on blends with 0.5 and 5.0wt% ZnO sonicated for 90 seconds. The FTIR spectra were recorded on uncured and cured specimens of these samples. The specimens were crushed to powder to minimize the absorption and limit saturation of the spectrum. These crushed specimens were placed on a KBr crystal and analyzed with a *Spectra Tech Continuum* FTIR device developed by the Thermo Electron Corporation. The spectra were obtained at a resolution of 4 cm^{-1} and with 128 scans. Finally, the background due to the atmosphere had to be removed to obtain the spectrum related to the resin.

Part III

Results and discussion

Chapter 6

Results on neat T-DDM and ZnO

This first chapter in Part III of this work addresses some of the results which were obtained on the neat T-DDM resin and on pure ZnO nanoparticle samples to characterize some of their properties.

6.1 Results on T-DDM

First, SEM was conducted on a sample of pure T-DDM benzoxazine resin to see what type of microstructure of the fractured section could be expected. Figure 6.1 illustrates the resulting fracture surfaces, where river patterns are visible. These river patterns result from the fragile fracture mechanism by cleavage, which explains the small teared-off parts on the edge of the ridges. Next to these river patterns the section surface is smooth.

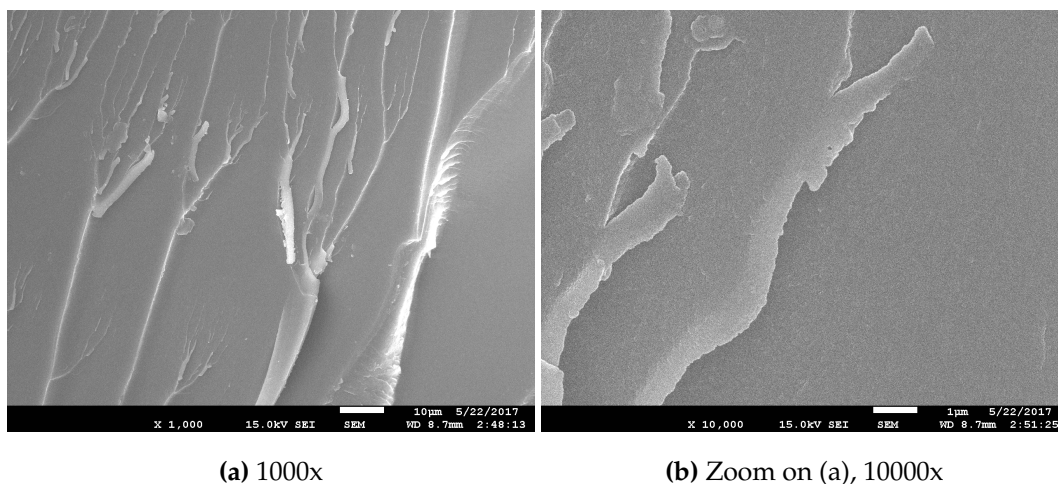


FIGURE 6.1: SEM micrographs at 15.0 kV on a sample of pure T-DDM benzoxazine resin.

Then, three different samples of neat T-DDM resin were analyzed by DSC and TGA. In DSC experiments, the neat T-DDM resin has an average heat of reaction of 279.0 Jg^{-1} and a peak temperature of 225°C . The evaluation of the thermal stability of T-DDM with TGA resulted in a char yield at 800°C of 43.6% and 5, 10, 20 and 30% degradation temperatures at respectively 306, 351, 402 and 446°C . These values, except the degradation temperatures, are listed in Table 6.1.

Because unexpected peaks appeared on some DSC curves of the neat resin, an experiment was conducted where a sample of the resin was heated to 130°C, cooled down to 30°C, and then heated to 300°C. The resulting curves are illustrated in Figure 6.2. Upon the first heating, an exotherm and an endotherm were found. These effects were associated to cold crystallization, due to a rearrangement of some amorphous regions into a crystalline phase, and the resulting melting of the resin. In the melting endotherm, several peaks are observed, which indicates that the crystalline structure is gradually dismantled. The first melting peak corresponds to the melting of the more flawed crystals, then a partial recrystallization occurs into more ordered crystal. The second melting peak corresponds to the melting of these more ordered crystals. The fact that the exothermic and endothermic peaks correspond to the same enthalpy further enforces the hypothesis of crystallization.

Furthermore, when cooling down, a crystallization from the melt was observed, and in the second heating almost no crystallization was found, with a large melting endotherm. These observations support crystallization as the origin for the unexpected peaks even more. Additionally, in DSC curves of partially cured blends, these peaks do not appear anymore. The T_g of the crystallized resin was observed at 40.4°C and a heat of reaction of 279.4 J g^{-1} was measured, which corresponds well with the value provided in Table 6.1.

Finally, if these peaks are not observed in all DSC curves, this is probably since the semi-crystalline behavior of benzoxazine precursors is dependent on their purity. Because different batches of T-DDM were over the whole of the experiments, differences in purity can be expected between them and, thus, the lack of the peaks due to crystallization and melting explained.

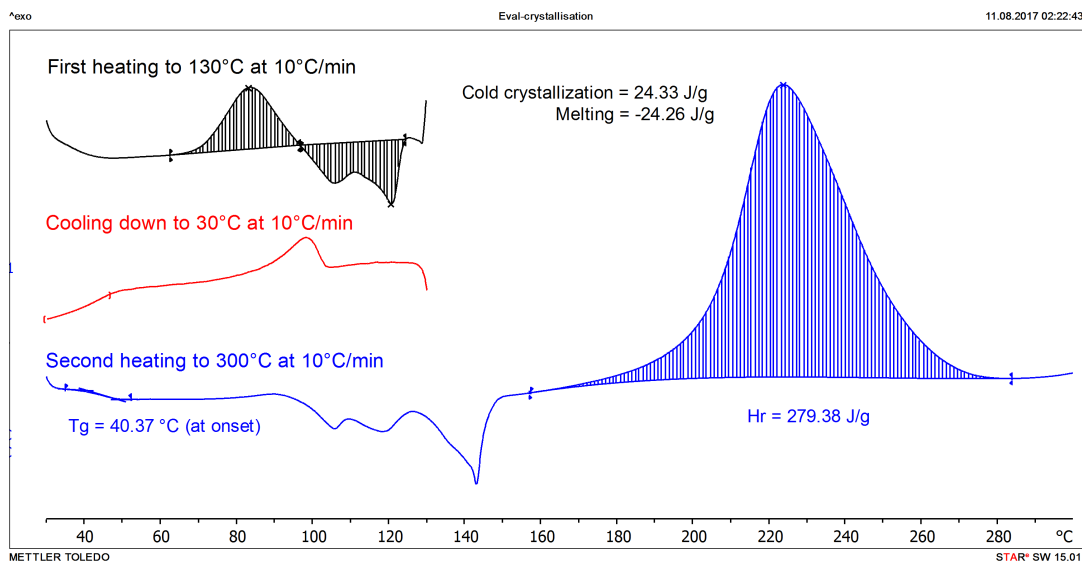


FIGURE 6.2: Crystallization in neat T-DDM resin.

In FTIR, the spectra shown in Figure 6.3 were obtained for the cured and uncured T-DDM. The spectra show that at least two types of polymerization reactions occur. The cross-linking of the benzoxazine via ROP is confirmed due to the decrease of certain characteristic peaks of the benzoxazine ring: (i) at 945 and 1500 cm^{-1} due to the tri-substituted benzene, (ii) at 1333 cm^{-1} due to the CH_2 agitation within the benzoxazine ring, and (iii) at 1226 cm^{-1} due to antisymmetric ether linkage $\text{C} - \text{O} - \text{C}$. Also, the appearance of a peak at 1480 cm^{-1} for tetra-substituted benzene is a

good argument for the occurrence of ROP. The second polymerization mechanism involves the condensation reaction between the hydroxyl functionalities originating from the tyrosol extremities of T-DDM. To support this, a decrease of the peak at 1120 cm^{-1} for the C – O stretching of alcohols [78] and an increase of the peak at 1480 cm^{-1} related to tetra-substituted benzene are observed. These observations are in line with the results put forward by Baqar [7].

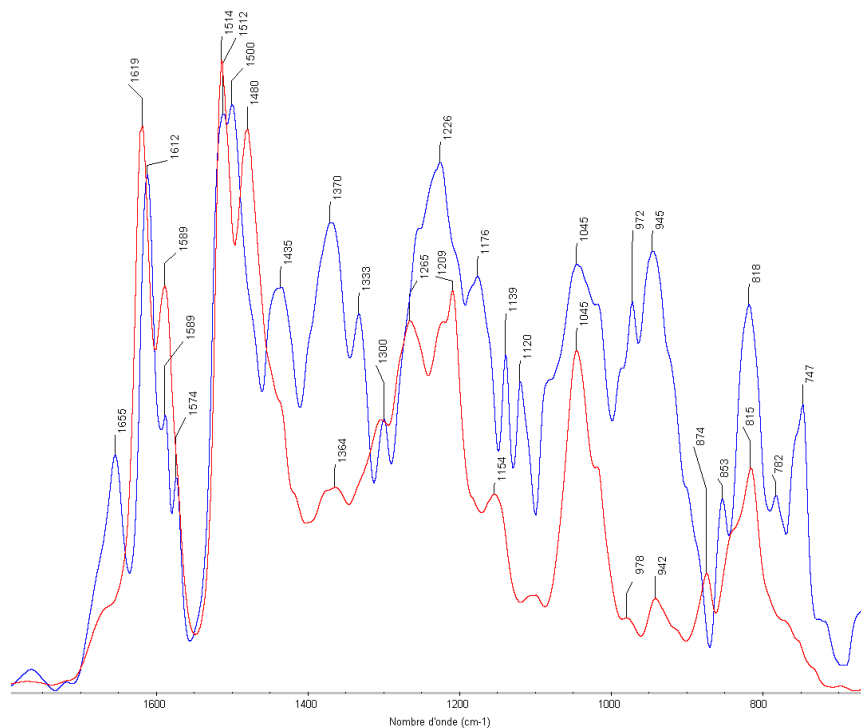


FIGURE 6.3: FTIR spectra in absorption of neat T-DDM from 650 to 1700 cm^{-1} . In blue the uncured sample and in red the cured sample of T-DDM.

TABLE 6.1: Heat of reaction H_r , peak temperature T_p and char yield CY of neat T-DDM and ZnO nanoparticles.

Sample	T-DDM	ZnO
H_r [J/g]	279.0 ± 5.7	-10.0 ± 0.4
T_p [°C]	225.1 ± 0.3	239.5 ± 1.3
CY [%]	43.6 ± 1.4	99.0 ± 0.1

6.2 Results on ZnO

An average particle size about 30.6 nm of diameter for the nanoparticles was obtained from TEM images with the *ImageJ* software, which is in good agreement with the particle size distribution provided by Umicore shown in Figure 5.1. An illustration of the original image and the image treated to determine the particle size is shown in Figure 6.6 for a blend at 5.0wt% ZnO sonicated for 90 seconds and at 10000 $\times$ magnification.

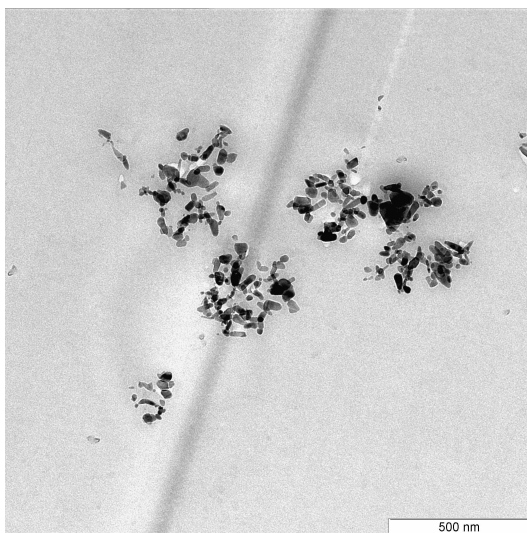


FIGURE 6.4: (a) Original image

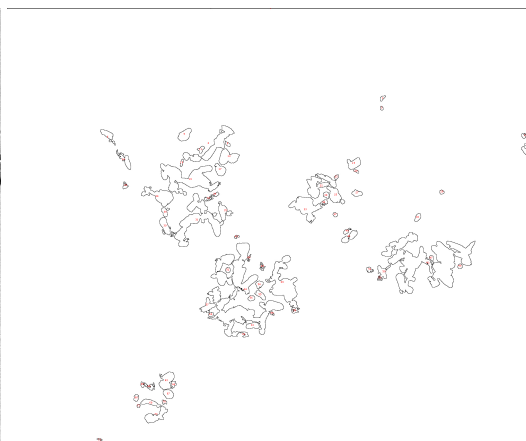


FIGURE 6.5: (b) Treated image

FIGURE 6.6: Evaluation of the average particle size: (a) TEM micrograph of blend with 5.0wt% ZnO, and (b) Image treated by the *ImageJ* software.

Also, three different samples of pure ZnO were analyzed by DSC and TGA. In DSC experiments, a small endothermic peak was found for ZnO nanoparticles around 239.5°C with a value of 10.0 Jg^{-1} . In a TGA experiment, the ZnO nanoparticles showed excellent thermal stability with 99.0% of the initial sample weight remaining at the end of the test. These values are listed in Table 6.1.

Chapter 7

Curing kinetics of T-DDM

This chapter will discuss the curing kinetics of the T-DDM benzoxazine resin based on DSC experiments, isothermal as well as non-isothermal. The resulting curves were treated and analyzed and will be studied to get information on the curing kinetics of T-DDM. The models used to establish the kinetic parameters were discussed in Chapter 2, and the T-DDM resin and DSC experiments were already presented in Chapter 5.

7.1 Analysis of the isothermal DSC curves and critical temperature

Isothermal experiments were run at temperatures between 160 and 220°C. Figure 7.1 compares the DSC curves of the isothermal part of the experiment method for 200 and 220°C. This figure distinctively shows that the curing reaction already started before the isothermal temperature was reached for 220°C, as the exothermal heat flow is above 0.2 at the beginning of the isothermal section. Moreover, the measured heat of reaction for the 220°C isothermal curve was 145.5 Jg^{-1} , while for 200°C it was 275.6 Jg^{-1} , which clearly proves a part of the reaction happens before the isothermal cure temperature. In comparison, the average total heat of reaction measured from non-isothermal DSC curves on the T-DDM precursor is 279.0 Jg^{-1} and the total heat of reaction, taking the residual heat into account, for the isothermal measurements at 200 and 220°C is respectively 283.3 and 145.5 Jg^{-1} . Thus, because the curing reaction started before the isothermal temperature was reached for temperatures above 200°C, these results are not considered.

Therefore, only the isothermal experiments between 160 and 200°C will be considered. The resulting curves of the isothermal part of the experiment are depicted in Figure 7.2 for 160, 180 and 200°C. At higher curing temperature, the maximum reaction rate increases and the curing reaction starts earlier than at lower temperature. Additionally, with increasing temperature the area below the curve grows as well, which means the conversion of the precursor to the cured resin increases.

Only one peak is observed on the DSC curves and, therefore, the heat of reaction is given by the integral of the peak with respect to the baseline. However, this is based on several assumptions. The first one is that a single chemical process is happening. The second one is that the recorded heat only results from the curing reaction. Finally, the whole reaction is supposed to take place at the exothermic peak. Thus,

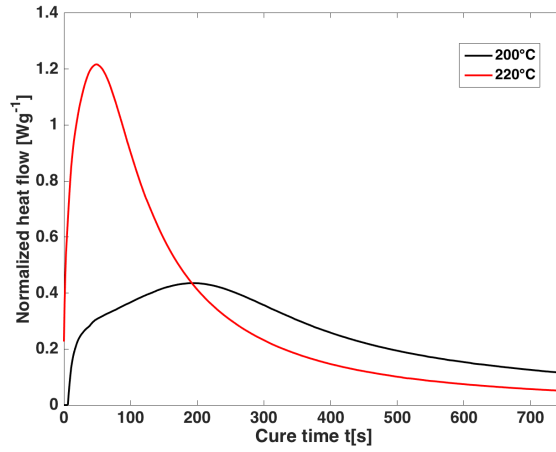


FIGURE 7.1: Curves from the isothermal DSC experiments for the T-DDM precursor at 200 and 220°C.

no reaction is supposed to occur before the sample reaches the isothermal cure temperature. It is to respect this final hypothesis that the DSC experiment at 220°C was dismissed.

Supposing all these assumptions are met, Equations (2.1) and (2.2) shown here below, are valid and can express the reaction rate and the conversion for a certain isothermal cure temperature.

$$\frac{d\alpha}{dt} = \frac{dH_r^{iso}}{dt} \cdot \frac{1}{H_r^{max}}$$

$$\alpha = \int_0^t \frac{dH_r^{iso}}{dt} dt \cdot \frac{1}{H_r^{max}} = \frac{H_r^{iso}}{H_r^{max}}$$

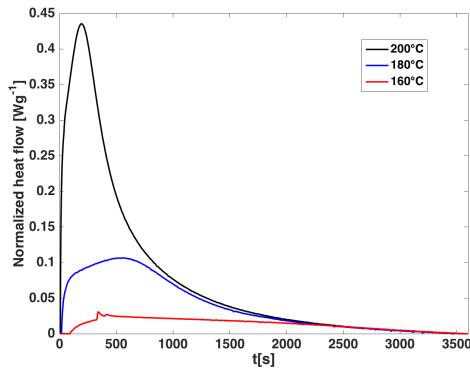


FIGURE 7.2: Curves from the isothermal DSC experiments for the T-DDM precursor at different cure temperatures.

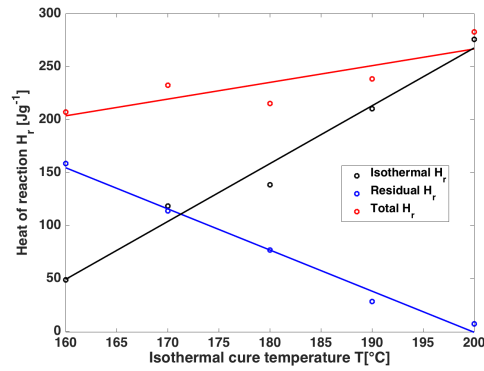


FIGURE 7.3: Heat generated by the curing reaction of the T-DDM precursor at different isothermal cure temperatures.

Figure 7.3 plots the heat of reaction H_r recorded from the isothermal experiments and the non-isothermal second runs to determine the residual heat, and shows the sum of both. For an increasing cure temperature, the heat of reaction measured in the isothermal tests gets bigger, while the residual heat of reaction decreases. The

total heat of reaction H_r^{tot} which sums both of those components, shows an increasing trend. Ideally, H_r^{tot} should be stable for at all temperatures because the resin is the same for all experiments. However, several factors can explain this increasing trend. First, the sensitivity limit of the DSC apparatus must be accounted for. At low reaction rates, which is the case at the lower temperatures of the tests, the DSC has trouble to detect that a reaction is occurring. Moreover, because of the lower reaction rate, the probability that some T-DDM monomers become entrapped within the crosslinked network grows, which makes it harder for them to react. Finally, the exact values for the isothermal, residual and total heat of reaction from the DSC measurements are listed in Table 7.1

TABLE 7.1: Isothermal, residual and total heat of reaction at different cure temperatures.

H_r	160°C	170°C	180°C	190°C	200°C
$H_r^{iso} [Jg^{-1}]$	48.5	118.3	138.3	210.2	275.6
$H_r^{res} [Jg^{-1}]$	177.1	113.8	76.6	28.2	7.7
$H_r^{tot} [Jg^{-1}]$	225.6	232.1	214.9	238.4	283.3

Under the assumption that the reaction rate of the crosslinking reaction is proportional to the exothermic heat measured in the tests [41], Equations 2.1 and 2.2 presented above are valid; and given the value of H_r^{max} at $279.0 Jg^{-1}$, the DSC curves can thus be converted to the reaction rate and the conversion using these equations. Figure 7.4, which illustrates the reaction rate and the conversion for the experiments at 160, 180 and 200°C, clearly shows that when the cure temperature increases the conversion does so as well; which is logical because the area underneath the curves increases.

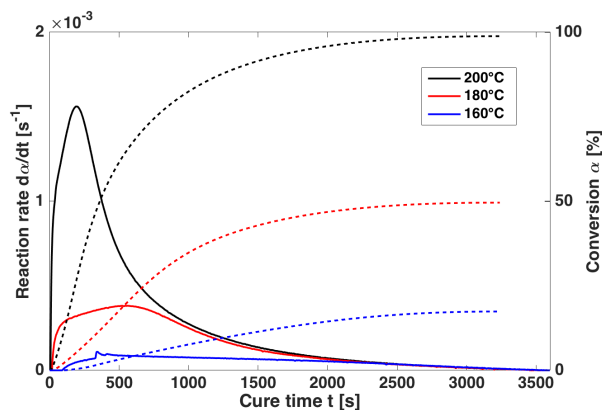


FIGURE 7.4: Reaction rate and conversion for the T-DDM precursor at different cure temperatures.

Furthermore, because the maximum reaction rate does not occur at time zero and an inflection point is observed in the curves representing the conversion versus the cure time, the curves for the reaction rate indicate that the reaction is probably autocatalytic - as it is the case for most benzoxazine resins. However, only the conversions at maximum reaction rate for 190 and 200°C are within the typical range between 20 and 40% conversion for autocatalytic reactions [43, 44]. This is potentially because certain structural rearrangements, which lead to a higher conversion, only occur at the higher temperatures [16].

The final conversion, the conversion at maximum reaction rate, and the maximum reaction rate for each isothermal experiment are presented in Table 7.2. The values in this table confirm that when the cure temperature increases, the maximum reaction rate and the conversion do so too.

TABLE 7.2: Maximum reaction rate, conversion at maximum reaction rate and final conversion at different cure temperatures.

	160°C	170°C	180°C	190°C	200°C
$d\alpha/dt_{MaxRate} [s^{-1}]$	$1 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$
$\alpha_{MaxRate} [\%]$	1.3	5.9	17.2	22.2	23.7
$\alpha_{final} [\%]$	17.4	42.4	49.6	75.3	98.8

In a final aspect of the isothermal experiments, the critical temperature T_{c0} below which no reaction occurs, was determined using the method developed by Sourour and Kamal [45]. Over the range of temperatures between 160 and 180°C, the residual extent of cure, $(1 - \alpha_{final})$, shows an exponential decrease and a linear correlation was found for the data, as is shown in Figure 7.5. Assuming the extrapolation of the data is valid at lower temperatures, an estimate of T_{c0} was found where the residual extent of cure reaches 100%. According to the correlation, a value of 150.7°C is found for the T-DDM resin. However, this result should be taken with caution as only three experimental points stand at the origin of the correlation and the determination factor R^2 for the correlation is 0.933. Even more, this value is certainly too high because a certain amount of reaction heat is already observed at 150°C for samples of T-DDM. Yet, T_{c0} gives an indication of the range of temperatures at which the reaction will first be observed. For instance, at 150°C, the conversion after one hour is still very low compared to 200°C: 22.6 versus 95.5%.

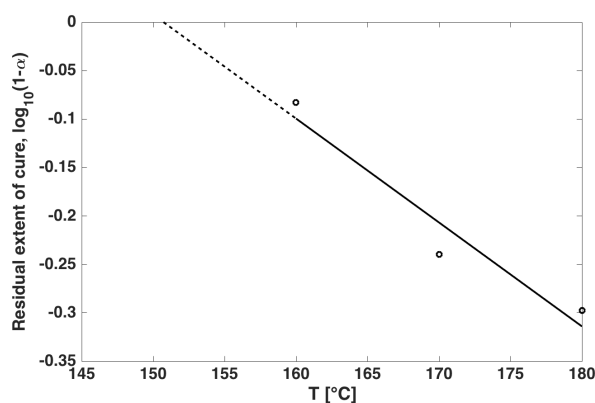


FIGURE 7.5: Variation of the residual extent of cure with the isothermal cure temperature.

The quantification of the kinetic parameters will be done using non-isothermal DSC experiments conducted at various heating rates, which do not require a mechanistic knowledge of the reaction.

7.2 Activation energy and order of reaction

The curves resulting from the non-isothermal experiments conducted at various heating rates between 30 and 300°C are illustrated in Figure 7.6. The main element which is interesting at this point is that for an increasing heating rate, the heat flow is more intense. Furthermore, a small delay in the onset of the curing is noted when the heating rate gets bigger. However, as is depicted in Figure 7.7, the conversion at the end is almost identical and the same delay is observed between the different heating rates.

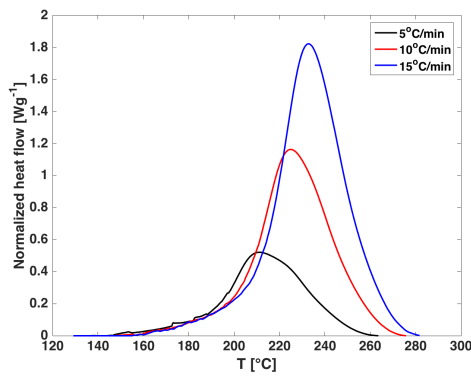


FIGURE 7.6: DSC curves from the dynamic experiments at 5, 10 and 15°C/min.

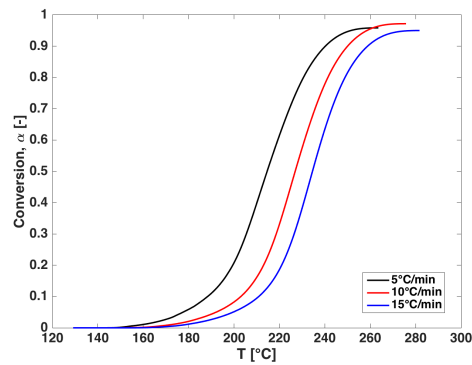


FIGURE 7.7: Conversion at 5, 10 and 15°C/min.

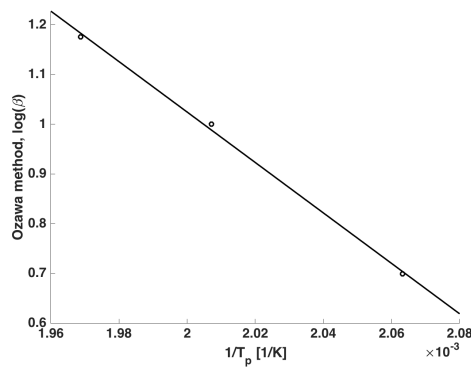


FIGURE 7.8: Illustration of the Ozawa method on dynamic DSC experiments.

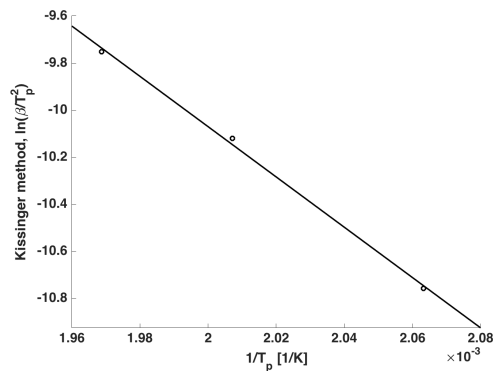


FIGURE 7.9: Illustration of the Kissinger method on dynamic DSC experiments.

First the methods of Ozawa [46] and Kissinger [47] were applied on the data from the DSC curves. These methods aim at determining the activation energy for the curing reaction. The graphs depicted in Figure 7.8 and Figure 7.9 show the resulting slope, respectively for the Ozawa and the Kissinger method.

To construct these graphs, the peak temperatures T_p , which are the temperatures at maximum reaction rate, were determined with the mean of the peak temperatures of three experiments for each heating rate β . The resulting average T_p were for a heating rate of 5, 10 and 15°C/min respectively 211.5, 225.1 and 234.8°C. Then, the Equations (2.4) and (2.6) were applied. Next, two other methods, the methods of Starink and Flynn-Wall-Ozawa, were used to compare the results. These methods

are based on Equations (2.7) and (2.8), respectively for the Starink and the Flynn-Wall-Ozawa method.

Based on the resulting slopes, the estimations of the activation energies for each method were computed. Those results, which are presented in Table 7.3, are fairly similar and show an average value of 89.7 kJ/mol for E_a . Additionally, these values are in the same range as the ones obtained by Ishida and Rodriguez [16] for a bisphenol-A based benzoxazine. With the Ozawa and Kissinger methods, they obtained respectively 107 and 99 kJ/mol for the BA-a resin.

TABLE 7.3: Activation energies for the different maximum peak methods.

Method	Ozawa	Kissinger	Starink	F-W-O
E_a [kJ/mol]	92.3	88.8	88.5	89.1

Finally, the four methods mentioned above were used as isoconversion methods to compare the activation energies obtained by both uses of the methods. Figure 7.10 illustrates the resulting E_a for a conversion between 20 and 80% and compares them with those at peak temperature. The range of values for the conversion was set between 20 and 80% because experimental errors are larger at the lowest and highest conversions. The conversion at peak temperature was chosen as the average peak conversion at the three heating rates. As is shown in the figure, the activation energy is higher when using the isoconversion methods. Moreover, there is an increase in E_a with conversion. This increase can be explained by the fact that at a higher conversion, less active sites remain for the residual unreacted precursors to react with. Also, above a certain level of conversion, these precursors become entrapped within the already cross-linked molecules. Thereby, increasing the activation energy necessary to pursue the curing reaction.

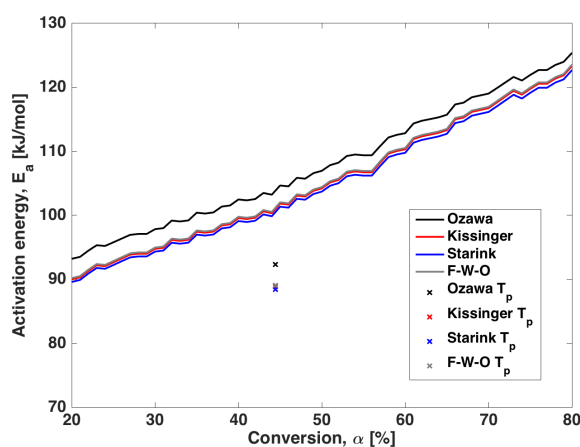


FIGURE 7.10: Activation energies versus conversion for the different isoconversion methods.

The accuracy of all above measurements is strongly dependent on one parameter, which is the maximum heat of reaction H_r^{max} . This parameter has been set at 279.0 Jg^{-1} according to dynamic DSC experiments conducted at a heating rate of $10^\circ\text{C}/\text{min}$. The value of H_r^{max} is theoretically given by the total heat of reaction for the material from its uncured state till it is completely cured. However, it can never

be sure that the recorded value corresponds to the real total heat of reaction. Some systems never reach 100% conversion because a certain mobility of the network is required to reach total conversion. Therefore, even with of a post-cure showing no residual exotherm, the value of H_r^{max} is not certain [16].

Another way to obtain the kinetic parameters is the reaction rate equation. With a multi-linear regression on the experimental data based on the general equation for the reaction rate of the curing, several parameters can be evaluated. In Subsection 7.1, it was established that the curing reaction of the T-DDM resin is autocatalytic. The reaction can thus be described with the general expression for autocatalytic systems given by Equation (2.9). This equation can be rewritten as Equation (2.11), shown again below, which was finally used to determine the values of the pre-exponential factor A , the activation energy E_a and the two exponents n and m with a multi-linear regression. The results of the regression are presented in Table 7.4.

$$\ln\left(\beta \cdot \frac{d\alpha}{dT}\right) = \ln(A) - \left(\frac{E_a}{RT}\right) + n \cdot \ln(1 - \alpha) + m \cdot \ln(\alpha)$$

TABLE 7.4: Kinetic parameters obtained from the multilinear regression of non-isothermal DSC curves.

β [°C/min]	A [s ⁻¹]	E_a [kJ/mol]	n	m
5	$3.99 \cdot 10^7$	90.2	1.6	0.6
10	$4.01 \cdot 10^7$	89.1	1.6	0.7
15	$4.00 \cdot 10^7$	88.0	1.7	0.8

With an increasing heating rate, it was found that E_a decreases a little. Also, the overall order of reaction, which is given by the sum of n and m increases gradually from 2.2 to 2.5. Additionally, the values for the activation energy are in good agreement with the values obtained using the Ozawa, Kissinger, Starink and Flynn-Wall-Ozawa methods with the peak temperature. They are, however, lower than when using the isoconversion criterion with those methods.

The results presented above depend on a series of assumptions. The first series of assumptions impact the measurement of the heat of reaction. First, it was assumed that only one reaction takes place during the polymerization of the resin. This is probably not true as there is strong evidence for the simultaneous occurrence of an exothermic reaction, linked to the ROP of the benzoxazine resin, and an endothermic reaction, due to the condensation polymerization of the hydroxyl functionalities of T-DDM. This was deduced from the FTIR spectra of T-DDM presented in Section 6.1 and the observations of Baqar on the resembling pHBA-DDM benzoxazine resin [7]. The second hypothesis is more difficult to verify, but one can suppose that the measured heat entirely originates from both types of polymerization reactions. Finally, the third assumption, which supposes no reaction takes place before the peak, is probably not entirely respected at the higher isothermal cure temperatures as it was shown that the reaction is already activated around 150°C.

For the maximum peak and isoconversion methods, they are valid for reactions with single activation energy and consider a single reaction. Again, due to the occurrence of two simultaneous reactions, probably with different activation energies, these methods only provide an estimation of E_a for the global reaction that is happening. Moreover, they require some approximations on the $p(y)$ temperature integral,

which adds a margin of error on the results.

Furthermore, it was supposed that the specific heat C_p was constant or followed a linear variation with the heating rate of the DSC experiments and the reaction rate followed an Arrhenius temperature dependence to transform (2.9) into (2.11) and determine the kinetic parameters.

Finally, errors resulting from the measuring limits of the DSC apparatus or from the inaccuracy of the multi-linear regression should be considered.

Conclusion on the curing kinetics

Isothermal DSC experiments showed that for an increasing cure temperature, the total heat of reaction H_r^{tot} increased, while it should remain constant. However, the expected increase of the isothermal heat of reaction H_r^{iso} and decrease of the residual heat of reaction H_r^{es} with an increasing cure temperature were found. From the shape of the isothermal curves, it was determined that the curing reaction is probably autocatalytic, which would be coherent with other benzoxazine resins. Also, a critical temperature T_{c0} , below which no reaction occurs, was found at 150.7°C. Nevertheless, this temperature is too high because heat of reaction is already recorded at 150°C.

Then, with the methods of Ozawa, Kissinger, Starink and Flynn-Wall-Ozawa the activation energy E_a , for which an average value of 89.7 kJ/mol was found, was evaluated based on dynamic DSC tests. A similar value for E_a was deduced from a multi-linear regression between the reaction rate equation and the DSC data. Moreover, this value is in the same range as for BA-a benzoxazine resins. However, E_a calculated by isoconversion methods yielded much higher values.

Finally, the multilinear regression allowed to estimate the overall order of reaction between 2.2 and 2.5.

Nonetheless, the accuracy of the different observations depends on a series of assumptions, which are most probably not all respected. For instance, there is strong evidence for the simultaneous occurrence of two polymerization reactions in T-DDM, one by ring-opening and the other by condensation, while the hypotheses assume only reaction takes place.

Chapter 8

Optimization of T-DDM cure cycle

The aim of this chapter is to present and discuss the results acquired to optimize the cure cycle of the T-DDM benzoxazine resin. Several criteria could have been selected for the optimization of this cure cycle. Yet, the minimization of the residual enthalpy after curing was chosen as optimization goal. The reason for this is that by a minimization of the residual enthalpy, the conversion of the monomer is maximized. Thus, maximizing several properties of the resin such as the glass transition temperature and modulus of the resin. Also, a reduction of the cure time was set as secondary objective in parallel with the minimization of the residual enthalpy.

This minimization of the residual enthalpy was obtained by applying several time and temperature profiles on the resin in isothermal DSC experiments. These isothermal DSC experiments were followed by a dynamic heating to measure the residual enthalpy. A direct measurement of the glass transition and the modulus as criteria for optimization would have been possible, but needed the use of another technique, namely Dynamic Mechanical (Thermal) Analysis or DMA. In DSC, the residual enthalpy and the T_g were measured.

In a first approach, the cure cycle of neat T-DDM was studied. Then, the potential alterations of this cycle due to the addition of zinc oxide were investigated. The numerical results of all tested cycles can be found in Figure A.1 of Appendix A.

8.1 Cure cycle of neat T-DDM

The curing cycle for T-DDM proposed by Materia Nova, which synthesizes this resin consists of several levels with increasing cure temperatures. This cycle, represented in Figure 8.1, was originally devised for another benzoxazine resin, namely pPDA. The distinct stages of the cure cycle were chosen to avoid overheating of the resin due to the exothermic reaction during the polymerization. The objective of this section is to determine another cure cycle which would insure a complete conversion for T-DDM, potentially shorter and with less levels than the basic cycle. This cure cycle aims at a complete cure and, thus, at the highest value of T_g for the T-DDM resin, which is at 167°C according to Materia Nova. With the initial cure cycle presented in the figure, a value of 166.4°C was obtained in DSC for T_g .

One aspect which should be borne in mind is that the optimization that will be proposed is based on DSC experiments. These DSC experiments use very little quantities of the material and are, therefore, not completely representative for what happens in a furnace where larger quantities of material are used and the control over temperature is less-well monitored. For instance, the residual enthalpy H_{res} of

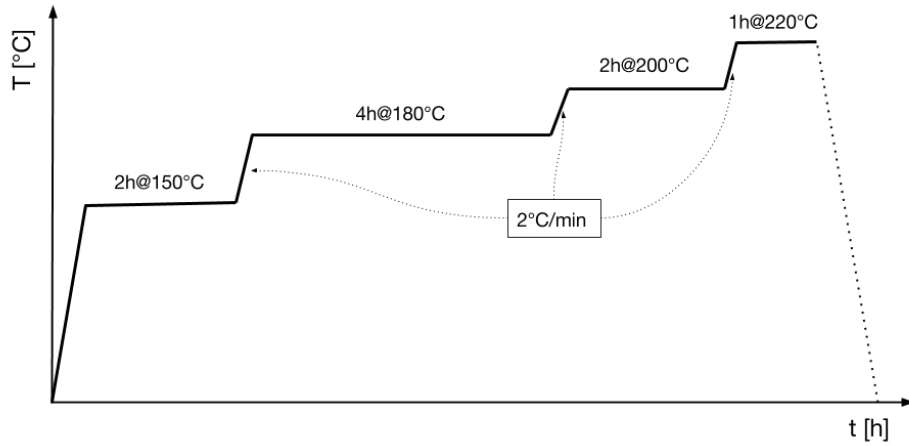


FIGURE 8.1: Cure cycle proposed by Materia Nova for T-DDM.

the cycle proposed in Figure 8.1 without the last step at 220°C was tested by DSC on samples which had followed this cycle either in a furnace or in DSC. While the sample analyzed completely by DSC showed no H_{res} at all, the one from the furnace showed a H_{res} of 33.2 Jg^{-1} .

The different series of experiments were presented in Chapter 5 in the subsection about the DSC methods. A first approach, to determine the rate of curing at different temperatures over a certain curing time, consisted of runs at four isothermal cure temperatures for five curing times. Those were respectively 150, 165, 180 and 200°C; and for 15, 30, 60, 90 and 120 minutes. H_{res} was then measured on the dynamic part of each experiment and the results were plotted in Figure 8.2a. The starting point of the curve was set at 279.0 Jg^{-1} , which is the enthalpy required to completely cure the neat T-DDM resin. Equation (8.1) gives the overall shape of the curves for each T_{cure} with an R^2 coefficient over 0.99 for each of them. The coefficients did vary with each T_{cure} : a decreases with temperature, b is slightly negative, and c globally increases with temperature.

$$H_{res} = 279.0 \cdot e^{-at_{cure}+b} + c \quad (8.1)$$

From these curves for the residual enthalpy and the conversion for a certain t_{cure} and at T_{cure} , shown in Figure 8.2b, could be determined using the following transformation:

$$\alpha = 100 \cdot \left(1 - \frac{H_{res}}{H_r^{max}}\right) \quad (8.2)$$

where the conversion α is expressed in [%] and H_r^{max} equals 279.0 Jg^{-1} . The main observations from this first series of experiments is that the conversion increases with the cure temperature. Also, the rate at which the conversion develops is strongly dependent on T_{cure} . At 150°C, the evolution of the conversion with curing time is almost linear. When the temperature increases gradually to 165 and 180°C, the conversion increases faster in the beginning of the cure and then this increase slows down gradually. At a T_{cure} of 200°C, a conversion of 90% is already reached after 27 minutes of curing. The conversion then evolves into an asymptotic behavior as the maximum conversion is slowly reached.

The evolution of the conversion curves is determining for the selection of an optimal cure temperature to avoid degradation of the material. Starting from the specific

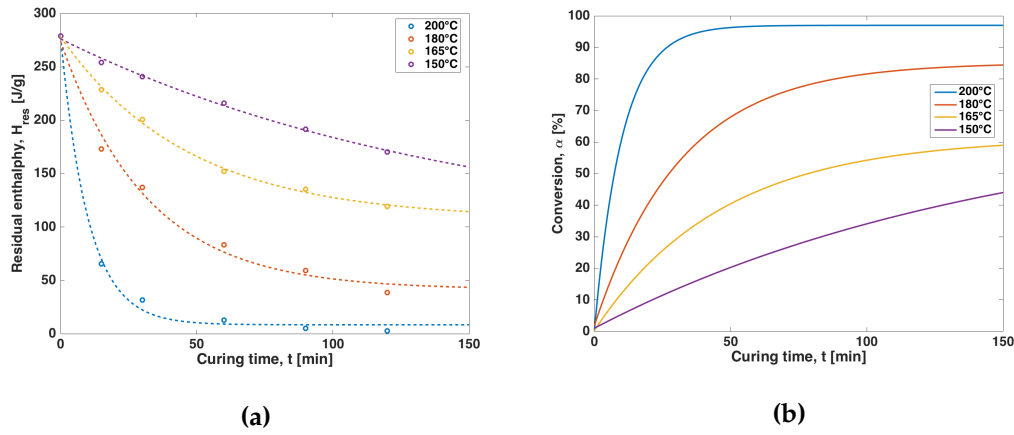


FIGURE 8.2: Results from experiments at one cure temperature: (a) Residual enthalpy after cure H_{res} , (b) conversion α .

heat capacity C_p of the benzoxazine and the curve of the conversion with cure time, the potential rise in temperature of the materials with time due to the exothermic curing reaction can be evaluated. For the neat T-DDM resin, C_p equals $1.65 \text{ J g}^{-1} \text{ K}^{-1}$ after T_g and before the onset of the cure reaction. Supposing no heat is transferred out of the material and a constant value of the C_p - two very unrealistic assumptions - an increase in temperature of 158.4°C should be observed for the T-DDM resin at a cure temperature of 200°C over 30 minutes of curing. In comparison, this would only be 23.0°C at a T_{cure} of 150°C . These values were computed from the heat of reaction H_r corresponding to the level of conversion at both cure temperatures. Then, from the definition of the specific heat, $C_p = H_r / \Delta T$, the increase temperature due to the reaction ΔT was found.

Based on TGA data of experiments conducted on cured T-DDM, this would lead to 11.3% of weight loss of the cured resin by degradation for a cure temperature of 200°C because of the additional 158.4°C brought by the heat of reaction. For a T_{cure} of 150°C , this degradation would be over ten times smaller, at 0.9%. Even if these values are excessive and unrealistic, due to the transfer of heat out of the sample and the variation of C_p with temperature and conversion, this illustrates that high cure temperatures can easily lead to an overheating of the resin and the degradation which results from it.

To obtain a better view of the dependence of the residual enthalpy with cure time and temperature, a tridimensional plot was constructed using a thin-plate spline interpolant fit of the data in Matlab. The resulting surface and contour plots are shown in Figure 8.3. From an analysis of these plots based on the objective of this cure cycle optimization, it is clear that the conversion develops too slow at 150°C , while it develops too fast at 200°C . Therefore, a compromise should be found with a T_{cure} in between these extremes. Additionally, because of the slowing down of the conversion rate once it reaches a certain level, a program combining several cure temperatures must be considered to keep the conversion increasing at a good rate.

Therefore, the next series of experiments were conducted using two isothermal cure temperatures.

First, times of 30, 60, 90 and 120 minutes at 150°C , followed by 120 minutes at 180°C were tested. The increased time at 150°C only slightly improved the final conversion

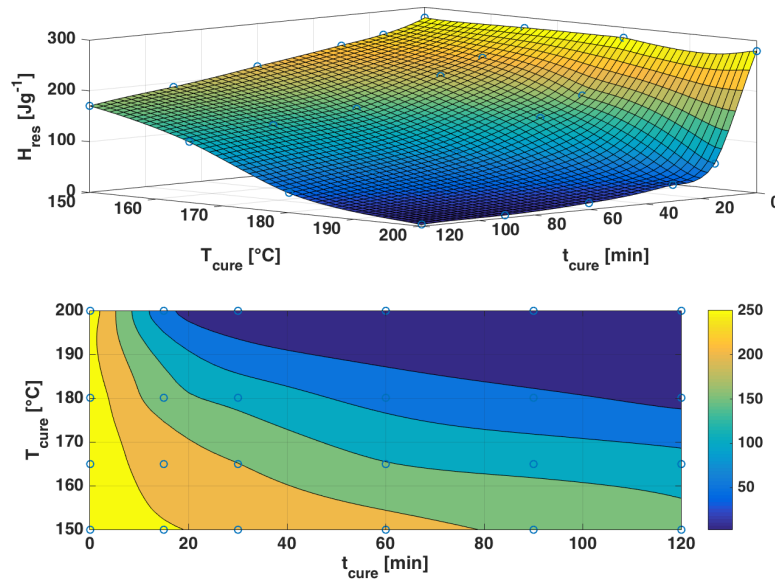


FIGURE 8.3: Evolution of the residual enthalpy H_{res} versus temperature and time of cure.

from 87.6 to 89.4%. In a second series of tests, the samples were subjected to 120 minutes of cure at 150°C and with increasing cure times at 180°C. The evolution of the residual extent of cure at 180°C is plotted in Figure 8.4. Based on the results at single isothermal cure temperatures, 38.9% of conversion was already reached after 120 minutes at 150°C. The residual 61.1% to be converted in polybenzoxazine decreases according to the curve shown in the figure during the second curing at 180°C. High levels of conversion are developed relatively fast as almost 80% is reached after one hour of cure at the second level. However, even after longer cure times at 180°C, the conversion seems to come to a standstill a little over 90%.

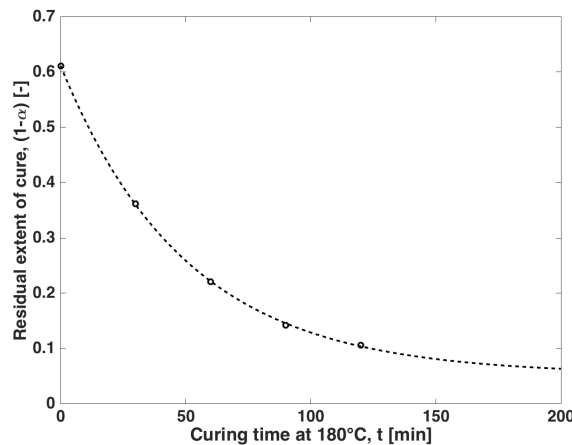


FIGURE 8.4: Residual extent of cure at 180°C after 120 minutes of cure at 150°C.

To reach a better conversion, other cycles were tested. In these cycles, the first cure temperature was set at 150, 165 or 180°C, while the second was set at 200°C. This value of 200°C was chosen to reach a better conversion than with 180°C. The

samples were kept during 60 minutes at the first T_{cure} and then for a varying time at the second. The reduction of the first stage of the cure cycle from 120 to 60 minutes was done in compliance to the previous series of tests where it was found that at 60 minutes of cure good level of conversion were already reached for the considered temperatures. Figure 8.5 shows the evolution of H_{res} during the second curing step at 200°C. After the first curing step at various T_{cure} and for each of these cure temperatures 22.6, 45.5 and 70.1% of conversion had respectively been reached. The figure shows that almost 100% conversion is attained after 90 minutes at the second T_{cure} , about 95% at 60 minutes, and approximately 90% after only 30 minutes. Because these percentages are almost independent of the first cure temperature, this temperature could be chosen accordingly to distribute as best as possible the curing of the resin.

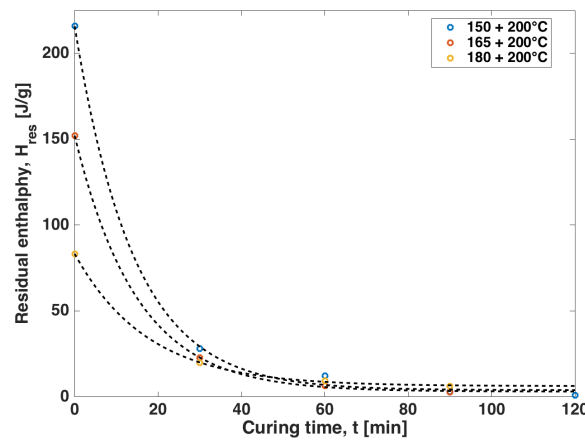


FIGURE 8.5: Evolution residual enthalpy during cure at 200°C after 60 minutes of cure at 150, 165 and 180°C.

In a similar fashion as for the cure experiments with a single T_{cure} , a surface and contour plot of the evolution of H_{res} during the second curing step was plotted in Figure 8.6. This means H_{res} was mapped as a function of t_{cure} at 200°C and T_{cure} of the first step. As mentioned above, the decrease of H_{res} over time is almost independent of the first cure temperature after 30 minutes of curing at 200°C. However, over the first 30 minutes, H_{res} decreases rapidly and this decrease is more marked for low first T_{cure} .

An improved cure cycle was then determined based on the results presented and discussed above. The main aspect of this cure cycle is its separation into two stages at different isothermal cure temperatures, the first one at an intermediate level and the second one at a higher cure temperature.

Based on the results, a temperature of 165°C for 60 minutes was chosen for the first step. After this step, a conversion of about 45.5% is reached. The choice of this cure temperature and the curing time was made in line with the results. On one hand, at a lower temperature, more time is needed to reach the same conversion; or for the same time, the conversion is too low and, therefore, the rate of conversion would be too high in the second step and risk degrading the material by excessive heat. On the other hand, for higher temperatures, the rate of conversion is too fast and the material risks damage if the reaction is not controlled, as illustrated previously with the computation of the potential temperature rise brought by the heat of reaction.

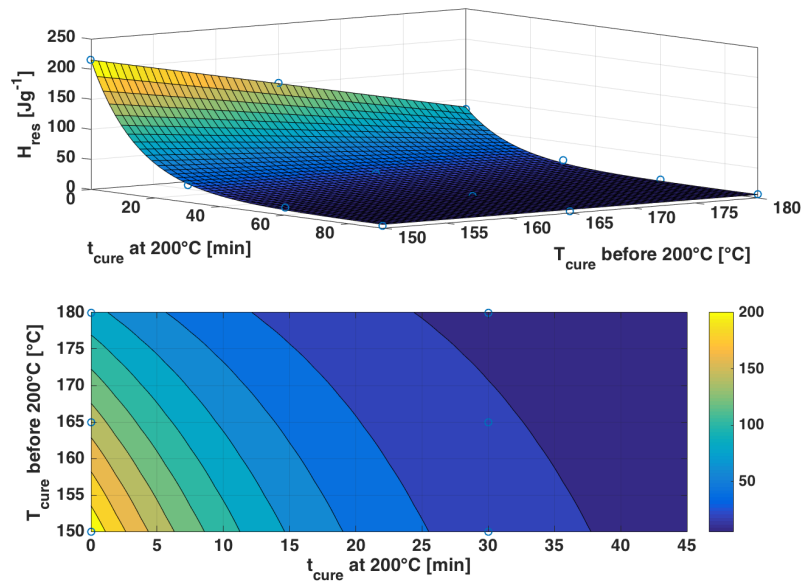


FIGURE 8.6: Evolution of the residual enthalpy H_{res} versus t_{cure} at 200°C and T_{cure} prior to before 200°C.

As can be seen on Figure 8.2b, after 60 minutes only 22.6% conversion is attained at 150°C, which is too low given the objectives of the improved cure cycle, while already 70.1 and 95.5% are obtained at respectively 180 and 200°C. Therefore, 165°C forms a good compromise between 150 and 180°C.

For the second step, a cure temperature of 200°C for 90 minutes was selected. As shown previously in Figure 8.4, 180°C does not reach a satisfactory conversion, even for longer curing times. Thus, a higher temperature of 200°C was chosen. Regarding the curing time, 90 minutes was judged reasonable as 99.0% of the conversion is obtained for this curing time.

To push the curing to a maximum, an additional level of 30 minutes at 220°C can be considered. Compared to the previous cycle that required almost 10 hours, this improved cycle reduces this time to under 3 hours without the step at 220°C and up to 3.5 hours with this step. This whole cycle is depicted in Figure 8.7.

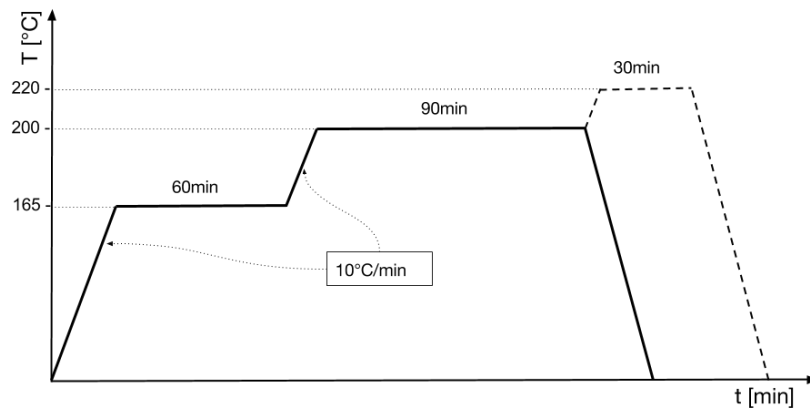


FIGURE 8.7: Improved cure cycle for the neat T-DDM resin.

8.2 Comparison with blend at 10wt% ZnO

Several experiments were also carried out on a blend containing 10wt% ZnO to evaluate the potential effect of ZnO on the cure cycle of the T-DDM benzoxazine resin. The different series of tests are detailed in Chapter 5. Additionally, the microstructure of T-DDM-ZnO blends and the dispersion of the ZnO nanoparticles within them, will be presented later in Chapter 9 because they are more pertinent in this section. SEM micrographs of the blends at 10wt% ZnO are presented in Figure 9.7.

First experiments with a single T_{cure} were reproduced. A comparison between the residual enthalpy for the neat resin and the blend is shown in Figure 8.8. The general trend apparent on the figure is that H_{res} is slightly higher for the blend than for the neat resin. This is especially marked at 180°C, whereas at 200°C they reach a similar value at a higher t_{cure} . The main reason for this is that the enthalpy required for a complete cure of the blend is higher than the one for neat T-DDM, 289.5 instead of 279.0 Jg^{-1} . This evolution of the heat of reaction with ZnO content will be discussed later in Chapter 9. Apart from this small shift in H_{res} , the decrease in the enthalpy is comparable to the one found for the neat resin. With increasing cure temperature, the conversion increases. Moreover, at low cure times, the rate of the curing reaction is very steep for a high cure temperature, and it flattens down at longer cure times.

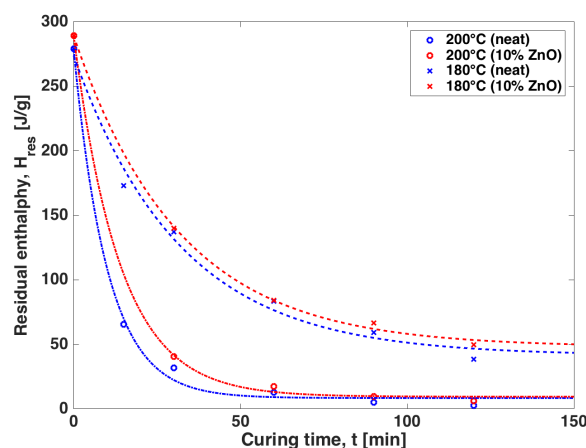


FIGURE 8.8: Comparison of the residual enthalpy H_{res} between neat T-DDM and a blend with ZnO at 180 and 200°C.

Figure 8.9a shows the residual extent of cure, which is the opposite of the conversion, for the experiments with 120 minutes at 150°C followed by 30, 60, 90 and 120 minutes at 180°C. Again, a lower conversion is reached by the blend. After 150 minutes of cure at 180°C, the conversion is about 85%, while a conversion over 90% was attained for the neat resin. Furthermore, for experiments with 60 minutes at 150°C and various times at 200°C, depicted in Figure 8.9b, the conversion is also lower than for neat T-DDM.

Due to the lower conversion of the blend composed of T-DDM with zinc oxide nanoparticles, two possibilities can be considered to adapt the cure cycle proposed in Figure 8.7. The first, is to require the additional level at 220°C to push the conversion

further. The second, is to increase t_{cure} either for both levels or only for the one at 200°C.

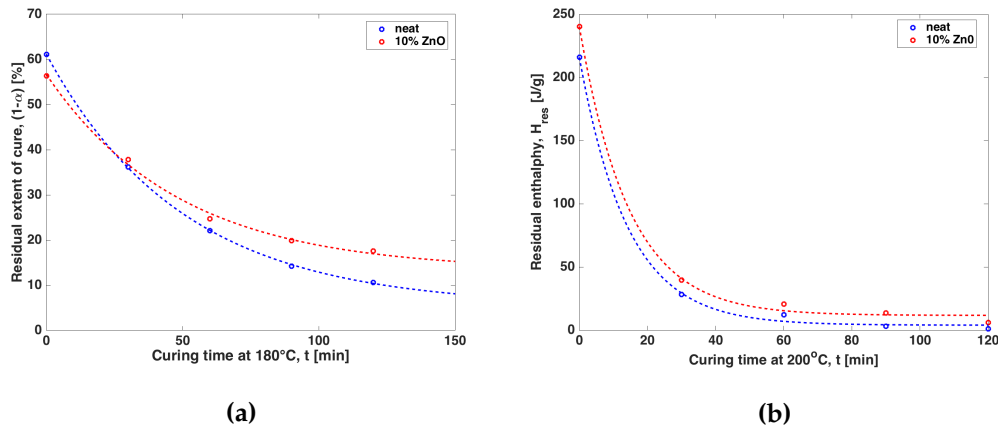


FIGURE 8.9: Results from the experiments with two T_{cure} : (a) 120 minutes at 150°C with varying times at 180°C, (b) 60 minutes at 150°C with varying times at 200°C.

8.3 Results for the improved cure cycle

An optimized cure cycle was proposed above, both for the neat resin as for a blend containing 10wt% ZnO. This cycle was applied on samples to measure its effectiveness through a measure of the residual enthalpy after curing. For the neat T-DDM, the cycle was applied on samples both in a DSC apparatus and a conventional furnace to evaluate the potential effect of a different environment on the final curing of the sample.

The values for H_{res} and T_g of the samples cured with DSC are listed in Table 8.1. Starting with the neat resin, after following the cure cycle with two levels at respectively 165 and 200°C, conversions of 99.2% on average were recorded. These conversions are in good accordance with the expected value. When extending the cure cycle with an additional level at 220°C, no residual enthalpy was measured at all. This means, the maximal measurable conversion was reached. Nevertheless, it is possible that the maximal real conversion is not yet reached and that it can further increase by a very small amount due to reactions occurring under the detection limit of the DSC apparatus. Another way, to indirectly approximate the extent of the cure, is to use the value of the glass transition temperature T_g . The values of the glass transition presented in the table are for both cycles very close to the ones obtained by the initial cycle, 166.39°C, and by Materia Nova, 167°C. This confirms that the specimens are almost completely to fully cured.

For the blend, the same observations can be made as in Section 8.2. For the same cure cycle, H_{res} remains higher than for the neat resin. A conversion of only 97.9%, compared to the 99.2% for the neat T-DDM, was reached after the cure cycle with two levels. Upon the addition of the third level to the cure cycle, this conversion increased to 99.2%. Therefore, in order to reach the maximal conversion for the blend at 10wt% ZnO, the cure time should be extended a little. For example, by increasing the time at 220°C from 30 to 45 or 60 minutes. However, it is interesting to observe that the T_g is already higher by approximately 4°C than for the neat samples due to

the addition of ZnO. Nevertheless, without a value for the ultimate T_g of the blends, it cannot be stated how close this value is to the ultimate value, and this increase could even be a little higher.

TABLE 8.1: H_{res} and T_g after curing in DSC. CC_1 : 60 minutes at 165°C plus 90 minutes at 200°C; CC_2 : CC_1 plus 30 minutes at 220°C.

Cure cycle	$H_{res} [Jg^{-1}]$			$T_g [^{\circ}C]$		
	T-DDM neat	10wt% ZnO		T-DDM neat	10wt% ZnO	
CC_1	2.2	2.3	6.0	167.5	165.8	171.4
CC_2	0.0	0.0	2.4	166.6	163.2	170.5

Table 8.2 lists H_{res} and T_g for the samples which had cured in the furnace by both cycles presented above. Two samples were cured for each cure cycle and for each of those samples two dynamic DSC runs were applied. As expected, the samples cured in the furnace showed more residual heat of reaction. The ones cured with CC_1 reached an average conversion of 82.6% and the average T_g was 146.7°C, which is much lower than the 166.6°C for the samples cured by DSC. With the additional level in CC_2 , H_{res} was much lowered and an average conversion of 99.2% was reached. However, the T_g did not increase accordingly and a value of only 152.2°C was reached. This value of T_g is not in accordance with the level conversion reached by the resin.

TABLE 8.2: H_{res} and T_g after curing in a furnace. CC_1 : 60 minutes at 165°C plus 90 minutes at 200°C; CC_2 : CC_1 plus 30 minutes at 220°C.

Cure cycle	$H_{res} [Jg^{-1}]$				$T_g [^{\circ}C]$			
	Sample 1		Sample 2		Sample 1		Sample 2	
CC_1	37.1	50.1	55.0	52.5	146.3	147.6	147.3	145.8
CC_2	2.7	2.7	2.7	1.3	153.0	152.9	151.3	151.6

Conclusions on the cure cycle optimization

In a series of isothermal tests followed by dynamic second heating to determine the residual enthalpy H_{res} , an improved cure cycle was devised for the curing of neat T-DDM to reach complete cure in the shortest time as possible. This improved cure cycle is composed of two steps and an additional step to push the degree of cure further: (i) 60 minutes at 165°C, (ii) 90 minutes at 200°C, and optionally (iii) 30 minutes at 200°C. The cure temperatures of the steps were chosen such that the curing could be sufficiently fast, whilst avoiding degradation by excessive heat from the exothermic reaction.

The results on this improved cure cycle show that it does not reach a complete cure for samples in DSC without the additional step at 220°C, but 99.2% of conversion are already reached before this last step. A T_g of 166.6°C on average was found, which corresponds well with the value provided by the manufacturer. Additionally, while this cycle is well-suited for the reticulation of the resin in DSC, it does not allow to reach a complete conversion for samples cured in a furnace. Also, the glass transition temperature for samples in a furnace is lower than expected. To improve both the conversion and the T_g when curing a furnace, increasing the time of the distinctive cure levels in the cycle should be considered. Yet, the time saved by this

cycle, even if decreased a little by the longer steps, is still significant compared to the initial cycle. Finally, for blends composed of T-DDM and ZnO nanoparticles, a slightly lower conversion was reached than for the resin, but the resulting T_g was higher. This lower conversion might result from the higher curing enthalpy of the blends compared to the neat resin.

Chapter 9

Effect of ZnO nanoparticles on T-DDM

This chapter focuses on the effect of zinc oxide nanoparticles on the properties of the T-DDM benzoxazine resin. First, blends with different weight concentrations of ZnO with T-DDM resin were produced. These blends were mainly sonicated to disperse the ZnO nanoparticles. However, some blends with various sonication times were also produced to measure the effect of sonication on the properties of the resulting nanocomposites. Secondly, the samples were studied by TEM and SEM to check whether a good dispersion of the ZnO nanoparticles was obtained. Then, in a third step, DSC and TGA experiments were conducted to find out the effect of the added particles to the curing reaction and the thermal stability of the benzoxazine resin. Finally, FTIR spectra were obtained to study the chemical interaction between ZnO and the T-DDM resin.

9.1 Dispersion of ZnO nanoparticles in the T-DDM matrix

TEM and SEM studies were conducted on the nanocomposite T-DDM–ZnO blends in order to confirm whether a good dispersion of the ZnO nanoparticles was reached for different compositions and at levels of sonication of 30, 90 and 270 seconds. First, the dispersion will be investigated with TEM micrographs and then with SEM micrographs. A certain amount of TEM and SEM micrographs will be presented in this section, additional micrographs can be found in Figures A.7 to A.12 of Appendix A.

9.1.1 TEM micrographs

As mentioned above, the TEM micrographs will first be discussed. These images contain artefacts which should be considered in their analysis. On all images, a sort of circular shadow is visible in their left bottom part. This shape is due to an effect in the TEM apparatus and must not be taken into account. Moreover, on some micrographs parallel scratches appear, sometimes with creases perpendicular to them. These scratches are the result of the slightly damaged edge of the diamond knife used for cutting the sections at 95 nm and as consequence of those scratches stresses appear in the cut sections, which lead to the perpendicular creases. This is especially clear on images (a), (c) and (d) of Figure 9.2. Finally, greyish zones with individual ZnO particles can be noticed on some images, for example on Figure 9.1b. These originate from the slicing of the sections, where individual particles are pulled from

larger aggregates and then immersed in the water used to recover the cut sections.

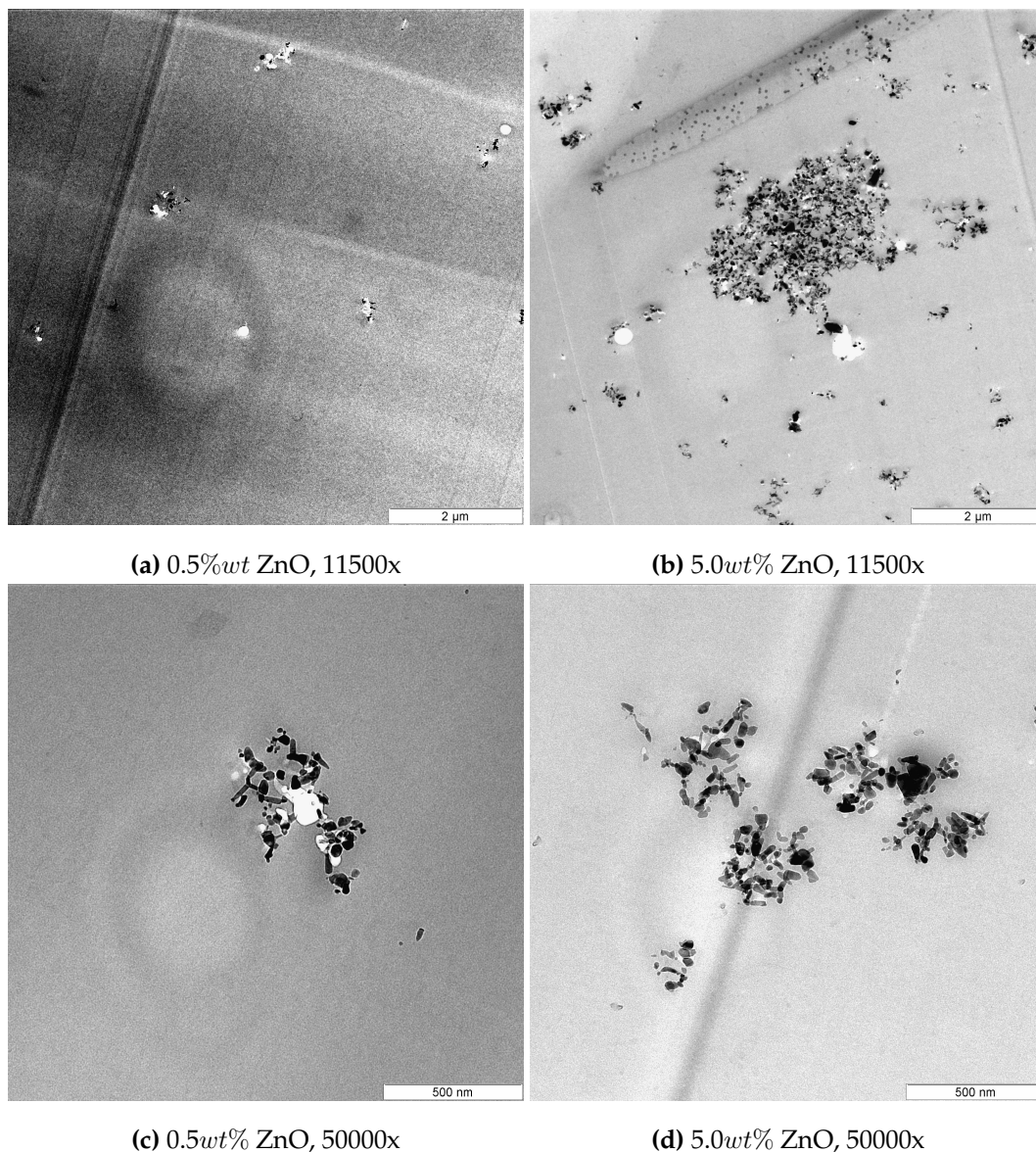


FIGURE 9.1: TEM micrographs at 120 kV on samples with 90s sonication.

The micrographs obtained with TEM on the samples at 90 seconds of sonication are illustrated in Figure 9.1.

The first two images, (a) and (b), compare the overall dispersion of the zinc oxide particles into the T-DDM matrix. From those images, it is clear that the ZnO particles mainly form small aggregates which are dispersed within the benzoxazine resin. Individual particles to small clusters of ZnO are also present in the samples. The origin of those particles and groups can be multiple, they were either originally dispersed in this way into the sample or displaced from larger aggregates when the sample was cut with the microtome. Probably, a bit of both causes is at their origin. Additionally, according to the images, the size of the aggregates tends to increase when the ZnO concentration is raised from 0.5 to 5.0wt%. Some larger aggregates appear in the 5.0wt% ZnO sample, as is shown in the figure, but in general the clusters remain well dispersed into the T-DDM matrix.

Micrographs (c) and (d) compare clusters found in both samples with a magnification of $50000\times$. While the cluster size is relatively similar on the images, they show that for $5.0wt\%$ of ZnO the aggregates have a tendency to stay grouped, probably because they come from larger aggregates which have started to break up with the sonication.

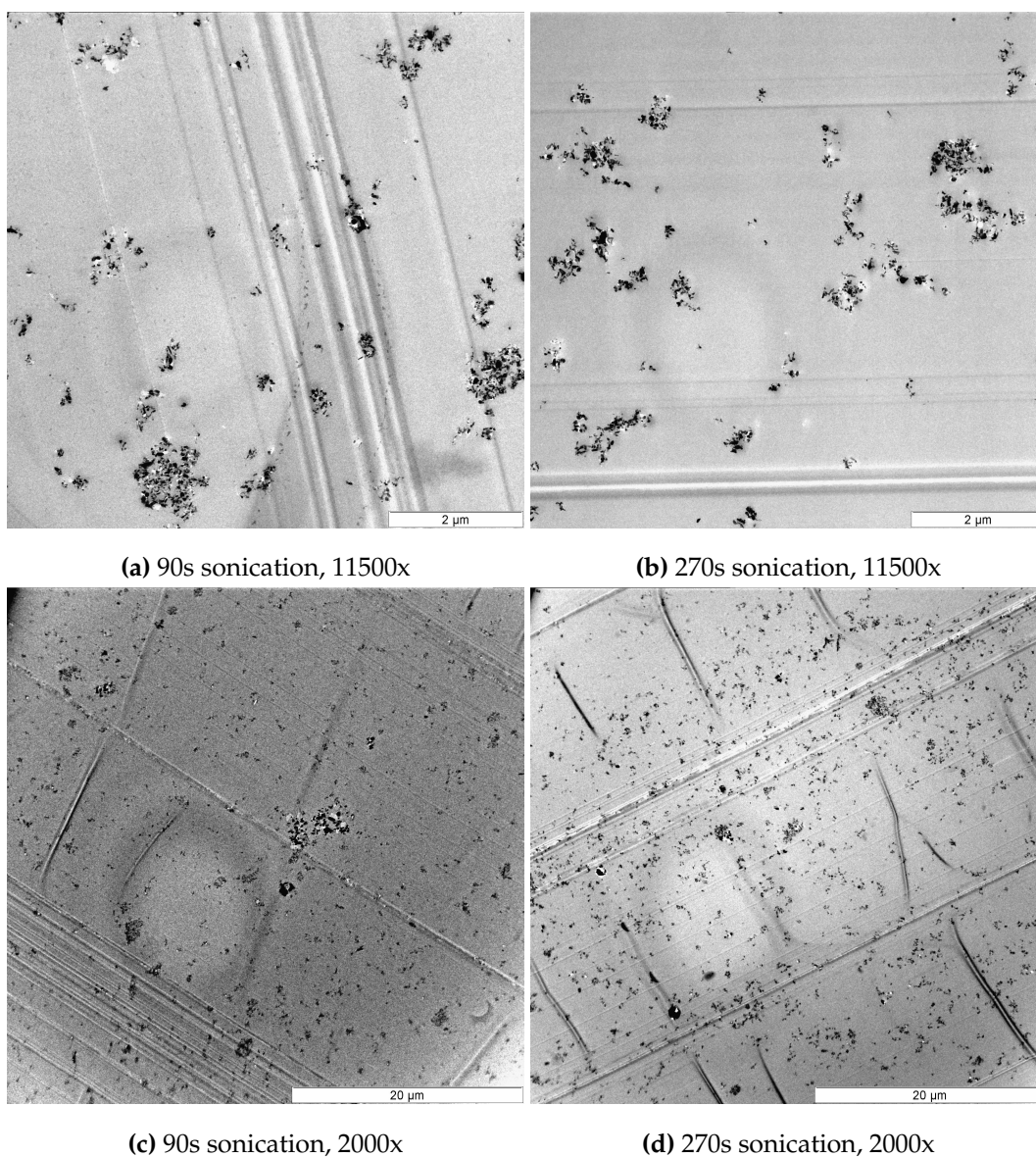


FIGURE 9.2: TEM micrographs at 120 kV on samples with $5.0wt\%$ ZnO.

Thus, the images obtained with TEM on samples with 90 seconds of sonication, allowed to conclude that the overall dispersion of ZnO nanoparticles is satisfactory. Although, some aggregates are observed, as the one shown in Figure 9.1b, smaller clusters dispersed over the whole sample are still present, thus leading to an acceptable dispersion on a larger scale.

Once the effect of the loading of ZnO on the dispersion was studied, the effect of a larger sonication time was analyzed with TEM for samples at $5.0wt\%$ ZnO with respectively 90 and 270 seconds of sonication. Micrographs of those samples are

shown in Figure 9.2.

With a longer sonication time, the larger ZnO clusters seem to be breaking up into smaller clusters but those clusters remain well dispersed. Yet, no significant change in the size and dispersion of the smaller clusters was detected.

A magnification of only $2000\times$ provided a good overview of the overall dispersion of ZnO in the samples. Images (c) and (d) illustrate this for the samples at respectively 90 and 270 seconds of sonication. These micrographs show that the dispersion is slightly improved when sonicating for a longer time. Most importantly, no large aggregates over $2\text{ }\mu\text{m}$ are present after 270 seconds of sonication in contrast to the sample sonicated for 90 seconds.

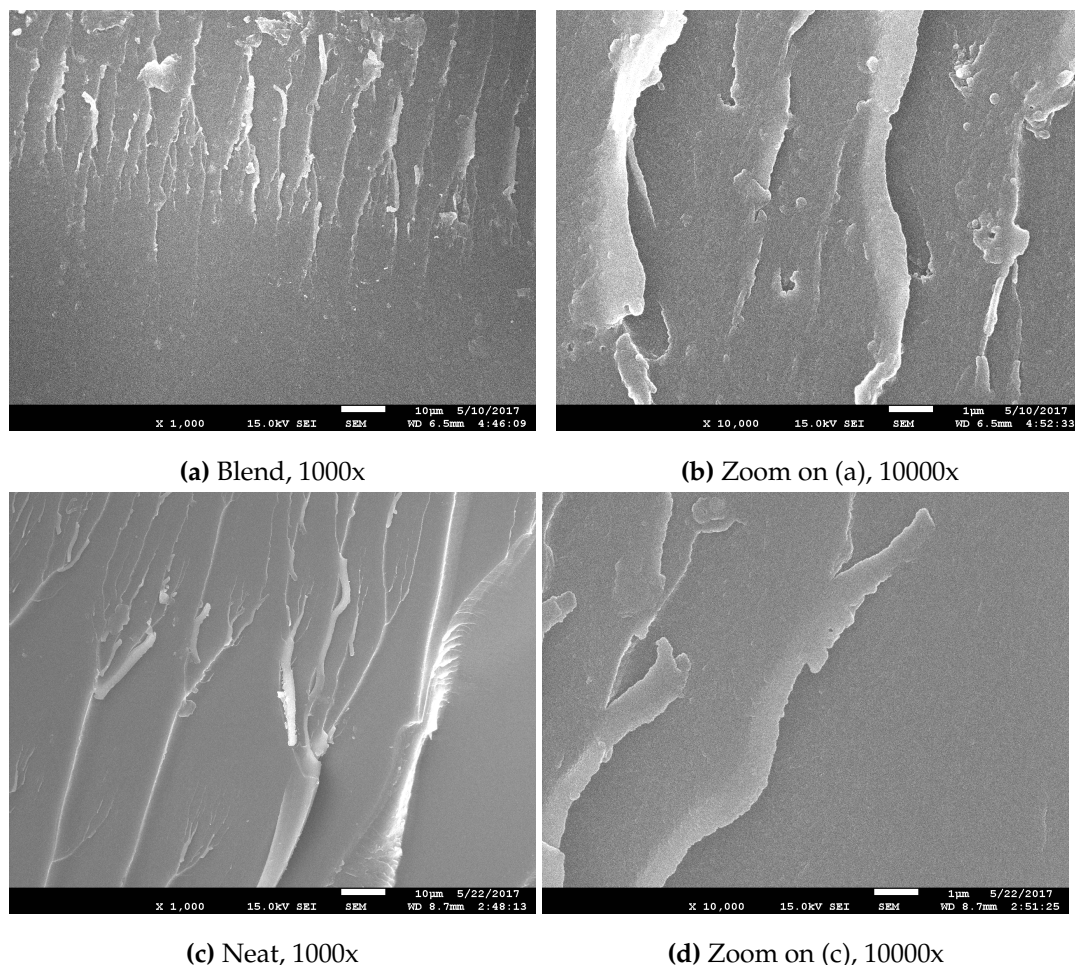


FIGURE 9.3: SEM micrographs at 15.0 kV on a sample with 0.5wt% ZnO and 30s sonication compared to the neat T-DDM resin.

9.1.2 SEM micrographs

Further studies were conducted with SEM. The first sample to be studied was one with 0.5wt% ZnO sonicated for 30 seconds. This sample was chosen to check whether large aggregates would be visible on a sample with low sonication time and having a small ZnO concentration. Figure 9.3 shows micrographs obtained with SEM at magnification of $1000\times$ and $10000\times$ and compares them to the neat resin. Image (a) and (c) give an overview of the fractured section of the nanocomposite and the neat resin respectively. Ridges with small teared-off fragments are visible and result from

the fracture mechanism of the material. On the image for the nanocomposite no evidence of aggregates is found. A further zoom on the sections, shown in image (b) and (d), reveals that the surface is rougher and more irregular for the blend. Small spherical particles are visible, which could be ZnO particles and small clusters, and in the top right corner of the image there even seems to be an aggregate of approximately $1\ \mu\text{m}$ in diameter. These observations cannot be confirmed with absolute certainty to be zinc oxide inclusions as they could also result from the fracture of the sample or appear with the metallization of the section. However, in comparison with the neat resin, which shows a very smooth surface except for the river patterns, there is strong evidence to associate the roughening of the surface and the small particles in the blend to the addition of ZnO nanoparticles.

Figures 9.4 and 9.5 illustrate sections of samples at $5.0\text{wt}\%$ ZnO with respectively 90 and 270 seconds of sonication time. A first observation which can be made is that the fracture surface is rougher for the sample sonicated for a shorter time. This could be the result of the ZnO particles forming larger clusters as was detected through the TEM analysis of these samples. However, no large aggregates seem to be located at the fracture surface of the sample with 90 seconds of sonication. Similar conclusions can be made as for the sample at $0.5\text{wt}\%$ ZnO, small clusters seem to be present but there is no conclusive evidence that they are ZnO nanoparticles.

The sample sonicated for 270 seconds, shown in Figure 9.5, has a smoother fracture surface, which could mean that a better dispersion in smaller clusters of ZnO is obtained, which would be in accordance with the results of the TEM studies. Image (b), which illustrates the section magnified 10000 times, shows no distinctive features that could be ZnO aggregates.

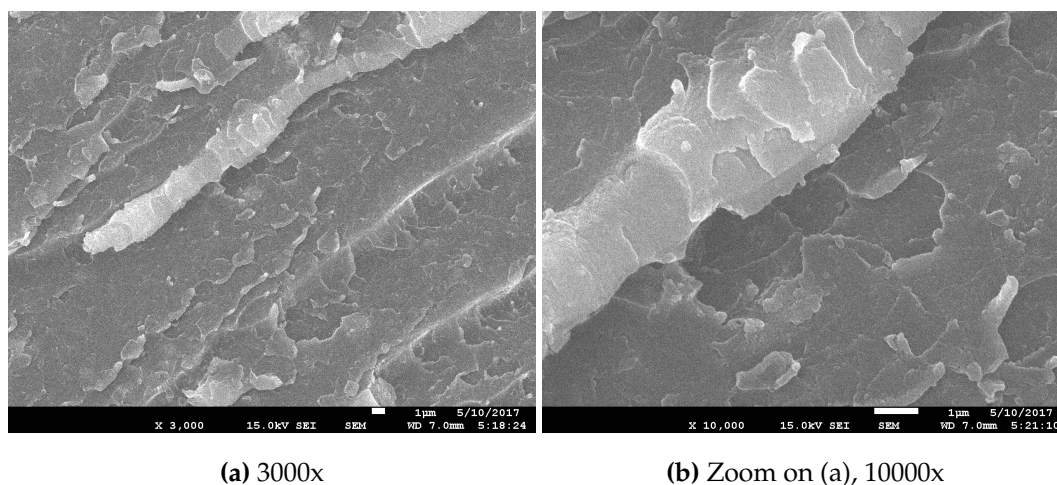


FIGURE 9.4: SEM micrographs at 15.0 kV on a sample with $5.0\text{wt}\%$ ZnO and 90s sonication.

Finally, a $45000\times$ magnification of the bottom right corner of image (a.) shows what could be a small aggregate of ZnO nanoparticles. The void observed between the particles could potentially be explained by the low solubility of ZnO in the chloroform which is used to dissolve the T-DDM benzoxazine resin. Namely, ZnO nanoparticles without surface functionalization, as is the case with the *Zano*®20 used in the blends with T-DDM, are not soluble in any polar or non-polar solvents [79]. Thus, chloroform being a non-polar solvent, this results in entrapped air within the

ZnO clusters and therefore a void can be observed within the T-DDM matrix. However, without additional images this hypothesis is difficult to confirm.

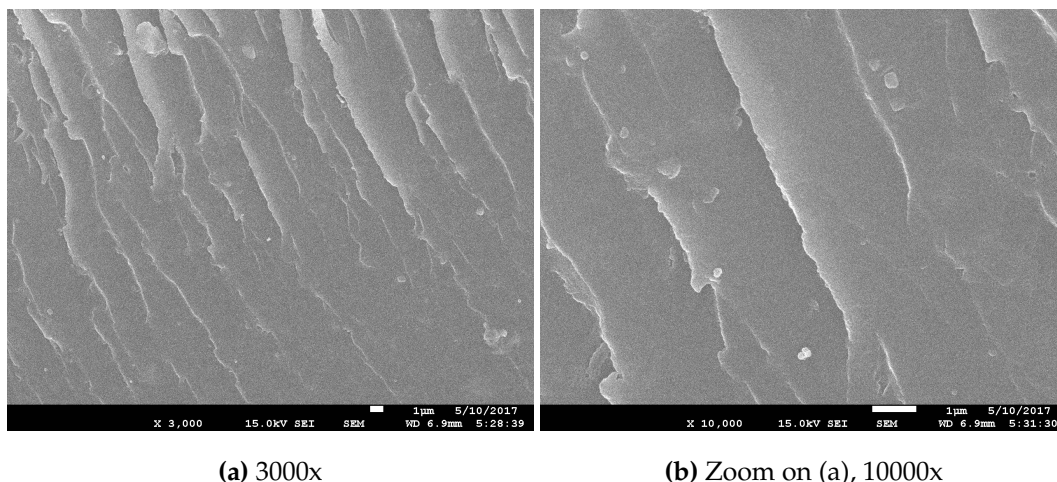


FIGURE 9.5: SEM micrographs at 15.0 kV on a sample with 5.0wt% ZnO and 270s sonication.

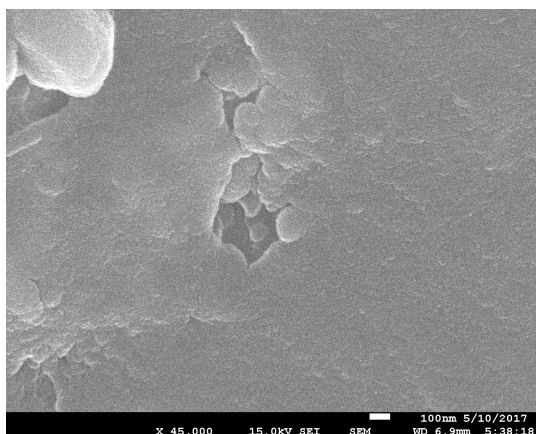


FIGURE 9.6: SEM micrograph at 15.0 kV on a sample with 5.0wt% ZnO and 270s sonication. Zoom on Figure 9.5a, 45000x.

Later, SEM analysis was made on a sample with a concentration of 10.0wt% ZnO to check whether large aggregates would appear in the samples and be visible on SEM micrographs. The resulting images for this sample sonicated for 90 seconds are presented in Figure 9.7. At a magnification of 5000 $\times$ it is already clear that the dispersion of the ZnO nanoparticles was less efficient. There seem to be some regions with large aggregates stuck together and other where ZnO particles are not detected. In image (b), a further magnification is applied. The presence of aggregates is well confirmed and they form a large clump of over 5 μm in size. Therefore, if a good dispersion was obtained for smaller amounts of ZnO at 90 seconds of sonication, this is no longer true at 10.0wt%. Their effect will be studied next with DSC and TGA analysis techniques.

Combining the various observations by TEM and by SEM on the dispersion of the ZnO nanoparticles within the T-DDM benzoxazine matrix, several conclusions

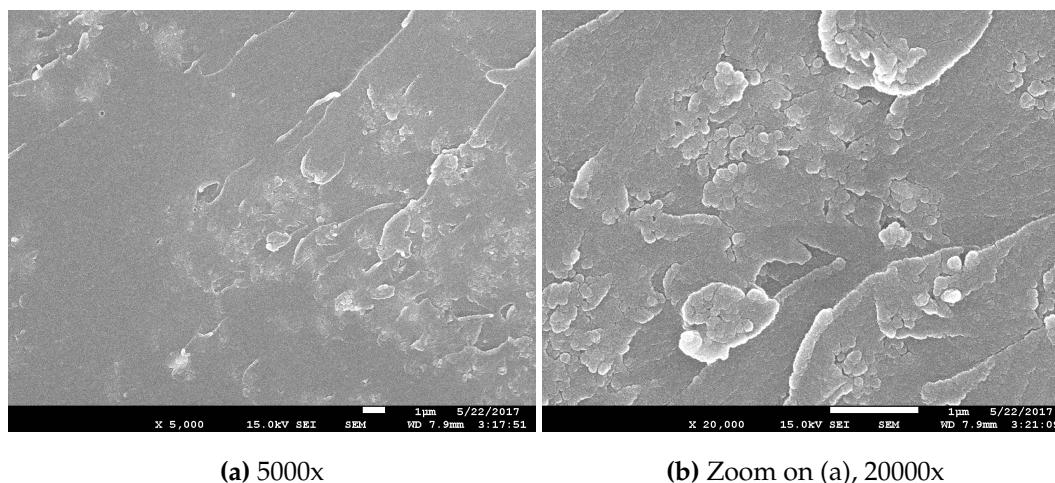


FIGURE 9.7: SEM micrographs at 15.0 kV on a sample with 10.0wt% ZnO and 90s sonication.

can be made. First, the dispersion was already judged sufficient at 90 seconds of sonication for both blends. Overall, the particles are well dispersed within the matrix in small clusters. Some larger clusters are also observed and their amount increases with the nanoparticles concentration in the blend. These clusters start breaking up at higher sonication times. Then, regarding the fracture surface of the samples, the surface is smooth with river cracks, indicating a fragile fracture, for the neat resin. With an increasing amount of nano-inclusions, the surface roughens and some clusters can be identified, and at 10wt% ZnO, some large aggregates are even visible. For an increasing sonication time, a smoothening of the surface is observed. Thus, the observations over thin sections, analyzed by TEM, and the fracture surface, analyzed by SEM, of the blends match. Increasing the ZnO concentration leads to larger clusters or even aggregates and increasing the sonication time disperses these clusters. Nevertheless, for blends at 0.5 and 5.0wt% ZnO, 90 seconds of sonication are already enough for an appropriate overall dispersion of the nanoparticles.

9.2 Analysis of the curing reaction of the blends

Once it was established that the dispersion of the zinc oxide nanoparticles was satisfactory for blends at 0.5 and 5.0wt% ZnO sonicated for 90 seconds, the first part of the thermal analysis was conducted by DSC. This part studies the curing reaction of the blends based on their heat of reaction and the temperature at maximum reaction rate or peak temperature. The results of the experiments will predominantly be presented graphically, however, the precise data are available in Figure A.2 of Appendix A.

The second part of the thermal analysis of the blends was done using TGA and will be discussed in the next section (Section 9.3).

Figure 9.8 depicts the typical curve obtained for the dynamic DSC experiments on the blends at a heating rate of 10°C/min between 30 and 300°C. The drop in the beginning of the curve at 30°C, is linked to the 5 minutes where an isothermal temperature is maintained to obtain a homogeneous starting temperature of 30°C over the whole sample. The small peaks appearing over the range of temperatures

between 60 and 130°C are the results of a crystallization, associated with the exothermic peak, followed by melting, associated to the endothermic peak. This behavior was also observed for the neat resin. Yet, crystallization is not observed on all samples, probably because of variations in the purity of the T-DDM batches. Some part of these peaks could also result from desolvation, if the sample was not sufficiently degassed, with the addition of an endothermic contribution.

However, the most significant feature is the peak related to the curing reaction of the T-DDM blend. For the blend at 5wt% ZnO shown in the figure, this curing reaction leads to a peak corresponding to an average enthalpy of reaction H_r of 271.3 Jg⁻¹ and with a maximum peak temperature T_p of about 225°C.

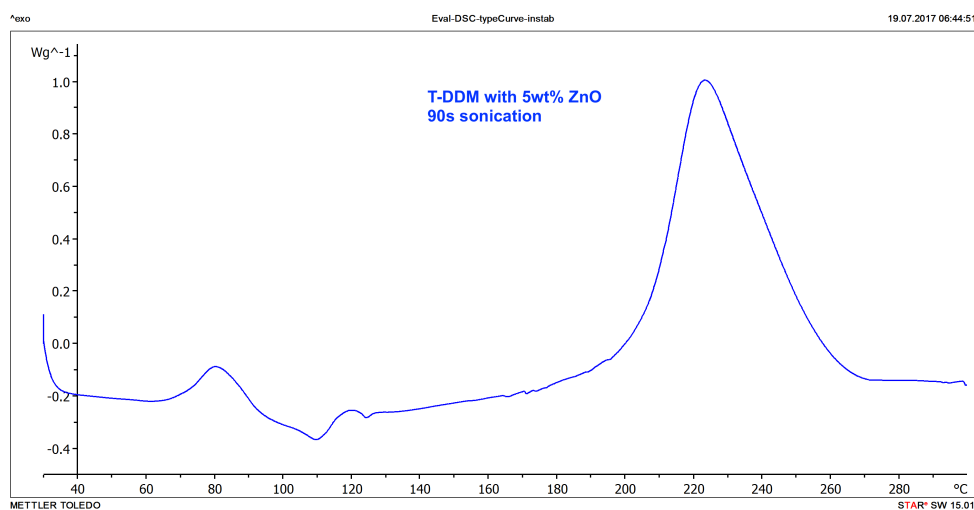


FIGURE 9.8: DSC curve for a blend of T-DDM with 5wt% ZnO, sonicated for 90s.

Two series of experiments were conducted. First, the effect of an increasing percentage of zinc oxide particles within the T-DDM matrix was studied. For this part of the DSC study, all blends had been sonicated for 90s. Then, in the second set of experiments, the effect of an increasing sonication time on blends with 0.5 and 5wt% ZnO was measured.

9.2.1 Effect of ZnO on T-DDM in DSC

The first series of experiments focuses on the effect of the addition of zinc oxide particles to the T-DDM benzoxazine matrix on some properties that can be measured by DSC. The maximum peak temperature and the heat of reaction, which is proportional to the area under the peak, have been recorded for this set of experiments. The general evolution of the peak related to the cross-linking reaction with the concentration in ZnO is shown in Figure 9.9. Overall, the peak area, and thus the enthalpy, decreases as the ZnO concentration increases. This decrease is at least partially due to the replacement of a fraction of the T-DDM resin with ZnO, which does not react on its own. Through the analysis of the DSC data, this will be studied in more detail. The onset and endset of the peak do not seem to change much due to the addition of ZnO, but the reaction rate globally slows down with the ZnO concentration. Finally, no distinctive conclusions can be made about the peak temperature at this stage of the analysis of the curves.

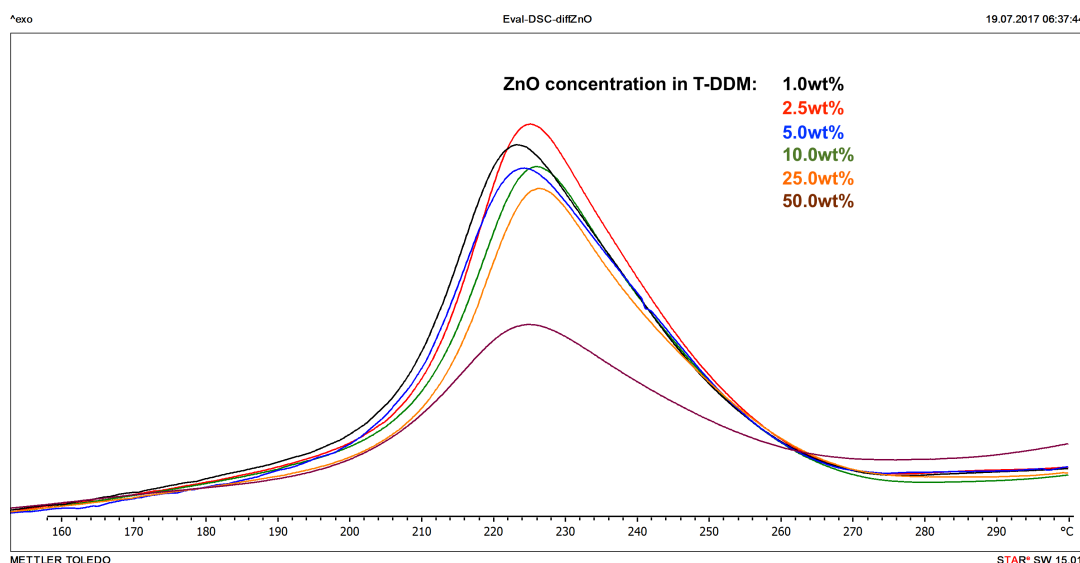


FIGURE 9.9: DSC curves of T-DDM blends with an increasing concentration of ZnO: 1, 2.5, 5, 10, 25, and 50wt% ZnO.

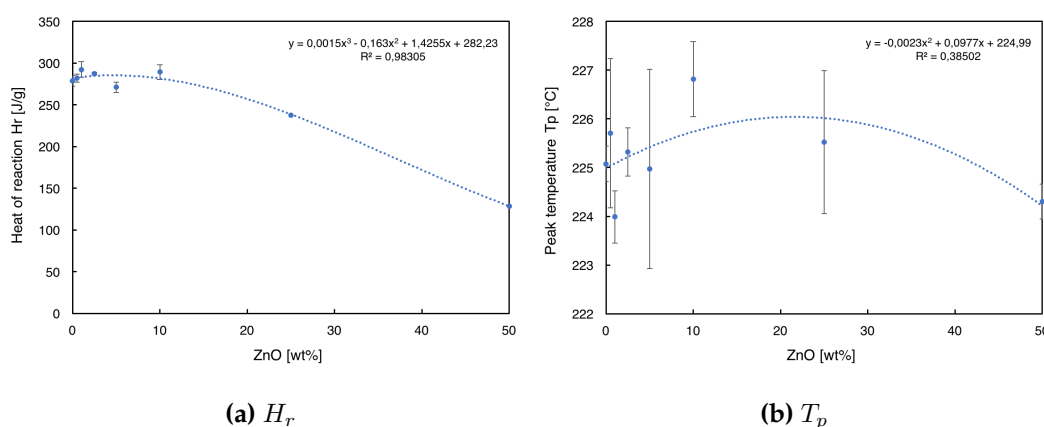


FIGURE 9.10: DSC data of T-DDM blends with different loadings of ZnO: (a) heat of reaction H_r , (b) peak temperature T_p . The brackets represent the 95% CI.

From the collected data, the mean values for the heat of reaction H_r and the peak temperature T_p were plotted with their CI against the ZnO concentration. These plots are shown in Figure 9.10. The data points representing H_r versus the ZnO fraction, were most adequately fitted with a third order polynomial. Due to the replacement of a fraction of the T-DDM resin with ZnO in Figure 9.9, it had already been predicted that a decline in H_r would be observed. However, this decline is not linear and there even is a small increase in the heat of reaction before it starts to decrease. This unexpected behavior will be discussed in a next paragraph.

Regarding the peak temperature T_p , a second order polynomial provided the most representative fit to the data, but given a factor of determination R^2 at 0.385 the validity of this fit must seriously be doubted. Given the small scale of the variations, between 223.0 and 227.5°C with the CI included, it may be assumed T_p is not much influenced by the amount of ZnO. The variations in T_p are most likely the result of differences in sample size and geometry as well as heterogeneities in sample composition. This being said, it is not excluded ZnO might have an effect on

T_p . However, due to the lack of precision of the data and the absence of additional data points, no conclusions can be made about the effect of zinc oxide on the peak temperature.

While the data on T_p are inconclusive, the fit for H_r with the ZnO concentration is much more in line with the data points and has an unexpected behavior worth investigating. To obtain the extent of the combined effect of ZnO and T-DDM on the enthalpy, the separate contributions of T-DDM and ZnO to the enthalpy were subtracted to the measured values. The contribution related to either T-DDM or ZnO on itself, were calculated based on the values in Table 6.1. These contributions were evaluated using Equations (9.1) and (9.2), where H_r^{TDDM} and H_r^{ZnO} represent the enthalpies measured for the pure samples of T-DDM and ZnO.

$$H_{TDDM} = H_r^{TDDM} \cdot \left(\frac{100 - wt\%ZnO}{100} \right) \quad (9.1)$$

$$H_{ZnO} = H_r^{ZnO} \cdot \frac{wt\%ZnO}{100} \quad (9.2)$$

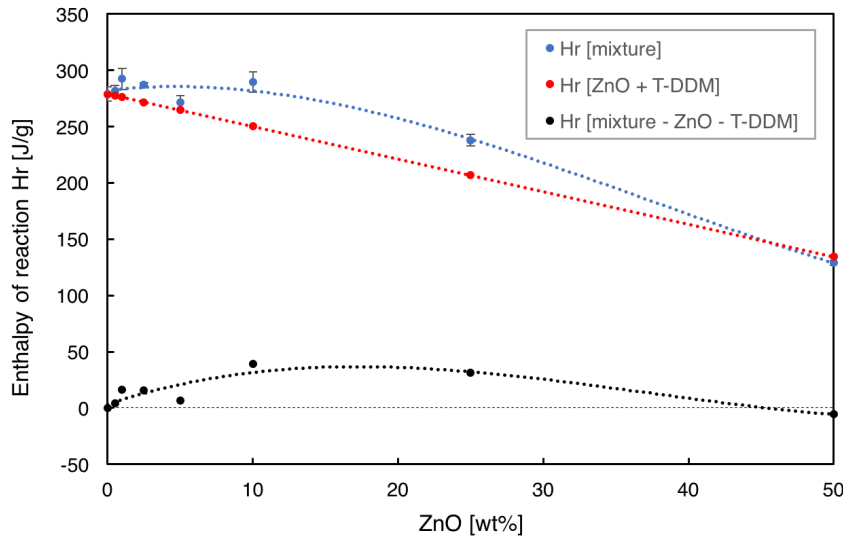


FIGURE 9.11: Heat of reaction versus ZnO concentration: DSC data compared to the expected decrease for H_r .

Figure 9.11 depicts the data for H_r of the blend, the summed value of the separate effects of T-DDM and ZnO, and the difference between both curves. This results in a residual H_r , which cannot be explained by the presence of ZnO and T-DDM separately. Thus, combining both components into a blend has a distinctive effect on the heat of reaction. When considering the data points obtained by DSC, the maximum of the recorded surplus in heat of reaction occurs at 10wt% ZnO, with a gain in H_r of 39.4 Jg^{-1} . For the residuals obtained by subtracting separate effects of T-DDM and ZnO to the fit, the resulting curve is maximized for 17.4wt% ZnO. In this case, the measured surplus in H_r is of 37.0 Jg^{-1} . These gains in enthalpy, offer an increase of the H_r expected from a rule of mixture of 15.8 and 16.1% at their respective ZnO concentrations.

9.2.2 Effect of the sonication time on T-DDM–ZnO blends in DSC

The effect of the sonication time was studied on blends with 0.5 and 5.0wt% ZnO. Sonication times of 30, 90 and 270 seconds were applied on the blend with the lower concentration in zinc oxide, while additional sonication times of 360 and 540 seconds were applied on the blend with 5.0wt% ZnO. The curves obtained by DSC for the different sonication times are illustrated in Figure 9.12. No significant effects linked to the increased sonication time can be observed in those curves. A more precise analysis of the DSC curves will try to determine the possible effect of sonication time on the enthalpy and the peak temperature.

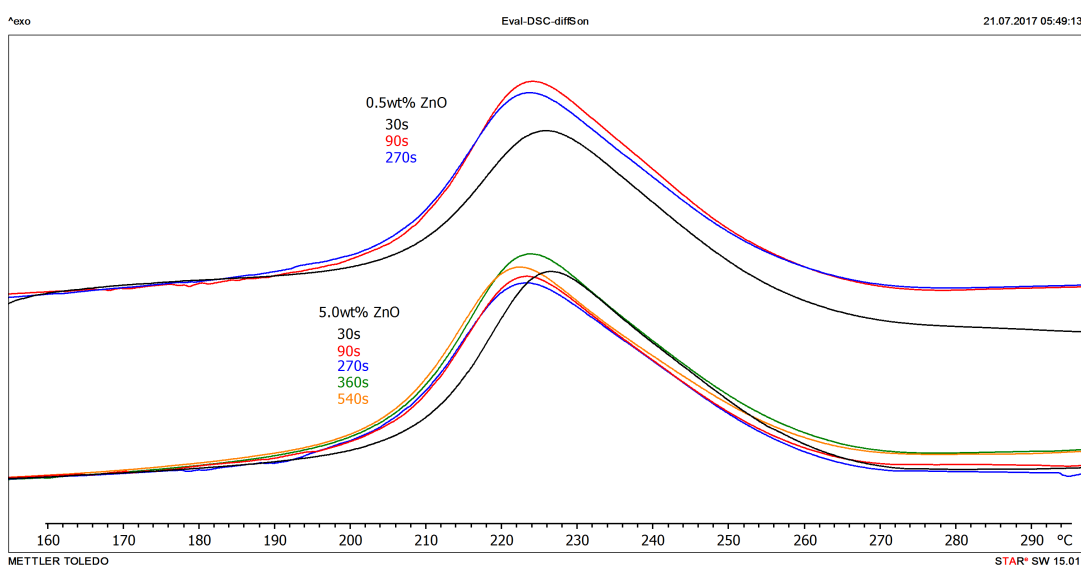


FIGURE 9.12: DSC curves for 0.5 and 5.0wt% ZnO blends with T-DDM: 30, 90, 270, 360, and 540 seconds sonication.

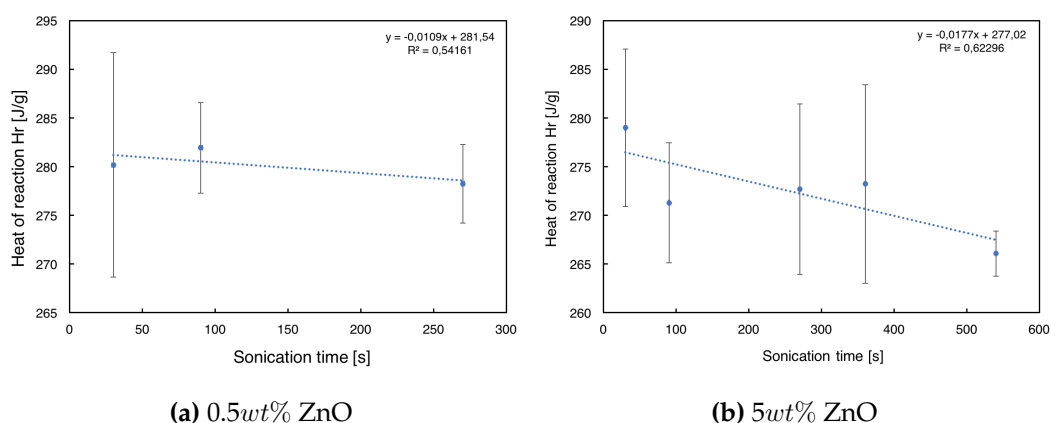


FIGURE 9.13: H_r of T-DDM blends with different sonication times: (a) 0.5wt% ZnO and (b) 5wt% ZnO. The brackets represent the 95% CI.

Regarding the heat of reaction, a decreasing trend is observed with sonication time for both ZnO concentrations, as shown in Figure 9.13. However, given the large margins of error and the small determination coefficients of the linear fitting curves,

it can be put in question whether this decrease is really linked to the increased sonication time. Additionally, this decreasing trend seems contradictory with the increased heat of reaction observed for the blends containing different ZnO loadings. It could be expected that this increase in enthalpy was related to interaction with the zinc oxide. And it was demonstrated in Subsection 9.1 that higher sonication times led to a better dispersion, thus increasing the possibility for interaction with ZnO. Therefore, an increase was anticipated instead of this small decrease. However, it is possible that sonication could lead to an advance of the reticulation, thereby decreasing H_r . Or that, some enthalpic interactions between the ZnO and the resin exist. Thus, due to the better dispersion, more of these interactions can take place and H_r drops a little. Additional sonication times should be applied on the blends to verify whether this decreasing trend persists. Moreover, for each data point, more tests would reduce the margins of error.

Again, for the peak temperature, a slight decrease with sonication time is recorded. The margins of error representing the 95% confidence intervals remain high, but the coefficient of determination is adequate. Furthermore, both fitted curves have almost the same equation, as if this decrease in T_p was independent of the ZnO fraction. Also, the decreasing trend for T_p is in line with the expectations. Longer sonication times lead to a better dispersion and a more homogeneous blend. Therefore, the ring-opening polymerization of the matrix can evolve more rapidly and there is a better access to ZnO nanoparticles for possible interactions. The reaction and the heat associated with it develop faster and reach the maximum of the exotherm peak at a lower temperature. Nevertheless, for more accurate results and fitting additional tests for each sonication time and the addition of different sonication times would be helpful.

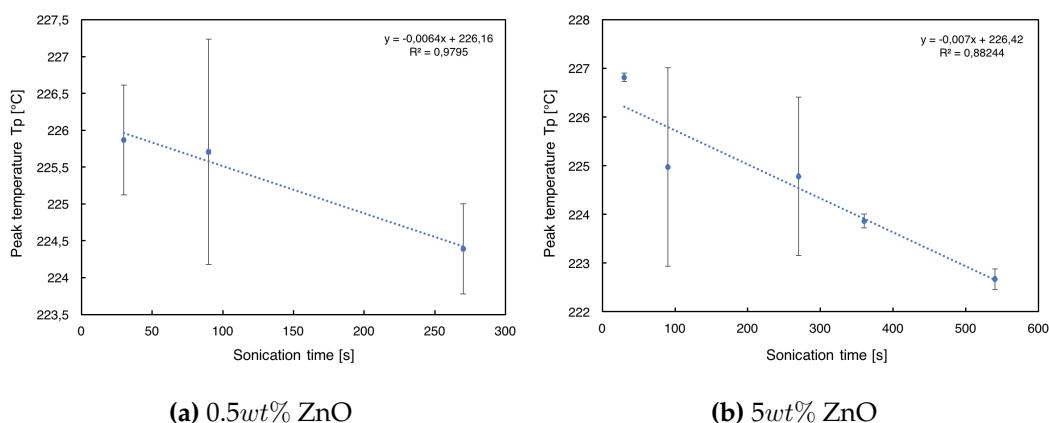


FIGURE 9.14: T_p of T-DDM blends with different sonication times: (a) 0.5wt% ZnO and (b) 5wt% ZnO. The brackets represent the 95% CI.

9.3 Analysis of the thermal stability of the cured blends

In the second part of the thermal analysis, TGA was used to analyze blends of different compositions and sonication times as detailed in Table 5.1 of Chapter 5. These analyses by TGA aim to establish the effect of ZnO nanoparticles on the thermal stability of the resin. In addition to the overall shape of the TGA curves, two criteria were studied to quantify the effect of zinc oxide particles on the thermal stability of the T-DDM benzoxazine resin. These criteria were the char yield at 800°C and the temperature at a certain percentage of degradation of the sample. The temperatures at 5, 10, 20 and 30% weight loss of the sample were recorded and respectively noted as T_{d5} , T_{d10} , T_{d20} and T_{d30} . These results were obtained in a similar fashion as for the DSC experiments, three samples were taken from each blend to be analyzed with TGA. While most data are presented graphically in this section, the numerical values are listed in Figures A.3 and A.4 of Appendix A.

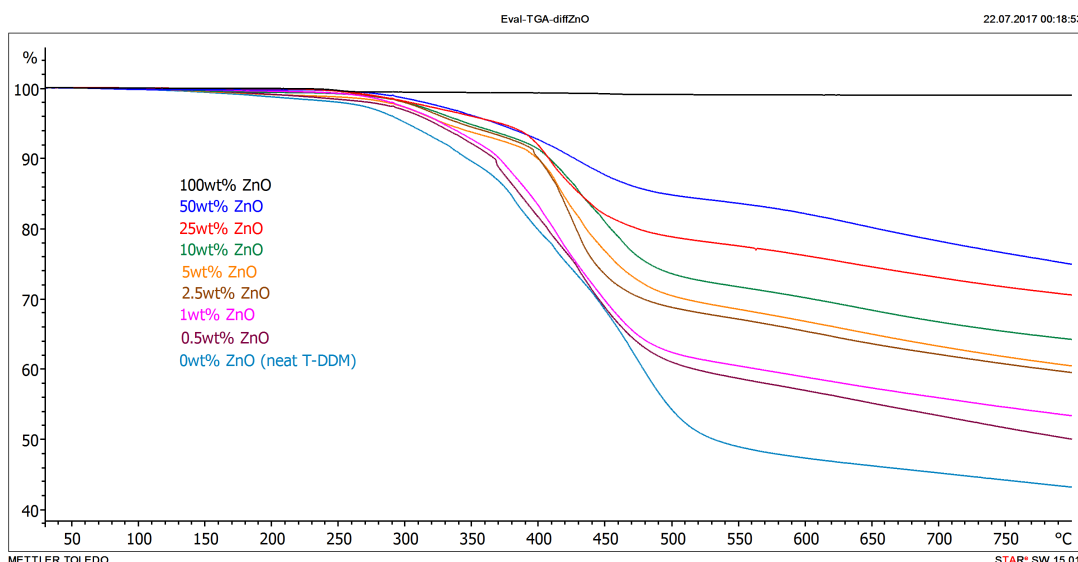


FIGURE 9.15: TGA curves of T-DDM blends with an increasing concentration of ZnO: 0.5, 1, 2.5, 5, 10, 25, and 50wt% ZnO. Curves of neat T-DDM and pure ZnO are added as reference.

Figure 9.15 represents the curves from the TGA analysis of samples with an increasing concentration in zinc oxide. The TGA curves of pure ZnO and T-DDM are added for comparison. The most interesting aspect of these curves is the increase in char yield due to the addition of ZnO. Benzoxazines are already known for their high char yields compared to other thermosetting resins. The addition of zinc oxide further improves this quality and the increase is higher than just the added weight of ZnO. Additionally, a shouldering of the curves, which increases with the amount of ZnO, delays the degradation of the blends. Thus, increasing the temperatures at a given percentage of degradation for each of those blends. For instance, T_{d5} increases from 306.1°C for the neat resin to 331.4 and 347.1°C for blends at 1 and 10wt% ZnO.

In a similar fashion as for the analysis of the DSC results, the data obtained with TGA will be treated, first, to study the effect of a varying concentration of ZnO on the blend, and then, to study the effect of the sonication time on two blends of different compositions.

9.3.1 Effect of ZnO on T-DDM in TGA

To begin the analysis of the effect zinc oxide nanoparticles on the T-DDM resin with TGA, the degradation mechanisms of the cured resin will be explored. Figure 9.16 shows the first derivative of the TGA curves for several blends and also for the neat resin and pure ZnO powder. By the definition of a derivative, these curves show, for each point of the initial TGA curves, the slope of the tangent on these curves. Therefore, the peaks observed in the figure correspond to specific degradation mechanisms, which occur at a certain temperature and then decrease. For the pure ZnO, no peaks are observed, except for a small dip around 250°C, probably due to the evaporation of water. The other curves, corresponding to the neat resin and the blends, show an initial degradation between 250 and 350°C.

Then, for the neat resin only, three main peaks are observed: a first between 350 and 400°C, a second between 400 and 430°C, and a third starting at 430°C and ending at 550°C. There certainly is an overlapping of these three peaks, because several degradation mechanisms can occur at once and no return to the starting line is observed. Based on the results of other studies on the degradation of benzoxazines resins presented in Subsection 1.1.4, the first peak could be associated with the cleavage of the C – N bond in the Mannich bridge. Then, the second peak should correspond to scission of C – C bonds. And the third peak, to the further degradation leading to the formation of char, which is strongly supported due to the long range of the peak from 430 to 550°C.

For the blends, several trends can be established. First, the separate peaks merge into one larger peak with shouldering. Then, there clearly is a delay of the degradation mechanisms visible by a shift of the peak to higher temperatures. Finally, the peak gains in intensity and becomes sharper between 0 and 5wt% of ZnO, and then decreases and becomes more diffuse with an increasing amount of ZnO. This can be explained, for the first effect, by the delay of the degradation and the occurrence of the greater part of the degradation at once by multiple mechanisms. The second effect, is due to the increasing amount of zinc oxide. This increasing amount will lead to a lower degradation of the material - as will be seen later - and, thus, to a decrease in intensity of the peaks of the derivative TGA curves.

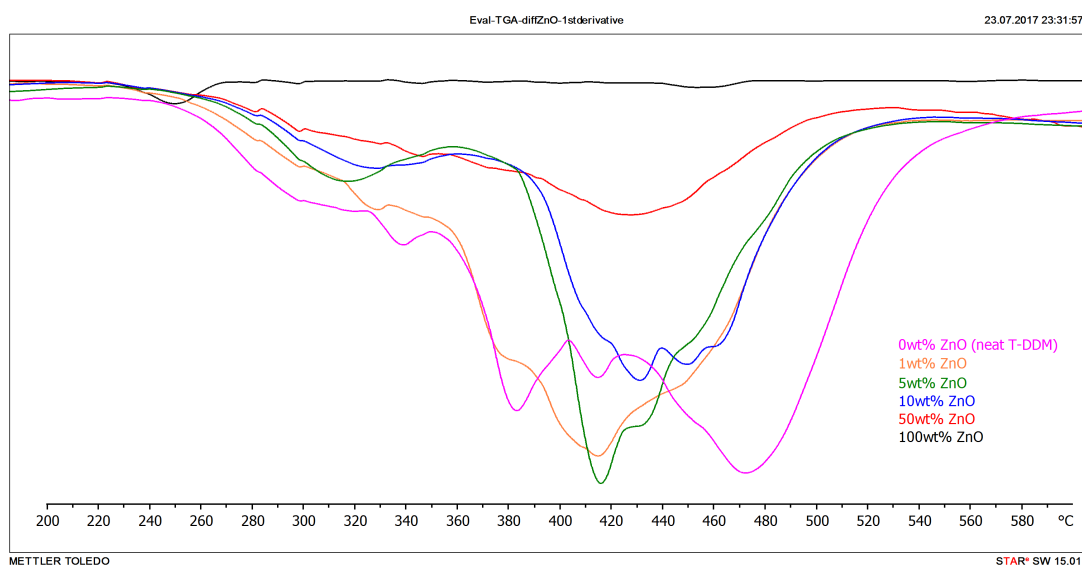


FIGURE 9.16: First derivative curve of the TGA measurements for loadings of ZnO of 0, 1, 5, 10, 50 and 100wt%.

Once the overall degradation mechanism was explored, the temperatures at four different degradation levels of the samples and over the studied range of ZnO concentrations in T-DDM benzoxazine are shown in Figure 9.17. For 5 and 10% weight loss of the samples, a sharp increase of the degradation temperature is observed for the lower concentrations in ZnO. Then, this increase levels off and the temperature continues to slightly increase in a plateau-like behavior. Equations (9.3) and (9.4) provided the best fit for the data over the selected range of ZnO concentration with determination factors of respectively 0.9411 and 0.9356. However, at higher ZnO concentrations those curves are bound to start increasing at some point since almost no weight loss is recorded for the pure ZnO. Therefore, a third order polynomial can be expected if data were collected on blends with a higher fraction of zinc oxide.

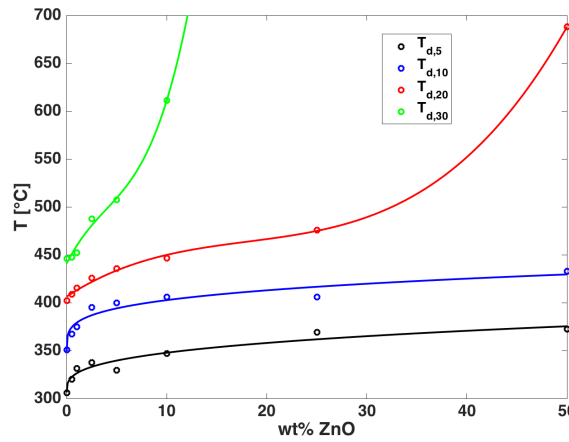


FIGURE 9.17: Evolution of degradation temperature with ZnO loading at for 5, 10, 20 and 30% weight loss.

A third order polynomial is also the type of equation which fits best the 20 and 30% degradation temperatures. The exact equations of the fitted curves on the data are given by Equation (9.5) and (9.6), with R^2 respectively 0.999 and 0.993. The increase in T_d begins fast to slow down into a plateau, followed by a sharp increase. When a higher degradation level is selected, the plateau length decreases and for T_{d30} this plateau has disappeared completely. Moreover, provided the fit follows the behavior of the blends accurately, a weight loss of 30% is never reached at 800°C over 13.7wt% ZnO. This value is 55.3wt% ZnO for T_{d20} .

$$T_{d5} = 306.3 + 20.0 \cdot X_{ZnO}^{1/3.16} \quad (9.3)$$

$$T_{d10} = 349.4 + 29.7 \cdot X_{ZnO}^{1/3.94} \quad (9.4)$$

$$T_{d20} = 0.006 \cdot X_{ZnO}^3 - 0.30 \cdot X_{ZnO}^2 + 6.81 \cdot X_{ZnO} + 406.4 \quad (9.5)$$

$$T_{d30} = 0.205 \cdot X_{ZnO}^3 - 2.41 \cdot X_{ZnO}^2 + 20.61 \cdot X_{ZnO} + 440.9 \quad (9.6)$$

Figure 9.18 shows the evolution of the char yield measured at 800°C with an increasing fraction of ZnO. On the figure, the dotted lines correspond to the value of the char yield after the subtraction of the individual effects of the T-DDM resin and ZnO nanoparticles respectively. The individual effects of T-DDM and ZnO were calculated as shown in Equation (9.9) and (9.10), where X_{ZnO} is the ZnO fraction

and 0.436 and 0.990 the final average char yields for T-DDM and ZnO at 800°C.

$$CY_{TDDM} = 0.436 \cdot (100 - X_{ZnO}) \quad (9.7)$$

$$CY_{ZnO} = 0.990 \cdot X_{ZnO} \quad (9.8)$$

Finally, these separate effects were both subtracted to the char yield. The resulting curve is particularly interesting as it shows a synergy: the combined effect of both components in the blend results in a char yield greater than the sum of their separate effects.

Equations (9.9) and (9.10) give the equations of the fitted curves to the char yield and for the synergy. The determination coefficients for those curves are respectively 0.996 and 0.971. From the fit to the synergy, the optimal ZnO concentration to improve the char yield could be calculated. At 10.8wt% ZnO, the intensity of the synergy reaches a maximum of 16.2%. Thereby, increasing the char yield of 38.9% for the fraction of neat T-DDM in the blend by a total 27.0% due to the addition of ZnO and of the synergy.

$$CY = 44.6 + 0.554X_{ZnO} + 10^{-4.95}(100 - X_{ZnO})^{2.97}X_{ZnO}^{0.36} \quad (9.9)$$

$$CY_{Syn} = 10^{-4.95}(100 - X_{ZnO})^{2.97}X_{ZnO}^{0.36} \quad (9.10)$$

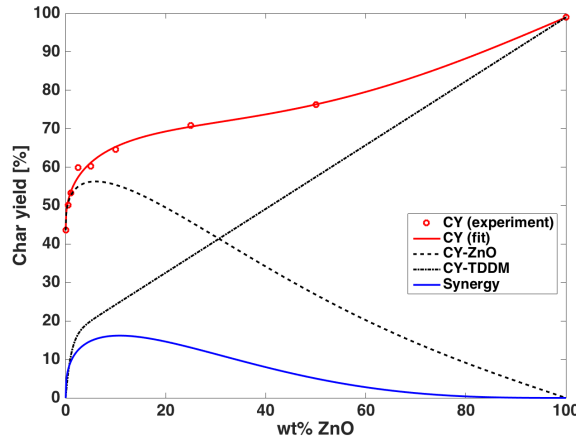


FIGURE 9.18: Char yield at 800°C versus ZnO fraction and synergic effect.

However, the fractions of zinc oxide linked to 80 and 70% char yield at 800°C, and thereby at 20 and 30% degradation, do not correspond well with those deduced from the degradation temperature curves. According to those curves they should be respectively at 55.3 and 13.7wt% ZnO. While a big difference is observed for the one at 30%, 22.8 with the char yield instead of 13.7wt%, the ones for 20% weight loss are closer together with 61.1 and 55.3wt% ZnO. This difference can probably be explained by the precision of the results. Although they are not displayed on the graph, the margins of error to form 95% confidence intervals are higher for the T_{d30} curve than for the T_{d20} one, which could explain the discrepancies between the values. To verify these values and find the most accurate, additional blends with the corresponding ZnO concentrations should be made and tested. The resulting data would also help to get curves to correspond more to the real evolution of the char yield and the degradation temperatures.

9.3.2 Effect of the sonication time on T-DDM–ZnO blends in TGA

Figure 9.19 depicts the aspect of the TGA curves and their first derivative for a nanocomposite at 5wt% ZnO sonicated for increasing times. There does not seem to be a general trend related to the sonication time on the degradation mechanism. In the derivative curves, the initiation of the degradation between 250 and 350°C is similar, however, not all samples start degrading at the same point. The ones that start degrading at a lower temperature, get their main degradation peak earlier and this peak is sharper than for the ones that start degrading at a higher temperature. But this behavior seems to be related to the blends themselves and not to the increased sonication time.

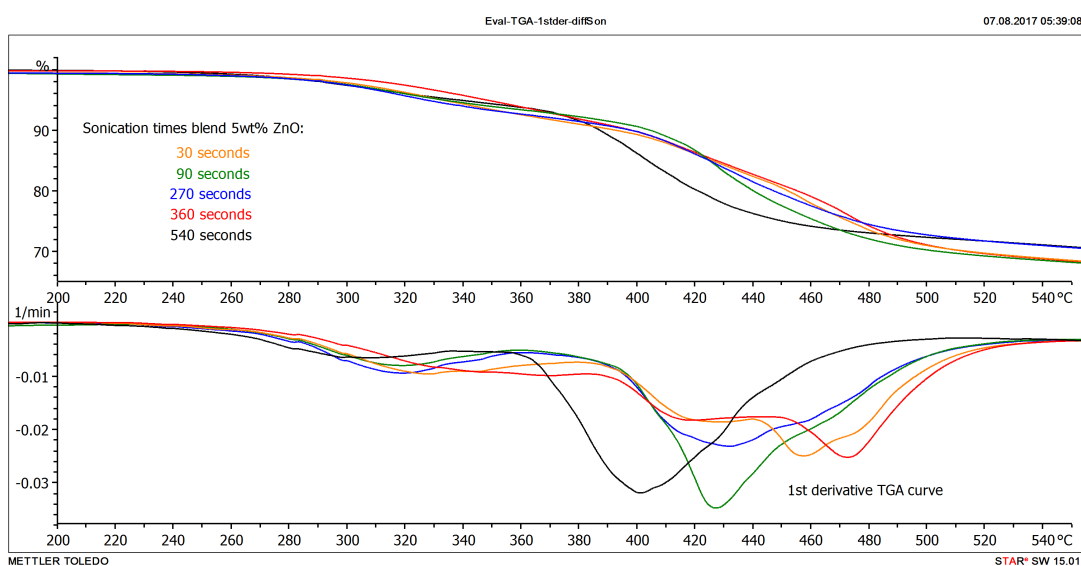


FIGURE 9.19: TGA curves and their first derivatives for measurements on the blends at 5wt% ZnO with sonication times of 30, 90, 270, 360 and 540 seconds.

The char yield and degradation temperatures were also studied with increasing sonication times for blends with 0.5 and 5.0wt% ZnO. Sonication times of 30, 90 and 270 seconds were applied on both blends and additional sonication times of 360 and 540 seconds on the blend with more zinc oxide.

Starting with the degradation temperatures, no distinctive trend could be found for both blends. Small fluctuations were observed that sometimes increased a little, while for other degradation levels or for the other blend, an opposing effect was found. Moreover, the values of R^2 were quite low. This led to the conclusion that the sonication time does not have a clear effect on the temperature at certain degradation levels. Therefore, the general aspect of the TGA curves is the similar for different sonication times and the sonication time should not influence the degradation mechanism. The graphs for the evolution of the degradation temperatures with sonication time are shown in Figures A.5 and A.6 of Appendix A.

Regarding the char yield, a small increase with the sonication time was observed. Figure 9.20 shows these curves for the tested blends. An increase of 1% in char yield was found when 200 seconds of sonication times were added. This increase, although being small, is probably related to the better dispersion of the ZnO within the T-DDM matrix at higher sonication times. A better dispersion allows more interactions with the ZnO and the T-DDM matrix. For example, the ZnO nanoparticles,

which do not degrade even at relatively high temperatures, can serve as support for the formation of char originating from the polymeric matrix. Thus, due to this better dispersion, a small increase of the thermal stability of the blend is found.

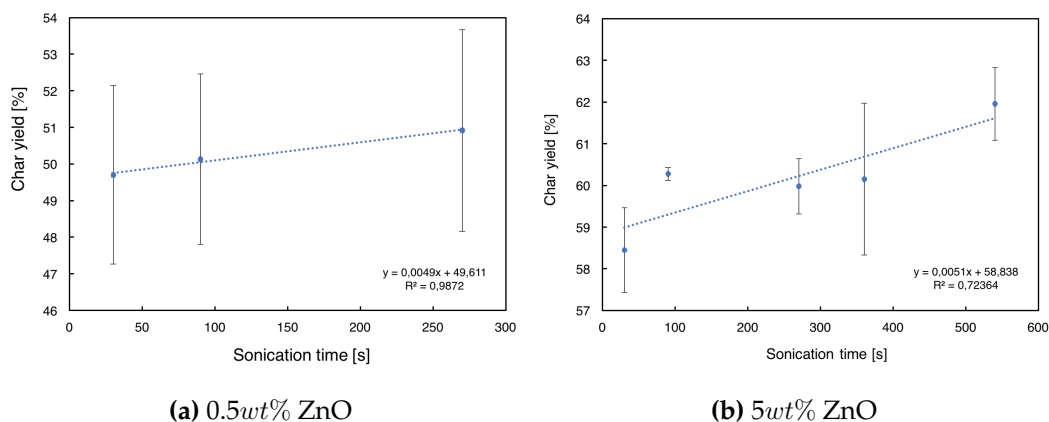


FIGURE 9.20: Char yield of T-DDM blends with different sonication times: (a) 0.5wt% ZnO and (b) 5wt% ZnO. The braquets represent the 95% CI.

9.4 Analysis of the T-DDM–ZnO interactions

This last section of the chapter on the effects of zinc oxide nanoparticles, presents the FTIR spectra of blends at 0.5 and 5.0wt% ZnO sonicated for 90 seconds. The objective of this part is to identify the interactions between the T-DDM matrix and the ZnO nanoparticles, because these interactions are potentially the origin of the increased thermal stability of T-DDM–ZnO blends. FTIR spectra of the blends were taken for uncured and cured samples. The spectra were also compared to the ones for the neat T-DDM resin, which were presented earlier in Figure 6.3.

Figure 9.21 represents the FTIR spectra for both blends in absorption. For each blend, the spectrum obtained for the uncured sample is compared to the one for the cured sample. These spectra confirm that a polymerization reaction occurs via ROP. Namely, the characteristic peaks linked to the benzoxazine structure all decrease or disappear on the spectrum for the cured sample. These peaks are the ones at about 945 and 1500 cm^{-1} associated with the tri-substituted benzene ring, at 1333 cm^{-1} due to CH_2 wagging in benzoxazine, and at approximately 1226 cm^{-1} due to the antisymmetric $\text{C} - \text{O} - \text{C}$ stretching. The peak at 1045 cm^{-1} related to the symmetric $\text{C} - \text{O} - \text{C}$ stretching is present in both spectra. Moreover, even though the peak at 1480 cm^{-1} due to the tetra-substituted benzene does not appear on the FTIR spectra of the cured nanocomposite samples, a shouldering and broadening around 1480 cm^{-1} of the peaks at 1509 and 1510 , respectively for the spectra of 0.5 and 5.0wt% ZnO blends, was observed and suggests the apparition of tetra-substituted benzene. Additionally, the peak at 1119 cm^{-1} due to $\text{C} - \text{OH}$ stretching of the hydroxyl functionalities of T-DDM disappears upon curing, which confirms a second polymerization mechanism based on a condensation reaction between the hydroxyl groups.

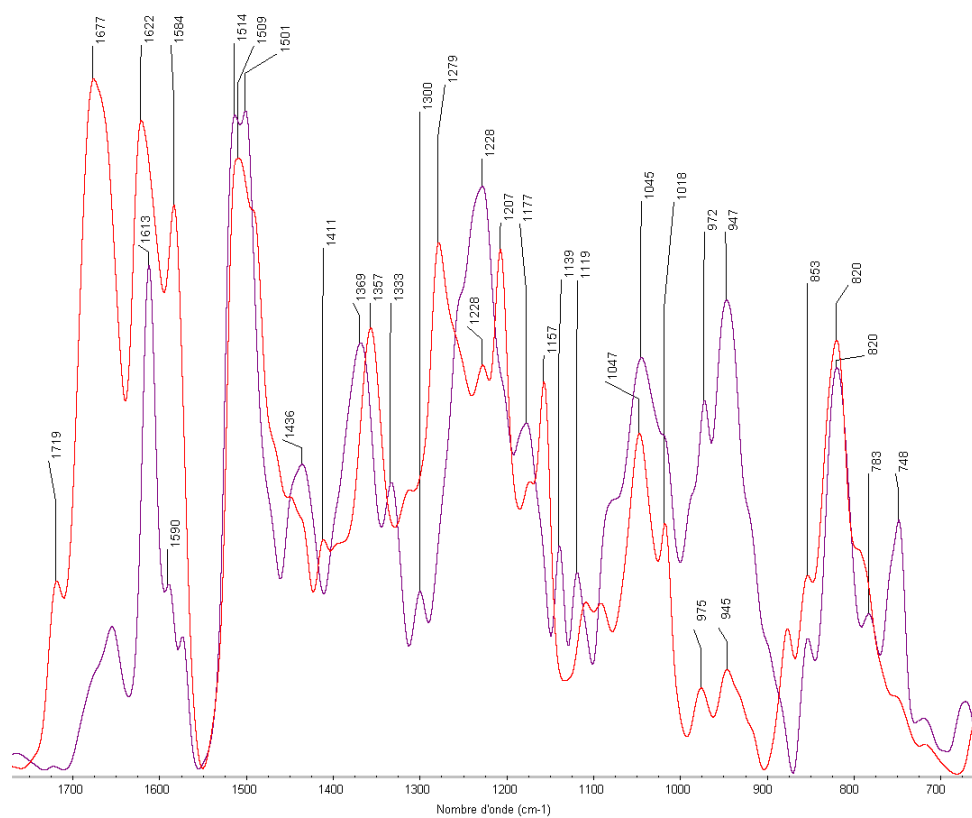
The apparition of the typical peaks associated with ZnO in the spectra was also analyzed. The spectrum of ZnO, presented earlier in Figure 3.3, has peaks over the studied range of wave numbers at 837 , 1402 and 1512 cm^{-1} . In the spectra for the

blends, a slight increase of the peaks at 1515 cm^{-1} was found. Moreover, a small peak appeared at 1412 cm^{-1} for the cured blends. These peaks could possibly be associated with the ones at 1402 and 1512 cm^{-1} of the spectrum of ZnO.

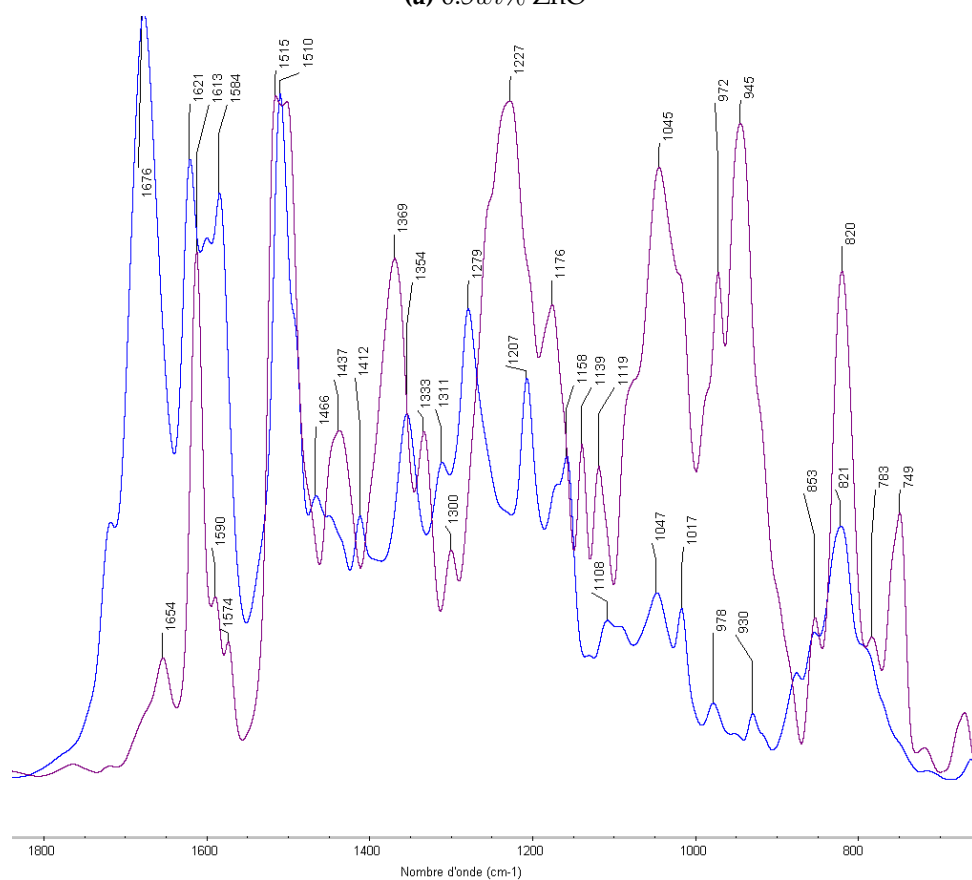
In order to get a better understanding of the effect ZnO has on the spectra of the blends, the spectra for the blend at $5.0\text{wt}\%$ ZnO were compared to the ones of neat T-DDM in Figure 9.22. Starting with the uncured samples, their spectra seem very similar. A closer study of the different peaks found that no additional significant peaks appeared due to the inclusion of ZnO. Yet, the intensity of some peaks was reduced or increased.

In the spectra for the cured samples, however, a distinctive difference was observed: a very strong peak appears at 1678 cm^{-1} . This peak was not observed at all for the cured sample of the neat resin. Therefore, this peak could be associated with an interaction between the zinc oxide and the benzoxazine matrix. The most evident possibility was to link this peak to carbonyl stretching. The carbonyl, $\text{C}=\text{O}$, stretching in this range could be associated with conjugated ketones [80]. Nevertheless, the formations of such compound due to ZnO seems difficult. According to Ghiotti [81] this peak is due to ZnH , with a secondary peak is found at 1707 cm^{-1} . This is already a better possibility, because a small shouldering peak is found around 1719 cm^{-1} for the blends. Yet, in their study these peaks were really small compared to the one found for the T-DDM–ZnO blends. Finally, the most probable origin for this peak is to attribute it to the hydroxyl group [82, 83]. Due to the presence of ZnO in the blends, the water produced by the condensation reactions of the hydroxyl groups is chemisorbed on the ZnO molecules and forms additional $\text{O}-\text{H}$ groups, which are detected at a wavenumber of 1678 cm^{-1} .

Nevertheless, this peak could also result from localized degradation of the resin. This peak is very close to the 1670 cm^{-1} found for the formation of an aliphatic Schiff base, $\text{CH}_2=\text{NR}$, due to a scission of the $\text{C}-\text{N}$ bond in the Mannich bridge. Therefore, if this last possibility is considered, it means that degradation occurs during the curing of the blend. But as this peak was not observed for T-DDM cured by the same cycle, the addition of ZnO would still be at its cause. Possibly, due to a catalytic effect around the ZnO nanoparticles that generates too much heat locally.

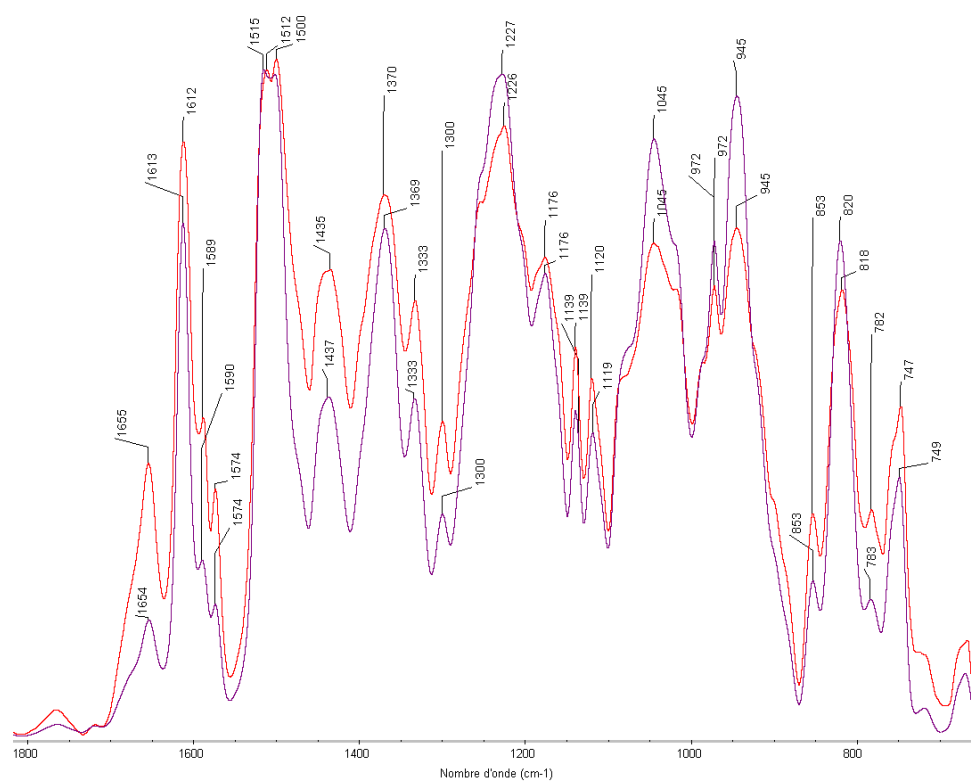


(a) 0.5wt% ZnO

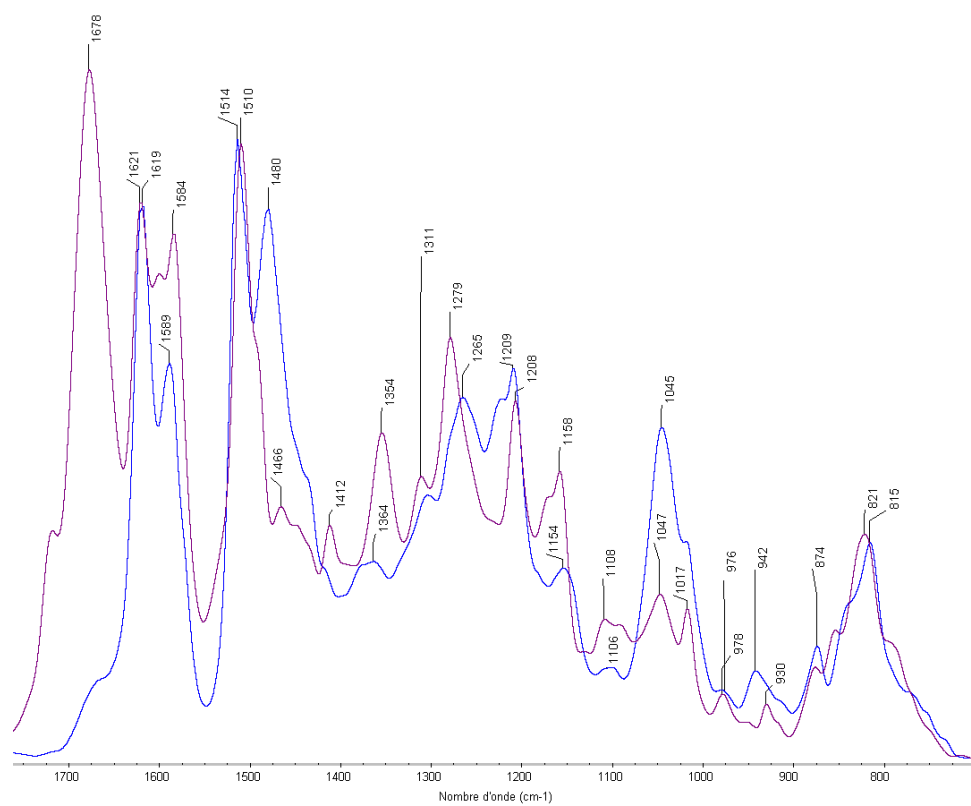


(b) 5wt% ZnO

FIGURE 9.21: Absorption FTIR spectra from 650 to 1800 cm^{-1} blends at : (a) 0.5wt% ZnO (purple uncured, red cured) and (b) 5wt% ZnO (purple uncured, blue cured).



(a) Uncured



(b) Cured

FIGURE 9.22: Absorption FTIR spectra from 650 to 1800 cm^{-1} comparing blend at 5wt% ZnO with neat T-DDM: (a) uncured (purple blend, red neat T-DDM) and (b) cured (purple blend, blue neat T-DDM).

Conclusion on the effect of ZnO on T-DDM

In a first aspect of the study on the effect of ZnO on T-DDM, the dispersion of the ZnO nanoparticles within the T-DDM matrix was studied by TEM. A sufficient dispersion was found for blends at 0.5 and 5.0wt% ZnO with 90 seconds of sonication. The dispersion was mainly in the form of small clusters of particles, which grew with an increasing concentration of ZnO. At 10wt% ZnO, some large aggregates were even found. With an increasing sonication time the larger clusters break up into smaller cluster. The addition of ZnO could also be confirmed by SEM micrographs of the fracture surface of samples. A roughening of the surface was observed when the ZnO loading increased. With longer sonication times, the fracture surface became smoother again.

Having established a correct dispersion was obtained, a thermal analysis of T-DDM–ZnO blends followed by DSC and TGA. A synergy was found for the enthalpy generated by the curing reaction. At 17.4wt% ZnO, the value of H_r is 37.0 Jg^{-1} higher than expected, thus, leading to an increase of H_r by 16.1%. With longer sonication times a decreasing trend of this heat of reaction was found. Nevertheless, the most significant improvement in properties due to the addition of ZnO nanoparticles was observed for the thermal stability by TGA. A brief discussion of the degradation mechanism showed that with the addition of zinc oxide nanoparticles, the distinctive degradation mechanisms of the neat resin merged together, and decreased in intensity once over 5wt% of ZnO were added. The degradation temperatures at certain levels of weight loss show a sharp increase for the first percentages of ZnO in the blend. T_{d5} and T_{d10} show only a small increase afterwards, while T_{d20} and T_{d30} are above 800°C over a certain ZnO concentration. Furthermore, a significant synergy was observed for the char yield at 800°C. At 10.8wt% ZnO, the value of CY is 16.2% over its expected value. Thus, adding a total contribution of 27%, due to the ZnO and the synergy, to the part of the char yield of the neat T-DDM present in the blend.

Finally, to explain the previous observations, FTIR was used to find possible interactions between the T-DDM resin and ZnO. While no significant effect was noticed in the spectra of the uncured blends, a peak at 1678 cm^{-1} appeared in the spectra of the cured blends. Several possible attributions of this peak were emitted. However, the most promising one explains this peak by additional O – H groups formed by water chemisorpted on the ZnO molecules. This water would originate from the condensation reaction in T-DDM that occurs alongside the ROP.

Conclusion

The aims of this master thesis were threefold. First, to establish the curing kinetics of the neat T-DDM benzoxazine resin. Second, to propose an optimized cure cycle for this benzoxazine. And third, to evaluate and discuss the origin of the effect of ZnO nanoparticles on the thermal stability of a composite blend, composed of these nanoparticles and T-DDM.

Starting with the curing kinetics, it was determined that the T-DDM benzoxazine precursor follows an autocatalytic curing mechanism. The reaction rate was found to match with the equation for autocatalytic reactions and a multi-linear regression was run to evaluate the kinetic parameters. An overall order of reaction in the range of 2.2 to 2.5 was observed and the value of the activation energy at approximately 90 kJ/mol agrees very well with the value obtained from peak temperature methods, such as the Kissinger method. However, the activation energies resulting from iso-conversion methods were higher and did not coincide well with the other results.

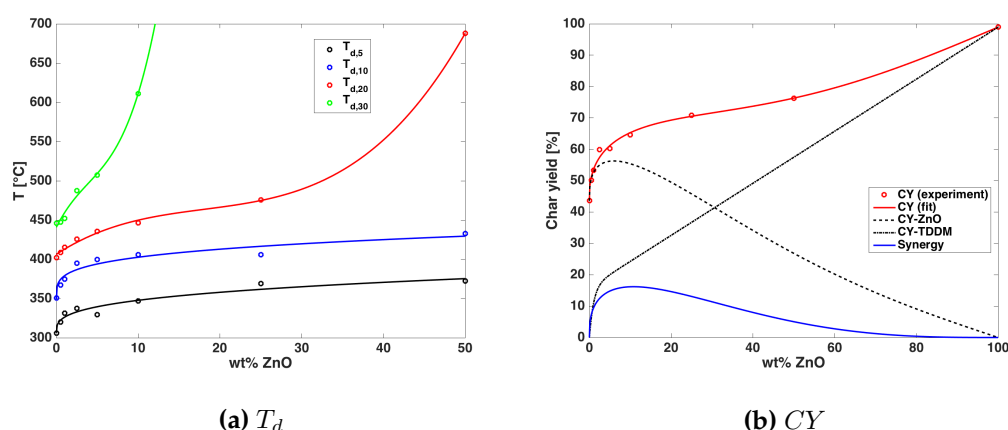
Based on this knowledge and a series of isothermal cure cycles, an improved cure cycle was then devised. The optimization of the cure cycle was targeted at maximizing the conversion of the precursor and, thus, at reaching its ultimate T_g . Considering the generation of heat by the exothermic curing reaction, the cycle was divided into two steps: 60 minutes at 165°C, followed by 90 minutes at 200°C. An additional step of 30 minutes at 220°C was considered to reach a complete conversion. Despite reaching the maximal conversion in DSC tests, this cycle could not fully cure the resin when applied in a furnace. Moreover, for a similar degree of conversion, the T_g was only 152°C for the samples cured in a furnace, while 167°C was reached in DSC. Finally, for a T-DDM–ZnO blend tested in DSC, the conversion was also lower than for the neat resin. However, a higher value of T_g was recorded at 171°C.

To reach optimal conversion for blends and for samples in the furnace, the duration of the different steps of the cure cycle should be extended. Nevertheless, this cycle would still be a huge gain in time compared to the basic cycle proposed by the manufacturer.

The main experimental part of this dissertation, and its primary objective, is to determine the effect of zinc oxide nanoparticles on the properties of the resin, and especially on its thermal stability. To do so, blends were prepared at various concentrations of ZnO and for different sonication times. These blends were analyzed by TEM and SEM to view the dispersion of the nanoparticles within the T-DDM matrix. At low concentration, the particles are dispersed in the form of small clusters.

With increasing loadings of ZnO, larger clusters and, at 10wt% ZnO, aggregates start appearing. The overall dispersion of the inclusions improved when the sonication time was increased. However, a decent dispersion was already found at a sonication time of 90 seconds for blends up to 5wt% ZnO.

In the thermal analysis, the sonification time often did not have a coherent effect on the thermal properties of the blends, and when an effect was found it was very limited. The effect of the amount of zinc oxide was, however, significant. In the study of the curing of the blends by DSC, an increase in the heat of reaction was found. This synergic effect was maximal around 17wt% ZnO with an increase of the expected value by 16%. Then, in a study conducted by TGA, the thermal stability of the blends was evaluated and their potential degradation mechanism studied. The degradation temperatures at different percentages of weight loss and the char yield at 800°C of the samples, illustrated in the figure below, increased significantly. Only a small fraction of ZnO nanoparticles are required for a consequential raise of the degradation temperatures at 5 and 10% of weight loss. Moreover, for the char yield, a synergic effect was found due to the addition of the nanoparticles. Around 11wt% ZnO, the synergy reaches a value of 16%. Thus, adding 27% of char yield, due to the ZnO and the synergy, to the part of the neat resin.



Thermal stability of T-DDM with the ZnO concentration: (a) degradation temperatures T_d , and (b) char yield CY .

This recurring synergy, both for the heat of reaction and the char yield, and the increase of the degradation temperatures, point to an interaction between the ZnO nanoparticles and the T-DDM resin. The potential origins of this interaction were studied by FTIR. While, no additional peaks were observed in the FTIR spectra of the uncured blends compared to the pure resin, a strong peak appeared at 1678 cm^{-1} for the cured blends. Several hypotheses were emitted to the assignment of this peak. It was assumed that the most probable explanation were additional O – H groups chemisorbed on the ZnO molecules, resulting from the water produced by the condensation reactions of the hydroxyl groups of T-DDM. These hydroxyl groups linked to T-DDM are good candidates for hydrogen bonding with the benzoxazine matrix. Therefore, bringing additional thermal stability to the resin and improving its properties.

Perspectives

This work brought to light some interesting aspects of the T-DDM benzoxazine resin and its use in nanocomposites with zinc oxide particles. However, many aspects still need to be considered. The most significant future works and perspectives will be listed in this conclusion. First of all, another master thesis regarding the addition of clay nanoparticles in the T-DDM was written concomitantly by Mathieu Roiseux and will highlight other interesting features of T-DDM. Regarding the objectives covered in this dissertation, a first work would be a deeper analysis of the curing kinetics of the resin as well as a study on its curing mechanism. Then, for nanocomposite blends with ZnO a study of the resulting mechanical properties by DMA and standardized tests would be interesting. Adding ZnO nanoparticles to the resin increases its thermal stability, but what are the effects on its mechanical properties? Also, a study on the effects of the combined addition of different nano-inclusion to the T-DDM benzoxazine would be useful.

Finally, the effects of the addition of ZnO nanoparticles to other benzoxazine resins could be considered. This was already done in another study by A. Raynaud [4], where he found an increased thermal stability, and by Rajamanikam et al. [64], where benzoxazine functionalized ZnO improved the tensile and flexural strength of a BA-a benzoxazine matrix. However, additional studies could prove useful to get a better understanding of the interactions between ZnO and benzoxazine resins.

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Appendix A

Supplementary information

A.1 DSC results

This section gathers the numerical data obtained with DSC in the experimental part. The data are subdivided according to the chapters in the results and discussion part of this work.

Cure cycle

Figure A.1 lists the values of H_{res} measured to establish the cure cycle and that were not yet presented numerically.

```
%% Hres for different cure cycles (10 refers to blend with 10wt% ZnO)
Hr_max = 278.9633; % [J/g] 0min of cure time (neat)
Hr10_max = 289.4566667; % [J/g] 0min of cure time (10%ZnO)

%% Single cure temperatures: 150, 165, 180 and 200°C

% neat
Hres_150 = [Hr_max, 254.08, 240.69, 215.90, 191.66, 170.40]; % [J/g] 0-15-30-60-90-120min of cure time at T
Hres_165 = [Hr_max, 228.44, 200.60, 152.10, 135.43, 119.18];
Hres_180 = [Hr_max, 173.00, 137.10, 83.30, 59.23, 38.47];
Hres_200 = [Hr_max, 65.51, 31.64, 12.67, 5.15, 2.72];

% 10%ZnO
Hres10_150 = [Hr10_max, 240.22, 163.21]; % [J/g] 0-60-120min of cure time at 150°C
Hres10_165 = [Hr10_max, 158.65]; % [J/g] 0-60min of cure time at 165°C
Hres10_180 = [Hr10_max, 140.14, 84.17, 66.53, 49.72]; % [J/g] 0-30-60-90-120min of cure time at 180°C
Hres10_200 = [Hr10_max, 40.70, 17.55, 9.61, 6.27]; % [J/g] 0-30-60-90-120min of cure time at 200°C

%% Cycles with 2 cure temperatures

% 120min at 150°C, different cure times at 180°C
H_150_diff180 = [170.40, 100.92, 61.69, 39.75, 29.70]; % [J/g] 0-30-60-90-120min of cure time at 180°C
H10_150_diff180 = [163.21, 109.60, 71.58, 57.61, 50.79];

% different cure times at 150°C, 120min at 180°C
H_diff150_180 = [38.47, 34.66, 33.58, 29.87, 29.70]; % [J/g] 0-30-60-90-120min of cure time at 150°C

% 60min at 150°C, different cure times at 200°C
H_150_diff200 = [215.90, 28.13, 12.25, 3.06, 1.03]; % [J/g] 0-30-60-90-120min of cure time at 200°C
H_165_diff200 = [152.10, 22.74, 6.49, 2.82]; % [J/g] 0-30-60-90min of cure time at 200°C
H_180_diff200 = [83.30, 19.90, 9.34, 6.30]; % [J/g] 0-30-60-90min of cure time at 200°C
H10_150_diff200 = [240.22, 39.48, 20.72, 13.65, 6.14];

% 60min at different T, 60min at 200°C
H_diffT_200 = [12.25, 6.49, 9.34]; % [J/g] 60min at 150-165-180°C before 60min at 200°C
H10_diffT_200 = [20.72, 16.48, 11.90];
```

FIGURE A.1: H_{res} values for the different cure cycles.

Effect ZnO

Figure A.2 summarizes the values of H_r , T_p , and of the onset of the peak T_{onset} for the various experiments conducted to study the effect of ZnO and of the sonication time in T-DDM–ZnO blends. These data helped construct the plots presented in Section 9.2.

	Hr	J/g	T_{peak} °C	T_{onset} °C	
0.5 ZnO	270s	1	282.32 Mean	224.39 Mean	203.68 Mean
		2	276.74 Standard Deviation	224.2 Standard Deviation	203.18 Standard Deviation
		3	275.7 Margin of Error	225 Margin of Error	203.68 Margin of Error
90s	1	279.19 Mean	224.15 Mean	225.7066667 Mean	204.82 Mean
		2	280.19 Standard Deviation	226.59 Standard Deviation	206.74 Standard Deviation
		3	286.64 Margin of Error	227.216992 Mean	204.8370145
30s	1	280.91 Mean	226.42 Mean	225.8666667 Mean	204.05 Mean
		2	289.97 Standard Deviation	225.14 Standard Deviation	206.4 Standard Deviation
		3	269.63 Margin of Error	225.1227979 Margin of Error	203.3446429
5.0 ZnO	540s	1	263.73 Mean	222.67 Mean	202.75 Mean
		2	267.49 Standard Deviation	222.5 Standard Deviation	202.75 Standard Deviation
		3	267.02 Margin of Error	222.8813977 Margin of Error	203.5138832
360s	1	267.35 Mean	223.2333333 Mean	222.4586023 Mean	203.6633333 Mean
		2	267.34 Standard Deviation	223.8633333 Standard Deviation	203.63 Standard Deviation
		3	285.01 Margin of Error	223.6992209 Margin of Error	203.0401045
270s	1	270.81 Mean	227.6833333 Mean	224.78 Mean	203.9766667 Mean
		2	281.19 Standard Deviation	224.36 Standard Deviation	206.3834177
		3	266.05 Margin of Error	223.61 Mean	201.5699157
90s	1	267.39 Mean	221.2866667 Mean	224.9733333 Mean	203.4566667 Mean
		2	268.96 Standard Deviation	227.02 Standard Deviation	202.82 Standard Deviation
		3	277.51 Margin of Error	224.29 Margin of Error	202.8253743
30s	1	270.75 Mean	229.0033333 Mean	226.77 Standard Deviation	207.19 Mean
		2	283.28 Standard Deviation	226.77 Standard Deviation	206.52 Standard Deviation
		3	282.98 Margin of Error	226.91 Margin of Error	206.84 Margin of Error
0.0 ZnO /	1	273.77 Mean	228.9633333 Mean	225.0766667 Mean	201.21 Mean
		2	278.04 Standard Deviation	225.42 Standard Deviation	200.9 Standard Deviation
		3	285.08 Margin of Error	225.02 Margin of Error	201.53 Standard Deviation
1.0 ZnO	90s	1	292.3 Mean	224.2 Mean	204.69 Mean
		2	284.23 Standard Deviation	224.32 Standard Deviation	204.56 Standard Deviation
		3	300.8 Margin of Error	223.44 Margin of Error	203.64 Margin of Error
2.5 ZnO	90s	1	285.89 Mean	225.32 Mean	206.91 Mean
		2	288.87 Standard Deviation	225.68 Standard Deviation	207.05 Standard Deviation
		3	287.4 Margin of Error	224.83 Margin of Error	206.13 Margin of Error
10.0 ZnO	90s	1	285.07 Mean	227.5 Mean	208.34 Mean
		2	284.81 Standard Deviation	227.14 Standard Deviation	206.24 Standard Deviation
		3	289.49 Margin of Error	226.81 Margin of Error	207.09 Margin of Error
25.0 ZnO	90s	1	241.34 Mean	227.76 Mean	206.0471606
		2	239.38 Standard Deviation	225.5233333 Mean	206.1733333 Mean
		3	232.56 Margin of Error	224.04 Margin of Error	202.7089002
50.0 ZnO	90s	1	130.2 Mean	222.3 Mean	200.57 Mean
		2	129.57 Standard Deviation	224.65 Standard Deviation	201.54 Standard Deviation
		3	126.63 Margin of Error	224.04 Margin of Error	201.94 Margin of Error
100.0 ZnO /	1	-9.61 Mean	-10.04666667 Mean	238.19 Mean	200.5528141
		2	-10.33 Standard Deviation	0.38370996 UL	240.9634764
		3	-10.2 Margin of Error	0.434200717 UL	238.009857

FIGURE A.2: Data from dynamic DSC experiments for the study of the effect of ZnO.

A.2 TGA results

Figure A.3 and A.4 list the data from TGA measurements on T-DDM–ZnO blends to study the effect of ZnO and of the sonication time. These data helped construct the plots presented in Section 9.3.

```

%% Char yield at 800°C
CY_00 = [42.65, 45.01, 43.09]; % [%]
CY_05 = [49.93, 48.18, 52.28];
CY_10 = [53.26, 53.33, 53.36];
CY_25 = [59.42, 59.91, 60.32];
CY_50 = [60.36, 60.34, 60.12];
CY_100 = [64.13, 64.79, 64.74];
CY_250 = [70.46, 70.55, 71.64];
CY_500 = [74.83, 77.61, 76.35];
CY_1000 = [98.92, 98.88, 99.05];

CY = 43.5833 50.1300 53.3167 59.8833 60.2733 64.5533 70.8833 76.2633 98.9500
% 0.0 0.5 1.0 2.5 5.0 10.0 25.0 50.0 100.0wt% ZnO

%% Temperatures at 5, 10, 20 and 30% weight loss
TD5_00 = [302.67, 315.50, 300.17]; % [°C]
TD5_05 = [321.33, 312.50, 325.67];
TD5_10 = [326.83, 333.67, 333.67];
TD5_25 = [340.00, 338.00, 334.00];
TD5_50 = [328.33, 328.00, 331.67];
TD5_100 = [345.50, 347.00, 348.67];
TD5_250 = [369.33, 371.17, 366.17];
TD5_500 = [367.00, 378.17, 372.00];

TD5 = 306.1133 319.8333 331.3900 337.3333 329.3333 347.0567 368.8900 372.3900
% 0.0 0.5 1.0 2.5 5.0 10.0 25.0 50.0wt% ZnO

TD10_00 = [348.00, 358.33, 345.50]; % [°C]
TD10_05 = [366.00, 363.00, 372.33];
TD10_10 = [370.00, 374.17, 380.00];
TD10_25 = [399.50, 395.83, 390.00];
TD10_50 = [398.50, 397.33, 404.00];
TD10_100 = [407.50, 406.33, 403.33];
TD10_250 = [407.33, 404.67, 406.17];
TD10_500 = [426.00, 440.50, 432.33];

TD10 = 350.6100 367.1100 374.7233 395.1100 399.9433 405.7200 406.0567 432.9433
% 0.0 0.5 1.0 2.5 5.0 10.0 25.0 50.0wt% ZnO

TD20_00 = [411.00, 398.33, 397.50]; % [°C]
TD20_05 = [406.33, 405.67, 413.67];
TD20_10 = [419.33, 415.17, 411.00];
TD20_25 = [433.17, 416.17, 427.83];
TD20_50 = [435.33, 431.33, 439.83];
TD20_100 = [449.00, 436.17, 453.67];
TD20_250 = [472.83, 474.33, 479.67];
TD20_500 = [651.50, 723.50, 688.33];

TD20 = 402.2767 408.5567 415.1667 425.7233 435.4967 446.2800 475.6100 687.7767
% 0.0 0.5 1.0 2.5 5.0 10.0 25.0 50.0wt% ZnO

TD30_00 = [453.83, 443.33, 441.33]; % [°C]
TD30_05 = [444.50, 441.50, 456.83];
TD30_10 = [458.33, 449.33, 448.50];
TD30_25 = [505.67, 479.83, 477.17];
TD30_50 = [506.83, 512.17, 502.83];
TD30_100 = [616.83, 615.17, 601.67];

TD30 = 446.1633 447.6100 452.0533 487.5567 507.2767 611.2233
% 0.0 0.5 1.0 2.5 5.0 10.0wt% ZnO

```

FIGURE A.3: Data from TGA experiments for the study of the effect ZnO.

		char yield		°C		T 5% degradation		°C		T 10% degradation	
%											
5.0 ZnO 540s	1	62.53 Mean	61.95333333333333	336.33	Mean	335.2766667	Mean	335.2766667	Mean	385.7766667	Mean
	2	61.08 Standard Deviation	0.769177049 UL	62.82372311	333.5	Standard Deviation	1.547460285 UL	337.0277506	Standard Deviation	1.687759857 UL	Standard Deviation
	3	62.25 Margin of Error	0.870389776 LL	63.08294356	336	Margin of Error	1.751083982 LL	333.5255827	Margin of Error	1.909844976 LL	Margin of Error
360s	1	60.25 Mean	60.14666667	347	Mean	343.5	Mean	343.5	Mean	393.11	Mean
	2	61.7 Standard Deviation	1.607492872 UL	61.96568267	343.33	Standard Deviation	3.418172026 UL	347.3679547	Standard Deviation	6.193246322 UL	Standard Deviation
	3	58.49 Margin of Error	1.819016002 LL	58.32765067	340.17	Margin of Error	3.867954701 LL	339.6320453	Margin of Error	7.008189185 LL	Margin of Error
270s	1	60.45 Mean	59.98	326	Mean	324.39	Mean	324.39	Mean	397.33	Mean
	2	60.17 Standard Deviation	0.588472599 UL	60.6459072	322	Standard Deviation	2.110995026 UL	326.7787719	Standard Deviation	6.891359324 UL	Standard Deviation
	3	59.32 Margin of Error	0.665907198 LL	59.3140928	325.17	Margin of Error	2.388771856 LL	322.0012281	Margin of Error	7.7981639 UL	Margin of Error
90s	1	60.36 Mean	60.27333333333333	328.33	Mean	329.3333333333	Mean	329.3333333333	Mean	398.5	Mean
	2	60.34 Standard Deviation	0.133166562 UL	60.42402272	328	Standard Deviation	2.030328381 UL	331.630824	Standard Deviation	3.561549288 UL	Standard Deviation
	3	60.12 Margin of Error	0.150689382 LL	60.12264395	331.67	Margin of Error	2.297490631 LL	327.0358427	Margin of Error	4.030198366 LL	Margin of Error
30s	1	59.3 Mean	58.45	326	Mean	326	Mean	326	Mean	391.67	Mean
	2	58.54 Standard Deviation	0.898387444 UL	59.46660242	322.5	Standard Deviation	5.082705972 UL	331.7515176	Standard Deviation	8.723447331 UL	Standard Deviation
	3	57.51 Margin of Error	1.016602416 LL	57.43339758	323.67	Margin of Error	5.751517569 LL	320.2484824	Margin of Error	9.871328552 LL	Margin of Error
0.5 ZnO 270s	1	53.73 Mean	50.91666667	323	Mean	322.5	Mean	322.5	Mean	369.83	Mean
	2	49.49 Standard Deviation	2.436500222 UL	53.67377556	322.67	Standard Deviation	0.603241245 UL	323.1826192	Standard Deviation	3.6667	Standard Deviation
	3	49.53 Margin of Error	2.757108893 LL	48.15955777	321.83	Margin of Error	0.682619187 LL	321.8173808	Margin of Error	1.853833086 LL	Margin of Error
90s	1	49.93 Mean	50.13	321.33	Mean	319.8333333333	Mean	319.8333333333	Mean	366	Mean
	2	48.18 Standard Deviation	2.057304061 UL	52.45801593	312.5	Standard Deviation	6.711351081 UL	327.4278025	Standard Deviation	3.63	Standard Deviation
	3	52.28 Margin of Error	2.328015926 LL	47.80198407	325.67	Margin of Error	7.59446914 LL	312.2388642	Margin of Error	5.389758413 UL	Margin of Error
30s	1	52.1 Mean	49.7	323.83	Mean	315.08	Mean	315.08	Mean	370.17	Mean
	2	47.93 Standard Deviation	2.155203007 UL	52.13879698	306.33	Standard Deviation	12.37436867 UL	329.0826591	Standard Deviation	355.17	Standard Deviation
	3	49.07 Margin of Error	2.438796976 LL	47.26120302	315	Margin of Error	14.00265906 LL	301.0773409	Margin of Error	362.5	Margin of Error
		T 20% degradation		°C		T 30% degradation		°C		T 30% degradation	
5.0 ZnO 540s	1	422.8 Mean	418.6666667	555.5	Mean	555.39	Mean	555.39	Mean	555.39	Mean
	2	412.5 Standard Deviation	5.448599208 UL	424.8322238	542	Standard Deviation	13.33534027 UL	570.4800808	Standard Deviation	13.33534027 UL	Standard Deviation
	3	420.7 Margin of Error	6.165557135 LL	412.5011095	568.67	Margin of Error	15.0900808 LL	540.2999192	Margin of Error	15.0900808 LL	Margin of Error
360s	1	442.5 Mean	449.6666667	482.67	Mean	512.1666667	Mean	512.1666667	Mean	512.1666667	Mean
	2	451.5 Standard Deviation	6.448514041 UL	456.9637132	541.33	Standard Deviation	29.33142058 UL	545.3576838	Standard Deviation	29.33142058 UL	Standard Deviation
	3	455 Margin of Error	7.297046494 LL	442.3696202	512.5	Margin of Error	33.19101709 LL	478.9756496	Margin of Error	33.19101709 LL	Margin of Error
270s	1	446.8 Mean	444.22	566.5	Mean	549.5533333333	Mean	549.5533333333	Mean	549.5533333333	Mean
	2	442 Standard Deviation	2.43850364 UL	446.9793759	512.83	Standard Deviation	31.83480223 UL	585.5771414	Standard Deviation	31.83480223 UL	Standard Deviation
	3	443.8 Margin of Error	2.759375931 LL	441.4606241	569.33	Margin of Error	36.02380806 LL	513.5295253	Margin of Error	36.02380806 LL	Margin of Error
90s	1	439.8 Mean	435.4966667	502.83	Mean	507.2766667	Mean	507.2766667	Mean	507.2766667	Mean
	2	431.3 Standard Deviation	4.252450274 UL	440.3086787	512.17	Standard Deviation	4.685993313 UL	512.5792699	Standard Deviation	4.685993313 UL	Standard Deviation
	3	435.3 Margin of Error	4.812012065 LL	430.6846546	506.83	Margin of Error	5.302603183 LL	501.9740635	Margin of Error	5.302603183 LL	Margin of Error
30s	1	451.8 Mean	445.3333333333	513.17	Mean	520.4433333333	Mean	520.4433333333	Mean	520.4433333333	Mean
	2	439.7 Standard Deviation	6.122681874 UL	452.2616728	504.83	Standard Deviation	20.25434604 UL	543.3628624	Standard Deviation	20.25434604 UL	Standard Deviation
	3	444.5 Margin of Error	6.928339463 LL	438.4049939	543.33	Margin of Error	22.91952903 LL	497.5238043	Margin of Error	22.91952903 LL	Margin of Error
0.5 ZnO 270s	1	412.7 Mean	414.8333333333	466.83	Mean	453.6666667	Mean	453.6666667	Mean	453.6666667	Mean
	2	410.8 Standard Deviation	5.419154301 UL	420.965571	441.67	Standard Deviation	12.62050844 UL	467.947854	Standard Deviation	12.62050844 UL	Standard Deviation
	3	421 Margin of Error	6.132237697 LL	408.7010956	452.5	Margin of Error	14.28118731 LL	439.3854794	Margin of Error	14.28118731 LL	Margin of Error
90s	1	406.3 Mean	408.5566667	456.83	Mean	447.61	Mean	447.61	Mean	447.61	Mean
	2	405.7 Standard Deviation	4.440555521 UL	413.5815359	441.5	Standard Deviation	8.124426134 UL	456.8034847	Standard Deviation	8.124426134 UL	Standard Deviation
	3	413.7 Margin of Error	5.024869279 LL	403.5317974	444.5	Margin of Error	9.19348471 LL	438.4165153	Margin of Error	9.19348471 LL	Margin of Error
30s	1	406.7 Mean	411.39	466	Mean	450.7233333333	Mean	450.7233333333	Mean	450.7233333333	Mean
	2	407.8 Standard Deviation	7.194108701 UL	419.5307508	444	Standard Deviation	13.26158487 UL	465.7299536	Standard Deviation	13.26158487 UL	Standard Deviation
	3	419.7 Margin of Error	8.140750775 LL	403.2492492	442.17	Margin of Error	15.00662025 LL	435.7167131	Margin of Error	15.00662025 LL	Margin of Error

FIGURE A.4: Data from TGA experiments for the study of the effect the sonication time on T-DDM–ZnO blends.

Figures A.5 and A.6 show the plots of the temperatures at 5, 10, 20 and 30% weight loss (T_d in [°C]) with sonication time (t_{son} in [s]) for blends at 0.5 and 5wt% ZnO.

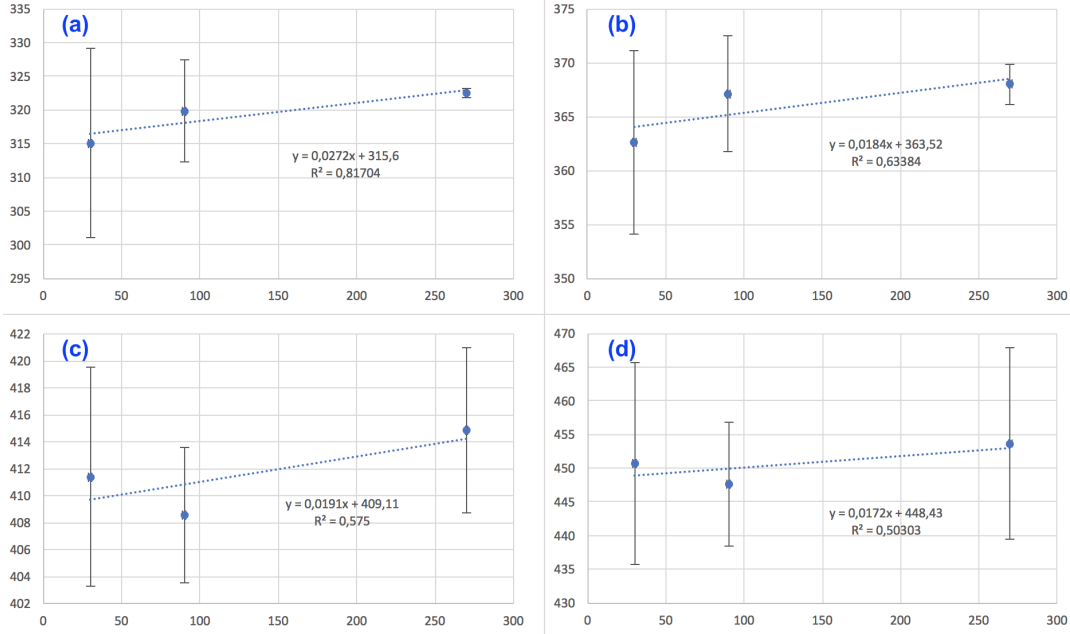


FIGURE A.5: Plots of T_d with sonication time on a blend with 0.5wt% ZnO: (a) T_{d5} , (b) T_{d10} , (c) T_{d20} , and (d) T_{d30} .

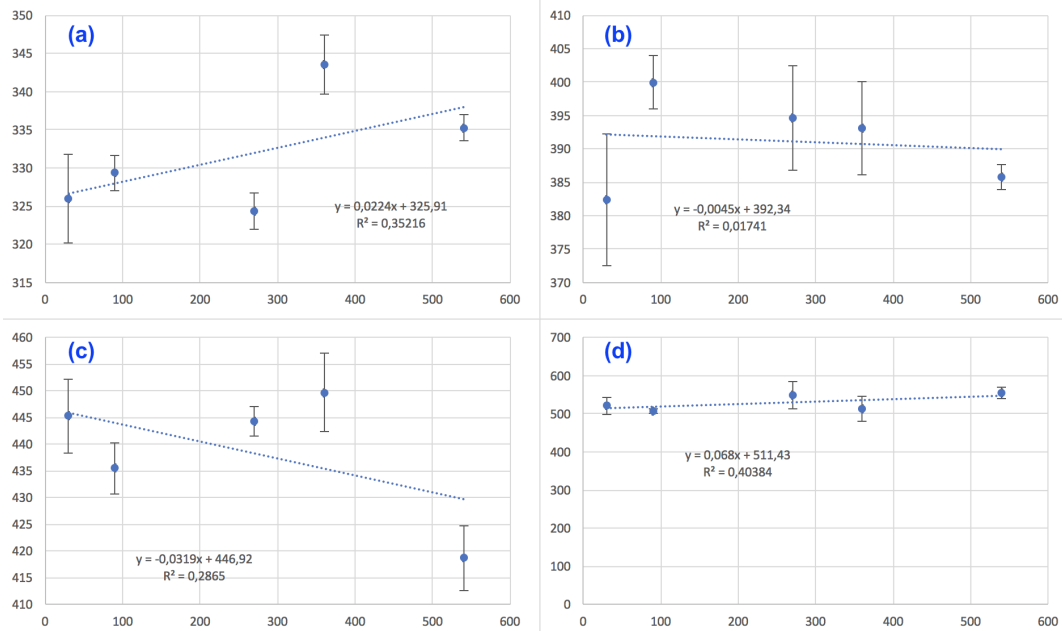


FIGURE A.6: Plots of T_d with sonication time on a blend with 5wt% ZnO: (a) T_{d5} , (b) T_{d10} , (c) T_{d20} , and (d) T_{d30} .

A.3 TEM images

This section gathers TEM images, which were not shown previously in this thesis, on the blends at 0.5 and 5.0wt% ZnO and with various sonication times. Figure A.7 and A.8 regroup these TEM micrographs at different magnifications.

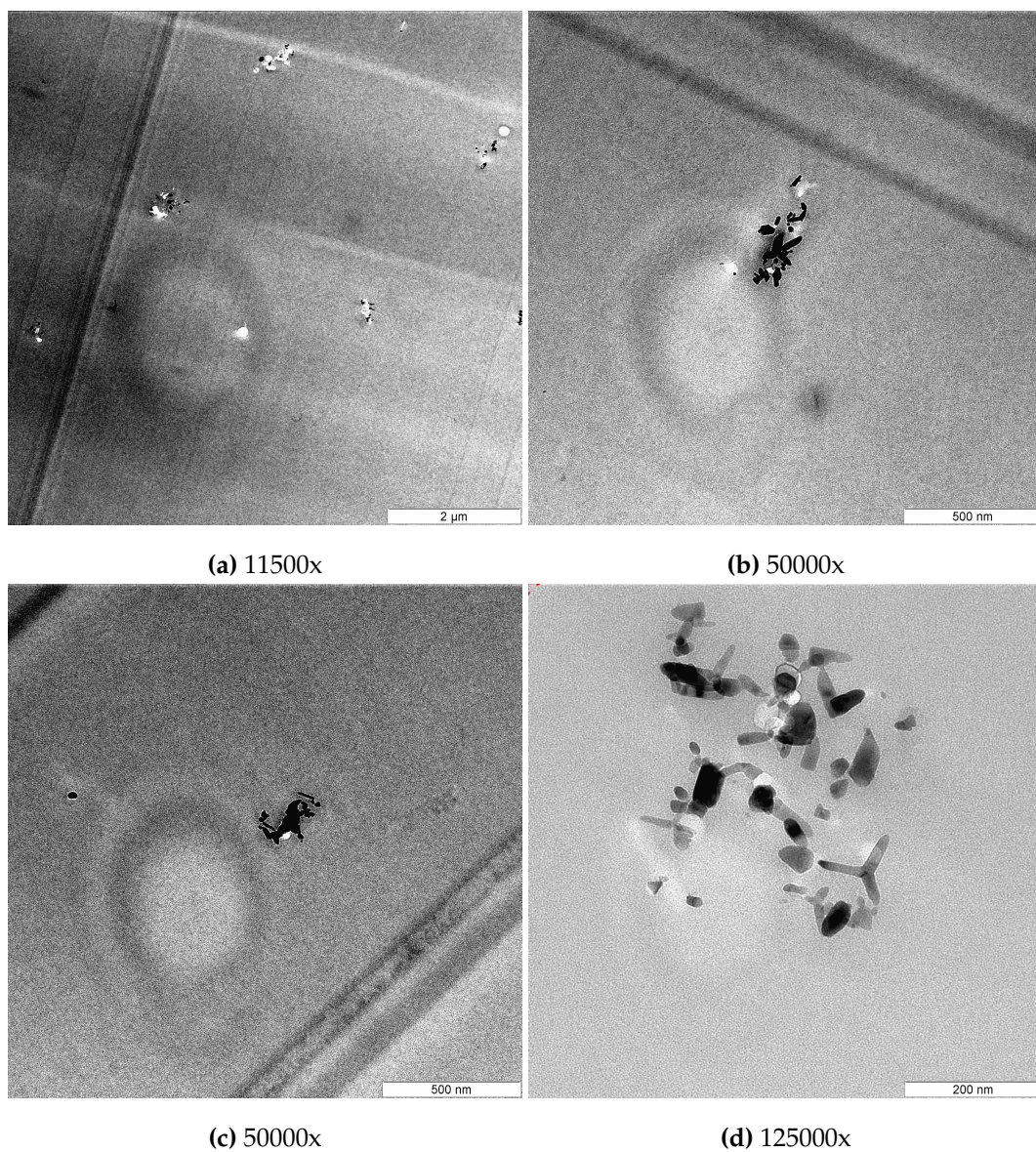


FIGURE A.7: TEM micrographs at 120 kV on blend at 0.5wt% ZnO with 90s of sonication.

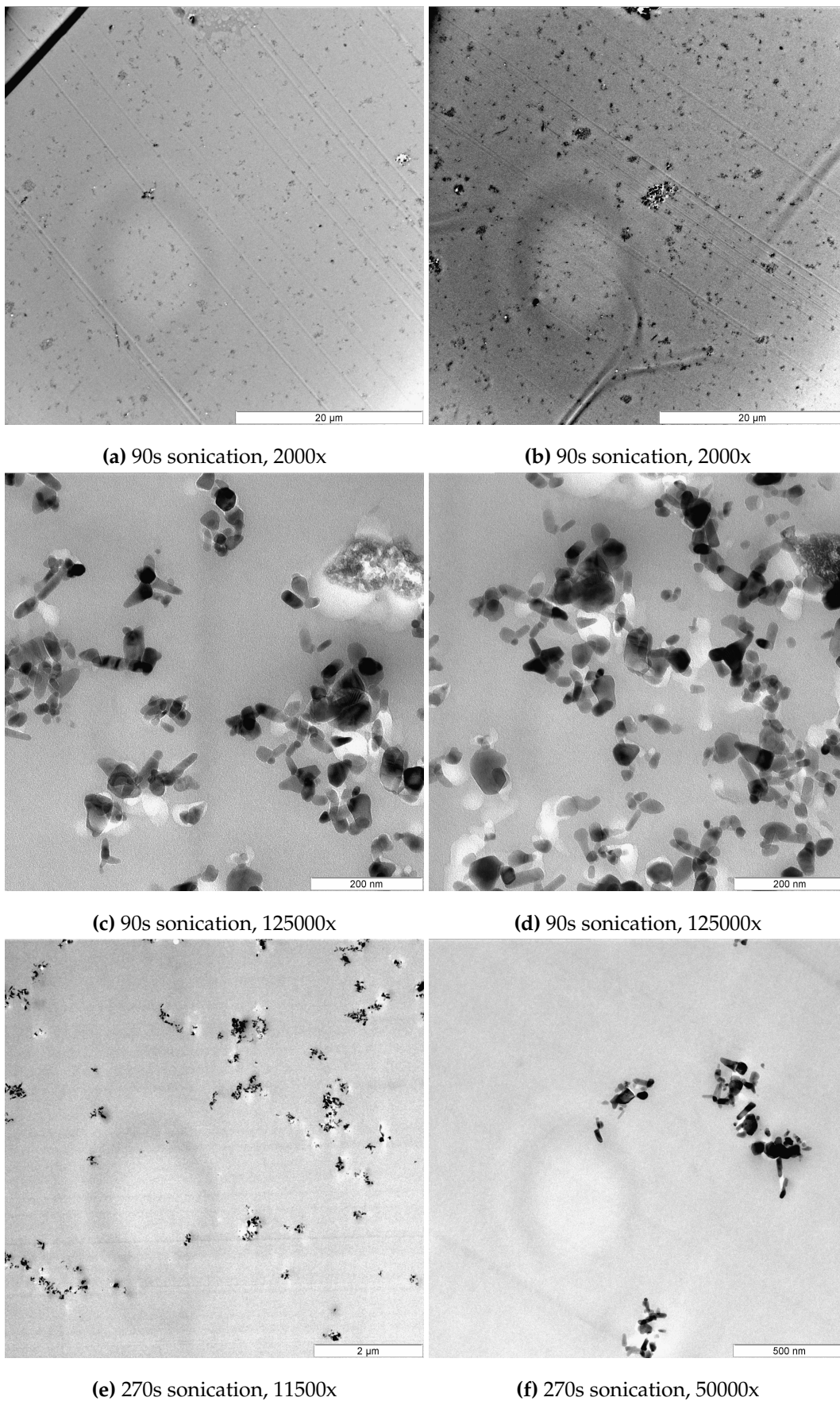


FIGURE A.8: TEM micrographs at 120 kV on blend at 5.0wt% ZnO with 90 and 270s sonication.

A.4 SEM images

This section presents SEM micrographs, which were not shown yet in this thesis. These SEM micrographs were obtained from neat T-DDM and nanocomposite blends at 0.5, 5.0 and 10.0wt% ZnO. Also, sonication times of 30, 90 and 270 seconds were applied on the blends.

Figure A.9 shows SEM micrographs at 1000 $\times$ magnification for several blends.

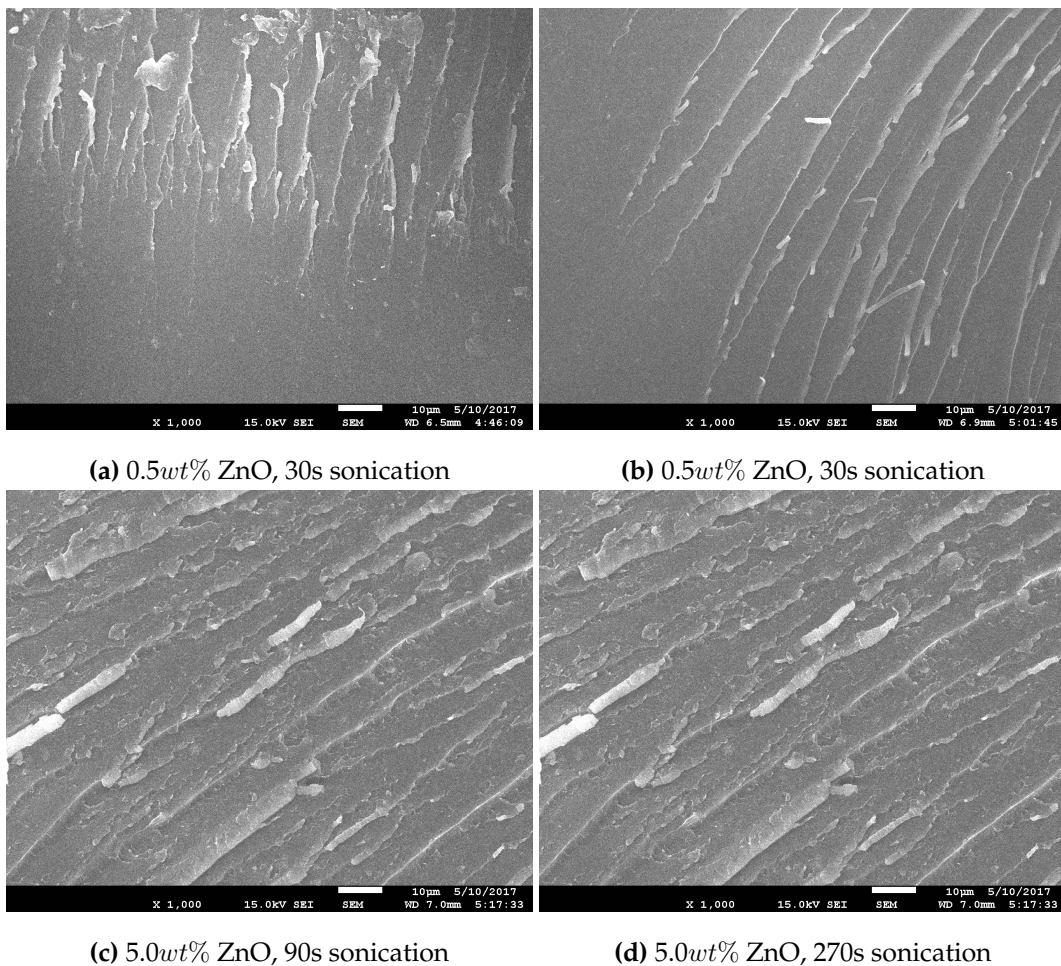


FIGURE A.9: SEM micrographs at 15 kV with 1000 $\times$ magnification on several blends.

Figure A.10 represents SEM images of the blend at 0.5wt% ZnO with 30 seconds of sonication at different magnifications.

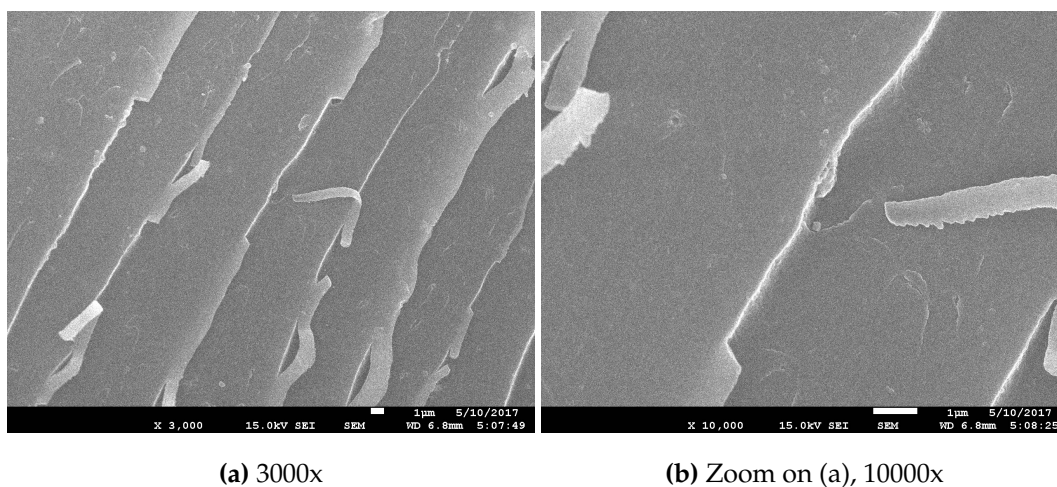


FIGURE A.10: SEM micrographs at 15 kV on blend at 0.5wt% ZnO with 30s of sonication.

Figure A.11 represents SEM images of the blend at 10.0wt% ZnO with 90 seconds of sonication at different magnifications.

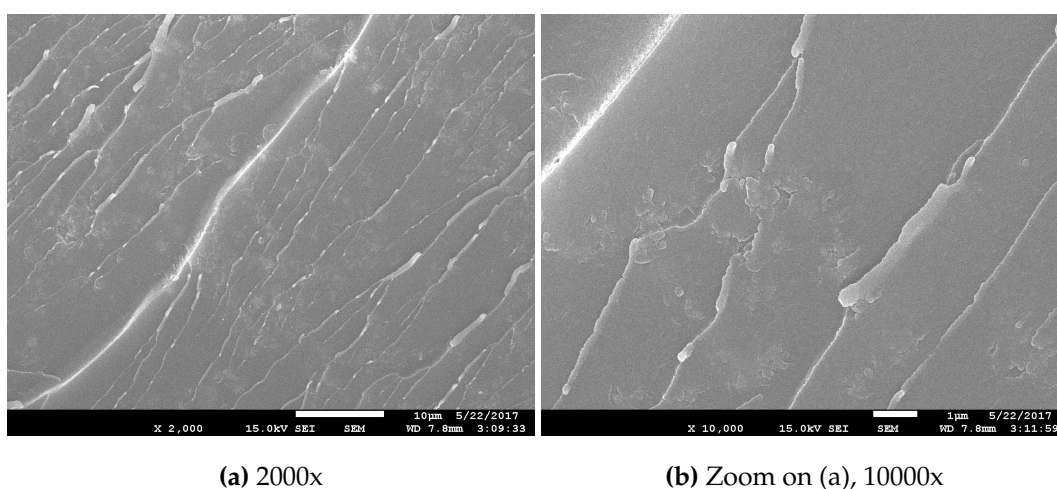


FIGURE A.11: SEM micrographs at 15 kV on blend at 10.0wt% ZnO with 90s of sonication.

Figure A.12 shows SEM micrographs of the neat T-DDM resin at different magnifications.

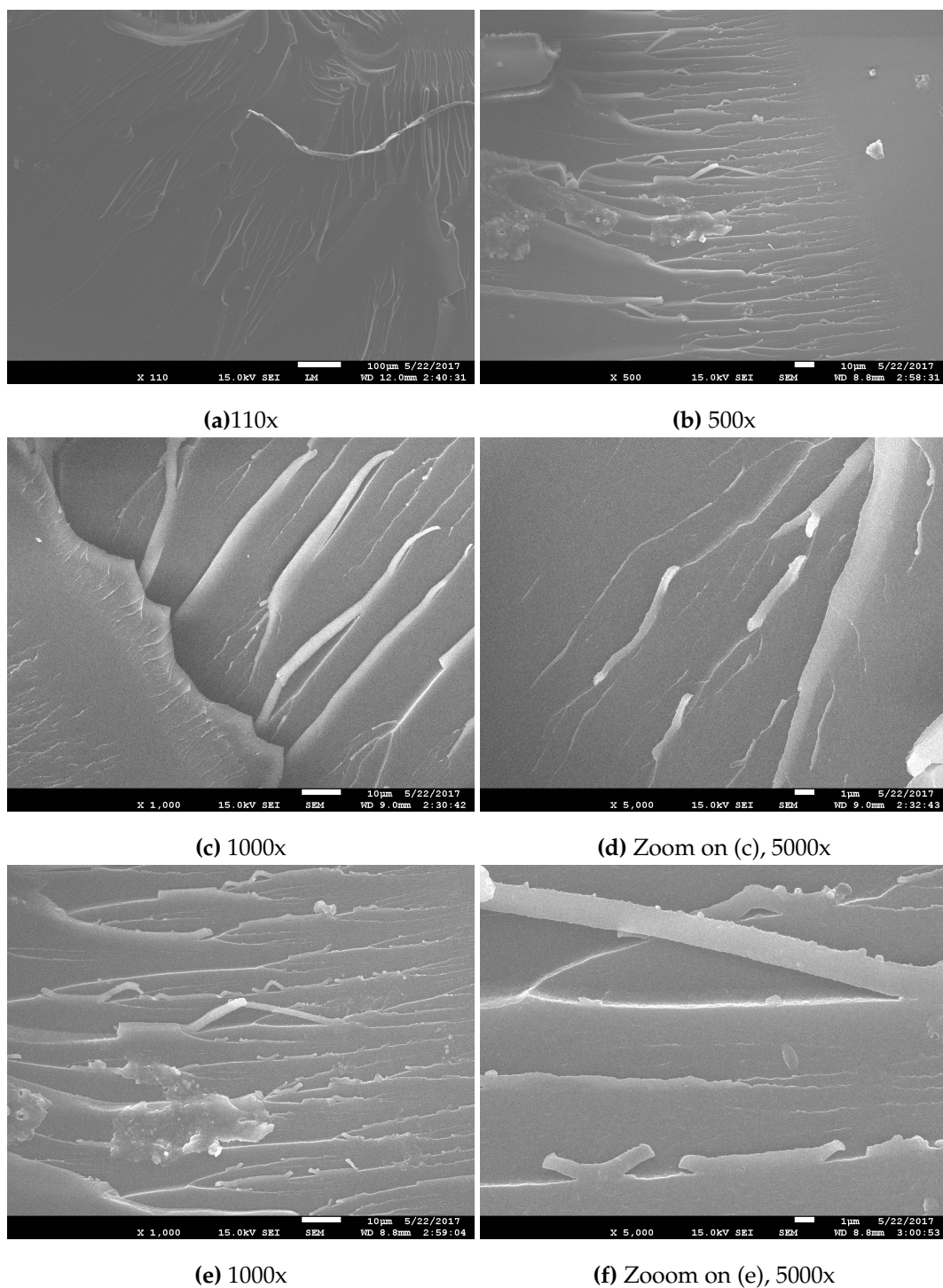


FIGURE A.12: SEM micrographs at 15 kV on the neat T-DDM resin.

A.5 FTIR spectra

This section groups the individual FTIR spectra of the neat resin and the blends at 0.5 and 5.0wt% ZnO for uncured and cured samples. These spectra focus on the region of interest for the benzoxazines, namely between 650 and 1800 cm^{-1} .

Figure A.13 shows the FTIR spectrum of the neat T-DDM resin in its cured form.

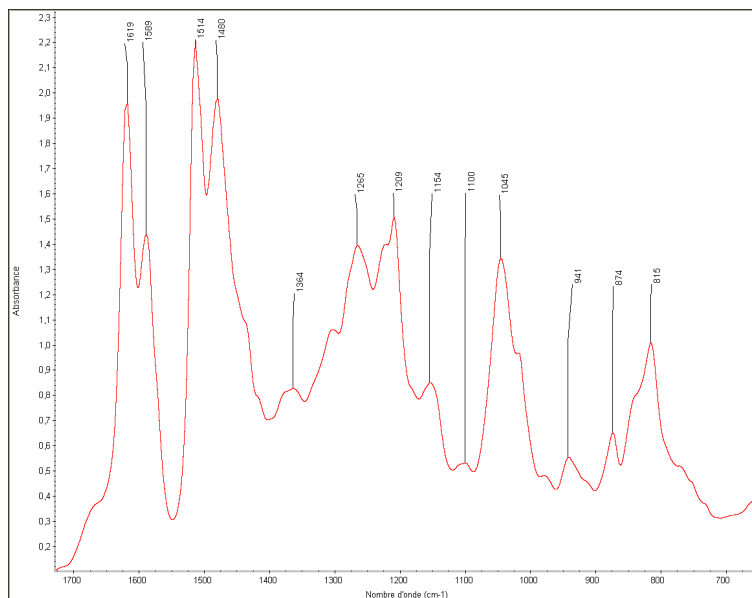
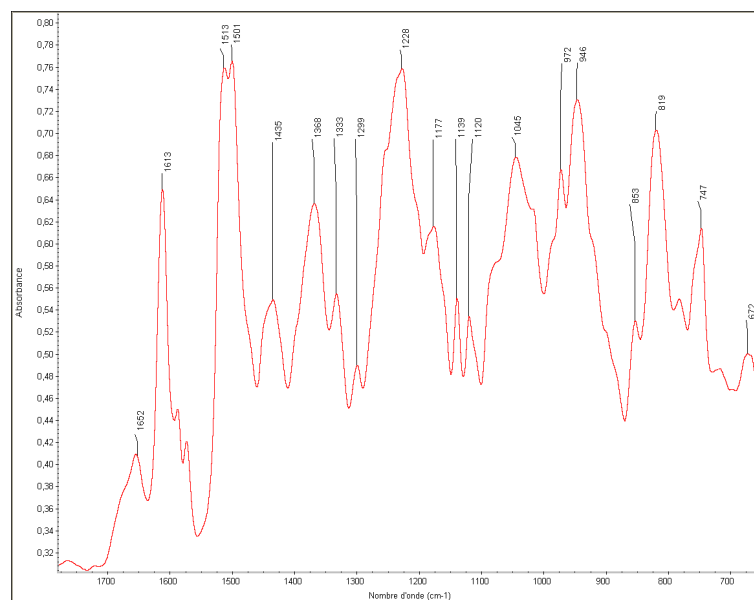
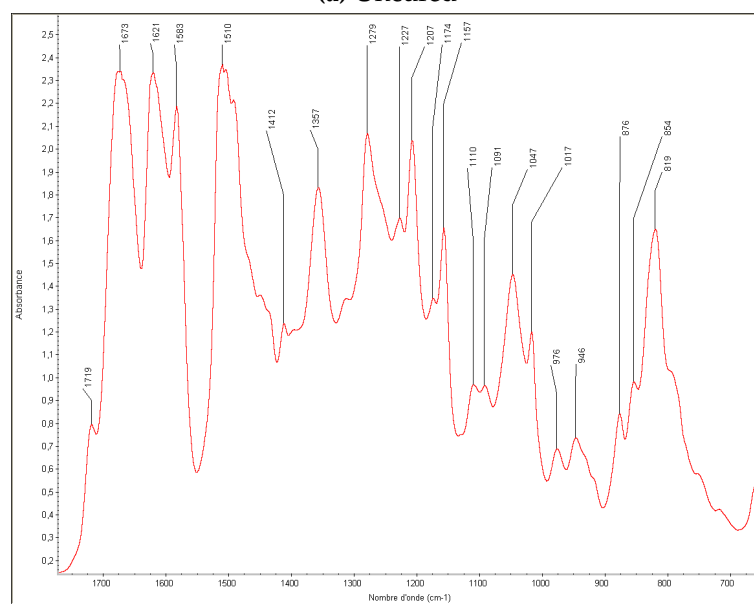


FIGURE A.13: FTIR spectrum in absorption of the cured neat T-DDM in the region of 650 to 1800 cm^{-1} .

Figure A.14 and A.15 show the spectra for the blends in their uncured and cured state.

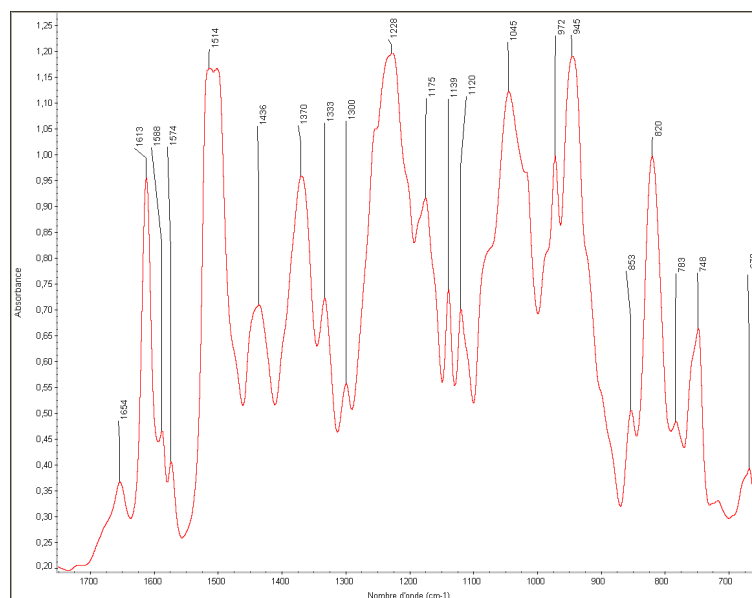


(a) Uncured

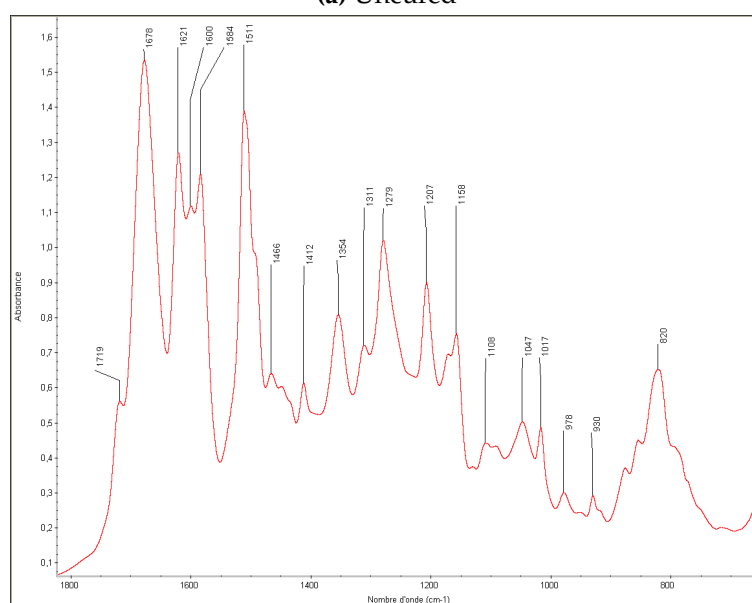


(b) Cured

FIGURE A.14: FTIR spectra in absorption of the blend at 0.5wt% ZnO in the region of 650 to 1800 cm^{-1} .



(a) Uncured



(b) Cured

FIGURE A.15: FTIR spectra in absorption of the blend at 5.0wt% ZnO in the region of 650 to 1800 cm^{-1} .

