THE CURING PROCESS OF LAYERED SILICATE/EPOXY NANOCOMPOSITES

LAHTI UNIVERSITY OF APPLIED SCIENCES
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Ilkka Nieminen

FOREWORD

I would like to thank the people who helped me in completing this study. First of all, I would like to thank my professor Pere Pagès Figueras and Teresa Lacorte, both from “Escola Tècnica Superior d’Enginyeríes Industrial i Aeronáutica de Terrassa”. They shared their knowledge and helped me with this study and all experiments.

Secondly, I would like to thank my family, especially for their support from Finland during the hard times of this thesis.

Lahti University of Applied Sciences
Faculty of Technology

NIEMINEN, ILKKA: The curing process of layered silicate/epoxy nanocomposites

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ABSTRACT

The industrial methods of processing polymeric thermoset matrix nanocomposites require a good knowledge of the matrix curing process. The dispersion of nanoparticles in the matrix effects the curing process due to the interaction between nanoparticles and the matrix at the atomic level, especially when the nanoparticles have been treated with a surfactant agent (alquilammonium) that is in competition with the reactive groups of the hardener.

This thesis investigates the curing process of a nanocomposite consisting of a trifunctional epoxy resin, montmorillonite (MMT) nanoparticles treated with octadecyl ammonium and a curing agent containing reactive primary amine groups. The curing reaction was followed using near-infrared spectroscopy (FT-NIR) concentrating on the decrease of primary amine and epoxy functional group bands.

The curing process was carried out using five weight percentages of MMT: 2, 5, 8, 10 and 12 wt%. The amount of MMT affected the mixing time of the mixture MMT/epoxy. After 5 minutes of manual mixing, an ultrasonic bath was used to obtain a good homogenous dispersion. The mixture times used were in the bath were, 1+1 hour for the 2wt%, 1 hours for the 5 and 8 wt% and 3 hours for the 10 and 12 wt%. For the curing process, the selected cycle was as follows: 4h at 100ºC, 2h at 150 ºC and 4h at 200 ºC.

The study revealed that the MMT nanoparticles accelerate the curing process, in particular in the first steps of the curing process, pointed out by the disappearing of the primary amine and epoxy group bands in the curing process. This was followed on the near-infrared region (NIR), by selecting the appropriate bands of the NIR spectra.

Keywords: trifunctional epoxy resin, modified montmorillonite, nanocomposites, FT-NIR; curing process.

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TIIVISTELMÄ

Tässä työssä tutkitaan nanokomposiitin jähmettymisreaktiota lämpötilaa nostettaessa ja sitä kuinka lämpötila vaikuttaa jähmettymiseen. Nanokomposiitti koostui modifioidusta montmorillionitista (MMT) ja trifunktionaalisesta epoksista. Tutkimus tehtiin vaihto-opiskelun aikana Katalonian yliopistossa, Espanjassa. Tutkimuksen valmistuttua vastaavanlaista menetelmää (FT-NIR), ei ollut vielä käytetty samanlaisessa tutkimuksessa mittatulosten saamiseksi.

Työ oli kaksiosainen: siihen kuuluivat nanokomposiitin valmistus sekä mittaustulosten kerääminen ja analysointi. Nanokomposiitti valmistettiin käyttäen ultraäänipesuria, uunia, mikroskooppia ja infrapuna spetroskopiaa(FTIR), jolla tarkkailtiin jähmettymistä. Ultraäänipesuri oli tärkeässä osassa prosessia, sillä oli erittäin tärkeää saada nanopartikkelit sekoittumaan tasaisesti epoksiin. Sekoitettua nanokomposiittia tarkkailtiin mikroskoopilla, jotta voitiin todeta, että sekoitus oli tasainen. Jähmettymistä seurattiin spetroskopialla (FTIR), jolla saatiin kerättyä tuloksia ja vertailtua niitä toisiinsa. Tärkeimpänä seuraamisen kohteena nähtiin ensisijainen amiini ja epoksiryhmä.

Tutkimuksessa saatujen tulosten pohjalta voidaan todeta, että modifioitu montmorillioinite partikkeli (MMT) kiihdyttää reaktiota. Tämä voitiin todeta ensisijaisen amiinin ja epoksiryhmän hävitessä kovettumisen kehittyessä. Kovettumista seurattiin spetroskopialla (FTIR) käyttäen NIR-skaalaa.

Avainsanat: trifuntionaalinen epoksihartsi, modifioitu montmorillionite, nanokomposiitti, FT-NIR; kovettumisreaktio

TERMINOLOGY

NANOCOMPOSITE
Composites with fillers the size of nano scale

FT-IR
Fourier Transform Infrared Spectroscopy

FT-NIR
Fourier Transform Near Infrared Spectroscopy

TGAP
Trifunctional epoxy resin

MMT
Montmorillonite

DDS
Hardener

CONTENTS

1. INTRODUCTION

Nanotechnology enters the market more heavily that ever before, seems to be one of the discussion topics of today. Everything has to be small and light also in the plastics industry. Nanocomposites have this advantage. They are light, the structure is small (particle size less than 100 nm), their mechanical and chemical properties are good, even better than the properties of steel. Thus, nanocomposites are widely used in civil engineering and in commercial aerospace.

Polymer matrix loaded with reinforcements which are nano-size can be called nanocomposites. When the inorganic material is dispersed homogenously in the polymer matrix, a great interfacial area is produced that gives better mechanical properties to the composites. This increases the realm in the field of material engineering and design engineering.

Nanocomposite fillers can be found in the form of nanopowder, nanorods, nanowires or nanotubes. They are either three-dimensional, such as nanopowder, or two-dimensional such as nanorods, nanowires and nanotubes. In this study, nanopowder called montmorillonite will be studied more closely.

The aim of this study is to report on the curing of a trifunctional epoxy resin in the presence of additional materials, nanoparticles and a hardener. The state of curing is studied by using FT-NIR.

This study was introduced at the National Congress of Materials in June 2008, in San Sebastián (Spain) .

2. PREVIOUS STUDIES

A study on the curing of layered silicate/epoxy nanocomposites using near infrared absorption spectroscopy (NIR), has not been done so far. However, there are several studies on using a different method such as Fourier transform infrared spectroscopy (FT-IR). As an example we can mention, *study of curing of layered silicate/trifunctional epoxy nanocomposites by means of FT-IR Spectroscopy* (Pagès, Lacorte, Lipinska, Carrasco, 2008).

3. MATERIALS

For this study, thermosets were studied as nanocomposites matrix. Nanocomposites are composites with a filler size of nano scale dispersed homogenously in the matrix resin.

For the preparation of the nanocomposite, three structural elements were needed. A trifunctional epoxy resin (TGAP) was used marketed as Araldite MY510 from Huntsman as the matrix. The used hardener was 4,4´diaminodiphenylsulfone marketed as HT-976-1 from Huntsman. In the reinforcement, nanoparticles consisted of montmorillonite (MMT) layered silicate, treated with surfactant octadecylammonium, with particle length ranging between 100-150 nm and thickness of 1 nm and marketed as Nanomer I.30 from Nanocor (Arlington Heights, Illinois) were used.

3.1. Thermosets

Epoxy resin, a type of polymer thermoset, receive a lot of attention in polymer science because of its low viscosity, high service temperatures as well as chemical resistance and stability. Compared to thermoplastics, thermosets are used more often in demanding applications, particularly as a matrix in polymer composite systems.

For differences between thermoplastics and thermosets can be found already when manufactured. When thermosets react and cure, they can not be returned back to their initial form and reprocessed like thermoplastics. If cured thermosets are subjected to high temperatures, they may soften but their molecular structure will be damaged, or may even burn eventually. This is because of the crosslinking of the chains during curing, as shown in Figure 1. Crosslinking is what ultimately gives thermosets their properties.

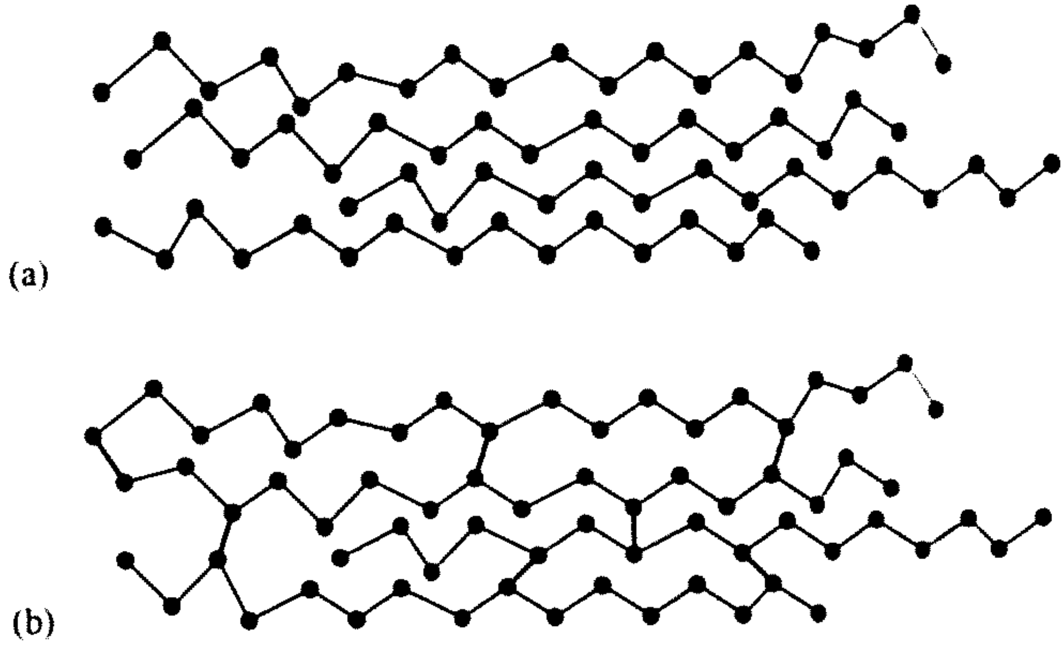


Figure 1. Epoxy resin crosslinking : a) before curing and b) a cured thermoset

Metals are often replaced by thermosets. Metallic materials are more sensible to chemical products due to corrosion. In addition, their weight-strength ratio is worse, they are heavy, their machining is expensive and they conduct electricity and heat. For example in these properties thermosets are much better.

Thermosets are polymers that are cured at a relatively high temperature, in order to allow crosslinking. Here are some examples of thermoset materials and their applications:

- Epoxy resins (coating, as dielectric material and road surfacing, structural pieces)
- Unsaturated Polyester Resins (adhesives, matrices of composite materials, moldings, films, and coatings)

- Polyimides (adhesives, matrices of composite materials, moldings, films, and coatings)
- Poly(arylene ether) (adhesives, matrices of composite materials, moldings, films, and coatings)
- Bakelite (sensors and matrices of composite materials)
- Melamine resin (composites)

(Brydson 1989, 724; Nasa 2008; FreePatentsOnline.com Masaaki, Akira 2002 2002; Jensen 2005; Qu, Yang, Li, Ma, 2007)

The processing methods of thermosets are limited compared to those of thermoplastics. Here are some of the molding methods used for thermosets:

- Injection molding
- Transfer molding
- Compression molding

(The Society of the Plastics Industry. 1999)

3.2. Epoxy

Epoxy resins are well known because of their wide use in many applications such, as in coating, as structural adhesives and as a matrix for composite materials. This is also the reason of their intense study in the recent years. Epoxy matrix is used to give good properties for composites. (Carrasco, Pagès, Lacorte, Briceño, JAPS, 2007, 1) This thesis focuses on the use of epoxy as a matrix for nanocomposite materials.

The history of epoxy resins goes all the way to the early 20th century. Scientists noticed that with heat epoxy got solid instead of just vanishing in the air. Lots of experiments were made, and the reaction with epichlorohydrin and bisphenol-A (2,2-bis(4-hydroxyphenyl)propane) yielded a material nowadays known as epoxy resin.(Britannica online 2008). For example, DGEBA, TGDDM and TGAP are epoxy resins. TGAP was used in this study.

Epoxy resins are built up from monomers, epoxy rings (see Figure 2) and benzene rings (see Figure 3). When this epoxy ring reacts during curing, it will release O.

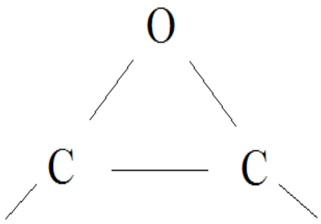


Figure 2. An epoxy ring

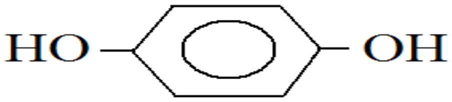


Figure 3. A Benzene ring

At the benzene ring, the OH group is the one which reacts when it is introduced to high temperature. The OH group gives better cross-linking for epoxy resins which is needed for example when manufacturing nanocomposites. When a mixture epoxy and benzene ring is introduced to heat, they react elaborating the mixture and the polycondensation with loss of H_2O, which is shown in Figure 4. (DOW Liquid Epoxy Resins, 6; Brydson, 1989, 697-703)

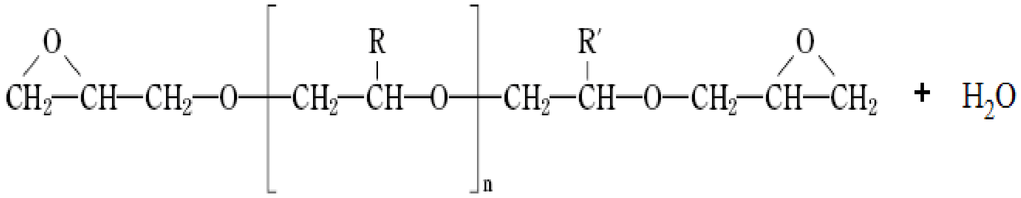


Figure 4. The chemical structure of epoxy resin

Epoxy resins are so called polyfunctional resins (levels from 2 to 5). But multifunctional resins (level from 3 to 5) are preferred in industry because of their better crosslinking density and glass-transition temperature. These properties, on the other hand, have an effect on the mechanical, thermal and adhesion performance in improving the properties. (Mustata, Bicu, 2000, 1) A trifunctional character was used in this work (see Figure 5). This was because more information was needed of the trifunctional epoxy resin, for there has not been so much research on it, especially with a NIR-scale. The epoxy was a commercial grade of p-aminophenol triglycidyl ether (TGAP) and name Araldite MY510 supplied by Huntsman. Further information about the epoxy resin can be found in Appendix 1.

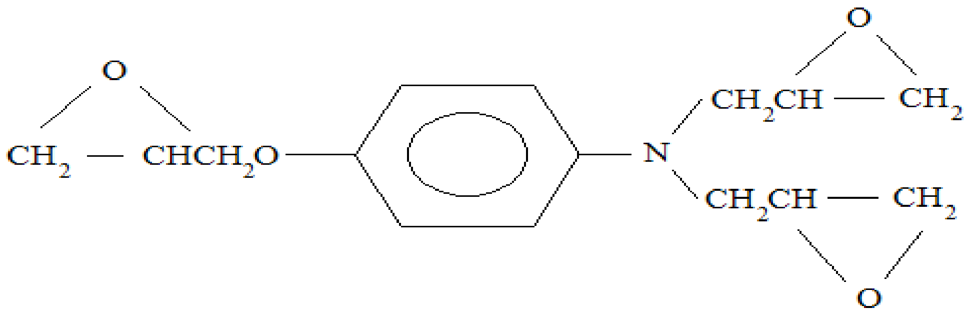


FIGURE 5. A trifunctional epoxy resin

The most important properties of epoxy were its viscosity 0.55- 0.85 Pa, the density of 1205-1225 kg/m^3 and a maximum water content of 0.2% at the temperature of 25°C.

3.3. Hardener

It is most common in these days in industry to use a hardener as a curing agent in the curing process and especially to choose a suitable one. Usually a primary or secondary amine based hardener is used to cause crosslinking between the epoxy chains. (Carrasco, Pagès, Lacorte, Briceño, 2007, 1) Table 1 lists some curing agents, their properties and applications. The hardened of this study was 4,4´diaminodiphenylsulfone (DDS, see Figure 6) marketed as HT-976-1, from Huntsman. The mix mass ratio was 100/52 (epoxy/DDS). Further information about the hardener can be found in Appendix 2.

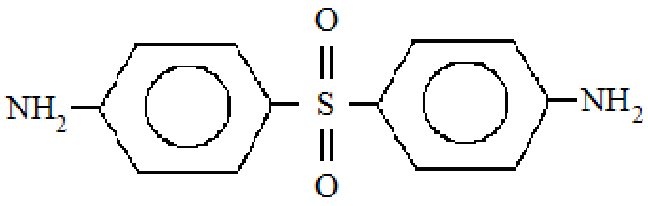
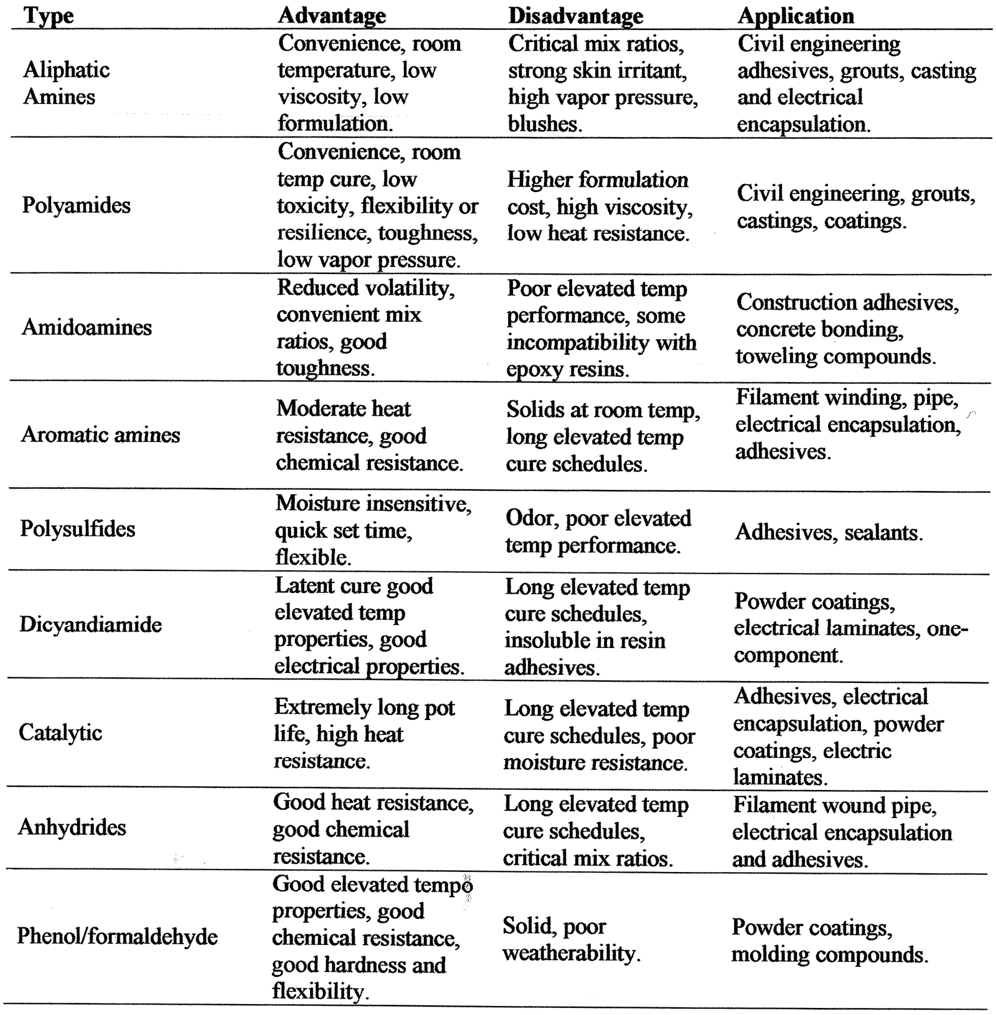


Figure 6. 4,4´diaminodiphenylsulfone (DDS)

Table 1. The most commonly used hardeners, their properties and applications. (Barrabes, 1997, 37)

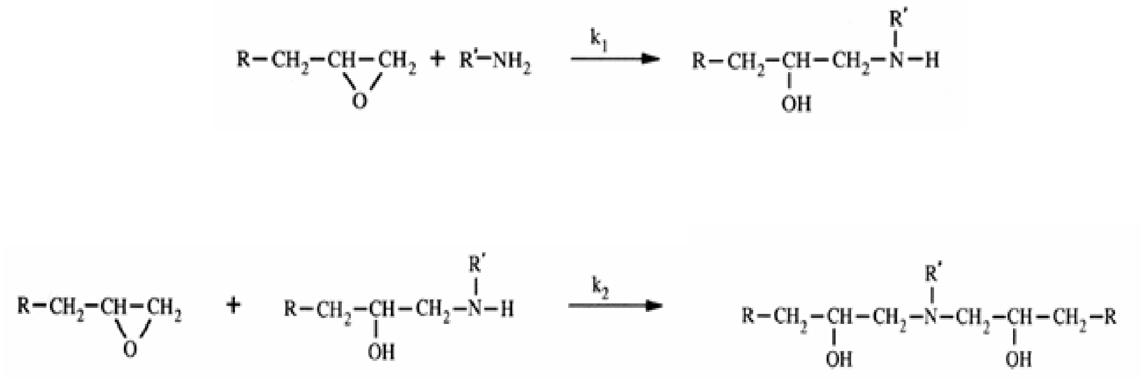


Type	Advantage	Disadvantage	Application
Aliphatic Amines	Convenience, room temperature, low viscosity, low formulation.	Critical mix ratios, strong skin irritant, high vapor pressure, blushes.	Civil engineering adhesives, grouts, casting and electrical encapsulation.
Polyamides	Convenience, room temp cure, low toxicity, flexibility or resilience, toughness, low vapor pressure.	Higher formulation cost, high viscosity, low heat resistance.	Civil engineering, grouts, castings, coatings.
Amidoamines	Reduced volatility, convenient mix ratios, good toughness.	Poor elevated temp performance, some incompatibility with epoxy resins.	Construction adhesives, concrete bonding, toweling compounds.
Aromatic amines	Moderate heat resistance, good chemical resistance.	Solids at room temp, long elevated temp cure schedules.	Filament winding, pipe, electrical encapsulation, adhesives.
Polysulfides	Moisture insensitive, quick set time, flexible.	Odor, poor elevated temp performance.	Adhesives, sealants.
Dicyandiamide	Latent cure good elevated temp properties, good electrical properties.	Long elevated temp cure schedules, insoluble in resin adhesives.	Powder coatings, electrical laminates, one-component.
Catalytic	Extremely long pot life, high heat resistance.	Long elevated temp cure schedules, poor moisture resistance.	Adhesives, electrical encapsulation, powder coatings, electric laminates.
Anhydrides	Good heat resistance, good chemical resistance.	Long elevated temp cure schedules, critical mix ratios.	Filament wound pipe, electrical encapsulation and adhesives.
Phenol/formaldehyde	Good elevated temp properties, good chemical resistance, good hardness and flexibility.	Solid, poor weatherability.	Powder coatings, molding compounds.

Before epoxy resin can begin the curing process, which happens under heat, a hardener has to be blend in with the epoxy. This is because after the curing initiate in epoxy, it will slowly get solid and mixing becomes hard. When the curing initiates, crosslinking occurs with epoxy group(s) and the crosslinking agent (hardener). The mixture turns from liquid to a gel after the hardener is added and mixed with epoxy. (Brydson, 1989, 703-704)

It is also very important to remove air from the mixture because air bubbles reduce mechanical properties. But for this study is was not important because mechanical properties were not studied.

The curing begins with a reaction, which is exothermical, with the epoxy group and a primary amine. In the second reaction, the epoxy group reacts with a secondary group (see Figure 7). The curing process of epoxy-amine is very complicated especially when using a multifunctional resin. At the end of the curing, the epoxy group and the primary amine disappear. (Carrasco, Pagès, Lacorte, Briceño, 2008, 1)



$$R-CH_2-\underbrace{CH-CH_2}_{O} + R'-NH_2 \xrightarrow{k_1} R-CH_2-\underset{OH}{CH}-CH_2-\overset{R'}{N}-H$$

$$R-CH_2-\underbrace{CH-CH_2}_{O} + R-CH_2-\underset{OH}{CH}-CH_2-\overset{R'}{N}-H \xrightarrow{k_2} R-CH_2-\underset{OH}{CH}-CH_2-\overset{R'}{N}-CH_2-\underset{OH}{CH}-CH_2-R$$

Figure 7. A curing reaction

When the nanocomposite is cured, it can be divided in to three different groups according to the dispersion of the clay (particles of very fine size) in the structure. We talk about composites, intercalated or exfoliated nanocomposites. In the composite structure, there is no infiltration between the matrix structures. In an intercalated composite, the additional molecules infiltrate in the matrix structure and in an exfoliated composite, silicate thick slabs are dispersed separately in the resin matrix (See Figure 8).(Xu, Bao, He, 2001, 1)

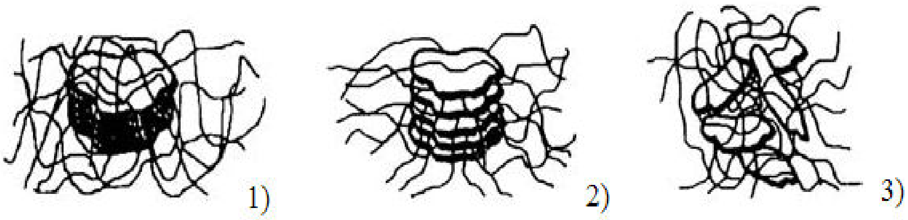


Figure 8. The structure of composites : 1) traditional composite 2) intercalated composite and 3) exfoliated composite

It is important to cure the nanocomposite in the right temperature to achieve the objective such as certain properties. There are studies on using different epoxy resin in the curing process. Most of them show that the exfoliation of silicate is more efficient in higher curing temperatures. This was because the molecules were moving more and the dispersion of the resin and the hardener platelets were much better in the matrix. On the other hand, a too low curing temperature might cause an intercalated structure. (Becker, Simon, 2005, 53-54).

3.4. Fillers for composites

Even though thermosets have good mechanical properties when cured, sometimes it is not enough. When working with composites, the properties of the final product have to be known before manufacturing it. Multiple studies are made to investigate the additional properties of thermosets. The most common interest is to achieve better mechanical and thermal properties. But nowadays composites are used also in household appliances, and therefore they have to be for example fire resistant. This has led scientists to study also composites which are fire-proof and water resistance. (Bockstaller, Mickiewicz, Thomas, 2005; Xu, Bao, He, 2001; Sun, Mayers, Xia, 2003)

Composite fillers can be found in different sizes and are usually named after them; micro-, nano- or composites. The purpose of adding fillers is not only to give better properties but also to decrease the price and the mold shrinkage. (Sun, Mayers, Xia, 2003, 1)

A composite filler can be either organic or inorganic, the second of the two being the must commonly used. In this study, Montmorillonite, an inorganic filler, was used. Some of the fillers most commonly used with thermosets are:

- Carbon fiber
- Aramid (Kevlar)
- Talc
- Fiberglass
- Sawdust

3.5. Montmorillonite (MMT)

Montmorillonite (MMT) (see Figures 9 and 10) is a clay mineral that can be encountered in a lot of places around the world. It got its name after Montmorillon, France, the place where it was found. It is a type of layered silicate due to its chemical structure, the formula for MMT is M^{+}_{y} $(Al_{2-y}Mg_{y})$ (Si_4) O_{10} $(OH)_2{\cdot}nH_2O$. (Montmorillonite 2001; Vali, Martin, Amarantidis, Morteani, 1993) In this study, the used MMT was organically modified, treated with the surfactant octadecyl ammonium. Octadecyl ammonium accelerates the curing reaction. Its particle length was from 100 to 150 nm and thickness of about 1nm. It was manufactured by Nanocor (Arlington Heights, Illinois, USA) and marketed as Nanomer I.30E.

Figure 9. Montmorillonite which is 3 cm long (Mindat.org, 2004)

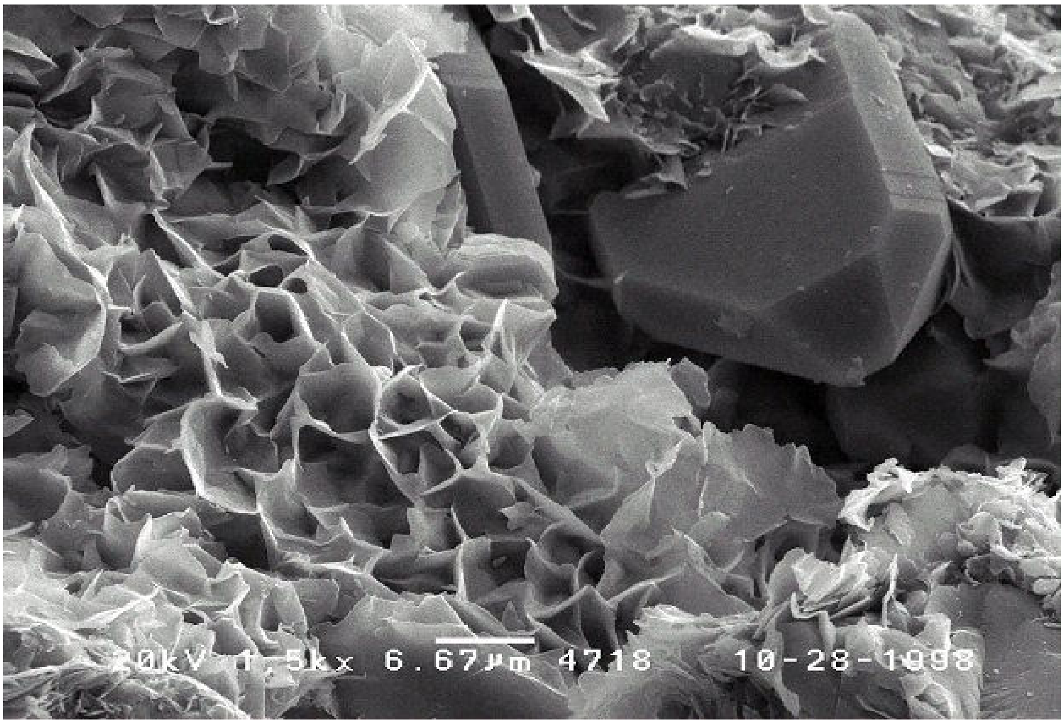


Figure 10. A SEM image of a core sample (Omni Laboratories 1998)

Montmorillonite is a phylosilicate ($Si_2O_5^{-2}$) type of mineral, belonging to the smectite group due to the 2:1 layer disposition. Smectites show a feature that allow them to intercalate molecules between their layers (see Figure 11), making them very useful as layered silicates. (Vali, Martin, Amarantidis, Morteani, 1993; Montmorillonite, Britannica online; Nelson, 2006) Further information about the montmorillonite can be found in Appendix 3.

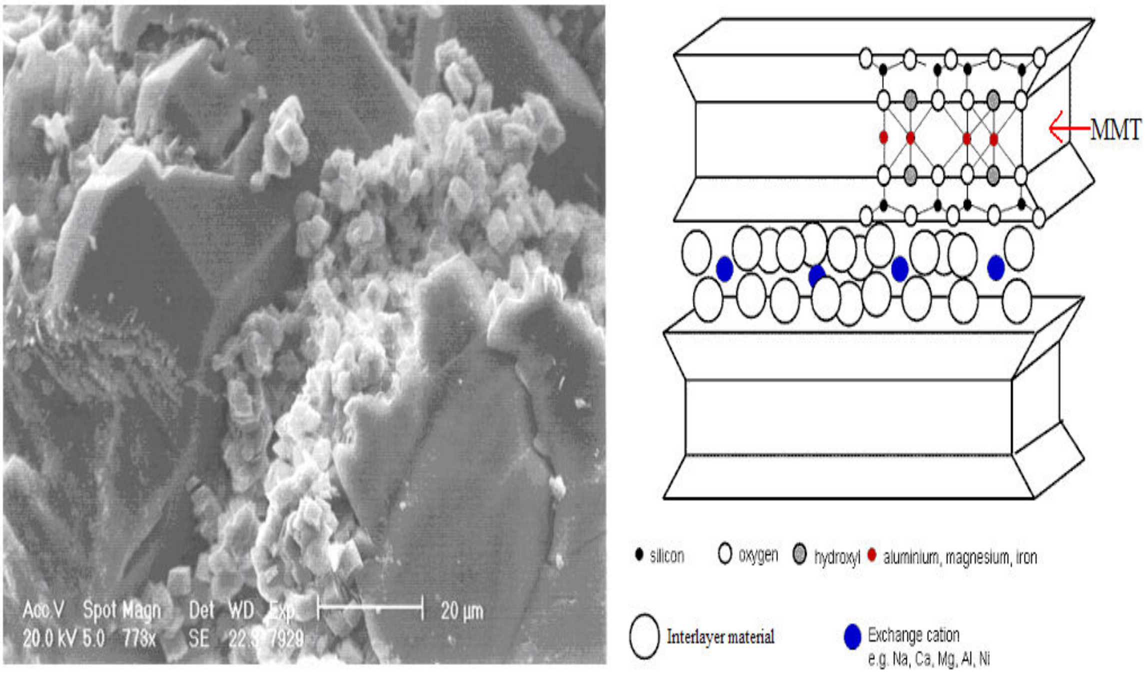


Figure 11. On the left, a SEM image and on the right, an image of intercalation between MMT platelets.

3.6. Composites and nanocomposites

Composites are materials prepared by dispersing different geometrically shaped reinforcements in a matrix. In the case of polymer based composites, thermosets are most commonly used as the matrix.

Ceramic, metallic or polymeric fibers or particles can be used as a reinforcing material, and can be placed either in bidimensional layers in the case of long fibers or else uniformly dispersed in the case of the short ones.(See Figure 12)

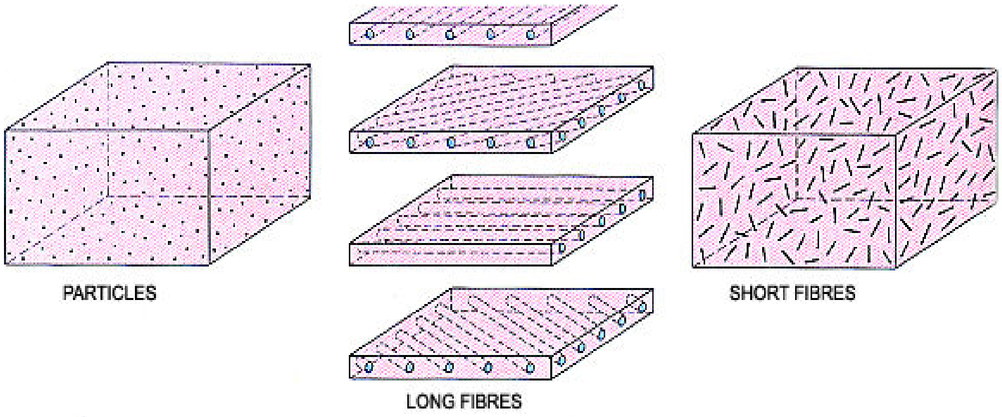


Figure 12. A figure of different kinds of reinforcing fibers and particles.(Investigación y Ciencia, p.160, December 1986)

Nanocomposites can be obtained when at least one of the dimensions of these fibres or particles are nanometric in size.

4. EQUIPMENT

4.1. Fourier transform infrared spectrometer (FT-IR)

FT-IR is a common tool used to analyze gases, liquids and solids. It can characterize the chemical functional groups (organic or inorganic) from unknown mixtures on the range of 14000-20 wavenumbers (cm^{-1}). This range can be divided in to smaller regions which are known as near-IR (14000-4000), mid-IR (4000-400) and far-IR (400-20). For this study, a Nicolet 6700 spectrophotometer was used. (Materials and Engineering Research Institute; NICOLET, 1986, 1)

The idea of Fourier transform infrared technique is based on the Lambert- Beer law. It is used to gather information of the infrared absorbance and the fourier transform is a process that calculates its value. To have a spectrum, a sample is introduced in an infrared spectrometer, the IR beam passing through the sample. The beam is divided into wavenumbers and each wave has a precise amount of energy. To make chemical bonds to vibrate, this energy is needed. Every chemical bond needs a precise amount of energy to make it vibrate. The energy of the transmitted and detected beam is compared and based on this calculation a spectrum is drawn (see Figure 13). (Materials and Engineering Research Institute)

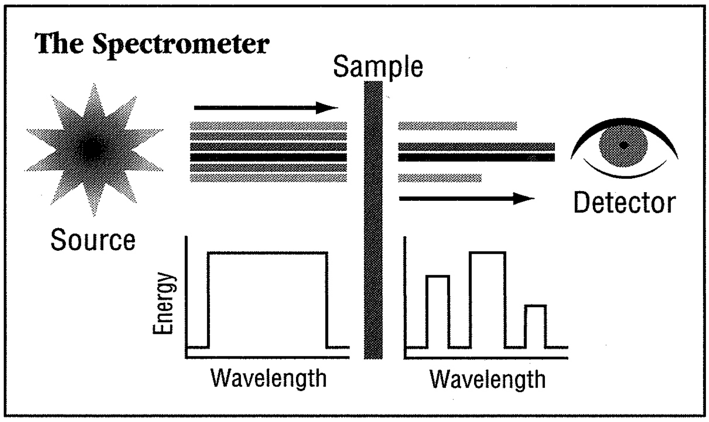


Figure 13. A beam path from the source to the detector

When samples are analyzed with FT-IR, a setup has to be made for the spectrum. Normally, 32 scans and a resolution of 4 is used, which was also the case in this study. 32 scans mean that FT-IR takes 32 scans from the sample. The resolution of 4 means that how detailed the spectrum is drawn. The smaller the number is, the more accurate the spectrum.

For this study, it was important to get information of epoxy (TGAP) and of primary amine during the curing process of nanocomposite which was manufactured. To gain this information, Fourier transform near-infrared was used (see Figure 14).

Figure 14. A Fourier transform infrared spectrometer and computer for monitoring the results.

4.2. Analytical balance

In order to determine the right mixture, with the right quantity of ingredients, a very accurate scale was needed. An analytical balance is used when a high degree of precision and measure materials are needed to within 0.0001 g. A Mettler H10W was used to measure the quantity of the materials for the mixture (see Figure 15).

Figure15. Analytical balance used for weighing the materials

4.3. Ultrasonic bath

Normally an ultrasonic bath is used for cleaning industrial components but it can also be used as a mixer for liquid and powder materials. An ultrasonic sound is a sound which uses frequencies which the human cannot hear. In ultrasonic bath, the ultrasound creates high and low pressure waves. Low pressure generates microscopic bubbles (cavitation) and high pressure collapses the bubbles which causes vast energy impulses on all directions. These impulses are the ones which make the particles move in the resin. In this Ultrasonic bath, the frequency was 42 kHz and its power was 130 W.

Before ultrasonic bath was discovered for mixing, acetone was used to put in the mixture of resin matrix and particles. This was to get a good dispersion. But because acetone was not good for the environment and health, its usage was cancelled. It was replaced with the ultra-sonic bath. There is a study on the comparison of these two methods which shows that the ultrasonic bath is as good as, or even better than using a solvent (Anglada, 2007, 235- 244). For the present study, the ultrasonic bath was used for mixing epoxy resin and montmorillonite (see Figure 16).

Figure 16. Epoxy/MMT in the ultrasonic bath

4.4. Oven

For the curing process, heat is needed even though the reaction is exothermic. When temperature was risen, it had to be done with caution so that the sample would not burn in the curing process. The temperature was risen 2,5°C/minute and the samples were eventually 9 hours in the oven (see Figure 17).

The samples were placed either between two classes or in the aluminium cup. The amount inside the glass was just a drop and in the cup there were about a few milliliters in the cup. But for the FT-NIR analysis, samples inside the glass were used. This was because the amount from the cup was too big for the analysis.

Figure 17. The Oven used for curing the composites.

4.5. Microscope

The dispersions of the clay in the resin were observed using a Leica polarising transmission optical microscope (see Figure 18). This was performed directly after the ultrasonic bath. From each sample, a drop was placed on glass slide covered with a slip.

Figure 18. A Leica polarising transmission optical microscope used for monitoring the dispersion

5. EXPERIMENTS

This study was started on 11 February 2008 at research the laboratory of the department of materials science and metallurgic engineering, at the Universitat Politècnica de Catalunya, in the academic campus of Terrassa. The following pieces of equipment were studied to find out about their functionality: analytical balance, ultra-sonic bath, optical microscope, oven and FTNIR spectrometer.

First the materials (epoxy resin, MMT and hardener) had to be weighed to prepare nanocomposite. The analytical balance was used for weighting. First the analytical balance had to be calibrated to get accurate results. The weight of the materials was a ten thousandth part of grams so the scale had to be very accurate. Epoxy was liquid and a bit hard to allocate so it was the factor which defined the quantity of the dose. MMT and hardener were in the form of powder so it was easier to allocate them. The amount of the portion could not be too big because the samples were put between two glasses and a big quantity of sample would have squeezed out. Before this study, an Omni-Cell NaCl windows circular 25mm diameter was used to introduce the example to the FT-IR. At the beginning it was examined, if glass influenced the results. The tests showed that glass does not influence the spectrum of the sample so it was used because it is much cheaper than NaCl crystal.

Epoxy and MMT were first mixed by hand and to make sure that the dispersion was good, the mixture was introduced to the ultrasound bath. The samples were in the bath from 1 to 3 hours depending on the amount of MMT, 2, 5, 8, 10 or 12 weight-percent (wt%). For 2wt% it was 1+1 hours because when the sample was examined with the microscope, after 1 hour in the ultrasound bath, the dispersion was not good enough. For 5 and 8 wt% 1 hour was needed and for 10 and 12 wt% 3 hours were needed in the ultrasound bath. The dispersion was always examined with a microscope. In Figure 19, the left sample was introduced to the ultrasonic bath and the dispersion was good. On the right, the sample was mixed by hand and the dispersion was not good enough.

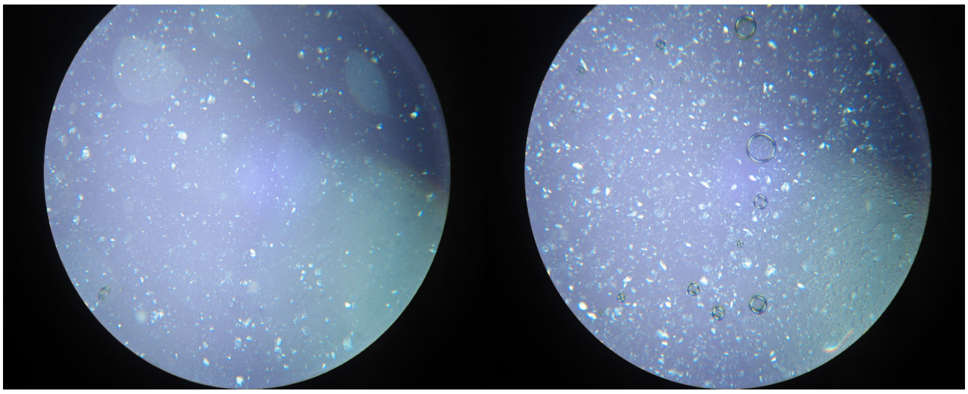


Figure 19. Microscope pictures of MMT (5%) mixed with epoxy using different methods

Montmorillonite particles had to be dispersed to the matrix resin very thoroughly to avoid aggregates in the example. These aggregates could cause weakness in the mechanical and thermal properties.

To mix the hardener in a mixture of epoxy/MMT, the mixture had to be heated because it was already like paste at a room temperature. When the mixture was liquid, in temperature of about 80ºC, the hardener was added little by little to avoid limps.

For the curing process, a mixture of hardener/epoxy/MMT was introduced to the oven. Examples were taken after number of hours in the oven as shown below:

2. Example: room temperature
3. Example: ½ h in 50ºC and ½h in 100 ºC
4. Example: 3½ h in 100 ºC
5. Example: 1h in 150 ºC
6. Example: 1h in 150 ºC
7. Example: 1h in 200 ºC
8. Example: 1h in 200 ºC
9. Example: 1h in 200 ºC
10. Example: 1h in 200 ºC

The examples were studied with FT-NIR and the results were gathered in tables which are analyzed later in this thesis. To be able to analyze the results is was very important to calculate α, it exposes the stage of curing.

The spectrums were analyzed by gathering the highest absorbance value at primary amine and epoxy band from every sample. For locating the highest value, Nicolet's program OMNIC was used. Using these values, the reduced absorbance was calculated as shown below.

Primary amine

$$\text{Reduced absorbance } (A_t) = \frac{\text{absorbance of primary amine band at time t}}{\text{absorbance of invariable band at time t}}$$

Epoxy

$$\text{Reduced absorbance } (A_t) = \frac{\text{absorbance of epoxy band at time t}}{\text{absorbance of invariable band at time t}}$$

Alpha (α) was calculated using the formula as shown below.

$$\alpha = 1 - \frac{A_t}{A_0}$$

In the formula A_t is the reduced absorbance at a time t and A_0 is the reduced absorbance at initiation (time=0h).

6. RESULTS AND DISCUSSION

As a first step in the present study, primary amine, epoxy and aromatic group bands were located on the different FT-NIR spectra. The study results from Varley, Liu and Simon (2006) were also taken into account when locating these bands. Also Table 2 was used for locating these bands (Poisson, Lachenal, Sautereau, 1996).

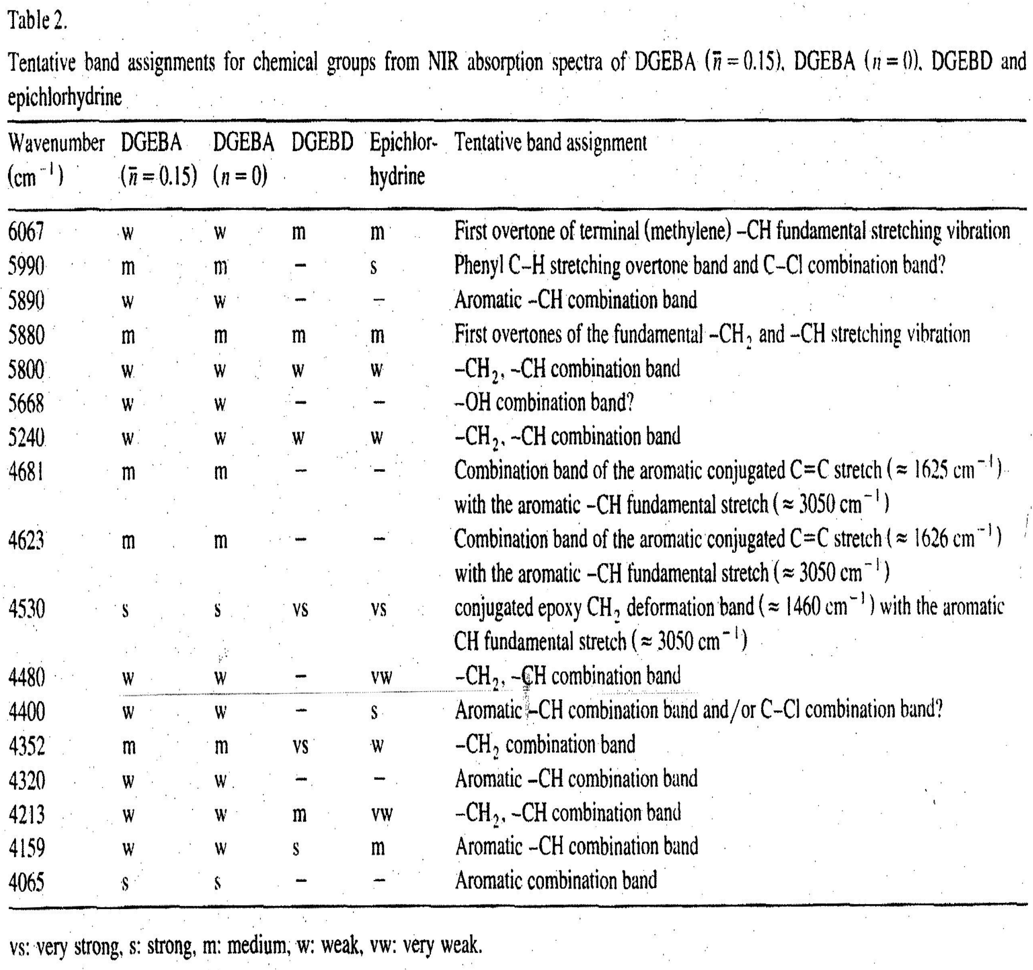


Table 2.

Tentative band assignments for chemical groups from NIR absorption spectra of DGEBA ($\bar{n} = 0.15$), DGEBA ($n = 0$), DGEBD and epichlorhydrine

Wavenumber (cm^{-1})	DGEBA ($\bar{n} = 0.15$)	DGEBA ($n = 0$)	DGEBD	Epichlor-hydrine	Tentative band assignment
6067	w	w	m	m	First overtone of terminal (methylene) –CH fundamental stretching vibration
5990	m	m	–	s	Phenyl C–H stretching overtone band and C–Cl combination band?
5890	w	w	–	–	Aromatic –CH combination band
5880	m	m	m	m	First overtones of the fundamental $-CH_2$ and –CH stretching vibration
5800	w	w	w	w	$-CH_2$, –CH combination band
5668	w	w	–	–	–OH combination band?
5240	w	w	w	w	$-CH_2$, –CH combination band
4681	m	m	–	–	Combination band of the aromatic conjugated C=C stretch ($\approx 1625\ cm^{-1}$) with the aromatic –CH fundamental stretch ($\approx 3050\ cm^{-1}$)
4623	m	m	–	–	Combination band of the aromatic conjugated C=C stretch ($\approx 1626\ cm^{-1}$) with the aromatic –CH fundamental stretch ($\approx 3050\ cm^{-1}$)
4530	s	s	vs	vs	conjugated epoxy CH_2 deformation band ($\approx 1460\ cm^{-1}$) with the aromatic CH fundamental stretch ($\approx 3050\ cm^{-1}$)
4480	w	w	–	vw	$-CH_2$, –CH combination band
4400	w	w	–	s	Aromatic –CH combination band and/or C–Cl combination band?
4352	m	m	vs	w	$-CH_2$ combination band
4320	w	w	–	–	Aromatic –CH combination band
4213	w	w	m	vw	$-CH_2$, –CH combination band
4159	w	w	s	m	Aromatic –CH combination band
4065	s	s	–	–	Aromatic combination band

vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

Epoxy (TGAP) was introduced to the FT-NIR to locate the characteristic epoxy group band. The earlier study by Varley, Liu, Simon (2006) and Table 2 point out that the epoxy group can be located at a wavenumber of 4530 cm^{-1}. Figure 20 was studied accurately only to confirm that the position of this band was slightly different (4526 cm^{-1}) than that of other similar studies. This was because chains have little movement due to the curing process, much like in Varley, Liu, Simon's (2006) study and in Table 2. Also different epoxy resins were used in both Varley, Liu, Simon's (2006) study as well as the data in Table 2.

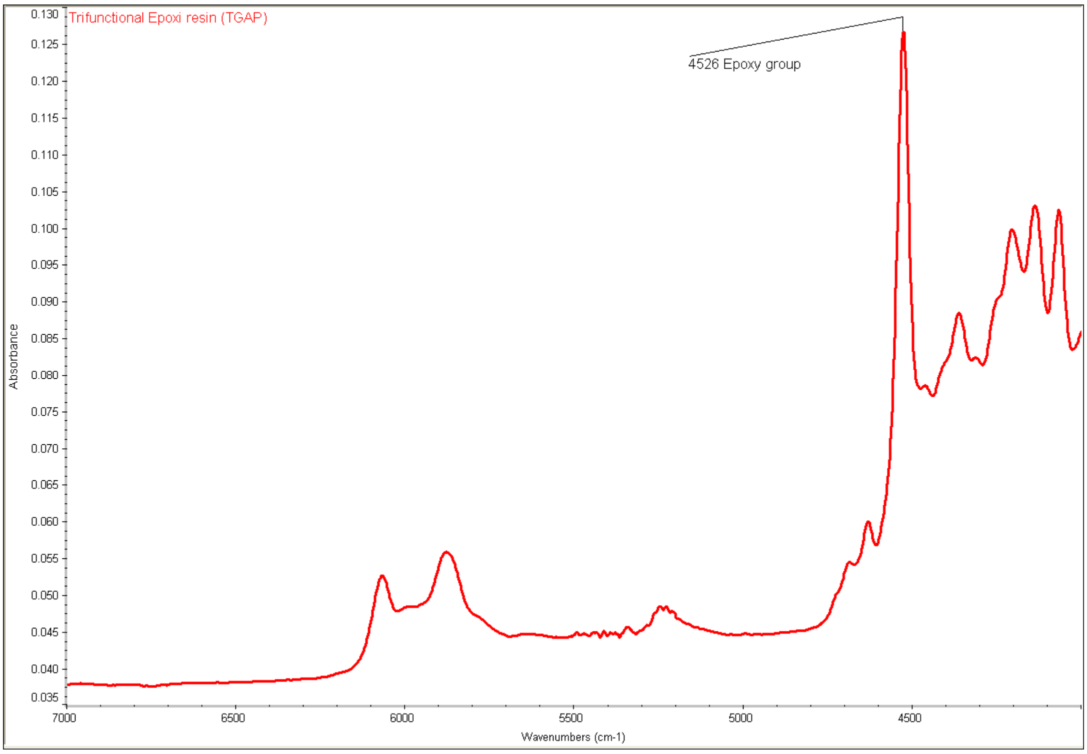


Figure 20. FT-NIR spectrum of the epoxy resin (TGAP)

Also, the hardener (DDS) was introduced to the FT-NIR to locate the characteristic primary amine group band. This group was found on the 5000-5100 cm^{-1} region as shown in Figure 21. When the mixture is cured, this primary amine group moves and can be more accurately located.

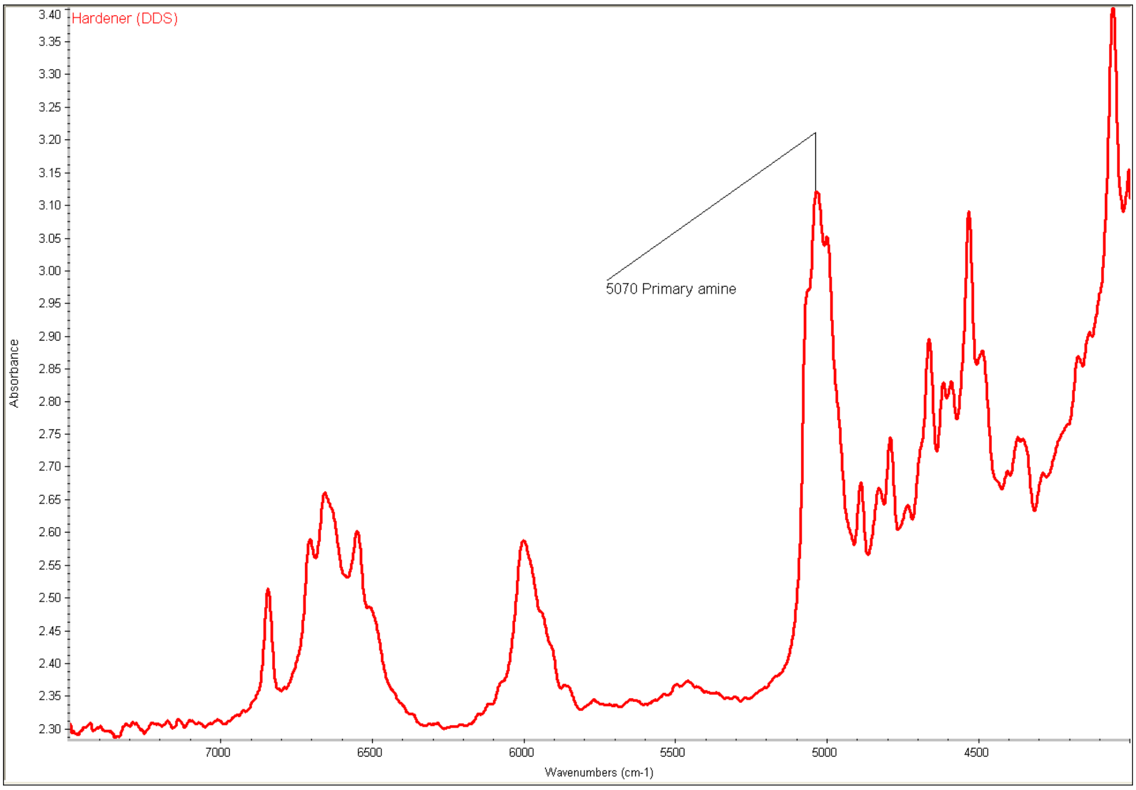


Figure 21. FT-NIR spectrum of the hardener (DDS)

To locate the invariant reference band a lot of research needed to be made. This was because there are different bands used as the invariable in the literature. Spectra were studied intensively to find an invariant reference band for this study. The following bands, 4623 cm^{-1} and 4057 cm^{-1}, were used in the calculations. These were compared and the results were more accurate when using the 4057 cm^{-1} band. Also 4623 cm^{-1} band shifted from 4627 to 4613 cm^{-1} due to the curing process as shown in Figure 22.

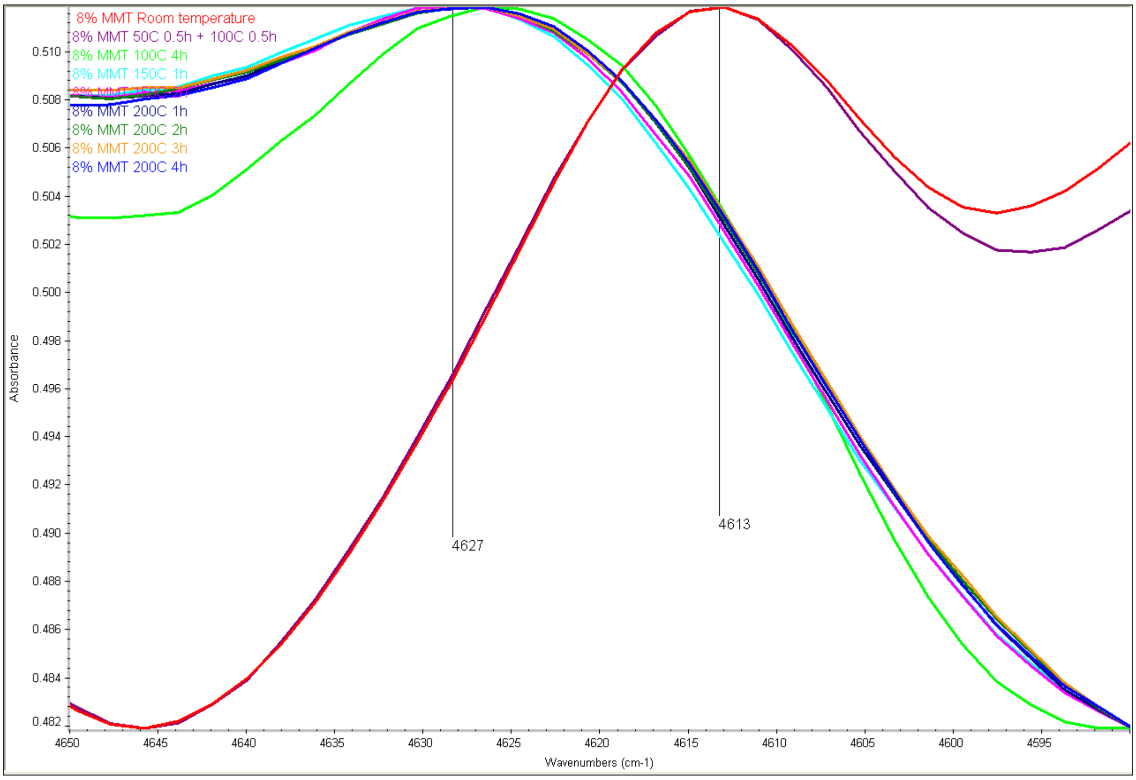


Figure 22. FT-NIR spectrum of the 4623 cm^{-1} band on curing process of 8% MMT

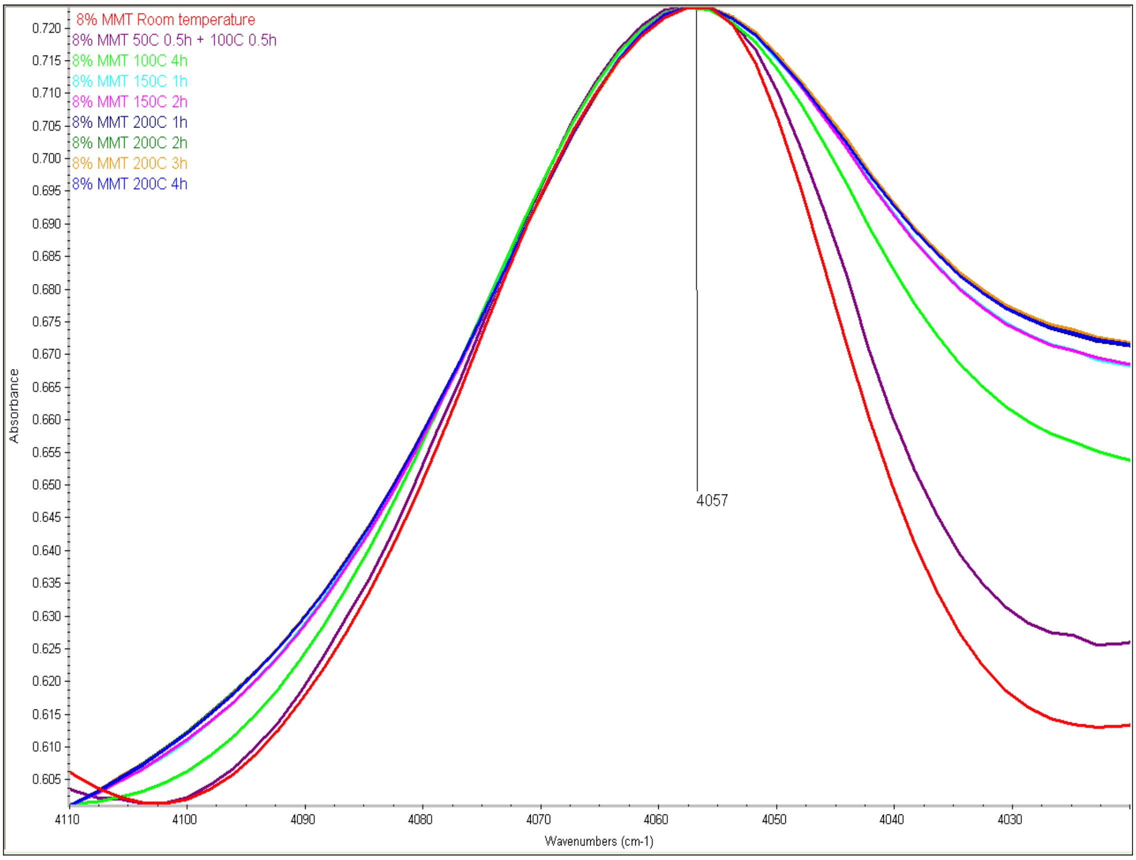


Figure 23. FT-NIR spectrum of 4057 cm^{-1} band on curing process of 8% MMT

The main interest was to study the evolution of the primary amine and epoxy resin bands during the curing process. These bands were found at 4530 cm^{-1} (epoxy) and 5070 cm^{-1} (primary amine). During the curing process, the epoxy peak changed between 4528-4514 cm^{-1}. The following figures show how the curing affects each mixture. Figures (24, 27, 30, 33 and 36) are the NIR spectra of the studied region, the others being close-ups of both the primary amine (Figures 25, 28, 31, 34 and 37) and epoxy band (Figures 26, 29, 32, 35 and 38) bands.

6.1. TGAP/ 2wt% MMT nanocomposite

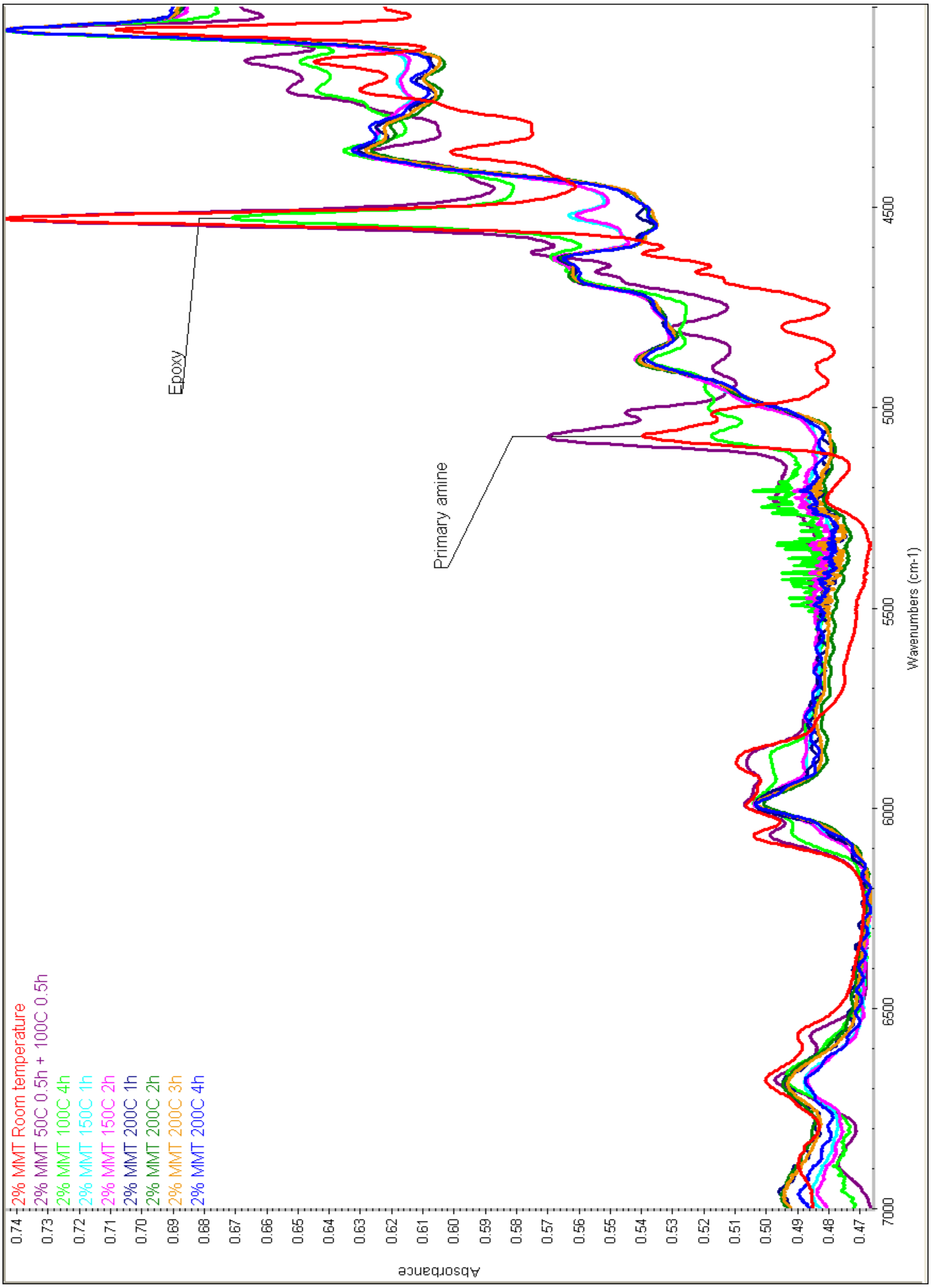


Figure 24. FT-NIR spectra showing all the thermal cycle of TGAP/ 2wt% MMT nanocomposites

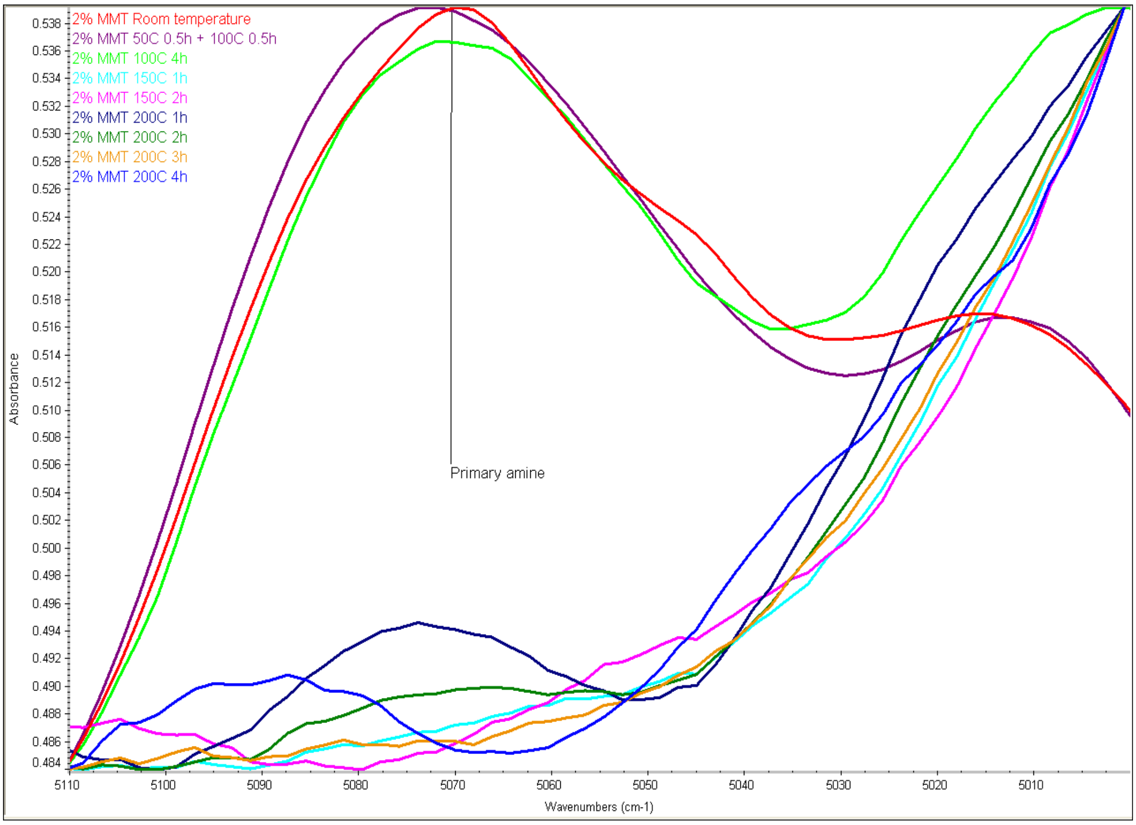


Figure 25. FT-NIR spectra showing all the thermal cycle of TGAP/ 2wt% MMT (primary amine).

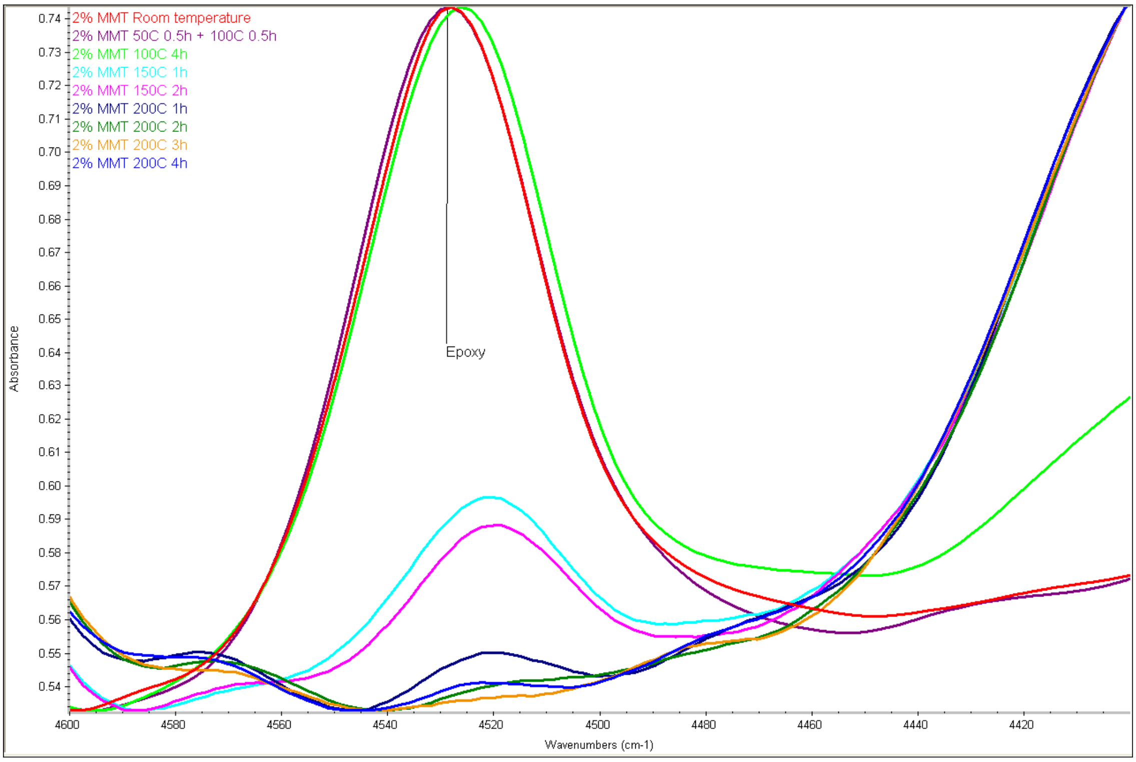


Figure 26. FT-NIR spectra showing all the thermal cycle of TGAP/ 2wt% MMT (epoxy).

6.2. TGAP/ 5wt% MMT nanocomposite

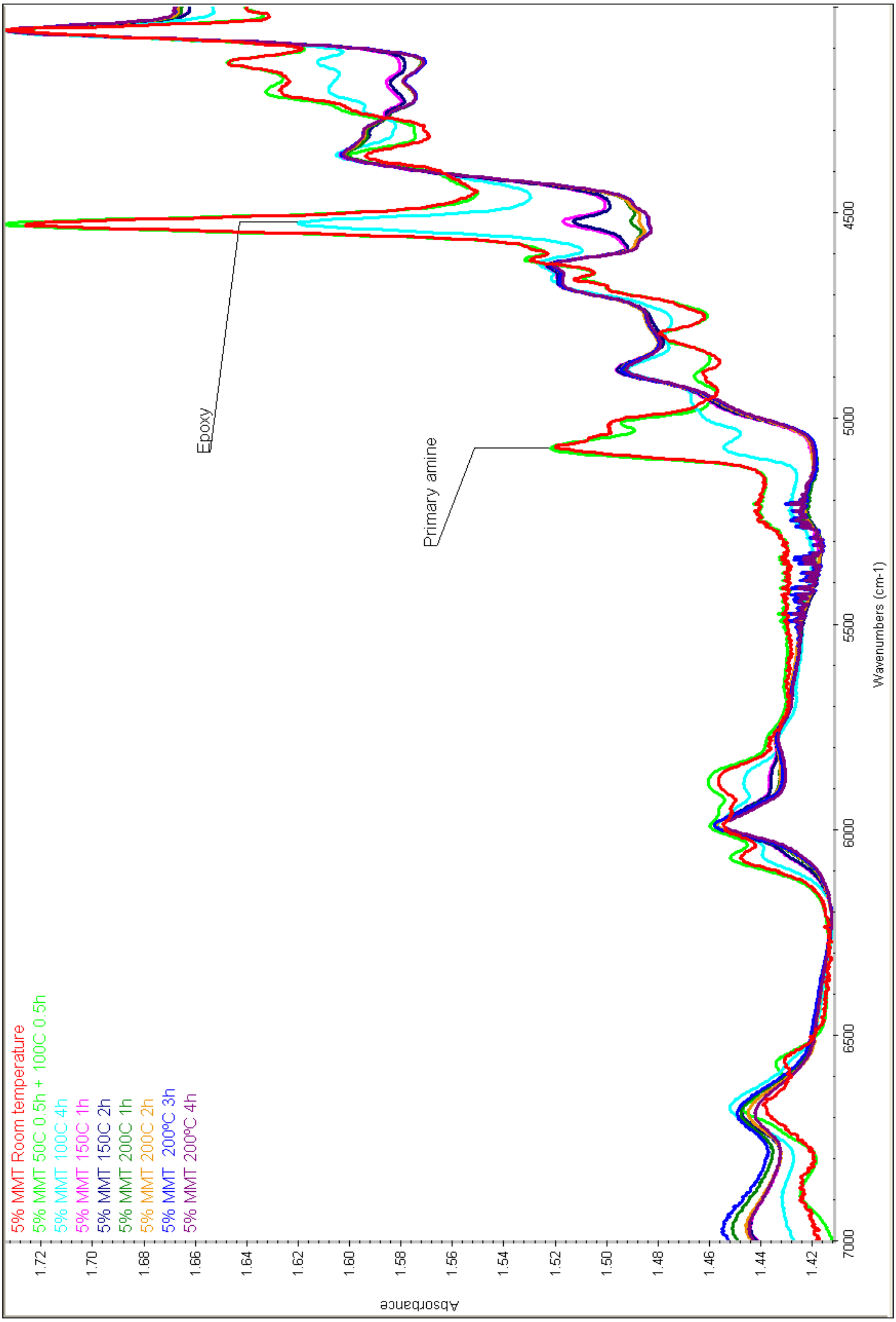


Figure 27. FT-NIR spectra showing all the thermal cycle of TGAP/ 5wt% MMT nanocomposites

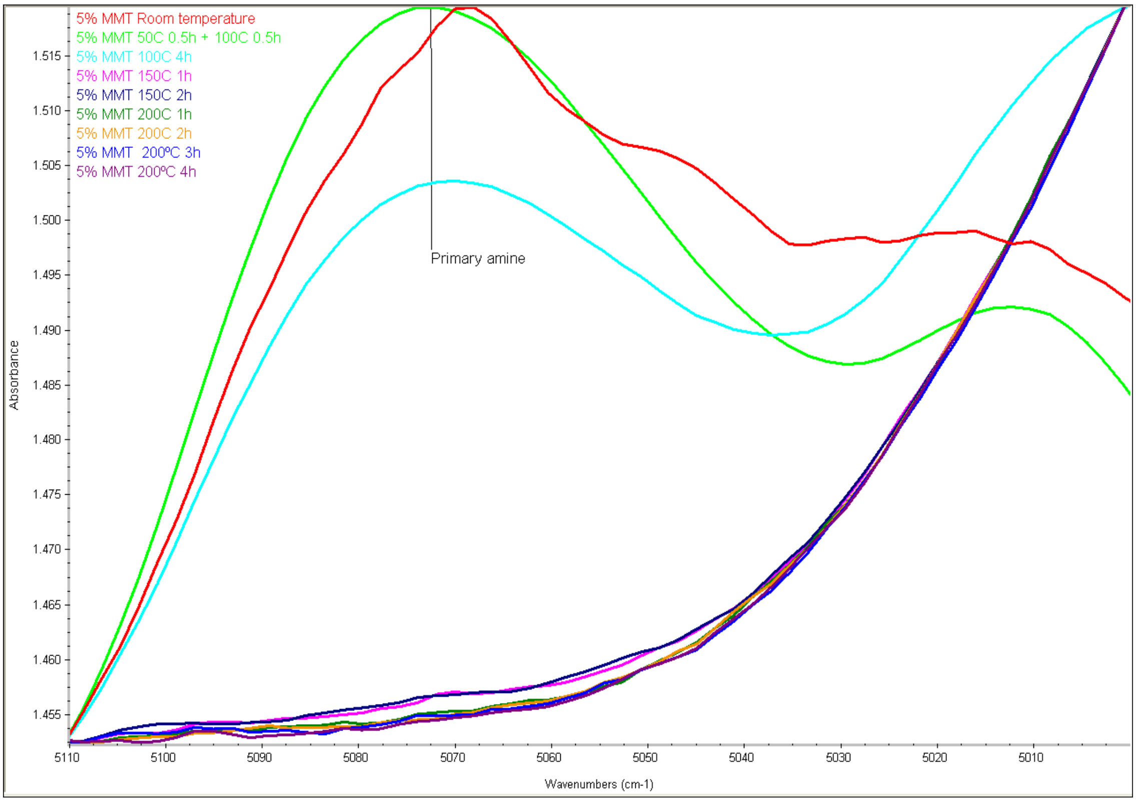


Figure 28. FT-NIR spectra showing all the thermal cycle of TGAP/ 5wt% MMT (primary amine).

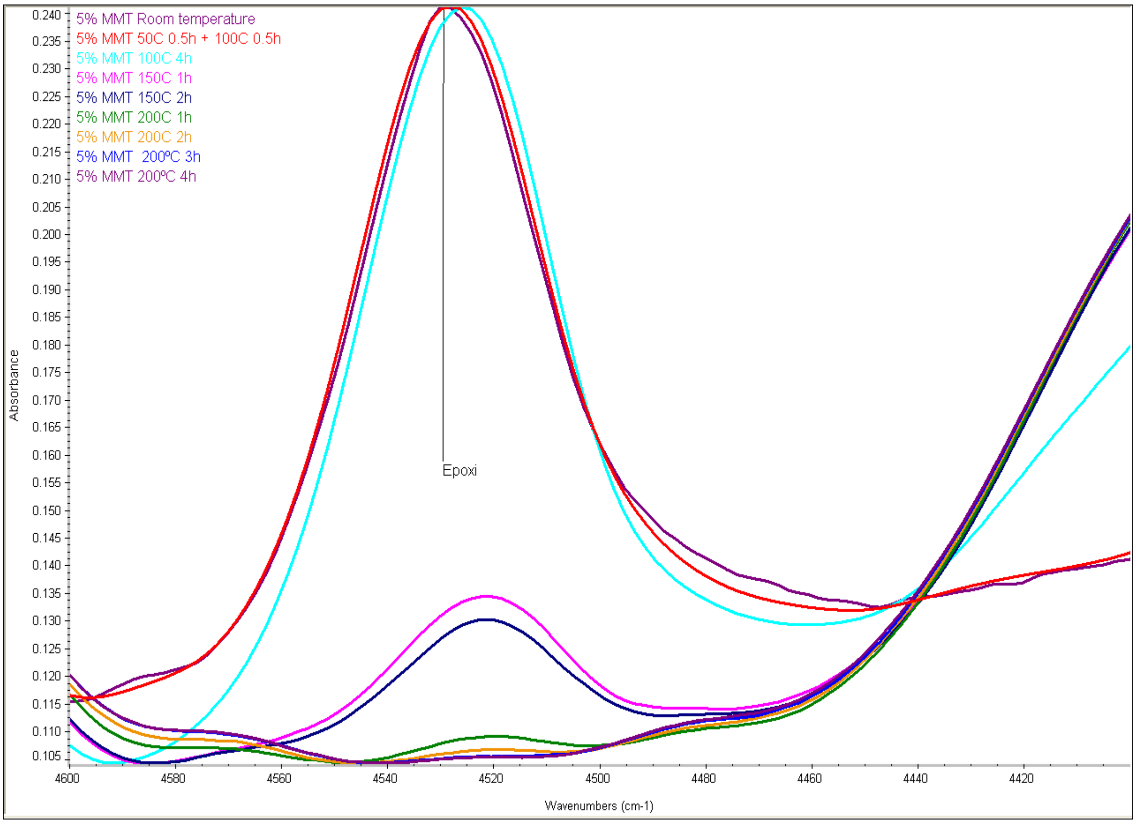


Figure 29. FT-NIR spectra showing all the thermal cycle of TGAP/ 5wt% MMT (epoxy).

6.3. TGAP/ 8wt% MMT nanocomposite

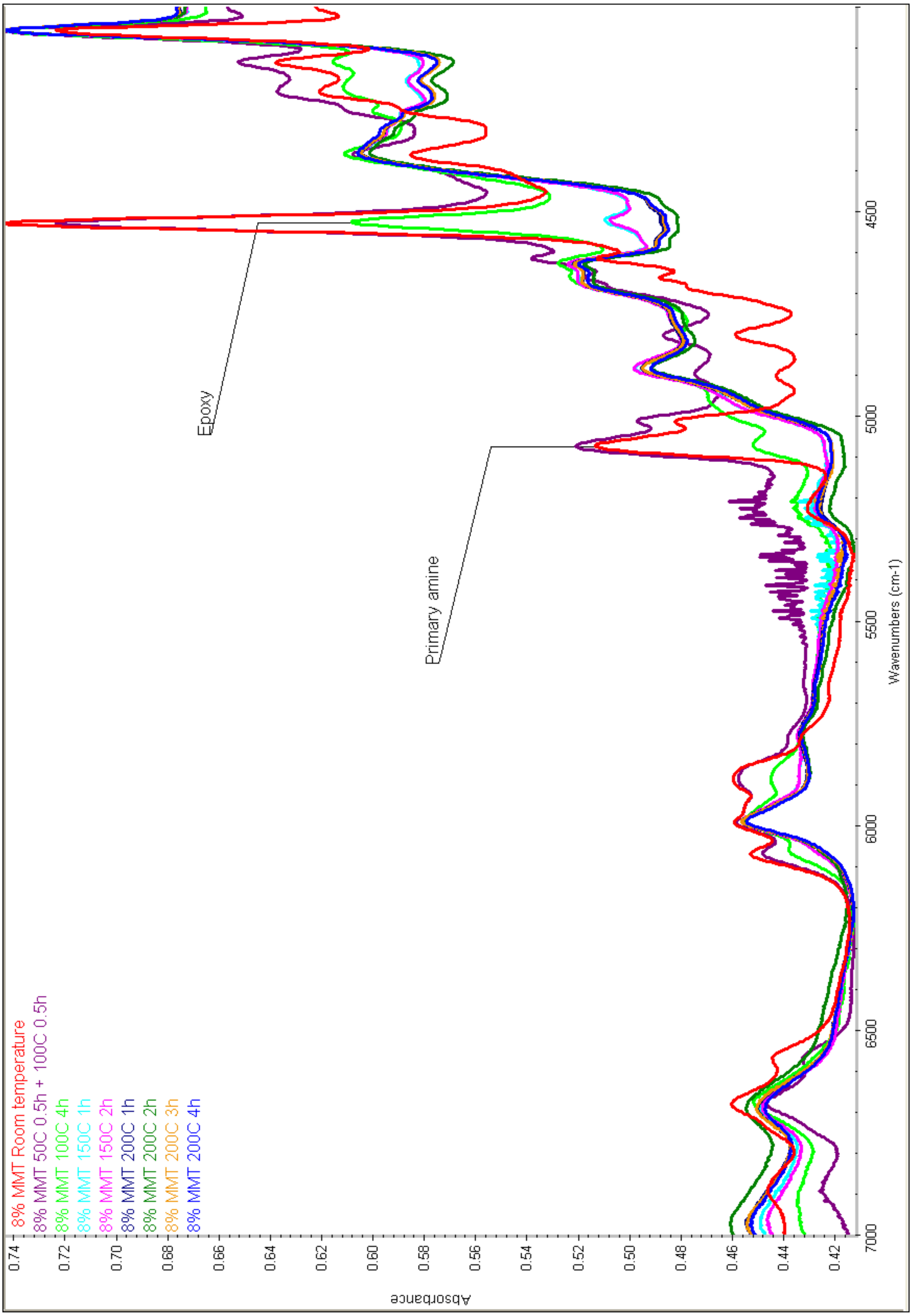


Figure 30. FT-NIR spectra showing all the thermal cycle of the TGAP/ 8wt% MMT nanocomposites

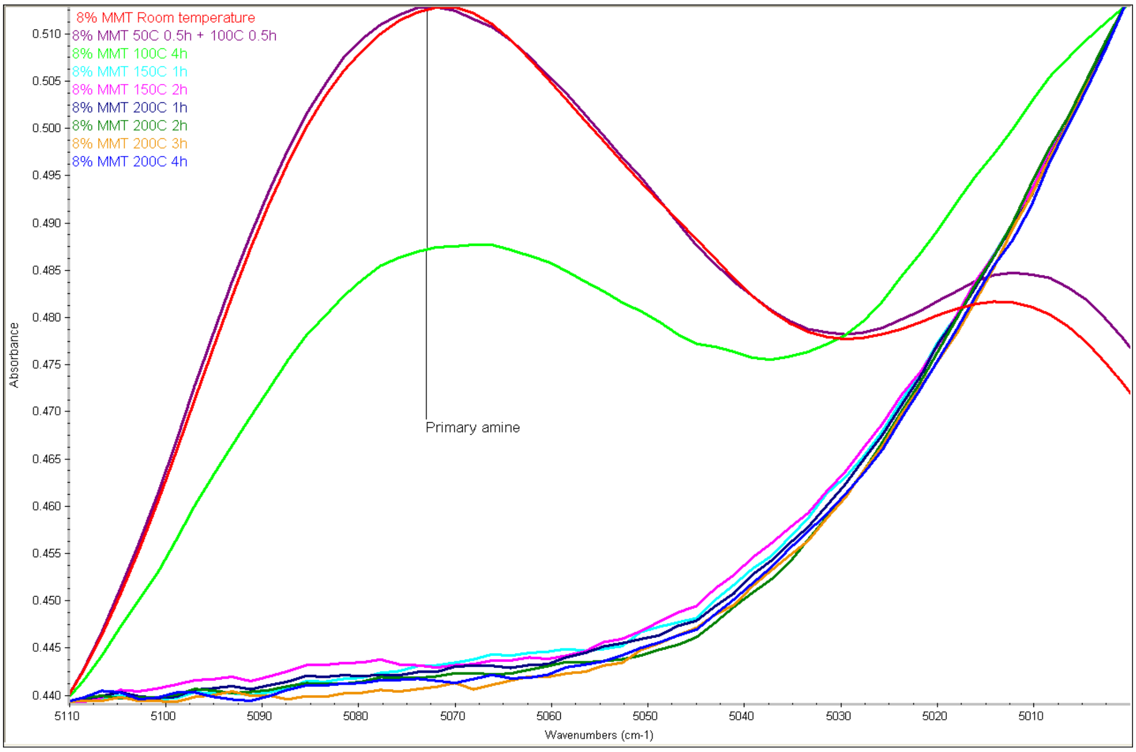


Figure 31. FT-NIR spectra showing all the thermal cycle of the TGAP/ 8wt% MMT (primary amine).

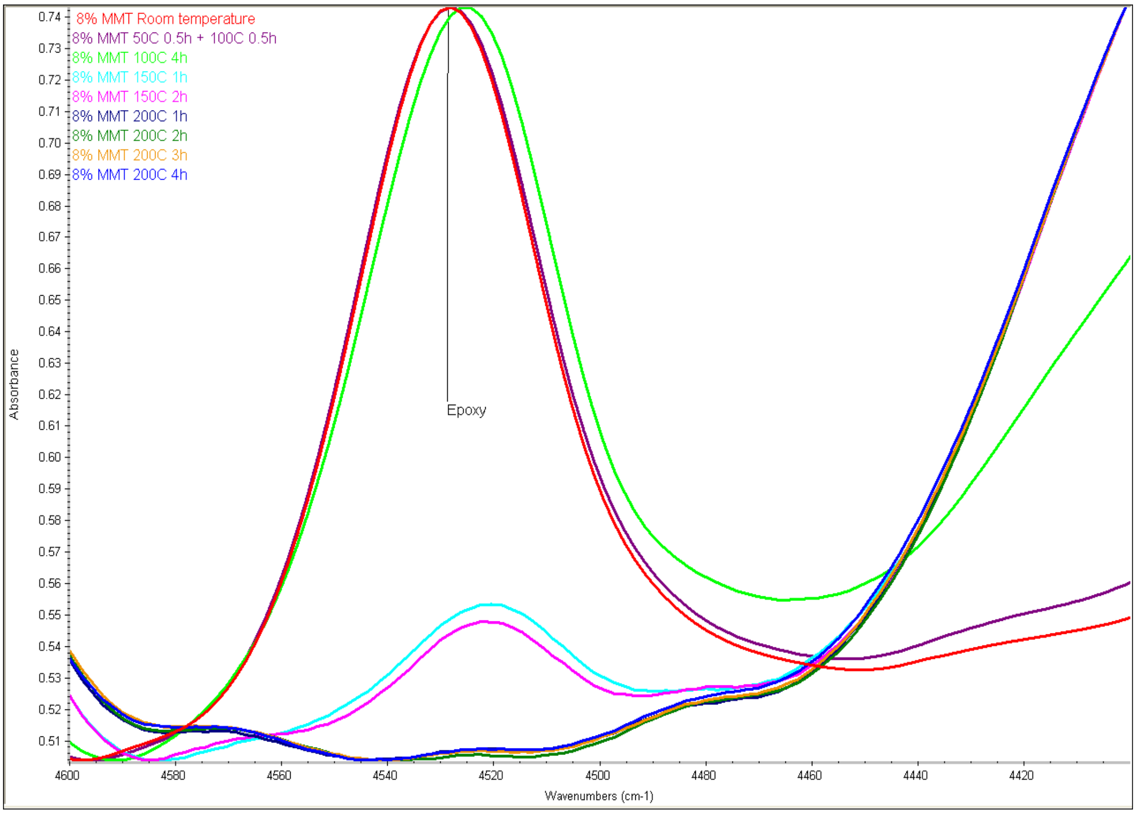


Figure 32. FT-NIR spectra showing all the thermal cycle of the TGAP/ 8wt% MMT (epoxy).

6.4. TGAP/ 10wt% MMT nanocomposite

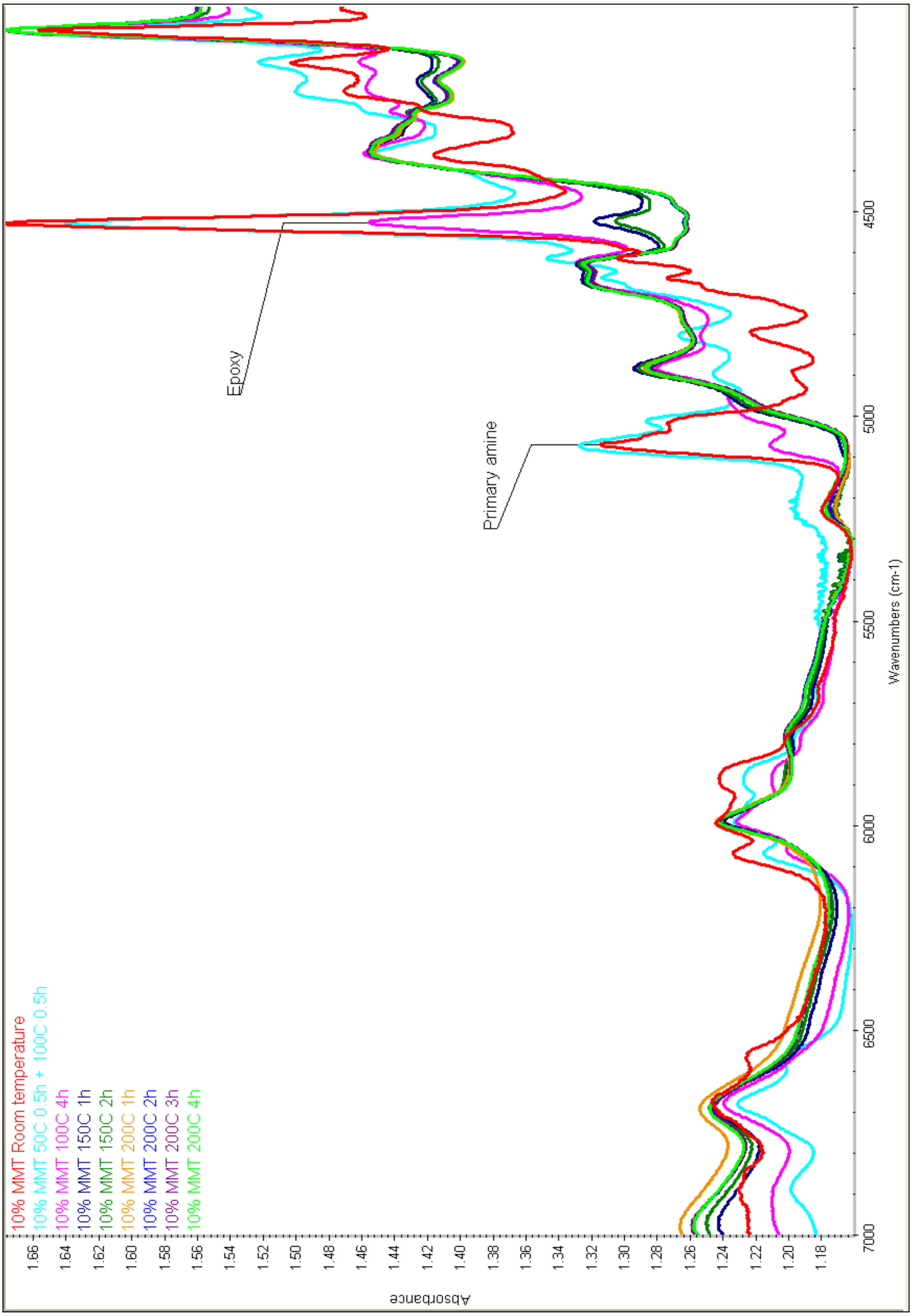


Figure 33. FT-NIR spectra showing all the thermal cycle of the TGAP/ 10wt% MMT nanocomposites

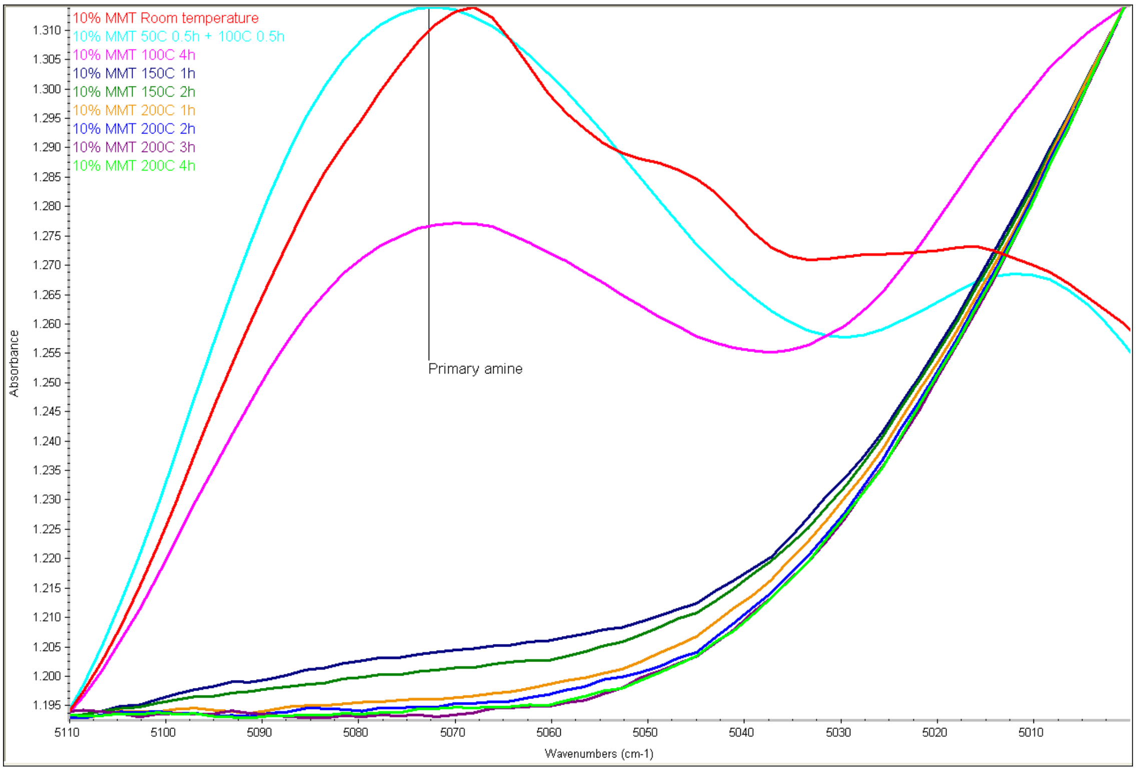


Figure 34. FT-NIR spectra showing all the thermal cycle of the TGAP/ 10wt% MMT (primary amine).

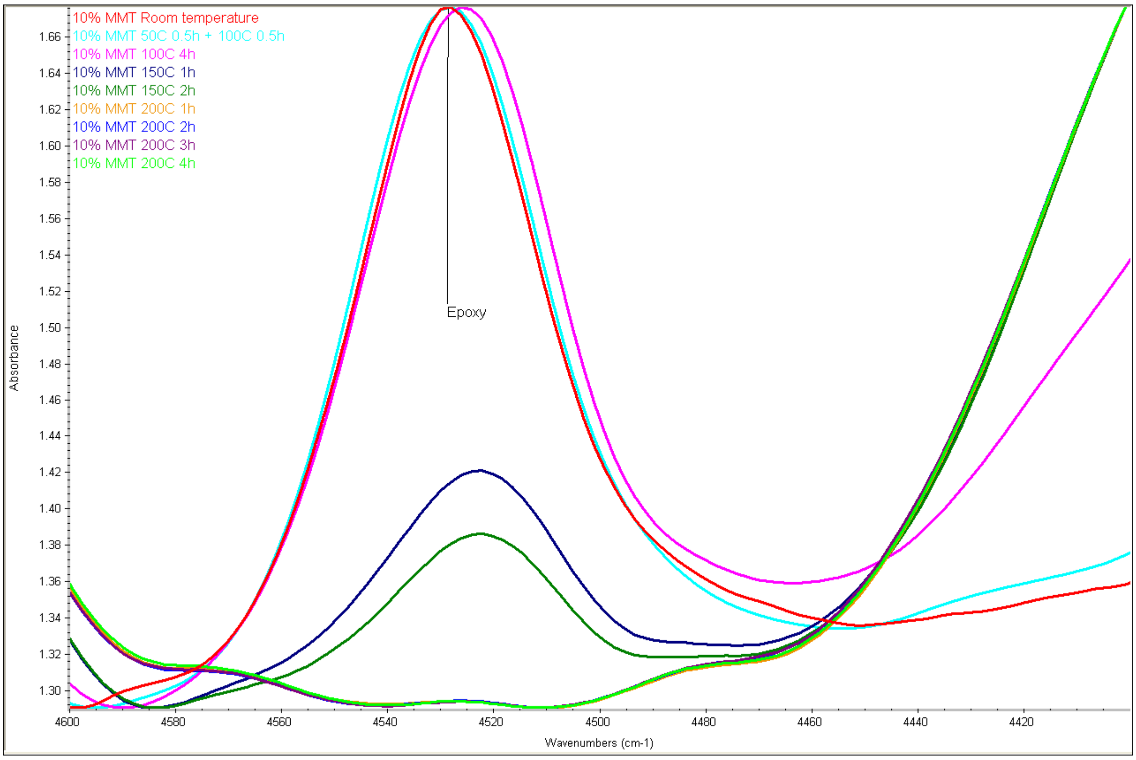


Figure 35. FT-NIR spectra showing all the thermal cycle of the TGAP/ 10wt% MMT (epoxy9.

6.5. TGAP/ 12wt% MMT nanocomposite

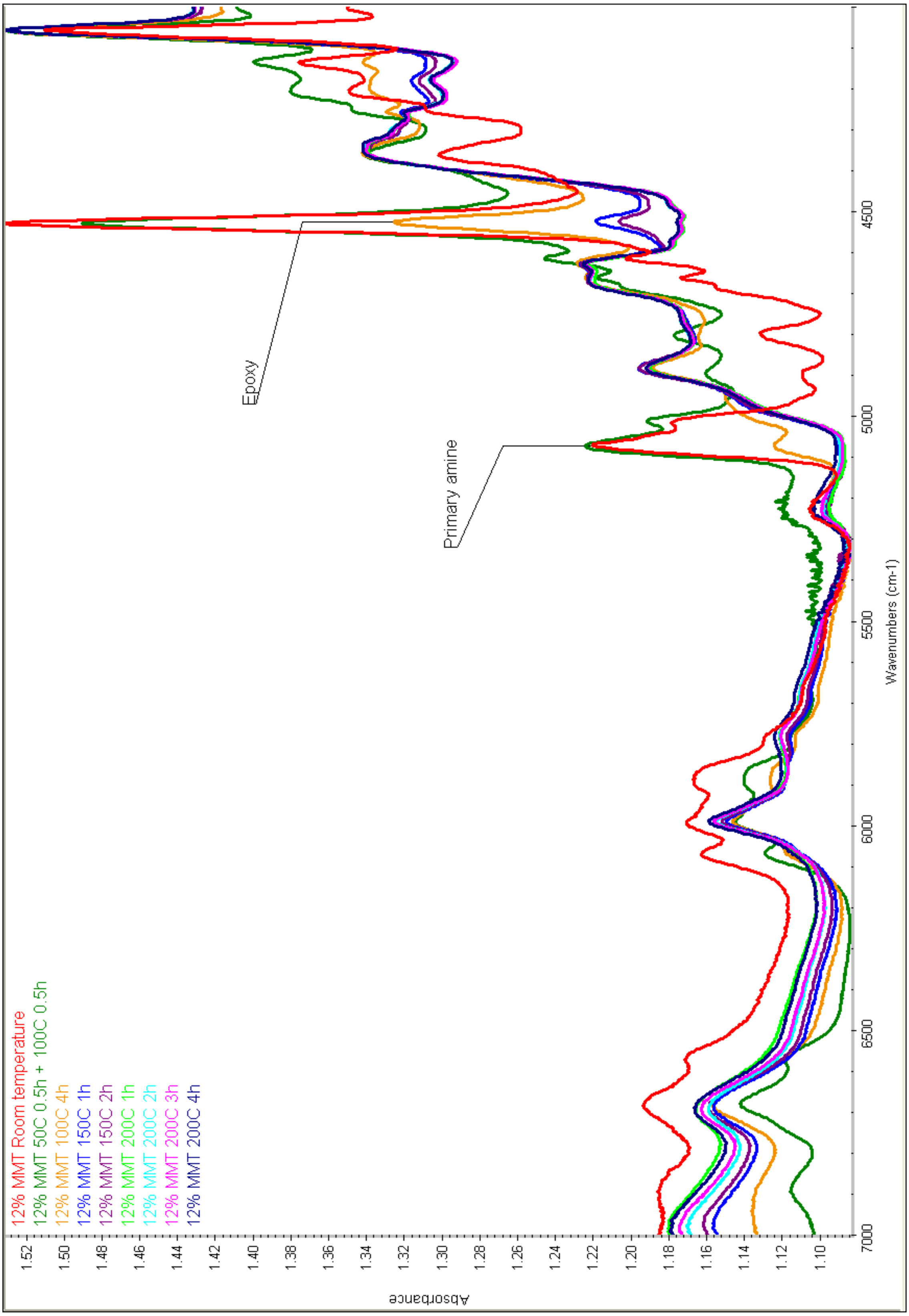


Figure 36. FT-NIR spectra showing all the thermal cycle of the TGAP/ 12wt% MMT nanocomposites

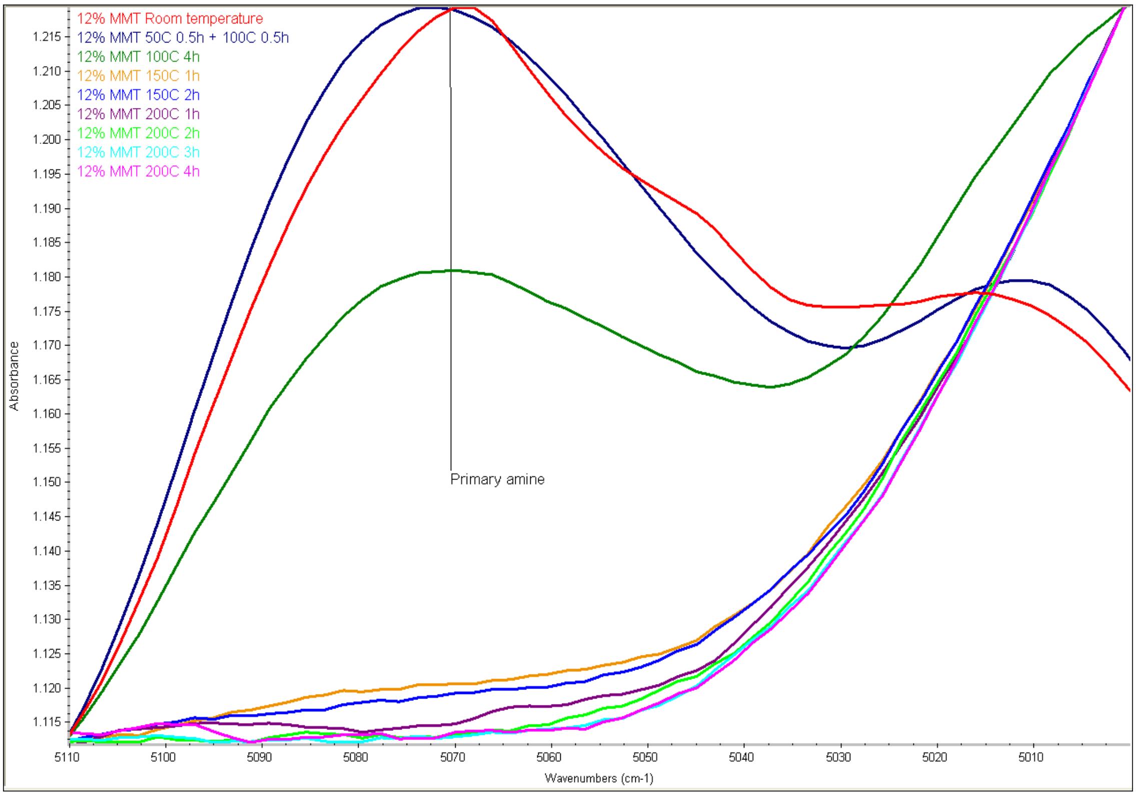


Figure 37. FT-NIR spectra showing all the thermal cycle of the TGAP/ 12wt% MMT (primary amine).

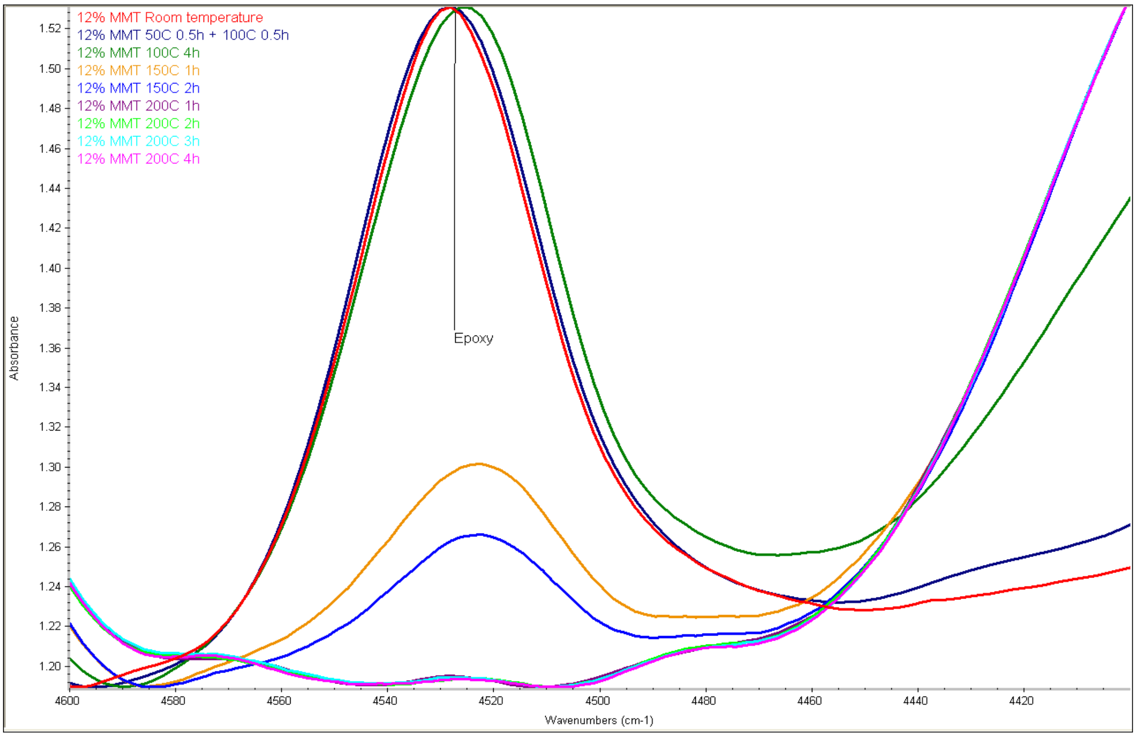


Figure 38. FT-NIR spectra showing all the thermal cycle of the TGAP/ 12wt% MMT (epoxy).

6.6. Curing conversion

Primary amine (see Table 3) and epoxy (see Table 4) conversion (α) values were calculated and, placed in a table for comparison reasons.

In the initial stages of curing, it was observed that a greater amount of MMT in the mixture led to higher conversions of both primary amine and epoxy. On the other hand, the stage of curing decreased after 1 hour of heat treatment with increasing the amount of MMT. The primary amine band disappeared faster than the epoxy band which is shown later in this chapter.

Table 3. Conversion (α) values for primary amine

T(ºC)	t accumulate (hours)	α (%) Primary amine(5070)				
		MMT				
		2%	5%	8%	10%	12%
25	0	0	0	0	0	0
100	1	13	13	41	15	37
100	2	34	40	61	46	60
100	3	37	57	73	68	72
100	4	66	74	84	79	85
150	5	100	100	100	100	100
150	6	100	100	100	100	100
200	7	100	100	100	100	100
200	8	100	100	100	100	100
200	9	100	100	100	100	100
200	10	100	100	100	100	100

The effect of the amount of modified montmorillonite can be seen after the first hour at 100ºC, the values of α of, 2, 5, 8, 10 and 12% MMT nanocomposites being respectively 13, 13, 41, 15 and 37. Curing is faster with increasing the amount of MMT. Full curing was reached after 5 hours of heat treatment on all the modified – MMT nanocomposites irrespective of the amount of the modified montmorillonite.

Table 4. Conversion (α) values for epoxy

T(ºC)	t accumulate (hours)	α (%) Epoxy (4528-4514 cm^{-1})				
		MMT				
		2%	5%	8%	10%	12%
25	0	0	0	0	0	0
100	1	7	3	30	26	34
100	2	13	21	41	39	47
100	3	18	29	50	49	58
100	4	35	46	62	65	69
150	5	83	86	91	90	91
150	6	85	89	91	93	93
200	7	98	99	100	100	99
200	8	100	100	100	100	99
200	9	100	100	100	100	100
200	10	100	100	100	100	100

Montmorillonite had a similar impact on the epoxy band, although curing was slower. Higher amounts of MMT speeded up the curing process. For example, after the first hour at 100ºC, nanocomposites with MMT contents of 2, 5, 8, 10 and 12% led to epoxide conversions of 7, 3, 30, 26 and 34. Full curing was achieved after 8 hours at 200ºC for all the nanocomposites.

From 4 to 5 hours of heat treatment, the results increased rapidly on both primary amine and epoxy. This region was studied intensely. Samples were taken every 15 minutes as shown in Tables 5 and 6.

Table 5. Conversion (α) values for primary amine between 4 and 5 hours

T(°C)	t accumulate (hour)	α (%) Primary amine(5070)				
		MMT				
		2%	5%	8%	10%	12%
100	4	66	74	84	79	85
150	4,25	100	100	100	100	99
150	4,5	100	100	100	100	100
150	4,75	100	100	100	100	100
150	5	100	100	100	100	100

Table 5 shows that primary amine cured after 4 hours and 15 minutes, except in the case of 12% of MMT/nanocomposites, although close to full curing stage (99%). Curing is really rapid after between 4 - 4.25 hours (average about 20%) (see figure 39) . 2, 5, 8, 10 and 12% MMT/nanocomposites curing rates were 34, 26, 16, 21 and 14%/15min.

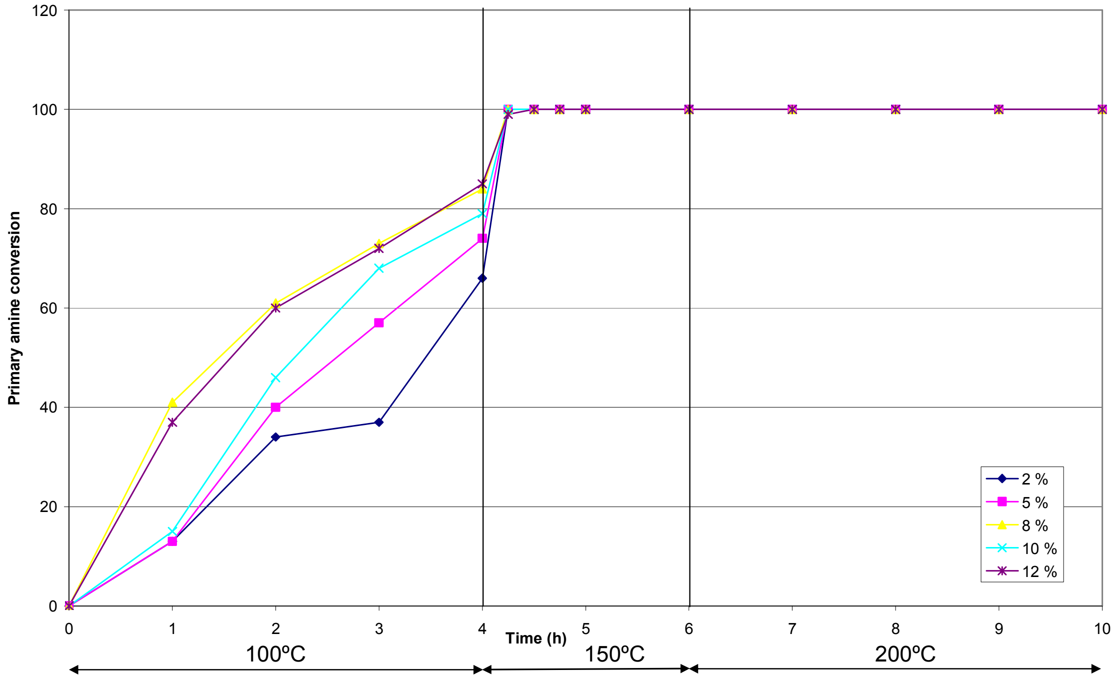


Figure 39. Conversion of primary amine

Table 6. Conversion (α) values for epoxy between 4 and 5 hours

T(ºC)	t accumulate (hour)	α (%) Epoxy(4528-4514 cm^{-1})				
		MMT				
		2%	5%	8%	10%	12%
100	4	35	46	62	65	69
150	4,25	69	76	87	86	88
150	4,5	71	80	86	88	88
150	4,75	77	82	89	89	90
150	5	83	86	91	90	91

For epoxy, curing was more controlled, as shown in Table 6 as observed previously for primary amine. Conversion increased rapidly between 4 - 4.25 hours like primary amine average of about 25% (see Figure 40). 2, 5, 8, 10 and 12% MMT/nanocomposites curing rate were 34, 30, 24, 21 and 19%/15min.

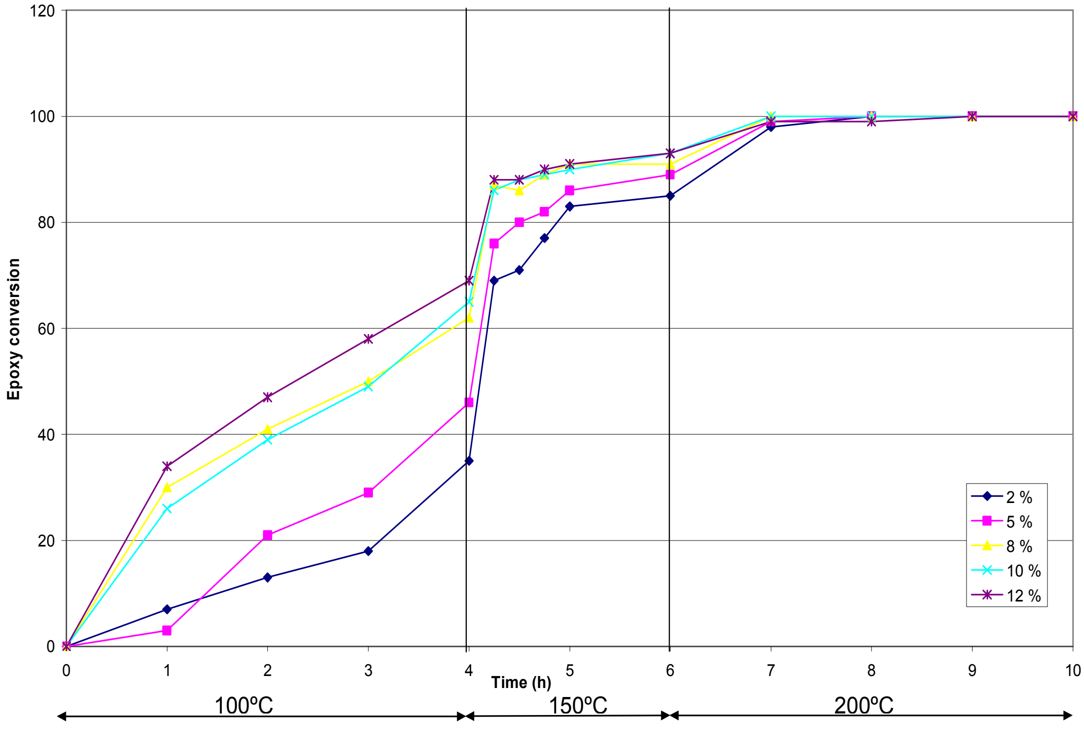


Figure 40. Conversion of Epoxy

The conversion of both the primary amine and the epoxy was compared to study their correlation (see Figure 41). It was shown earlier that primary amine cured more quickly than epoxy. However, this did not affect the correlation values because they were excellent, as shown in Figure 41. For 2, 5, 8, 10, 12% MMT correlations were 0,93, 0,96, 0,97, 0,96 and 0,97.

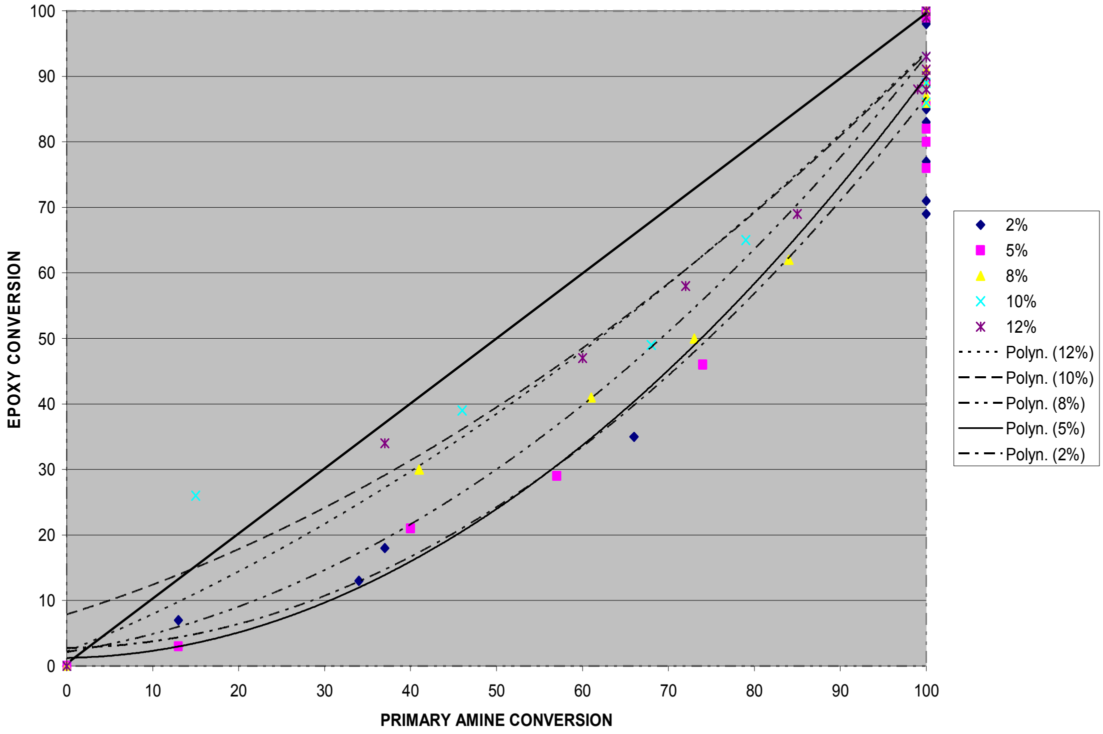


Figure 41. Comparison of epoxy and primary amine conversions with different amounts of MMT

7. CONCLUSIONS

Nanocomposites can be taken as a noteworthy option in industries. It may have better mechanical properties than metals, not to mention chemical properties. It has vast utilization ratio and it can be modified with additives, such as nanoparticles.

It is important to get MMT homogeneously dispersed into the matrix. For industrial use and for this study using the ultrasonic bath was a good alternative.

The environment and especially the health of people is at risk when using a solvent.

The aim of this study was to follow the resin curing reaction using FTIR and especially region of near- infrared (NIR). The used composite consisted of a trifunctional epoxy resin, an aromatic amine hardener (DDS) and a modified montmorillonite with octadedyl ammonium. The modification of MMT affected the curing stage by accelerating it.

In the initial stage of curing it was already observed that modification of MMT was effecting the curing process. A bigger quantity of MMT, speeded up the curing right after one hour at 100ºC. 2, 5, 8, 10 and 12% proportions of MMT, conversions were for primary amine 13, 12, 41, 15, 37% and for epoxy 7, 3, 30, 26 and 34. After first hour curing, conversion increased smoothly until 4 hours when the conversions rapidly increased. The conversion increased on average 22% for primary amine and 33% for epoxy between the 4th and 5th hour.

To get more accurate results between the 4th and 5th hour, it was decided to analyze that interval more closely. Samples were taken every 15 minutes with FT-NIR. It was observed that curing was still rapid from 4 to 4,25 hours at 100ºC for both primary amine (20% /15min) and epoxy (25% /15min). In the future, more detailed studies need to be conducted on this area. After 4 hours and 15 minutes conversions increased moderately because most of the crosslinking had happened so the movement of molecules was limited.

The results of Pagès, Lacorte, Lipinska and Carrasco (2008) implied that, conclusions were similar to this study meaning that a bigger wt% accelerates the reaction. The results shown in this study demonstrate that FT-NIR is a much more accurate technique than FT-IR. Nonetheless, more research must be conducted, particularly on the use of different epoxies, hardeners and particles in order to be sure that FT-NIR is as good for other types of molecule bonds.

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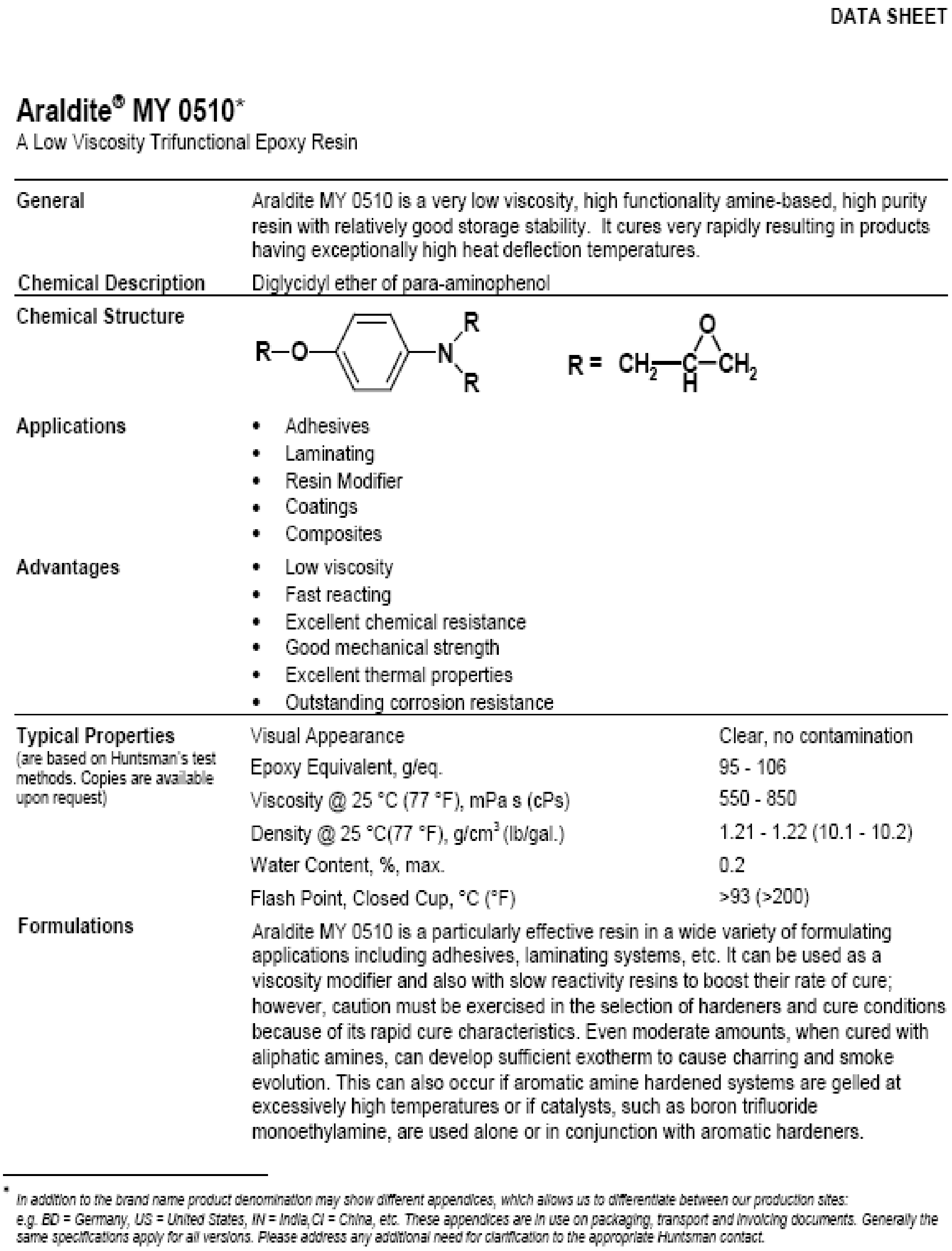
APPENDICES

APPENDIX 1	Trifunctional epoxy resin data sheet
APPENDIX 2	Hardener (DDS) data sheet
APPENDIX 3	Montmorillonite data sheet

APPENDICES 1/1



DATA SHEET

Araldite® MY 0510*

A Low Viscosity Trifunctional Epoxy Resin

General Araldite MY 0510 is a very low viscosity, high functionality amine-based, high purity resin with relatively good storage stability. It cures very rapidly resulting in products having exceptionally high heat deflection temperatures.

Chemical Description Diglycidyl ether of para-aminophenol

Chemical Structure

Applications

- Adhesives
- Laminating
- Resin Modifier
- Coatings
- Composites

Advantages

- Low viscosity
- Fast reacting
- Excellent chemical resistance
- Good mechanical strength
- Excellent thermal properties
- Outstanding corrosion resistance

Typical Properties
(are based on Huntsman's test methods. Copies are available upon request)

Visual Appearance	Clear, no contamination
Epoxy Equivalent, g/eq.	95 - 106
Viscosity @ 25 °C (77 °F), mPa s (cPs)	550 - 850
Density @ 25 °C(77 °F), g/cm^3 (lb/gal.)	1.21 - 1.22 (10.1 - 10.2)
Water Content, %, max.	0.2
Flash Point, Closed Cup, °C (°F)	>93 (>200)

Formulations Araldite MY 0510 is a particularly effective resin in a wide variety of formulating applications including adhesives, laminating systems, etc. It can be used as a viscosity modifier and also with slow reactivity resins to boost their rate of cure; however, caution must be exercised in the selection of hardeners and cure conditions because of its rapid cure characteristics. Even moderate amounts, when cured with aliphatic amines, can develop sufficient exotherm to cause charring and smoke evolution. This can also occur if aromatic amine hardened systems are gelled at excessively high temperatures or if catalysts, such as boron trifluoride monoethylamine, are used alone or in conjunction with aromatic hardeners.

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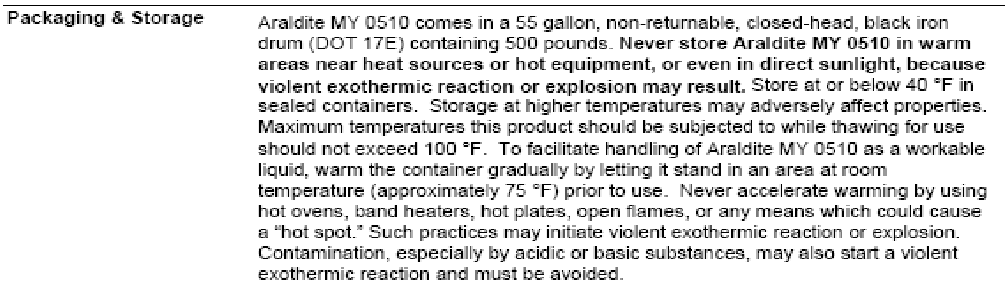
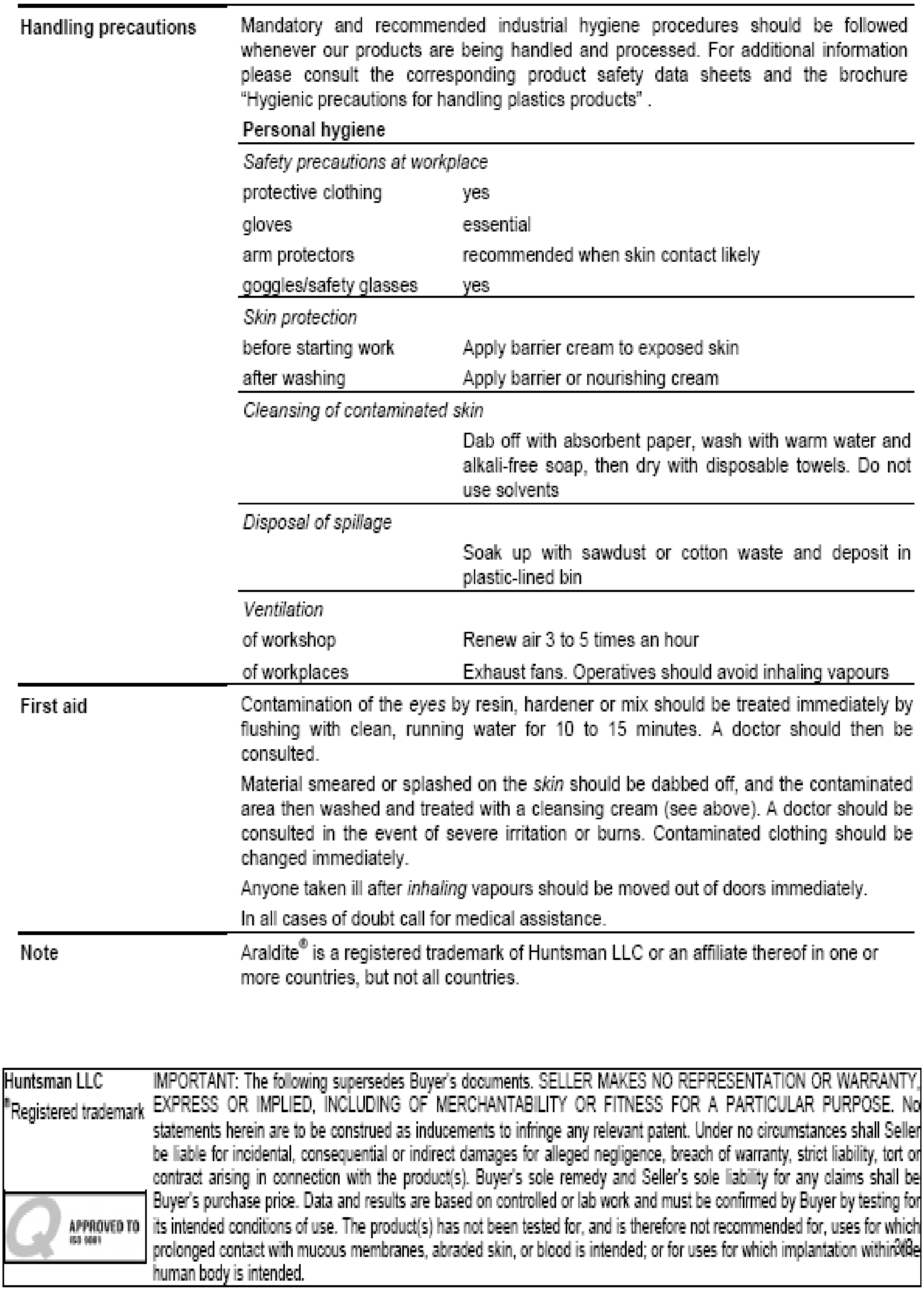
* *In addition to the brand name product denomination may show different appendices, which allows us to differentiate between our production sites: e.g. BD = Germany, US = United States, IN = India,CI = China, etc. These appendices are in use on packaging, transport and invoicing documents. Generally the same specifications apply for all versions. Please address any additional need for clarification to the appropriate Huntsman contact.*



Packaging & Storage Araldite MY 0510 comes in a 55 gallon, non-returnable, closed-head, black iron drum (DOT 17E) containing 500 pounds. **Never store Araldite MY 0510 in warm areas near heat sources or hot equipment, or even in direct sunlight, because violent exothermic reaction or explosion may result.** Store at or below 40 °F in sealed containers. Storage at higher temperatures may adversely affect properties. Maximum temperatures this product should be subjected to while thawing for use should not exceed 100 °F. To facilitate handling of Araldite MY 0510 as a workable liquid, warm the container gradually by letting it stand in an area at room temperature (approximately 75 °F) prior to use. Never accelerate warming by using hot ovens, band heaters, hot plates, open flames, or any means which could cause a "hot spot." Such practices may initiate violent exothermic reaction or explosion. Contamination, especially by acidic or basic substances, may also start a violent exothermic reaction and must be avoided.

APPENDICES 1/2



Handling precautions	Mandatory and recommended industrial hygiene procedures should be followed whenever our products are being handled and processed. For additional information please consult the corresponding product safety data sheets and the brochure "Hygienic precautions for handling plastics products" .	
	Personal hygiene	
	Safety precautions at workplace	
	protective clothing	yes
	gloves	essential
	arm protectors	recommended when skin contact likely
	goggles/safety glasses	yes
	Skin protection	
	before starting work	Apply barrier cream to exposed skin
	after washing	Apply barrier or nourishing cream
	Cleansing of contaminated skin	
		Dab off with absorbent paper, wash with warm water and alkali-free soap, then dry with disposable towels. Do not use solvents
	Disposal of spillage	
		Soak up with sawdust or cotton waste and deposit in plastic-lined bin
	Ventilation	
	of workshop	Renew air 3 to 5 times an hour
	of workplaces	Exhaust fans. Operatives should avoid inhaling vapours
First aid	Contamination of the *eyes* by resin, hardener or mix should be treated immediately by flushing with clean, running water for 10 to 15 minutes. A doctor should then be consulted. Material smeared or splashed on the *skin* should be dabbed off, and the contaminated area then washed and treated with a cleansing cream (see above). A doctor should be consulted in the event of severe irritation or burns. Contaminated clothing should be changed immediately. Anyone taken ill after *inhaling* vapours should be moved out of doors immediately. In all cases of doubt call for medical assistance.	
Note	Araldite® is a registered trademark of Huntsman LLC or an affiliate thereof in one or more countries, but not all countries.	

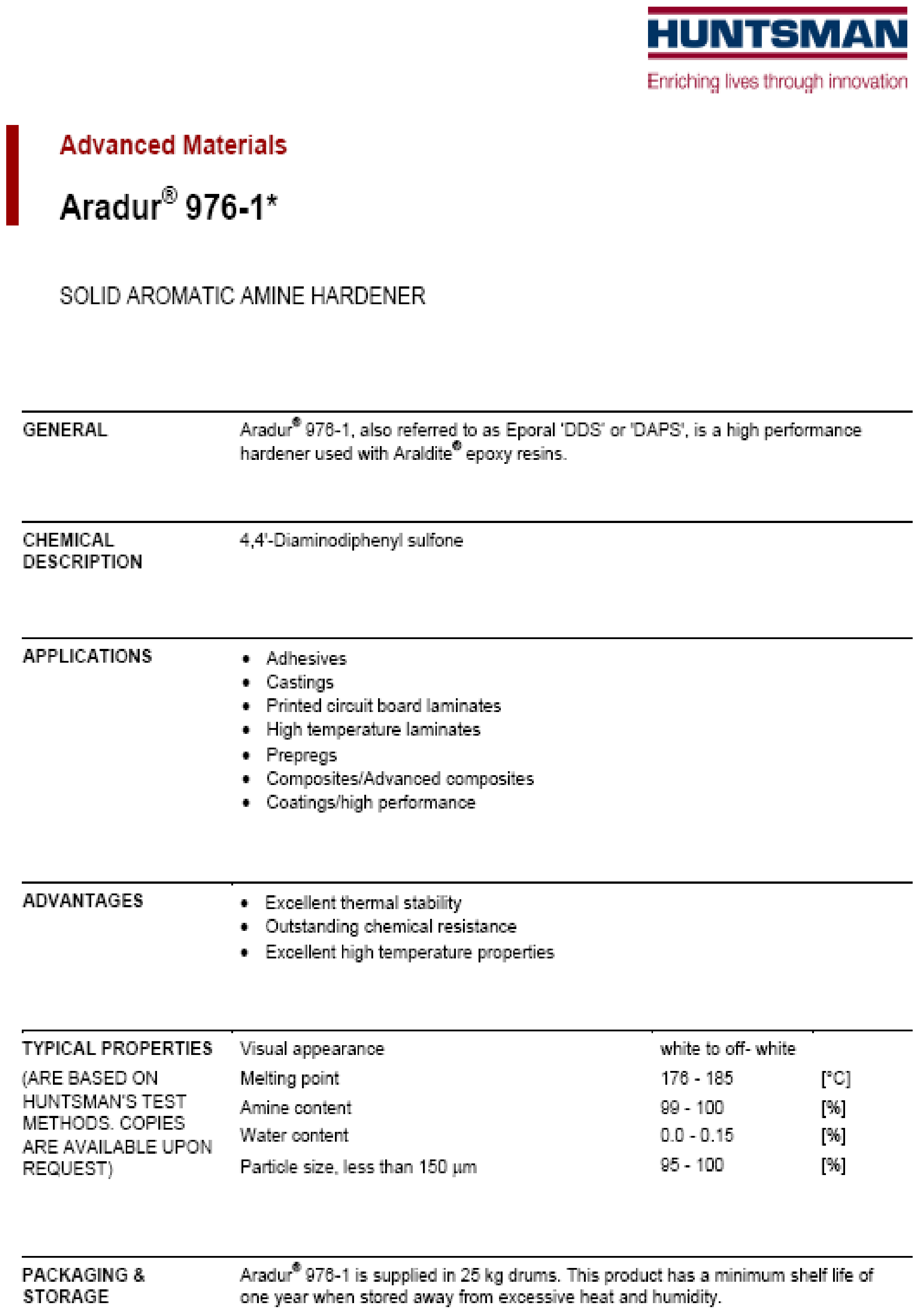
Huntsman LLC
®Registered trademark

APPROVED TO ISO 9001

IMPORTANT: The following supersedes Buyer's documents. SELLER MAKES NO REPRESENTATION OR WARRANTY, EXPRESS OR IMPLIED, INCLUDING OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. No statements herein are to be construed as inducements to infringe any relevant patent. Under no circumstances shall Seller be liable for incidental, consequential or indirect damages for alleged negligence, breach of warranty, strict liability, tort or contract arising in connection with the product(s). Buyer's sole remedy and Seller's sole liability for any claims shall be Buyer's purchase price. Data and results are based on controlled or lab work and must be confirmed by Buyer by testing for its intended conditions of use. The product(s) has not been tested for, and is therefore not recommended for, uses for which prolonged contact with mucous membranes, abraded skin, or blood is intended; or for uses for which implantation within the human body is intended.

3/3

APPENDICES 2/1



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Advanced Materials

Aradur® 976-1*

SOLID AROMATIC AMINE HARDENER

GENERAL

Aradur® 976-1, also referred to as Eporal 'DDS' or 'DAPS', is a high performance hardener used with Araldite® epoxy resins.

CHEMICAL DESCRIPTION

4,4'-Diaminodiphenyl sulfone

APPLICATIONS

- Adhesives
- Castings
- Printed circuit board laminates
- High temperature laminates
- Prepregs
- Composites/Advanced composites
- Coatings/high performance

ADVANTAGES

- Excellent thermal stability
- Outstanding chemical resistance
- Excellent high temperature properties

TYPICAL PROPERTIES

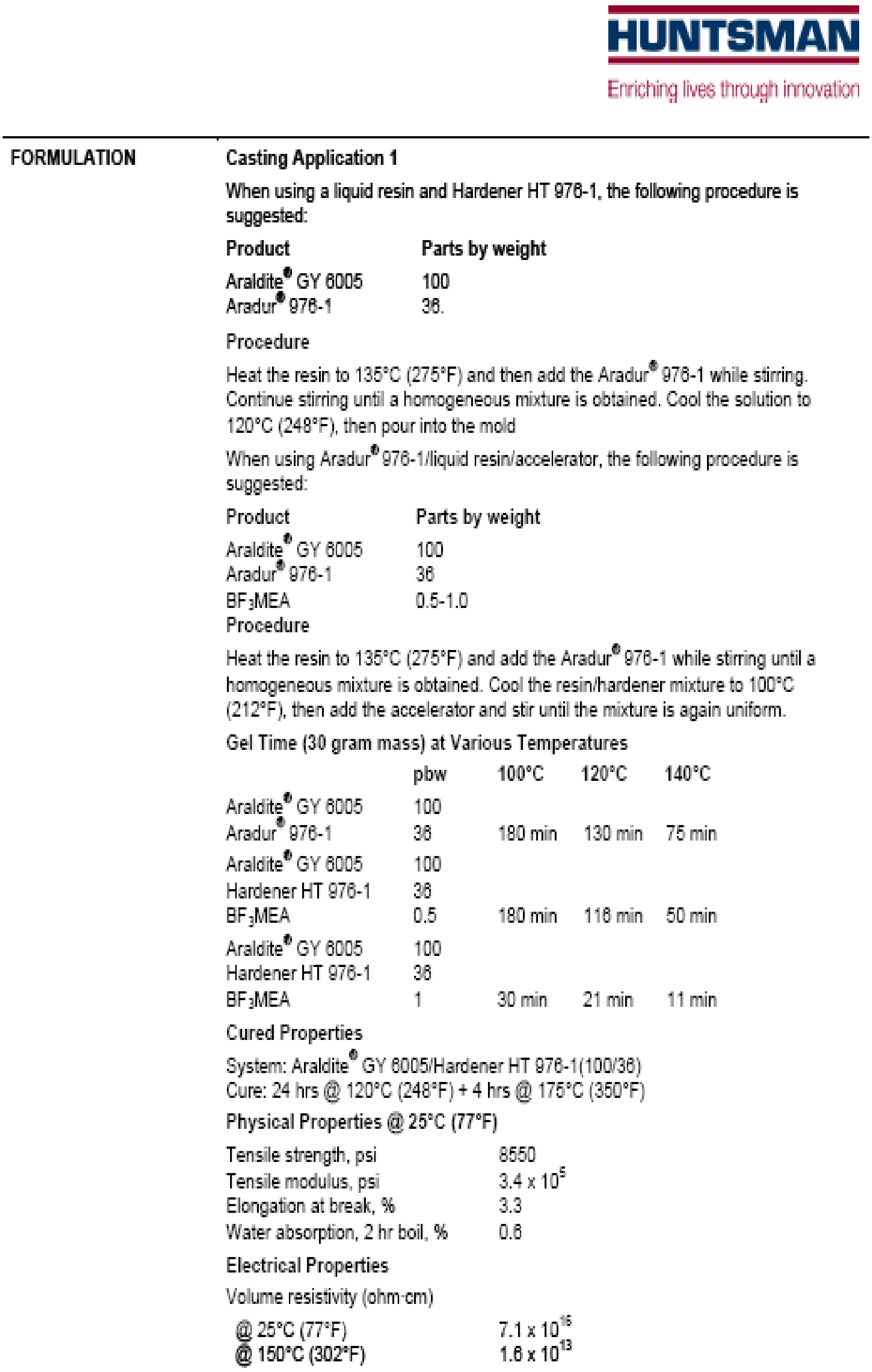
(ARE BASED ON HUNTSMAN'S TEST METHODS. COPIES ARE AVAILABLE UPON REQUEST)

Visual appearance	white to off- white	
Melting point	176 - 185	[°C]
Amine content	99 - 100	[%]
Water content	0.0 - 0.15	[%]
Particle size, less than 150 µm	95 - 100	[%]

PACKAGING & STORAGE

Aradur® 976-1 is supplied in 25 kg drums. This product has a minimum shelf life of one year when stored away from excessive heat and humidity.

APPENDICES 2/2



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FORMULATION

Casting Application 1

When using a liquid resin and Hardener HT 976-1, the following procedure is suggested:

Product	Parts by weight
Araldite® GY 6005	100
Aradur® 976-1	36.

Procedure

Heat the resin to 135°C (275°F) and then add the Aradur® 976-1 while stirring. Continue stirring until a homogeneous mixture is obtained. Cool the solution to 120°C (248°F), then pour into the mold

When using Aradur® 976-1/liquid resin/accelerator, the following procedure is suggested:

Product	Parts by weight
Araldite® GY 6005	100
Aradur® 976-1	36
BF_3MEA	0.5-1.0

Procedure

Heat the resin to 135°C (275°F) and add the Aradur® 976-1 while stirring until a homogeneous mixture is obtained. Cool the resin/hardener mixture to 100°C (212°F), then add the accelerator and stir until the mixture is again uniform.

Gel Time (30 gram mass) at Various Temperatures

	pbw	100°C	120°C	140°C
Araldite® GY 6005	100			
Aradur® 976-1	36	180 min	130 min	75 min
Araldite® GY 6005	100			
Hardener HT 976-1	36			
BF_3MEA	0.5	180 min	116 min	50 min
Araldite® GY 6005	100			
Hardener HT 976-1	36			
BF_3MEA	1	30 min	21 min	11 min

Cured Properties

System: Araldite® GY 6005/Hardener HT 976-1(100/36)
Cure: 24 hrs @ 120°C (248°F) + 4 hrs @ 175°C (350°F)

Physical Properties @ 25°C (77°F)

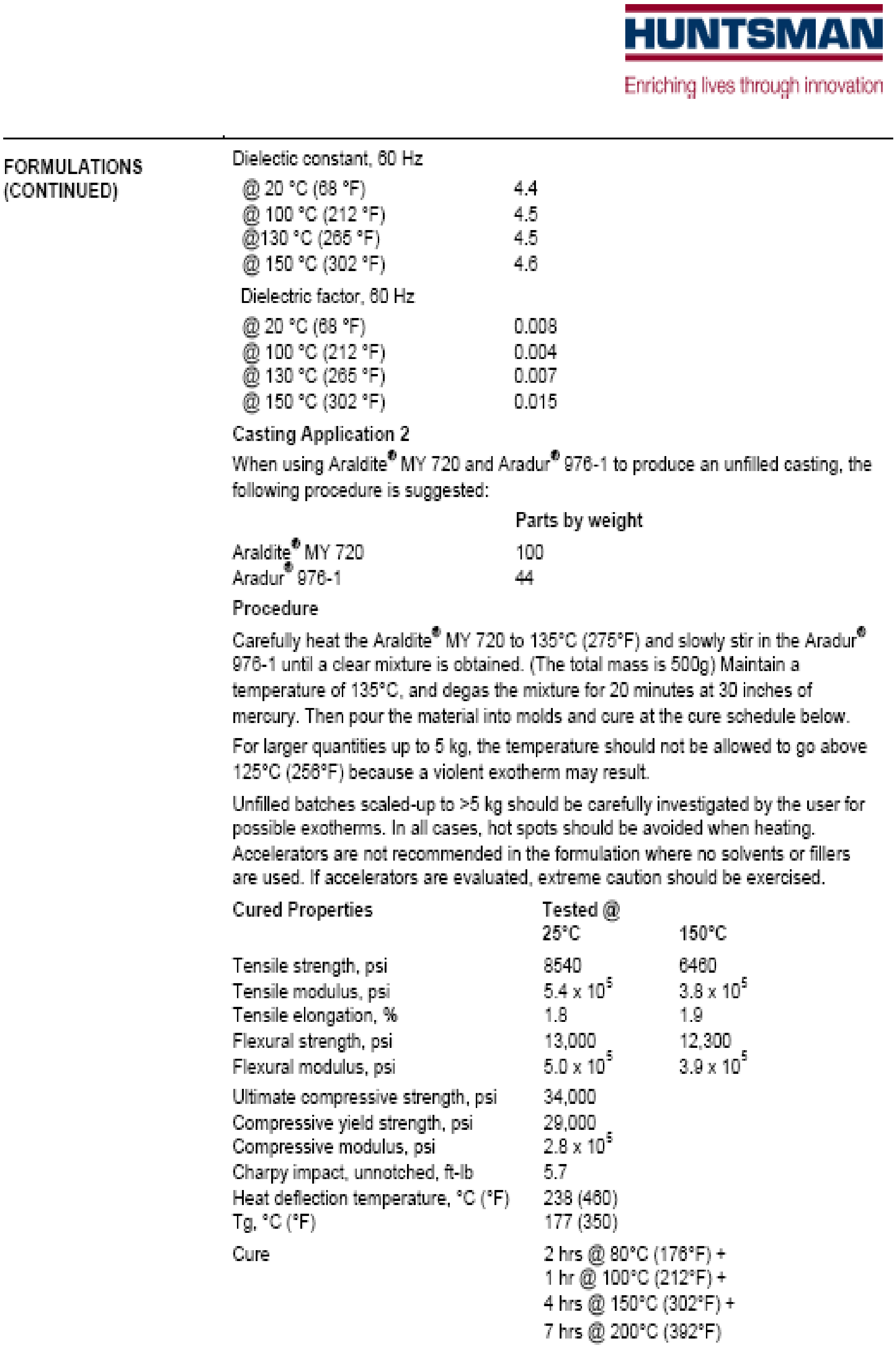
Tensile strength, psi	8550
Tensile modulus, psi	3.4×10^5
Elongation at break, %	3.3
Water absorption, 2 hr boil, %	0.6

Electrical Properties

Volume resistivity (ohm·cm)

@ 25°C (77°F)	7.1×10^{16}
@ 150°C (302°F)	1.6×10^{13}

APPENDICES 2/3



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FORMULATIONS (CONTINUED)

Dielectic constant, 60 Hz

@ 20 °C (68 °F)	4.4
@ 100 °C (212 °F)	4.5
@130 °C (265 °F)	4.5
@ 150 °C (302 °F)	4.6

Dielectric factor, 60 Hz

@ 20 °C (68 °F)	0.008
@ 100 °C (212 °F)	0.004
@ 130 °C (265 °F)	0.007
@ 150 °C (302 °F)	0.015

Casting Application 2

When using Araldite® MY 720 and Aradur® 976-1 to produce an unfilled casting, the following procedure is suggested:

	Parts by weight
Araldite® MY 720	100
Aradur® 976-1	44

Procedure

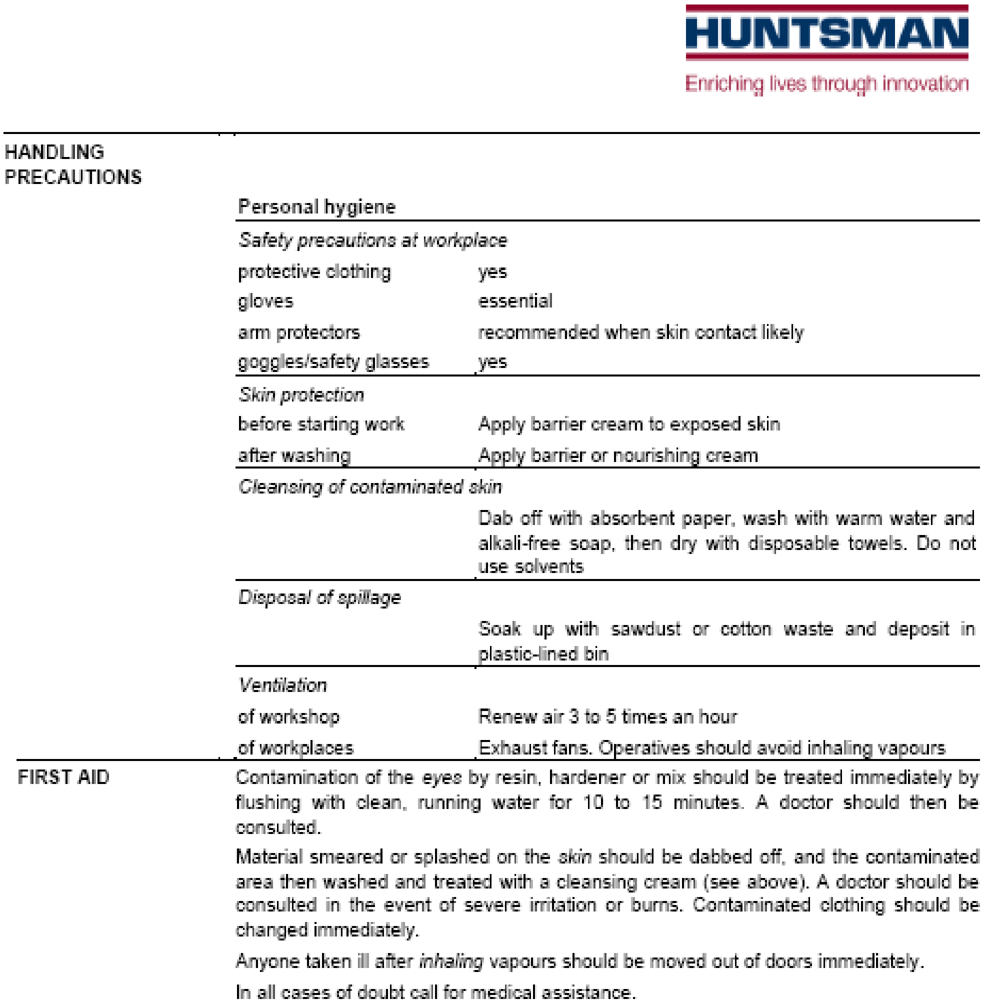
Carefully heat the Araldite® MY 720 to 135°C (275°F) and slowly stir in the Aradur® 976-1 until a clear mixture is obtained. (The total mass is 500g) Maintain a temperature of 135°C, and degas the mixture for 20 minutes at 30 inches of mercury. Then pour the material into molds and cure at the cure schedule below.

For larger quantities up to 5 kg, the temperature should not be allowed to go above 125°C (256°F) because a violent exotherm may result.

Unfilled batches scaled-up to >5 kg should be carefully investigated by the user for possible exotherms. In all cases, hot spots should be avoided when heating. Accelerators are not recommended in the formulation where no solvents or fillers are used. If accelerators are evaluated, extreme caution should be exercised.

Cured Properties	**Tested @**	
	25°C	**150°C**
Tensile strength, psi	8540	6460
Tensile modulus, psi	5.4 x 10^5	3.8 x 10^5
Tensile elongation, %	1.8	1.9
Flexural strength, psi	13,000	12,300
Flexural modulus, psi	5.0 x 10^5	3.9 x 10^5
Ultimate compressive strength, psi	34,000	
Compressive yield strength, psi	29,000	
Compressive modulus, psi	2.8 x 10^5	
Charpy impact, unnotched, ft-lb	5.7	
Heat deflection temperature, °C (°F)	238 (460)	
Tg, °C (°F)	177 (350)	
Cure	2 hrs @ 80°C (176°F) + 1 hr @ 100°C (212°F) + 4 hrs @ 150°C (302°F) + 7 hrs @ 200°C (392°F)	

APPENDICES 2/4



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HANDLING PRECAUTIONS

Personal hygiene

Safety precautions at workplace	
protective clothing	yes
gloves	essential
arm protectors	recommended when skin contact likely
goggles/safety glasses	yes
Skin protection	
before starting work	Apply barrier cream to exposed skin
after washing	Apply barrier or nourishing cream
Cleansing of contaminated skin	
	Dab off with absorbent paper, wash with warm water and alkali-free soap, then dry with disposable towels. Do not use solvents
Disposal of spillage	
	Soak up with sawdust or cotton waste and deposit in plastic-lined bin
Ventilation	
of workshop	Renew air 3 to 5 times an hour
of workplaces	Exhaust fans. Operatives should avoid inhaling vapours

FIRST AID

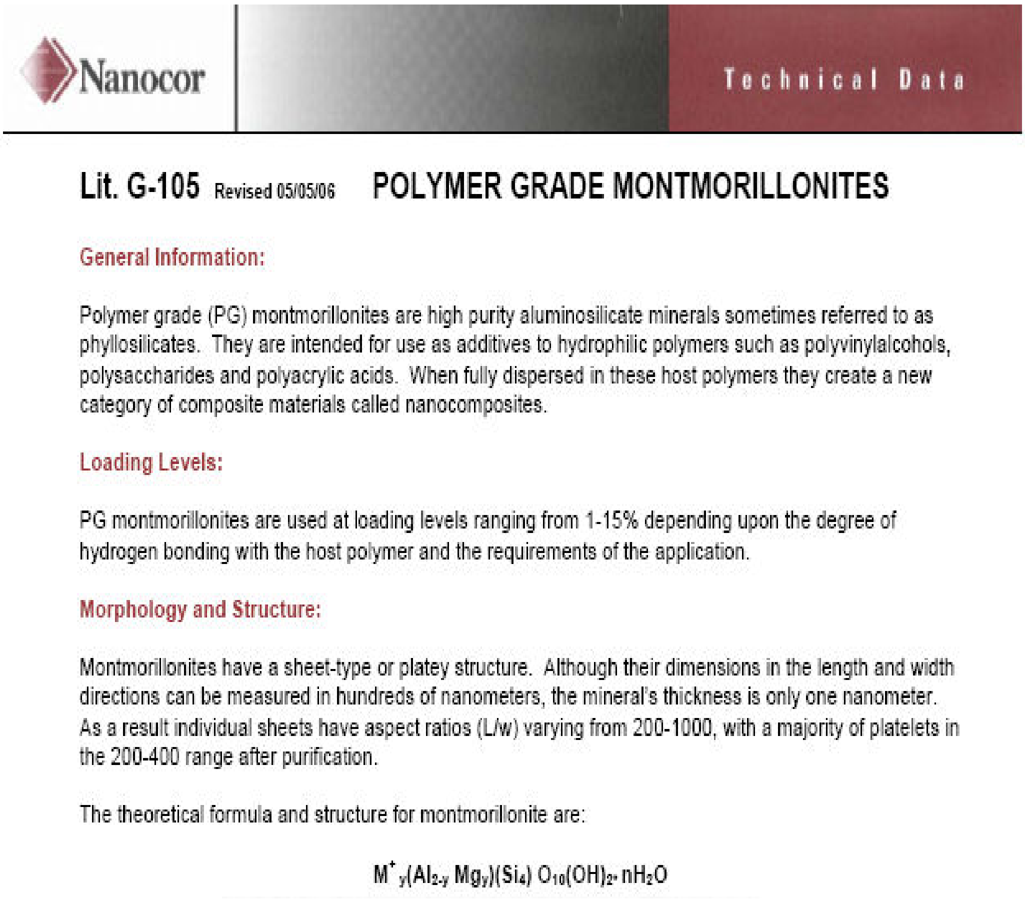
Contamination of the *eyes* by resin, hardener or mix should be treated immediately by flushing with clean, running water for 10 to 15 minutes. A doctor should then be consulted.

Material smeared or splashed on the *skin* should be dabbed off, and the contaminated area then washed and treated with a cleansing cream (see above). A doctor should be consulted in the event of severe irritation or burns. Contaminated clothing should be changed immediately.

Anyone taken ill after *inhaling* vapours should be moved out of doors immediately.

In all cases of doubt call for medical assistance.

APPENDICES 3/1



Nanocor

Technical Data

Lit. G-105 Revised 05/05/06 POLYMER GRADE MONTMORILLONITES

General Information:

Polymer grade (PG) montmorillonites are high purity aluminosilicate minerals sometimes referred to as phyllosilicates. They are intended for use as additives to hydrophilic polymers such as polyvinylalcohols, polysaccharides and polyacrylic acids. When fully dispersed in these host polymers they create a new category of composite materials called nanocomposites.

Loading Levels:

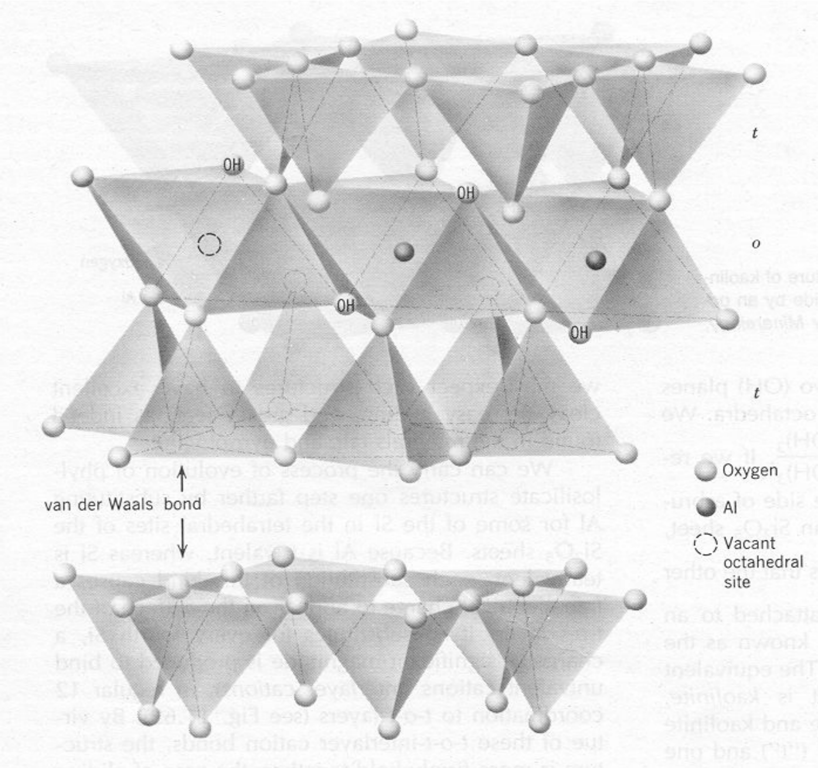
PG montmorillonites are used at loading levels ranging from 1-15% depending upon the degree of hydrogen bonding with the host polymer and the requirements of the application.

Morphology and Structure:

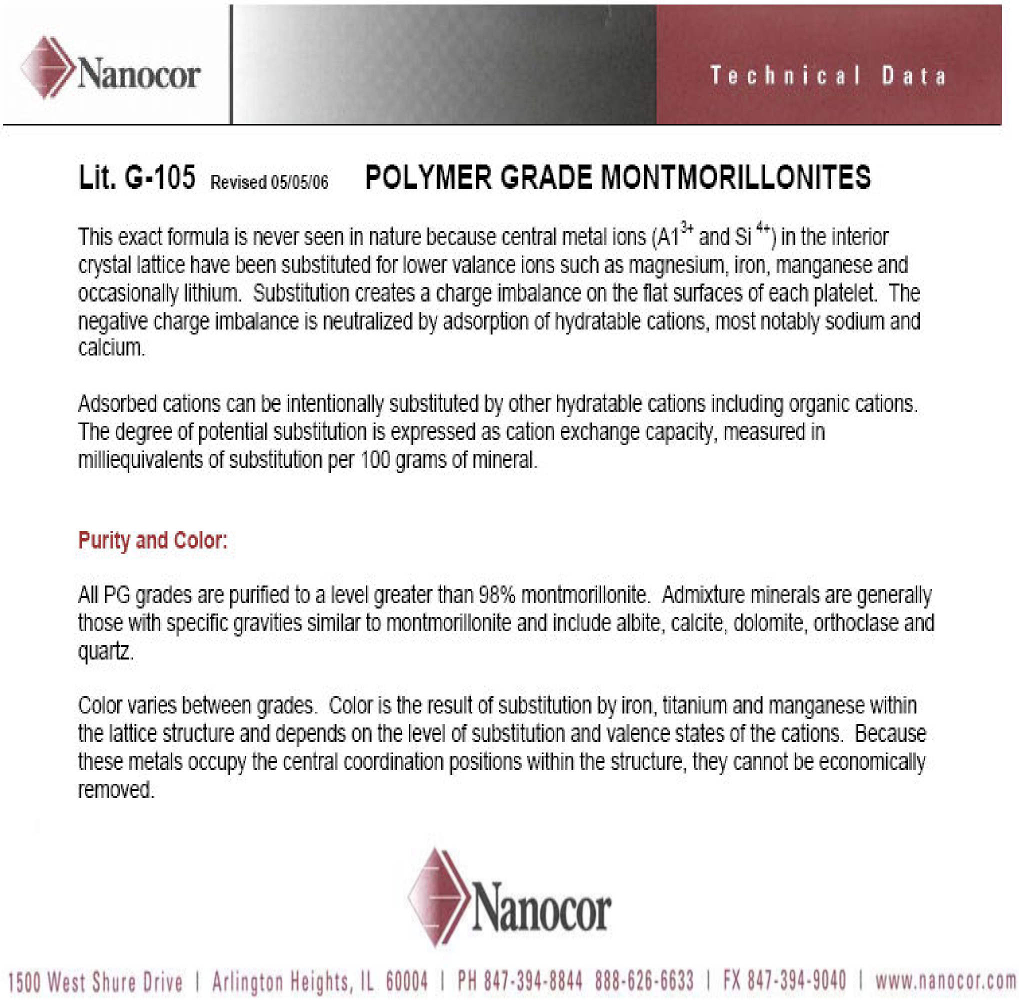
Montmorillonites have a sheet-type or platey structure. Although their dimensions in the length and width directions can be measured in hundreds of nanometers, the mineral's thickness is only one nanometer. As a result individual sheets have aspect ratios (L/w) varying from 200-1000, with a majority of platelets in the 200-400 range after purification.

The theoretical formula and structure for montmorillonite are:

$$M^{+}_{y}(Al_{2-y}Mg_{y})(Si_{4})O_{10}(OH)_{2}\cdot nH_{2}O$$



APPENDICES 3/2



Nanocor

Technical Data

Lit. G-105 Revised 05/05/06 POLYMER GRADE MONTMORILLONITES

This exact formula is never seen in nature because central metal ions (A1^{3+} and Si $^{4+}$) in the interior crystal lattice have been substituted for lower valance ions such as magnesium, iron, manganese and occasionally lithium. Substitution creates a charge imbalance on the flat surfaces of each platelet. The negative charge imbalance is neutralized by adsorption of hydratable cations, most notably sodium and calcium.

Adsorbed cations can be intentionally substituted by other hydratable cations including organic cations. The degree of potential substitution is expressed as cation exchange capacity, measured in milliequivalents of substitution per 100 grams of mineral.

Purity and Color:

All PG grades are purified to a level greater than 98% montmorillonite. Admixture minerals are generally those with specific gravities similar to montmorillonite and include albite, calcite, dolomite, orthoclase and quartz.

Color varies between grades. Color is the result of substitution by iron, titanium and manganese within the lattice structure and depends on the level of substitution and valence states of the cations. Because these metals occupy the central coordination positions within the structure, they cannot be economically removed.

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1500 West Shure Drive | Arlington Heights, IL 60004 | PH 847-394-8844 888-626-6633 | FX 847-394-9040 | www.nanocor.com