ALTERNATIVE FORMALDEHYDE-FREE PARTICLEBOARD COMPOSITIONS BASED ON EPOXIDIZED VEGETABLE OILS

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1- INTRODUCTION

1.a- IMPLICATIONS FOR SUSTAINABILITY

Wood flour is the main ingredient of particleboard, since it represents 70 to 95% of it. This project does not affect its role, but aims at limiting the toxicity of the resin used as a binder for wood flour. The use of formaldehyde in conventional petroleum-based particleboard binders has been indentified as a hazardous element. The California Air Resources Board has set new emissions standard for particleboards. From the first of January 2009, particleboards sold in California had to produce levels of formaldehyde no higher than 0.18 ppm[1].

This study aims at replacing the conventional resins by formaldehyde–free alternatives from renewable resources. The chosen alternative resins are epoxidized vegetable oils, as they are characterized as practically non-toxic[2]. Most of the study is devoted to optimizing the curing of the chosen epoxidized vegetable oils with different crosslinkers, bearing in mind to limit the overall toxicity of the final products.

1.b– PROJECT BACKGROUND

Particle board is an engineered wood product manufactured from wood particles (i.e. wood chips, sawmill shavings, saw dust) and a binder (to glue the wood particles together). These are extruded to form sheets[3]. Its main applications are furniture, cabinetry, floor underlay, stair treads. Figure 1[4] shows an example of a commercially available particleboard coupon.

The conventional binders used in particleboards are the following[5]:

Figure 1: Particleboard coupon

(1) **Urea Formaldehyde (UF)** – Urea formaldehyde was conventionally used for the manufacture of particleboards. But the curing of UF continues even after manufacturing. The degassing of formaldehyde continues over time and it is also prone to acid hydrolysis.

(2) **Melamine Formaldehyde (MF)** – Melamine formaldehyde has a lower emission rate as compared to UF, but it does not eliminate the problem of emission completely. It is more expensive than UF.

(3) **Phenol formaldehyde** – Phenol formaldehyde has better water resistance than UF and it is more expensive. It has 90% less formaldehyde emission. But it has occupational exposure concerns. Also the raw material used in the making of aromatic hydrocarbon, i.e. phenol, is a chemical of concern.

(4) **Methylene diphenyl diisocyanate (MDI)** – One of the raw material used in the making of MDI is MDA (4,4-methylenedianiline), which is classified as a human carcinogen. Conversion to MDI involves phosgene. MDI is primarily a respiratory tract irritant

(effect: asthma), a skin, eye, mucous membrane irritant (effect: contact dermatitis) and a sensitizer.

Formaldehyde is characterized by various toxicity attributes, leading to the following health issues[6,7]:

- **Acute (short-term) health effects :** Irritation of the eyes, nose, throat and skin; Skin contact results in severe irritation and burns and some formaldehyde may pass through the skin; When inhaled, formaldehyde causes narrowing of the bronchi resulting in coughing, wheezing, chest pains, and bronchitis.
- **Chronic (long-term) health effects:** Formaldehyde is a known human carcinogen; Prolonged exposure may cause dermatitis and asthma attacks; Formaldehyde exposure is a potential reproductive hazard.

There are different possible strategies to reduce the formaldehyde exposure from particleboards[8], among which the following can be found:

- Modified urea formaldehyde resins with scavenger additives (i.e. melamine), to reduce the rate of emissions of formaldehyde
- Use of other formaldehyde resins (i.e. phenol formaldehyde), with higher cross-linking density hence lower formaldehyde emissions in use
- Use of alternate fossil fuel-based binders containing no added formaldehyde, such as methylene diphenyl diisocyanate (MDI)
- Use of alternate binders based on renewable resource materials, such as vegetable oil.

We choose to investigate this last idea. Hence the objective of our research project is to replace the hazardous conventional formaldehyde based binders by resins from renewable sources, giving similar properties than the former, keeping in mind the cost-effectiveness.

2- MATERIALS AND METHODS

2.a- MATERIALS

▪ RESINS:

The alternative for the conventional formaldehyde based binders are chosen in such a way that the resins are derived from renewable resources and are as eco-friendly as possible. The chosen binders are based on three epoxidized vegetable oils, namely Epoxidized Linseed Oil (ELO) (Figure 2), Epoxidized Soybean Oil (ESO) (Figure 3) and Epoxidized Castor Oil (ECO) (Figure 4).

The ELO[9] was donated by Chemtura Corporation under the tradename Drapex 10.4, its oxirane content is equal to 9 %, according to the producer. ELO is FDA approved for incidental food contact[10].
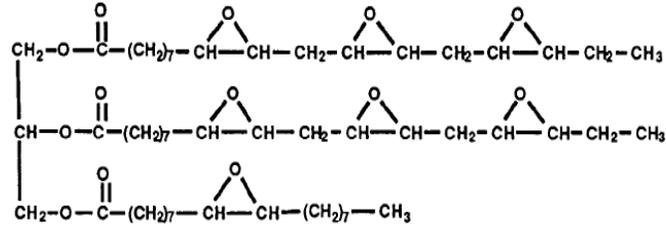
Figure 2: Chemical structure of Epoxidized Linseed Oil (ELO)

The ESO[11] was donated by the Chemtura Corporation, under the tradename Drapex 6.8, Chemtura. Its Oxirane Oxygen is reported as 7 % according to the producer. ESO is FDA approved for direct addition to food for human consumption[12].
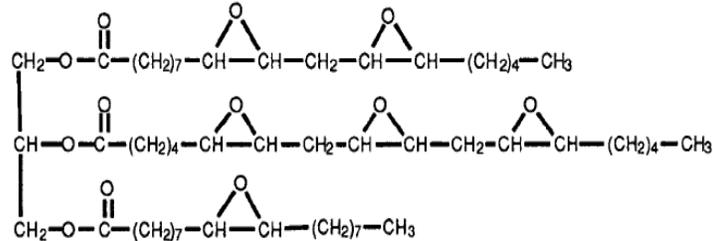

Figure 3: Chemical structure of Epoxidized Soybean Oil (ESO)

The ECO was donated by Hexion, under the tradename Heloxy 505[13]. Its weight per epoxide is 601 g/eq according to the producer.
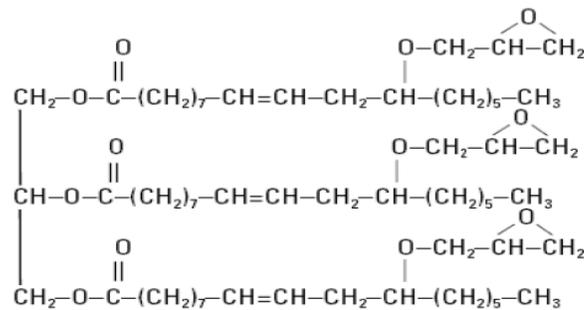
Figure 4: Chemical structure of Epoxidized Castor Oil (ECO)

For the sake of comparison with the actual binders used in particleboards, two formaldehyde based resins were purchased: a urea formaldehyde resin (Cymel U-65) and a melamine formaldehyde resin (Cymel 303) resin. The catalyst used in the curing of the formaldehyde based resins is dodecylbenzenesulfonic acid, purchased from Sigma-Aldrich.

   ▪ **CROSSLINKERS:**

The crosslinkers (Table 1; Figures 5-8) for the curing of these bioepoxies are also chosen in such a way that their level of toxicity is as minimal as possible. Most of the following study is

devoted to optimizing the curing conditions of the various resin – crosslinker couples in order to achieve a high degree of cross-link density in the binder and a low percentage of extractables.

Table 1: Used crosslinkers

| Crosslinker Name	Chemical Family
L-Tryptophan[14]/L-Lysine[15]	Amino Acid
TETA (Triethylenetetramine)[16]	Polyimine
PEI (PolyethyleneImine) [17] ($M_n \sim 600$)	Polyimine
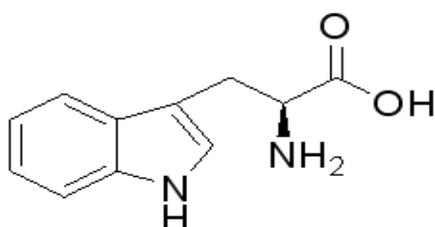
Figure 5: Chemical structure of L-Tryptophan [Sigma-Aldrich, T0254]
Chemical name: (S)-2-Amino-3-(3-indolyl)propionic acid, L-α-Amino-3-indolepropionic acid
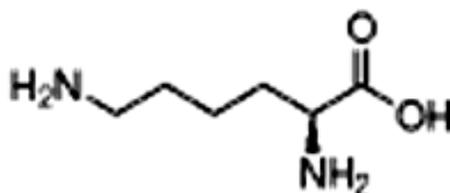
Figure 6: Chemical structure of L-Lysine [Sigma-Aldrich, L5501]
Chemical name: (S)-2,6-Diaminocaproic acid
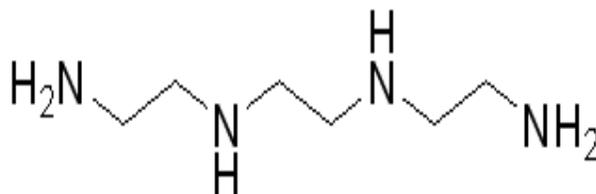
Figure 7: Chemical structure of
Triethylenetetramine [Sigma-Aldrich, 90462]

$$H_2N\text{-}(\text{-}CH_2CH_2N\text{-})_x\text{---}(\text{-}CH_2CH_2NH\text{-})_y\text{-}H$$

$$(CH_2CH_2NH_2)_z$$
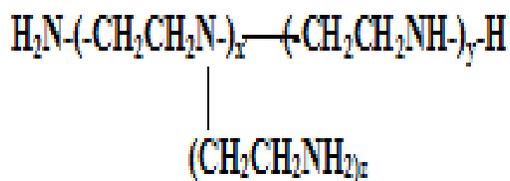
Figure 8: PolyethyleneImine [Polysciences Inc.]

TETA and PEI are highly alkaline and may act as sensitizers. However, PEI is commonly used by biochemists in presence of mammalian cells[18,19].

- **BASIC REACTIONS:**

The basic epoxy chemistry lies in the ring opening reaction of the oxirane ring (epoxide group) with either an amine or an acid. The crosslinking agents chosen are all amine based and they undergo the basic two-step reaction presented on Figures 9 & 10 [20].
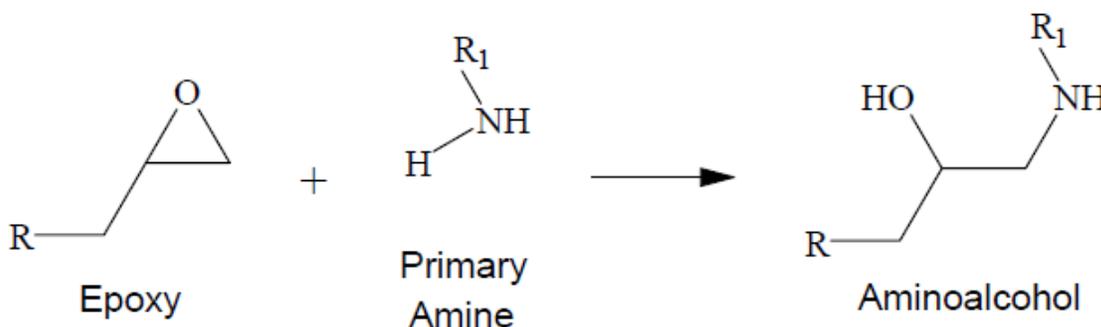
Figure 9: 1st step: Reaction of the epoxy group with a primary amine
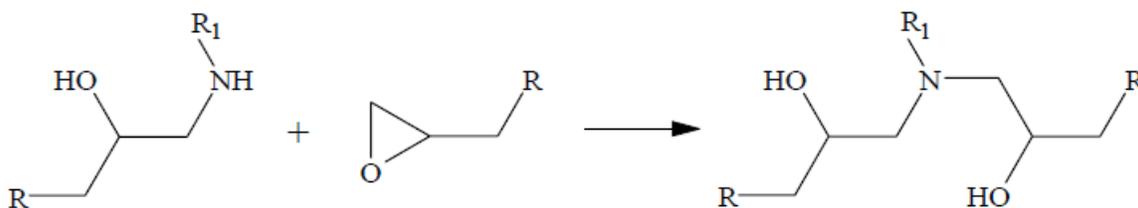
Figure 10: 2nd step: Reaction with a secondary amine

For each of the resin – crosslinker couple, the stoichiometric ratios needed for the crosslinking reaction have been calculated (see Appendix A-1 to A-10). Those stoichiometric ratios are used as a starting point for the curing reaction of the resins; they are further optimized as explained in section 2-b.

- **INCORPORATION OF NANOCLAY:**

An extension to the preparation of the bioepoxy based binders consists in adding nanoparticles in the form of nanoclay. As these clays are commonly found and naturally occurring, they are generally recognized as safe and represent a hazard only as a nuisance dust at very high airborne concentrations. Likewise, the alkylammonium modifiers used to compatibilize the nanoclay are found in fabric softeners and detergents with a long safety history, and are known to be biodegradable in the environment.

The nanoclay will help to ensure that the chosen bioepoxies display levels of stiffness and creep resistance similar to conventional binders. They also represent a promising avenue to enhance the fire[21], barrier[22] and moisture resistance of the polymer, with only a few weight percent loading of nanoparticles.
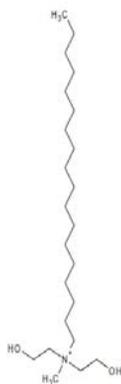
Figure 11: Chemical structure of Cloisite 30B

This concept will be applied to the binder families that are the most promising. The nanoclay chosen is Cloisite 30B[23] (Southern Clay Products), a natural montmorillonite modified with bis(2-hydroxyethyl)methyltallowammonium cations (see Figure 11).

Three different loading levels of the clay in the bioepoxies, namely 1 wt%, 2 wt% and 4 wt%, are investigated. These nanoclays were introduced in the optimized ELO - PEI system.

2.b- METHODS

- **SAMPLE PREPARATION**

For each chosen couple of resin – crosslinking agent, the resin is mixed with the crosslinking agent in a speed mixer (FlackTek DAC-150FV SpeedMixer) (Figure 12)[24] at 3540 rpm for 2 minutes; this device ensures the degassing of the liquid mixture as well as a homogeneous mixing.

The mixture is poured onto an aluminum pan and cured in a convection oven. All the tested curing times and curing temperatures for the optimization are gathered in Table 2. In all cases, the oven heating rate is set to 3.3°C/min. Once cured, the sample is left in the shut-off oven for 2 ½ hrs (in order to ensure no thermal stress build-up in the sample).

Table 2: Set of tested conditions

Curing temperatures (°C)
120°C
160°C

Curing time (hrs)
3
6
12
18

Figure 12: Speed Mixer

- **SOLVENT UPTAKE ANALYSIS[25]**

The optimization of the bioepoxies curing is carried out through a solvent uptake analysis. The idea behind this test is to swell the cured sample in a good solvent; this enables to extract all of the unreacted monomers from the sample, and also to evaluate the level of crosslink density in the produced network.

The first step of the solvent uptake analysis consists in finding a right solvent for the sample. A good solvent is a solvent in which the sample swells reasonably well (so that the unreacted monomers can actually escape), but not so much that the chemical pressure makes it burst. For each of the resin – crosslinking agent couple, one or two good solvents are found out of the various solvents that are tested. An illustration is given on Figure 13.

For each resin – crosslinking agent couple and each selected solvent, the crosslink density is quantified through the parameter Vr, given by the following equation:

$$V_r = \frac{\text{volume of unswollen polymer matrix}}{\text{volume of swollen polymer matrix}}$$

$$= \left(\frac{V_{dry}}{V_{swollen}} \right)$$

$$= \left(\frac{m_{dry}}{\rho_{matrix}} \right) \div \left(\frac{m_{dry}}{\rho_{matrix}} + \frac{m_{swollen} - m_{dry}}{\rho_{solvent}} \right)$$

$$= \left[1 + \left(\frac{m_{swollen} - m_{dry}}{m_{dry}} \right) \left(\frac{\rho_{matrix}}{\rho_{solvent}} \right) \right]^{-1}$$

where,

   $m_{swollen}$ – Weight of the sample in the swollen state after a particular given time
   m_{dry} – Weight of the equilibrated swollen sample after it as been vacuum dried
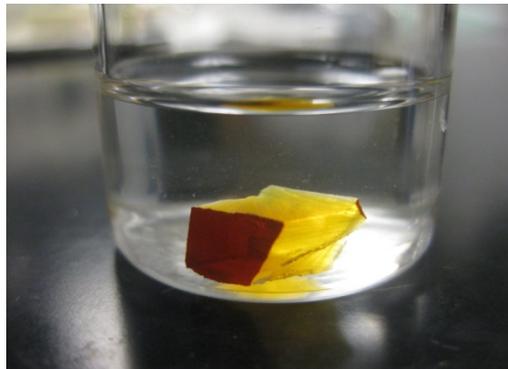
Figure 13: ELO - PEI sample in acetone during the solvent uptake analysis

The lower the value of *Vr*, the higher the degree of swelling the system undergoes in the particular solvent which implies the lower its crosslinks density. **The solvent uptake parameter value *Vr* is directly proportional to the crosslink density.**

For each resin – crosslinking agent couple and each selected solvent, the amount of extractables in the system is determined by the following equation:

$$\%Extractables = \left(\frac{W_i - W_f}{W_i} \right) \times 100$$

where, W_i – Initial weight of the cured sample before it is immersed in solvent
   W_f – Final weight of the vacuum dried sample after the swelling analysis
   % Extractables – Amount of unreacted monomers in the cured sample

- **OPTIMIZATION OF THE CURING PARAMETERS**

The curing reaction of the bioepoxies with the various curing agents has to be optimized in terms of:
(1) The curing time
(2) The curing temperature
(3) The resin to hardener ratio

In order to carry out the optimization of the curing parameters, a stoichiometric mixture of the bioepoxy and the curing agent is prepared and it is cured at different temperatures and for different times. The crosslink density and the extent of the cure are then evaluated through an equilibrium solvent uptake analysis (see the previous section for details). Depending upon the results, the resin to hardener ratio, along with the curing time and the curing temperature are modified. A set of conditions is said to be optimized if the cured bioepoxy has the highest level of crosslink density and the lowest amount of extractables.

- **DENSITY MEASUREMENTS**

The density of the cured sample is determined by calculating first the mass of the specimen in air and then the mass of the specimen immersed in a liquid (water is used as a reference). Its apparent mass upon immersion is determined and its specific gravity (relative density) is then calculated. This test is carried out at room temperature. Such a procedure is in accordance to the **ASTM Standard D792 – 08**.

- **SAMPLE PREPARATION FOR MECHANICAL TESTING**

A silicone mold is designed and created (see Figure 14) in order to produce the flexure bars for the mechanical testing; the silicone was purchased from Freeman Manufacturing and supply company.
The flexure bars of the optimized ELO - PEI and the ESO - PEI systems are prepared by pouring the chosen mixture of resin and crosslinking agent into the slots of the mold; the mold is then first transferred to a vacuum oven and undergoes a cycle of purging at primary vacuum (to remove any gas from the poured mixture). Right after the mold is placed in a convection oven (already heated) for the desired amount of curing time. The oven is shut off after that period, and the mold is allowed to go back to room temperature. Once the resin samples are removed, the mold is cleaned with ethanol (so that it does not swell the silicone) to remove any traces of unreacted monomers left on it.
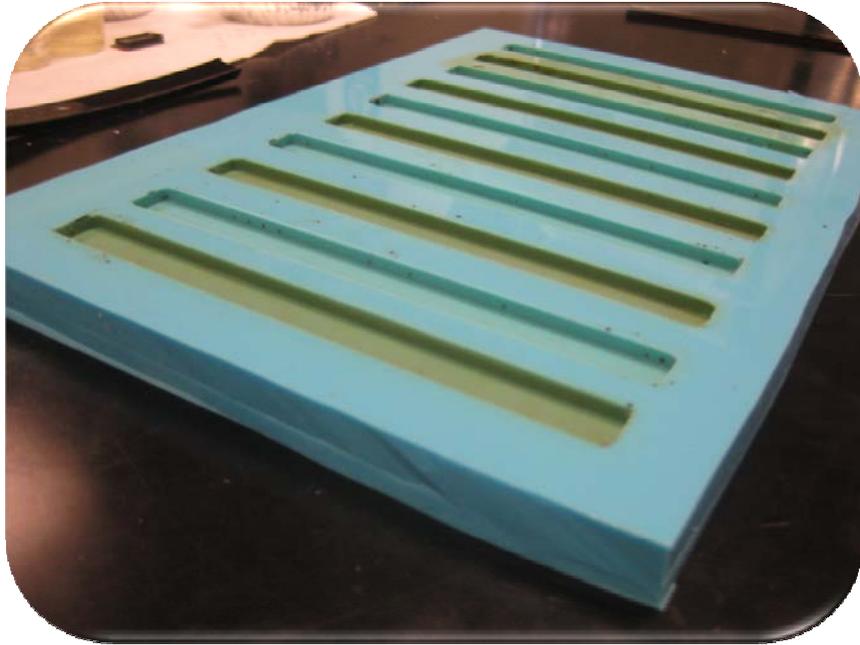
Figure 14: Home-made silicone mold for flexure bar processing
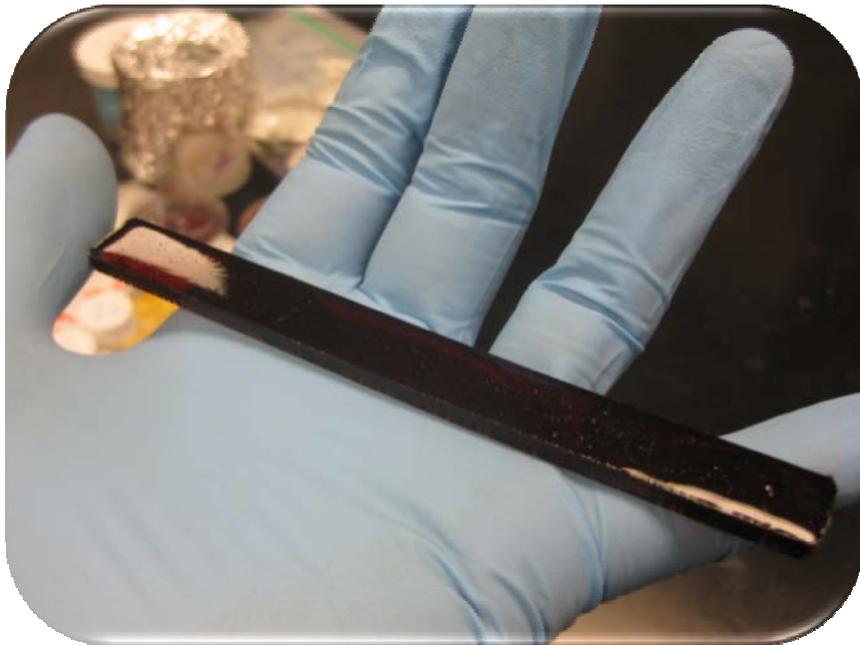
Figure 15: Flexure bar prepared thanks to the silicone mold
(ELO - PEI [1:1.4] cured at 160°C for 18 hrs)

An example of a cured flexure bar is presented on Figure 15.

▪ **MECHANICAL TESTING**

The mechanical tests are performed on a Dynamic Mechanical Analyser (DMA) TA Q800 DMA. This device enables to measure the storage modulus, the loss modulus and therefore the damping capacity of the resin. The tests are performed in a three-point bend configuration, and most of them are carried out at room temperature.

3- RESULTS & DISCUSSIONS:

3.a- OPTIMISATION OF THE CURING CONDITIONS

3.a.1- *Epoxidized Linseed Oil (ELO) and Epoxidized Soybean Oil (ESO) with PolyethyleneImine (PEI)*

As a first step, the densities of the ELO and ESO cured with PEI in stoichiometric conditions are determined as presented in Table 3.

Table 3: Densities of the ELO and ESO cured systems

ELO/PEI	g
Wt. of the dried sample	0.2198
Wt. of the sample in water	0.0117
Specific gravity (g/cc)	1.0562
Density (kg/m^3)	1053.6

ESO/PEI	g
Wt. of the dried sample	0.2668
Wt. of the sample in water	0.0013
Specific gravity (g/cc)	1.0049
Density (kg/m^3)	1002.4

The cured ELO and ESO systems are swollen in different solvents. The best solvent is chosen as the one allowing both a high amount of extractables and an important swelling of the system (i.e. a low value of *Vr*), while maintaining the system integrity. The second parameter *Vr* is chosen as the primary indicator in case of ambiguity. For both the ELO - PEI and the ESO - PEI systems, the amount of extractables with respect to the swelling solvent is presented on Figure 16, while the evolution of the solvent uptake parameter *Vr* with respect to the swelling solvent is presented on Figure 17. Tables B-1 and B-3 (in the Appendix) gather the values of the percentage of extractables in the ELO and ESO systems for the various tested solvents. Tables B-2 and B-4 present the kinetics of the swelling for those systems.
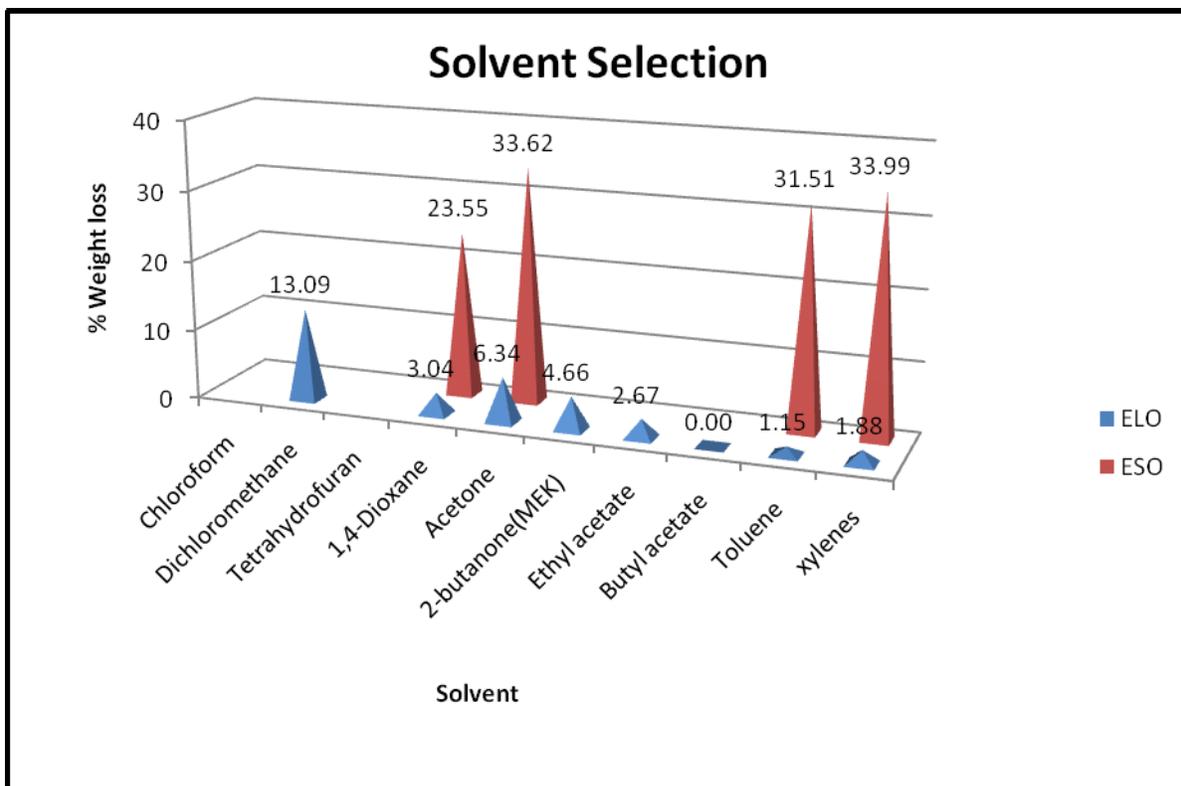
Figure 16: Amount of extractables in various solvents for the ELO and the ESO systems
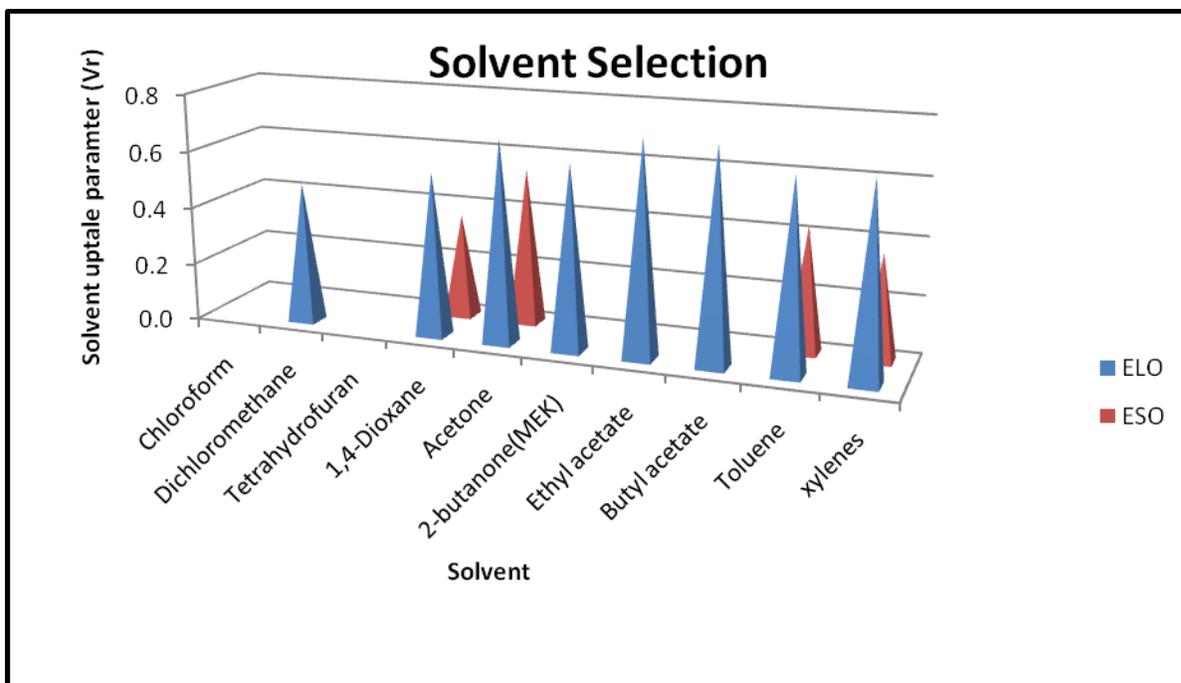
Figure 17: Values of *Vr* in various solvents for the ELO and the ESO systems

From the swelling analysis, it is concluded that **dichloromethane** is the best solvent for the **ELO** cured samples (later on **acetone** will be chosen as the back-up solvent) and **acetone** and **xylenes** for the **ESO** cured samples. The selected solvents give the maximum swelling i.e. the minimum value of *Vr*, indicating that the cured systems swell the most without any disintegration in these solvents, thus removing all the possible unreacted monomers from the cured resin.

It is to be noted here that the mentioned solvents are used to characterize the level of crosslinking occuring during the resin curing. In no case do they intervene in the curing of the bioepoxies. Once the optimization of the curing is achieved, the solvents will no longer be used in the materials processing steps.

Once the best solvent is selected for the respective bioepoxies, the **optimization of the curing time** is performed. First, the curing time is optimized by curing the bioepoxies at different curing times (3 hrs, 6 hrs, 12 hrs and 18 hrs) keeping the curing temperature constant and mixing stoichiometric amounts of the resin and the crosslinking agent. One of the cured samples is presented on Figure 18.

Figure 18: ELO - PEI cured at 160°C for 18 hrs

Ultimately, the network should have the highest crosslink density (this will ensure that the number of unreacted monomers is minimal). Crosslinks do not swell: If a material has many crosslinks, the degree of swelling will be minimal and the parameter V_r (as defined in section 2-b) will be as high as possible (approaching one). Also, the percentage of extractables should be as low as possible (close to zero).

Table 4 gathers the data for the weight loss and the parameter *Vr* at the various tested curing times. The data are also presented on Figures C-1 and C-2 in the Appendix. One can notice that the parameter *Vr* is the highest at the longest curing time. This means that a curing time of 18 hours for both the ELO - PEI and the ESO - PEI systems will ensure as high a crosslink density as possible. This is confirmed by the values of the percentage of extractables: they are the lowest at 18 hours of curing, meaning that a minimum amount of monomer is left unreacted after that amount of curing time.

As a result, the **optimized curing time was set to 18 hours**.

Table 4: Solvent uptake values for the samples cured for different curing times

Curing time (hrs)	% Weight loss			Solvent uptake (final) (Vr)		
	Dichloromethane	Acetone	Xylenes	Dichloromethane	Acetone	Xylenes
3	13.09	33.62	33.99	0.4915	0.5569	0.3757
6	16.31	17.53	13.41	0.4469	0.6081	0.5110
12	8.59	10.54	7.72	0.5556	0.6542	0.5673
18	8.25	7.25	6.49	0.5926	0.6555	0.5756
	ELO	ESO	ESO	ELO	ESO	ESO

As a next step, the **optimization of the curing temperature** is performed for both bioepoxies. The ELO and ESO are cured with the PEI at two different temperatures: 160°C (as previously performed) and 120°C; the samples are then compared through a solvent uptake analysis. This experiment is also performed to check if the dark top layer (see Figure 18) on the bioepoxies could be prevented. The dark layer on the bioepoxies is indeed thought to be linked to an oxidation reaction triggered by the high curing temperatures.

Assuming that the reaction rate doubles every increase by one degree in the temperature, it is estimated that the curing at 120°C would take 48 hours to lead to a similar crosslink density as the one carried out at 160°C for 18 hours.

Table 5: Solvent uptake values of the samples cured at different curing temperatures

Curing temperature	Curing time (hrs)	% Weight loss			Solvent uptake (final) (Vr)		
		DCM	Acetone	Xylenes	DCM	Acetone	Xylenes
160°C	3	13.09	33.62	33.99	0.4915	0.5569	0.3757
	6	16.31	17.53	13.41	0.4469	0.6081	0.5110
	12	8.59	10.54	7.72	0.5556	0.6542	0.5673
	18	8.25	7.25	6.49	0.5926	0.6555	0.5756
120°C	24	-	21.92	15.24	-	0.5658	0.4964
	48	12.18	15.2	13.09	0.5146	0.6161	0.5339
	60	15.32	-	-	0.4706	-	-
		ELO	ESO	ESO	ELO	ESO	ESO

On Table 5, one can observe that the ELO and ESO systems need to be heated up to a temperature of 160°C, as the samples cured at 120°C give a higher amount of unreacted monomers as compared to the samples cured at 160°C, despite the longer curing time. Also,

prolonging the curing did not help in leading to a better network as the values of extractables at 60 hours of curing at 120°C are worse than the ones at 160°C: a compromise need to be established between crosslinking the network further and minimizing the degradation by oxidation.

Once the curing time and the curing temperature are optimized, the **resin to hardener ratio** needs to be fine-tuned. An excess of 10% to 90% (i.e. a 1:1.1 to 1:1.9 ratio) for the ELO - PEI system and ratios of 1:0.8 to 1:1.4 for the ESO - PEI system are investigated. A solvent uptake analysis is carried out to characterize the percentage of extractables (*% extractables)* in the cured products and the solvent uptake parameter *Vr*. The optimized systems are the ones exhibiting the lowest amount of extractables (with a *% extractables* close to zero) and the highest amount of crosslinks (i.e. a *Vr* parameter close to one).

As presented on Figure 19 to Figure 21 (data can be found in Appendix D-1), in the ELO system the addition of an excess of the curing agent improves the network (i.e. gives a lower value of *% extractables*). As a matter of fact, the excess of crosslinking agent induces more reaction of the ELO oxirane rings with the PEI amine groups, thereby decreasing the amount of unreacted monomers left in the final product.
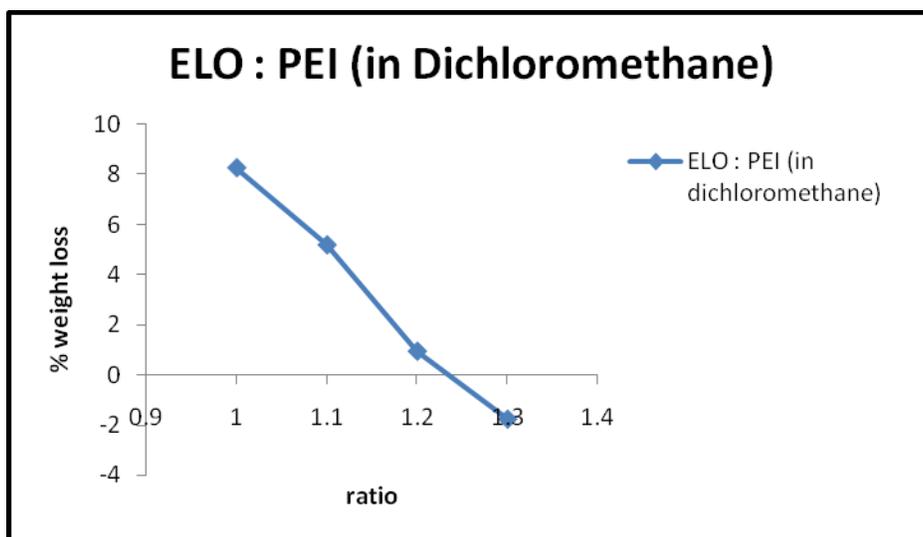
Figure 19: Amount of extractables vs. resin-to-hardener ratio for the ELO - PEI swollen in dichloromethane (The samples disintegrated for ratios above 1:1.3, as dichloromethane was the strongest solvent)
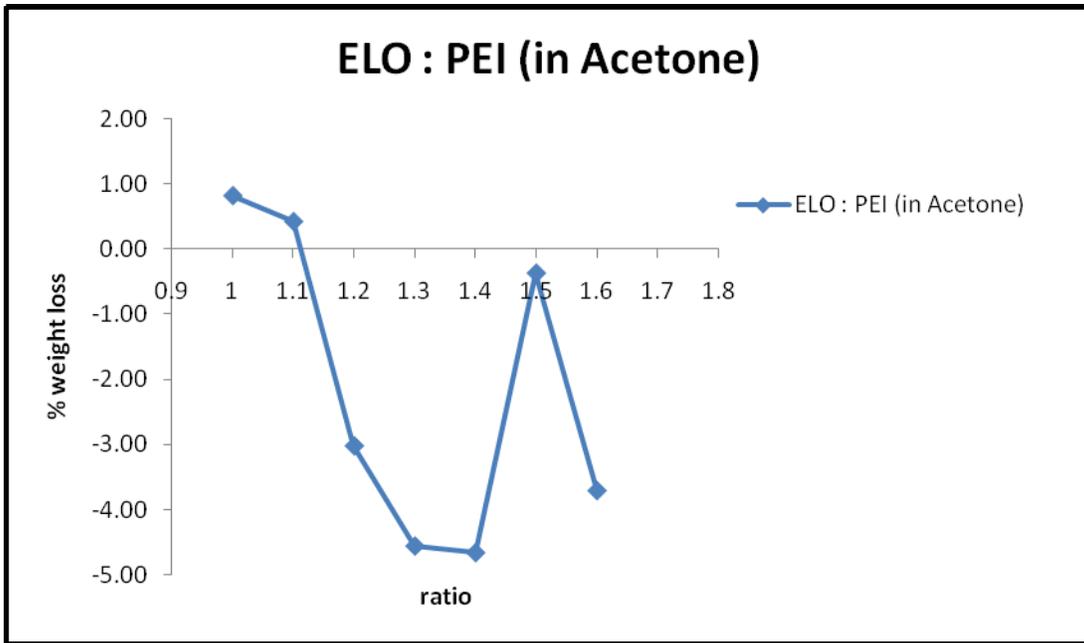
Figure 20: Amount of extractables vs. resin-to-hardener ratio for the ELO - PEI swollen in acetone
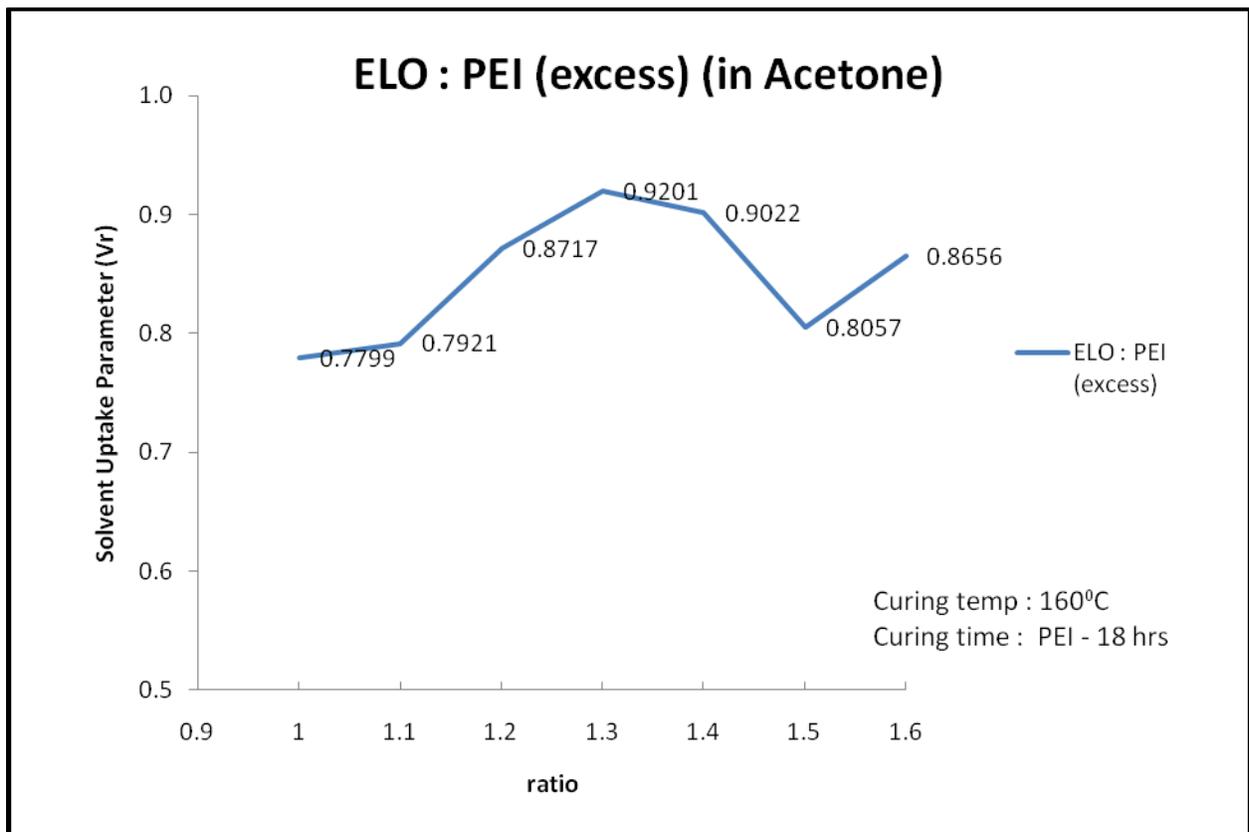

Figure 21: Solvent uptake parameter *Vr* vs. resin-to-hardener ratio for the ELO - PEI swollen in acetone

The optimized composition corresponds to the lowest point on the *% extractables* curve, or the highest point in the *Vr* curve. In this case, the ratios 1:1.3 and 1:1.4 lead to very similar results. As the *Vr* parameter is more reliable than the *% extractables* (because of the experimental error associated with the solvent) the solvent uptake parameter *Vr* value is chosen to define the optimized ratio. As its *Vr* value is the highest, the ratio 1:1.3 is considered as the optimized one for the ELO - PEI system.
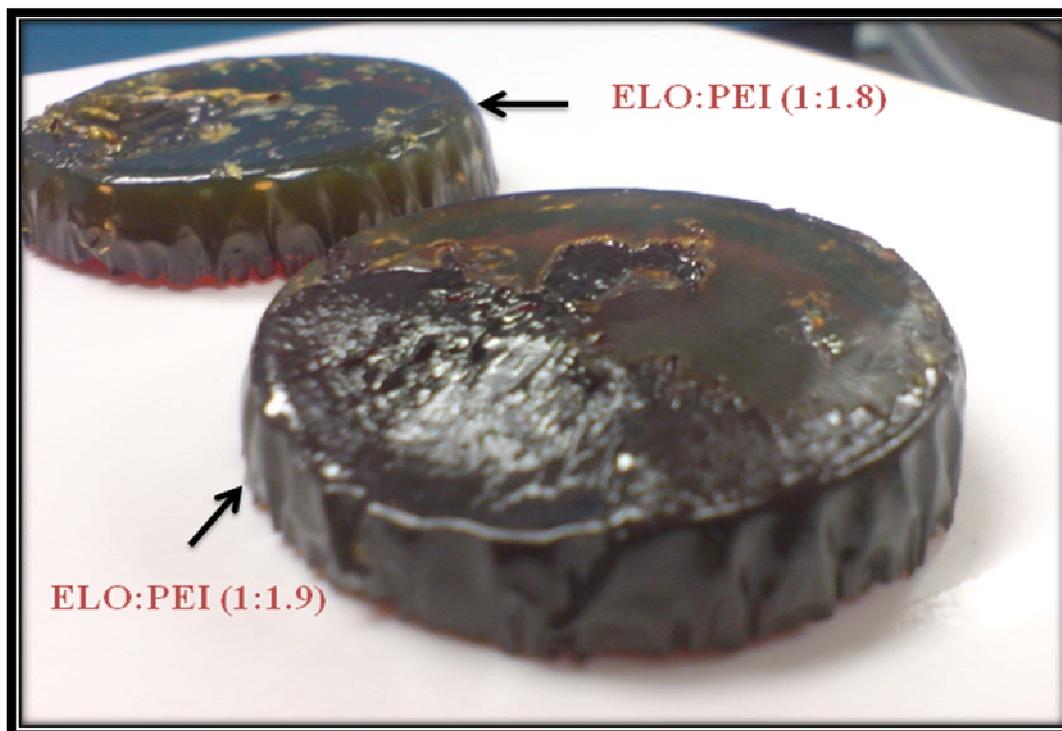
Figure 22: Deformed samples (from the bottom) of ELO - PEI (at ratios of 1:1.8 and 1:1.9) cured at 160°C for 18 hrs

During the optimization, systems with ratios as high as 1:1.9 are produced to check on the influence of higher crosslinking agent on the network density above the ratio 1:1.6. It is observed that above a ratio of 1:1.7, the samples would deform during processing (as illustrated on Figure 22). This could be associated with some degradation or side reactions occurring at high hardener concentrations, that could increase the kinetics of the curing reaction, hence leading to inhomogeneous and unusable samples.

Following are the optimization curves for the ESO – PEI system. Figure 23 and Figure 24 correspond to the solvent uptake in acetone, while Figure 25 and Figure 26 correpond to the solvent uptake in xylenes.
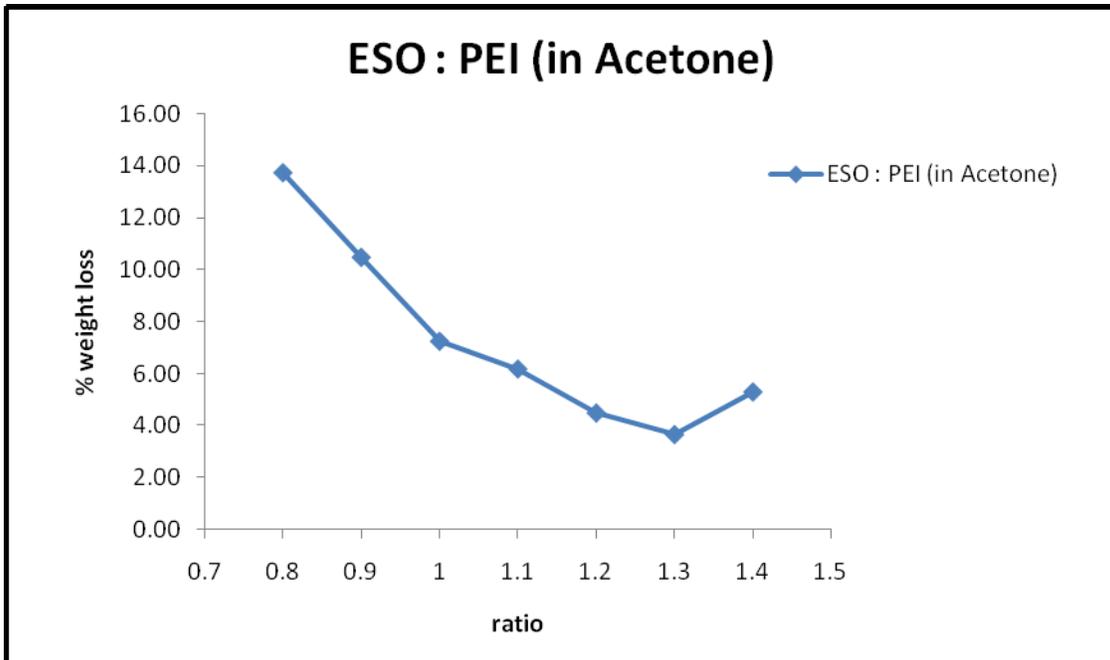
Figure 23: %weight loss vs. resin-to-hardener ratio for the ESO - PEI samples swollen in acetone
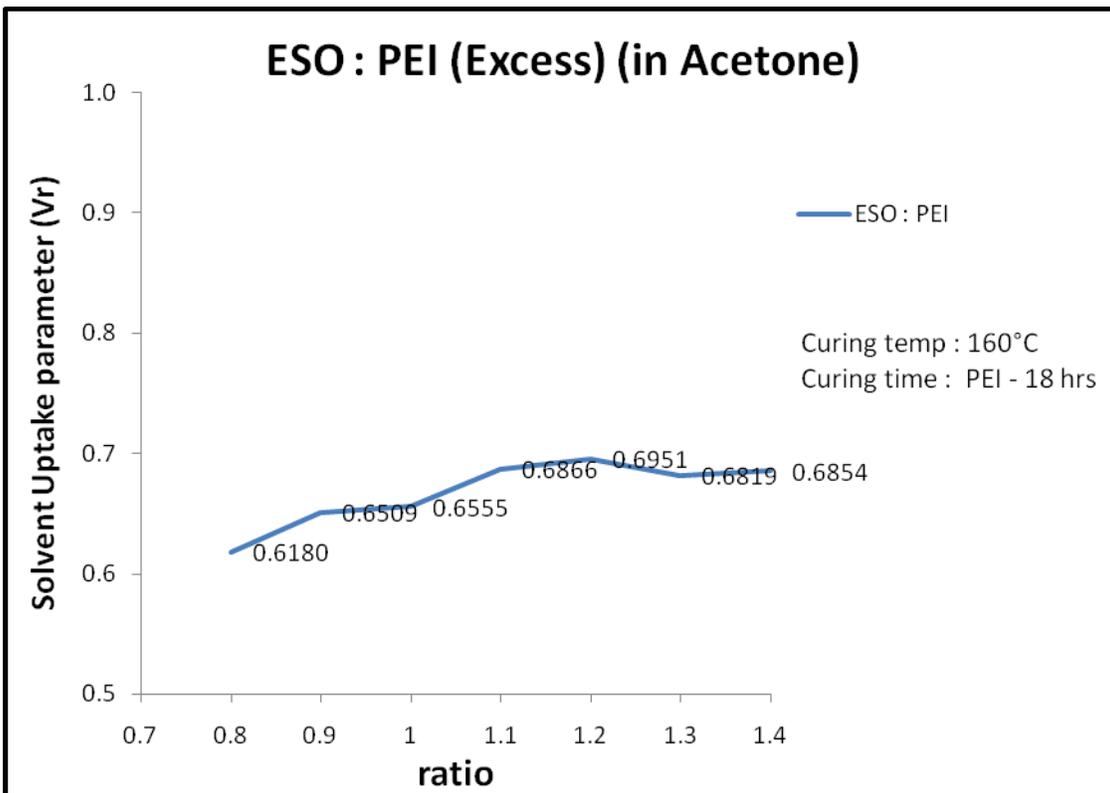
Figure 24: Solvent uptake parameter Vr vs. resin-to-hardener ratio for the ESO - PEI samples swollen in acetone
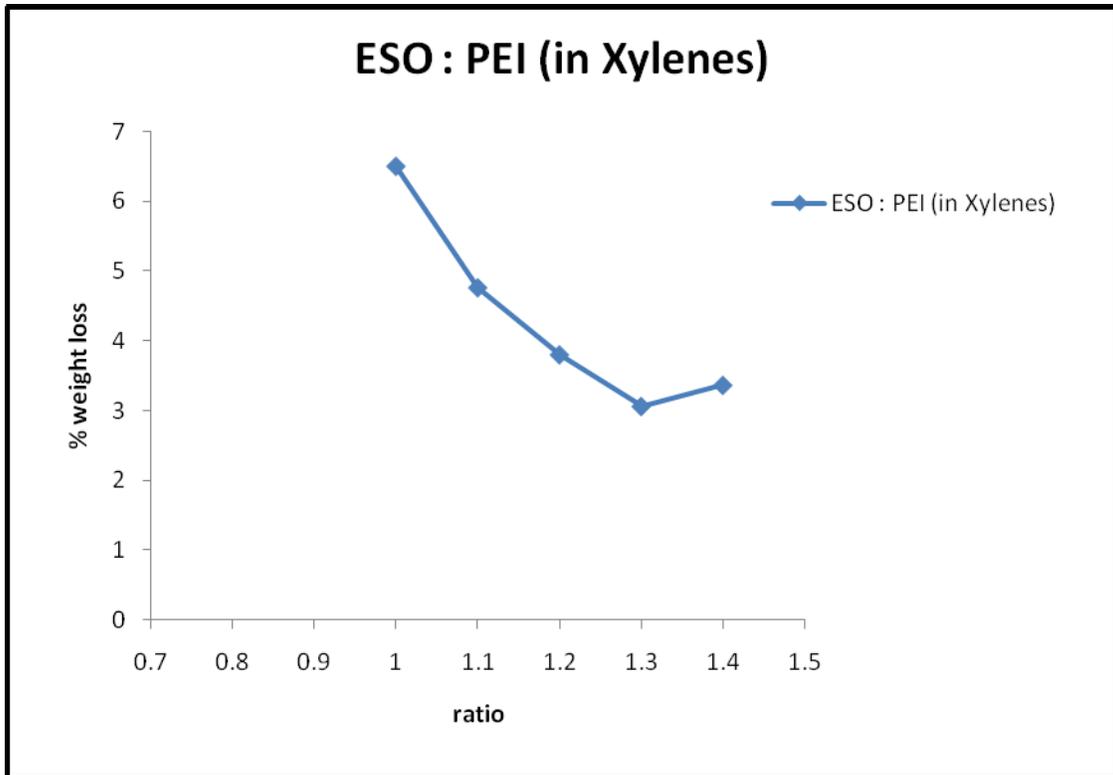
Figure 25: %weight loss vs. resin-to-hardener ratio for the ESO - PEI samples swollen in xylenes.
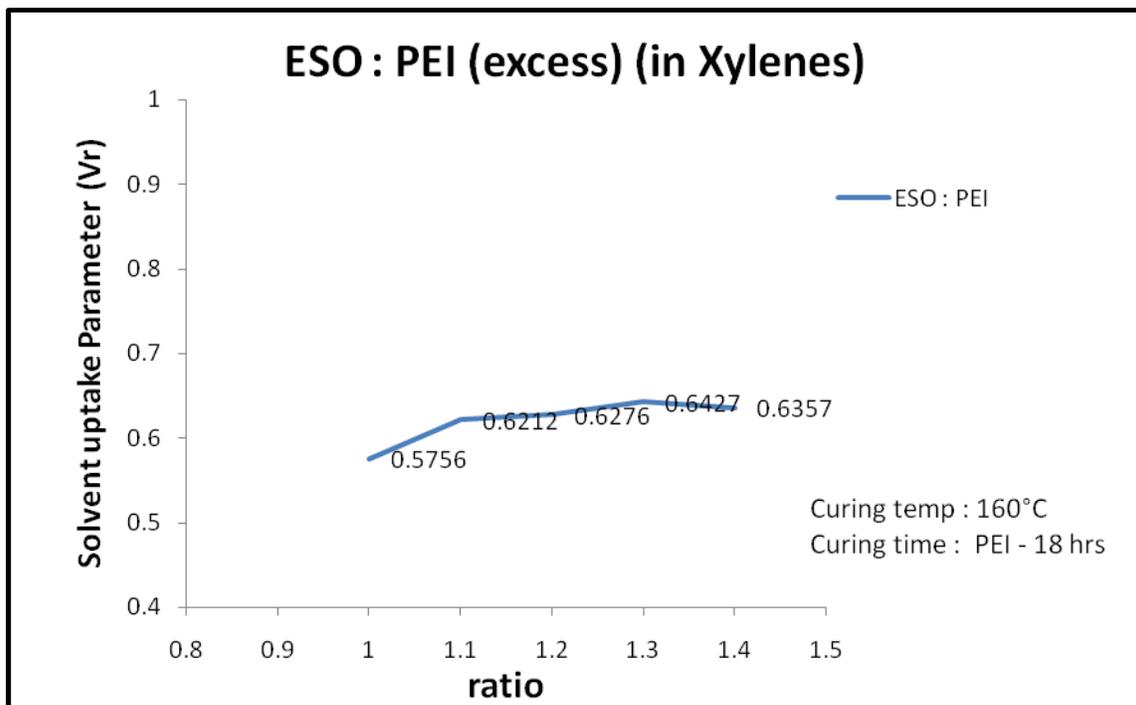
Figure 26: Solvent uptake parameter *Vr* vs. resin-to-hardener ratio for the ESO - PEI samples swollen in xylenes

The highest value of *Vr* are reached at ratios between 1:1.2 and 1:1.4; the differences between the parameters are then so limited that they are attributed to experimental error. As a result, the average of a ratio of 1:1.3 was chosen as the optimized ratio for the ESO - PEI system.

3.a.2- Epoxidized Linseed Oil (ELO) and Epoxidized Soybean Oil (ESO) with Triethylene Tetra Amine (TETA):

The second chosen curing agent, Triethylene Tetra Amine (TETA), has been also studied in the same way as the PEI, by optimizing the curing conditions and the resin-to-hardener ratio.
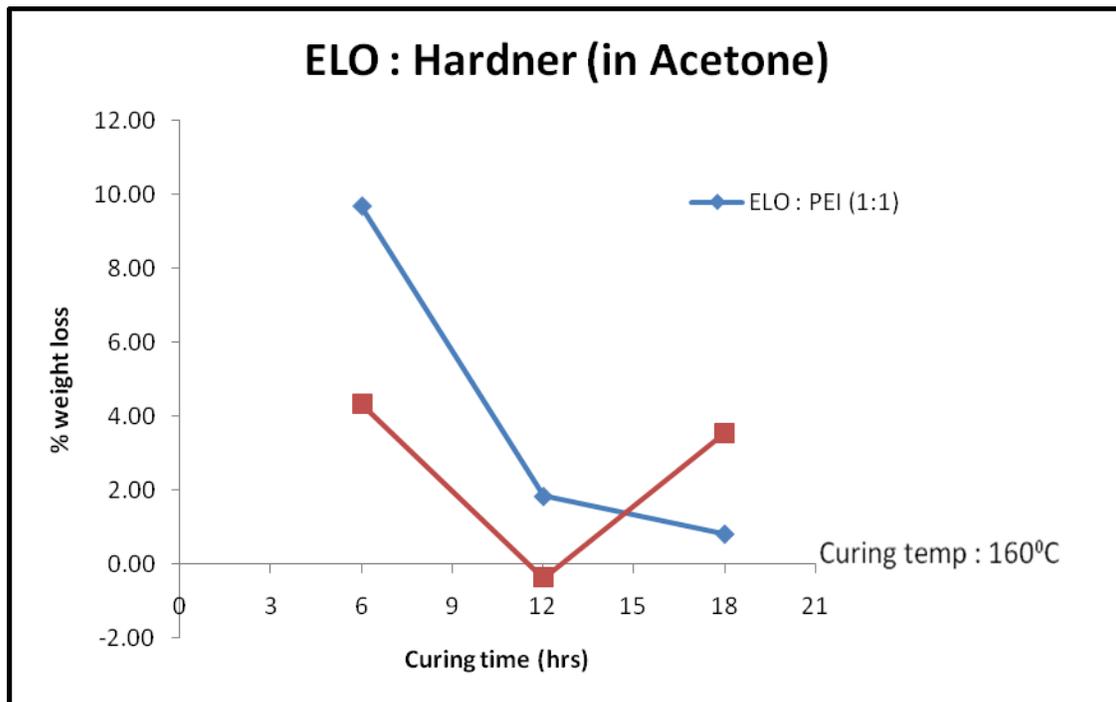
Figure 27: Comparison of % weight loss vs. curing time for the ELO cured with PEI or TETA

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As compared on Figure 27, the optimized curing time for the ELO - PEI system is 18 hrs, whereas for the ELO - TETA system the optimized curing time is 12 hrs. Under this set of conditions, the *% extractables* reaches a minimal value (i.e. fewer amounts of unreacted monomers) than could be reached in the ELO - PEI system.
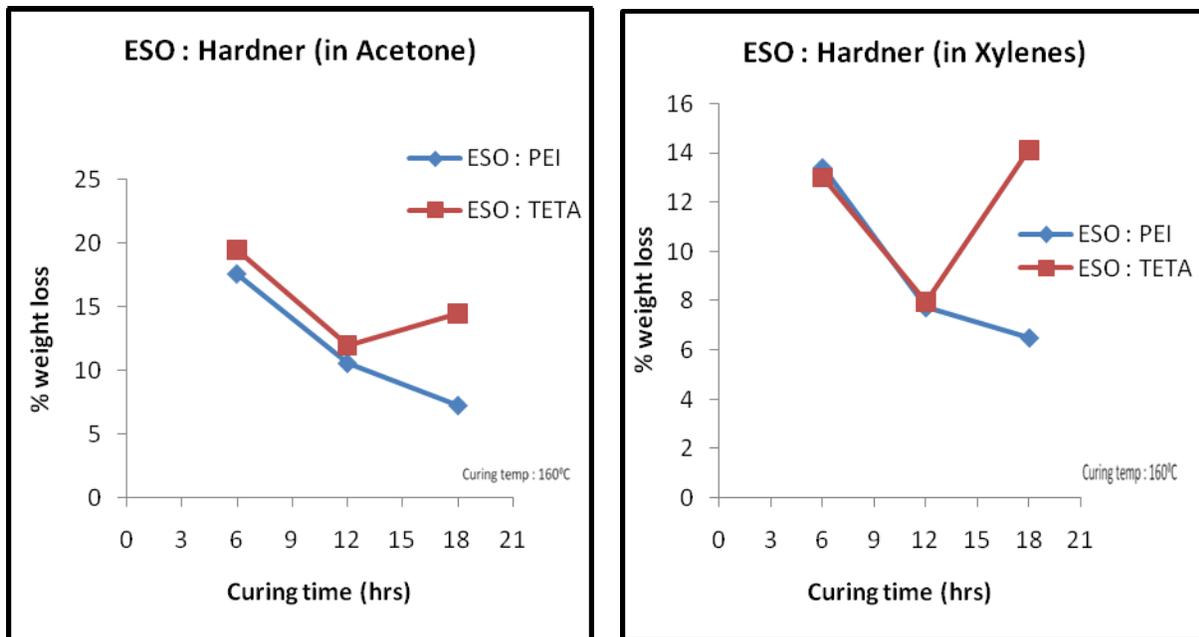
Figure 28: Comparison of % weight loss vs. curing time for the ESO cured with PEI or TETA.

Likewise for the ESO - TETA system, it is observed on Figure 28 that the optimized curing time is 12 hrs.

The next optimization step consists in adjusting the resin-to-hardener ratio. Samples with an excess of 10% to 60% (i.e. 1:1.1 to 1:1.6) of the curing agent (TETA) are produced for the ELO system and samples with ratios of 1:0.9 to 1:1.4 are produced for the ESO system. A solvent uptake analysis is carried out to characterize the *% extractables* in the cured product and the solvent uptake parameter *Vr*.
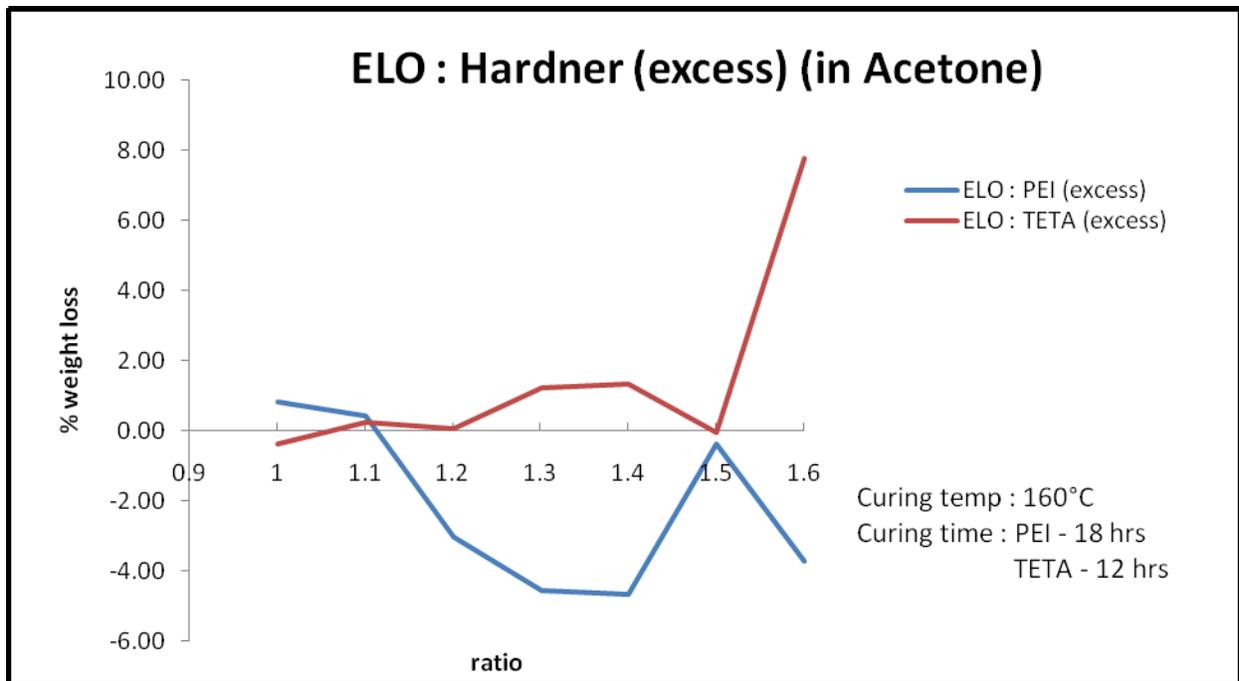
Figure 29: Comparison of the % weight loss vs. different ratios of PEI or TETA for the ELO based resins.
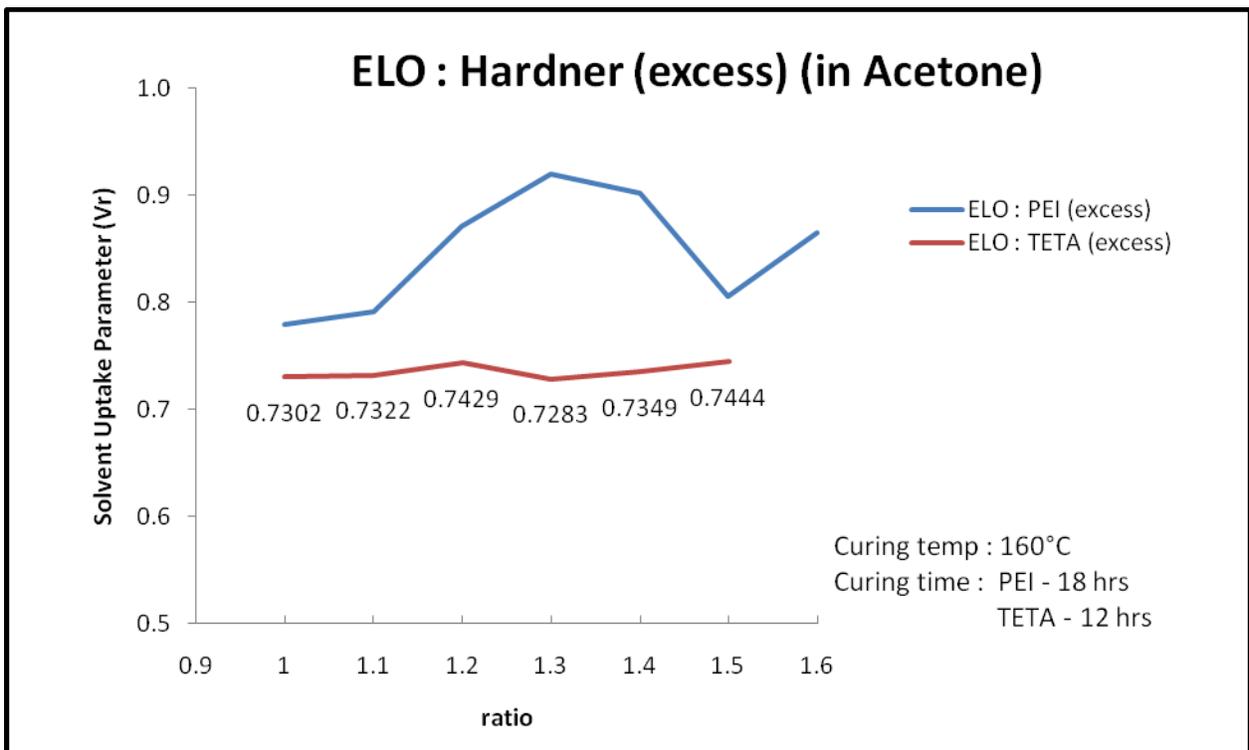
Figure 30: Comparison of *Vr* vs. different ratios of PEI or TETA for the ELO based resins

As for the **ELO - TETA system**, resin-to-hardener ratios of 1:1 to 1:1.2 cured for 12 hours lead to very limited amount of extractables (Figure 29). As already noted, when the % extractables are very similar, the solvent uptake parameter Vr is taken as the choice parameter. As compared on Figure 30; the highest values of Vr are reached for a ratio of 1:1.2; and for ratios higher than 1:1.5. The higher ratios lead to deformed samples (in a similar way as what was observed for the ELO – PEI system). As a result, the resin-to-hardener ratio 1:1.2 is considered the optimized ratio for the PEI – TETA system.
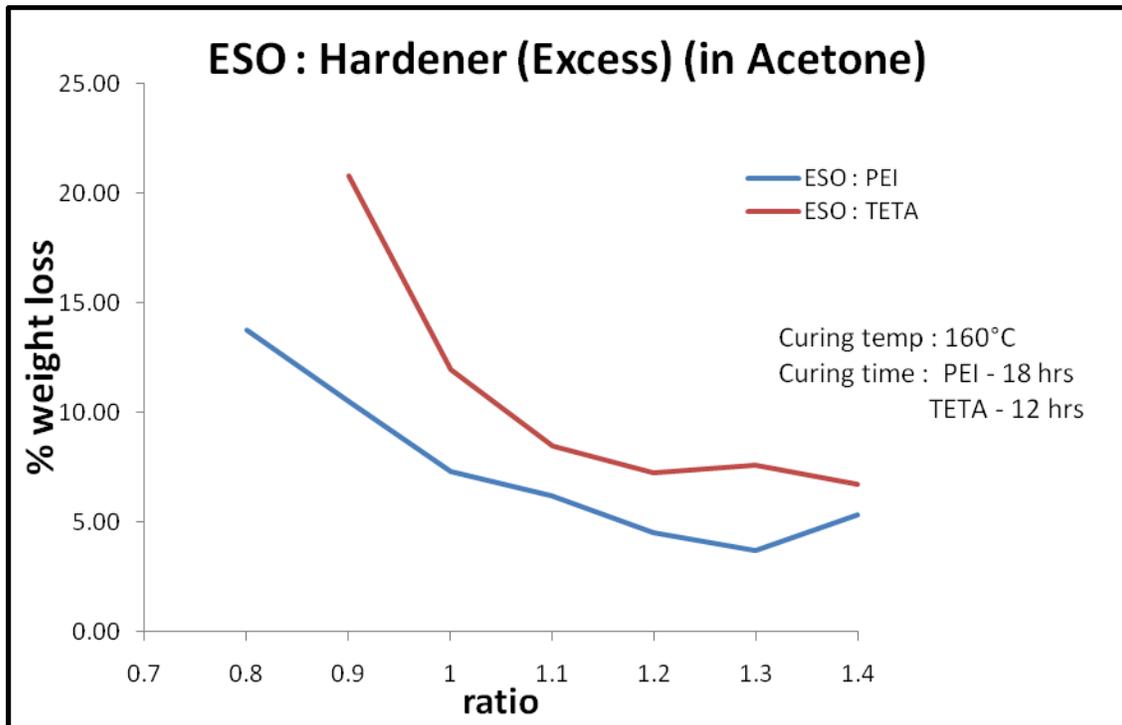
Figure 31: Comparison of the % weight loss vs. different ratios of PEI or TETA for the ESO based resins
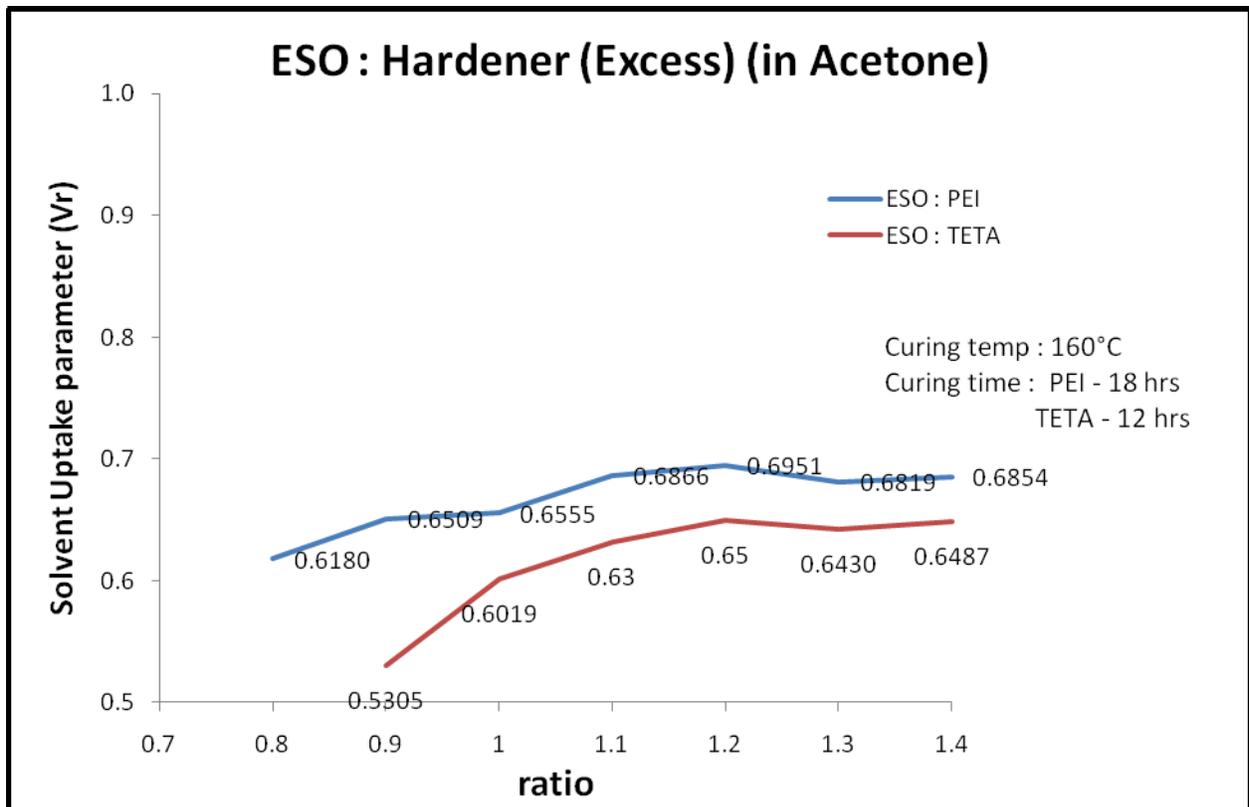
Figure 32: Comparison of the *Vr* vs. different ratios of PEI or TETA for the ESO based resins
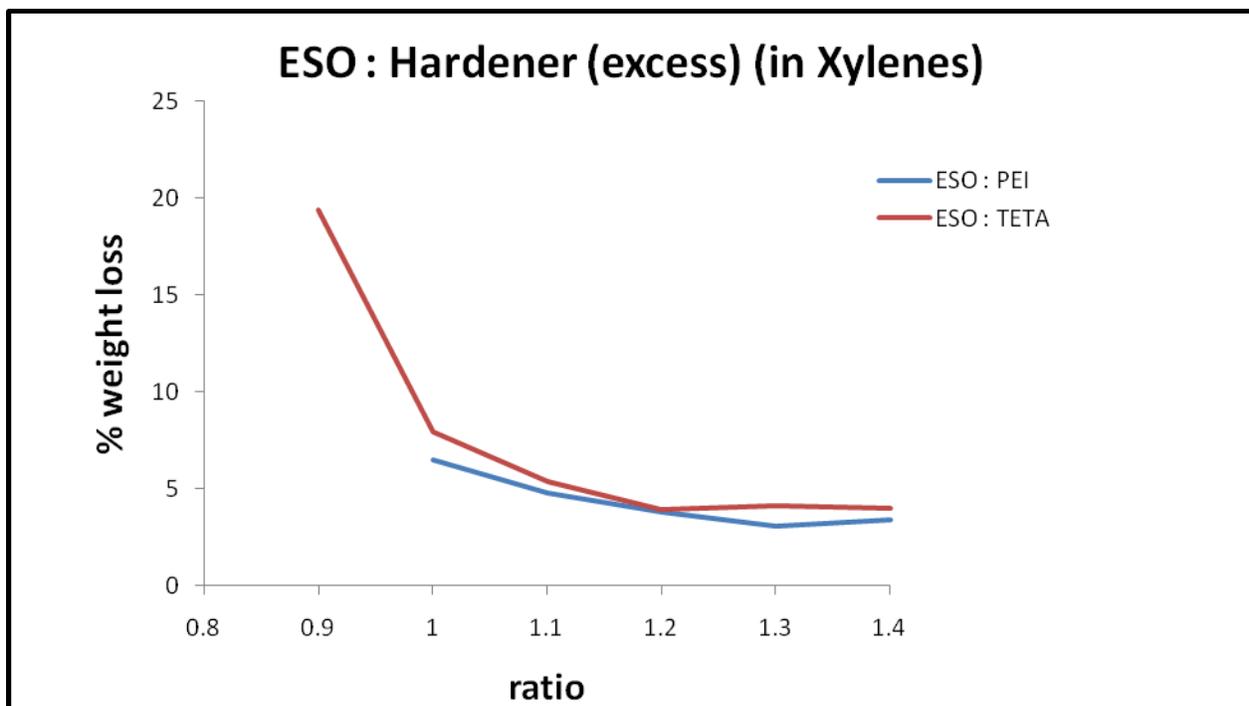
Figure 33: Comparison of the % weight loss vs. different ratios of PEI or TETA for the ESO based resins
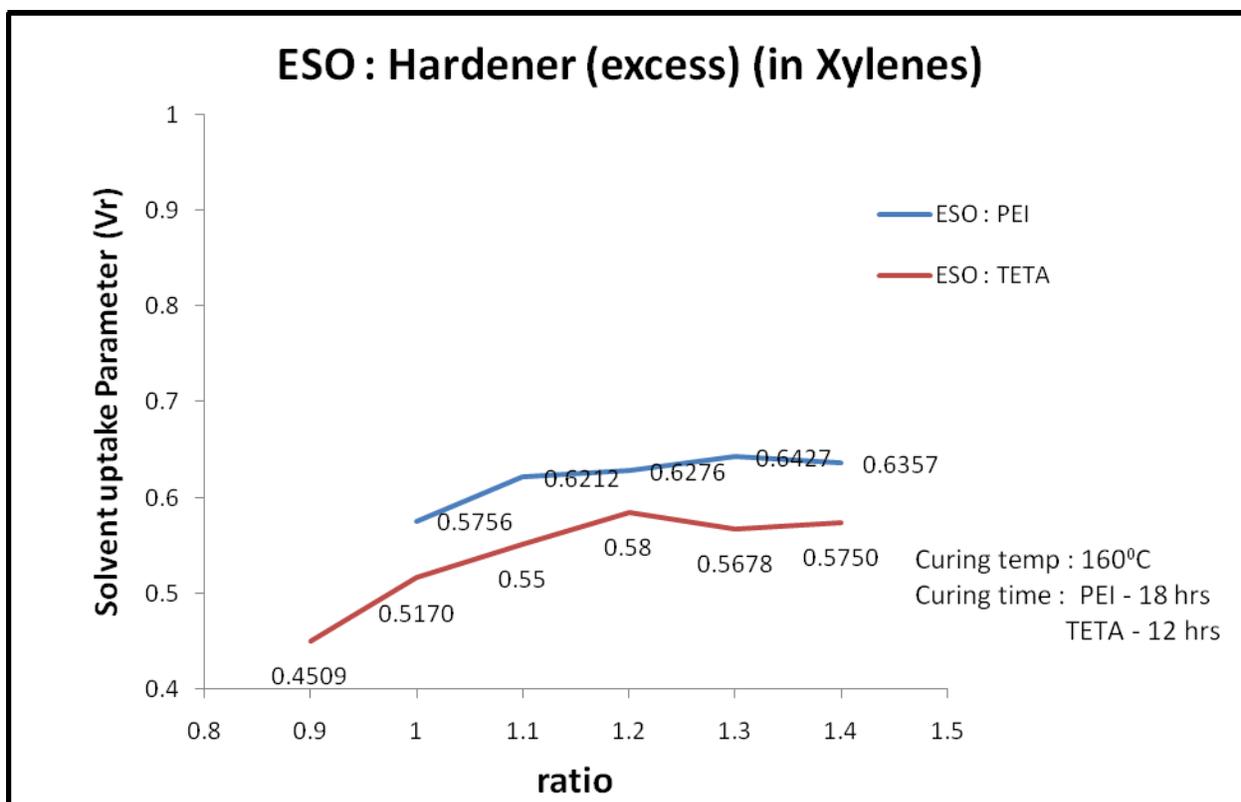
Figure 34: Comparison of the % weight loss vs. different ratios of PEI or TETA for the ESO based resins

As for the ESO - TETA cured at 12 hrs at 160°C, both solvents (acetone and xylenes) show the same trend. (Figure 31 and Figure 33) with respect to the *% extractables*. The curve levels off at a ratio of 1:1.2. Here again, the *Vr* values are taken as the choice parameter, since the *% extractables* are very similar. **1:1.2** appears as the optimum ratio for the **ESO - TETA**, as *Vr* reaches a maximum at this concentration on Figure 32 and Figure 34.

Figures E-1 and E-2 in the Appendix section compare the ELO and ESO systems for the two curing agents already studied; it clearly shows that the ELO system is better than the ESO system in terms of the *% extractables* and the crosslink density. The optimized ELO system has lower (no) unreacted monomer left in the final product and also has a higher solvent uptake parameter *Vr* (crosslink density) as compared to the ESO system. It is also observed that the rigidity (stiffness) of the ELO based samples is better than the ones of the ESO based samples.

When the curing agents are compared, the PEI gives a better network as compared to the TETA. This is because the PEI is highly branched (functional) as compared to the TETA and can react with the oxirane rings of the ELO easily, although it is true that the TETA would be more mobile (because of the structure) as compared to the PEI (which is bulky).

Initially the L-Tryptophan is chosen as one of the curing agents for the bioepoxies. The bioepoxies are liquids in nature while the L-Tryptophan is solid (i.e. a coarse powder). So as to achieve a homogenous mixing of the amino acid with the bioepoxies, it is attempted to reduce the L-Tryptophan into a fine powder through freeze-drying: the principle consists in freezing the material (thanks to liquid nitrogen), then in reducing the pressure surrounding the powder and adding enough heat to allow the frozen solvent in the sample to sublime. A solution of L-Tryptophan and distilled water is created, a small amount of NH_4OH is added to it. This solution is frozen in liquid nitrogen and then freeze-dried.

Both the as-received L-tryptophan and the freeze-dried L-tryptophan are mixed in stoichiometric ratios with the bioepoxy and cured at 160°C for various times (namely 3 hrs, 6 hrs, 12 hrs and 18 hrs). All samples dissolved during the solvent uptake test, meaning that the L-tryptophan, both in the as-received form and in the fine powder form, did not lead to any network; they are therefore useless as crosslinking agents.

L-Lysine (which belongs to the same family of amino acids; it is basically an aliphatic form of the aromatic L-Tryptophan) is thought as an alternative. The L-Lysine (like the L-Tryptophan) had to be freeze-dried to be reduced in fine powder. Despite its water solubility, the L-lysine did not get reduced in powder form through the freeze-drying process, as illustrated on Figure 35 (left). Trials are made on a range of different concentrations (from 3 wt% to 70 wt%) of the L-Lysine in water, but no attempt is successfull. As in the case of the L-Tryptophan, the as-received L-Lysine is mixed with ELO in stoichiometric ratios, but the reaction does not lead to any network; the final product is a thick viscous liquid with small chunks on the surface (Figure 35, right).

Figure 35: Chunks of L-lysine (left) and cured sample of L-lysine and ELO (right)

3.a.4- Curing of Epoxidized Castor Oil(ECO) with PolyethyleneImine (PEI) (Mw-600&10,000)

The curing of the Epoxidized Castor Oil (ECO) is investigated because it is expected that the ECO will be more efficient than the other investigated epoxidized vegetable oils in that:
(1) ECO should cure at room temperature
(2) The curing time shouldld be less as compared to the ESO or the ELO
(3) Less amount of hardener should be needed for curing
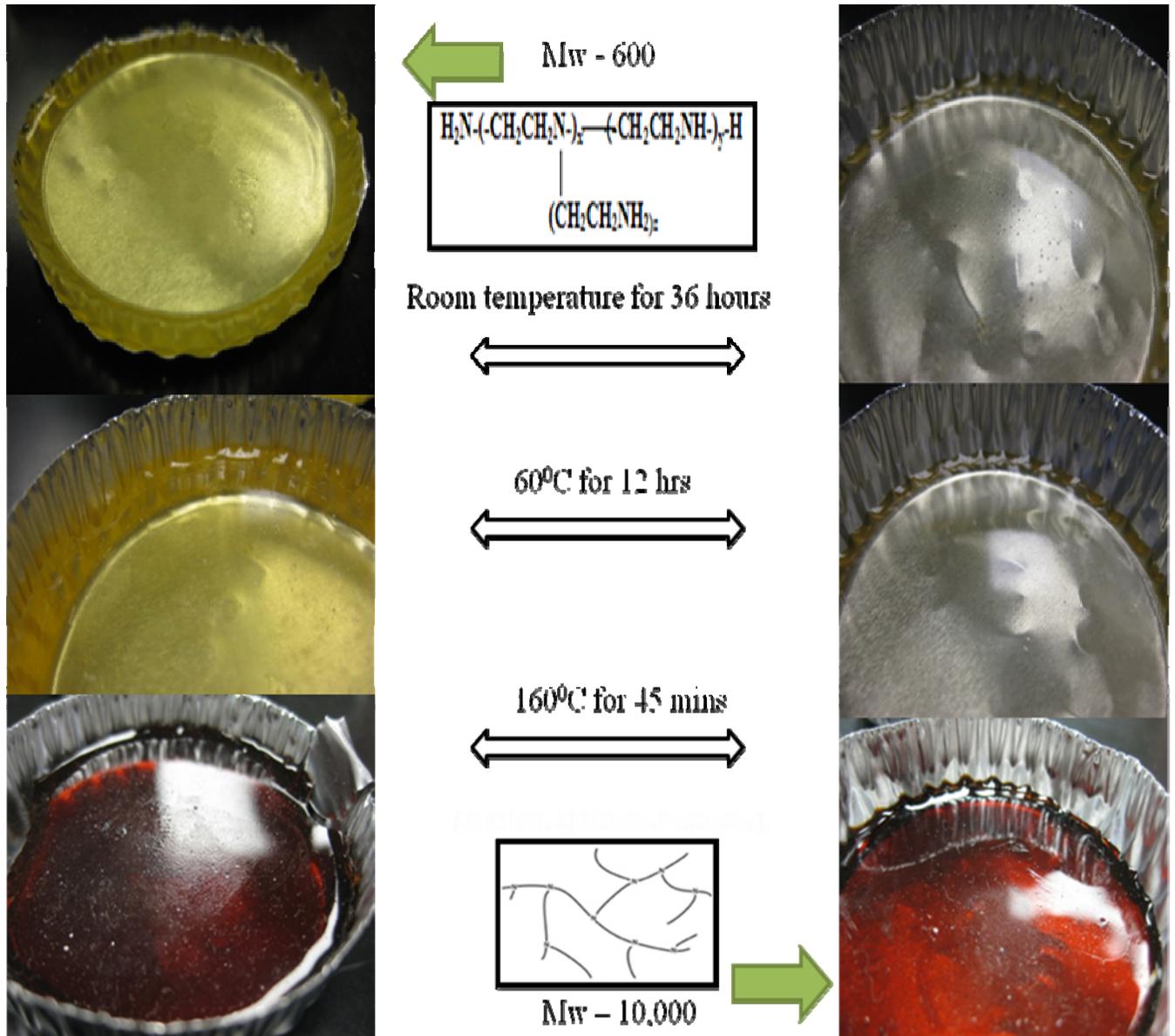
Figure 36: Curing of the Epoxidized Castor Oil (ECO) with PEI (Mw-600 on the left and Mw-10,000 on the right)

Figure 36 gives a visual comparison between the ECO cured with a PEI of small molecular weight (Mw-600) and one of higher molecular weight (Mw-10,000). It is observed that the molecular weight of the PolyethyeleneImine (PEI) used for the curing of the ECO does not make any difference in the stiffness of the final sample. This is linked to the effective amine hydrogen equivalent weight which is almost the same in the two tested cases. Heating the resin at a higher temperature does not affect the stiffness of the sample much, but it increases the curing kinetics.
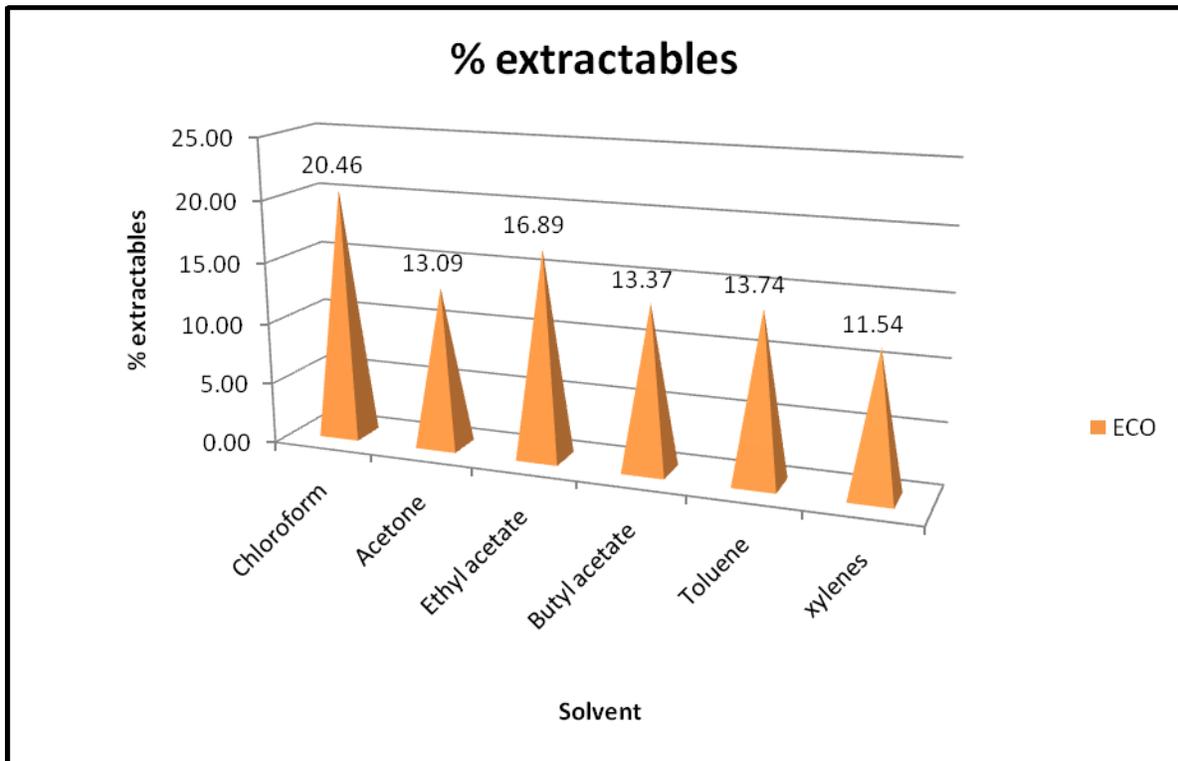
Figure 37: Comparison of the % weight loss vs. solvent for the ECO - PEI system
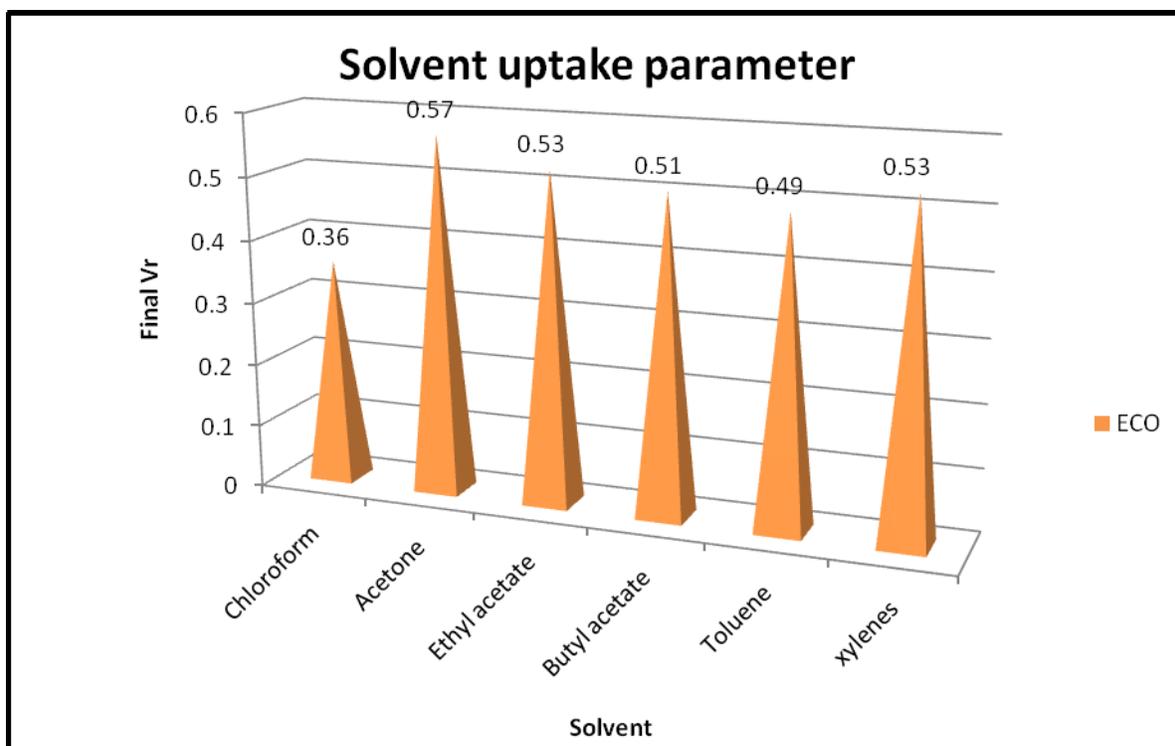
Figure 38: Comparison of the *Vr* vs. solvent for the ECO - PEI system

From the swelling analysis (see Figure 37 and Figure 38), one can conclude that **Ethyl acetate** and **Acetone** are the best solvents for the **ECO** cured samples. The solvents selected give the maximum swelling i.e. the minimum value of *Vr*, indicating that the cured systems swelled the most without any disintegration in these solvents, thus removing all the possible unreacted monomers from the cured resin. The solvents also give the highest value of *% extractables*. The chloroform is not chosen as it would disintegrate the low cross-linked products (during optimization) and acetone is chosen although it is not the best solvent, because it would be easier to compare all the bioepoxies with one common solvent.

Nevertheless, the ECO systems in general are not as rigid as the ELO and ESO systems (this was evaluated by bending the samples). As a result, the study of the ECO – PEI systems is not carried any further.

3.a.5 - Optimization of the formaldehyde based resins

A urea formaldehyde (UF) based resin and a melamine formaldehyde (MF) based resin are prepared so as to compare the bioepoxies with the conventionally used formaldehyde based binders in particleboards.

The MF resin is cured with a dodecylbenzenesulfonic acid as a catalyst for various set of conditions (Table 6 and Table 7).

Table 6: Curing conditions and results of the UF resin

Curing temperature (°C)	Curing time (hrs)	Catalyst loading level	Results
125	48	1%	Dissolved in all solvents, except xylenes
175	3	1%	Foamed
150	12	1%	Foamed
150	12	0.25%	Foamed
150	12	0.10%	Foamed
137	96	0.10%	Brittle, dissolved in most of the solvents
137	96	0.25%	Rigid, shattered in most solvents and dissolved in chlorine based solvents

Table 7: Curing conditions and results of the MF resin

Curing temperature (°C)	Curing time	Catalyst loading level	Comments
125	3 hrs	1%	Foamed
125	24 hrs	0.10%	Fragmented (escaping byproducts forming bubbles in the resin)
125	24 hrs	0.25%	Flexible, rigid product, but dissolved in some solvents
125	48 hrs	0.25%	Still dissolves in some solvents
150	3 hrs	0.25%	Foamed
150	96 hrs	0.10%	Rigid, shattered in the chosen solvent (i.e. 2-butanone/toluene)
137	96 hrs	0.10%	Rigid, shattered in the chosen solvent (i.e. 2-butanone/toluene)
137	96 hrs	0.25%	Brittle, does not shatter in solvents except chlorine based solvents
137	96 hrs	0.50%	Foamed, shattered in dichloromethane
137	24 hrs	0.25%	To reduce the curing time of the **optimized sample** (Bubbling of the byproducts)
137	36 hrs	0.25%	To reduce the curing time of the **optimized sample** (Bubbling of the byproducts)
137	48 hrs	0.25%	To reduce the curing time of the **optimized sample** (Bubbling of the byproducts)
137	60 hrs	0.25%	To reduce the curing time of the **optimized sample** (Bubbling of the byproducts)
137	72 hrs	0.25%	To reduce the curing time of the **optimized sample** (Bubbling of the byproducts)

As noted in the observations, the curing of the formaldehyde based resins is impaired by various problems: either the system is undercured (i.e. does not form a network) and simply dissolves in a solvent; or the system leads to a material so heavily crosslinked that it shatters

under the chemical pressure of a solvent; or the system starts curing so fast it generates gas that is trapped in it and leads to a foam (see illustration on Figure 39) .

Formaldehyde based resins are known to cure fast; as a result, they are generally compression-molded or hot-pressed in industrial settings to extract any by-products; this leads to samples without bubbles. Unfortunately we do not have access to something else but a convection oven to prepare our samples. One decent set of conditions is isolated (see the yellow-highlight in Table 7) where a correct sample is produced from the MF based resin. A solvent selection is then performed on this sample, as presented on Figure 40 and Figure 41.

It is concluded that **2-butanone** and **Toluene** are the best solvents for the MF system, as they give the highest percentage of extractables and the least solvent uptake parameter *Vr*.

Given the difficulty in preparing bulk samples, the study on the formaldehyde based resin has been deliberately interrupted at this point, to focus on the core of the research project, the binder from renewable resources.

Figure 39: Foamed MF sample with a catalyst loading level of 0.28 wt% at 140°C
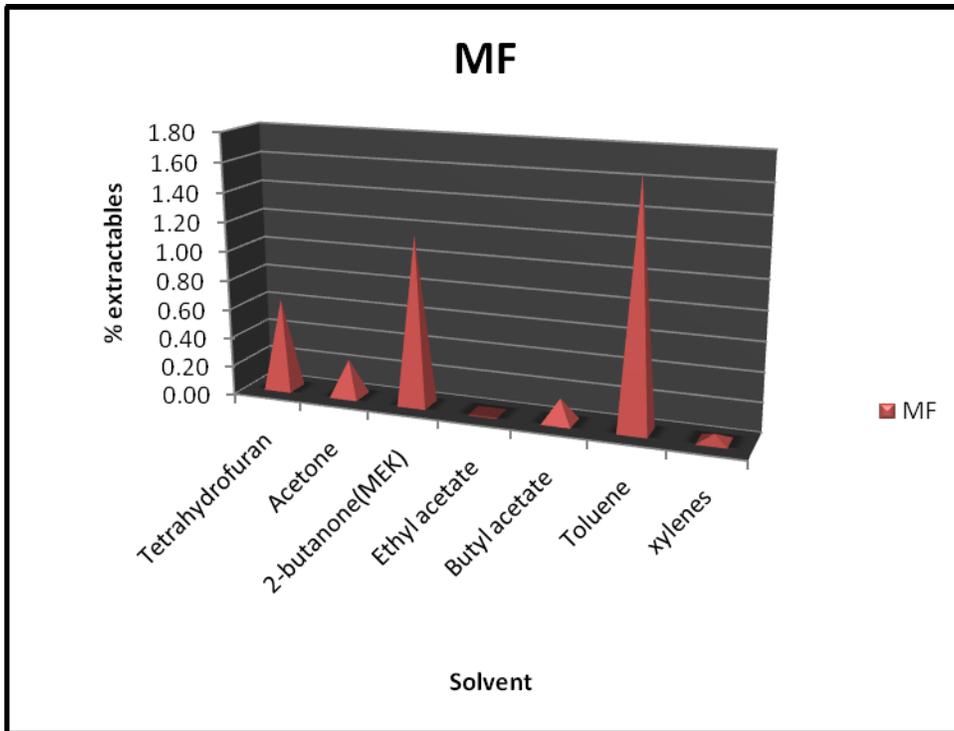
Figure 40: Solvent selection for the MF resin (comparing *% extractables*).
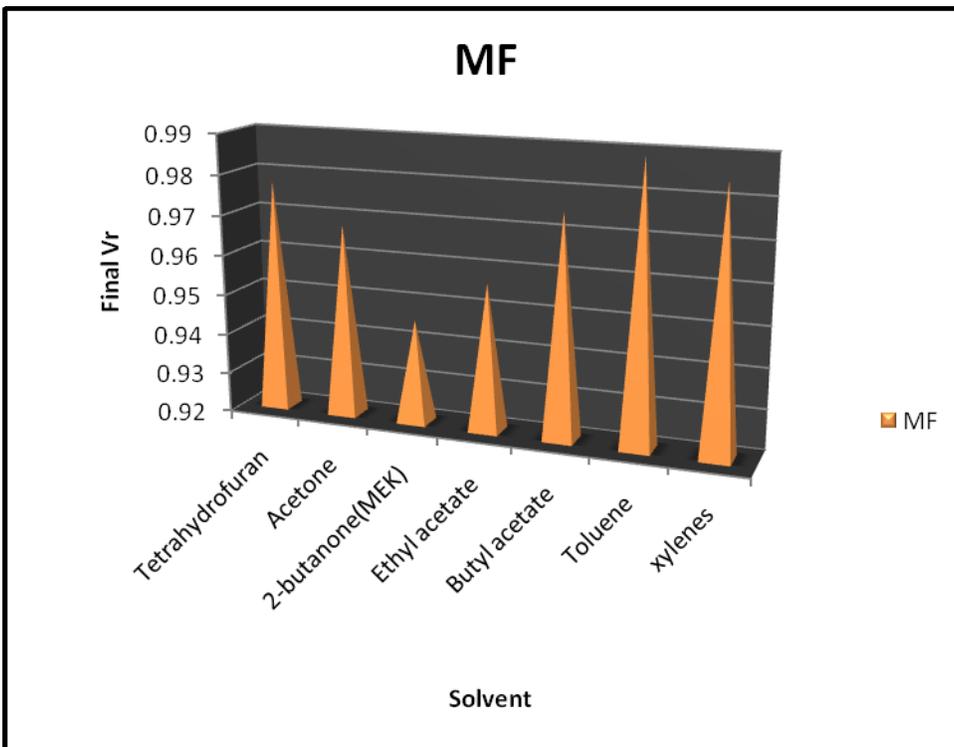
Figure 41: Solvent selection for the MF resin (comparing final *Vr*).

3.b- MECHANICAL TESTING OF THE BIOEPOXY SYSTEMS

3.b.1- Sample preparation

Degassing of bubbles is always an issue with thermosets (see Figure 42). To overcome this problem, the best solution is adding a degassing step to the preparation route. The resin and hardener solution is poured into the mold and then kept under vacuum (with the pump is running) overnight. It then undergoes three cycles of vacuum and purge, which removes the bubbles completely. The mold is then transferred to a preheated convection oven for curing at the required curing temperature.
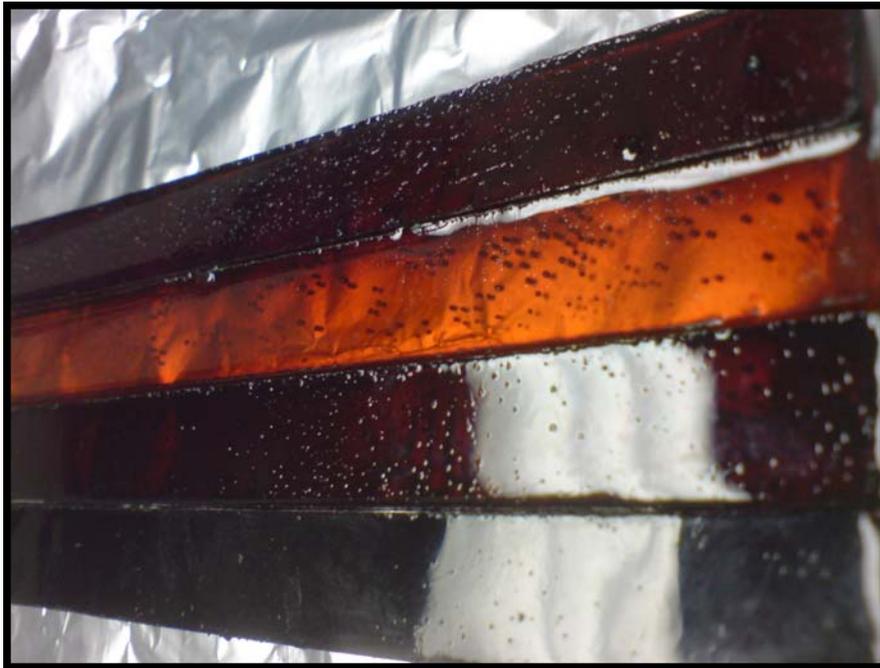
Figure 42: Flexure bars with bubbles made of ELO - PEI (1:1.4) cured at 160°C for 18 hrs without and with Cloisite 30 B (nanoclay) loading level of 2 %wt.

The samples with nanoclay in them show poor surface finish at the bottom of the flexure bars (Figure 43). It turns out to be linked to the use of a silicone mold and is not related to the clay presence. This problem is solved with the degassing technique.
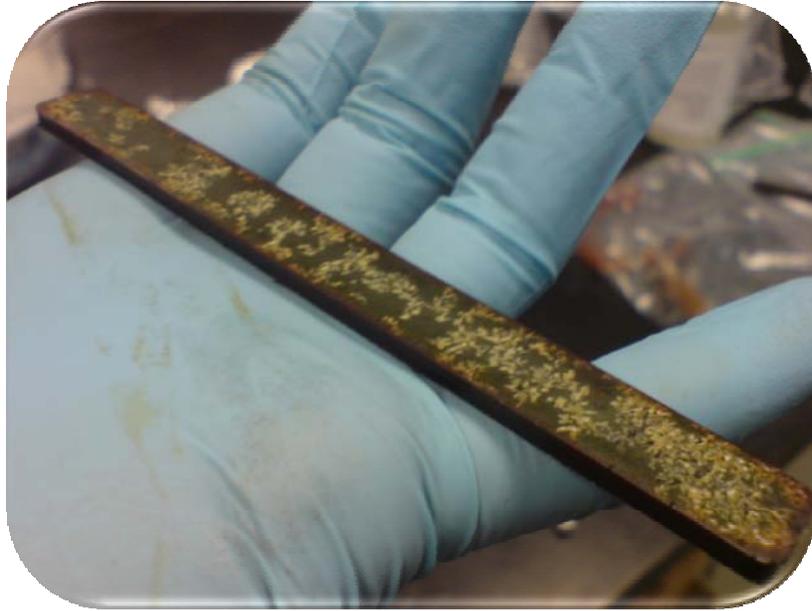
Figure 43: Bottom of the flexure bar made of ELO - PEI (1:1.4) cured at 160°C for 18 hrs with Cloisite 30 B (nanoclay) loading level of 2 %wt

3.b.2– First series of experiments

As a first set of mechanical experiments, a selection of samples having undergone different preparation routes was tested (see Table 8). A three-point bend test was performed on each sample at room temperature. The results are presented on Figure 44.

The ELO - PEI optimized flexure bars that are tested for mechanical properties (by DMA) are cured at 160°C for 18 hrs and their ratio of the ELO to PEI is 1:1.3.

Table 8: First set of samples tested by DMA

Sr. No.	Parameters
1	w/o degassing w/o conditioning
2	w/o degassing with conditioning
3	with degassing w/o conditioning (Dark)
4	with degassing w/o conditioning (Clear)
5	with degassing w/o conditioning (2 wt% Clay)
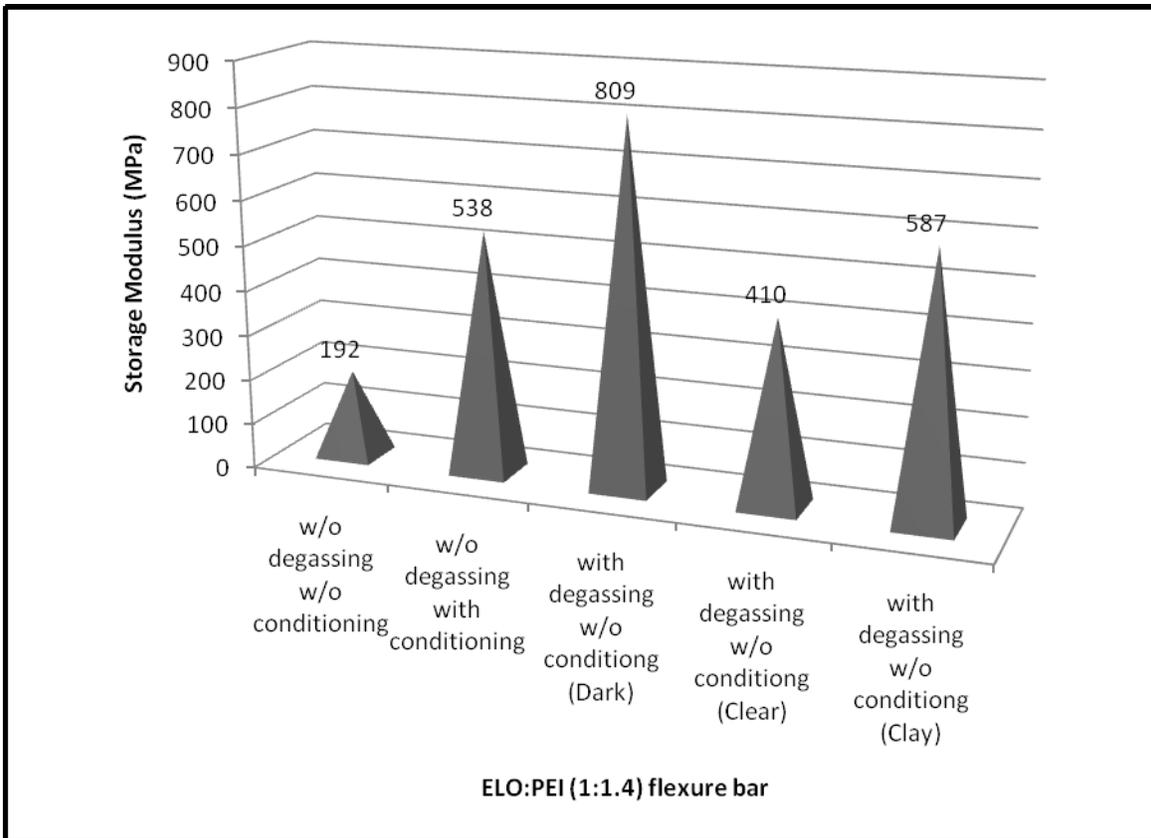
Figure 44: Storage modulus of the samples cured under different conditions.

First it should be noted that the results do not indicate a clear trend on the role of degassing: the bubbles in the samples are expected to play a role on the strength of the materials, but not on the modulus.

Most remarkably, the resin with the optimized composition shows a lot of variability in its storage modulus, as can be observed with the clear and dark degassed but not conditioned samples. This is linked to the thermal gradient experience by the various samples of the same mold while curing, and is further investigated in the following section.

Finally, the addition of the Cloisite 30B (nanoclay) at a loading level of 2 wt% leads to a potential increase in the modulus value. This will need to be confirmed on several samples, when the resin values would have less variability.
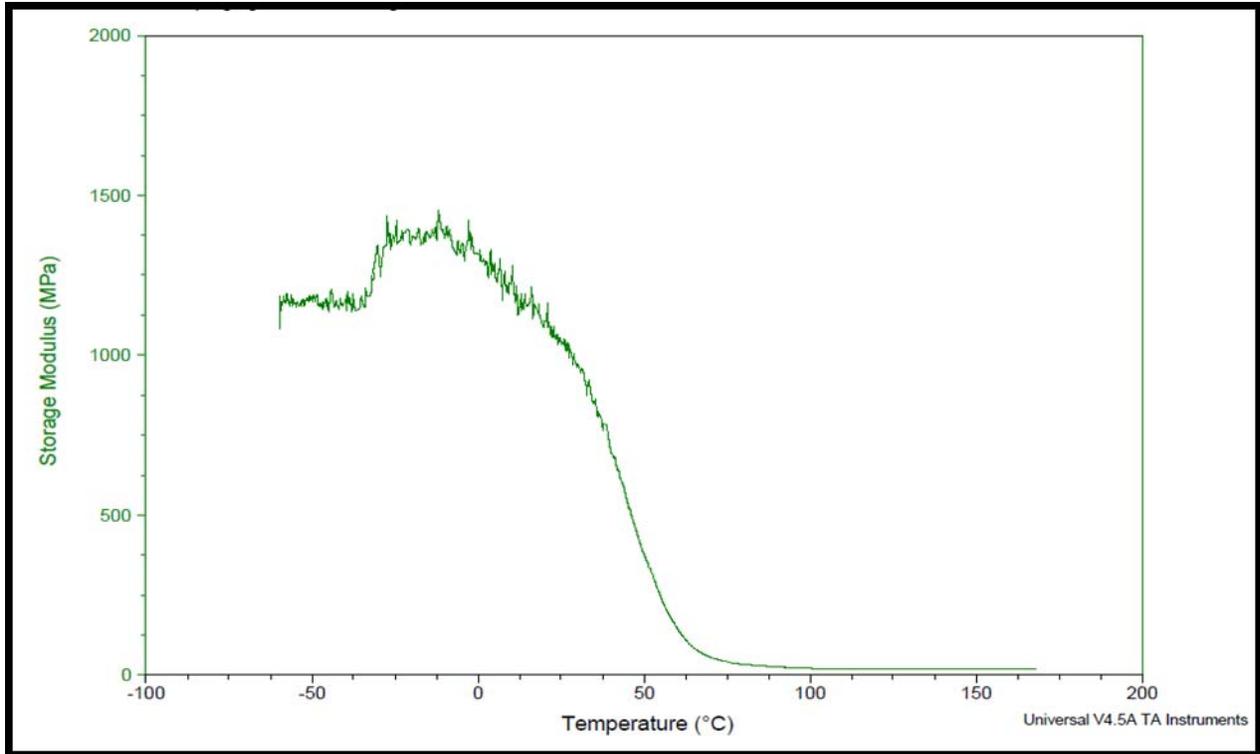
Figure 45: Storage modulus vs. temperature of the flexure bar which was degassed and not conditioned, from -60°C to 170°C at 30°C/min

A degassed (but non-conditioned) sample of the pure resin is submitted to a DMA test from -60°C to 170°C at 3°C/min as presented on Figure 45. While the modulus reaches values as high as 1.4 GPa at low temperatures, it can be noted that the main relaxation temperature of the resin is around 50°C; which is relatively close to room temperature. This could be of concern in industrial applications, as a change in a few degrees around room temperature could lead to tremendous change in the mechanical behavior. Again, further investigations on the repeatability of those results would help to better characterize the behavior of the bioepoxy.
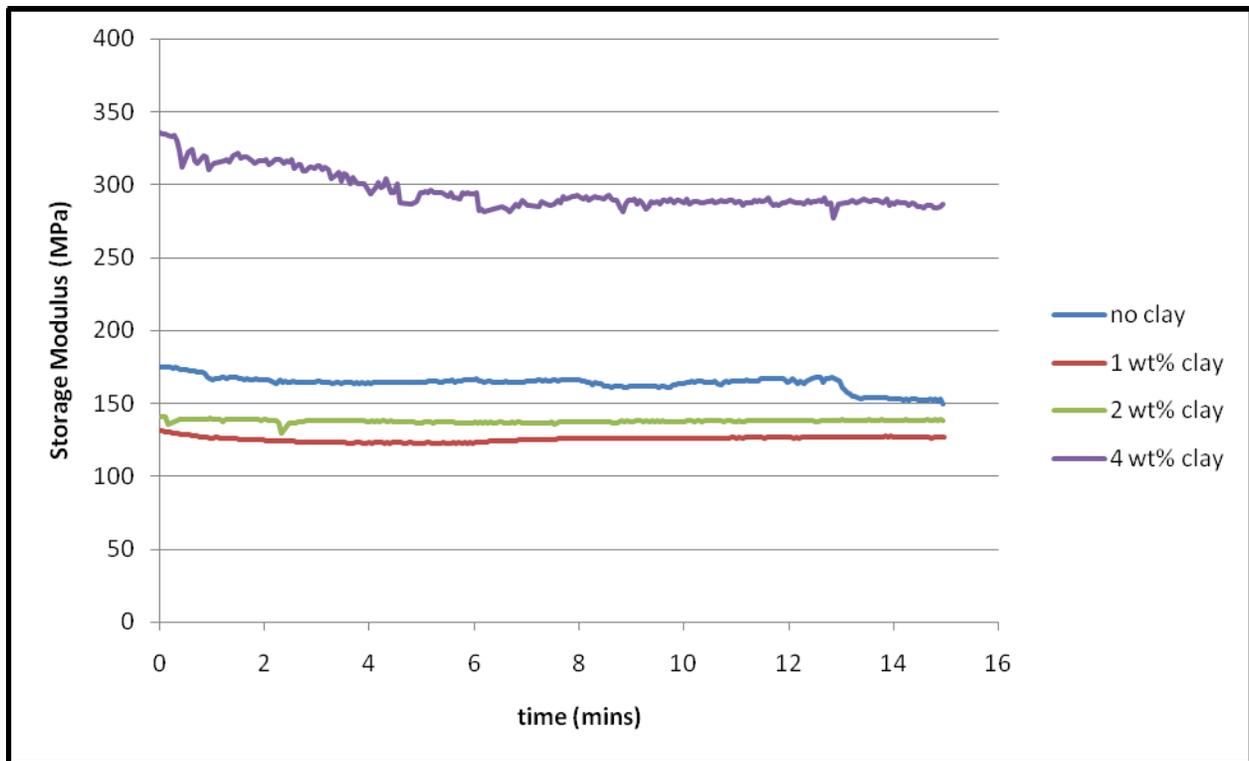
Figure 46: Effect of the clay presence on the sample modulus evolution with time

Isothermal DMA tests are used to compare the stiffness of the samples with respect to different clay concentrations (Figure 46). The samples are made of ELO - PEI (1:1.3)cured at 160°C for 18 hrs , with the different loading levels of clay (1wt%, 2wt% and 4 wt%). The samples are tested at 30°C with a three-point bend test. It is seen that as the loading of the clay increases, the modulus value of the flexure bars increases. All the clay samples are prepared under the same conditions in the same batch. But the neat polymer has been prepared in a different batch. The heating profile of the neat bioepoxy could have been different, which could explain the relative position of the non-filled samples compared to the filled ones.

3.c– INVESTIGATION OF THE CURING CONDITIONS

One of the major problems that arose during the investigation is the reproducibility of the flexure bars made with the silicone mold. The samples prepared for the optimization of the curing conditions in the aluminum pans appear stiffer as compared to the flexure bars prepared in the silicone mold. It is possible that the heating profile of the silicone mold is different than the one of the aluminum pans. In order to achieve reproducible stiff flexure bars with the silicone mold, InfraRed (IR) images (thanks to a FLIR system) are captured on the aluminum pan and on the silicone mold to find the surface temperatures (**Figure 47**). This gives us useful information regarding the difference in the heating profile and also the heating gradient within the silicone mold. It is seen that the set oven temperature (320°F) is different from the surface temperature of the silicone mold (~308°F) and the aluminum pan (180°F).
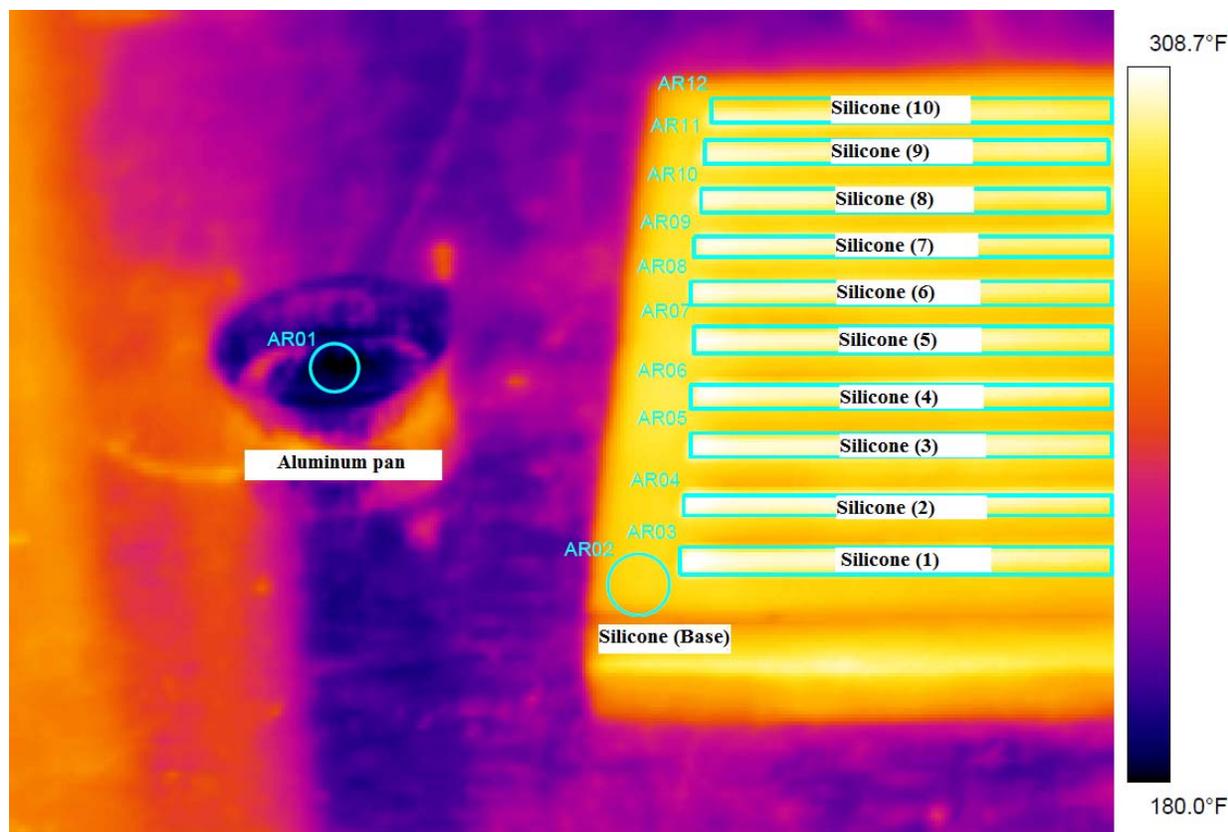
Figure 47: IR imaging of the aluminum pan and silicone mold at the set curing temperature (160°C – 320°F) for the bioepoxies

A complete IR imaging analysis is carried out to determine the heating profile of both molds and it is seen that at the set curing temperature (160°C) of the oven, the silicone mold is at a higher temperature as compared to the aluminum pan (Figure F-1). The bioepoxies undergo degradation at high temperatures and lose their stiffness. Therefore, the oven should be set at a lower temperature to get stiff samples, cured using the silicone mold.

The temperature gradient in the silicone mold was also checked with the IR imaging. The temperatures at the different locations were mostly uniform (Table F-1, Figure F-2). Thus, it is recommended to use the convection oven for reproducibility of the flexure bars. The vacuum oven gives a temperature gradient due to non-uniform heating of the mold at the different locations.

4- CONCLUSIONS AND RECOMMENDATIONS

Throughout this project, the curing of the bioepoxies (ELO and ESO) has been optimized with two curing agents, TETA (Triethylenetetramine) and PEI (PolyethyleneImine). The optimization has been performed by varying the curing time, the curing temperature and the ratio of the resin to crosslinking agent, and by checking the effect of those parameters on the network formation through a solvent uptake analysis.

The optimized conditions are gathered in Table 9:

Table 9: Optimized curing conditions for the achieved bio-derived binders

Resin	Hardener	Curing temperature (°C)	Curing time (hrs)	Ratio
ELO	PEI	160°C	18 hrs	1 : 1.3
ESO	PEI	160°C	18 hrs	1 : 1.3
ELO	TETA	160°C	12 hrs	1 : 1.2
ESO	TETA	160°C	12 hrs	1 : 1.2

Among the bioepoxies, the ELO systems seem to form a better network as compared to the ESO system. This is because the ELO has a higher oxirane oxygen content (9 %) as compared to the ESO resin (7 %). With respect to the curing agents, the PEI seems to be a better hardener, as it is highly functional (branched) as compared to the TETA. The amount of TETA (1.2) required for curing the biopeoxy is less compared to the PEI (1.3) though, as the TETA is more mobile than the PEI (which is bulky).

The curing of the bioepoxy with the amino acids has not been successful at the moment because none of the amino-acids could be reduced in a fine enough powder to mix with the resin. An alternative to this issue is the use of Calcium Lysinate & Magnesium Lysinate (commercialized by Scandinavian Formulas), which would provide the needed amino-acids in the form of a fine powder.

Flexure bars for the mechanical testing have been prepared and a dynamic mechanical analysis has been carried out on the optimized ELO - PEI system. The problem of bubbles has been solved by the degassing technique. The problem of the temperature homogeneity in the oven has led to flexure bars with inconsistent properties and needs to be further addressed. IR imaging gives useful information regarding the heating profile and it is expected that the silicone mold will give stiffer flexure bars, when cured at a lower temperature. Storage moduli ranging from 200 to 800 MPa in the cured bioepoxy samples have been achieved (current industrial binders have a modulus in the 1,000 to 2,000 MPa range). The incorporation of nanoclay could lead to some modulus enhancement, but the inconsistent resin properties do not allow for any conclusion on the role of the nanoclay as of now.

A reproducibility study is the next needed step in this study so as to evaluate the range of variability for the modulus of the given bioepoxies. Following that study, the influence of the clay loading and the wood flour loading on the bioepoxies will have to be characterized. In particular, it is recommended to perform the following tests on coupons of the obtained materials: dynamic mechanical analysis for the storage modulus evaluation; Impact strength using an instrumented drop impact tester (ASTM D3763); Fracture face analysis via field emission scanning electron microscopy (FE-SEM); Immersion testing (ASTM 1037-06a); Fire properties testing (Heat release and mass loss rates, heat of combustion)

The optimized biopeoxies (with/without nanoclay) will be compared with the conventional formaldehyde based binders (MF/UF) used for particleboards, in order to assess the viability of the proposed approach.

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APPENDIX

APPENDIX A: **Calculations of the stoichiometric ratios of resin to crosslinking agent:**

Appendix A gives the calculations of the stochiometric ratios of each of the used chemical reactions. Those stoichiometric ratios are used as a basis for the curing of the resins, and have been further optimized.

A-1: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of PEI - ELO

   (1) Epoxide Equivalent Weight (EEW) :

Given: Oxirane Oxygen (%) = 9 %
EEW   = Mass of polymer to give one mole of oxirane oxygen.
       0.09/16 =5.625 mmol of oxirane per g of polymer
EEW   = 1000/5.625
       = 177.77 g of polymer for one mole of oxirane oxygen.
Amine Hydrogen Equivalent Weight (AHEW) :
       Given: Amine Value : 20 mmol/g.solid

                   Amine Rate (%) :
                   Primary   : 35%
                   Secondary   : 35%
                   Tertiary   : 30%

Amine hydrogen equivalent weight (AHEW) = $\dfrac{\text{Amine molecular weight}}{\text{Number of available hydrogens}}$

$\text{AHEW} = \dfrac{1{,}000}{[2 \times \text{primary amine content (meq/g)}] + (\text{secondary amine content (meq/g)})}$

AHEW   = 1000/([2*20*0.35]+[20*0.35*1])
        = 1000/21
         = 47.62

   (2) Amount of curing agent required
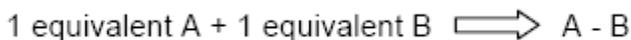
 1 equivalent A + 1 equivalent B $\Longrightarrow$ A - B
A = Resin (ELO),   B = Curing agent (PEI),   A-B = Cured Product
           47.62 g of PEI → 177.77 g of Drapex 10.4

Ratio of Curing agent - Resin (PEI - ELO) =   **1 : 3.75** (Theoretical value)

A-2: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of PEI - ESO

Oxirane Oxygen (%) = 7 %
Epoxide Equivalent Weight (EEW) = 228.57 g
Amine Value = 20 mmol/g.solid
Amine Hydrogen Equivalent Weight (AHEW) = 47.62 g

Therefore, ratio of the PEI - ESO = **1:4.79** (Theoretical value)

A-3: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of TETA - ELO

Oxirane Oxygen (%) = 9 %
Epoxide Equivalent Weight (EEW) = 177.77 g
Amine Value of TETA = 1443 mg of KOH / g
Amine Hydrogen Equivalent Weight (AHEW) = 38.87 g of TETA per one mole

Therefore, ratio of the PEI - ESO = **1 : 4.57** (Theoretical value)

A-4: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of TETA - ESO

Oxirane Oxygen (%) = 7 %
Epoxide Equivalent Weight (EEW) = 228.57 g
Amine Value of TETA = 1443 mg of KOH / g
Amine Hydrogen Equivalent Weight (AHEW) = 38.87 g of TETA per one mole

Ratio of Curing agent - Resin (TETA - ESO) = **1 : 5.88** (Theoretical value)

A-5: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of L-Tryptophan - ELO

Oxirane Oxygen (%) = 9 %
Epoxide Equivalent Weight (EEW) = 177.77 g
Amine Hydrogen Equivalent Weight (AHEW) = 68.07g

Therefore, ratio of the L-Tryptophan - ESO = **1 : 2.61** (Theoretical value)

A-6: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of L-Tryptophan - ESO

Oxirane Oxygen (%) = 7 %
Epoxide Equivalent Weight (EEW) = 228.57 g
Amine Hydrogen Equivalent Weight (AHEW) = 68.07g

Therefore, ratio of the L-Tryptophan - ESO = **1 : 3.357** (Theoretical value)

A-7: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of L-Lysine - ELO

Oxirane Oxygen (%) = 9 %
Epoxide Equivalent Weight (EEW) = 177.77 g
Amine Hydrogen Equivalent Weight (AHEW) = 36.55g

Therefore, ratio of the L-Tryptophan - ESO = **1 : 4.864** (Theoretical value)

A-8: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of L-Lysine - ESO

Oxirane Oxygen (%) = 7 %
Epoxide Equivalent Weight (EEW) = 228.57 g
Amine Hydrogen Equivalent Weight (AHEW) = 36.55g

Therefore, ratio of the L-Tryptophan - ESO = **1 : 6.254** (Theoretical value)

A-9: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of PEI - ECO

Weight per Epoxide = 601 g/eq
Amine Value = 20 mmol/g.solid
Amine Hydrogen Equivalent Weight (AHEW) = 47.62 g

Therefore, ratio of the PEI - ECO = **1 : 12.62** (Theoretical value)

A-10: Calculation of Epoxide Equivalent Weight and Amine Hydrogen Equivalent Weight and ratio of PEI-10,000 - ECO

Weight per Epoxide = 601 g/eq
Amine Value = 20 mmol/g.solid
Amine Hydrogen Equivalent Weight (AHEW) = 52.91g

Therefore, ratio of the PEI - ECO = **1 : 11.36** (Theoretical value)

APPENDIX B: Solvent selection for the ESO - PEI and ELO - PEI systems

Appendix B indicates the best solvent to be used for the ELO- PEI and ESO - PEI cured samples

Table B-1: Calculation of the amount of extractables for the ELO - PEI cured samples

Sr. No.	Solvent	Initial weight (W_1)(g)	Final weight (Wf)	% Weight loss	Density of the solvent (ρ_s)(g/cc)	Density of the matrix (ρ_m)(g/cc)
1	Chloroform	0.1025	0.072	**29.76**	1.48	1.056223
2	Dichloromethane	0.1367	0.1188	**13.09**	1.326	1.056223
3	Tetrahydrofuran	0.0885	0.073	**17.51**	0.889	1.056223
4	1,4-Dioxane	0.0756	0.0733	**3.04**	1.034	1.056223
5	Acetone	0.0899	0.0842	**6.34**	0.791	1.056223
6	2-butanone(MEK)	0.103	0.0982	**4.66**	0.806	1.056223
7	Ethyl acetate	0.0936	0.0911	**2.67**	0.893	1.056223
8	Butyl acetate	0.1144	0.1144	**0.00**	0.881	1.056223
9	Toluene	0.0866	0.0856	**1.15**	0.865	1.056223
10	Xylenes	0.1062	0.1042	**1.88**	0.88	1.056223

Table B-2: Evolution of *Vr* vs. time for the ELO cured samples

Sr. No.	Solvent	Solvent Uptake (48 hrs)	Solvent Uptake (72 hrs)	Solvent Uptake (96 hrs)	Solvent Uptake (120 hrs)	Solvent Uptake (144 hrs)	Solvent Uptake (168 hrs)	Solvent Uptake (192 hrs)	Solvent Uptake (216 hrs)
1	Chloroform	*	*	*	*	*	*	*	*
2	Dichloromethane	0.4284	0.4424	0.4679	0.4685	0.4692	0.4686	0.4912	0.4915
3	Tetrahydrofuran	0.3822	0.3938	*	*	*	*	*	*
4	1,4-Dioxane	0.5138	0.5160	0.5255	0.5309	0.5534	0.5617	0.5661	0.5661
5	Acetone	0.6179	0.6620	0.6676	0.6940	0.6979	0.6933	0.6986	0.6994
6	2-butanone(MEK)	0.5382	0.6196	0.6290	0.6349	0.6497	0.6386	0.6492	0.6386
7	Ethyl acetate	0.6477	0.6685	0.6803	0.6906	0.7183	0.7137	0.7163	0.7362
8	Butyl acetate	0.6490	0.6919	0.8133	0.7878	0.7373	0.7255	0.8809	0.7367
9	Toluene	0.6355	0.6198	0.7481	0.6443	0.6601	0.6632	0.6601	0.6576
10	Xylenes	0.5865	0.6459	0.8120	0.6449	0.6406	0.6488	0.6556	0.6688

* Could not be measured as the polymer disintegrated during the tests

Table B-3: Calculation of the amount of extractables for the ESO cured samples

| Sr. No.	Solvent	Initial weight $(W_1)(g)$	Final weight (W_f)	% Weight loss	Density of the solvent $(\rho_s)(g/cc)$	Density of the matrix $(\rho_m)(g/cc)$
1	Chloroform	0.1144	0.0586	48.78	1.48	1.004896
2	Dichloromethane	0.1203	0.0587	51.21	1.326	1.004896
3	Tetrahydrofuran	0.2317	0.1221	47.30	0.889	1.004896
4	1,4-Dioxane	0.1728	0.1321	23.55	1.034	1.004896
5	Acetone	0.1621	0.1076	33.62	0.791	1.004896
6	2-butanone(MEK)	0.2293	0.1737	24.25	0.806	1.004896
7	Ethyl acetate	0.1591	0.1255	21.12	0.893	1.004896
8	Butyl acetate	0.1729	0.1062	38.58	0.881	1.004896
9	Toluene	0.152	0.1041	31.51	0.865	1.004896
10	Xylenes	0.1627	0.1074	33.99	0.88	1.004896

Table B-4: Evolution of *Vr* vs. time for the ESO cured sample

Sr. No.	Solvent	Solvent Uptake (48 hrs)	Solvent Uptake (72 hrs)	Solvent Uptake (96 hrs)	Solvent Uptake (120 hrs)	Solvent Uptake (144 hrs)	Solvent Uptake (168 hrs)	Solvent Uptake (192 hrs)	Solvent Uptake (216 hrs)
1	Chloroform	*	*	*	*	*	*	*	*
2	Dichloromethane	0.2675	*	*	*	*	*	*	*
3	Tetrahydrofuran	0.2174	0.2707	0.2848	0.2713	0.2684	0.2875	*	0.2861
4	1,4-Dioxane	0.3617	0.3358	0.3417	0.3478	0.3633	0.3742	0.4708	0.3745
5	Acetone	0.5009	0.4326	0.4621	0.4818	0.5206	0.4899	0.8521	0.5569
6	2-butanone(MEK)	0.3896	0.4487	0.4498	*	*	*	*	0.4438
7	Ethyl acetate	0.5466	0.5333	0.5509	*	*	*	*	0.5408
8	Butyl acetate	0.4140	0.3539	*	*	*	*	*	0.4347
9	Toluene	0.3622	0.3727	0.3781	0.3787	0.3805	0.3918	0.4429	0.4451
10	Xylenes	0.3216	0.3190	0.3304	0.3442	0.3531	0.3685	0.4205	0.3757

* Could not be measured as the polymer disintegrated during the test

**APPENDIX C: Optimization of the curing time**
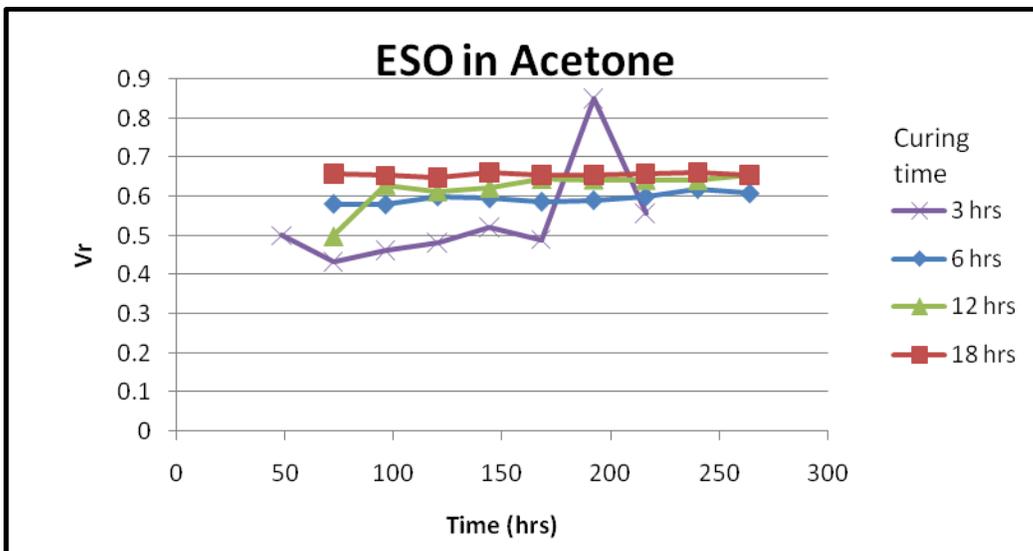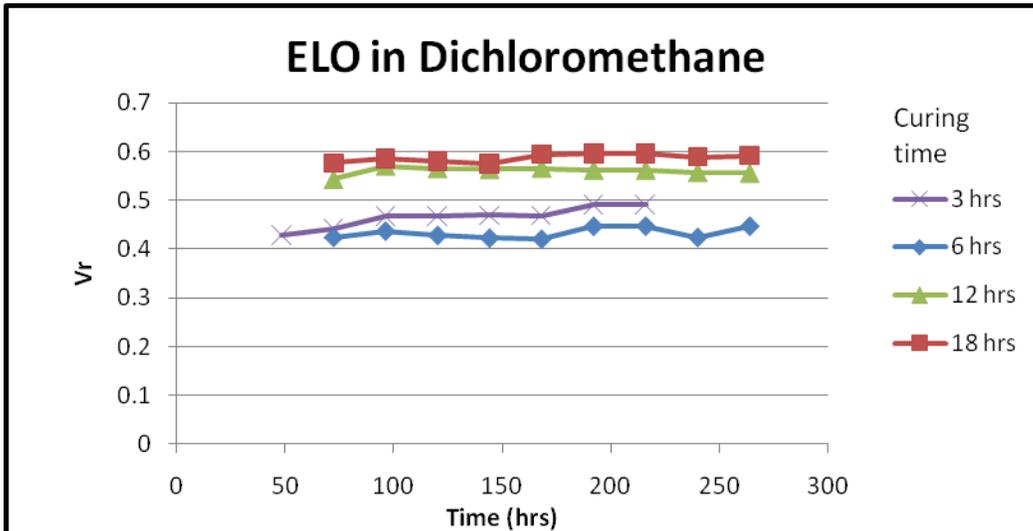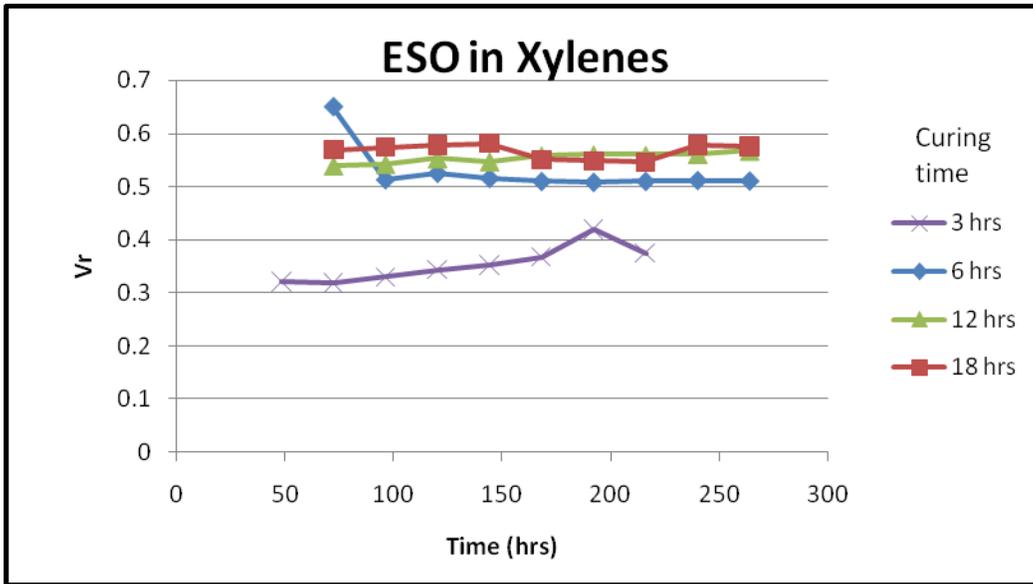
**Figure C- 1: Evolution of *Vr* with respect to curing time for the ELO and the ESO systems**
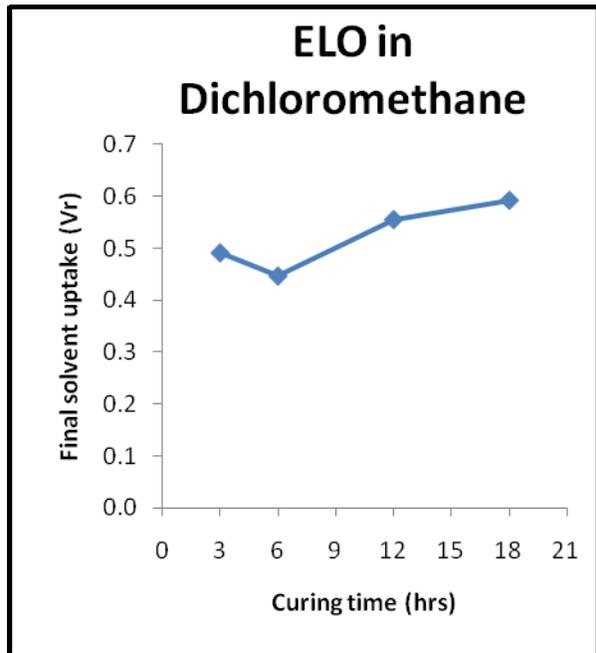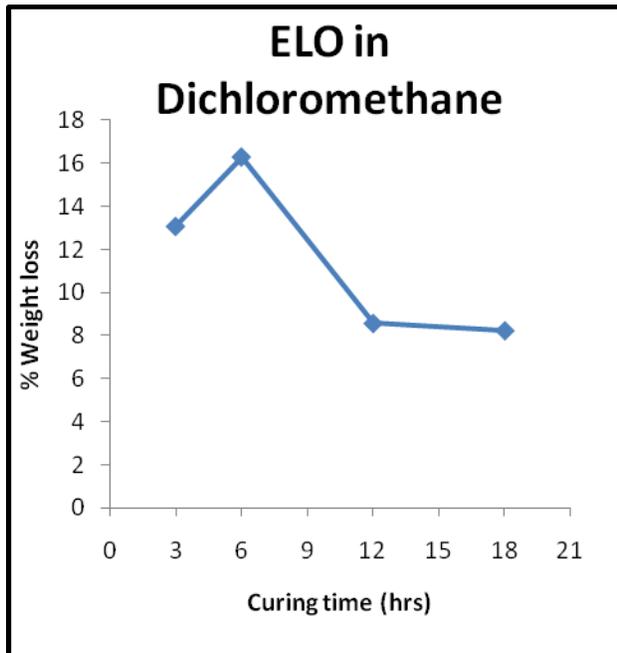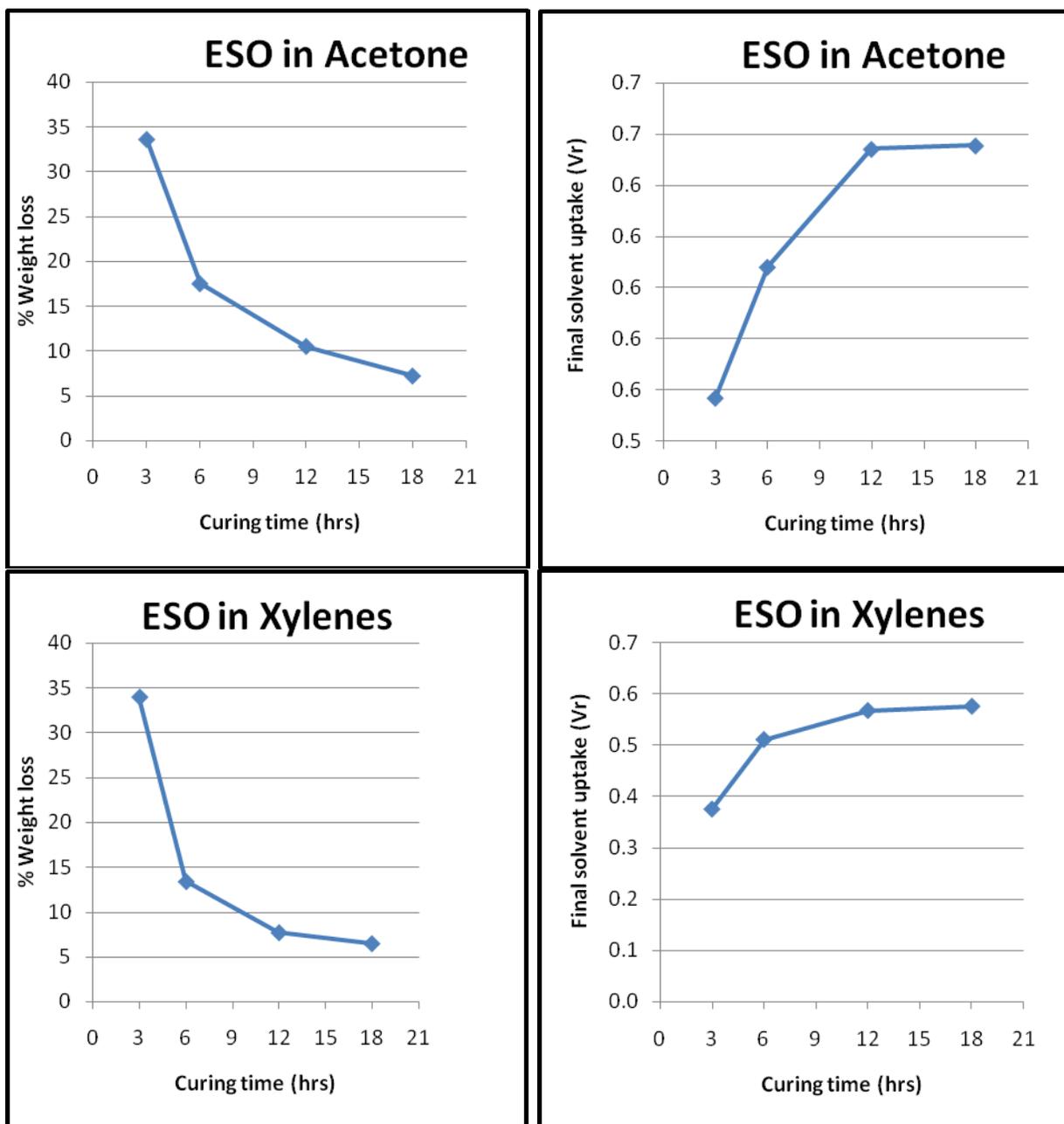
Figure C-2: Evolution of the amount of extractables and *Vr* with respect to curing time for the ELO - PEI and the ESO - PEI systems

APPENDIX D: Optimization of the resin to hardener ratio

Table D-1: Comparison of the solvent uptake values of the optimized bioepoxies cured at 160°C and the samples cured with an excess of PEI

Curing agent	Resin : Hardener	Curing time (hrs)	% Weight loss				Solvent Uptake (*Vr*)				Equilibrium
			DCM	Acetone	Acetone	Xylenes	DCM	Acetone	Acetone	Xylenes	
PEI	1: 1	3	13.09	-	33.62	33.99	0.4915	-	0.5569	0.3757	After 216 hrs
	1: 1	6	16.31	9.68	17.53	13.41	0.4469	0.6365	0.6081	0.5110	After 264 hrs
	1: 1	12	8.59	1.83	10.54	7.72	0.5556	0.7545	0.6542	0.5673	After 264 hrs
	1: 1	18	8.25	0.81	7.25	6.49	0.5926	0.7799	0.6555	0.5756	After 264 hrs
	1: 1.1	6	-	-	16.85	12.50	-	-	0.5912	0.5271	After 216 hrs
	1: 1.1	12	-	-	6.46	3.37	-	-	0.6621	0.6285	After 216 hrs
	1: 1.1	18	5.18	0.42	6.18	4.76	0.6045	0.7921	0.6866	0.6212	After 216 hrs
	1: 1.2	6	-	-	13.02	12.80	-	-	0.6309	0.4908	After 216 hrs
	1: 1.2	12	-	-	5.63	5.04	-	-	0.6495	0.6174	After 216 hrs
	1: 1.2	18	0.94	-3.02	4.49	3.79	0.6022	0.8717	0.6951	0.6276	After 216 hrs
	1: 1.3	12	-	-	4.68	2.56			0.6659	0.6404	After 216 hrs
	1: 1.3	18	-	-4.55	3.66	3.06	-	0.9201	0.6819	0.6427	After 192 hrs
	1: 1.4	12	-	-	3.71	3.04	-	-	0.6833	0.6358	After 216 hrs
	1: 1.4	18	-1.76	-4.65	5.30	3.36	0.6278	0.9022	0.6854	0.6357	After 192 hrs
	1: 1.5	18	-	-0.37	-	-	-	0.8057	-	-	After 240 hrs
	1: 1.6	18	-1.86	-3.70	-	-	0.6295	0.8656	-	-	After 240 hrs
	1: 0.8	6	-	-	20.13	19.47	-	-	0.5801	0.4697	After 192 hrs
	1: 0.8	18	-	-	13.73	-	-	-	0.6180	-	After 192 hrs
	1: 0.9	6	-	-	14.76	17.22	-	-	0.6072	0.4982	After 192 hrs
	1: 0.9	18	-	-	10.48		-	-	0.6509	-	After 192 hrs

* Optimized curing time, Optimized ratio of resin to hardener

Table D-2 Comparison of the Solvent Uptake Values of the Optimized Samples (ELO/ESO) Cured at 160^{0}C and the Sample Cured by taking Excess of Curing Agent (TETA)

Curing	Resin :	Curing	% Weight loss				Solvent Uptake (Final) (Vr)	Equilibrium

TETA			DCM	Acetone	Acetone	Xylenes	DCM	Acetone	Acetone	Xylenes	
	1: 0.9	6	-	-	28.41	22.49	-	-	0.4630		After 240 hrs
	1: 0.9	12	-	-	20.79	19.35	-	-	0.5305	0.4509	After 240 hrs
	1: 1	6		4.35	19.49	13.01	*	0.6940	0.5412	0.4263	After 240 hrs
	1: 1	12	9.27	-0.37	11.98	7.95	0.4805	0.7302	0.6019	0.5170	After 240 hrs
	1: 1	18	-	3.55	14.48	14.14	*	0.7057	0.6061	0.4923	After 240 hrs
	1: 1.1	6	-	3.05	-	-	*	0.7092	-	-	After 240 hrs
	1: 1.1	12	-	0.24	8.51	5.35	-	0.7322	0.63	0.55	After 240 hrs
	1: 1.1	18	-	2.15	-	11.50	*	0.7365	*	0.5312	After 240 hrs
	1: 1.2	6	2.99	1.66	-	-	0.5538	0.7472	-	-	After 240 hrs
	1: 1.2	12		0.07	7.23	3.93		0.7429	0.65	0.58	After 240 hrs
	1: 1.2	18	3.05	0.55	12.20	11.13	0.5818	0.7660	0.6180	0.5410	After 240 hrs
	1: 1.3	6	-	-	12.87	7.23	-	-	0.5913	0.5241	After 240 hrs
	1: 1.3	12	-	1.22	7.61	4.14	-	0.7283	0.6430	0.5678	After 240 hrs
	1: 1.3	18	-	1.95	-	-	-	0.7589			After 240 hrs
	1: 1.4	6	-	-	11.31	4.94	-	-	0.6049	0.5386	After 240 hrs
	1: 1.4	12	-	1.31	6.74	3.97	-	0.7349	0.6487	0.5750	After 240 hrs
	1: 1.4	18	-	-0.29	-	-	-	0.7641	-	-	After 240 hrs
	1: 1.5	12	-	-0.04	-	-	-	0.7444	-	-	After 240 hrs
	1: 1.5	18	-	1.24	-	-	-	0.7468	-	-	After 240 hrs
	1: 1.6	12	-	7.75	-	-	-		-	-	After 240 hrs
	1: 1.6	18	-	-1.47	-	-	-	0.7805	-	-	After 240 hrs
			ELO		ESO		ELO		ESO		

* Optimized curing time, Optimized ratio of resin to hardener

**APPENDIX E: Comparison of the bioepoxies**
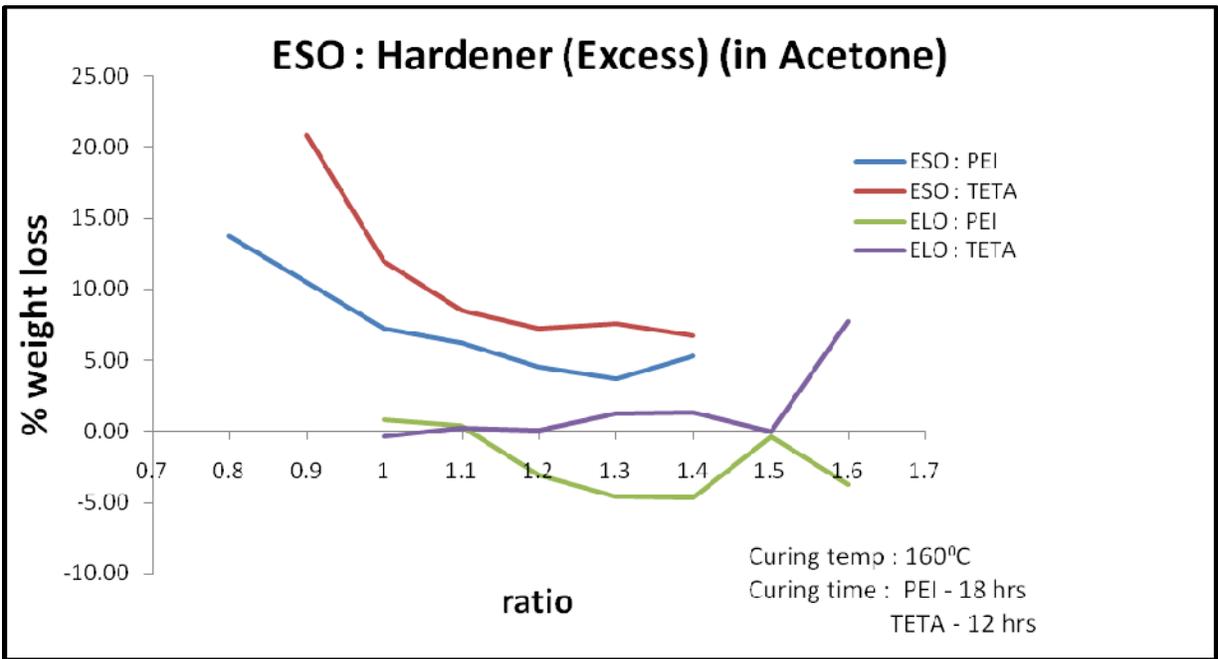
Figure E-1: Comparison of the weight loss in the ELO and ESO systems with respect to different ratios of hardener (PEI or TETA)
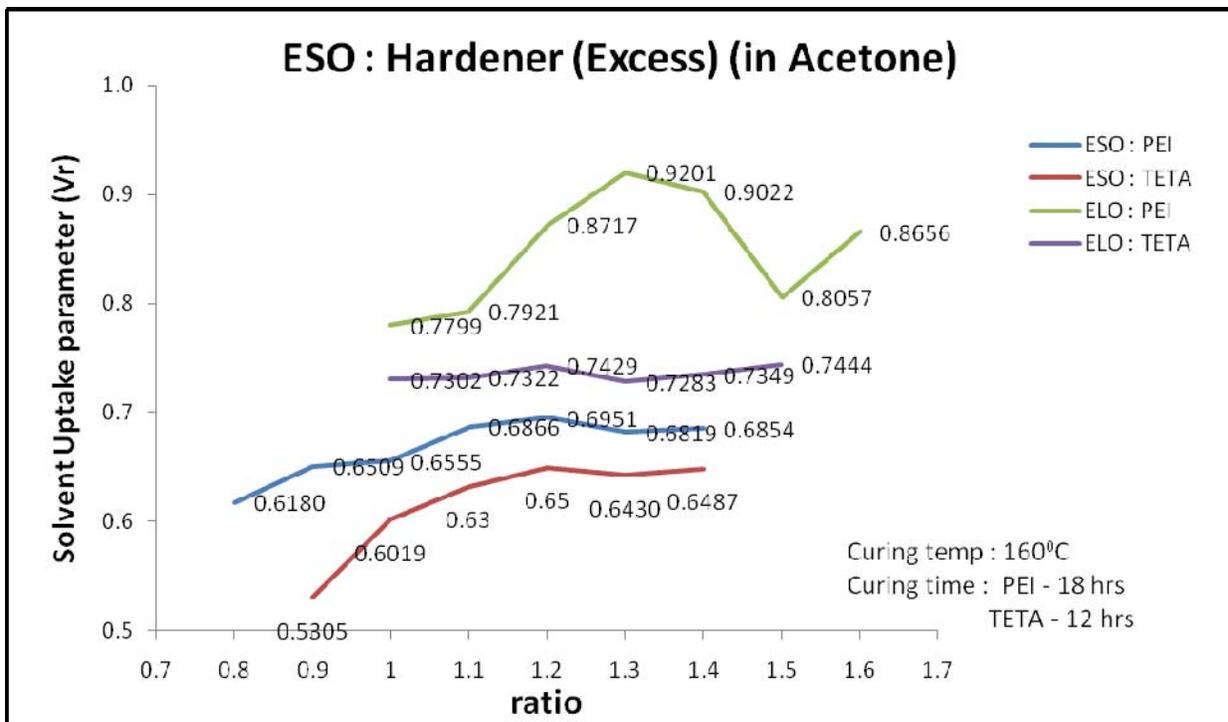

Figure E-2: Comparison of *Vr*. for the ELO and the ESO systems with respect to different ratios of hardener (PEI & TETA)

APPENDIX F: IR Imaging analysis
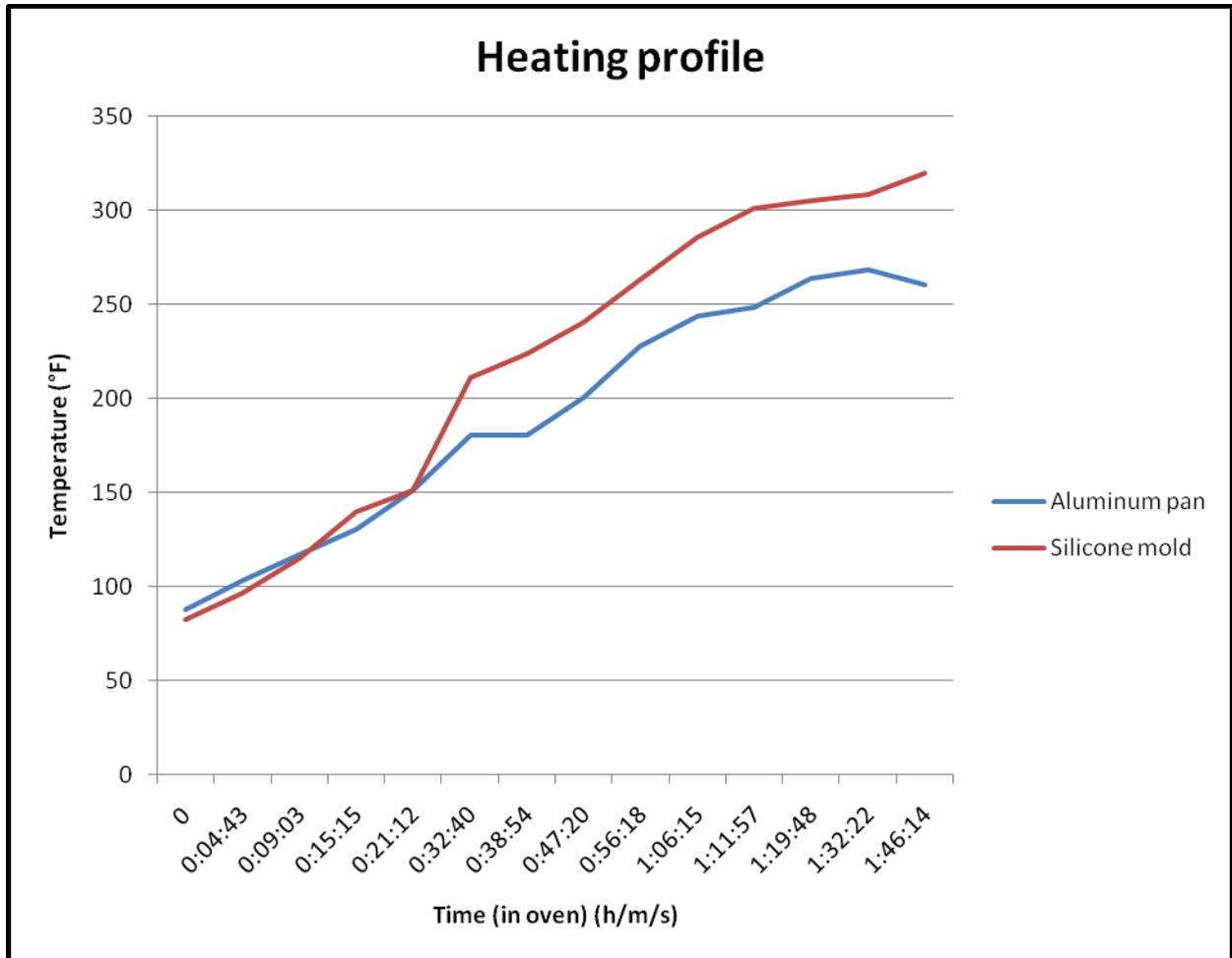
Figure F-1: Comparison of the heating profile in the silicone mold and in the aluminum pan as measured by IR imaging

Table F-1: Temperature at different locations of the molds in the convection oven

| Heating	Oven temp (°F)	Label	Mold	Min (°F)	Max (°F)	Max-Min	Avg (°F)	Std. Dev
1 hr 49 mins	320	AR01	Aluminum	176	212.5	36.5	190.2	7.7
		AR02	Silicone(B)	274.2	293.2	19	290.3	3.7
		AR03	Silicone (1)	289.7	310.1	20.4	298.9	4
		AR04	Silicone (2)	291.6	309.2	17.6	300.6	3.6
		AR05	Silicone (3)	292.4	308.8	16.4	299.9	3.5
		AR06	Silicone (4)	289.9	307.8	17.9	298.9	4
		AR07	Silicone (5)	289.1	308.3	19.2	298.4	3.7
		AR08	Silicone (6)	290.8	307	16.2	298.4	3.5
		AR09	Silicone (7)	292.3	306.9	14.6	298.9	3.2
		AR10	Silicone (8)	290.8	305.6	14.8	298.1	3.3
		AR11	Silicone (9)	292.6	304.7	12.1	298.3	2.5
		AR12	Silicone (10)	289.2	303.7	14.5	296.8	3.4
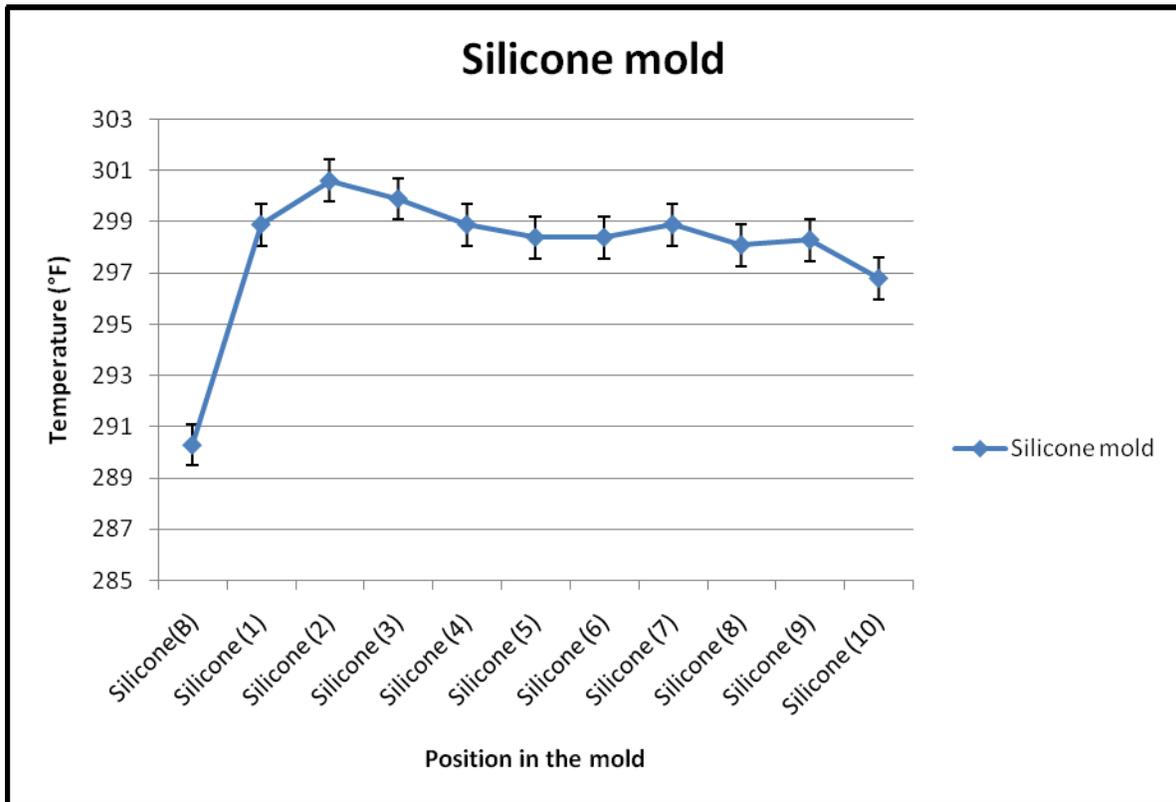
Figure F-2: Uniformity of the heating at different locations in the silicone mold in the convection oven