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## Ferulic bio-based monomers for UV-curing



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## **RIASSUNTO**

Questo lavoro di tesi si focalizza sulla sintesi di monomeri foto-reticolabili e sulla caratterizzazione dei film derivati tramite fotopolimerizzazione attraverso l'analisi di proprietà termiche, meccaniche e reologiche.

Nel contesto di uno sviluppo sostenibile e nella ricerca di alternative all'utilizzo di fonti derivanti dal petrolio, questa tesi si pone come obbiettivo quello della valorizzazione di un derivato della lignina: l'acido ferulico (FA). Esso è presente nei cereali, in alcuni tipi di ortaggi e come detto precedentemente può essere estratto dalla lignina.

Il primo capitolo presenta il background di questa ricerca, mentre il secondo descrive in modo dettagliato le caratteristiche chimiche della molecola, le tecniche di funzionalizzazione adoperate e le possibili applicazioni finali con considerazioni riguardanti la tecnica di fotopolimerizzazione.

L'acido ferulico fa parte della famiglia di acidi cinnamici insieme all'acido sinapico e a quello caffeico (Figura 1). La presenza dell'anello benzenico conferisce rigidità e stabilità termica alla molecola. Negli ultimi anni si è studiata la sua omopolimerizzazione nel tentativo di replicare la struttura chimica del polietilene tereftalato (PET). L'acido ferulico inoltre, si presenta ad una vasta gamma di funzionalizzazioni data la presenza di tre gruppi funzionali nella sua struttura: il fenolo, l'acido carbossilico e il doppio legame. Attualmente l'FA viene utilizzato come antinfiammatorio, antiossidante, assorbitore di raggi UV e nel packaging alimentare.



Figura 1: struttura chimica degli acidi cinnamici.

La tecnica di polimerizzazione adottata in questo lavoro di tesi è la fotopolimerizzazione. Questa scelta è stata dettata poiché rispetto al curing termico presenta numerosi vantaggi tra cui: tempi di reazione più brevi, minor consumo energetico, la possibilità di evitare l'utilizzo di solventi e temperature elevate. La fotopolimerizzazione può avvenire per via radicalica o via ionica. In questo studio verrà approfondita la reazione tiolo-ene che viene definita "reazione click" siccome la reazione è stechiometrica, garantisce alte percentuali di conversione e può avvenire in svariate condizioni. La particolarità di questa reazione radicalica è il fatto di procedere secondo un

meccanismo a stadi: inizio, propagazione e terminazione. Quando il fotoiniziatore viene irraggiato strappa l'idrogeno allo zolfo formando un radicale che attaccata un doppio legame C=C, in questo modo si origina un legame S-C. Come prodotto si forma anche un altro radicale tiolo che a sua volta può attaccare un altro doppio legame carbonio-carbonio. Un importante vantaggio di questa reazione è l'assenza dell'inibizione da ossigeno, questo rende non necessario l'utilizzo di atmosfere inerti. Questa caratteristica deriva dalla labilità del legame che l'ossigeno forma con il radicale -S•.

Il terzo capitolo si focalizza nelle prime sottosezioni sulla presentazione delle tecniche utilizzate per valutare la sintesi dei derivati dell'FA e sulle tecniche di caratterizzazione dei coatings ottenuti. Tutti i metodi usati per valutare la sintesi hanno confermato l'ottenimento dei prodotti desiderati. I test eseguiti sui film hanno permesso di valutarne le proprietà termiche, meccaniche e reologiche.

La sezione 3.3 è dedicata alla descrizione delle sintesi utilizzate. La prima sintesi eseguita ha avuto come obbiettivo l'allilazione dei due gruppi funzionali principali: il fenolo e l'acido carbossilico. Successivamente si è cercato di isomerizzare il mono allile. Si è eseguita inoltre un'idrogenazione del doppio legame seguita da una successiva allilazione del derivato creato.

La prima sintesi, Schema 1, ha seguito i passaggi seguenti: solubilizzazione dell'idrossido di sodio e acido ferulico in etanolo, aggiunta di cloruro di allile, riflusso e agitazione della miscela per una notte a 55 °C. Le condizioni di reazione sono state settate in base a uno studio precedentemente condotto su una molecola simile. La reazione è stata termina con l'abbassamento della temperatura; a cui sono seguiti: l'evaporazione del solvente, il trattamento con acido, estrazione con dietil-etere e trattamento con solfato di magnesio. La reazione è stata monitorata mediante la tecnica di cromatografia strato sottile (TLC) e spettroscopia di risonanza magnetica nucleare protonica (<sup>1</sup>H-NMR). Il prodotto ottenuto ha mostrato la presenza di reagente iniziale in tracce.

Tenendo conto della difficoltà nel purificare il prodotto si è scelto di sostituire: il cloruro di allile con il bromuro di allile, l'idrossido di sodio con il carbonato di potassio e si è utilizzato l'acetone come solvente. Le condizioni di reazione sono state mantenute invariate.



Schema 1: allilazione dell'acido ferulico.

Tramite la reazione con il bromuro di allile si sono ottenuti due prodotti: il mono allile (A1FA) e il bi allile (A2FA). Il mono-allile è stato ottenuto tramite il trattamento con idrossido di sodio.

La reazione di mono allilazione ha previsto, come in precedenza, la dissoluzione dell'acido ferulico in acetone, quindi l'aggiunta il carbonato di potassio (4 equivalenti rispetto al FA) e l'addizione di bromuro di allile. La reazione è avvenuta a 55 °C per una notte ed è terminata con riduzione della temperatura e la filtrazione del solido. Il solvente residuo viene fatto evaporare e il prodotto viene disciolto in una miscela di etanolo e idrossido di sodio 2 M. La soluzione viene riscaldata a 70 °C per circa 2 ore e, una volta raffreddata, viene trattata con acido cloridrico. Questo permette la precipitazione del prodotto, che una volta filtrato, viene fatto essiccare in vuoto per una notte in modo da eliminare le ultime tracce di solvente. La resa della reazione è stata del 95 %. Il monitoraggio è stato fatto con TLC mentre la caratterizzazione del prodotto è stata effettuata sia con <sup>1</sup>H-NMR che con l'analisi di spettroscopia di risonanza magnetica nucleare al carbonio (<sup>13</sup>C-NMR). Per confermare i risultati si sono anche effettuate analisi di spettrocopia IR di riflettanza totale attenuata (ATR-FTIR).

La sintesi del propenile derivato dal A1FA è avvenuta tramite due diverse possibili reazioni. La prima ha previsto una reazione con 18-corona-6 (18-c-6) e il potassio t-butossido (t-ButOK) in dimetilsolfossido (DMSO). La reazione avviene a 50-60 °C per una notte. Dopo il raffreddamento, la soluzione è stata trattata con acido cloridrico, il prodotto desiderato precipita e viene filtrato. La seconda via utilizzata prevede l'uso del catalizzatore di Grubbs di seconda generazione.

La reazione di bi allilazione (A2FA) ha avuto uno step iniziale identico alla reazione di monoallilazione: solubilizzazione dell'acido ferulico in acetone, aggiunta di carbonato di potassio e di bromuro di allile, agitazione e riflusso per 24 ore a 55 °C. I passaggi successivi sono stati: diminuzione della temperatura, filtrazione del solido, estrazione del prodotto con diclorometano. Come in precedenza, sono state utilizzate analisi di caratterizzazione: TLC e <sup>1</sup>H-NMR per monitorare la reazione; FTIR, <sup>1</sup>H-NMR e <sup>13</sup>C-NMR per caratterizzare il prodotto. La resa della reazione si è attestata al 82 %.

Un ulteriore sintesi è stata l'idrogenazione del FA. L'acido ferulico, disciolto in metanolo, viene addizionato in un pallone da 500 mL (sigillato tramite tappo in gomma), dove precedentemente è stato introdotto il catalizzatore Pd/C ed è stato eliminato l'ossigeno tramite insufflaggio di azoto. La reazione è iniziata fornendo un'atmosfera di idrogeno all'interno del pallone e dura per 24 ore a temperatura ambiente. Una volta terminata la reazione, la soluzione è stata filtrata per eliminare il catalizzatore e il solvente è stato eliminato tramite rotoevaporazione. Il prodotto finale, h-FA, è stato caratterizzato con le tecniche precedenti. In questo caso la resa è stata del 95 %.

La reazione di mono e bi allilazione è stata eseguita, nella stessa metodologia descritta in precedenza, su questo nuovo prodotto. Si sono ottenuti così due nuovi prodotti: h-A1FA e h-A2FA. Le rese delle reazioni sono state del 96 % e 93 % rispettivamente.

Come ultima sintesi si è optato per una esterificazione dell'acido residuo su entrambi i mono allili derivati ottenendo così due esteri, EA1FA e h-E1FA derivanti rispettivamente dal A1FA e h-A1FA. In questo caso la sintesi ha previsto la solubilizzazione del reagente in metanolo, l'aggiunta di acido solforico (H<sub>2</sub>SO<sub>4</sub>) come catalizzatore della reazione che avviene riscaldando a una temperatura di 60 °C sotto riflusso per circa 20 ore. Una volta terminata la reazione il prodotto è stato estratto con acetato di etile lavando la soluzione con una soluzione satura di bicarbonato di sodio e cloruro di sodio. La soluzione è trattata con solfato di magnesio per eliminare tracce di acqua. Infine, si ha l'evaporazione del solvente. Il prodotto EA1FA lo si è ottenuto con una resa del 90 %, invece per h-EA1FA la resa è stata 94 %.



Schema 2: esterificazione del derivato h-A1FA.

La sezione 3.4 mostra uno studio fatto sulla possibile fotodimerizzazione del bi allile derivato, A2FA. La presenza del gruppo cinnamico all'interno della molecola presenta la possibilità di una reazione di ciclo addizione [2+2] al doppio legame con formazione del dimero. Questa avviene grazie all'esposizione di raggi UV con  $\lambda > 250$  µm. Studi precedenti rivelano la possibilità di interazione in modo reversibile, che risultano in una creazione ed eliminazione del doppio legame a seconda della lunghezza d'onda dei raggi UV che irradiano la molecola.

La reazione è stata monitorata con RT-FITR variando la temperatura del cristallo in modo da poter esaminare una possibile influenza della stessa sulla reazione. Il prodotto è stato analizzato anche con altre tecniche, in modo da confermare il primo risultato della misura in tempo reale, quali <sup>1</sup>H-NMR e cromatografia di esclusione molecolare (SEC). Un'ultima tecnica usata è stata la misura UV-VIS di una soluzione 0.02 g/mL sottoposta a irraggiamento UV.

La sezione 3.5 descrive la formulazione dei film. I prodotti utilizzati sono stati: A2FA, h-A2FA e h-EA1FA. Si procede tramite reazione tiolo-ene utilizzando un fotoiniziatore radicalico. Il tiolo usato è stato trimetilolpropano tris(3-mercaptopropionato) invece il fotoiniziatore è stato Irgacure 819. Lo Schema 3 riporta un'illustrazione della reazione di reticolazione.

La formulazione dei film ha previsto un rapporto stechiometrico 1:1 di equivalenti di tiolo e doppio legame e una percentuale in peso di fotoinizaitore dello 0.5 % phr cioè calcolata sul totale della resina impiegata per il coating.



*Schema 3:* fotopolimerizzazione tra h-A2FA e TMP con uno zoom sulla creazione del nuovo legame.

L'esposizione ai raggi UV è stata garantita da una lampada al mercurio Dymax ECE 5000 Flood con intensità di 110 mW/cm<sup>2</sup>. Il tempo di irraggiamento è stato di 1 minuto per la formazione dei film. Le analisi di caratterizzazione sono state: analisi foto-reologica per indagare la cinetica di reazione, analisi FTIR per valutare la conversione attraverso uno studio pre e post curing, analisi termica dinamo meccanica (DMTA) e calorimetria differenziale a scansione (DSC) per studiare proprietà meccaniche e termiche.

Il quarto capitolo descrive gli esiti ottenuti per quanto riguarda la parte di sintesi dei prodotti e le proprietà dei film.

La sezione 4.1 riguarda l'allilazione. La reazione 1C ha portato ad una conversione totale del reagente di partenza, confermata dai dati NMR. Si è così ottenuto il composto monofunzionale A1FA e il bifunzionale A2FA. I risultati FTIR, mostrati in Figura 2, convalidano le analisi precedenti in quanto si notano la scomparsa del picco relativo al fenolo e lo shift del picco relativo al carbonile visto la formazione del legame estere.



Figura 2: spettri FTIR dei derivati dell'acido Ferulico.

La reazione di idrogenazione ha portato alla formazione del prodotto desiderato verificato tramite analisi FTIR e NMR. La reazione di allilazione di questo derivato ha originato il monofunzionale, h-A1FA, e il bifunzionale, h-A2FA. La Figura 3 presenta gli spettri <sup>1</sup>H-NMR dei composti ottenuti a partire dall'idrogenazione dell'FA.



*Figura 3:* spettri NMR dei composti derivati dall'idrogenazione dell'acido Ferulico e successiva allilazione.

La reazione di esterificazione, eseguita su entrambi i monomeri monofunzionali, ha portato alla formazione di due prodotti che sono stati caratterizzati tramite analisi NMR e FTIR come in precedenza.

Per quanto riguarda la reazione di isomerizzazione, il prodotto è stato sintetizzato ma la procedura di purificazione ha riscontrato alcuni problemi. Il primo problema raffrontato è la tendenza di reazione da parte del propenile con l'acido, il secondo è l'utilizzo di DMSO come solvente, questo risulta essere difficoltoso nella rimozione una volta terminata la reazione.

La sezione 4.6 è dedicata ai risultati della fotodimerizzazione. Le misure spettroscopiche in tempo reale (RT-FTIR), Figura 4, fanno notare i seguenti cambiamenti: shift dei picchi del carbonile da 1705 cm<sup>-1</sup> a 1740 cm<sup>-1</sup>; riduzione dell'area dei picchi da 1660 a 1550 cm<sup>-1</sup>, responsabili dello stretching dei doppi legami cinnamici; riduzione del valore massimo di assorbanza del picco a 1100 cm<sup>-1</sup> del gruppo cinnamico. Questo permette di affermare che la reazione di dimerizzazione è avvenuta e la variazione dei segnali chiave dei gruppi funzionali coinvolti è la conferma.



Figura 4: spettro in tempo reale della reazione UV di fotodimerizzazione del A2FA.

Le analisi NMR confermano i risultati antecedenti in quanto si vede una variazione degli integrali responsabili degli idrogeni in posizione  $\alpha$  e  $\beta$  rispetto a quelli in posizione 11 e 11' appartenenti al gruppo allilico. La figura 5 illustra i risultati ottenuti.



*Figura 5:* spettri NMR prima, verde scuro, e dopo, verde chiaro, l'esposizione agli UV del campione A2FA. Viene evidenziata a lato la variazione del valore degli integrali prima e dopo l'esposizione e nei quadrati tratteggiati rossi vengono evidenziati i nuovi picchi.

Le ulteriori analisi effettuate, SEC-DMF, confermano la presenza di una nuova molecola avente circa peso molecolare doppio rispetto al reagente di partenza, dando così una prova aggiuntiva della avvenuta reazione.

In ultima analisi anche la misura UV-VIS effettuata sulla soluzione conferma una riduzione del picco di assorbanza responsabile del doppio legame verificando così la reazione di dimerizzazione.

La caratterizzazione dei coatings, sezione 4.7, ha conseguito i seguenti risultati.

In primo luogo, il test di fotoreologia ha permesso di conoscere la cinetica di reazione per le due principali formulazioni e l'effetto dell'aggiunta del monomero monofunzionale. Il monomero A2FA è meno reattivo della formulazione contenente h-A2FA, Figura 6, data la pendenza minore di crescita del modulo e il periodo iniziale di induzione prima dell'avvio della reazione. Inoltre, il modulo raggiunto per la formulazione A2FA è minore del secondo.

Il secondo risultato importante è l'effetto dell'aggiunta di co-monomero, h-EA1FA: il modulo finale diminuisce all'aumentare della percentuale di monofunzionale. Questo risultato è spiegabile considerando la minore densità di reticolazione, conseguenza dell'introduzione del monofunzionale. La Figura 7 presenta questo risultato.



Figura 6: andamento del modulo delle due formulazioni principali per il test fotoreologico.



Figura 7: variazione del modulo secondo la percentuale di monofunzionale addizionata.

Come seconda analisi si è eseguito uno studio pre e post curing attraverso un'analisi FTIR.

I punti chiave in quest'analisi sono la scomparsa dei due picchi responsabili della presenza del tiolo (S-H 2550 cm<sup>-1</sup>) e del doppio legame (C=C 1540 cm<sup>-1</sup>). Durante la reazione di cross-link questi gruppi funzionali reagendo formano il legame e il segnale iniziale scompare. In Figura 8a, 8b e 8c viene evidenziato questo cambiamento nello spettro relativo alle composizioni testate. Il calcolo delle conversioni, Tabella 1, e l'analisi degli spettri hanno portato al test di un ulteriore formulazione differente considerando A2FA come trifunzionale. Infatti, valutando la conversione del monomero A2FA considerato come bifunzionale, la reazione non va a completezza, la reazione del tiolo si attesta attorno al 85 %, invece considerando A2FA come trifunzionale la conversione del tiolo è pressoché totale e si ha una marcata riduzione del segnale C=C rispetto al caso bifunzionale, evidenziata anche in Figura 8c. In questo modo si stabilisce la possibilità di reazione anche del doppio legame cinnamico. Questo fatto viene altresì evidenziato dallo shift verso destra del segnale del carbonile attorno ai 1700 cm<sup>-1</sup>.



Figura 8: risultati FTIR per la resina A2FA.



*Figura 8b:* FTIR pre e post foto reticolazione per la resina contenente h-A2FA.



Figura 8c: spettri pre e post cura per il coating A2FA trifunzionale.

Successivamente si è studiata la risposta meccanica del materiale in temperatura attraverso un'analisi DMTA. I risultati sono mostrati in Figura 9. La  $T_g$  viene valutata come picco di Tan $\delta$  e il valore più alto è stato di 24.1 °C per A2FA trifunzionale, poi 20.1 °C per A2FA e infine 0.6 °C per h-A2FA. A2FA trifunzionale origina più cross-link che, irrigidendo la struttura, fanno aumentare la  $T_g$  e il modulo nel plateau gommoso. Per quanto riguarda la  $T_g$  della resina h-A2FA la forte diminuzione di circa 20 °C è dettata dalla variazione di struttura chimica. La presenza del doppio legame cinnamico rinforza e irrigidisce il network facendo aumentare la temperatura di transizione vetrosa del network.



*Figura 9:* T<sub>g</sub> dei coating analizzati tramite DMTA.

La Figura 10 infine riporta i risultati ottenuti in termini di modulo elastico. Anche quest'ultimo valore è in accordo con i precedenti. Il valore maggiore di E' è stato ottenuto per A2FA trifunzionale. Il valore intermedio si ha per h-A2FA il quale, a differenza della resina A2FA, raggiunge maggiore conversione, quindi un numero maggiore di cross-links fa aumentare il modulo nel plateau gommoso. Infine, il valore più basso di E' è stato ottenuto per la resina A2FA considerata come bifunzionale. I valori di E' nel plateau gommoso per quanto riguarda A2FA bifunzionale e h-A2FA sono anche in accordo con i valori ottenuti durante i test fotoreologici.

L'introduzione del monomero monofunzionale risulta in un abbassamento della  $T_g$  e del modulo E'. Questi risultati sono stati usati per il calcolo della densità di reticolazione tramite l'equazione 1.

$$v_c = \frac{E'}{3RT} \tag{1}$$

dove  $v_c$  è il numero di moli per unità di catena per unità di volume, E' è il modulo nel plateau gommoso, R è la costante dei gas e T è la temperatura valutata come T<sub>g</sub> + 50 °C.

La tabella 1 riassume i valori ottenuti in base alle differenti tecniche utilizzate. Come si può vedere una percentuale maggiore di co-monomero porta a una riduzione della densità di cross link visto la minor possibilità di reticolare che è intrinseca a un monomero monofunzionale.



Figura 10: andamento di E' in funzione della temperatura, analisi DMTA.

Formulation	Conversioni (S-H)	T <sub>g</sub>	Е'	$\nu_{\rm c}$
	0⁄0	°C	Ра	mmol/cm <sup>3</sup>
A2FA	86	20.1	2.08E+06	258
A2FA (trifunctional)	99	24.1	6.38E+06	781
A2FA+5% h-EA1FA	85	18.1	1.04E+06	130
A2FA+10% h-EA1FA	85	17.6	5.65E+05	71
A2FA+15% h-EA1FA	83	12.8	2.60E+05	33
h-A2FA	99	0.6	5.38E+06	711
h-A2FA+5% h-EA1FA	100	-0.2	4.87E+06	645
h-A2FA+10% h-EA1FA	100	-2.4	3,75E+06	500
h-A2FA+15% h-EA1FA	99	-5.0	2,85E+06	384

*Tabella 1:* calcolo della densità di reticolazione secondo i risultati della DMTA e conversioni ottenute dall'analisi FTIR.

L'ultima caratterizzazione effettuata è stata l'analisi DSC. Il dato rilevante di questa misura è la determinazione della  $T_g$ . I risultati presentano lo stesso trend visto per l'analisi DMTA e questo conferma la validità di entrambe le analisi. Anche in questo caso la resina avente A2FA, considerato come trifunzionale, ha presentato la più alta  $T_g$ , Figura 11. Inoltre, come in precedenza, all'aumentare della percentuale di co-monomero si ha una riduzione della  $T_g$  (Figura 12) considerando la diminuzione di cross-links all'interno del network.



Figura 11: risultati analisi DSC per i coating studiati.



*Figura 12:* trend di diminuzione della  $T_g$  proporzionale all'aumento di monomero monofunzionale nelle rispettive formulazioni principali. A2FA in rosso e h-A2FA in blu. In verde è stata riportata la curva per A2FA trifunzionale.

Le conclusioni sono riportate nel capitolo 5.

Come primo obiettivo si sono riusciti a sintetizzare monomeri sensibili agli UV, in particolare mono e bi funzionali. La parte di sintesi ha coinvolto reazioni di idrogenazione, allilazione ed esterificazione. Le sintesi sono state effettuate seguendo modelli standard, ma in particolare nell'allilazione si è testato per la prima volta l'uso di allile clorica e acetone come reagenti con l'acido Ferulico.

La formulazione di coating ha ottenuto buoni riscontri utilizzando i reagenti liquidi, in particolare A2FA, h-A2FA e h-EA1FA.

La caratterizzazione fotoreologica ha evidenziato una reazione estremamente rapida per il monomero h-A2FA rispetto al A2FA, il quale, nonostante un breve tempo di induzione, riesce a reticolare. L'analisi FTIR ha indicato la reattività possibile del gruppo cinnamico testimoniata dall'aumento di conversione finale quando si è testato il monomero A2FA come trifunzionale. Le

analisi termomeccaniche hanno evidenziato l'influenza della struttura chimica, in particolare come la presenza del doppio legame cinnamico faccia variare le proprietà del reticolo. Infatti, la  $T_g$  è più alta per la formulazione avente il doppio legame (A2FA), che irrigidendo la struttura, fa innalzare la temperatura di transizione vetrosa. Il valore del modulo nel plateau gommoso rispecchia i valori di conversione con un valore massimo per la formulazione con A2FA trifunzionale. Il network creato ha una densità di cross-link più elevata che comporta un modulo maggiore rispetto alle formulazioni precedenti. Le analisi DSC confermano il trend visto per le analisi DMTA convalidando i risultati finali.

## 1. Introduction

#### 1.1. Sustainable development goals introduced by the United Nations

The United Nation (UN) in 2015 has adopted an agreement based on 17 goals in order to create a better future for the planet. Their ami is to solve the environmental, social and humanitarian issues. The government were in agreement to set the deadline on 2030. The goals number 9 and 13, which concern the sustainable industrialization and the climate action respectively, are the most relevant with the concept of this work.

The purpose of this study is to investigate bio-based renewable materials in order to avoid the fossil-fuel derivates and to reduce the greenhouse gases emission [1].

#### 1.2. Aim of the study

Plastics comprise a large variety of materials with outstanding mechanical and chemical properties. Nowadays they have become almost irreplaceable in our life. A study reports that approximately 8300 Mt of virgin plastic have been produced and 6300 Mt of plastic waste have been discarded in 2015. Only 9 % of the total plastic waste has been recycled. The remaining plastic amount has been disposed as following: approximately 12 % has been incinerated, 79 % has been either placed on landfill or thrown on the natural environment [2]. In order to reduce the plastics environmental impact, different strategies have been proposed such as the development of greener protocols and the use of bio-based polymers [3].

Due to their customizable properties, polymer coatings are an ideal choice in many applications.

The scope of this study is to investigate bio-based monomers with the aim of finding a replacement of conventional petroleum-based polymers in the field of coating technology.

The synthesis protocols were selected taking into consideration all the possible green alternatives. In order to select the best sustainable route, the UV-curing technology was chosen as cross-linking method over conventional thermal curing. In fact, the UV-curing has many advantages over the thermal one. For example, it has a lower energy consumption and requires shorter reaction time.

This work starts with the detailed description of the synthesis of some Ferulic acid derivatives (Section 3.3). A particular section (Section 3.4) is dedicated on the photodimerization in which particular stress is given to the formation of this particular molecule. Then the UV-curing of some of those derivatives is described (Section 3.5) followed by a deep investigation on the thermal and mechanical properties of the obtained films (Section 4).

### 2. Background

#### 2.1. Ferulic acid

Ferulic acid (FA) is a naturally occurring trans-cinnamic acid derivated (HCAs) [4]. It was discovered in the 1866 as a component of *Ferula foetida* Reg. (*Umbelliferae*), the name of the molecule derives from the plant from which it is extracted [5]. FA belongs to p-hydroxycinnamic family along with caffeic acid and sinapic acid. It is a phenolic compound its structure is showed in Figure 2.1 [6].

In nature FA is produced in the metabolic network that rise lignin, coumarins, ligands, and flavonoids; its synthesis follows the shikimate pathway [7]. Thus, ferulic acid is present in all type of the plants, in particular in the outer birch bark [8]. The total amount of FA is different in whole grain with respect to the one in the bran, but it also varies according to the cereal species considered [9].



Figure 2.1: structure of hydroxycinnamic acid [6].

Among the different biomass, lignin is the second most diffuse organic biopolymer (after cellulose) representing 30 % of biosphere organic carbon. FA is present as cross-linker between lignin and polysaccharides to ensure rigidity in cell walls. Lignin can be obtained as by-product of pulp and paper industry without damaging as well as from the food production of crops and cereals. However, the process used for the separation of the different biopolymers affects the final quality of the extracted compounds [10].

FA is present in plant tissue in two different forms: conjugate and free. It is usually concentrated in the bran of grains, peel of fruits, roots and peel of vegetables. [11] The conjugated form is often esterified with specific polysaccharides and it is mostly in the trans-isomeric form [12]. In the maize the FA content is around 3-4 % of the dry weight representing from 216 to 2400 mg for 100 g of product [13]. This percentage is almost the same considering different types of fruit [7].

HCAs have obtained a crucial role in the polymer innovation since they have good mechanical and chemical properties originated by presence of an aromatic ring inside the chemical structure. They also can be functionalized to adapt the material properties according specific applications.

Ferulic acid can be synthetized in a green way the FA by following an enzymatical protocol. For example, Uraji et al. [14], reports the success of the enzymatic production of FA from defatted rice bran. This group also suggested that the enzymes (a-L-arabinofuranosidase, multiple xylanases, and an acetyl xylan esterase) derived from *Streptomyces* can be used for the extraction of FA from sources like raw rice bran, wheat bran and corncob. Another study presents the use of *Immobilized Candida Antarctica lipase B* (CALB) to obtain the bio-based monomer [15].

The main roles of Ferulic acid are antioxidant, antiallergic, anti-inflammatory and antimicrobial. It can be used as anticancer agent and since it can adsorb UV can be used in cosmetic to protect the skin [12]. FA can also be considered as a promising bio-block monomer to substitute some of the oil-base monomers already used. There are several examples in literature about the possibility to mimic the behavior of PET with FA as starting material [16]. PET is one of the most common petroleum-based thermoplastic material. Many researchers are trying to find greener materials to replace PET. In this use the FA becomes a polyester but it can be an interesting starting block for polyurethanes, epoxide and phenolic resins as well [10] [17] [18] [19] [20].

Compounds that can respond to external factors, such as light, pH or change in temperature have become more and more important in the recent years. This is due to the fact that they have triggerable properties. Photo-responsive materials such as o-nitro benzyl, anthracene, cinnamoyl and coumarin have been deeply investigated [21].

In FA the cinnamate group reacts when it is exposed to appropriate wavelengths of light. There are several studies in literature that reports the cross-linking and the consecutive cyclobutane ring formation [22] [23] [24] [25]. The reaction is called [2+2] cycloaddition and it is a photo-dimerization. The most important characteristic of this reaction is the reversibility of the cyclobutan ring formation. In fact, when the monomers are exposed to UV-light with  $\lambda > 250 \ \eta m$  they form dimers but if the dimers are irradiated with UV light at  $\lambda < 250 \ \eta m$  the reaction goes in opposite direction originating again the monomers [4].

#### 2.2. UV-curing

The curing is the polymerization mechanism that forms chemical bonds between monomers and oligomers in order to form a thermoset network or a thermoplastic material. The network is formed when the monomers are irradiated by UV light and they have two or more functional groups into the structure that are reactive, in case of only one active group the final result is a linear chain of polymer without crosslinks. The photoinitiator plays a central role since it has UV-sensible groups that start the reaction.

The network gives interesting final properties to the polymer and industrially speaking there are many advantages in the products derived from this reaction, such as rigidity and thermal stability. These are used in several different areas, for example one of the common and very wide is the coating industry. The polymer network can be formed in different ways, thermally or using UV light. The UV curing has mainly developed in the last years since it provides economic and environmental advantages compared to thermal curing. For example, the UV-curing is faster and requires less amount of energy. Nowadays is commercially available a huge variety of UV lamps, photoinitiatiors and UV curable materials [26].

Light is an external stimulus that can provide the energy to break bonds and create new bonds to link the different chains. The source can be UV or visible according to the absorbance of the functional groups present into the formulation. The polymerization can be free radical or ionic (cationic in most of the case but also anionic) according to the nature of the active species that start the reaction. The photocontrol gives importance in the study of different monomers and initiators for many industrial applications such as coatings, inks and adhesives [27].

A common formulation contains three key components:

- A photoinitiation that generate the active species; according to the formulation, multiple photoiniziations can be utilized to reach different percentage of crosslink in the thickness of the irradiated film.
- Active monomers or oligomers having multifunctional groups.
- A reactive diluent, if necessary, that has the function of adjusting viscosity in order to apply the formulation on the substrate [28].

This study is focused on the synthesis of UV -curable monomers. Particular attention is given to the thiol-ene reaction. The next section will present an introduction of this particular reaction with particular stress on its advantages over other synthesis and on the properties of the obtained materials.

## 2.2.1. Thiol-ene reaction

The thiol-ene reaction is defined as "click" reaction, since it has several advantages compared to other reactions:

- It proceeds as (near) quantitative conversion of the thiol and double bond in thioether formation.
- It is applicable in several condition, by radical pathway or via catalytic process (Michael addition).
- It is insensitive to water and oxygen so mild condition can be applied to the reaction;
- The reaction is flexible in term of type of ene and thiol that can be used, so the properties become tunable according to the structure of the monomer used, the range of variation includes several orders of magnitude and finally it is very rapid and can be completed in few seconds [29] [30].

The mechanism is a combination of chain-growth and step-growth since it proceeds by chain process with three steps: initiation, propagation and termination. The Figure 2.2. represents the general mechanism. The initiation is the activation of the thiol by means of photoinitiatior. When the photoinitiatior is irradiated by the right light source it produces radical that can attack the thiol. Then the propagation is a two steps path that involves first the addiction of the thiol radical to the C=C yielding an intermediate radical, then the second step is a chain transfer to a second molecule of thiol giving the final product. This gives the contemporaneous generation of a new radical that can continue the reaction. The possible termination can include typical radical-radical coupling processes.



Figure 2.2: mechanism of click reaction [30].

## 3. Experimental procedure

#### 3.1. Materials

Ferulic acid (FA) was supplied by Sigma-Aldrich and it was used without any further treatment. Allyl bromide, allyl chloride, sodium hydroxide (NaOH), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), Pd 10% on activated carbon were all provided from Sigma-Aldrich. Potassium t-butoxide (t-ButOK) was supplied by Lanchaster Synthesis. 18-crown-6 (18-c-6) and MgSO<sub>4</sub> were provided by Acros Organic. Acetone and methanol (CH<sub>3</sub>OH), ethyl acetate (EtOAC) were all supplied by RWV Chemicals, while dimethyl sulfoxide (DMSO) and dichloromethane (DCM) were provided by Merk KGaA. Hydrochloric acid, HCl 37 %, and sulphuric acid (H<sub>2</sub>SO<sub>4</sub> 95%) was supplied by RWV Solvent. NMR analysis were performed with two different standards: deuterated chloroform, CDCl<sub>3</sub>, and dimethyl sulfoxide, DMSO- $d_6$  provided by RWV Chemicals. The trimethylolpropane tris(3-mercaptopropionate), TMP, was supplied by Sigma-Aldrich and the photoiniziator Irgacure 819, was provided by Basf.

#### 3.2. Method

#### 3.2.1. Thin Layer Chromatography

One good technique for monitoring reactions is thin layer chromatography (TLC). TLC is a separation technique, called also planar chromatography, that uses the different spreading of the sample's components due to affinity with mobile and stationary phase. TLC is a common technique used in the laboratory since it is easy, fast, non-expensive and the result is almost real time [31]. A typical set up is showed in the Figure 3.1.



*Figure 3.1:* schematic view of TLC, the silica plate is positioned in a becker, or TLC box where there is a solvent mixture that drags the sample through the plate [32].

The solvent phase is the mobile one that spreads along the plate towards the opposite edge. It is applied on a plate, that can be made of glass or metal. In the plate there is the stationary phase which consist of a layer of uniform size particles fixed on the substrate. Particles are usually made by silica, alumina or cellulose. The separation of the components will take place according to the affinity between the three actors, components affinity towards the mobile phase and stationary phase. The output of this test will provide an estimation on the numbers of different compounds present in the sample. The principles behind this technique are the differences in the polarity or in the molecular weight of the components. For example, silica bed separates according to the polarity of the solvent: larger and more polar molecules may be isolated by their lack of mobility, so they may stay near the origin, while smaller and non-polar molecules can diffuse easily in the plate.

In this work, TLC was used to investigate the evolution of all the reactions. Silica layer was used as stationary phase while the solvent was an ethyl acetate and heptane mixture. Usually the volume ratio between ethyl acetate and heptane was 1:1 but different ratios were used as well in order to drag the different components through the plate making a proper separation between them.

#### 3.2.2. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a widely diffused analytic method. It can be used for both qualitative and quantitative analysis. NMR is nondestructive method and can be performed in a liquid or solid state, Figure 3.2 [33].



Figure 3.2: schematic representation of NMR instrument [34].

NMR spectroscopy uses the lowest radiation irradiation energy to permit excitation, relaxation of single NMR-active nuclei along the compounds. The energy given to the sample only interacts with the spin quantum state. If a magnetic field,  $B_0$ , is generated, the quantum number of a proton can have two different states,  $m_I = +1/2$  and  $m_I = -1/2$ , Figure 3.3. The first state has lower energy and tends to align parallel to the external magnetic field, while the second has higher energy and tends to make straight with an antiparallel configuration [34].

The Equation 3.1 gives the relation between energy and magnetic field strength, higher is the strength higher is the difference in the energy gap of the two states. Usually the range of frequencies varies from 20 to 900 MHz.

$$\Delta E = hv \tag{3.1}$$



*Figure 3.3:* energy difference between the two spin states depending on the external magnetic field strength [34].

Each active nucleus gives a characteristic signal due to both resonance frequency and the magnetic field. The most important feature is that surrounding atoms can modify the magnetic field, this provides a chemical shift in the peaks.  $B_{eff}$  can be stronger or weaker than  $B_0$ . Higher electronic density means  $B_{eff}$  weaker so the signal will show upfield on the right of a spectrum, instead if  $B_{eff}$  is stronger the peaks will move on the left of the spectrum. De-shielding is caused by neighboring atoms with high electronegativity (oxygen, halogens, etc.).

This is the reason why protons <sup>1</sup>H are non-equivalent in many compounds, since protons within a compound generate diverse magnetic fields thus giving different shifts in H-NMR spectra. Due to this behavior NMR is an excellent method to follow a reaction [33].

Another important aspect is the number n of the proton neighbors. This gives the splitting pattern of the peaks. The general rule is n+1, where n is the number of neighboring spin-coupled nuclei. For example, if there are two protons as neighbors the resultant peak will be a triplet. In all cases the central peak is stronger than the other lateral peaks as consequence of Pascal's triangle. So, for a doublet the intensity will be the same for the two peaks.

In this study, NMR was conducted on a Bruker AM 400. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at 400 MHz and 101 MHz respectively.  $CDCl_3$  and DMSO were used as reference for the analysis that was carried out with MestReNova version 9.0.0 – 12821 (Mesterlab Research S.L 2013).

#### 3.2.2. Fourier transform infrared

FTIR (Fourier transform infrared) spectrometers are widely used as qualitative or quantitative method in organic synthesis, polymer science and food analysis. This type of spectroscopy is based on mid-IR, region of frequencies between 2.5  $\mu$ m and 25  $\mu$ m (i.e. 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>), including the fundamental vibration of the functional groups of organic molecules, such as carbonyl stretching, alcohol vibration, C=C double bond vibrations. The vibration energy is quantic, and the general Equation 3.2 is:

$$E_{vib} = \left(v + \frac{1}{2}\right) hv \tag{3.2}$$

The system adsorbs only at determined energy meaning determinate wavelength. The base principle is sending infrared radiation on a sample that interacting with the chemical bond (change the angle or the distance between the atoms) produces an absorption of the initial radiation.

A common FTIR spectrometer involves a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer. The source generates radiation which passes from the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal by the amplifier and analog-to-digital converter. The computer gives the final spectrum by the calculation of Fourier transform. The following Equation 3.3 is a common form of the Fourier transform with unitary normalization constants:

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt$$
(3.3)

For the mid-IR region, the most used source is a silicon carbide heated to about 1200 K giving output as black body.

The heart of any FTIR spectrometer is an interferometer. The design consists of a beam splitter, a compensating plate, and a pair of mirrors. The light generated by polychromatic infrared sources is collimated towards the beam splitter. Ideally, 50 % of the light is directed on the fixed mirror and the other in the direction of the moving mirror. Then, the light is redirected toward the beam splitter and focused on the sample. The difference between the two paths generates the retardation or optical path difference (OPD) that creates constructive and destructive interference, so a well-defined wavelength reaches the sample. The result of scanning is an interferometer. The interferogram obtained is a plot of the intensity of signal versus OPD. The processing is done by Fourier transformation that gives the spectrum.

The set-up ATR-FTIR (Attenuated Total Reflection Fourier Transform IR Spectroscopy) allows to reduce some problems regarding FTIR as preparation of the sample and reproducibility. The sample in this case is positioned over a crystal as reported in Figure 3.4. The crystal has high refractive angle, so the beam goes through the sample for 0.5  $\mu$ m - 5  $\mu$ m and then is redirected toward the crystal where it is reflected toward the detector. The detector measures the difference in the evanescent wave induced by the interaction with the material. Solid and liquid materials can be analyzed, this analysis can provide qualitative or quantitative results.

One virtuous advantage of FTIR is the possibility to follow in real time a certain reaction seeing the shift and the change in the peaks according to the chemical bonds modification occurring in the reaction. This is called RT-FTIR real time FTIR. The reaction can be followed at different setting temperatures since the crystal can be heated, a photo-chemical reaction can also be tracked.

In this study, the ATR-FTIR analysis was carried out using a Perkin-Elmer Spectrum 2000 FT-IR instrument (Norwalk,CT) equipped with a single reflection accessory unit (Golden gate) from Graseby Specac Ltd (Kent, England) and TGS detector using the Golden Gate set up. Each spectrum was collected after 16 scans with a resolution of 4 cm<sup>-1</sup> in a wavelenght range from 600 to 4000 cm<sup>-1</sup>. Instead, the data of RT-FTIR were collected as a single scan each 6 second with resolution of 4 cm<sup>-1</sup>. The light source used for the irradiation was a Hamamatsu L5662 equipped with a standard-medium pressure 200 W L6722-01 Hg-Xe lamp and provided with optical fiber on the sample surface. The UV intensity was measured by means of a Hamamatsu UV-light power meter (model C6080-3) calibrated for the main emission at 365 nm. The intensity was about 100 mW/cm<sup>2</sup>. Spectrum software v. 10.5.1 and TimeBase® were used to process the data of FTIR and RT-FTIR respectively. The setup is represented in the Figure 3.4. This instrument was used to analyze the monomers during the synthesis and to perform the photo dimerization.

The instrument used for the characterization of the different formulations was a Nicolet iS 50 Spectrometer. Data pre and post curing were collected as 32 scans with a spectral resolution of 4.0 cm<sup>-1</sup>. In order to follow the curing, RT-FTIR were performed with the same instrument. All these data were recorded and handled with the software Omnic from Thermo Fischer Scientific. The lamp was a Hamamatsu LIGHTINGCURE LC8 equipped with an optic fiber.



Figure 3.4: schematic block of RT-FTIR set up for the experiment.

#### 3.2.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) is one of the most popular method to determine the glass transition temperature ( $T_g$ ) of a polymer. The DMTA analysis involves the application of a constant oscillatory input (stress or strain) to the sample while increasing the temperature.

If a polymer material is subjected to a sinusoidal stress, its response is a combination of two contribute: elastic, which corresponds to storage modulus named E' and viscous, loss modulus named E''.

The equation 3.4 reports the formula of the applied stress:

$$\sigma = \sigma_0 \sin \omega t$$

The equation 3.5 reports the formula of the applied strain response:

### $\mathcal{E}(t) = \mathcal{E}_0[\sin(\omega t)\cos\delta + \cos(\omega t)\sin\delta]$

The ratio of loss modulus to the storage modulus represents the damping factor named Tan $\delta$  value that corresponds to the dissipated energy stored for cycle of deformation. The  $T_g$  of the material can be evaluated from the Tan $\delta$  peak and it is one of the most important parameters for a thermoset polymer since is correlated with the crosslink density. In fact, higher crosslinks density means higher  $T_g$  and this can be correlated with the conversion as well.

The glass transition temperature is a very important polymer characteristic since the properties of the thermoset change dramatically from a glassy state ( $T < T_g$ ) when the material behave like solid, stiff and rigid, to a rubbery state ( $T > T_g$ ) when the material is more flexible since the cooperative segmental mobility is activated.

In this work, the DMTA analysis was performed with Triton Technology instrument. The parameters of the measures are the following: 3 °C/min as heating rate, the starting temperature was set as -40 °C with an applied tensile stress frequency of 1 Hz. The measurements were stopped after the appearance of the plateau in the storage modulus. Liquid nitrogen was used to cool down the chamber. The analyzed samples had an average dimension of  $0.4 \times 0.8 \times 12$  mm.

(3.4)

(3.5)

#### 3.2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermo-analysis widely used to measure the material response to temperature variation. The test is performed in a chamber where two different crucibles are present: the first one for the sample and the second one for the reference (Figure 3.5). The instrument is able to measure the difference between the heat flows coming from the two crucibles as a function of temperature and time. This difference is detected by thermocouples. The final output of this measurements is a thermogram. This analysis can be used to compare materials or study thermal processes. In fact, for example  $T_g$  of different materials are detectable and they are comparable if the same heating ramps and temperature cycles are used in the analysis. This allows to compare thermal properties of materials [35].



Figure 3.5: general scheme of DSC apparatus [35].

The preparation of the sample consists of placing 5 to 10 mg of material in a crucible with or without a lid. The crucible can be made of gold, aluminum or platinum. It is also possible to select a proper atmosphere for this analysis.

In this study 40  $\mu$ L aluminum pans were used. The DSC analysis was performed on a Mettler Toledo DSC-1 equipped with Gas Controller GC100. The method used was the follow: the starting temperature was set as 30 °C; the first heating goes from 30 to 100 °C; then the temperature was maintained at 100 °C for 2 minutes in order to stabilize the sample, after that the chamber was again cooled until -50 °C is reached and then this temperature was maintained for 4 min, finally was applied a second heating from -50 °C to 100 °C. The heating and the cooling rates were set at 10 °C/min and the analysis was performed in a nitrogen atmosphere with a flow rate 20 mL/min. The first heating ramp was used to remove the thermal history of the different sample making comparable the different data of the performed analyses. The data were analyzed with Mettler Toledo STARe software V9.2.

#### 3.2.5. Size exclusion chromatography

Size exclusion chromatography (SEC) is a convenient method to determine the average molecular weight and the molar mass distribution (MWD) of polymer. The principle is the separation of the polymer chains by their molecular hydrodynamic volumes or sizes. The polymer is dissolved in the appropriate solvent and injected in a column. The stationary phase has well defined porous size so the smaller molecules can enter into these pores thus elute later in the time, blue peak in the Figure 3.6, whereas the big molecules are too large to enter in these small voids, so they are eluted earlier in time since they have to follow a shorter routes. The technique is relative, so calibration is necessary. The calibration has to be done with a standard polymer with a known molecular weight and with similar chemical structure to the polymer in analysis. This permits to have similar interaction in the column to compare the retention time, time of elution, of the polymers [36].



*Figure 3.6:* principles of SEC, the retention time changes according to the size of the different polymer injected into the column [37].

In this study was performed the SEC-DMF (dimethylformamide) analysis. The DMF was mixed with 0.01 M LiBr as mobile phase. The instrument was TOSOH EcoSEC HLC-8320GPC equipped with an EcoSEC RI detector. The calibration was done using narrow linear polystyrene standard with a molecular weight ranging from 376 g/mol to 18100 g/mol. Corrections in the interpretation of the results can be done using the toluene as internal standard of the used solvent.

#### 3.2.6. Photo-rheology

This technique combines the rheology study with the application of a UV/visible radiation in order to register the in-time changes in mechanical properties occurring with the process of the cross-linking reactions. The liquid formulation is placed on top of quartz then the rheology measurement starts. After a certain amount of time, the UV light is turned on and start to irradiate

the sample. This technique is very useful to investigate the kinetics of the reaction. Good comparison can be done between different formulation comparing for example the curve slopes, the induction time and the reaction velocity. The first one is useful to understand the kinetics, higher slope means higher reactivity as well as the second one, in fact a lack of induction time means that the reaction starts immediately. All parameters are very important to reach the optimal condition for the irradiation time to reach the best properties.



*Figure 3.7:* scheme of a rheometer used for the analysis. The sample is positioned between the quartz and the disk plate.

For this research was utilized the Anton Paar MC 302 instrument. The light source come from Hamamatsu LIGHTINGCURE LC8 equipped with an optic fiber. The intensity of the UV light was around 30 mW/cm<sup>2</sup>. The conditions for the tests were the following: frequency of 1 Hz, strain of 1 %, the lamp was switched on after 30 seconds. The rheometer was set as plate-plate, the accessory had a 2.5 cm. The distance between the crystal and the plate was 200  $\mu$ m which corresponds approximately to 150  $\mu$ L of formulation.
# 3.3. Synthetic procedure

### 3.2.3. Allylation of Ferulic acid

The synthesis of the allylated ferulic acid (A1FA) was performed in different paths in order to find the best result in terms of conversion and final yield. The protocols are described below, and the Scheme 1 shows the different condition used for each reaction.



Scheme 1: allylation of Ferulic acid.

The reaction 1A follows the following steps which were selected according to previous work on similar compound [38]. Sodium hydroxide (90 mg) was dissolved in ethanol in a round bottom flask under agitation; FA (210 mg) was added when the NaOH was dissolved completely. After the dissolution of FA the solution was heated, by means of oil bath, to 55 °C and allyl chloride (123  $\mu$ L) was added drop-wise through a septum using a syringe. The allyl chloride selectively reacts with the phenolic alcohol this is the reason why it was used in this protocol. A reflux is applied in order to avoid the evaporation of the solvent and the allyl chloride. The solution was left in stirring condition at T = 55 °C for one day. The reaction was stopped by decreasing the temperature of the oil bath and eliminating the reflux. The round bottom flask was left under the fume hood for 30 min in order to remove the allyl chloride in excess. The solvent was roto evaporated at 40 °C. The final extraction was performed with diethyl ether as organic phase and a solution of HCl 6 N as water phase. In order to obtain the final acid molecules, HCl solution was added to decrease the pH. The pH was monitored with a pH-indicator strip. The organic phase was dried using MgSO<sub>4</sub> and filtered. Diethyl ether was removed using a rotary evaporator at 30 °C.

The reaction 1B was performed to obtain the allylated product. In this case the selected solvent was acetone and the selected base was potassium carbonate. The FA (230 mg) was dissolved in the solvent in a round bottom flask. Then were added both the base (490 mg) and the allyl chloride (133  $\mu$ L). The reaction was then equipped with a reflux and heated up with a vigorous stirring. The reaction was carried out for 24 hours then the work up was the same as described in the previous paragraph.

The other protocols follow the procedure written by other researchers and, in this case the starting material was the same as the reagents used in those studies.

For the reaction 1C allyl chloride was substituted with allyl bromide while the solvent and the base,  $K_2CO_3$  remained the same. FA (5.21 g) was dissolved in a round bottom flask with 60 mL of acetone, then the base (14.82 g) was added under stirring. The allyl bromide (5.8 mL) was subsequently added, and then the solution was heated at T = 55 °C. The system was left to react overnight. The Figure 3.8 shows a photo of the experiment set-up used and a TLC analysis used to analyze the obtained product [39] [40] [41].



Figure 3.8: on the left, glass instrumentation used for the reaction; on the right, TLC of reaction.

The last protocol used (reaction 1D in scheme 1) contemplate the addition of 18-crown-6 in the mixture. This is a catalyst and it was used in small amount (1 % wt). The other conditions remained the same as the previous protocol. The reaction was performed with FA (2.1 g), allyl bromide (2.3 mL) and  $K_2CO_3$  (5.91 g).

The workup of these last types of synthesis started with decreasing the temperature and removing the reflux, in order to get rid of the allyl bromide in excess. When the temperature was decreased, filtration was performed, and the solvent was evaporated. Then the residue was dissolved in a mixture (60:40) of ethanol and NaOH 2M (the amount of NaOH was calculated each time according to the starting moles of reagent). The solution was refluxed for two hours. After the cooling down the HCl was added into the solution. The introduced amount of HCl was calculated in order to neutralize the base and to form the desired acid product. The pH was measured by pH strip. A precipitate was formed. The suspension was left stirring for half an hour then it was filtrated. The solid was collected, dried overnight and then yield was evaluated. The Figure 3.9 shows how the solution and the precipitate look like in the two sequential stages and the final product stored in a vial.



*Figure 3.9:* on the left, solution of NaOH and EtOH after the reflux; in the center, solution after the precipitation by adding HCl; on the right, A1FA stored in a vial.

All the reactions were monitored with TLC to verify the synthesis and the final products were analyzed by NMR and FTIR analysis.

A1FA (monoallylated ferulic acid)

1C. Whitish powder, 5.99 g, 95 % yield.

<sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$  12.20 (s, 1H), 7.51 (d, J = 15.9 Hz, 1H), 7.32 (d, J = 2.0 Hz, 1H), 7.18 (dd, J = 8.3, 2.0 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.04 (ddt, J = 16.1, 10.6, 5.3 Hz, 1H), 5.45 – 5.22 (m, 2H), 4.59 (d, J = 5.3 Hz, 2H), 3.81 (s, 3H).

<sup>13</sup>C NMR (101 MHz, DMSO-d6) δ 168.31, 150.02, 149.64, 144.55, 133.98, 127.74, 122.92, 118.27, 117.27, 113.46, 111.09, 69.29, 56.12.

1D. Whitish powder, 2.24 g, 76 % yield.

1H NMR (400 MHz, Chloroform-d)  $\delta$  7.73 (d, J = 15.9 Hz, 1H), 7.16 – 7.05 (m, 2H), 6.88 (d, J = 8.2 Hz, 1H), 6.32 (d, J = 15.9 Hz, 1H), 6.08 (ddt, J = 17.3, 10.6, 5.4 Hz, 1H), 5.48 – 5.28 (m, 2H), 4.66 (dt, J = 5.4, 1.5 Hz, 2H), 3.92 (s, 3H).

 $^{13}\mathrm{C}$  NMR (101 MHz, Chloroform-d) & 172.22 , 150.68 , 149.75 , 147.14 , 132.82 , 127.37 , 123.04 , 118.62 , 114.97 , 112.99 , 110.37 , 69.91 , 56.12 .

# 3.2.4. Isomerization of allyl derivate

Rearrangements on the first product (iso-A1FA) were performed following procedures founded in literature on similar compounds [42] [43] [44] [45]. The Scheme 2 shows the illustrations of these reactions.



Scheme 2: isomerization of mono-allyl derivate.

The rearrangement of the product previous synthetized was done according to different routes that include these phases. The allylated ferulic acid (1.02 g), t-ButOK (0,97 g) and 18-c-6 (2.30 g) were placed in a 100 mL round bottom flask. Several solvents were tried but the most effective was the DMSO. The reactions occurred overnight at 50-60 °C under strong stirring. The reactions progresses were monitored by TLC. The NMR analysis was used to analyze the final products. The workup of this reaction consists of a HCl addition. The product precipitates in the solution Then the final compound was filtrated. The compound was used without any other purifications.

Another strategy adopted to obtain the isomerization was the catalytic reaction in which secondgeneration Grubbs catalyst was used as catalyst in combination with 4 mol % of the reagent [46] [47] [48]. The reaction was carried out in air and MeOH was used as solvent. Since the reactions were heated, a reflux system was always required.

iso-A1FA (propenyl derivate of allyl ferulic acid)

Whitish powder, 0.73 g, crude.

<sup>1</sup>H NMR (400 MHz, DMSO-d6) δ 7.53 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.21 (dd, J = 8.3, 1.9 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.53 – 6.42 (m, 2H), 4.91 (p, J = 6.8 Hz, 1H), 3.85 (s, 3H), 1.64 (dd, J = 6.8, 1.8 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, DMSO-d6) δ 167.75, 149.32, 147.81, 143.73, 141.33, 129.35, 122.14, 117.86, 115.72, 111.54, 106.83, 55.88, 9.37.

### 3.2.5. Esterification allyl derivate of Ferulic acid

The esterification was performed by following a protocol found in literature [49]. A1FA (0.92 g) was dissolved in methanol,  $H_2SO_4$  was added in catalytic amount to speed up the reaction and to act as dehydrating agent moving the equilibrium toward the ester production. The solution was refluxed overnight. After cooling down the system, it was performed an extraction using EtOAC

as organic solvent and water (Figure 3.10). The water phase was extracted other three-time to ensure a complete removal of the product. The organic layers were combined and washed with saturated solution of NaHCO<sub>3</sub> and successively with a solution of NaCl. They were dried over MgSO<sub>4</sub> and the final stage was the evaporation of the solvent.

This reaction (Scheme 3) was monitored by TLC and the product was analyzed by NMR and FTIR analysis.



Scheme 3: esterification of allyl derivate.

EA1FA (methyl ester of allyl derivate of ferulic acid)

Whitish powder, 0.89 g, 90 % yield.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.65 (d, *J* = 16.0 Hz, 1H), 7.13 – 7.05 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.10 (ddt, *J* = 17.2, 10.6, 5.4 Hz, 1H), 5.44 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.33 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.67 (dt, *J* = 5.4, 1.5 Hz, 2H), 3.93 (s, 3H), 3.82 (s, 3H).

 $^{13}\mathrm{C}$  NMR (101 MHz, Chloroform-d)  $\delta$  167.64 , 150.11 , 149.55 , 144.75 , 132.76 , 127.57 , 122.35 , 118.38 , 115.56 , 112.88 , 110.08 , 69.75 , 55.94 , 51.61 .



*Figure 3.10:* on the left, extraction of organic phase, EtOAC, with aqueous phase in order to obtain pure product; on the right, product EA1FA collected in a vial.

## 3.2.6. Double allylation of ferulic acid

The double allylation (A2FA) was conducted modifying the previous procedure according to the protocol found in literature. Scheme 4 reports the compound generic structures and condition of the reaction [41].



Scheme 4: double allylation of Ferulic acid.

FA (2.08 g) and potassium carbonate (5.91 g) were placed in two neck round bottom flask and acetone was used as solvent. The mixture was stirred to allow the dissolution of FA then allyl bromide (2.35 mL) was added. The reaction was left at 55 °C for about 20 hours. Then the mixture was filtered and the solvent was evaporated. Subsequently the extraction with dichloromethane was performed: water layer was extracted three times then the organic layer was dried over MgSO<sub>4</sub> to give the product. Finally, the evaporation of the solvent was performed with rotavapor system. The A2FA was used without further purification. TLC was used to monitor the reaction. The Figure 4.11 shows the reaction result (the spot representing the reagent disappeared while a new spot representing the product appeared). The NMR analysis confirms the presence of the desired product.

A2FA (double allyl derivate of ferulic acid)

Yellow-orange liquid, 2.39 g, 82 % yield.

<sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$  7.61 (d, J = 15.9 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.21 (dd, J = 8.3, 1.9 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.58 (d, J = 15.9 Hz, 1H), 6.01 (dddt, J = 20.9, 17.4, 10.6, 5.4 Hz, 2H), 5.43 - 5.20 (m, 4H), 4.63 (ddt, J = 29.3, 5.4, 1.5 Hz, 4H), 3.82 (s, 3H).

<sup>13</sup>C NMR (101 MHz, DMSO-d6) δ 166.10, 149.82, 149.17, 144.88, 133.42, 132.84, 127.02, 122.78, 117.75, 117.70, 115.34, 112.89, 110.70, 68.81, 64.30, 55.64.



*Figure 3.11:* on the left, TLC at the end of the reaction; on the right, A2FA collected in a vial at the end of the extraction.

# 3.2.7. Hydrogenation of Ferulic acid

The protocol follows a procedure reported in literature [50] [51]. The Scheme 5 represents the reaction. FA (20 g) was dissolved in methanol (100 ml) under stirring. Pd on activated carbon (2 g) was placed in a round bottom flask. A septum was used to close the bottom flask (very thigh) and argon was shuffled inside to remove all the air present (it can be removed thanks to a needle insert into the septum that is removed at the end of the operation). The solution of FA was added into the flask with a syringe then H<sub>2</sub> was blowed in. The Figure 3.12 shows two different reaction steps. The mixture was stirred overnight at room temperature in H<sub>2</sub> atmosphere then the Pd was filtrated through a glass filter (pour 5). The solvent was evaporated to obtain the product as powder.



*Scheme 5:* saturation of  $\alpha - \beta$  double bond.

The reaction was monitored by NMR analysis in order to stop the reaction when the total conversion of the reagent was achieved.

h-FA (hydrogenated ferulic acid)

Whitish powder, 19.21 g, 95 % yield.

<sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  6.86 – 6.82 (m, 1H), 6.70 (d, J = 7.4 Hz, 2H), 3.87 (s, 3H), 2.89 (t, J = 7.7 Hz, 2H), 2.66 (t, J = 7.7 Hz, 2H).

 $^{13}\mathrm{C}$  NMR (101 MHz, Chloroform-d)  $\delta$  178.95 , 146.59 , 144.25 , 132.21 , 120.99 , 114.55 , 111.07 , 56.02 , 36.10 , 30.49 .



*Figure 3.12:* on the left: Pd and reagent dissolved in  $CH_3OH$  under Ar with the septum very thigh; in the center, setup of the  $H_2$  atmosphere during the reaction time; on the right: the final product collected in a vial.

# 3.2.8. Allylation of hydrogenated Ferulic acid

The mono allylation followed the same procedure used for the allylation of Ferulic acid, the Scheme 6 reports the structure of the reagent, of the product and the reaction conditions [6] [41].



Scheme 6: allylation of saturated Ferulic acid.

h-FA (3.33 g) was dissolved in acetone, 50 mL,  $K_2CO_3$  (9.38 g) was added and then allyl bromide was provided with a micropipette (3.55 mL). The mixture was heated at 55 °C for 24 hours under reflux with a strong stirring. TLC shows complete conversion of the starting material as shown in the Figure 3.13. After cooling down the solution the mixture was filtrated, and the solvent was evaporated. The residue was dissolved in NaOH 2 M and EtOH (75 mL and 50 mL respectively), then the solution was heated at T = 70 °C with a reflux for 2 hours. When the solvent was filtrated (Figure 3.12 right) and dried in a vacuum oven for one night. Recrystallization was operated on the previous solution and other amount of product was given.



*Figure 3.13:* on the left, TLC of the reaction after 24 hours; on the right, final filtration of the product after precipitation.

h-A1FA (monoallyl derivate of hydrogenated ferulic acid)

Yellowish powder, 3,85 g, 96 % yield

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  10.67 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.79 – 6.70 (m, 2H), 6.10 (ddt, *J* = 16.2, 10.6, 5.4 Hz, 1H), 5.46 – 5.37 (m, 1H), 5.33 – 5.25 (m, 1H), 4.61 (d, *J* = 5.4 Hz, 2H), 3.88 (s, 3H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H).

 $^{13}\mathrm{C}$  NMR (101 MHz, Chloroform-d)  $\delta$  178.94 , 149.41 , 146.55 , 133.48 , 133.17 , 120.03 , 117.87 , 113.66 , 112.06 , 69.99 , 55.90 , 35.81 , 30.25 .

Also the double allylation (h-A2FA) was performed following protocol already used in literature for FA. Scheme 7 reports the generic structure od both the reagent and the product and the reaction conditions [41].



Scheme 7: double allylation of hydrogenated Ferulic acid.

The h-FA (3.22 g) and potassium carbonate (9.10 g) were placed in two necked round bottom flask, acetone was added as solvent. The mixture was stirred to allow the dissolution of FA then allyl bromide (3.45 mL) was added. The reaction was left at 55 °C for one day under reflux (Figure 3.14). Then the mixture was filtered, the solvent was evaporated, and the extraction with dichloromethane was performed. The water layer was extracted three times then organic layer was dried using MgSO<sub>4</sub>. Finally, the evaporation of the solvent was performed with rotavapor. The h-A2FA was used without further purification.



*Figure 3.14:* on the left, picture of the glass ware used in the synthesis; on the right, h-A2FA stored in a vial.

h-A2FA (double allyl derivate of hydrogenated ferulic acid)

Yellow liquid, 4.24 g, 93 % yield.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  6.80 (d, *J* = 8.1 Hz, 1H), 6.75 – 6.65 (m, 2H), 6.07 (ddt, *J* = 17.4, 10.6, 5.4 Hz, 1H), 5.90 (ddt, *J* = 17.3, 10.5, 5.7 Hz, 1H), 5.44 – 5.18 (m, 4H), 4.58 (dq, *J* = 5.7, 1.4 Hz, 4H), 3.86 (s, 3H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.64 (dd, *J* = 8.4, 7.1 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.58, 149.39, 146.47, 133.53, 133.51, 132.16, 120.07, 118.22, 117.83, 113.65, 112.06, 70.00, 65.13, 55.89, 36.10, 30.59.

# 3.2.9. Esterification of allyl derivate of h-FA

The esterification procedure was found in literature [49]. h-A1FA (2.01 g) was dissolved in methanol (40 mL), H<sub>2</sub>SO<sub>4</sub> was added in catalytic amount. The solution was refluxed overnight at T = 60 °C. After cooling down the solution, the product was extracted by EtOAC. The organic layers were combined and washed with saturated solution of NaHCO<sub>3</sub> and NaCl, dried over MgSO<sub>4</sub>. Finally, the solvent was evaporated. The product obtained was an orange liquid (Figure 3.15).

This reaction, represented in the Scheme 8, was monitored by TLC and the final product was analyzed by NMR and FTIR analysis.



Scheme 8: esterification of allyl hydrogenated Ferulic acid.



Figure 3.15: h-EA1FA collected in a vial.

h-EA1FA (methyl ester of allylated hydrogenated ferulic acid)

Orange-brown liquid, 1.99 g, 94 % yield.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  6.79 (dd, J = 8.1, 1.9 Hz, 1H), 6.74 – 6.66 (m, 2H), 6.07 (dddd, J = 15.9, 12.7, 6.5, 4.4 Hz, 1H), 5.43 – 5.20 (m, 2H), 4.57 (ddt, J = 5.4, 2.8, 1.5 Hz, 2H), 3.85 (d, J = 2.1 Hz, 3H), 3.66 (d, J = 2.5 Hz, 3H), 2.89 (td, J = 7.7, 1.8 Hz, 2H), 2.60 (td, J = 7.9, 1.8 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 173.48, 149.49, 146.57, 133.65, 120.14, 117.92, 113.75, 112.15, 70.09, 55.99, 51.70, 36.06, 30.71.

# 3.3. Photodimerization

The dimerization reaction was directly performed on the FTIR crystal. Few droplets of the solution were placed on the surface of the detector and then were covered by a KBr disk. The KBr was used to avoid contact with air during the measurement and to create a very thin film. The reactions were performed at different temperature, 30 °C, 40 °C, 50 °C, 75 °C, 100 °C. The lamp was switched on when the temperature was stable. The measurements performed at 100 °C required a stabilization time of 120 seconds. The irradiation lasted 10-15 then the measure continued without any UV irradiation to check the possibility of reversibility in the reaction. The intensity of the mercury lamp was set around 100 mW/cm<sup>2</sup> for all experiments.

<sup>1</sup>H-NMR analysis was performed on the reacted at 50 °C. SEC-DMF was performed on three different samples, one reacted at 30 °C and two at 50 °C.

The last measurement was done using a solution of A2FA. The UV-VIS analysis was performed on 0.02 g/mL sample solution in DCM. The exposure times were 15 s and 25 s. The lamp used was the one used for the FTIR in the previous experiment.

#### 3.4. Film formulation and curing parameters

The prepared films had 1 : 1 as molar ratio between double bond and thiol. The amount of photoinitiatior added in each formulation was 0.5 % wt of the total of mass of the resins (phr). The used photoinitiatior was Irgacure 819 in accordance to previous works [25] [38]. The Scheme 9 shows the formation of the h-A2FA polymer network as result of UV irradiation in which are highlighted the links between the thiol and the double bond unit.

The double allylated liquid products were mixed with TMP then the solution ultrasonicated in order to obtain an homogeneous dispersion of the two components. The photoinitiatior was subsequently added and dispersed using the ultrasound bath as well. A mold in silicon (Figure 3.16) was used to create the samples. The UV irradiation was performed with the Dymax ECE 5000 Flood lamp. The irradiation time was 1 minute with a lamp intensity of 110 mW/cm<sup>2</sup>.

In order to investigate the influence of a co-monomer into the network, formulations with the addition of the h-EA1FA monomer were also analyzed. The evaluated compositions are reported in the Table 3.1.

The percentage of co-monomer must be calculated as molar ratio between the bifunctional monomer and the co-monomer itself. The amount of thiol was calculated on the sum of the ene equivalent in total of the two comonomers.

The films were tested using different techniques: photo-rheology, FTIR pre and post curing DMTA and DSC.

Film formulation	Main monomer,	Co-monomer,	Thiol-ene ratio
	% molar ratio	% molar ratio	
1	A2FA, 100%	-	1:1
2	A2FA trifunctional, 100%	-	1:1
3	A2FA, 95%	h-EA1FA, 5%	1:1
4	A2FA, 90%	h-EA1FA, 10%	1:1
5	A2FA, 85%	h-EA1FA, 15%	1:1
6	h-A2FA, 100%	-	1:1
7	h-A2FA, 95%	h-EA1FA, 5%	1:1
8	h-A2FA, 90%	h-EA1FA, 10%	1:1
9	h-A2FA, 85%	h-EA1FA, 15%	1:1

Table 3.1: compositions of the different formulations used in this study.



Scheme 9: photopolymerization of a A2FA - TMP formulation.



*Figure 3.16:* silicon mold used to create the sample. The thickness of each parallelepiped changes from 0.2 mm to 1.5 mm.

# 4. Result and discussion

## 4.1. Allylation of FA

The 1A protocol leads to the formation of allyl derivatives but the reaction was uncompleted since there were still traces of ferulic acid. This could be explained by many reasons listed below:

- Not complete deprotonation of the phenolic hydrogen due to the fact that the base selected may first deprotonate the acid and then the phenol;
- Slow reaction kinetic which increases the reaction;
- Mutual reactivity between FA and allyl chloride that does not allow complete conversion.

Thus, allyl bromide was chosen to substitute allyl chloride. The reactivity of allyl bromide is higher than the previous one, it can react with both carboxylic acid and phenol groups [52]. The mechanism of the reaction is a nucleophilic substitution, called  $S_N 2$  where the nucleophile is the ferulic acid in deprotonated form, the leaving group is the halogen and the electrophile is the allyl radical. General mechanism is presented in Figure 4.1.

The deprotonation is achieved with the use of  $K_2CO_3$  as a base. The ratio was 4 equivalents of base to 1 equivalent of Ferulic acid. These can ensure a complete and rapid deprotonation of phenol and carboxylic.



*Figure 4.1:* S<sub>N</sub>2 reaction showing the mechanism, bimolecular participation of nucleophile and leaving group [53].

Two monomers were obtained: A1FA and A2FA. The main difference with the first protocol can be found in the reaction work up. During the A1FA reaction NaOH was used to avoid the esterification reaction since allyl bromide can react with the carboxylic part of the molecule. The protonation was achieved with the addition of HCl. The A2FA reaction follows the same protocols except for the use of NaOH. The final extraction was performed in order to the organic material from aqueous soluble impurities, like salt.

These two molecules were obtained in high conversion and high purity as confirmed by the NMR analysis, both H-NMR and C-NMR. Figure 4.2 shows the A1FA NMR spectra in which is

clear present the final product without trace of starting material. From these A1FA spectrum it can be noted the presence of new peak from 6 to 5.5 ppm which can be attributed to the allyl group as well as the disappearance of phenol peak at 9.5 ppm.



*Figure 4.2:* <sup>1</sup>H-NMR (DMSO-d<sub>6</sub> as solvent) of monoallylated FA (A1FA), violet spectrum, and FA orange spectrum.

The protocol named 2D involves the use of 18-crown-6 as catalyst. The catalyst had the effect of reduce the activation energy. Two different reactions were compared in the same time interval in order to understand the effect of the 18-c-6. The figure 4.3 shows a higher conversion when the catalyst is used. In fact, in this case it is clearly possible to observe the disappearance of the initial FA peaks.



*Figure 4.3:* effect of 18-c-6 on the reaction: the orange spectrum represents the reaction without catalyst while the violet one is the reaction with the catalyst.

# 4.2. Isomerization

The isomerization reaction successfully leads to the formation of the desired product however it was difficult to purify it. The isomerization reaction requires mild conditions with temperature below 100 °C in order to avoid the Claisen rearrangement. The impossibility to heat over 100 °C limited the use of the Grubb catalyst, that in other protocol headed to high conversion and easy reaction.

Alternatively, a strong base, t-ButOK, in aprotic solvent DMSO was selected as method to form the isomer. The desired product was obtained but the elimination of DMSO and 18-c-6 generated problems. The DMSO solvent has a high boiling point 189 °C so it is very difficult to eliminate. Five to six washing with DCM were required to obtain a purified product.

The final acidification with HCl leads to the reverse reaction (reformation of starting material) since the propenyl is a better leaving group then allyl. The treatment with acid can lead to the reformation of the phenol group.

Column chromatography was used to get rid of the 18-c-6 but the acidic structures of the stationary phase interacted with the product, as mentioned before. At the exit of the column the product was the ferulic acid. The interaction with acid leads to the elimination of propyl group and to the formation of phenol. This is an interesting result since the propenyl group can be used to protect phenol in other reactions that need to shield this particular functional group.

### 4.3. Esterification

EAFA was obtained from the A1FA and h-A1FA following the simple method described before. The reaction led to high yield and pure product without side reactions. This reaction is a condensation reaction between alcohol and acid forming water, the general equation is represented in the scheme 9.



Scheme 9: general esterification between a carboxylic acid and alcohol.

The role of  $H_2SO_4$  is to promote the elimination of the water creating a good leaving group in the acid part. The mechanism of the reaction is represented in the Figure 4.4. The protonation in the first stage allows the attack of the alcohol to the carbon of the acid which has a partial positive charge. The tautomerism is presence of different structural isomers (same chemical formula but different bonding) that can readily interconvert each other's. The last step is the deprotonation which implicates reformation of the acid catalyst.



Figure 4.4: mechanism of esterification using acid catalyst [54].

The analysis of the product was done by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FTIR analysis. The FTIR results can be summarized in two points:

• In the region from 3500 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> it is possible to observe the disappearance of -OH stretching peak. The phenol group signal is only present in the starting material Figure 4.5.

• The shift of the C=O stretching peak from 1680 cm<sup>-1</sup> to 1704 cm<sup>-1</sup> can be possible due to the formation of the ester.

The spectra were corrected with common base line and normalized with the 1508 cm<sup>-1</sup> peaks which is attribute to the benzyl ring which is expected to remain unchanged in all the materials analyzed.



*Figure 4.5:* spectra of the FA derivates in which is possible to observe the disappearance of -OH peak at 3400 cm<sup>-1</sup> and shift of C=O peak in the region between 1600 and 1500 cm<sup>-1</sup>.

# 4.4. Hydrogenation

The hydrogenation of Ferulic acid was performed with Pd, in form of Pd-C (Pd adsorbed on carbon). The result was very satisfactory since it was obtained a total conversion and an very high yield. It was possible to perform this reaction with an high amount (20 g) of starting material.

The mechanism consists in the reaction between  $H_2$  and the cinnamoyl group present in the molecule. The Pd decreased the activation energy in this reaction. Since this reaction was exothermic the experiment was conducted at room temperature. A strong stirring condition was required to assure an homogeneous mixing among the hydrogen in the atmosphere, the metal and the ferulic acid. Its general scheme is reported in the Figure 4.6.

The <sup>1</sup>H-NMR result showed complete conversion without any side reactions. This is showed in the Figure 4.7 where all the peaks present in the product were attributes to h-FA.



1. Hydrogen atoms and C=C double bonds being attached to metal surface;

2. An hydrogen atom is transferred to the previous double bond;

3. A second hydrogen is linked to the alkene;

4. The saturated product leaves the metal surface.

Figure 4.6: mechanism of hydrogenation [55].



*Figure 4.7:* <sup>1</sup>H-NMR spectra after the hydrogenation, shift for the peak  $\alpha$  and  $\beta$  towards lower ppm,  $\alpha$ ' and  $\beta$ '. (Peak 8 in h-FA is present but it is very broad with this magnification is not so visible).

# 4.5. Allylation of hydrogenated FA derivatives

The allylation followed the same protocol described before (2C). The reagent ratio was h-FA : allyl bromide :  $K_2CO_3 = 1 : 2.4 : 4$  with a maintained temperature of 55 °C for 24 hours. The yield and purity of the product were confirmed by the NMR analysis Figure 4.8.



*Figure 4.8:* <sup>1</sup>H-NMR of mono and double allylated derivates from h-FA.

# 4.6. Photodimerization

The sample A2FA was used to study the behavior of the cinnamoyl double bond C=C when it is exposed to UV, Figure 4.9. Experiments were performed at different temperature ranging from room temperature up to 100 °C with the previous described set up.

In order to evaluate the possible dimerization, real time FTIR was performed with the UV mercury lamp. The most relevant results were the following:

- Shift in the C=O peak, from 1705 cm<sup>-1</sup> to 1740 cm<sup>-1</sup> that may be attribute to the change in the molecular structure in proximity to the carboxylic bond (Figure 4.10).
- Reduction in the average area of the peaks ranging from 1660 cm<sup>-1</sup> to 1550 cm<sup>-1</sup>. This region can be attribute to the stretching of C=C, so a reduction of this area suggests a decrease in the number of double bonds. This can be due to the disappearance of cinnamoyl group and formation of cyclobutane ring.
- Appearance of a peak at 1200 cm<sup>-1</sup> which can be attribute to the stretching of C-H in combination with the reduction in the absorbance of the peak at 1100 cm<sup>-1</sup> representing the C=C in cinnamic group. This suggests the formation of cyclobutane ring.



*Figure 4.9:* real time spectra of the A2FA, in which is possible to observe the reduction of the cinnamoyl peak at  $1100 \text{ cm}^{-1}$ .



*Figure 4.10:* result of RT-FITR measurement, zoom between 1800 and 1550 cm<sup>-1</sup>. The picture highlights the shift of the C=O bond vibration peak.

Other techniques were also used to confirm the RT-FTIR data.

In the <sup>1</sup>H-NMR spectrum of the product new peaks, which can be attributed to the presence of the dimer, appeared and the double bond peak integral decreased with respect to the allyl function of the starting material, see Figure 4.11. These results are in good agreement with FITR results. The presence of multiple new peaks, red dash rectangles in the Figure 4.11 can be explained by the presence of head-tail or tail-tail reactions. The analyzed product was a mixture of monomers and dimers, so it was difficult to isolate only the dimers peak. However, the integration of the c and  $\beta$  peaks in comparison to the allyl peak called 11-11' confirmed the consumption of the cinnamoyl double bond. In fact, the ratio between the two groups, allyl and cinnamoyl, changed after the UV explosion and the reduction of cinnamoyl can be explained by mutual reaction of two cinnamoyl groups leading to formation of dimer.

• Start material  $\delta_{11-11}: \delta_{\alpha}: \delta_{\beta} = 2:1:1.03$ 



• After irradiation  $\delta_{11-11}$ :  $\delta_{\alpha}$ :  $\delta_{\beta} = 2: 0.62: 0.69$ 

*Figure 4.11:* result of <sup>1</sup>H-NMR analysis. Initial A2FA spectrum (bottom) and A2FA spectrum after UV exposure (top).

Another analysis was performed by SEC-DMF. According to the principle of this technique, if the product is bigger than starting monomers, the eluting time will be shorter. The Figure 4.12 and 4.13 shows that a new peak appears on the sample exposed to the UV radiation. The software elaboration reports that the corresponding mass of this new peak was about the double of the starting material. This result could be further optimized since the SEC-DMF was not calibrated for this molecular weight plus the polystyrene used to calibrate had different functional group than the material used (which could have led to different column interactions).



*Figure 4.12:* on the left graph of the SEC-DMF analysis, the selected peak is the A2FA while the other is the solvent's signal; on the right the MW analysis derived from the software, only reagent is present.



*Figure 4.13:* on the left graph of the SEC-DMF analysis, the selected peaks are the proof of presence of new molecule, the dimer; on the right the MW analysis derived from the software, reagent is present but dimer as well since the peak in correspondence of double mass of reagent.

The solution of A2FA was tested with UV-VIS measurement. The Figure 4.14 shows the result. After 15 and 25 seconds of the exposure there was a reduction in the absorbance in the double bond region. The small concentration is the reason for less time required than in RT-FTIR where the sample was pure and not diluted.

One other good result was the possibility to understand the match between the emission spectra of the mercury lamp used and the absorbance of the component. The Hamamatsu lamp has important emission peaks at 365 nm, 334 nm and 312 nm. The last two are in the absorbance region of the material (Figure 4.14) so the reaction can happen. Moreover, the high level of the absorbance, 1.5 Abs, could explain the low conversion seen in the NMR result. Dissolving all the sample used for RT-FTIR the conversion in <sup>1</sup>H-NMR did not reach high level as shown before since the UV cannot reach the all thickness of the sample.



*Figure 4.14:* UV-VIS data, red line represents the initial point while the dash line and dot line represent 15 s of explosion and 25 s respectively.

# 4.7. Film characterization

The characterization of the different coatings was performed using different techniques in order to study the kinetics reaction, the reactivity of the starting materials and thermal and mechanical properties of the cured networks.

The different cross-link kinetics were studied using the photo-rheometer. The obtained samples are shown in the Figure 4.15. The color of h-A2FA samples were less yellowish than the A2FA ones.

Focusing on the analyzed data there can be done two different comparisons: the influence of the different monomers on the kinetics and the influence of different percentage of co-monomer in the two formulations. Concerning the first comparison (Figure 4.16): the h-A2FA storage modulus has a higher slope and reached the plateau faster than the A2FA. Moreover, after the lamp was switched on the h-A2FA reaction started immediately whereas the A2FA required an induction time. From these considerations it is clear that the h-A2FA reaction has a higher reactivity and a faster reaction kinetic than the A2FA one. The total conversion time was different, the plateau for h-A2FA was reached faster than for the other one so, for the successive study of conversion was chosen a different irradiation time: one minute for h-A2FA and 2 minutes for A2FA.



*Figure 4.15:* top A2FA films, bottom h-A2FA films. From left to right the percentage of co-monomer increases from left to right in these amounts: 0% - 5% - 10% - 15%.



Figure 4.16: photo-rheology comparison between the h-A2FA and A2FA formulations.

The Figure 4.17 shows the result obtained on the formulation containing different percentage of co-monomer. In this case is clear that the co-monomer influenced only the final value of the storage modulus. The kinetic of the cross-link reaction was not influenced by presence of co-monomer. The curves followed the same trend with almost the same slope. The difference was in

the final value of the modulus, the h-A2FA without any co-monomer reached higher value than the formulation with 15 %. Moreover, a trend can be seen: the reduction of modulus was proportional to the increase in the co-monomer percentage. For both A2FA and h-A2FA films the formulations with 15 % of h-EA1FA gave the lowest modulus. The reason can be attribute to the mono-functionality of the added co-monomer which decrease the cross-links density.



*Figure 4.17:* photo-rheology results of the tested composition for the A2FA on the left, and hA2FA on the right.

The FTIR was used to show the success of the cross-linking reaction. This analysis was conducted by collecting the spectrum before and after the curing. The Figure 4.18 represents the A2FA spectra variation at different time intervals. The Figure 4.19 reports the h-A2FA spectra in which there can be clearly seen both reduction of the thiol peak at 2590 cm<sup>-1</sup> and the reduction of the double bond peak at 1640 cm<sup>-1</sup>.

In order to calculate the final conversion, the Equation 4.1 was used.

$$Conversion = 1 - \frac{A^{thiol/ene}}{A^{ref}}$$
(4.1)

where  $A^{ref}$  is the area ration between the area after and before the irradiation of the reference peak which is expected to remain unchanged during the whole reaction. In this case as reference was chosen the following peak: stretching of the double bond C=C in the benzene ring, at 1550 cm<sup>-1</sup>.

A<sup>thiol/ene</sup> is the area ration between the area collected after and before the irradiation of the thiol or ene peak. The results are summarized in the Table 4.1.



*Figure 4.18:* FTIR spectra of the A2FA formulation evaluated in three different conditions: pre curing, after one minute and after two minutes of irradiation. S-H peak is around 2550 cm<sup>-1</sup> and ene peak is in the region between 1650 and 1550 cm<sup>-1</sup>.

*Table 4.1:* calculated final conversion of the different formulation according to the FTIR results. Irradiation under Dymax UV lamp with an intensity of  $110 \text{ mW/cm}^2$ .

Film formulation	Conversi	ion (%)
	S-H	C=C
A2FA	86	-
A2FA (trifunctional)	99	-
A2FA+5% h-EA1FA	85	-
A2FA+10% h-EA1FA	85	-
A2FA+15% h-EA1FA	83	-
h-A2FA	99	98
h-A2FA+5% h-EA1FA	100	98
h-A2FA+10% h-EA1FA	100	96
h-A2FA+15% h-EA1FA	99	98



*Figure 4.19:* FTIR spectra pre and post curing after one minute. The disappearance of the thiol and the double bond have been highlighted.

The formulations with h-A2FA reached higher conversion than the others. The trend was around complete conversion for both the thiol and the double bond. This confirms the stochiometric reaction, one double bond reacts with one thiol, so the reaction is defined as click photopolymerization

The A2FA total conversion was around 85 % for the thiol, while the conversion of the double C=C was much lower (Figure 4.18).

Since the conversion after two minutes was still not complete and the peak relative to double bond did not disappeared suggest the taking place of a reaction involving the cinnamoyl double bond. The cinnamoyl double bond may react with the thiol as well, while in the thiol : ene molar ratio evaluated only the allyl group were considered as active groups into the photocuring reaction. This is the reason why A2FA monomers was then considered as trifunctional. The results obtained by changing the formulation ratio shows an almost complete thiol conversion. However, further test should be done in order to understand the reactivity of the two type of the double bonds present into the monomer. The figure 4.20 reports the A2FA spectra. It is possible to observe a change in the thiol signal which completely disappeared with respect to previous signal reported in Figure 4.18. Moreover, the reduction of the ene region was more visible than formulation in which A2FA was evaluated as bi-functional.



*Figure 4.20:* FTIR spectra of A2FA formulation evaluated as trifunctional; pre and post (one minute and two minutes of irradiation).

The DMTA analysis was performed to investigate the thermo-mechanical properties of the obtained films. In this analysis particular stress was given to the peak of the damping factor which can be attribute to the  $T_g$  and to the values of the storage modulus E'. The films were cured in the silicon mold shown before and the results are reported in the Figure 4.21.

Like before two studies were conducted: the influence of the co-monomer into the formulations and a comparison between the A2FA and h-A2FA formulations.

The Figure 4.22 reports the DMTA of the formulation containing the co-monomer in different percentages into the monomer A2FA and h-A2FA respectively. As expected, it is possible to observe a reduction in the  $T_g$  increasing the amount of co-monomer. This is reasonable since the h-EA1FA is mono-functional and it gives less possibility to cross-link. The  $T_g$  is directly related to the cross-link density so a decrease in the density means reduction in  $T_g$ . The structure is more flexible, and the cooperative segmental mobility can start at lower temperature. In the Figure 4.21 it is clear that the height of tan  $\delta$  is decreasing when the percentage of co-monomer increases: the peak maximum decrease since less cross-links are present and broadens which indicate a decrease of network homogeneity. This trend is also shown in the decrease of E'. The h-A2FA samples had better homogeneity with respect to A2FA once since they have a sharper Tan $\delta$  peak. One possible explanation of this behavior can be found in the dispersion of the co-monomer which was more difficult in the A2FA formulations.



Figure 4.21: films of A2FA used for DMTA.



Figure 4.22: Tano curves of A2FA samples (left) and of h-A2FA samples (right) with different amount of co-monomer.

Comparing the A2FA and h-A2FA formulations there can be seen a difference of about 20 °C on the Tan $\delta$  peak. The lower T<sub>g</sub> for the h-A2FA, despite an higher total conversion, can be explained with the difference in the chemical structure of the monomer. In fact, the absence of the double bond made the network more flexible this is the reason why the formulation has lower T<sub>g</sub>. The double bond in the A2FA is conjugated to the benzyl ring and this can increase the network stiffness. The A2FA value of T<sub>g</sub> and the storage modulus evaluated considering the monomer as trifunctional was higher the one evaluated considered as bi-functional. The data was in good agreement with the higher conversion calculated in the FTIR analysis.

The Figure 4.23 reports the Tan $\delta$  curves acquired for the three compositions described in the previous paragraph. The Table 4.2 resumes all the data.



Figure 4.23: peak of Tano for the h-A2FA, A2FA (bifunctional) and A2FA (trifunctional).

Film formulation	T <sub>g</sub> (°C)
A2FA	20.1
A2FA (trifunctional)	24.1
A2FA+5% h-EA1FA	18.8
A2FA+10% h-EA1FA	17.0
A2FA+15% h-EA1FA	14.8
h-A2FA	0.6
h-A2FA+5% h-EA1FA	-0.2
h-A2FA+10% h-EA1FA	-2.4
h-A2FA+15% h-EA1FA	-5.0

**Table 4.2:**  $T_g$  evaluated by DMTA analysis.

The DMTA analysis is also useful to compare the storage modulus in a range of temperatures. Figure 4.20 shows the trend of the storage modulus for the tested compositions. The increase on the co-monomer affects the modulus which decrease with higher co-monomer percentage.

The better conversion for the A2FA considered as trifunctional has a higher cross-link density and enhanced final mechanical properties with respect to the A2FA considered as bifunctional.



*Figure 4.24:* E' curves of A2FA in red evaluated as bifunctional and in green evaluated as trifunctional (left); the E' trend for the h-A2FA (right) with different co-monomer concentrations.

The A2FA modulus reached lower value than the h-A2FA (Figure 4.25), this is in agreement with the photo-rheology data and with the calculated conversion. In fact, also in the photo-rheology the reached plateau for the modulus was lower in the A2FA than in h-A2FA formulation and the lower conversion for this last one contributes to explain the lower value. Considering the A2FA trifunctional the obtained modulus was higher than the other obtained for the other two compositions. This can be explained with a higher number of reactive sites.

From the DMTA analysis it is also possible to evaluate the cross-link density. The Equation 4.2 derives from the statistically theory of rubber elasticity and gives an estimation of the strand density, density of cross-links.

$$v_c = \frac{E'}{3RT} \tag{4.2}$$

where  $v_c$  is the number of mole per unit chains per unit volume of the cross-linked network, E ' is the storage modulus evaluated in the rubbery plateau, R is the gas constant and T is the temperature evaluated as  $T_g + 50$  °C.



*Figure 4.25:* comparison between the storage modulus of the h-A2FA, A2FA bifunctional and A2FA trifunctional of the network.

All the data are summarized in the Table 4.3. The highest cross-link density was reached using A2FA trifunctional while the h-A2FA one was lower than A2FA trifunctional but higher than A2FA bifunctional. This can explain why the storage modulus of h-A2FA is higher than the A2FA bifunctional. The differences among the  $T_g$  values can be explained by looking into the chemical structure of the monomers; in fact, the presence of the cinnamoyl double bond improves the network stability and increases its rigidity, since it is a conjugated double bond with the benzyl ring.

The introduction of the co-monomer decreased the cross-link density as expected since the monomer was monofunctional. The network flexibility increases while the cross-link density decreases.

Formulation	Conversion (S-H)	$T_{ m g}$	Е'	Vc
	0⁄0	°C	Ра	mmol/dm <sup>3</sup>
A2FA	86	20.1	2.08E+06	258
A2FA (trifunctional)	99	24.1	6.38E+06	781
A2FA+5% h-EA1FA	85	18.1	1.04E+06	130
A2FA+10% h-EA1FA	85	17.6	5.65E+05	71
A2FA+15% h-EA1FA	83	12.8	2.60E+05	33
h-A2FA	99	0.6	5.38E+06	711
h-A2FA+5% h-EA1FA	100	-0.2	4.87E+06	645
h-A2FA+10% h-EA1FA	100	-2.4	3.75E+06	500
h-A2FA+15% h-EA1FA	99	-5.0	2.85E+06	384

*Table 4.3:*  $v_c$  and DMTA data.

The  $T_g$  obtained from the DSC analysis shows the same trend as the one obtained with the DMTA. All the data are collected in the Table 4.4. The DSC curves are reported in the Figure 4.26. Increasing the amount of co-monomer in the A2FA formulations it is possible to observe a reduction in the  $T_g$  values (Figure 4.27) while the A2FA trifunctional formulation shows the highest  $T_g$  as expected. The Figure 4.28 shows the DSC curves of A2FA mono and trifunctional and h-A2FA to highlight the differences on the  $T_g$  in the main formulations as done for DMTA analysis.

Film formulation	Т <sub>g</sub> (°С)
A2FA	6.0
A2FA (trifunctional)	15.0
A2FA+5% h-EA1FA	4.5
A2FA+10% h-EA1FA	2.5
A2FA+15% h-EA1FA	0.5
h-A2FA	-7.5
h-A2FA+5% h-EA1FA	-8.0
h-A2FA+10% h-EA1FA	-9.5
h-A2FA+15% h-EA1FA	-11.0

*Table 4.4:*  $T_g$  evaluated by DSC analysis.



Figure 4.26: graph of the different DSC curves for the formulation containing h-A2FA.



Figure 4.27: graph of the different DSC curves for the formulation containing A2FA.


Figure 4.28: graph of the different DSC curves for the three most important formulation.

## 5. Conclusion

This study demonstrate that the Ferulic acid can be successfully modified in order to obtain promising starting materials in the field of UV curable coatings.

It was possible to obtain high reaction yield in the hydrogenation, allylation and esterification reactions. Mono and bi functional monomers were synthetized and deeply analyzed by NMR, both proton and carbon, FTIR and TLC.

In this work was also investigated the [2+2] photodimerization which showed an interesting high conversion. However, even if it was possible to obtain the desired product, it was impossible to isolate it. The reversibility of this photodimerization could be used as marker of ageing or changing in environmental conditions [21] [56].

The liquid products, A2FA, h-A2FA and h-EA1FA were further used in combination with a thiol monomer order to create a new series of thiol-ene UV-curable coatings.

The reaction kinetics and the final thermo-mechanical properties of the cured films were fully investigated by different techniques.

The formulation containing the A2FA (trifunctional) had higher  $T_g$  and higher E' in the rubber region than A2FA (bifunctional).

The importance of the chemical structure on the final properties was also evaluated. The presence of the cinnamoyl double bond made the network more rigid and more stable in temperature so the  $T_g$  of A2FA was higher than the  $T_g$  of h-A2FA.

The flexibilization of the network as a consequence of the monofunctional addition was verified by means of photo-rheology, DSC and DMTA analysis. The cross-link density, the Tg and the storage modulus decrease while the amount of monofunctional increase.

The E' values were analyzed by taking into consideration the reaction conversion and the network chemical structure. The formulation containing A2FA (trifunctional) showed the highest cross-link density due to the highest E' value in the rubber plateau.

Further work in the optimization of allylation reaction and in the purification of the final mixture could be done maybe considering new eco-friendly solvent alternatives. The isomerization procedure can also be improved by enhancing the solvent extraction and by increasing the final conversion.

In conclusion, this work demonstrates the feasibility of using Ferulic acid as a green starting monomer for developing UV-curable coatings. This provides the framework for future studies aimed to further investigate these promising materials.

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