UNIVERSITAT ROVIRA I VIRGILI

HETERO-MICHAEL ADDITION TO SUNFLOWER OIL DERIVATIVES AS PRECUSORS OF POLYMERIC MATERIALS

Maryluz Moreno Rueda

Dipòsit Legal: T.65-2014

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.

Maryluz Moreno Rueda

HETERO-MICHAEL ADDITION TO SUNFLOWER OIL DERIVATIVES AS PRECURSORS OF POLYMERIC MATERIALS

PhD Thesis

Supervised by Dr. Marina Galià i Clua and
Dr. Joan Carles Ronda i Bargalló

Departament de Química Analítica
i Química Orgànica

UNIVERSITAT ROVIRA I VIRGILI

Tarragona
2013

UNIVERSITAT
ROVIRA I VIRGILI
Departament de Química Analítica
i Química Orgánica

c/ Marcel.li Domingo, s/n
Campus Sescelades
43007, Tarragona
Telf. 977 559 769
Fax. 977 558 446

Marina Galià i Clua, Catedrática de Universidad, y Joan Carles Ronda Bargalló, Catedrático de Universidad, del Departamento de Química Analítica y Química Orgánica de la Universidad Rovira i Virgili.

Hacen constar:

Que el presente trabajo, titulado “Hetero-Michael addition to sunflower oil derivatives as precursors of polymeric materials”, que presenta Maryluz Moreno Rueda para la obtención del título de Doctor, ha sido realizado bajo nuestra dirección en el Departamento de Química Analítica y Orgánica de esta Universidad y que cumple los requisitos para poder optar a la Mención Europea.

Tarragona, 22 de julio de 2013

Prof. Marina Galià i Clua   Prof. Joan Carles Ronda i Bargalló

A mi familia

Al final de una de las etapas más enriquecedora en mi formación profesional y personal, quiero expresar mis agradecimientos a todas las personas que han contribuido de una u otra forma en la realización de esta tesis.

En primer lugar a la Universidad Rovira i Virgili por la beca otorgada para la realización de esta tesis doctoral.

A la Prof. Virginia Cádiz por darme la oportunidad de pertenecer a su grupo de investigación y por estar siempre dispuesta a escuchar. A mis directores de tesis la Prof. Marina Galià y el Prof. Joan Carles Ronda. A Marina por su dedicación, comprensión y paciencia durante todos estos años, también te agradezco por ayudarme a crecer. A Joan Carles por su entusiasmo y colaboración en el laboratorio; mi conocimiento en síntesis y material de laboratorio se incrementó considerablemente. También quiero agradecer al Dr. Gerard Lligadas por la ayuda oportuna y sus comentarios constructivos en las reuniones de grupo, a los profesores del área: Prof. Sergio Castillón, Dra. Yolanda Díaz, Prof. Maribel Matheu, Dr. Toni Reina, y especialmente a la Prof. Àngels Serra por ser la más cercana.

I would like to thank Prof. José Maria Kenny, Prof. Luigi Torre and Dr. Ilaria Armentano from University of Perugia in Italy for accepting me in their group and your support and interest on my work. A special thanks to, Dr. Samantha, Dr. Elena, Dr. Debora, Dr. Maurizio, Dr. Roberto, Dr. Franco, Dr. Silvia, Dr. Marco, Francesca, Mado and Leo (el che). Grazie a tutti voi per tutti!

Quiero expresar mi agradecimiento al personal del Servei de Recursos Científics i Tècnics de la URV: Martí Yebras, Antonio de la Torre, Francesc Gispert, Rosa Ras, a las chicas de Microscopía Mercè Moncusí, Mariana Stefanova, Núria Argany, Rita Marimon Picó y a Ramón Guerrero por estar siempre dispuesto a sintonizar nuevamente el fósforo, por la paciencia y el optimismo que te caracteriza. Un especial agradecimiento a las secretarias y técnicos del departamento: Avelina, Olga, Eulalia, Dunia, Juan Luis, Tere y Taïs por las mejores tartas del Barça.

A mis compañeros y amigos de los laboratorios 326 y 327. Mis Suspoleros son muchas las experiencias vividas, las alegrías, las tristezas, los sueños y los momentos compartidos durante estos cuatro años de mi vida en Tarragona. A Marta por las pizzas, caminatas y tiempo compartido, a Lucas por ser un gran guía turístico y por aparecer de repente cuando menos lo espero, Kike mi antiguo y nuevo compañero de trabajo. Rodolfo amigo, gracias por compartir tu visión de la vida, los pequeños detalles hacen la diferencia!. A Cristina por ese viaje compartido gracias ti creo que conozco muy bien Berlín. Mis Turcas Zeynep y Alev quienes han traído nuevos aires y sabores al laboratorio. Sí, estoy hablando del Baklava, gracias por compartir vuestra cultura. A Mariola, Xavi, Ignasi, Danfeng y Marc el niño del laboratorio y a Camilo coterráneo, compañero de master, de laboratorio y de doctorado, amigo en la vida, gracias por estar ahí.

A los Sucreros porque siempre están dispuestos a compartir y ayudar. A Miriamcita mejor conocida como Miriamcienta por ser la más amigable, A Isma porque siempre estas atento a ayudar, a las niñas Emma y Miriam por su alegría, A Sebastián, Pep, Xavi, Mariam y especialmente a Isidro por ser un gran amigo y por el reencuentro. A Idoia feliz por animarme y hacerme sonreír. A los chicos del laboratorio 330, A los que ya son doctores Silvana, Foix, Mireia, Cristina M. y a los que están en proceso: Suryakant, Marjorie, Cristina A., Cris y Daylin; especialmente a mis antiguos compañeros de piso Adrian y Asta. Adrian aun te recuerdo practicando tus canciones y Asta has sido una gran amiga, gracias a ti y a tu familia por acogerme en Lituania y hacerme sentir una más de tu hogar. Rubab thanks for your friendship.

A las hermanitas Arasa y vuestra familia de quienes aprendí el amor por Deltebre. Estrella de verdad iluminas. Mercè molt bona xiqueta, gracias por tu amistad, apoyo y energía durante esta última etapa. ¡Siempre recordaré las dunas!

A las personas que conocí durante estos años, son tantas y tengo tanto por agradecer pero especialmente a Paulita, Yanine, Julian y Said mi ciberamigo, Gozde y a los antiguos amigos; pero que han llegado a Tarragona Natacha y Luis gracias por los paseos. Also I would like to thank my dear Idente's family in Italy.

A mis compañeros de master en Madrid de quienes siempre llevaré un hermoso recuerdo en mi corazón. Al Dr. Daniel Lopéz quién por primera vez me abrió las puertas de la investigación en España. A Ester y Rosiña por seguir en contacto durante todo este tiempo. A Yeli por ser mi familia en Madrid.

A mis amigos en Colombia, por los pocos encuentros en cafés, en restaurantes y hasta en los aeropuertos. Especialmente a Saida, Ciro, Alix, Felipe, Susan y Omar por tantas conversaciones por skype. A la familia Pinto Maquilon por su constante apoyo, especialmente a la Sra. Alcira y a mi médica favorita July. A Leito por sus llamadas y consejos para la vida.

A Dios quien ilumina el sendero por donde continuo caminando y al tesoro más grande que hay en mi vida, mi familia. A mis padres Santiago y Flor por su gran amor, por ser mis guías, mi apoyo, mi refugio y consuelo y la inspiración para seguir adelante. A mis hermanos Alex y Elkin. Alex gracias por secundar cada una de mis decisiones, por mis sobrinos Daniel y Sarita quienes alegran mis fines de semana. Elkin mejor amigo y confidente en todas las etapas de mi vida, gracias por siempre tener la palabra exacta y la frase perfecta. Ina gracias por quererme y comprenderme tanto. Nonita María agradezco cada una de tus oraciones. Familia gracias a su amor me levanto cada día y quiero ser mejor. Los Amo y no hay palabras para expresar mis sentimientos tan solo un cálido abrazo en la distancia y esperar ansiosamente el momento en que nuestra familia se vuelva a reunir.

Finalmente, a Edwin mi amigo, mi compañero de viaje, de aventuras y el amor de mi vida. Gracias por querer siempre lo mejor para mí, por apoyarme en todas mis decisiones, por brindarme alegría y fortaleza en los momentos más difíciles; por los sacrificios realizados y porque caminar de tu mano lo ha hecho más fácil. Te amo.

Maryluz

Table of contents

Chapter 1

Chapter 2

Chapter 3

Chapter 1

Introduction, scope and objectives

In this chapter, the origin of concepts such as sustainable development and Green Chemistry and their connection with the area of polymer research and industry are described. Moreover, this chapter is giving a general idea about vegetable oils as renewable resources, their composition and reactivity. The objectives of this Thesis as well as a brief description of the organization of the manuscript are included in the last part of the chapter.

> *"The true book of philosophy, the book of nature is written in characters unknown to our alphabet" Galileo*

Sustainable Development

In 1980, the International Union for the Conservation of Natural Resources (IUCN) published the World Conservation Strategy (WCS) which provided a precursor to the concept of sustainable development. “'This is a kind of development that provides real improvements in the quality of human life and at the same time conserves the vitality and diversity of the Earth. The goal is development that will be sustainable.”[1] In 1987, the term “sustainable development” came out of the United Nations Commission on Environment and Development (Bruntland Commission) and was defined as “the development that meets the needs of the present without compromising the ability of future generations to meet their own needs”[2]

In June 1992, the United Nations Conference on Environment and Development (UNCED) was held in Rio de Janeiro and adopted an agenda for environment and development in the 21st Century. Agenda 21: A Program of Action for Sustainable Development contains the Rio Declaration on Environment and Development, which recognizes each nation’s right to pursue social and economic progress and assigned to States the responsibility of adopting a model of sustainable development. For the first time also, the lifestyle of the current civilization was addressed in Principle 8 of the Rio Declaration. The urgency of a deep change in consumption and production patterns was expressly and broadly acknowledged by State leaders. Agenda 21 further reaffirmed that sustainable development was delimited by the integration of the economic, social and environmental pillars.[3]

On 24th December 2009 the United Nations (UN) General Assembly adopted a Resolution (A/RES/64/236) agreeing to hold the United Nations Conference on Sustainable Development (UNCSD) in 2012 - also referred to as 'Rio+20' or 'Rio 20'. The Conference seeks three objectives: securing renewed political commitment to sustainable development, assessing the progress and implementation gaps in meeting already agreed commitments, and addressing new and emerging challenges. The Member States have agreed on the following two themes for the Conference:

green economy within the context of sustainable development and poverty eradication, and institutional framework for sustainable development.[4]

Since UNCED, sustainable development has become part of the international lexicon. The concept has been incorporated in many UN declarations and its implementation, while complex has been at the forefront of world's institutions and organizations working in the economic, social and environmental sectors. However, they all recognize how difficult it has proven to grant the environmental pillar the same recognition enjoyed by the other two pillars despite the many calls by scientists and civil society signaling the vulnerability and precariousness of the Earth since the 1960s.

In relation to chemical sciences, the Environmental Protection Agency coined a new term in 1998 that collected the ideals of sustainability applied to chemistry: Green Chemistry, also called Sustainable Chemistry. Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. The Green Chemistry is based on Twelve Principles.[5] These Twelve Principles as articulated by Anastas and Warner serve as a guide for developing more environmentally-benign products and processes.

1. Prevention: It is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less Hazardous Chemical Syntheses: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing Safer Chemicals: Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. Using Safer Solvents and Auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of Renewable Feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. Reduce Derivatives: Unnecessary derivatization (use of blocking groups, protection/deprotection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents, generate waste and consume energy.
9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for Degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for Pollution and Prevention: Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The concept and practice of Green Chemistry forms the core of developing a strategy for a sustainable chemical industry and, indeed, a sustainable world. The most prestigious award available in the field of chemistry, the Novel Prize in Chemistry, also recognized the importance of new green procedures when in 2005 The Royal Swedish Academy of Sciences has decided to award to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock for the development of the metathesis method in organic synthesis.

Green Chemistry is increasingly seen as a powerful tool that researchers must use to evaluate the environmental impact of different chemical technologies. Many attempts are being made not only to quantify the *greenness* of a chemical process but also to factor in other variables such as chemical yield, the price of reaction components, safety in handling chemicals, hardware demands, energy profile and ease of product workup and purification.[6]

The main challenges of green chemistry and engineering can be summarized as

- Utilizing renewable instead of scarce resources
- Avoiding toxic dangerous chemicals in safer processes to obtain safer products
- Minimizing energy use
- Minimizing waste and resource use, reusing products, recovering and recycling materials

making processes globally more efficient.

Because polymers are one of chemicals produced in largest quantities, the use of renewable resources, energy saving and waste reduction in the production, processing and recycling of polymeric materials are important issues in greener polymer chemistry. Many efforts in this direction have been made during the last years. Presidential Green Chemistry Challenge Awards, which began in 1995 as an effort to recognize individuals and businesses for innovations in green chemistry, awarded improvements in polymer chemistry. Some outstanding examples are the Greener Synthetic Pathways Award in 2005, for Archer Daniels Midl, (Company Novozyme) for developing NovaLipid™, low trans fats and oils produced by enzymatic interesterification of vegetable oils using lipozyme; the Greener Chemical Award in 2007 for Cargill Inc. for developing BiOH polyols from soybean oil and the Academic Award in 2012 for Professor Geoffrey W. Coates, (Cornell University) for synthesizing biodegradable polymers from carbon dioxide and carbon monoxide. [7]

Renewable Resources in Polymer Chemistry

There are two types of natural resources in the world: renewable and non-renewable. Renewable resources are those that are replenished through biogeochemical and physical cycles. By contrast, non-renewable resources do not replenish themselves, or, as in the case of fossil fuels, do so only at a very slow rate. Renewable resources include solar energy, wind, falling water, the heat of the earth (geothermal), plant materials (biomass), waves, ocean currents, temperature differences in the oceans and the energy of the tides. Although renewable resources have been used for various purposes for centuries, there is currently a significant focus on expanding and optimizing this use in the form of new technologies fit for the 21st century.[8] Those renewable resources may be the source of power for renewable energy and also feedstock for the chemical industry.

The use of renewable raw materials as a feedstock for the production of materials, chemicals and other biobased products can save fossil resources and reduce negative impacts on the environment.[8] It can also support the agricultural and forestal sector, and generate multiple applications, for example, biomaterials or biobased chemicals. Many renewable resources have been used in the chemical industry (table1.1).[9]

The most important renewable resource is plants. It was estimated that around 120 billion tons carbon in biomass, equivalent to 80 billion tons of oil equivalents (toe), are generated globally year by year by photosynthesis.[10] In 2004, the global primary energy supply was 11.2 billion toe and was estimated to be 20.6 billion toe in 2030.[11] Nowadays, only about 5% of biomass are used by man. From a chemical point of view, about 75% of biomass are carbohydrates, 20% lignins and only about 5% fats and others. Clearly, the detailed knowledge of the chemistry of these biomolecules will be absolutely necessary on the way to a sustainable usage of biomass as renewable feedstock.[12]

The first synthetic thermoplastic materials, cellulose esters, followed by two other types of modified natural oligomers, namely linoleum from linseed oil and vulcanized rubber appeared during the second half of 19th century. From then, the study and application of polymerization reactions both in renewable resources and monomers from fossil-based chemicals has grown enormously. A progressive shift in favor of the oil-based resources dominated the scene of macromolecular synthesis by the end of the last century and this state of affairs still reflects today’s reality. Several factors are steadily pushing to the return to the exploitation of renewable resources. Fossil resources are dwindling, their prices fluctuate with an overall tendency to rise and the industrial activities associated with their transformation into commodity chemicals and polymers are often ecologically unsound.

Table 1.1 Principal renewable raw materials*

Raw Materials	Plants and other sources	Applications
Plant oils, animal fats	Rape, sunflower, olive, soybean, oil palm, fish oil	Lubricants, surfactants, paint additives, polymers
Proteins: gelatin, Casein and other	Animal tissue, milk protein, yeast extracts	Pharmaceutical products, photo films, paper coating, glues, paints, polymers
Sugar, molasses, syrup	Sugar beet sugar cane	Bulk and fine chemicals, polymers, cosmetics (alkyl polyglycosides), pharmaceuticals
Starch, starch derivates, syrups	Wheat, potato, maize, other cereals, rice, cassava	Paper starch, glues, binders, chemicals, cosmetics, polymers, textile, starch, bioethanol
Wood	Soft wood, hard wood tropical hard wood	Construction, wood, packaging, furniture, derived timber products paper
Natural fibers	Hemp, flax, nettle, cotton kenaf, jute, abaca, sisal, ramie	Textiles, nonwovens (insulating material), fiber reinforced plastics, paper

* Obtained from European Topic Centre on Sustainable Consumption and Production.[9]

The use of biomass as a resource has developed rapidly in recent years, and it will become an important contributor to available resources in the future. Biomass sets itself aside from the other renewable resources since the energy it contains is stored as chemical bonds. This characteristic allows biomass to be used for several purposes apart from electricity and heat generation, such as the production of chemicals. Indeed, biomass is the only renewable source of useful carbon atoms. The concept of the “biomass refinery” puts forward an approach, similar to that of the classical petrol counterpart, in which each of the different components of a given natural resource is isolated by chemical or biochemical means with the aim of turning them into useful products. Although biomass is annually renewable, it is still a scarce and limited industrial resource, especially when produced in a sustainable manner, and it is important to use it in the most efficient way.[8]

The field of polymers from renewable resources is undergoing a remarkable development in both quantitative and qualitative terms as highlighted in the literature.[13-18] The above citations give an overview on opportunities and challenges, which are critical to promote biorefinery in the production of renewable chemicals, monomers and polymers.

Vegetable oils as renewable feedstock in polymer chemistry

Oils and fats of vegetable origin are historically as well as currently one of the most important renewable feedstock of the chemical industry. In the last 10 years production of the nine major vegetable oils has risen from 80 to 133 million tonnes (66%), mainly due to increases in palm (24.2 million tonnes), sunflower (15 million tonnes), soybean (11.5 million tonnes), and rapeseed oil (8.6 million tonnes).[10]

The 26.2 million tonnes of non-food uses of the major plant oils included about 11 million tonnes of biodiesel. The difference of about 15 million tonnes was used mainly in the chemical industry. Thus, the importance of fats and oils as renewable feedstock for the chemical industry is steadily increasing.[19]

According to the statistics, it will be important to introduce and to cultivate more and new plants containing fatty acids with interesting and desired properties for chemical utilization while simultaneously increasing the agricultural biodiversity. The problem of the industrial utilization of food plant oils has become more urgent with the development of the global biodiesel production.[20] The cultivation of the respective plants for the production of these oils would increase the agricultural biodiversity, an important aspect of a sustainable utilization of renewable feedstocks. Moreover, classic breeding as well as genetic engineering will be necessary to improve the oil yield and the fatty acid composition for chemical utilization.[21,22]

Vegetable oils: composition and reactivity

The word ‘‘oil’’ is used for triglycerides that are liquid at ordinary temperatures. A triglyceride is an ester product obtained from one molecule of glycerol and three molecules of fatty acids (Figure 1.1). It can also be artificially produced from the reaction of glycerol and fatty acids.[23]

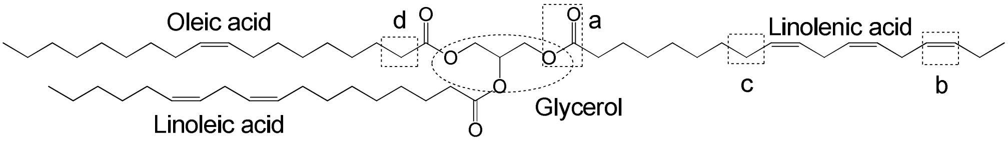


Figure 1.1 General structure and reactive positions of triglycerides (In this example, with oleic, linoleic and linolenic acids): ester groups (a), C=C double bonds (b), allylic positions (c) and α positions of ester groups (d).

The fatty acids contribute from 94–96% of the total weight of one molecule triglyceride oil. Some fatty acids are saturated and some of them are unsaturated; furthermore unsaturated fatty acids can have one or more double bonds. Additionally, some natural fatty acids have other functional groups, with acid chains having hydroxyl, epoxy, or double bonds (Figure 1.2).

Different vegetable oils contain differing composition of fatty acids depending on the plant and the growing conditions.[24] The main vegetable oils and their fatty acid content are recorded in the Table 1.2

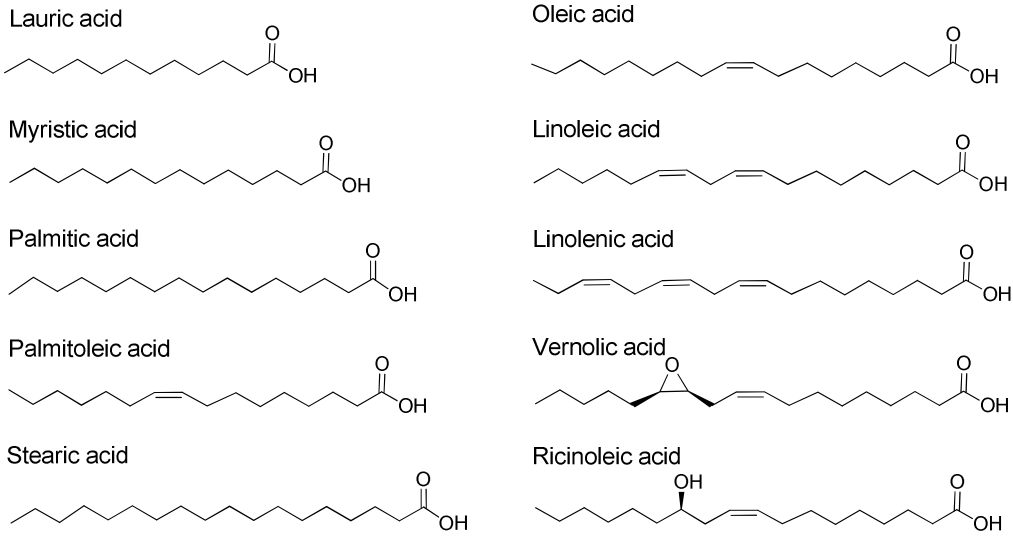


Figure 1.2 Some fatty acids in natural oils.

Table 1.2 Fatty acid composition of some common plant oils.

Acids Oils	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Formula	$C_{12}H_{14}O_2$	$C_{14}H_{28}O_2$	$C_{16}H_{32}O_2$	$C_{18}H_{36}O_2$	$C_{18}H_{34}O_2$	$C_{18}H_{32}O_2$	$C_{18}H_{30}O_2$
DB*	-	-	-	-	1	2	3
Sunflower	0	0	6	4	28	61	0
Palm kernel	50	15	7	2	15	1	0
Soybean	0	0	10	5	21	53	8
Linseed	0	0	5	4	22	15	52
High Oleic sunflower**	0	0	7	3	83	2	4

*Number of double bond, ** Obtained from genetically engineered seeds.

The physical state of vegetable oils depends on both the nature and the distribution of the fatty acids. Generally, higher melting point vegetable oils are obtained with more carbons in the fatty acid chain, a lower number of carbon–carbon double bonds, an E (trans) configuration and conjugation of the carbon–carbon double bonds.

The degree of unsaturation a vegetable oil is perhaps the most relevant parameter. It is usually determined by measuring the iodine value (IV) and represents the amount of iodine (mg) that reacts with the carbon–carbon double bonds in 100 g of vegetable oil; the larger value indicates more carbon–carbon double bonds per vegetable oil triglyceride. Thus, vegetable oils can be classified as drying oils (IV > 130), semi-drying oils (100 < IV < 130), and non-drying oils (IV < 100).[25] Drying oils have been extensively used in coatings, lacquers, paints and inks and constitute one of the first examples of using vegetable oils in polymer chemistry.

Newly developed genetic engineering techniques are likely to make unique contributions to the expansion of vegetable oils available to the chemical industry, such as increasing the content of individual fatty acids or dramatically changing the oil quality by the introduction of a new fatty acid. Whitin this context, “high oleic” sunflower (minimum 80% oleic acid content) produced using techniques based on genetic engineering have been developed by Dupont. It exhibits greater stability and resistance to oxidation over time compared to other natural oils.

Triglycerides contain several reactive positions that can act as starting points in different reactions: ester groups (a), C=C double bonds (b), allylic positions (c), and α positions of ester groups (d) (Figure 1.1). These can be used to perform natural oils transformation following three main routes (Figure 1.3).[26]

The first one is the direct polymerization through groups present in triglycerides, such as internal double bonds, which can be polymerized using different methods. Although straightforward, the direct polymerization of triglycerides do not provide polymeric materials with the mechanical and thermal properties required for some applications. Moreover, low crosslinking degrees are usually obtained which are accompanied by high soluble fractions for that reason the triglyceride-based materials had not been used for structural applications because of their low rigidity and strength. To overcome these drawbacks olefinic monomers such as styrene, divinylbenzene, norbornadiene, or dicyclopentadiene are usually copolymerized with vegetable oils.[27]

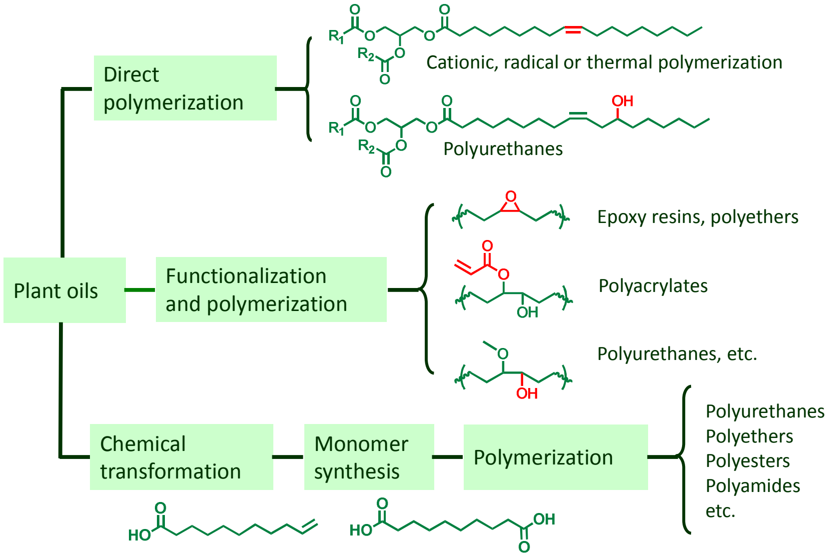


Figure 1.3 General strategies for the synthesis of plant oil-based polymers.[26]

The copolymerization of soybean oils with styrene and divinylbenzene can be achieved using BF_3OEt_2 modified with methyl oleate or norwayfish oil ethyl ester as initiator, as both are miscible with vegetable oils.[28] Styrenic monomers containing Si, B and P have been used to produce materials with improved flame retardant properties. [29,30]

The second route is the functionalization of the triglyceride double bonds to introduce readily polymerizable groups. This approach solves the drawback of the low reactivity of natural triglycerides, which usually only contain double bonds. For the synthesis of cross-linked structures, the epoxidation of the C=C double bonds is one of the most important functionalization reactions, that can be achieved by environmentally friendly procedures such as catalyzed chemical oxidation with hydrogen peroxide[31,32] or by enzymatic oxidation.[33] In addition the epoxidation reaction makes triglycerides capable of reacting via ring-opening obtaining a wide number of products.[34-36] One of the most important product from this process are the polyols.[37] These polyols can react with diisocyanates to produce vegetable oil based polyurethane thermosets [38] or waterborne polyurethane dispersions.[39]

The third route explored consists of using plant oil-derived chemicals like 10-undecenoic and oleic acids to produce tailor made monomers. The fatty acids have been used for a long time by polymer scientists for the development of polymeric structures, both directly and as building blocks for the synthesis of more sophisticated monomers.[24] Recent contributions show a growing interest in the use of fatty acids as precursors of monomers; not only because of their renewability, but also because of the properties they can provide to the final polymers.

The challenge to progressively replace fossil feedstocks by material arising from plant derived renewable resources implies not only the development of new original reactions and catalysts but also the application of well-established reactions to the functionalization of vegetable oils. Moreover, there is a need to develop environmentally friendly monomer and polymer synthesis strategies to keep moving towards more sustainable polymer chemistry and the reactions termed “click chemistry” are consistent this aim.

The singlet oxygen “ene” reaction is one of the highest investigated processes in organic chemistry to functionalize the allylic C-H bonds of unsaturated compounds. This reaction was discovered in 1948 by Schenck,[40] who demonstrated that allylic hydroperoxides are readily prepared by reaction of alkenes with photochemically generated singlet oxygen. The mechanism of this reaction has been widely studied and it is actually well-established.[41] For synthetic applications, the unsaturated substrate can be photoxygenated “in situ” with singlet oxygen generated by means of a high pressure sodium-vapor lamp and tetraphenylphorphyrin (TPP) as sensitizer in an oxygen saturated medium, to give a mixture of isomeric allylic hydroperoxides (Figure 1.4). This reaction has been used to oxidize the allylic position of fatty acids and their derivatives.[42] The mild conditions utilized and the use of oxygen, as the only reagent, makes this process particularly favorable from both economic and ecological viewpoint.

The allylic hydroperoxides resulting from photoperoxidation of the allylic positions can undergo a number of different transformations.[43-45] A common transformation of allylic hydroperoxides is their reduction to the corresponding hydroxylic compounds (Figure 1.4). The mixture of allylic hydroperoxides can be reduced "in situ" to a mixture of secondary allylic alcohols using diverse common reducing agents. The resulting hydroxyl containing tryglicerides can be esterified with acryloil chloride thus being a method of direct acrylation, alternative to the traditional method used to obtain acrylate oils. [44,45]

Other interesting reaction is the conversion of the hydroperoxides into a regioisomeric mixture of enones, which can be carried out in the presence of acetic anhydride and pyridine or tertiary amines[46,47] (Figure 1.4). This reaction has been scarcely used with fatty acids and their derivatives. This environmentally friendly chemical procedure was applied for first time to obtain enone-containing triglycerides from high oleic sunflower oil.[48]

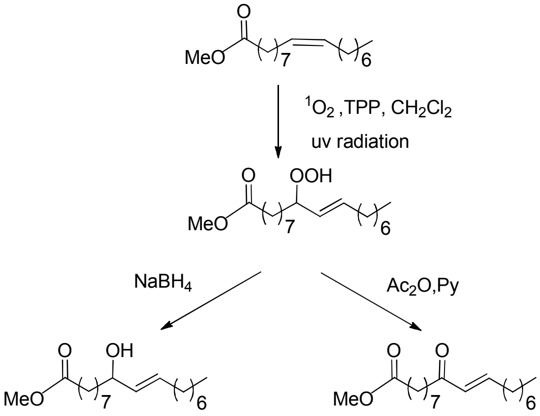


Figure 1.4 Photooxygenation with singlet oxygen and transformation of the resulting hydroperoxides in allylic alcohols or α-β-unsaturated ketones.

The aza-Michael addition has been used as crosslinking reaction of the enone-containing derivatives to produce thermosets by crosslinking with diamines. After the initial aza-Michael addition at high temperatures, a set of cascade reactions occur leading to quinoline moieties that causes the improvement of the thermal and mechanical properties of these thermosets.[49]

This curing process is much faster than the corresponding nucleophilic attack over the epoxide ring and in this way, enone-containing triglycerides could be considered as interesting alternative to epoxidized oils. Following the criteria of Sustainable and Green Chemistry, Sharpless introduced the concept of Click Chemistry in 2001. This concept encompasses a wide range of reactions characterized by selectivity, facile experimental set-up, applicability in aqueous and aerobic systems, and tolerance to a variety of functional groups, quantitative yields, and minimal synthetic work-up.[50] Even though the specific chemistries that were proposed to represent click reactions are not new, in fact most of these reactions have been well known for years; Sharpless concept has led to a significant change in the same strategies and the overall approach to synthetic problems. The click philosophy is based on the concepts of modularity and orthogonality: building blocks for a final target are made individually and subsequently assembled by means of click reactions. While the main application of click chemistry was originally envisaged to be in the synthesis of biologically active molecules, the click concept has had a great influence in polymer chemistry. For the design of functionalized macromolecular architectures, the efficiency of click conjugations combined with the lack of side products and facile purification led to a strong practical value. Moreover, the modular concept facilitates the synthesis of polymer materials that would not have been achievable otherwise and it also greatly increases the range of structures that can be prepared. Nevertheless, many chemists use the term click to describe their reactions even though they often not proceed to high conversions or require tedious purification procedures. A set of requirements that should be fulfilled in order for a reaction to be designated as click in the context of synthetic macromolecular chemistry has been pointed out. In addition to the original definition by Sharpless, a true click reaction in macromolecular synthesis should allow using equimolar amounts of the building blocks and should reach a very high yield to avoid complex purification techniques. Moreover, a click reaction should proceed on a reasonable timescale and require no tedious fine-tuning of reaction conditions.[51]

Initially the Cu (I) catalyzed azide-alkyne clycloaddition attracted most of the attention in polymer chemistry; however, this concept can be extended too many other highly eficient reactions, such as nucleophilic substitutions, radical additions, Michael additions as well as Diels-Alder and retro Diels-Alder reactions. Among the multiple reactions that have been accepted into the click chemistry realm, the radical addition of thiols to C=C bonds, which is currently called thiol-ene addition, is absolutely the champion in the field of oleochemistry.[52]

Scope and objectives

As above explained, research into the exploitation of renewable resources is of great importance from both environmental and economical aspects. The development of polymers from renewable resources is consistent with the aim of global sustainability and is also receiving considerable attention since the availability of crude oil will become severely restricted within the foreseeable future. Other issues as energy saving and waste reduction in the production, processing and recycling of polymeric materials and design of safer materials are also important in sustainable polymer chemistry. Guided by this green philosophy, there is a need to develop environmentally friendly monomer and polymer synthesis strategies to keep moving toward more sustainable polymer chemistry.

The main objective of this thesis was to develop new biobased polymers from vegetable oils as renewable resources. To achieve this goal, the experimental work was focused on exploiting the reactivity of the enone derivatives of high oleic sunflower oil to prepare different monomers for polymer synthesis by using different methodologies. The specific objectives were:

- To explore the phospha-Michael and the thiol-Michael additions to the methyl oleate enone derivative as new routes to the synthesis of new monomers from vegetable oils.
- To prepare phosphorus-containing sunflower oil thermosets with enhanced flame retardant properties as halogen-free safer materials.
- To develop new functionalized thermoplastic polyesters by enzymatic polymerization.
- To carry out the post-polymerization modification of the linear polymers.
- To develop new biobased nanocrystalline cellulose nanocomposites.

Chapter two describes the synthesis and characterization of new flame retardant materials by phospha-Michael addition. The experimental procedures and the results of the studies performed in this chapter have been published in Journal of Polymer Science Part A: Polymer Chemistry 2012, 50, 3206-3212 and Journal of Polymer Science Part A: Polymer Chemistry 2013, 51, 1808-1815.

Chapter 3 is focused on the synthesis of a novel monomer from methyl oleate by thiol-Michael addition, its enzymatic polymerization as well as the post-polymerization functionalization. The results of these studies have been published in Green Chemistry (DOI: 10.1039/C3GC41346B). A second part of this chapter describes the preparation of new crystalline cellulose nano-biocomposite.

References

1 World Conservation Strategy, I., UNEP and WWF. http://www.unep.org/geo/geo3/english/049.htm (accessed: Mar 13, 2013).

2 Brundtland, G. H., World Commission on Environment and Development. http://www.un-documents.net/our-common-future.pdf (accessed Mar 13, 2013).

3 UN. Conference on Sustainable Development. http://www.uncsd2012.org/history.html (accessed: Mar 11, 2013).

4 UN. General Assembly of the United Nations. http://www.un.org/en/ga/64/resolutions.shtml (accessed: Mar 13, 2013).

5 Anastas, P. T. W., J. C., Ed. Green Chemistry: Theory and Practice ,; Oxford University Press: New York, 1998.

6 Anastas, N.; Warner, J. In Green Chemistry Education: Changing the Course of Chemistry; American Chemical Society: Washington, 2009, p 117-136.

7 Environmental. Protection Agency United States. http://www.epa.gov/greenchemistry/pubs/pgcc/presgcc.html (accessed Mar 15, 2013).

8 Vennestrøm, P. N. R.; Osmundsen, C. M.; Christensen, C. H.; Taarning, E. Angew. Chem. Int. 2011, 50, 10502-10509.

9 Almut, J. G., J.; Raschka, A.; Carus,M.; Piotrowski, S.; Scholz, L., Use of renewable raw materials with special emphasis on chemical industry. http://scp.eionet.europa.eu/publications/Use%20of%20RRM/wp/WP2010_1 (accessed Abr 1, 2013)

10 IPCC. Climate change. In: Working Group I Report: The Physical Science Basis. http://www.ipcc.ch (accessed: Abr 12, 2013).

11 International Energy Agency. World Energy Outlook 2006. OECD/IEA: Paris (France), 2006.

12 Metzger, J. O. Eur. J. Lipid Sci. Technol. 2009, 111, 865-876.

13 Montero De Espinosa, L.; Meier, M. A. R. Eur. Polym. J. 2011, 47, 837-852.

14 Belgacem, M. N.; Gandini, A. Monomers, Polymers and Composites from Renewable Resources; Elsevier Science, 2008.

15 Yao, K.; Tang, C. Macromolecules 2013, 46, 1689-1712.

16 Gandini, A. Green Chem. 2011, 13, 1061-1083.

17 Gandini, A. Macromolecules 2008, 41, 9491-9504.

18 Raquez, J. M.; Deléglise, M.; Lacrampe, M. F.; Krawczak, P. Prog. Polym. Sci. 2010, 35, 487-509.

19 Gunstone, F. D. Lipid Technology 2013, 25, 24-24.

20 Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. Angew. Chem. Int. 2011, 50, 3854-3871.

21 Dyer, J. M.; Stymne, S.; Green, A. G.; Carlsson, A. S. Plant. J. 2008, 54, 640-655.

22 Cahoon, E. B.; Shockey, J. M.; Dietrich, C. R.; Gidda, S. K.; Mullen, R. T.; Dyer, J. M. Curr. Opin. Plant. Biol. 2007, 10, 236-244.

23 Seniha Güner, F.; Yağcı, Y.; Tuncer Erciyes, A. Prog. Polym. Sci. 2006, 31, 633-670.

24 Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. Chem. Soc. Rev. 2007, 36, 1788-1802.

25 Bailey, A. E.; Swern, D.; Applewhite, T. H.; Formo, M. W. Bailey's Industrial oil and fat products; Wiley, 1985.

26 Ronda, J. C.; Lligadas, G.; Galià, M.; Cádiz, V. Eur. J. Lipid Sci. Technol. 2011, 113, 46-58.

27 Lu, Y.; Larock, R. C. ChemSusChem 2009, 2, 136-147.

28 Li, F.; Hanson, M. V.; Larock, R. C. Polymer 2001, 42, 1567-1579.

29 Sacristán, M.; Ronda, J. C.; Galià, M.; Cádiz, V. Biomacromolecules 2009, 10, 2678-2685.

30 Sacristán, M.; Ronda, J. C.; Galià, M.; Cádiz, V. Polymer 2010, 51, 6099-6106.

31 Lane, B. S.; Burgess, K. Chem. Rev. 2003, 103, 2457-2474.

32 Grigoropoulou, G.; Clark, J. H.; Elings, J. A. Green Chem. 2003, 5, 1-7.

33 Uyama, H.; Kuwabara, M.; Tsujimoto, T.; Kobayashi, S. Biomacromolecules 2003, 4, 211-215.

34 Esen, H.; Küsefoğlu, S. H. J. Appl. Polym. Sci. 2003, 89, 3882-3888.

35 Petrović, Z. S.; Guo, A.; Zhang, W. J. Polym. Sci. Part A: Polym. Chem. 2000, 38, 4062-4069.

36 Behera, D.; Banthia, A. K. J. Appl. Polym. Sci. 2008, 109, 2583-2590.

37 Javni, I.; Zhang, W.; Petrović, Z. S. J. Appl. Polym. Sci. 2003, 88, 2912-2916.

38 Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. Biomacromolecules 2007, 8, 1858-1864.

39 Lu, Y. S.; Larock, R. C. Biomacromolecules 2007, 8, 3108-3114.

40 Schenck, G. Naturwissenschaften 1948, 35, 28-29.

41 Greer, A. Acc. Chem. Res. 2006, 39, 797-804.

42 Samadi, A.; Martínez, L. A.; Miranda, M. A.; Morera, I. M. Photochem. Photobiol. 2001, 73, 359-365.

43 Frimer, A. A. Chem. Rev. 1979, 79, 359-387.

44 Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 1159-1167.

45 Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 4051-4063.

46 Kornblum, N.; DeLaMare, H. E. J. Am. Chem. Soc. 1951, 73, 880-881.

47 Ohloff, G. Pure Appl. Chem. 1975, 43, 481-502.

48 Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 6843-6850.

49 Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2010, 48, 869-878.

50 Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Angew. Chem. Int. 2001, 40, 2004-2021.

51 Barner-Kowollik, C.; Du Prez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; Van Camp, W. Angew. Chem. Int. 2011, 50, 60-62.

52 Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 2111-2124.

Chapter 2

Polymers from renewable resources: enone-containing high oleic sunflower oil as precursor of flame retardant thermosets

Chapter 2 is focused on the development of plant oil-based flame retardant polymers by phospha-Michael addition to the enone-containig trygliceride.

> *"Great works are performed not by strength, but by perseverance." Samuel Johnson*

The Michael addition reaction

The Michael addition, named for Arthur Michael, is a versatile synthetic methodology for the efficient coupling of electron poor olefins with a vast array of nucleophiles. The reaction, which is also commonly termed conjugate addition, has recently gained increased attention as a polymer synthesis strategy for tailored macromolecular architectures.[1] The Michael addition benefits from mild reaction conditions, high functional group tolerance, a large host of polymerizable monomers and functional precursors as well as high conversions and favorable reaction rates[2]

This reaction lends itself to both step growth[3] and chain growth polymerization[4] and has been employed in the synthesis of linear, graft, hyperbranched, dendritic and network polymers. Furthermore, post-polymerization modification and coupling of biological and synthetic polymers are often facilitated by the Michael reaction.[5] These features make the Michael addition reaction well-suited to numerous emerging technologies including biomedical applications such as gene transfection,[6] cell scaffolds[7] and tissue replacements.[2]

The Michael addition reaction produces a wide range of polymers from diverse monomers; polymers which are prepared in environments in which other polymerization mechanisms will not operate. In biological applications such as protein derivatization, high temperatures, oxidizing radicals and organic solvents are not feasible and the mild Michael addition reaction conditions are favorable. Furthermore, the Michael addition has found utility for the synthesis of crosslinked polymers such as hydrogels,[8] thermoset resins and coatings[9] where rapid cure and high conversions are necessary for performance. Few polymerizations offer sufficient rates to permit room temperature cure and industrial coatings are often limited to toxic and environmentally hazardous agents. The Michael addition proceeds rapidly at room temperature, offers low cure times and involves less toxic precursors. Nonlinear optical materials can also be obtained using the Michael addition which benefits from the absence of volatile byproducts.[10] The Michael addition has been widely used in classical polymer chemistry such as the anionic polymerization of alkyl methacrylates and cyanoacrylates.

The Michael addition involves the addition of a nucleophile, also called a “Michael donor”, to an activated electrophilic olefin, the “Michael acceptor” resulting in a “Michael adduct”, as shown in Figure 2.1

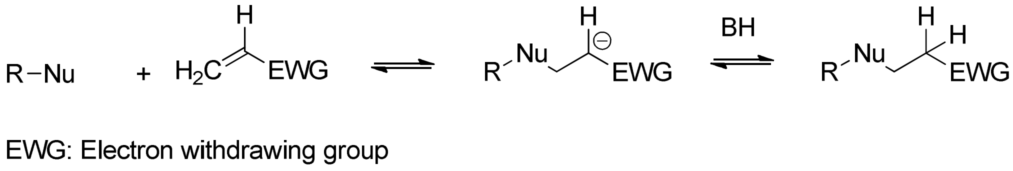


Figure 2.1.Schematic representation of the Michael addition reaction[1]

Although this reaction is generally considered the addition of enolate nucleophiles to activated olefins, a wide range of functional groups possess sufficient nucleophilicity to perform as Michael donors. Reactions involving non-enolate nucleophiles such as amines, thiols, and phosphines are typically referred to as Michael type additions or hetero-Michael additions.

The Michael acceptor possesses an electron withdrawing and resonance stabilizing activating group, which stabilizes the anionic intermediate. Michael addition acceptors are far more numerous and varied than donors, due to the plethora of electron withdrawing activating groups that enable the Michael addition to olefins and alkynes. Acrylate esters, acrylonitrile, acrylamides, maleimides, alkyl methacrylates, cyanoacrylates and vinyl sulfones serve as Michael acceptors and are commercially available. Less common, but equally important, vinyl ketones, nitro ethylenes, α,β-unsaturated aldehydes, vinyl phosphonates, vinyl pyridines, azocompounds and even β-keto acetylenes and acetylene esters also serve as Michael acceptors.[11] It is important to note that the product of the first Michael addition has a remaining active methylene hydrogen in many cases, which can undergo a second addition to another Michael acceptor.

The reactivity of the acceptor will decrease if the substituent of the α,β-unsaturated carbonyl compound is electron rich, such as in the case of alkyl, aryl or carboethoxy substituted olefins such as styrene derivatives or vinylethers. Sterics are also an important factor. The larger the groups substituted at the α and β positions, the slower the reaction rate and differences in reactivity between acceptors require differences in nucleophilicity of the Michael donors. For instance, alkyl methacrylates are relatively poor Michael acceptors and strong nucleophiles are necessary for successful Michael additions. Better acceptors such alkyl acrylates or acrylamide accept weaker amine and thiol nucleophiles.

Typical solvents for Michael additions include methanol, ethanol, diethylether, tetrahydrofuran, benzene, xylene, dioxane and mixtures of these solvents. Protic solvents are desirable being the solvent selection depending on the solubility of catalyst, donor and acceptor. In some cases, reactions are carried out in absence of solvents, especially for network or coating applications.

The most widely applied Michael transformation is the base catalyzed one. The choice of base catalyst has tremendous effect on the reaction kinetics since nucleophile concentration is highly dependent on the relative base strength. Bases such as hydroxide, tretramethylguanidine, triethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) have been used.

Aside from the traditional base-catalyzed reaction, Michael addition can be catalyzed or initiated with certain strong nucleophiles being phosphines one of the most active catalysts of this type.

Although base catalysts are most prominently used in the Michael addition the reaction is also catalyzed with acids, particularly in the case of Lewis acids. Some of the earlier examples include the use of boron trifluoride, aluminum trichloride and zinc chloride. Besides these conventional compounds a myriad array of metal centered Lewis acid catalysts has been developed in view of the potential applications in asymmetric synthesis.[12] Metal salts or complexes derived from In (III), Bi (III), Ru (III), Rh (III), Ir (III), Ni (II), Pd (II), Pt (IV), Cu (II) and Au (I and III) are the most extensively explored. However, not all these catalysts can be applied to different types of nucleophiles. A strong Bronsted acid Tf_2NH was found to be capable of catalyzing different Michael additions[13] as well as the lewis acid $VO(OTf)_2$.[14]

Most asymmetric reactions carried out with these chiral catalysts are conducted in organic solvents and several efforts have been made to develop newer and simpler methodologies for Michael additions that lead to the development of various base and acid catalysts and novel reaction media such as water and ionic liquids. For example asymmetric Michael reactions catalyzed by $Sc(OTf)_3$-chiral bipyridine complex at room temperature in water afforded the desired products in high yields with high selectivities.[15]

The Aza-Michael Addition Reaction

The nitrogen-donor version of the Michael addition is often referred to as the aza-Michael reaction. Since amines can act as both nucleophiles and bases, no additional base is typically needed in these reactions. Primary amines can react with two equivalents of acceptor to form tertiary amines. The secondary amines are more nucleophilic than primary amines and are therefore more reactive in the aza-Michael reaction. However, it is worth noting that this is highly dependent on the electronic and steric environment of the amine. For example, 1,4-butanediol diacrylate was allowed to react with 1-(2-aminoethyl) piperazine in an equimolar ratio (Figure 2.2).[16]

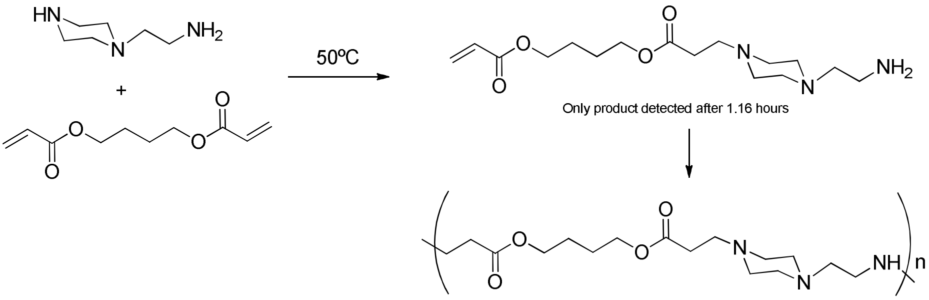


Figure 2.2 Higher reactivity of secondary amines in aza-Michael addition reactions.

During the initial part of the experiment, it was found that there was exclusive reaction with the secondary amine present in the piperazine ring. Only upon longer reaction times, did reaction occur with the primary amine, which led to polymerization.

Numerous examples of step-growth Michael addition polymerizations exist. Perhaps the earliest example is poly(amidoamine)s, which were synthesized from bisacrylamides and diamines. A second class of step-growth polymers are derived from bis-maleimides and diamines. Michael addition polymerization mechanisms were broadly applied to the design of hyperbranched polymers and graft copolymers. Dendrimers have traditionally been synthesized using Michael addition reactions, and in fact, Tomalia et al. synthesized the first dendrimer poly(amido amine) (PAMAM) using Michael additions. Moreover, network polymers can be synthesized using aza-Michael addition offering applications in diverse areas such as high performance composites and coatings. Bismaleimide-based networks are used in high performance fiber reinforced composite materials and also in thermoset resins.[17]

The aza Michael addition has been applied to the synthesis of crosslinked polymers derived from vegetable oils.[18]

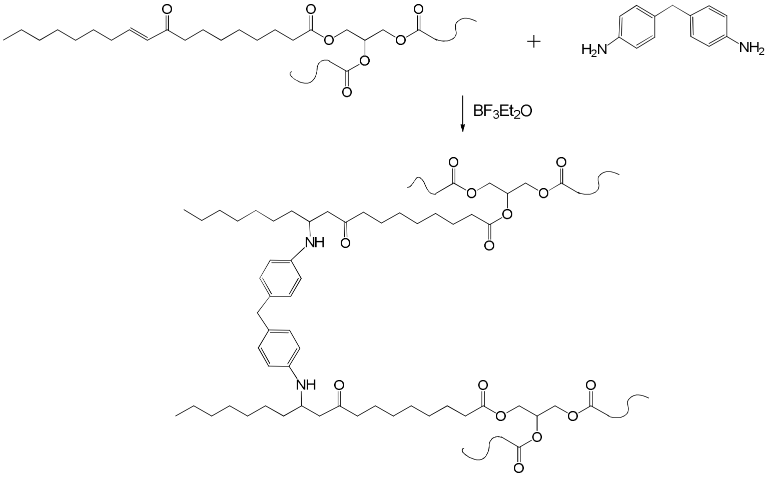


Figure 2.3 Aza-Michael addition of diaminodiphenylmethane (DDM) to enone containing triglyceride.

In the figure 2.3 a enone-containing triglyceride derivative reacted with diaminodiphenylmethane (DDM) in presence of $BF_3.Et_2O$ to obtain the expected aza-Michael adduct as a soft material.[18]

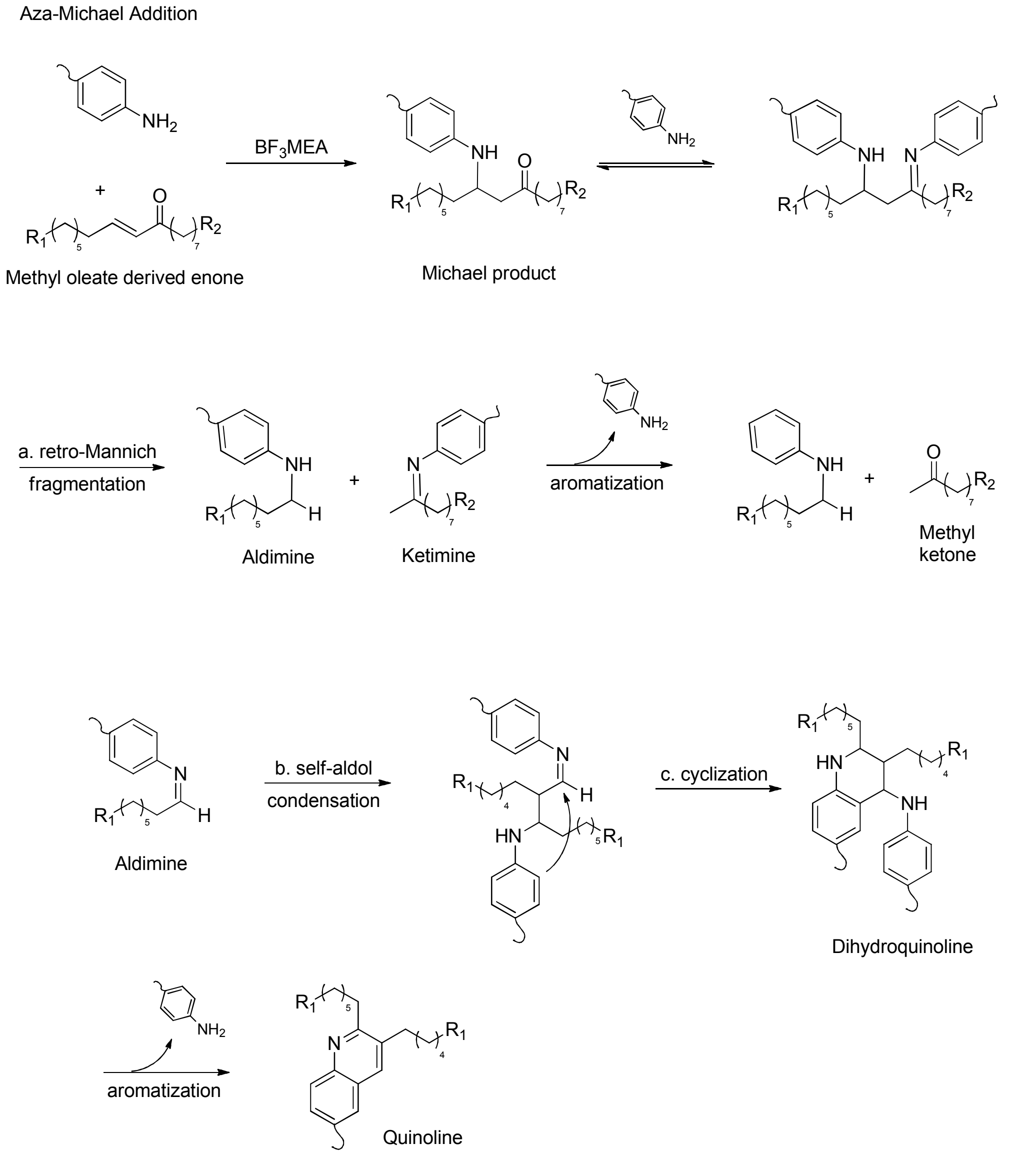


Figure 2.4 Proposed self-aldol condensation of the aldimine and further cyclization and aromatization to give quinoline.[19]

Further heating of this product lead to a harder material as a consequence of a set of consecutive reactions(Figure 2.4): a) a retro-Mannich type fragmentation leading to ketimine and aldimine moieties, b) a self-condensation of the aldimine fragment, c) a cyclization of the resulting conjugate followed by deamination and aromatization, leading to trisubstituted quinoline moieties that act as additional crosslinking sites.[18]

The Phospha-Michael Addition Reaction

Phosphorus containing monomers and polymers have been the subject of extensive research due to their peculiar and interesting properties arising from the different possible chemical environments of phosphorus atom.[20] Phosphorinated moieties can be introduced onto polymers by polymerization of monomers bearing the phosphorus atom or by grafting of the phosphorus based group onto the polymer.

Phosphorus containing materials can be employed for a large range of technological applications.[21,22] They are largely used in industry because of their aptitude to bind metals[23] and due to their interesting complexing properties.[24] Recently, the development of free halogen materials due to largest legislation gave phosphorinated polymers new opportunities to be used in flame retardancy.[25] Polymeric materials bearing phosphonic sites were also developed in alternative energy production because they have been involved in proton conducting fuel cell membranes.[26] The interest in phosphorus-based materials used in the biomedical field is growing because they proved to be biodegradable and biocompatible, showed reduced protein adsorption and led to strong interactions with dentin or bones.

The addition of a phosphorus nucleophile to an acceptor-substituted alkene or alkyne, known as a phospha-Michael addition is one of the most versatile and powerful tools for the P-C bond formation.[27,28] It is most commonly promoted by bases, acids, microwaves, transition metals and radical initiators. Olefinic acceptors bearing carbonyl, nitro, sulfones, sulfoxides or phosphonate groups as well as alkynic acceptors have been described. Moreover, several nucleophiles comprising Ph_3P, $R_2P(O)H$, $R_2P(OR')$, $RP(OR')_2$, $(RO)_3P$ or R_2PH can be used. Depending on both the acceptor and the nucleophile, many different reaction pathways are accessible and products with numerous substitution pattern can be generated. This offers the possibility to access many diversely functionalized monomers and polymers.

Flame retardant polymeric materials

The massive use of polymeric materials in our everyday life is driven by their remarkable combination of properties, low weight and ease of processing. However, polymers are also known for their relatively high flammability; most often accompanied by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications. The design and production of new polymer materials with flame retardant properties match with the principles of green chemistry as one of the main driving forces is producing safer final products and avoiding the use of dangerous materials and intermediates.

Polymer combustion

Polymers are highly combustible because of their chemical structure, made up mainly of carbon and hydrogen. The combustion reaction involves two factors: one or more combustibles (reducing agents) and a combustive (oxidizing agent). The combustive is generally the oxygen in the air. The whole process usually starts with an increase in the temperature of the polymeric material due to a heat source, to such an extent that it induces polymer bond scissions. The volatile fraction of the resulting polymer fragments diffuses into the air and creates a combustible gaseous mixture (also called fuel). This gaseous mixture ignites when the auto-ignition temperature (defined as the temperature at which the activation energy of the combustion reaction is attained) is reached, liberating heat. Alternatively, the fuel can also ignite at a lower temperature (called the flash point) upon reaction with an external source of intense energy (spark, flame, etc.)

The life span of the combustion cycle depends on the quantity of heat liberated during the combustion of the fuel. When the amount of heat liberated reaches a certain level, new decomposition reactions are induced in the solid phase, and therefore more combustibles are produced. The combustion cycle is thus self-maintained (Figure 2.5).[29]

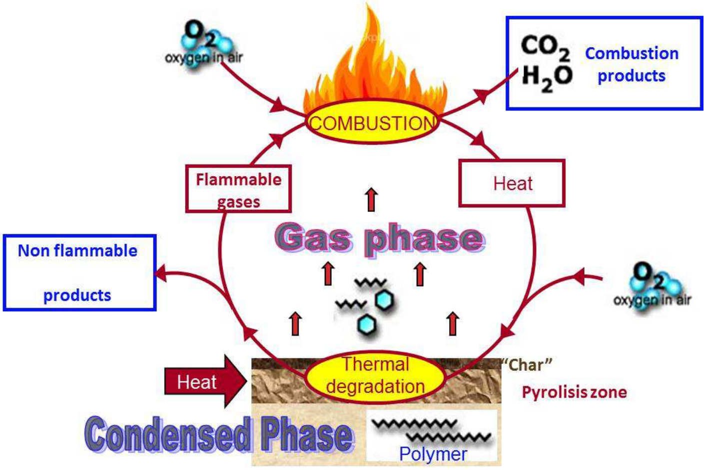


Figure 2.5 Combustion cycle.[29]

The thermal decomposition of a polymer (i.e. covalent bond dissociation) is an endothermic phenomenon, which requires an input of energy. The energy provided to the system must be higher than the binding energy between the covalently linked atoms (200–400 kJ/mol for most C–C bonds). The decomposition mechanism is highly dependent on the weakest bonds, and also on the presence or absence of oxygen in the solid and gas phases. Generally, thermal decomposition is the result of a combination of the effects of heat and oxygen. We can therefore distinguish between non-oxidizing thermal degradation and oxidizing thermal degradation.

Non-oxidizing thermal degradation is generally initiated by chain scissions under the simple effect of temperature (pyrolysis). This scission involves varying degrees of material depolymerization. The initial scission depends on several factors: the presence of oxygen atoms in the chain and catalyst residues, former residues of oxidation, chemical defects in polymer chains and the existence of weak bonds along the chain, particularly at the end, which can initiate unzipping reactions. Chain scission can occur in two ways:

- By formation of free-radicals in this case, the reaction does not stop at this stage because these radicals start a chain/cascade reaction, which occurs under both oxidizing and non-oxidizing conditions.

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 \longrightarrow R_1\text{-}CH_2^{\bullet} + R_2\text{-}CH_2^{\bullet}$$

- By migration of hydrogen atoms and the formation of two stable molecules, one of which has a reactive carbon–carbon double bond.

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \longrightarrow R_1\text{-}CH{=}CH_2 + R_2\text{-}CH_3$$

In oxidizing thermal conditions, the polymer reacts with oxygen in the air and generates a variety of low molecular weight products: carboxylic acids, alcohols, ketones, aldehydes, etc. This degradation also releases very reactive species, i.e. $H\cdot$ and $HO\cdot$

Flame retardants

Flame retardants are compounds that reduce the chances of a fire starting by providing increased resistance to ignition. Even if ignition does occur, flame retardants will act to delay the spread of flame, providing extra time in the early stages when fire can be extinguished or an escape can be made. They can be added to or applied as a treatment to materials such as plastics, textiles, of timbers, as flame retardant additives. Alternatively they can be incorporated during the production process as a chemical modification of the polymer or by synthesis of flame retardant monomers that were further homo- or copolymerized. These are known as reactive flame retardants.

Mechanism of action

In function of their nature and composition, flame retardants can either act physically or chemically by performing their activity in the condensed phase, in the gas phase or in both.[30]

The gas-phase activity of flame retardants is based on their interference in the reactions that maintain the combustion cycle.

Radical species formed during the polymer degradation react with oxygen producing the combustion propagation through the following reactions.

$$1)\quad H^{\cdot} + O_2 \longrightarrow HO^{\cdot} + O^{\cdot}$$

$$2)\quad O^{\cdot} + H_2 \longrightarrow HO^{\cdot} + H^{\cdot}$$

$$3)\quad HO^{\cdot} + CO \longrightarrow CO_2 + H^{\cdot}$$

The most exotermic reaction is 3 which provide the most energy to maintain the flame. Some flame retardants, typically halogenated flame retardants, release hydrogen halides during their thermal degradation which effectively interfere the radical propagation reactions by forming highly stable halogen radicals.

$$4)\quad RX \longrightarrow HX + R^{\cdot}$$

$$5)\quad H^{\cdot} + HX \longrightarrow H_2 + X^{\cdot}$$

$$6)\quad HO^{\cdot} + HX \longrightarrow H_2O + X^{\cdot}$$

Volatile low valence phosphorous species have been described to also act in the gas phase by this mechanism.[30]

The condensed phase mechanism implies a chemical interaction between the flame retardant and the polymer through two main modes of interaction: dehydration and crosslinking. Both contribute to the formation of char, a solid residue that protects the polymer by isolating the non-burned surface from the heat source and preventing the volatile species to reach the flame and feed it.

In some cases, flame retardants promote the formation of the named intumescent char which is a form of foamed char with high insulating capacity. Additionally, some flame retardants decompose forming a vitrified layer that acts as a physical insulating layer between the gas phase and the condensed phase (Figure 2.6).

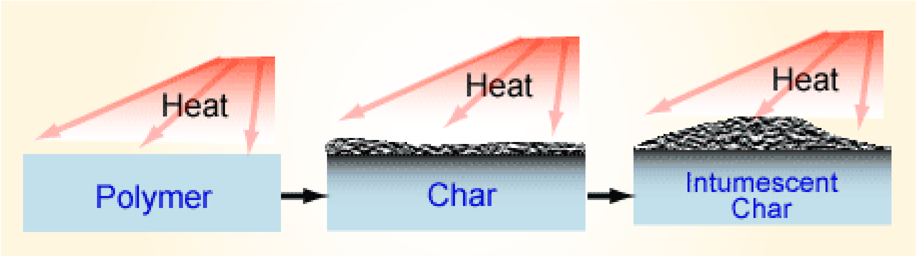


Figure 2.6 Intumecent layer formation[31]

Other mechanisms that contribute to flame reatardancy are:

- The decomposition of some flame retardant additives such as hydrated alumina is strongly endothermic inducing a temperature decrease by heat consumption.
- The decomposition of some flame retardants releases large amounts of inert gases (H_2O, CO_2, NH_3, etc.) in which the combustible gas mixture is diluted, limiting the concentration of reagents and the possibility of ignition.

As mentioned above flame retardants can be classified in two main categories namely additives and reactives.[32]

Additive flame retardants are generally incorporated mechanically during the transformation process and do not react at this stage with the polymer. They are cost effective and more widely applicable than reactive flame retardants but usually high loads are needed to reach flame retardancy (10-40%). Furthermore, since additives are mechanically blended with the polymer, migration can take place during the usage period.

Reactive flame retardants: unlike additive flame retardants, these are usually introduced into the polymer during synthesis (as monomers or precursor polymers) or in a post-reaction process (e.g. via chemical grafting) and thus they are chemically bonded to the polymer. Even more expensive, the synthesis of intrinsic flame retardant polymers though the design of flame retardant monomers, enables a better control of the final polymer properties. Moreover they are considerably more effective and low levels of modification (1-3%) have comparable effects to those achieved with relatively high loadings of flame retardant additives and the migration problems associated with additives are avoided.[25]

Flame retardants can be also classified according to their chemical nature in the Figure 2.7

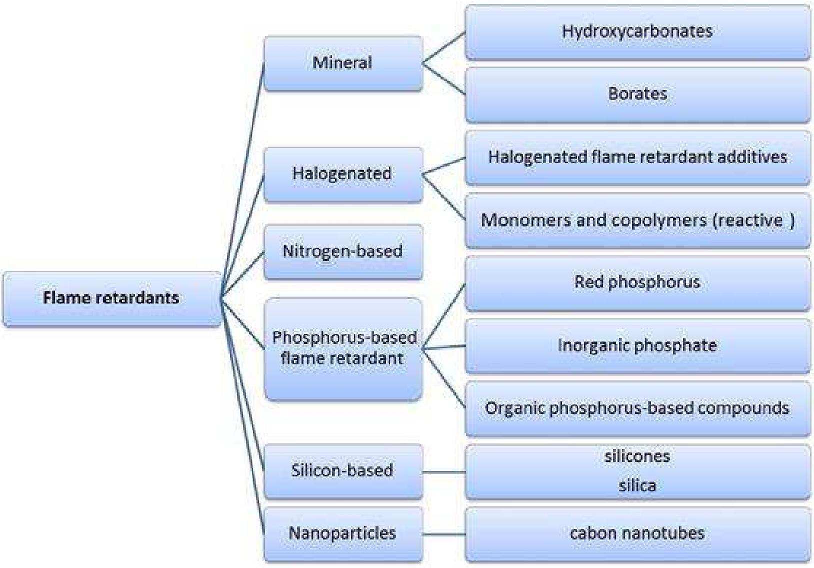


Figure 2.7 Clasification of flame retardants according to their chemical nature.

Beside the omnipresent mineral salts, oxides and other inorganic fillers (metal hydroxides, antimony oxides, stannates, etc), organic flame retardants can be roughly classified in two groups: halogenated flame retardants and non-halogenated flame retardants. This classification obeys the nowadays concerns about environment and health protection. Until now, industry is dominated by halogenated flame retardants because very little amounts are needed to infer good flame retardancy to polymers, they are cheap and versatile. However, during combustion toxic decomposition products like halogenated dibenzodioxines and dibenzofuranes and corrosive gases like hydrogen bromide are released. Moreover, some of the halogenated flame retardants are non-easily degradable and accumulate in the environment being classified as persistent organic pollutants (POPs).

Non halogenated flame retardants stand as the alternative to overcome these drawbacks. There is an immense range of organic non-halogenated flame retardants based on heteroatoms like phosphorus, nitrogen, silicon and boron.[25] Among them, phosphorus-based flame retardants have been extensively studied and proved to act efficiently mostly in the condensed phase with no significant environmental concerns.

Phosphorus-based flame retardants

The use of phosphorus compounds to infer flame retardant properties to polymeric materials is well established[33] Phosphorus-based flame retardants can be inorganic (ammonium pyrophosphate), organic, or elemental (red phosphorus). The range of organic phosphorus-based flame retardant products is extremely wide, including phosphates, phosphonates, phosphinates and phosphine oxides. These phosphorated flame retardant agents can be used as additives or incorporated into the polymer chain during its synthesis, and are known to be active in the condensed and/or vapor phase and sometimes may operate simultaneously in both phases.

Phosphine oxides[34] and phosphonates[35] have been proven to act in the gas phase through the formation of PO· radicals which terminate the highly active flame-propagation radicals (H· and HO·). These radicals are formed after the decomposition of the parent compound which implies that flame inhibition does not depend on the form of the parent compound, provided that the parent breaks down in the flame.[35]

$$1)\quad (P) \longrightarrow PO^{\bullet} + P^{\bullet} + P_2$$

$$2)\quad PO^{\bullet} + H^{\bullet} \longrightarrow HPO$$

$$3)\quad HO^{\bullet} + PO^{\bullet} \longrightarrow HPO + {}^{\bullet}O^{\bullet}$$

$$4)\quad P_2 + PO^{\bullet} \longrightarrow PO^{\bullet} + P^{\bullet} \quad \text{and so on.....}$$

Volatile phosphorated compounds are among the most effective combustion inhibitors since phosphorus-based radicals are, on average, five times more effective than bromine and ten times more effective than chlorine radicals.[29]

In the condensed phase mechanism, thermal decomposition of phosphorus flame retardants leads to the production of phosphoric acid, which is further dehydrated to polyphosphoric acid. The water released dilutes the oxidizing gas phase and polyphosphoric acid promotes condensation and dehydration reactions in the surface of polymer giving rise to unsaturated carbonaceous species that make up a residue that protects the polymer surface from the flames, limits the volatilization of fuel and prevents the formation of new free-radicals (Figure 2.8).

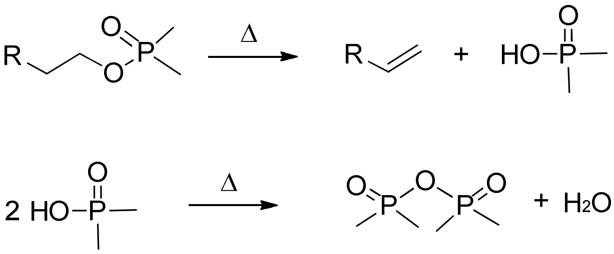


Figure 2.8 Condensed phase mechanism of phosphorus-based flame retardants.

The carbonization process takes place through several stages[36] During the process, in addition to polyphosphoric acid being formed, also reducing compounds such as phosphites can be present. They reduce carbon oxidation in favor of char.[37]

Phosphate, phosphonate and phosphinate based flame retardants have been the most widely used in polymer materials. The P-O bond possess quite high thermal stability (ΔH_{dis} about 85 Kcal/mol), however presents poor hydrolytic stability[38] that limits the range of application of the final polymeric materials. On the other hand, phosphine oxides present a P-C bond, which has a lower reactivity, being more stable and having a higher hydrolytic stability. Moreover, the P-C bond also has quite high thermal stability (ΔH_{dis} about 65 Kcal/mol).[39]

As commented above, the disadvantages of additives make the reactive approach a more suitable way to flame retardant polymeric materials. In this way increasing research is now being directed at the synthesis of phosphorus-based flame retardant polymers. Some recently published examples include polyphosphonates,[40] phosphonate –based polyurethanes,[41] polyether-esters[42] and polymethacrylates[43] phosphate containing Nylon,[44] phosphine oxide-based epoxy resins[45], polybenzoxazines[46], polyesthers[47], and a variety of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-containing derivatives[48,49]

Laboratory fire testing

The flammability of polymers can be characterized by their ignitability, flame-spread rate and heat release. Depending on the targeted application of the polymeric material, one or more of these flammability criteria need to be measured by appropriate flammability tests. There are numerous small-, intermediate- or full-scale flammability tests used in industrial or academic laboratories for either screening materials during product development or testing manufactured products, this chapter will only cover one of the most commonly used laboratory test methods: limited oxygen index.

Limited Oxygen Index: LOI

The LOI test is a widely used research and quality control tool for determining the relative flammability of materials. This test was first proposed in 1966 by Fenimore and Martin. Standardized in France (NF T 51-071) and in the United States (ASTM D 2863), the LOI test is now subject to an international standard (ISO 4589).[50] The value of the LOI is defined as the minimal oxygen concentration [O_2] in a oxygen/nitrogen mixture [O_2/N_2] required to just support candle-like downward burning of a vertically mounted test specimen. Hence, higher LOI values represent better flame retardancy. This test method is generally reproducible to an accuracy of 0.5%.

The LOI is expressed as: $LOI = 100 \times ([O_2]/([O_2]+[N_2]))$

According to ISO 4589, the LOI is measured on $80x10x4mm^3$ specimens placed vertically at the center of a glass chimney (Figure 2.9). The mixture of gases flows upstream through this chimney and is homogenized by being passed through layers of glass beads. After a 30-s purge of the column, the top of the specimen is ignited, like a candle. As air contains 21% oxygen, materials with an LOI below 21 are classified as ‘‘combustible’’ whereas those with an LOI above 21 are classified as ‘‘self-extinguishing’’, because their combustion cannot be sustained at ambient temperature without an external energy contribution

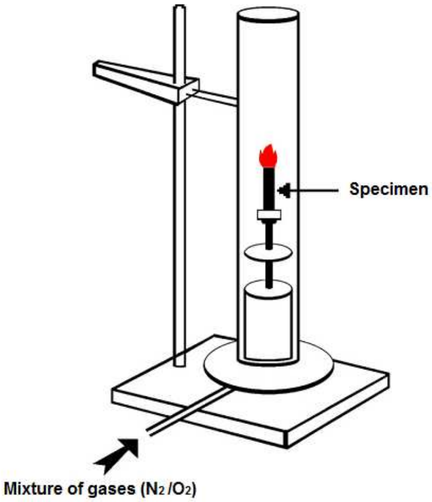


Figure 2.9 Experimental set-up for LOI measurement

References

1 Mather, B. D.; Viswanathan, K.; Miller, K. M.; Long, T. E. Prog. Polym. Sci. 2006, 31, 487-531.

2 Vernon, B.; Tirelli, N.; Bächi, T.; Haldimann, D.; Hubbell, J. A. J. Biomed. Mater. Res. Part A 2003, 64A, 447-456.

3 Vaccaro, E.; Scola, D. A. CHEMTECH 1999, 29, 15-23.

4 Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. In Polysiloxane Copolymers/Anionic Polymerization; Springer: Berlin, 1988, p 87-143.

5 Morpurgo, M.; Veronese, F. M.; Kachensky, D.; Harris, J. M. Bioconjugate Chem. 1996, 7, 363-368.

6 Richardson, S. C. W.; Pattrick, N. G.; Stella Man, Y. K.; Ferruti, P.; Duncan, R. Biomacromolecules 2001, 2, 1023-1028.

7 Ferruti, P.; Bianchi, S.; Ranucci, E.; Chiellini, F.; Caruso, V. Macromol. Biosci. 2005, 5, 613-622.

8 Rizzi, S. C.; Hubbell, J. A. Biomacromolecules 2005, 6, 1226-1238.

9 Pavlinec, J.; Moszner, N. J. Appl. Polym. Sci. 1997, 65, 165-178.

10 Abbotto, A.; Beverina, L.; Chirico, G.; Facchetti, A.; Ferruti, P.; Gilberti, M.; Pagani, G. A. Macromol. Rapid Commun. 2003, 24, 397-402.

11 Gimbert, C.; Lumbierres, M.; Marchi, C.; Moreno-Mañas, M.; Sebastián, R. M.; Vallribera, A. Tetrahedron 2005, 61, 8598-8605.

12 Desimoni, G.; Faita, G.; Jørgensen, K. A. Chem. Rev. 2006, 106, 3561-3651.

13 Wabnitz, T. C.; Yu, J.-Q.; Spencer, J. B. Chem.Eur. J. 2004, 10, 484-493.

14 Lin, Y.-D.; Kao, J.-Q.; Chen, C.-T. Org. Lett. 2007, 9, 5195-5198.

15 Ueno, M.; Kitanosono, T.; Sakai, M.; Kobayashi, S. Org. Biomol. Chem. 2011, 9, 3619-3621.

16 Wu; Liu, Y.; He; Chung; Goh. Macromolecules 2004, 37, 6763-6770.

17 Curliss, D. B.; Cowans, B. A.; Caruthers, J. M. Macromolecules 1998, 31, 6776-6782.

18 Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 6843-6850.

19 Montero de Espinosa, L.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2010, 48, 869-878.

20 Monge, S.; Canniccioni, B.; Graillot, A.; Robin, J.-J. Biomacromolecules 2011, 12, 1973-1982.

21 Huang, S.-W.; Zhuo, R.-X. Phosphorus. Sulfur. Silicon. Relat. Elem. 2008, 183, 340-348.

22 Queffélec, C.; Petit, M.; Janvier, P.; Knight, D. A.; Bujoli, B. Chem. Rev. 2012, 112, 3777-3807.

23 Essahli, M.; Colomines, G.; Monge, S.; Robin, J.-J.; Collet, A.; Boutevin, B. Polymer 2008, 49, 4510-4518.

24 Matczak-Jon, E.; Videnova-Adrabińska, V. Coord. Chem. Rev. 2005, 249, 2458-2488.

25 Lu, S.-Y.; Hamerton, I. Prog. Polym. Sci. 2002, 27, 1661-1712.

26 Jiang, F.; Kaltbeitzel, A.; Meyer, W. H.; Pu, H.; Wegner, G. Macromolecules 2008, 41, 3081-3085.

27 Enders, D.; Saint-Dizier, A.; Lannou, M.-I.; Lenzen, A. Eur. J. Org. Chem. 2006, 29-49.

28 Lenker, H. K.; Richard, M. E.; Reese, K. P.; Carter, A. F.; Zawisky, J. D.; Winter, E. F.; Bergeron, T. W.; Guydon, K. S.; Stockland, R. A. J. Org. Chem. 2012, 77, 1378-1385.

29 Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J. M.; Dubois, P. Mater. Sci. Eng. R. 2009, 63, 100-125.

30 Horrocks, A. R.; Price, D. Fire Retardant Materials; Woodhead Publishing: Cambridge, 2001.

31 Specialchem, S. A., Chemical Effect Condensed Phase. http://www.specialchem4polymers.com/tc/flame-retardants/index.aspx?id=9305 (accessed May, 2013).

32 Salamone, J. C. Concise Polymeric Materials Encyclopedia; CRC Press: New York, 1996, p 2397-2411.

33 Ebdon, J. R.; Price, D.; Hunt, B. J.; Joseph, P.; Gao, F.; Milnes, G. J.; Cunliffe, L. K. Polym. Degrad. Stab. 2000, 69, 267-277.

34 Shmakov, A. G.; Shvartsberg, V. M.; Korobeinichev, O. P.; Beach, M. W.; Hu, T. I.; Morgan, T. A. Mendeleev Commun. 2007, 17, 186-187.

35 Jayaweera, T. M.; Melius, C. F.; Pitz, W. J.; Westbrook, C. K.; Korobeinichev, O. P.; Shvartsberg, V. M.; Shmakov, A. G.; Rybitskaya, I. V.; Curran, H. J. Combust. Flame 2005, 140, 103-115.

36 Delobel, R.; Le Bras, M.; Ouassou, N.; Descressain, R. Polym. Degrad. Stab. 1990, 30, 41-56.

37 Hörold, S. Polym. Degrad. Stab. 1999, 64, 427-431.

38 Beach, M. W.; Rondan, N. G.; Froese, R. D.; Gerhart, B. B.; Green, J. G.; Stobby, B. G.; Shmakov, A. G.; Shvartsberg, V. M.; Korobeinichev, O. P. Polym. Degrad. Stab. 2008, 93, 1664-1673.

39 Quin, L. D. A Guide to Organophosphorus Chemistry; John Wiley & Sons, 2000.

40 Ranganathan, T.; Zilberman, J.; Farris, R. J.; Coughlin, E. B.; Emrick, T. Macromolecules 2006, 39, 5974-5975.

41 Chen, H.; Luo, Y.; Chai, C.; Wang, J.; Li, J.; Xia, M. J. Appl. Polym. Sci. 2008, 110, 3107-3115.

42 Canadell, J.; Mantecón, A.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 1980-1992.

43 Edizer, S.; Sahin, G.; Avci, D. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 5737-5746.

44 Yang, H.; Yang, C. Q.; He, Q. Polym. Degrad. Stab. 2009, 94, 1023-1031.

45 Spontón, M.; Ronda, J. C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 2142-2151.

46 Spontón, M.; Ronda, J. C.; Galià, M.; Cádiz, V. Polym. Degrad. Stab. 2009, 94, 145-150.

47 Hoffmann, T.; Pospiech, D.; Häußler, L.; Komber, H.; Voigt, D.; Harnisch, C.; Kollann, C.; Ciesielski, M.; Döring, M.; Perez-Graterol, R.; Sandler, J.; Altstädt, V. Macromol. Chem. Phys. 2005, 206, 423-431.

48 Spontón, M.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. Polym. Degrad. Stab. 2009, 94, 1693-1699.

49 Yang, S.-C.; Kim, J. P. J. Appl. Polym. Sci. 2007, 106, 2870-2874.

50 Camino, G.; Costa, L.; Casorati, E.; Bertelli, G.; Locatelli, R. J. Appl. Polym. Sci. 1988, 35, 1863-1876.

Phospha-Michael Addition to Enone-Containing Triglyceride Derivatives as an Efficient Route to Flame Retardant Renewable Thermosets

---

"Wanderer, there is no road, the road is made by walking." Antonio Machado

Chapter 2. J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 3206-3213

Phospha-Michael Addition to Enone-Containing Triglyceride Derivatives as an Efficient Route to Flame Retardant Renewable Thermosets

Maryluz Moreno, Gerard Lligadas, Joan C. Ronda, Marina Galià, Virginia Cádiz

Departament de Química Analítica i Química Orgánica, Universitat Rovira i Virgili,
C/ Marcel.lí Domingo s/n,
Tarragona 43007, Spain

Abstract

A novel phosphorus-containing vegetable oil (PETR) was prepared through phospha-Michael addition of a diphenylphosphine oxide to the enone derivative of high-oleic sunflower oil (ETR). The reaction was investigated using the enone derivative of methyl oleate under conventional thermal heating and microwave irradiation. The kinetic study showed a great enhancement of reaction rate for the microwave-initiated addition.The crosslinking of ETR with diaminodiphenylmethane (DDM) via aza-Michael addition was also investigated under microwave irradiation, showing a noticeable acceleration of the curing. The new phosphorus-containing triglyceride was crosslinked with DDM to obtain phosphorus-containing vegetable oilbased thermosets of different phosphorus contents. Limiting oxygen index values from 26.4 to 35.0 for the final materials were obtained, demonstrating that the flame retardant properties of vegetable oil-based thermosets can be improved by adding covalently bonded phosphorus to the polymer.

Keywords

Aza-Michael addition; flame retardance; heteroatom-containing polymers; microwave irradiation; phospha-Michael addition; renewable resources.

Introduction

Recently, the use of nonpetrochemical feedstocks for the development of designed polymeric materials has received particular attention due to environmental and economic concerns.[1,2] Plant oils are considered to be one of the cheapest and most abundant biological sources available, and their use as annually renewable platform chemicals has numerous advantages, including low toxicity and inherent biodegradability.[3,4] Synthetic polymeric materials are used in many areas, and thus, the fire hazards associated with the use of these materials are of great concern for both users and manufacturers. Plant oil-based materials, just than many other currently used polymeric materials, are flammable, being this flammability a shortcoming in some applications. Halogen-based flame retardant polymers and additives have been a cost-effective solution for flame retardant applications. However, there is now an increased global emphasis on discontinuing the use of halogenated compounds due to the release of toxic gases on combustion that are harmful to both humans and environment. According to the sustainability issues, there exists the need to develop flame retardant materials that preserve the efficacy of function while reducing risk and toxicity to human health and environment.[5] Phosphorus-based polymers are a well-established class of flame retardant materials, which are preferred to the widely applied halogenated flame retardants due to health and environment reasons [6,7] The main component of plant oils are triglycerides, the product of esterification of glycerol and three fatty acids. Triglycerides have been used in the synthesis of crosslinked polymers by three main approaches. The first one takes advantage of the naturally occurring functional groups in triglycerides, such as internal double bonds, alcohols, and epoxides, which can be directly polymerized. However, the reactivity of triglycerides is limited, and a second strategy is their functionalization prior to polymerization, widening the synthetic possibilities by introducing easily polymerizable functional groups. The third strategy is the use of fatty acids, isolated from oils, to obtain useful monomers that can be used as building blocks for the synthesis of crosslinked polymers. [8-10]

The challenge to progressively replace fossil feedstocks by materials arising from plant-derived renewable resources implies not only the development of new original reactions and catalysts but also the application of well-established reactions to the production of new tailor-made compounds capable to produce competitive performance materials. The singlet oxygen promoted ‘‘ene’’ reaction is one of the highest investigated processes in organic chemistry to functionalize the C-H bonds of unsaturated compounds. Schenck[11] demonstrated that allylic hydroperoxides are readily prepared by reaction of alkenes with photochemically generated singlet oxygen. The mechanism of this reaction has been widely studied, and it is actually well established.[12] This reaction has been used to oxidize the allylic position of fatty acids and their derivatives.[13] The mild conditions utilized, and the use of oxygen, as the only reagent, makes this process particularly favorable from both economic and ecological viewpoint.

The allylic hydroperoxides resulting from the photoperoxidation can be converted into a regioisomeric mixture of enones by treatment with acetic anhydride and pyridine or tertiaryamines. We have applied this environmentally friendly chemical procedure to obtain enone-containing triglycerides from high-oleic sunflower oil.[14] The reactivity of these enone groups toward aromatic primary amines was evaluated, and the results indicated that the aza-Michael reaction proceeds in a very efficient way, and thus the enone-containing triglycerides can be considered as interesting precursors of crosslinked polymers. From a detailed study of the curing process at high temperatures we concluded that after the initial aza-Michael reaction, a set of cascade reactions occur that finally lead to a quinoline-containing thermoset.[15]

To further extend the applications of the enone-containing triglycerides, we focused on using the phospha-Michael addition of secondary phosphine oxides as a straightforward method for developing phosphorus-containing vegetable oilbased thermosets. In this study, the reactivity of diphenyl phosphine oxide (DPO) with the enone derivative of methyloleate (EMO) as model compound, both under conventional heating and microwave irradiation, has been investigated by means of a ^{1}H NMR kinetic experiment. In a further step, the phospha-Michael addition to the enone-containing triglyceride and its crosslinking with diaminodiphenylmethane (DDM) allowed us to obtain new flame retardant vegetable oil-based thermosets.

Experimental

Materials

High-oleic sunflower oil (minimum 80% oleic acid) was supplied by Coreysa. Methyl oleate (75%; Alfa Aesar), chlorodiphenyl phosphine (Aldrich), *meso*-tetraphenylporphyrin (Aldrich), borontrifluoride diethylethearate (BF_3OEt_2; Aldrich), 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD), DDM (Aldrich), triethylamine (Scharlau), and acetic anhydride (Scharlau) were used as received. Toluene was dried over sodium/benzophenone and dichloromethane over P_2O_5, both distilled immediately before use. TLC plates (aluminum sheets 20 x 20 cm^2 silica gel 60 F 254 Merck) were developed by spraying with sulfuric acid/anisaldehyde ethanol solution and heating at 200 ^{0}C. Enone derivatives of methyl oleate (mixture of methyl-9-oxo-10-octadecenoate and methyl-10-oxo-8-octadecenoate) (EMO) and high-oleic sunflower oil (ETR, 2.4 α,β-unsaturated ketones per molecule) have been obtained following a reported procedure.[14] DPO was obtained as previously described.[16]

Kinetic Measurements

Kinetic experiments were carried out by ^{1}H NMR using rubber septa sealed NMR tubes. The precise amounts of a 1 M solution of EMO and 1 M solution of DPO in dry deuterated toluene were introduced using general vacuum-line techniques.The proper amount of 0.06 M solution of $BF_3 \cdot OEt_2$ or 0.06 M solution of TBD in dry deuterated toluene as a catalyst was added (1% of catalyst).

The reaction was monitored at 60 ^{0}C. For microwave reactions, glass vials were placed inside the microwave reactor (10 mL) and subjected to microwave irradiation (150 and 300 W). Overheating of the reaction mixtures was avoided by cooling with compressed air. Samples at different reaction times were obtained and analyzed by ^{1}H NMR spectroscopy.

Phospha-Michael Addition of DPO to the Enone Derivative of High-Oleic Sunflower Oil (ETR)

ETR (0.2 g) and 0.05 g of DPO (molar ratio enone/phosphine1:0.5) were mixed in a round-bottomed flask, and 1% mol of $BF_3 \cdot OEt_2$ was added. The stirred reaction mixture was heated at 90 ^{0}C for 4 h. Samples were taken and analyzed by IR and ^{1}H NMR spectroscopy.

Table 1. Thermal- and Microwave-Initiated Reactions.

	DPO[a] (mol)	DDM[a] (mol)	T (^{0}C)	(W)	t (h)	IF (%)
1	0.5		90		2	41[b]
	0.5		120		12	51
2	0.5	0.5	90		4	63
			120		12	
3		1	90		4	48
			120		12	
4		1		150	3	70
5		1		300	3	48
6	0.5	0.5		150	3	36
7	0.5	0.5		150	6	44
8	0.5	0.5		150	3	38
				300	6	
9	0.30	0.70	90		5	60
			120		12	
10	0.23	0.77	90		5	65
			120		12	
11	0.15	0.85	90		5	75
			120		12	
12	0.08	0.92	90		5	76
			120		12	

[a] Mols of DPO and DDM per 1 mol of enone
[b] Enone conversion.

Curing Reactions

Thermally initiated curing reactions were carried out as follows.The required amounts of ETR, DPO, and DDM (Table1) were melted and then mixed, and $BF_3 \cdot OEt_2$ (1% mol) was added to the mixture. The resulting liquid was put into apreviously heated (60 ^{0}C) mold. The mixture was heated at 90 ^{0}C and postcured at 120 ^{0}C. The microwave-initiated curing was carried out by irradiating the samples at 150 and

300W. The soluble part of the cured samples was extracted by refluxing 0.5 g of each sample thoroughly triturated in 50 mL of CH_2Cl_2 during 4 h.

Instrumentation

The microwave-irradiated polymerizations were carried out using a CEM Discover monomodal microwave reactor with an IR temperature sensor and operating at a maximum power of 300 W.^{1}H NMR 400 MHz and ^{13}C NMR 100.6 MHz NMR spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform, $CDCl_3$ as solvent and TMS as internal standard. The crosslinking process was monitored with a JASCO 680 FTIR (attenuated total reflection, ATR) spectrophotometer with a resolution of 4 cm^{-1} in the transmittance mode. An ATR accessory with thermal control and a diamond crystal (Golden gate heated single-reflection diamond ATR, Specac Teknokroma) was used to determine FTIR/ATR spectra.

Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer using N_2 as a purge gas (10 mL min $^{-1}$) at scan rates between 5 and 20 ^{0}C min $^{-1}$. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as a purge gas, in the 30–800 ^{0}C at scan rates of 10 ^{0}C min $^{-1}$.

The limiting oxygen index (LOI) values (ASTM D 2863) as the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion of materials were measured on a Stanton Redcroft instrument provided with an oxygen analyzer.The dimensions of the polymer bars were 100 x 6 x 3 mm^3.

Results and discussion

The synthesis of the enone derivatives from methyl oleate and from high-oleic sunflower oil has been carried out by an environmentally friendly chemical procedure previously described by us.[14] A mixture of allylic hydroperoxides was obtained using the singlet oxygen ‘‘ene’’ reaction and further transformed into a regioisomeric mixture of enones in the presence of acetic anhydride and triethylamine.

In the first part of this work, we carried out the model study of the phospha-Michael addition of DPO onto the EMO. The phospha-Michael addition is probably one of the most important tools for phosphorus–carbon bond formation and is most commonly promoted by bases, acids, microwaves, transition metals, and radical initiators.[17] Different investigations have been carried out focusing on phosphorus nucleophiles of general structure $R_2P(O)H$.[18] This reaction is normally conducted under basic conditions, either in the presence of a basic catalyst or using a strong base in stoichiometric amounts. An interesting alternative to this base-catalyzed addition is the analogous microwave-assisted conversion under neat conditions, that is, without any solvent or catalyst.[19] The Michael addition of P(O)H groups has also been conducted stereoselectively, both with chiral P nucleophiles and with chiral Michael acceptors.[20]

In this context, the addition of the secondary phosphine oxide to the enone methyl oleate derivative has been carried out without catalyst and using $BF_3.OEt_2$ or TBD as catalyst and toluene-d_8 as solvent. In this way, the same amounts of 0.5 M solution of the enone were mixed with a 0.5 M solution of diphenylphosphine oxide in sealed NMR tubes (molar ratio 1:1). The necessary amount of a 0.06 M solution of the catalyst was added to obtain a 1% molar solution. The reactions were monitored at 60 ^{0}C through the disappearance of the characteristic double bond signals at 6.05 and 6.75 ppm, and the appearance of the multiplet signal at 3.17 ppm corresponding to the methine directly bonded to the phosphorus moiety (Fig 1). We used the signal at 3.65 ppm corresponding to the methyl in the ester group as internal reference. Different studies focused on the issue of 1,2- versus 1,4-addition to unsaturated carbonyl compounds.[17] The 1,2-addition product arises from a kinetic reaction control, and the 1,4-addition product is thermodynamically more stable, being obtained at high temperature. In our case, there was no evidence of 1,2-addition to the carbonyl group.

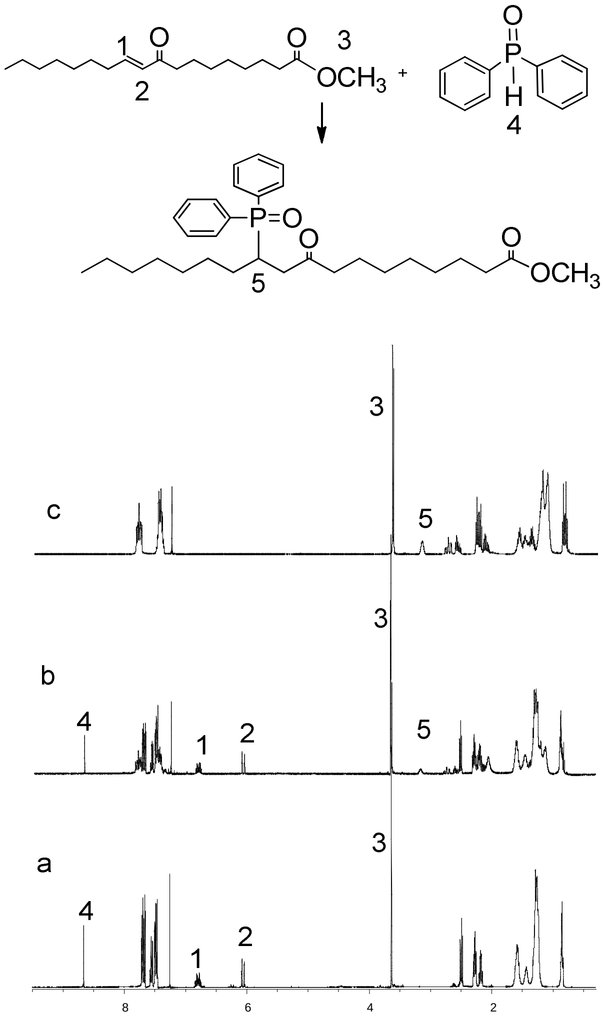


Figure 1. ^{1}H NMR spectra (CDCl$_3$/TMS, ppm) of the EMO/DPO reaction mixture for different reaction times. (a) 0 min, (b) 30 min, and (c) 8 h.

Figura 2 (a) shows the conversion versus time for the catalyzed and uncatalyzed experiences. As can be seen, the reaction occurs faster when using either acid or basic catalysts and reaches a high degree of conversion after 8 h.

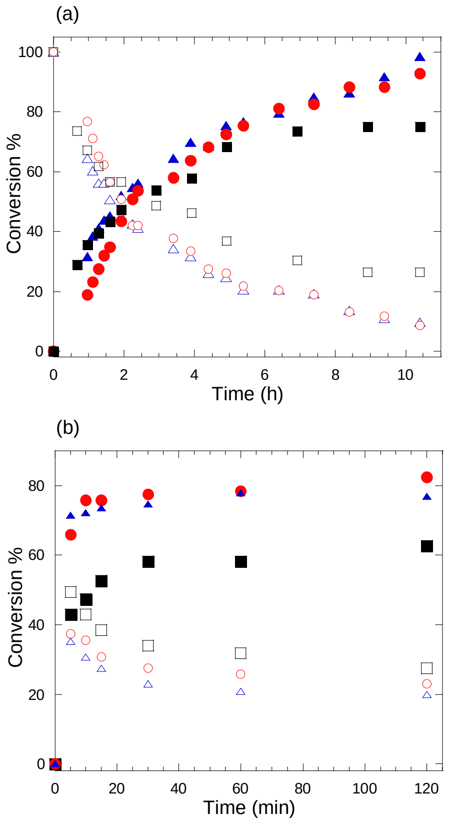


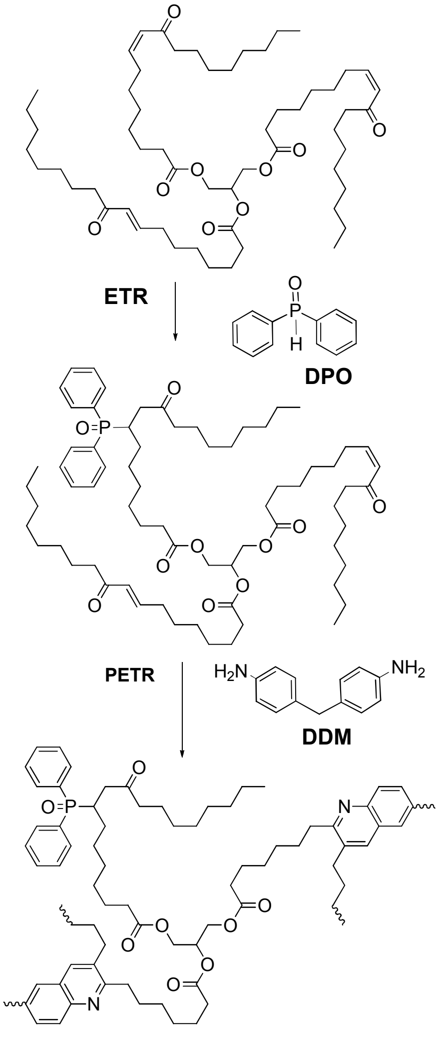
Figure 2. Conversion degree versus time for the phospha-Michael addition of DPO to EMO (a) conventional heading and (b) microwave irradiation (open symbols for the EMO consumption and solid symbols for the formation of the addition product).

The addition of P(O)-H bonds to a variety of alkenes has been successfully accomplished using microwave irradiation,[21] with the best results obtained when the alkene contained an activating group. In addition to terminal alkenes, disubstituted olefins were also hydrophosphinylated. When the alkene contained a CO-R unit, there was no evidence of addition to carbonyl group. We investigated the addition of DPO to EMO without catalyst and using $BF_3{\cdot}OEt_2$ or TBD as catalyst and toluene as solvent by irradiation at 150 W. The reactions were followed by ^1H NMR, and Figure 2(b) shows the conversion versus time for the catalyzed and uncatalyzed experiences. The maximum values of conversion degrees are lower than that obtained by conventional thermal heating, but the times needed to achieve similar conversions are much lower in the three sets of experiments. The acceleration of the reaction is noteworthy, and the addition proceeds six times faster than in conventional heating conditions.

As part of our studies on the development of new approaches for the synthesis of phosphorus-containing flame retardant vegetable oil-based thermosets, we planned the synthesis of high sunflower oil derivatives by phospha-Michael addition followed by aza-Michael addition to its enone derivative. The phospha-Michael addition provides phosphorus–carbon bond formation and allows us to control the phosphorus content of the final thermoset. The aza-Michael reaction initiates a set of cascade reactions that finally lead to a quinoline-containing crosslinked material.

In the following set of experiments, we examined the addition of DPO to the enone derivative of high-oleic sunflower oil (ETR, Scheme 1 Table 1). The reaction was carried out in bulk at 90 ^{0}C by mixing the reactants in a 1:0.5 enone/phosphine oxide molar ratio and by adding 1% mol of a $BF_3{\cdot}OEt_2$ as a catalyst. The reaction was monitored by IR spectroscopy through the disappearance of signal at 2390 cm $^{-1}$, attributed to P-H bond. ^{1}H NMR spectroscopy showed the intensity decrease of the characteristic double bond doublet signals at 6.05 and 6.75 ppm and the appearance of the multiplet signal at 3.17 ppm corresponding to the methine directly bonded to the phosphorus moiety (Figure 3) After 2 h of reaction, a 41% of conversion was reached, and no higher values are observed after 4 h of reaction. In this way, a phosphorus-containing high-oleic sunflower oil derivative (PETR) with a 69% of the initial enone content was obtained. The curing reaction of PETR with DDM was carried out by mixing both compounds in a 1:1 enone/amine ratio and heating at 120 ^{0}C for 12 h, according to the previously described reaction conditions.[15] IR spectroscopy allowed monitoring the crosslinking process. In the spectrum of ETR, carbonyl ester band appears at 1736 cm^{-1} and conjugated ketone carbonyl signals appear at 1692 cm^{-1} (C=O) and 1630 cm^{-1} (C=C). After DPO addition, the intensity of the conjugated double bond band decreases, and there is a shift of the ketone carbonyl band to higher wavenumbers because of the appearance of the nonconjugated ketone. Moreover, the broadening of the signal at 1190 cm^{-1} can be attributed to the presence of the P=O group. After the crosslinking process, new signals at 1510 and 1610 cm^{-1} corresponding to the quinoline units are also observed. The crosslinking reaction gave a material with an insoluble fraction of 51%.

According to the proposed crosslinking primary amine–enone mechanism,[15] the final properties of the material are crosslinking temperature-dependent. After the aza-Michael addition, a retro-Mannich-type fragmentation, self-condensation of the aldimine fragment and its cyclization followed by deamination and aromatization take place. Initial addition and fragmentation occur at lower temperatures, while the increase in crosslinking temperatures promotes the aromatization. To improve the final material properties, we studied the phospha- and aza-Michael additions to the ETR in one pot by carrying out the reaction of 1:0.5:0.5 enone/phosphine oxide/amine ratio and heating at 90 ^{0}C for 4 h and at 120 ^{0}C for 12 h. The extraction of the final material gave higher insoluble fraction (63%) than in the previous two step process. This fact could be due to a more effective aza-Michael addition at lower temperatures, thus favoring the formation of the aza-Michael adduct and its fragmentation previous to the aromatization process. Moreover, a better miscibility of the reactants is achieved when mixed in one step. Increasing temperature or reaction times did not increase the insoluble fraction.



Scheme 1. Phospha-Michael DPO addition to ETR and crosslinking with DDM.

The use of microwave irradiation in polymer chemistry is an emerging field of research that evolved from the investigation of various polymerization techniques to the material synthesis.[22,,23] In view of the above-described faster phospha-Michael addition reaction, we examined the effect of microwave irradiation on the crosslinking of ETR, DPO, and DDM. Curing reactions have been described to proceed slightly faster under microwave irradiation during the early stage of the process.[24] Microwave irradiation induces rapid crosslinking, creating a molecular network, which is rigid enough to trap unreacted functional groups, thus causing a lower degree of cure. It has also been shown that dielectric properties change, as cure reaction proceeds due to changes in the network structure. Microwave heating is based on dielectric heating, where the polar molecules, that have a permanent dipole moment, try to align to the applied electromagnetic field resulting in rotation, friction, and collision of molecules, and thus, heat generation. As a result, the heating rate and efficiency of microwave heating strongly depends on the dielectric properties and the relaxation times of the reaction mixture.[25,26] In this case, DDM has a low polarity, whereas ETR and DPO have a higher polarity. These differences of monomer polarities could yield modification of polymerization behavior by microwave irradiation.[27]

We performed the crosslinking process under microwave irradiation, and first experiments were focused on the curing of nonphosphorylated ETR with DDM (Table 1). To compare the microwave-induced crosslinking with that produced by thermal treatment, a sample containing 1:1 enone/amine molar ratio and 1% mol of $BF_3{\cdot}OEt_2$ was also obtained by conventional heating 4 h at 90 ^{0}C and 12 h at 120 ^{0}C. The material after a soxhlet extraction with dichloromethane gave an insoluble fraction of 48%. For the microwave curing, the sample was irradiated at 150 W for 3 h, and the yield of insoluble fraction increased to 70%. No higher contents of insoluble fraction were observed for longer reaction times, and an increase of irradiation power to 300 W for 3 h decreases the content of insoluble fraction to 48%. This effect can be explained taking into account the crosslinking mechanism aforementioned. The aza-Michael addition occurs at lower temperature, being a necessary previous step to the higher temperature fragmentation and aromatization processes. By comparing experiments with and without microwave irradiation, an increase in insoluble fraction content is observed under microwave irradiation compared to the conventional heating conditions. In addition, the acceleration of the reaction is noteworthy and crosslinking proceeds five times faster than in conventional heating conditions.

In view of the feasibility of the microwave-induced phospha-Michael addition to EMO and aza-Michael crosslinking of ETR, we examined the crosslinking process of ETR, DPO and DDM under microwave irradiation. A sample containing 1:0.5:0.5 enone/phosphine oxide/amine molar ratio and 1% mol of $BF_3{\cdot}OEt_2$ was irradiated at 150 W for 3 h, and a material containing a 38% of insoluble fraction was obtained (Table 1). By increasing reaction time to 6 h, a higher content of insoluble material was extracted from the polymer (44%). The effect of a postcuring was also investigated, and a sample with the same composition was irradiated at 150 W for 3 h and 300 W for 6 h. After extraction of the polymer, a 38% of insoluble fraction was obtained. In this case, the comparison with the conventional heating experiments shows an acceleration of the reaction, but a material with slightly lower content of insoluble fraction was obtained.

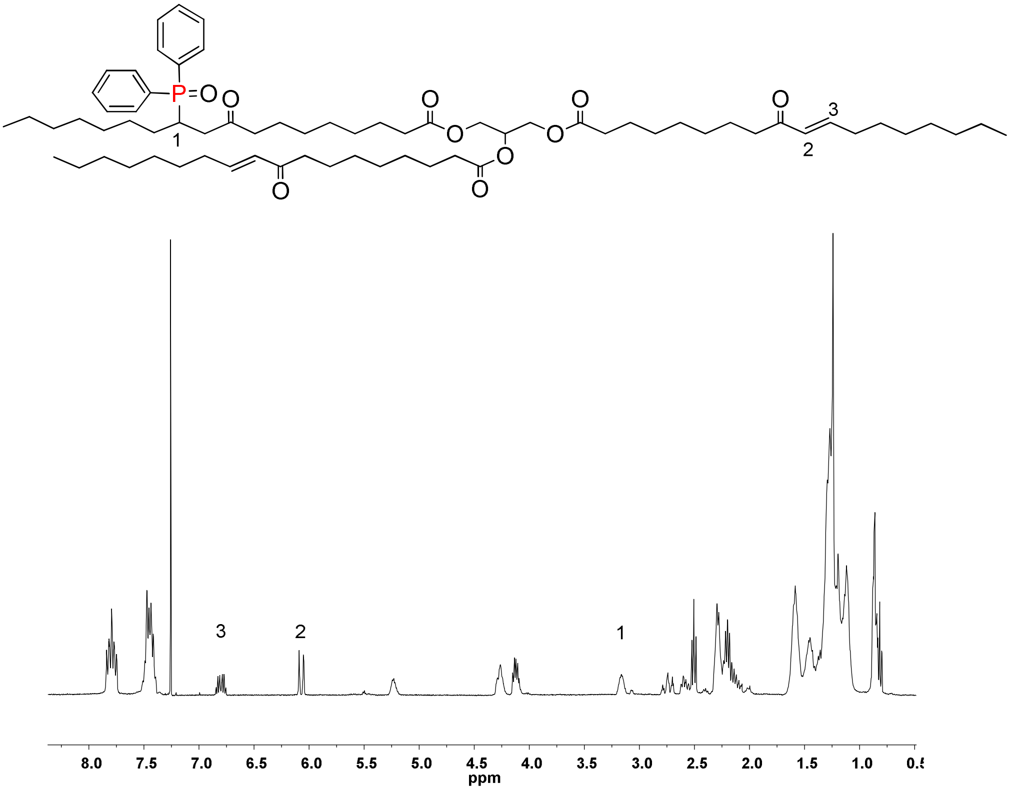


Figure 3. ^{1}H NMR spectrum of PETR (CDCl$_3$/TMS, ppm).

Once demonstrated that the phospha-Michael addition and the aza-Michael crosslinking can be carried out under conventional heating conditions and by microwave irradiation, our next aim was to control the phosphorus content in the polymers regarding their flame retardant properties. It is well known that percentages of 2–3 wt % are enough to infer flame retardant properties to polymers.[6] Under conventional heating, samples were obtained by mixing the melted components in a previously heated mold and cured at 90 ^{0}C for 5 h and postcured at 120 ^{0}C for 12 h (Table 1). To obtain different phosphorus-containing materials, the reactions were carried out by varying the DPO/DDM ratio (Table 2).

Table 2. Thermal and Flame Retardant Characterization of the Polymers.

		DSC	**TGA (N_2)**			**TGA (O_2)**			**LOI%**
Sample	***%P***	**T_g (ºC)**	**$T_{5\%}$(ºC)**	**T_{max} (ºC)**	**Char (%)**	**$T_{5\%}$ (ºC)**	**T_{max} (ºC)**	**Char (%)**	**O_2(v/v)**
3	0	-5	278	397/470	7	288	347/482/693	0	21.2
9	0.4	-10	313	405/464	9	312	442/480/716	0	26.4
10	0.8	-9	318	419/461	12	329	431/467/697	4	28.0
11	1.2	-17	314	414/458	10	300	429/474/707	0	31.0
12	1.6	-9	315	402/454	12	304	416/445/675	3	35.0
2	2.6	-3	332	395/454	16	317	388/442/581	8	34.0

As can be expected, a higher content of insoluble fraction is obtained, when the amount of DDM increased. The glass transition temperature of the polymers was obtained by DSC, and values between -17 and -3 ^{0}C were obtained. As the phosphorus content increases, the content of strongly polar phosphoryl groups increases, that cause restriction in segmental mobility and would increase Tg. As the enone functionality decreases, the crosslinking degree of the polymer decreases, and Tg should shift to lower temperatures. Due to these two opposite effects, no significant trends on Tg values can be observed.

To examine the effect of the phosphorus content on the thermal stability and decomposition behavior, TGA data under nitrogen and air atmospheres were determined and analyzed. In our previous studies,[28] we described the thermal degradation of phosphorus-containing triglyceride thermosets. The main degradation products of the triglyceride structure are long-chain fatty acids, esters, acrolein, and substituted ketenes. Moreover, the formation of several aromatic phosphorus volatiles after cleavage of the CAP bond was observed. Different evolved phosphorus species are oxidized to phosphoric acid and remain in the solid residue, thus forming a glass-like polyphosphoric acid that protects the burning surface. According to these results, a gas-phase flame retardancy mechanism in combination with a condensed-phase mechanism was proposed.

Table 2 summarizes the thermogravimetric data under nitrogen and air atmospheres. The temperatures of the 5% of weight loss of the phosphorus-free resin are lower than that of the phosphorus-containing polymers both under nitrogen and under air. The derivative plots show that under nitrogen the degradation process consist of two main steps, whereas under air three maximum weight loss rates are involved, indicating the existence of more complex processes. Under air atmosphere and above 500 ^{0}C, polymeric materials undergo a weight loss due to the char formed oxidized. It can be seen that the weight loss rate of the phosphorus-containing polymers is lower than that of the phosphorus free resin in this thermo-oxidative degradation. In this retarded-degradation phenomenon, the phosphorus groups promote an insulating protective layer that prevents the combustible gases from transferring to the surface of materials,increases thermal stability at higher temperatures, and improves fire resistance. Char yield ranges from 7 to 16% under nitrogen and from 0 to 8% under air atmosphere. These low residues could indicate that volatile compounds are released upon heating, according to the existence of a gas-phase mechanism in combination to the condensed phase mechanism.

The flame retardancy of the polymers was evaluated using the LOI value, and the results are listed in Table 2. The phosphorus-free polymer gave a LOI of 21.2, and the addition of phosphorus increases LOI values even when the phosphorus content is low, thus indicating that these polymers no longer burn in ambient air without complementary oxygen and show excellent flame retardant properties.

Conclusions

The phospha-Michael addition has been successfully applied to obtain phosphorus-containing high sunflower oil derivatives, both under conventional heating and under microwave irradiation. The kinetic study using model compounds showed a great enhancement of reaction rate for the microwave-initiated addition. The crosslinking of enone-containing triglyceride with aromatic diamines via aza-Michael addition under microwave irradiation has shown a noticeable acceleration of the curing.

The new phosphorus-containing enone derivative has shown high reactivity toward amines thus allowing the crosslinking via aza-Michael addition. Both reactions can be done in one step, thus providing a promising route to phosphorus-containing renewable thermosets. The increase in LOI values as a consequence of the incorporation of phosphorus covalently attached to the polymer suggests that these materials are very interesting for applications that require flame resistance.

Acknowledgments

Financial support by the MICINN (Ministerio de Ciencia e Innovacion; MAT2008-01412 and MAT2011-24823) is gratefully acknowledged.

References

1 Gandini, A.; Belgacem, M. N. Monomers, Polymers and Compositesfrom Renewable Resources; Elsevier: Oxford, UK, 2008.
2 Gandini, A. Green Chem. 2011, 13, 1061–1083.
3 Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J.O.; Schäfer, H. J. Angew. Chem. Int. Ed. 2011, 50, 3854–3871.
4 Montero de Espinosa, L.; Meier, M. A. R. Eur. Polym. J. 2011,47, 837–852.
5 Wilkie, C. A.; Morgan, A. B. Fire Retardancy of Polymeric Materials, 2nd ed.; CRC Press: Boca Raton, FL, 2010.
6 Lu, S. Y.; Hamerton, I. Prog. Polym. Sci. 2002, 27, 1661–1712.

7 Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J. M.; Dubois, Ph. Mater. Sci. Eng. R 2009, 63, 100–125.

8 Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. Chem. Soc. Rev. 2007, 36, 1788–1802.

9 Galia, M.; Montero de Espinosa, L.; Ronda, J. C.; Lligadas, G.; Cadiz, V. Eur. J. Lipid. Sci. Technol. 2010, 112, 87–96.

10 Ronda, J. C.; Lligadas, G.; Galia, M.; Cadiz, V. Eur. J. Lipid Sci. Technol. 2011, 113, 46–58.

11 Schenck, G. O. Naturwissenschaften 1948, 35, 28–29.

12 Greer, A. Acc Chem Res 2006, 39, 797–804.

13 Hui, S. P.; Yosahimura, T.; Murai, T.; Chiba, H.; Kurosawas,T. Anal. Sci. 2000, 16, 1023–1028.

14 Montero de Espinosa, L.; Ronda, J. C.; Galia, M.; Cadiz, V. J.Polym. Sci. Part A: Polym. Chem. 2008, 46, 6843–6850.

15 Montero de Espinosa, L.; Ronda, J. C.; Galia, M.; Cadiz, V. J.Polym. Sci. Part A: Polym. Chem. 2010, 48, 869–878.

16 Quin, I. D.; Montgomery, R. E. J. Org. Chem. 1963, 28,3315–3320.

17 Enders, D.; Saint-Dizier, A.; Lannou, M.-I.; Lenzen, A. Eur. J. Org. Chem. 2006, 29–49.

18 Öhler, E.; Zbiral, E. Liebigs Ann. Chem. 1991, 229–236.

19 Stockland, R. A.,Jr.; Taylor, R. I.Thompson, L. E.; Patel, P. B.Org. Lett. 2005, 7, 851–853.

20 Zhao, D.; Mao, L.; Yang, D.; Wang, R. J. Org. Chem. 2010, 75, 6756–6763.

21 Ide, D. M.; Eastlund, M. P.; Jupe, C. L.; Stockland, R. A.,Jr. Curr. Org. Chem. 2008, 12, 1258–1278.

22 Kempe, K.; Becer, C. M.; Shubert, U. S. Macromolecules 2011, 44, 5825–5842.

23 Ebner, C.; Bodner, T.; Stelzer, F.; Wiesbrock, F. Macromol. Rapid Commun. 2011, 32, 254–288.

24 Zhang, D.; Crivello, J. V.; Stoffer, J. O. J. Polym. Sci. Part B: Polym. Phys. 2004, 42, 4230–4246.

25 Lidström, P.; Tierney, J.; Wathey, B. Tetrahedron 2001, 57, 9225–9283.

26 Hayes, B. L. Microwave Synthesis: Chemistry at the Speed of Light; CEM Publishing: Matthews, NC, 2002.

27 Stange, H.; Greiner, A. Macromol. Rapid Commun. 2007, 28, 504–508.

28 Montero de Espinosa, L.; Ronda, J. C.; Galia, M.; Cadiz, V. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 4051–4063.

Flame Retardant High Oleic Sunflower Oil-Based Thermosetting ResinsThrough Aza- and Phospha-Michael Additions

"Science, is made up of mistakes, but they are mistakes which it is useful to make, because they lead little by little to the truth." Jules Verne

Chapter 2. J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 1808-1815

Flame Retardant High Oleic Sunflower Oil-Based Thermosetting ResinsThrough Aza- and Phospha-Michael Additions

Maryluz Moreno, Gerard Lligadas, Joan C. Ronda, Marina Galià, Virginia Cádiz

Departament de Química Analítica i Química Orgánica, Universitat Rovira i Virgili,
C/ Marcel.lí Domingo s/n,
Tarragona 43007, Spain

Abstract

Phosphorus-containing thermosetting resins derived from high oleic sunflower oil were prepared through phospha-Michael addition of a difunctional secondary phosphine oxide, the 1,3-bis(phenylphosphino)propane dioxide on the α,β-unsaturated ketone derived from high oleic acid (ETR). The aim of this approach was to introduce phosphorus and to crosslink the material in one single step. Materials with increasing aromatic content were also prepared by addition 4,4'-diaminodiphenylmethane and co-crosslinking through aza-Michael addition. The kinetics of the phospha and aza-Michael additions was investigated using the enone derivative of methyl oleate (EO) in presenceof $BF_3 \cdot Et_2O$ as catalyst and in absence of catalyst at different temperatures. Competitive experiments showed that phospha-Michael addition proceeds faster than the aza-Michael addition. The new triglyceride-based thermosets containing up to 4.2% of P, were characterized and their thermal and flame retardant properties evaluated. Limiting oxygen index values increase from 21.5 for the phosphorus free material up to 38.0 for the final material with 4.2% P content. These results demonstrate that the flame retardant properties of vegetable oil-based thermosets can be significantly improved by adding covalently bonded phosphorus to the polymer.

Keywords

Crosslinking; flame retardant; Michael addition; renewable resources; triglycerides

Introduction

The development of environmentally compatible polymers is one of the current challenges in polymer chemistry. The scarcity of non-renewable resources encouraged the scientific community to develop and commercialize new biobased products that can alleviate the wide-spread dependence on fossil fuels and enhance security, the environment and the economy.[1] Among the renewable raw materials, natural oils are the most widely used renewable resource for the chemical and polymer industries.[2] The main component of the triglyceride vegetable oils are saturated and unsaturated fatty acids. Although they have double bonds which can be used as reactive sites in coatings, for obtaining high performance polymeric materials the introduction of more reactive functional groups, such as hydroxyl, epoxy, or carboxyl groups, is much more suitable.[3,4]

In an effort to extend the use of natural oils in polymer chemistry, we described the synthesis of a new triglyceride derivative with α,β-unsaturated carbonyl groups.[5] This enone-containing triglyceride can be obtained following an environmentally friendly chemical procedure from high oleic sunflower oil and shows high reactivity towards aromatic amines producing polymeric networks by aza-Michael addition under relatively mild conditions ($T < 90\ ^0C$). The aza-Michael addition of 4,4'-diaminodiphenylmethane (DDM) to these enone-containing triglycerides resulted in a reliable and straightforward procedure to prepare thermosetting resins. We demonstrated that when the curing process is carried out at higher temperatures (i.e., 120 ^0C) or when in presence of a catalysts (BF_3), the initial aza-Michael adduct undergoes a series of chemical transformations leading to the formation of trisubstituted quinoline rings in the structure.[6] This aromatization process resulted in an increase in crosslinking density and notably improved the final material performance extending its potential applications.

For most of the applications (coatings, adhesives, electric, and electronic devices, etc.) safety regulations call for materials with fire retardant properties among the key properties. Because of the composition of triglycerides, plant oil based polymers are flammable, just like many other currently used polymeric materials. Therefore, the use of flame retardants to reduce the combustibility of polymers is an important part of the development of plant oil based polymeric materials. In this way, the synthesis of flame-retardant polymers from bromoacrylated plant oil triglycerides was reported.[7] However, it is known that bromine-containing flame-retardant resins release hydrogen bromide during combustion which is toxic and corrosive.[8] The concept of sustainable development requires fire retardant technologies to be developed that have a minimum impact on health and the environment throughout the life cycle of the fire-resistant material: starting from its synthesis, via fabrication, use, and recycling to its final disposal. Therefore, the search for new environmentally friendly flame-retardant polymeric materials is of large current interest. Phosphorus based polymers, for instance, are an effective and well established class of flame retardant materials.[9] They have a good flame retardant performance and are preferred to the widely applied halogenated flame retardants due to environmental and health reasons.[10] In a recent work, we explored the phospha-Michael addition of secondary phosphine oxides to enone groups as a reliable way to introduce covalently bonded phosphorus moieties into the triglyceride structure.[11] Secondary phosphine oxides are convenient and readily available phosphorus precursors that undergo addition to α,β-unsaturated systems under mild conditions.[12–14] The resulting tertiary phosphine oxides have proven to be effective flame retardants[15–16] and have a superior thermal and hydrolytic stability when compared to the phosphate, phosphonate, or phosphinate moieties which have a limited range of applications.[18]

Phospha-Michael addition of diphenylphosphine oxide (DPO) to the enone triglyceride showed to be an excellent method to covalently link phosphorus to the triglyceride molecules but producing a crosslinked network required the additional reaction with a difunctional aromatic amine though an azamichael addition. As part of the reactive enone groups were reacted to introduce the phosphorous moieties, the resulting thermosets had good flame retardance but limited mechanical properties due to their low crosslinking degree.[11] In this work, we explore the possibility of using a difunctional secondary phosphine oxide, the 1,3-bis(phenylphosphino)propane dioxide (BPPO), to introduce phosphorus and to crosslink the material in only one step.

Experimental Section

Materials

High oleic sunflower oil (minimum 80% oleic acid) was supplied by Coreysa. Methyl oleate (EO; 75%) (Alfa Aesar), 1,3-Bis(phenylphosphino)propane 90–95% (Strem), meso-tetraphenylporphyrin (TPP) (Aldrich), borontrifluoride diethylethearate ($BF_3 \cdot OEt_2$) (Aldrich), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), diaminodiphenylmethane (DDM) (Aldrich), triethylamine (Scharlau) and acetic anhydride (Scharlau) were used as received. Toluene was dried over sodium/benzophenone, dichloromethane over P_2O_5 and isopropanol oversodium, all dry solvents were distilled immediately before use. TLC plates (Aluminium sheets 20 x 20 cm^2 silica gel 60F 254 Merck) were developed by spraying with sulphuric acid/anisaldehyde ethanol solution and heating at 200 ^{0}C. Enone derivative of EO (mixture of methyl-9-oxo-10-octadecenoate and methyl-10-oxo-8-octadecenoate) has been obtained following a reported procedure[5] which similar to the reported for the synthesis of ETR. BPPO was obtained as previously described.[19]

Synthesis of the α,β-Unsaturated Ketone Derivative of High Oleic Sunflower Oil

In a 450 mL standard immersion-well photochemical reactor with a 400 W high pressure sodium vapour lamp, high oleic sunflower oil (70 g, 79.1 mmol), TPP (0.02 g, mol) and dichloromethane (400 mL) were introduced. Cold water was circulated through the lamp jacket, while a gentle stream of oxygen was bubbled through the stirred reaction mixture. After a few minutes, the lamp was turned on and the reaction was monitored by TLC (hexane/ethyl acetate, 5:1). After 4 h of irradiation the total disappearance of isolated double bonds and formation of the intermediate allylic hydroperoxides was observed. The lamp was turned off and the reactor was placed into a water bath. Acetic anhydride (24.60 mL, 260.9 mmol) and triethylamine (18.20 mL, 130.4 mmol) were added with stirring at room temperature. After 30 min TLC (hexane/ethyl acetate, 5:1) confirmed the formation of the enone and the complete disappearance of the hydroperoxide. The solvent was then eliminated at reduced pressure. The reaction mixture was diluted with ethyl acetate (500 mL) and washed successively with water, saturated $NaHCO_3$, HCl (10%, v/v) and saturated NaCl. After drying over $MgSO_4$ and concentrating under reduced pressure, the product was obtained as a triglyceride mixture with 2.2 α,β-unsaturated ketones per molecule (determined by ^{1}H NMR spectroscopy). Further purification was achieved by crystallization, at 5 ^{0}C, from hexane (200 mL) obtaining a product with 2.4 α,β-unsaturated ketones per molecule (determined by ^{1}H NMR) with 76% yield.

FTIR: 1740 cm^{-1} (ester C=O, st), 1696 cm^{-1} (C=O,s-cis, st), 1673 cm^{-1} (C=O, s-trans, st), 1629 cm^{-1} (C=C, st), 1162 cm^{-1} (C-O, st).

^{1}H NMR (CDCl3, TMS, δ ppm): 6.78-6.70 (3H, m, H-11), 5.99 (3H, dd, J_{10-11}= 16 Hz, J_{10-12}= 1.6 Hz, H-10), 5.22-5.16 (1H, m, H-19), 4.24-4.20 (2H, m, H-20), 4.06 (2H, dd, $J_{20'-20}$= 11.6 Hz, $J_{20'-19}$= 6.0 Hz, H-20´), 2.44 (6H, t, J_{2-3}=7.2 Hz, H-8), 2.25-2.21 (6H, m, H-2), 2.15-2.09 (6H, m, J_{12-11}≈ J_{12-13}= 7.3 Hz, H-12), 1.58-1.43 (12H, m, H-3 H-7), 1.43-1.30 (6H, m, H-13), 1.30-1.10 (42H, m, aliphatic chain), 0.83-0.76 (9H, m, H-18).

^{13}C NMR (CDCl$_3$, TMS, δ ppm): 200.76 (C-9), 200.65 (C-9´), 173.21-172.66 (C-1 C-1´), 147.33, 146.86 (C-11), 130.42-130.30 (C-10), 68.94-68.89 (C-19), 62.05 (C-20), 40.12-39.94 (C-8), 34.11-33.89 (C-2), 32.47-32.35 (C-12), 31.95-31.76 (C-16), 29.72-28.79 (C-Al), 28.13-27.92 (C-13), 24.86-24.67 (C-3), 24.29-24.15 (C-7), 22.72-22.64 (C-17), 14.15-14.10 (C-18).

Kinetic Measurements

Kinetic experiments were carried out by ^{1}H NMR using rubber septa sealed NMR tubes. The precise amounts of a 2 M solution of EO, 1 M solution of BPPO, and 1 M solution of DDM in dry deuterated toluene were introduced using general vacuum-line techniques. In catalyzed experiments, the proper amount of 0.06 M solution of $BF_3{\cdot}OEt_2$ in dry deuterated toluene as a catalyst was added (1% of catalyst). The reaction was monitored at 70 and 100 ^{0}C by ^{1}H NMR spectra at different reaction times.

Table 1. Insoluble fractions obtained after curing mixtures of ETR/BPPO, ETR/DDM, and ETR/BPPO/DDM at different molar ratios, temperatures, and times in presence or absence of TBD or BF_3Et_2O as curing catalysts.

Exp.	ETR/BPPO/DDM molar ratio	Catalyst [a]	Curing T (ºC)	Curing Times (h)	IF (%)[b]
1	1:1:0	none	90	4	68
			120	12	
2	1:1:0	TBD	90	4	67
			120	12	
3	1:1:0	$BF_3.Et_2O$	90	4	76
			120	12	
4	1:1:0	$BF_3.Et_2O$	90	4	76
			120	24	
5	1:1:0	$BF_3.Et_2O$	90	4	78
			140	12	
6	1:0:1	$BF_3.Et_2O$	90	4	86
			120	12	
7	1:0.3:0.7	$BF_3.Et_2O$	90	4	84
			120	12	
8	1:0.3:0.7	$BF_3.Et_2O$	90	4	87
			140	12	
9	1:0.5:0.5	$BF_3.Et_2O$	90	4	88
			120	12	
10	1:0.7:0.3	$BF_3.Et_2O$	90	4	88
			120	12	

[a] 1 mol% respect to the double bond content.

[b] Insoluble fraction in dichloromethane.

Addition Product of 1,3-Bis(phenylphosphino)propane oxide (BPPO) to the Enone Derivative of EO

In a shlenk type flask 0.38 g of EO (1.2 mmol), 0.15 g (0.5mmol) of BPPO, and 2 mL of dry toluene were introduced under argon. The reaction mixture was stirred at 90 ^{0}C for 4h and the resulting oil purified by column chromatography using neutral silica gel and ethyl acetate as eluent. After concentration and drying, 0.32 g (62%) of product were isolated as a colorless oil.

Curing Reactions

The required amounts of ETR, BPPO, and DDM (Table 1) were melted in a flask. Then, the necessary amounts $BF_3 \cdot OEt_2$ or TBD (1 mol %) were added to the mixture. The resulting liquid was poured into a previously heated (60 ^{0}C) glass mold and the mixture heated at 90 ^{0}C for 4 h and post-cured at 120 or 140 ^{0}C for 12 or 24 h.

Polymer Fractionation

The insoluble part of the cured samples was isolated by extracting 0.5 g of sample in 50 mL of refluxing CH_2Cl_2 for 4h. The percentage of the soluble and insoluble fractions was determined by weighting the dry fractions.

Instrumentation

^{1}H NMR 400 MHz and ^{13}C NMR 100.6 MHz NMR spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform, $CDCl_3$ as solvent and TMS as internal standard. The crosslinking process was monitored with a JASCO 680 FTIR (ATR) spectrophotometer with a resolution of 4 cm^{-1} in the transmittance mode. An attenuated-totalreflection accessory with thermal control and a diamond crystal (Golden gate heated single-reflection diamond ATR, Specac Teknokroma) was used to determine FTIR/ATR spectra.

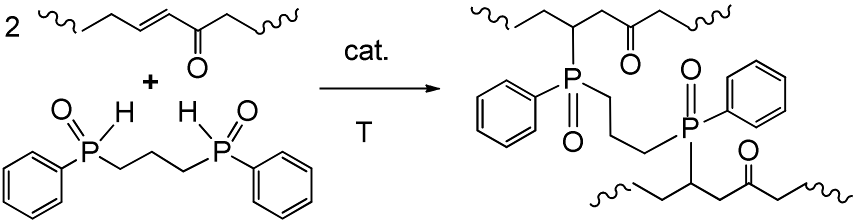
Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer using N_2 as a purge gas (10 mL/min) at scan rates between 5 and 20 ^{0}C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as a purge gas, in the 30–800 ^{0}C range at scan rates of 10 ^{0}C/min.

The limiting oxygen index (LOI) values (ASTM D 2863), as the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion of materials, were measured on a Stanton Redcroft instrument provided with an oxygen analyzer. The dimensions of the polymer bars were 100 x 6 x 3 mm^3.

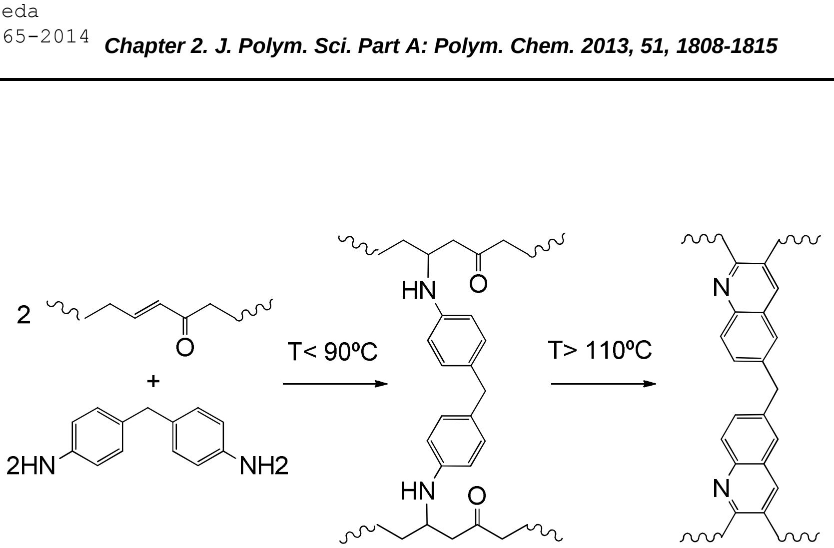
Results and discussion

As commented above, the aim of this work is to explore the phospha-michael addition of the 1,3-BPPO to a triglyceride containing 2.4 α,β-unsaturated ketone groups per molecule derived from high oleic sunflower oil (ETR). The difunctional nature of BPPO is expected to allow introduction of phosphorus an contribute to the network formation at the same time (Scheme 1)

To prepare thermosetting resins with different phosphorus content, the enone containing triglyceride was cured in presence of different amounts of DDM and BPPO. The addition of aromatic amines to these α,β-unsaturated ketone groups has been studied by us and leads to networks with improved properties due to the formation of quinoline units as crosslinking points.[6] These quinoline moieties are the result of a set of cascade reactions produced when the initial aza-Michael adduct is heated over 110 ^{0}C or when the aza-Michael addition process is carried out in presence of a catalyst like $BF_3 \cdot Et_2O$ (Scheme 2).



Scheme 1. Schematic representation of the crosslinking process by phospha-Michael addition of BPPO to the enone containing triglycerides.



Scheme 2. Schematic aza-Michael addition of DDM to the enone containing triglycerides and its posterior transformation in quinoline groups at higher temperatures.

The enone-containing triglyceride was synthesized from high oleic sunflower oil following a procedure already described by us[5] consisting of the selective hidroperoxydation of the allylic positions of the high oleic sunflower oil (>80% of oleic acid) followed by the dehydration of the resulting regioisomeric hydroperoxyde mixture using acetic anhydride. The product used in this work contained 2.4 enone groups per triglyceride molecule according to the ^{1}H NMR analysis. BPPO was prepared from commercial grade 1,3-bis(phenylphosphino)propane by air oxidation in anhydrous isopropanol following a described procedure.[19] According to ^{31}P NMR spectroscopy the starting diphosphine contained 5.9% of 1-phenylphosphetane as impurity. The ^{31}P NMR spectrum of the resulting crude product was characterized by an intense signal at 26.0 ppm, which confirms the formation of the 1,3-bis(phenylphosphino)propane oxide, and a small signal at 40.8 ppm which, according to the literature,[20] can be assigned to the 1-phenylphosphetane oxide formed by oxidation of the starting diphosphine impurity. This impurity (5.8% in the crude mixture by ^{31}P NMR) could be conveniently eliminated by recrystallization in dry benzene. The ^{1}H and ^{31}P NMR spectra of the resulting BPPO were in good accordance with the data reported in the literature from the spectra recorded in deuterated benzene.[19,21]

To carry out kinetic and mechanistic experiments we used the enone derivative of the EO as model compound. This product was synthesized using the same procedure described for the triglycerides but starting from pure EO.[5] The resulting pale yellow oil consists of a mixture of essentially pure methyl 10-oxo-8-octadecenoate and methyl 9-oxo-10-octadecenoate.

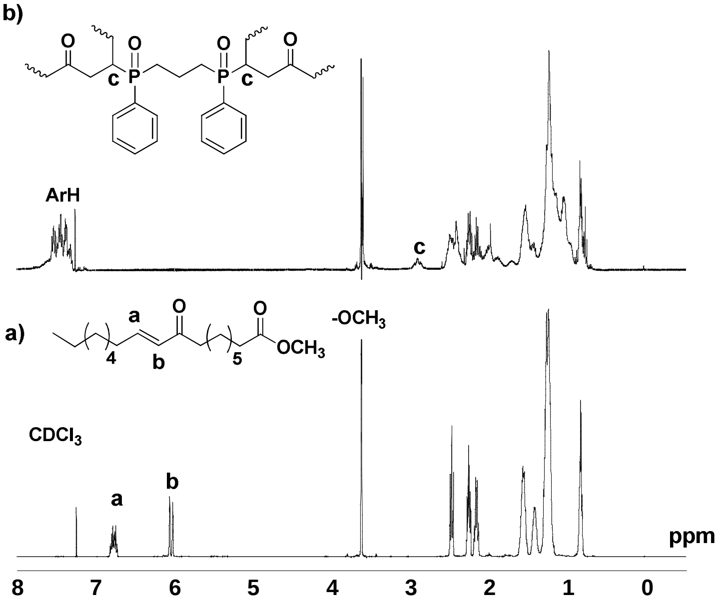


Figure 1. ^{1}H NMR spectra recorded in $CDCl_3$ of (a) EO and (b) product of the addition of BPPO to EO.

First, we studied the phospha-Michael addition of BPPO to the enone group. For this purpose, mixtures of BPPO and methyl enone oleate in a 1:2 mole ratio were heated at 70 and 100 ºC in dry deuterated toluene. The reaction was monitored by ^{1}H NMR and the percentage of unreacted enone calculated from the intensity of the doublet at about. 6.0 ppm (Figure 1). To follow the formation of the double phospha-Michael adduct, previously we synthesized a sample of this product by reaction of BPPO with a slight excess of methyl enone oleate and subsequent purification by column chromatography. The NMR characterization of this product indicates that the formation of the new P-C bond can be followed by the appearance of a characteristic methyne signal at about 2.9 ppm in the ^{1}H NMR spectrum and a singlet at 46.8 ppm in the ^{31}P NMR spectrum. The unequivocal assignment of this signal was carried out on the basis of gHSQC bidimensional correlations and by selective irradiation experiments. In all measurements, the intensity of the methyl ester signal at 3.6 ppm was used as internal reference.

In Figure 2, the results of these kinetic experiments are collected. As can be seen at 70 ^{0}C the reaction proceeds smoothly and after 24 h about 30% of the starting enone still remains unreacted. Increasing the temperature to 100 ^{0}C produces notable reaction acceleration, the enone being completely consumed in about 12 h. Formation of the double phospha-Michael adduct proceeds in a parallel way reaching a plateau at around 94% conversion probably because of the consumption of some BPPO in side reactions. The ^{31}P NMR analysis of the crude mixture shows a main peak at 46.7 ppm, which corresponds to the expected product. One additional small peak 19.7 ppm can be also observed, which, according to the chemical shift, could be due to some mono addition product.

It is well known that the aza and phospha-Michael additions can be activated by different catalyst.[22–24] In a previous work,[11] we studied the addition of DPO to the same methyl enone oleate in presence of boron trifluoride diethylether complex ($BF_3 \cdot Et_2O$) and 1,5,7-triazabyciclo[4,4,0]dec-5-ene (TBD) the former being more effective. So, we decided to follow the reaction at 100 ^{0}C in presence of 1 mol % of $BF_3 \cdot Et_2O$. As can be seen in Figure 2, in these conditions the reaction proceeds faster and consumes the enone in few hours. Moreover, the conversion of the phospha-Michael adduct seems to be higher indicating that in presence of this catalyst the side reactions are minimized or even suppressed.

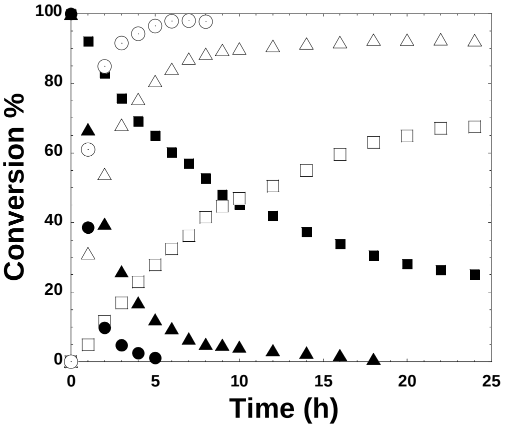


Figure 2. Evolution of the EO compsumption (dashed symbols) and the phospha-Michael adduct formation (hollow symbols) versus time. a) ■ and □ at 70 ^{0}C, b) ▲and ∆ at 100 ^{0}C and c) ● and ○ at 100 ^{0}C in presence of 1% of BF_3·Et_2O. Conditions [BPPO] 0.4M, BPPO-enone ratio 1:2, solvent toluene-*d*$_8$.

We also carried out a competitive experiment in which the reactivity of BPPO and DDM toward the EO was measured. For this purpose, reagents were dissolved in deuterated toluene in a BPPO:DDM:EO ratio of 0.25:0.25:1 in presence of 1 mol % of BF_3·Et_2O. The mixture was heated at 100 ^{0}C and the reaction followed by ^{1}H NMR. The formation of the aza-Michael product was determined from the intensity of the new signal at about. 3.9 ppm which corresponds to the methyne attached to the amino group.[5] (Figure 3) shows the relative rates for both reactions.

As can be seen, under these conditions, phospha-Michael addition proceeds faster than aza-Michael addition. In both cases, a plateau is reached before the complete consumption of the enone probably because of the lower reactivity of the mono addition product.

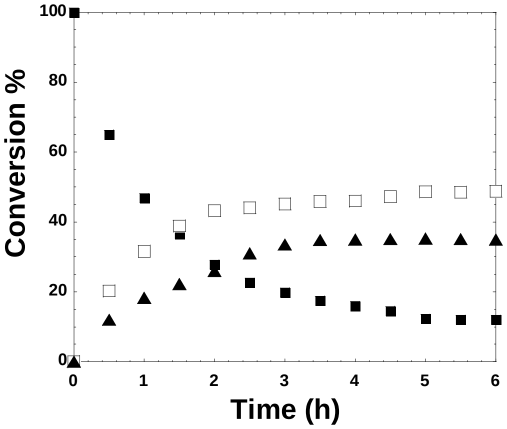


Figure 3. Reaction of EO with BPPO and DDM at 100 ^{0}C in presence of 1 mol% of $BF_3.Et_2O$ versus time. a) ■ consumption methyl enone oleate b) □ formation of the phospha-Michael adduct c) ▲formation of the aza-Michael adduct. Conditions [BPPO] = [DDM] 0.2M, BPPO:DDM:EO ratio 0.25:0.25:1, solvent toluene-*d*$_8$.

To prepare thermosetting materials with different phosphorus content, mixtures of ETR and BPPO and ETR, BPPO, and DDM with 1 mol % of $BF_3 \cdot Et_2O$ were prepared. Also, some experiments with TBD as catalyst and without catalyst were carried out as reference. The curing conditions were determined according to the results of a previous study[11] and by taking into account the DSC plot of a mixture of ETR and BPPO which shows a broad curing exotherm starting at about 80 ^{0}C with a maximum at 120 ^{0}C. Thus, samples were cured by heating at 90 ^{0}C for 4 h and at 120 ^{0}C for 12h. The amount of crosslinked material was determined by continuous extraction with dichloromethane. Longer curing times (24 h) or higher curing temperatures (140 ^{0}C) were also tested with no noticeable improvement in the percentageof crosslinked fraction. In Table 1, the composition of samples and characteristics of the different experiments are collected.

Experiments 1–3 were carried out in order to confirm the catalyst activity tested with the enone model compound. It is clear from the results of experiment 3 that $BF_3 \cdot Et_2O$ improves the phospha-Michael addition also in the case of ETR. Experiments done without catalyst or in presence of a basic catalyst (TBD) show about 10% decrease the yield of crosslinked material. Experiments 4 and 5 demonstrate that longer curing times (24 h, exp. 4) and higher curing temperatures (140.^{0}C, exp. 5) do not increase the amount of crosslinked fraction due to the phospha-Michael addition noticeably. The NMR spectroscopic analysis of the soluble fractions reveals that uncrosslinked fractions are composed mainly of saturated fatty acid chain triglycerides and some BPPO addition products. The ^{1}H NMR spectra of these fractions show the absence of either enone or P-H groups in significant amounts. Starting ETR contains an average of 2.4 enone groups per triglyceride molecule which indicates significant amounts of triglyceride molecules with one or more saturated aliphatic chains. These triglyceride molecules are able to react with BPPO to give only dimeric or low molecular weight oligomeric species but not a networked material. The analysis of the ^{1}H NMR signals intensity ratio of these soluble fractions, reveal one to two triglyceride aliphatic chains per aromatic ring. This relatively high aromatic content suggests that in these soluble fractions BPPO are linked through only one of the active sites. The analysis of the ^{31}P NMR spectra shows two main signals at 50 and 18 ppm which, as commented above, can be related with the 1,4-addition products of BPPO to one or two enone groups. Moreover, a low intensity signal at about 45 ppm, can be observed. This signal according to its chemical shift[25] could correspond to a small percentage of 1,2-addition product which was not detected in the study with model compounds.

As mentioned in the introduction, materials obtained by phospha-Michael addition would have a low crosslinking degree and consequently lower networked polymer fraction than those obtained in presence of dichloromethane. The increase of insoluble fraction due to the formation of the quinoline crosslinking points formed at high temperatures is clear when comparing experiments 6 (reference material without BPPO) and 7–10 with those obtained in absence of DDM. In all cases a neat increase of about 10% in insoluble fraction can be observed. Again, an increase in the curing temperature (Exp. 8) did not show a significant increase in the amount of crosslinked fraction.

Table 2. Thermal characteristics (by DSC and TGA), phosphorus content and LOI values for selected thermosets.

		DSC	TGA (N_2)			TGA (O_2)			LOI
Exp.	**P(%)**	**T_g (ºC)**	**$T_{5\%}$(ºC)**	**T_{max} (ºC)**	**Char (%)**	**$T_{5\%}$ (ºC)**	**T_{max} (ºC)**	**Char (%)**	**% O_2**
6	0.0	-5	323	428/466	8	326	424/458/585	0	21.5
7	1.6	-10	323	405/448	13	326	408/443/597	1.6	35.0
8	1.6	-11	320	398/454	12	327	403/442/600	1.9	35.7
9	3.05	-16	318	393/456	12	323	402/436/614	3.5	37.0
10	4.2	-23	312	392/450	11	319	395/433/619	4.7	38.0
3	5.8	-8	276	396/446	14	259	364/426/623	5.9	---

The resulting orange materials were characterized by DSC and TGA (Table 2).

All materials behave as rubbers and consequently show T_g values bellow room temperature. The highest T_g values correspond to both two-component systems whereas three-component ones depict lower T_g values. As observed for similar materials obtained using ETR, DDM, and DPO,[11] T_g values would be directed by two main parameters. First, the crosslinking density, which according to the reagents functionality should be quite similar for all synthesized materials. The second is the BPPO/DDM ratio which influences T_g values due to two main effects. A high percentage of DDM in the mixture should increase the T_gs due to the introduction of rigid aromatic moieties. In the same way, a high percentage of DPPO, must also increase the T_g value due to the strong polar interactions established between P=O groups.

Results in Table 2 confirm these effects for both two-component systems but indicate that for three-component systems the effect due to the decrease in aromatic moieties is not as important as the effect produced by the increase in the percentage of phosphoryl groups. This fact can be explained taking into account that for three-component formulations the presence of DDM networking points could disrupt somewhere the interaction between phosphoryl groups. In any case, the decrease in the amount of aromatic moieties seems to be the dominant variable since the lower the amount of DDM the lower the T_g value.

Thermal stability of these materials was evaluated by TGA under nitrogen and air atmosphere [Figure 4(a,b) and Table 2]. Under nitrogen and air atmosphere, all thermosets were stable bellow 300 ^{0}C and have a 5% weigh loss around 320 ^{0}C with the exception of the ETR/BPPO system (Exp. 3). Under nitrogen, all materials present two main degradation steps with maximum weight loss rates at about 400 and 450 ^{0}C. The temperatures of 5% weight loss and maximum degradation rate show a decrease with the percentage of BPPO in the mixture. This behavior can be related to the lower thermal stability of P-C bonds (264, KJ/mol) when compared with C-C, C-O, C-N, and C-H bonds (346, 358, 305, and 411 KJ/mol respectively).[26]

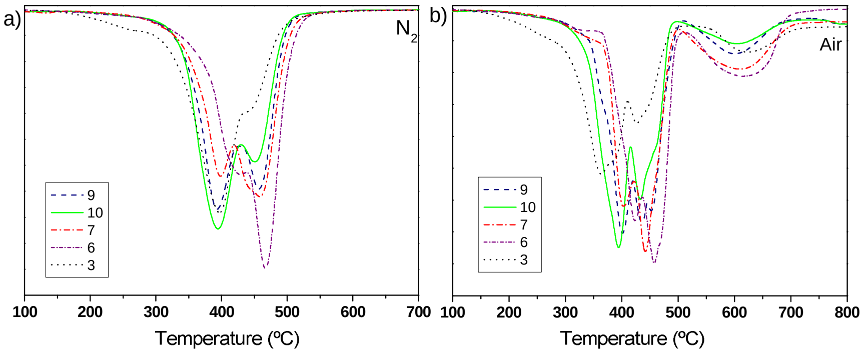


Figure 4. TGA first derivative curves of thermosets 3, 6, 7, 9, and 10 under nitrogen (a) and under air (b).

At 800 ^{0}C, phosphorus containing thermosets yield 11–14% of char yield whereas the phosphorus-free material yields only 8% char. Thermal degradation of phosphorus containing compounds lead to the formation of polyphosphoric acid which catalyzes dehydration, condensation and cyclation reactions in the condensed phase favouring the formation of char instead of volatile degradation products. The formation of char is also favored by the presence of aromatic rich fractions.This effect can be observed in polymer 7 with only 1.6% of P but with a highest DDM content (13% of char).

Under oxygen atmosphere, the same trends can be observed but an additional degradation step with a maximum degradation temperature at 580–620 ^{0}C can be observed. This high temperature process is associated to the thermoxydative degradation of the carbonaceous residue promoted by the presence of P. As can be seen in Figure 4(b) and Table 2, there is a direct relationship between this degradation and the phosphorus content in the material. As higher is the percentage of phosphorus in the residue, higher is the temperature of the maximum and lower the weight loss associated to this phenomenon.

It is well known that phosphorus acts in the condensed phase by delaying the degradation of the carbonaceous residue and consequently, the residue obtained at 800 ^{0}C under oxygen for the phosphorus free resin is 0% and increases progressively as the phosphorus content does. Finally, the influence of phosphorus on the combustion behavior of these vegetable oil-based thermosets was evaluated using the LOI value which measures the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support the flaming combustion of the material under standard conditions.

The results collected in Table 2 show a LOI value of 21.5 for the phosphorus-free resin which indicates that this material is not flame retardant. The presence of 1.6% of phosphorus produces a remarkable increase in the LOI value to 35.0. This LOI value increases progressively with the phosphorus content until a maximum value of 38.0 for the thermoset containing 4.7% of P. These values show that this important improvement on the flame retardant properties is related to the presence of phosphorus although the amount of phosphorus is not so significant. It is known that low phosphorus contents are sufficient to infer flame retardant properties to polymers and that high contents do not usually give better results.[27,28]

Conclusions

The combination of aza-Michael addition of DDM and phospha-Michael addition of a difunctional phosphine oxide has been successfully applied to produce phosphorus-containing sunflower oil derivatives. The kinetic study using model compounds showed that phospha-Michael-additions to the enone groups proceeds faster that the addition of aromatic amines and shows the positive effect of $BF_3 \cdot Et_2O$ in the enhancement of the reaction rate.

The introduction of phosphorus and crosslinking of these formulations can be carried out in a single step under quite mild conditions yielding high oleic sunflower oil thermosetting coatings with tuneable phosphorus-content. The incorporation of covalently bonded phosphorus notably increases the LOI values indicating that these materials are very appropriate for applications that require flame resistance.

Acknowledgments

Financial support by the MICINN (Ministerio de Ciencia e Innovacion) (MAT2008-01412 and MAT2011-24823) is gratefully acknowledged.

References

1 J. J. Bozell, M. Patel, Eds.; Feedstocks for the Future: Renewable for the Production of Chemicals and Materials; ACS Symposium Series 921; American Chemical Society: Washington, DC, 2006.
2 U. Biermann, W. Friedt, S. Lang, W. Lu¨ hs, G. Machmüller, J. O. Metzger, M. R. Klaas, H. J. Schäfer, M. P. Schneider, Angew. Chem. Int. Ed. Engl. 2000, 39, 2206–2224.
3 F. S. Güner, Y. Yagci, A. T. Erciyes, Prog. Polym. Sci 2006,31, 633–670.
4 M. A. R. Meier, J. O. Metzger, U. S. Schubert, Chem. Soc.Rev. 2007, 36, 1788–1802.

5 L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz,J. Polym. Sci Part A: Polym. Chem. 2008, 46, 6843–6850.

6 L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz,J. Polym. Sci Part A: Polym Chem. 2010, 48, 869–878.

7 T. Eren, S. H. Küsefoglu, J. Appl. Polym. Sci. 2004, 91,2700–2710.

8 D. Purser, In Fire Retardant Materials; A. R. Horrocks, D. Price, Eds.; CRC Press: Boca Raton FL, 2001; pp 69–127.

9 P. Jain, V. Choudary, I. K. Varma, J. Macromol. Sci. Polym. Rev. 2002, 42, 139–183.

10 S. Y. Lu, I. Hamerton, Prog. Polym. Sci. 2002, 27, 1661–1712.

11 M. Moreno, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz,J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 3206–3213.

12 R. A. Stockland, R. I. Taylor, L. E. Thompson, P. B. Patel, Org. Lett. 2005, 7, 851–853.

13 D. Enders, A. Saint-Dizier, M.-L. Lannou, A. Lenzen, Eur. J.Org. Chem. 2006, 71, 29–49.

14 S. Sobhani, Z. P. Parizi, S. Rezazadeh, J. Organomet. Chem. 2011, 696, 813–817.

15 G. Ribera, L. A. Mercado, M. Galia, V. Cadiz, J. Appl. Polym. Sci. 2006, 99, 1367–1373.

16 M. Sponton, J. C. Ronda, M. Galia, V. Cadiz, J. Polym. Sci Part A: Polym. Chem. 2007, 45, 2142–2151.

17 L. Montero de Espinosa, J. C. Ronda, M. Galià, V. Cádiz, J.Polym. Sci Part A: Polym. Chem. 2009, 47, 4051–4063.

18 P. W. Morgan, B. C. Herr, J. Am. Chem. Soc. 1952, 74,4526–4529.

19 B. Walter, R. Schöps, W. Kolbe, D. Scheller, Zeitschrift für Chem. 1979, 19, 417–418.

20 E.-Y. Yao, J. Szewczyk, L. D. Quin, Synthesis 1987, 3,265–267.

21 J. T. Yeh, L. R. Avens, J. L. Mills, Phosphorus Sulfur Silicon 1990, 47, 319–232.

22 T. C. Wapnitz, J.-Q. Yu, J. B. Spencer, Chem. Eur. J. 2004, 10, 484–493.

23 D. Enders, A. Saint-Dizier, M.-I. Lannou, A. Lenzen, Eur. J. Org. Chem. 2006, 29–49

24 B. D. Mather, V. Kalpana, K. M. Miller, T. E. Long, Prog. Polym. Sci. 2006, 31, 487–531.

25 B. A. Arbuzov, G. N.Nikonov, Erastov, O.A Russ. Chem. Bull. 1986, 35, 588–592

26 U. Quittmann, L. Lecamp, W. El Khabit, B. Youssef, C. Brunel, Macromol. Chem. Phys. 2001, 202, 628–635.

27 X.-G. Ge, G. Wang, Z. Hu, X. Xiang, J.-S. Wang, D.-Y. Wang, C. P. Liu, Y.-Z. Wang, J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 2994–3006.

28 M. Sponton, L. A. Mercado, J. C. Ronda, M. Galià, V. Cádiz,Polym. Degrad. Stab. 2008, 93, 2025–2031

Chapter 3

Thiol-Michael addition as a tool for synthesis of biomaterials

In this Chapter, the thiol-Michael addition to the enone derivatives of trigycerides have been applied to develop new thermoplastic and thermosetting materials.

"The best way to make your dreams come true is to wake up". Paul Valery

Thiol-Michael Addition

Apart from the traditional thiol-ene free radical additions, reactions between a thiol and an electron deficient "ene" also occur readily. Depending on the substrate, this reaction has been refered to as thia-Michael, thiol-Michael, thio-Michael, sulfa-Michael and more recently thiol-maleimide click and thiol-based click reaction.[1] In this thesis we simply refer to this click reaction as a thiol-Michael reaction, being the ene electron deficient, such as in acrylates, methacrylates, maleimides, α,β-unsaturated ketones, fumarates, acrylonitrile, cynamates and crotonates. Traditionally, a wide variety of catalysts have been used to initiate the thiol-Michael addition including strong bases, metals, organometallics an Lewis acids.[2]

Recently, thiol-maleimide click reactions using tertiary amine as a catalyst have been described to effectively functionalize degradable polyesters or to synthesize block copolymers by reaction between polymers selectively end-functionalized with maleimide and thiol groups.[3] This reaction was used also for the synthesis of nanoparticle surfaces functionalized with water soluble linear acrylate-based copolymers. These reactions proceed with high conversions under mild conditions and examples of efficient use of thiol-ene click chemistry to generate a range of functionalized materials have been reported.

The conjugate or Michael addition of thiols have been studied since 1940's.[4] From a traditional or fundamental start point the hydrothiolation of an activated C=C bond is readily accomplished under base catalysis with reagents such as sodium methoxyde, benzyltrymethylammonium hydroxide, and even relatively weak organobases such as triethylamine. The accepted mechanism for such reactions is given in Figure 3.1. The base, abstracts a proton from the thiol generating a potent nucleophilic thiolate anion, that attacks the electrophilic β carbon of the C=C generating the intermediate carbon-centered anion, itself a very strong base that abstracts a proton yielding the thiol-Michael addition product with concomitant regeneration of the base catalyst.[5]

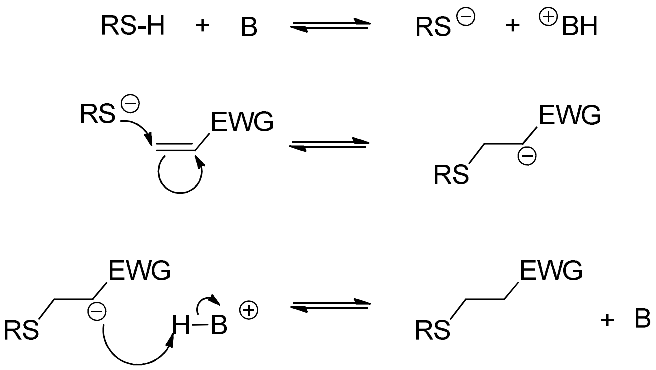


Figure 3.1 The base catalysed hydrothiolation of an activated C=C bond.

One important area in which the traditional base mediated thiol-Michael reaction has found extensive application is in the preparation of α- and ω- functional polymers and copolymers commonly, but not exclusively, derived from polymers or copolymers synthesized by RAFT.

While the traditional base-catalyzed thiol-Michael reaction is a highly versatile process significant efforts are being expended on the development of novel catalytic systems that efficiently and cleanly effect such thiol-Michael additions. A strategy of using primary or secondary amines or even more powerful and efficient nucleophilic alkylphosphine catalysts for extremely efficient thiol-Michael addition has emerged during the last few years. The use of primary amines, which act as nucleophilic catalysts rather than as simple bases, was first noted in 1967[6] and was not followed up for use in material applications until 2003.[7] The primary/secondary amine and phosphine nucleophilic catalysts are particularly efficient and provide a simple highly efficient process for catalyzing the addition. A proposed mechanism for such a nucleophile mediated thiol-Michael addition reactions is given in Figure 3.2. The nucleophile (amine or phosphine) undergoes conjugate addition to the activated C=C bond generating the strong intermediate carbanion that deprotonates the thiol, generating a thiolate anion that then enters an anionic chain process in which the thiolate anion undergoes direct thiol-Michael addition, regenerating the strong carbanion that deprotonates more thiol with concomitant generation of the thiol-Michael product.

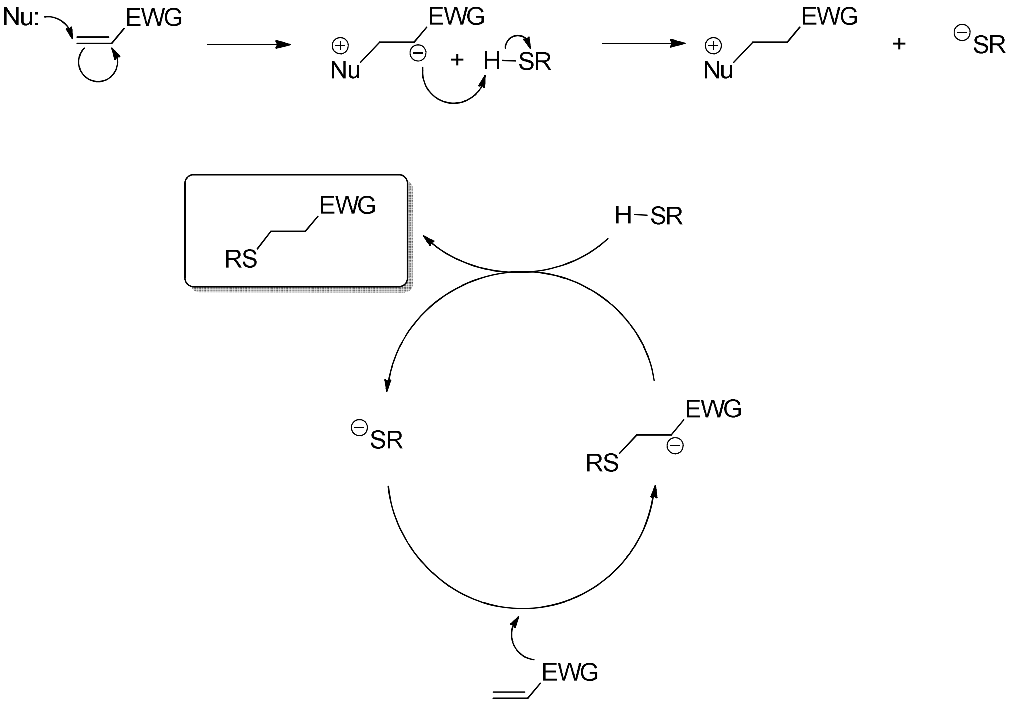


Figure 3.2 Proposed mechanism for the nucleophile-mediated hydrothiolation of an activated C=C bond.

Under appropriate conditions, nucleophile-mediated conjugate additions do proceed with exceptional click characteristics as exemplified in the convergent synthesis of star polymers and the preparation of branched thioethers.[8,9]

The light controlled reactions in both polymer chemistry and materials science are challenging and needed to expand and diversify the photo-mediated click reaction toolbox. Recently, light-mediated methods to control the thiol-Michael reaction which would have a significant impact in several material fabrication strategies have been described. The utilization of 2-(2-nitrophenyl)propyloxycarbonyl as a photolabile primary amine cage enables the thiol-Michael click reaction to be photo-triggered.[10]

Lewis acids have been used successfully in thiol-Michael additions. Asymmetric Michael reactions of thiols with enones mediated with chiral catalysts are among the most efficient methods for the preparation of optically active sulfides. Also several chiral catalysts have been developed and most asymmetric reactions have been carried out in organic solvents.[11] $Sc(OTf)_3$ chiral bipyridine complex at room temperature in water without using any organic solvent catalyzes the Michael reaction to afford the desired sulfide in high yields with high enantioselectivity.[12]

Anphoteric vanadyl triflate catalyze Michael additions with N-, P- and C- centered protic nucleophiles. The partially positive charged V center in V=O is Lewis acidic enough to first activate a carbonyl electrophile (step I in Figure 3.3)

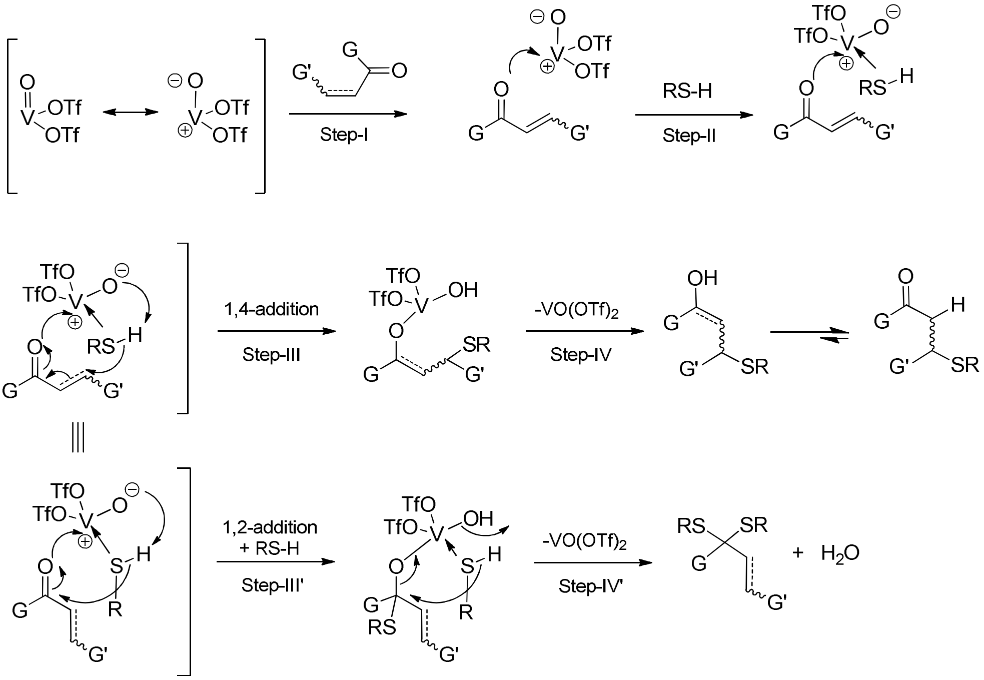


Figure 3.2 Scheme of postulated mechanisms for thiol-Michael-type 1,4-addition and thioacetalization (1,2-addition) to a given α,β-enone catalyzed by amphoteric vanadyl triflate.[13]

Conversely, the partial negatively charged O center in V=O serves as a Lewis base to promote a subsequent proton transfer of a coordinated, protic sulfur nucleophile (step II) during the 1,4- or 1,2-addition event (step III or III’). The resultant S,O-acetal in the

1,2-addition undergoes a second 1,2-addition to a thioxocarbenium ion intermediate leading to the corresponding dithioacetal (Step-IV’). In both scenarios, the reactions proceed in a sequential push–pull type pathway toward the substrate pair.[13]

In this chapter we used the thiol-Michael addition to the methyl oleate enone derivative to obtain an hydroxyester. The enzymatic polymerization of the hydroxyester has been used for the synthesis of sulfide-ketone-functionalized polyesters that can be further chemically modified. The same reaction has been used to crosslink the sunflower oil enone derivative to produce matrices for the preparation of fully renewable cellulose nano-biocomposites.

Enzymatic synthesis of functional polyesters.

Aliphatic polyesters are among the most widely used biodegradable polymers in environmental and biomedical fields. Generally, these polymers are synthesized via chemical polycondensation reactions using a wide range of catalysts, such as acetates of manganese, zinc, calcium, cobalt and magnesium, antimony and titanium oxides. However, these reactions are usually conducted at temperatures of 180–280ºC, and cause undesirable side reactions such as dehydration of diols and β-scission of polyesters to form acid and alkene end groups.[14] Meanwhile, high reaction temperatures are not suitable for thermally or chemically unstable monomers and functional groups, including siloxane, epoxy and vinyl moieties. In addition to temperature concerns, trace residues of metallic catalysts can cause unfavorable effects on environment and toxicity in biomedical applications. Moreover traditional chemical catalysts generally lack selectivity and the designed functional polyesters are hard to produce. Thus, the discovery of new and versatile polycondensation catalysts to catalyze reactions under mild conditions with chemo, regio and enantioselectivity, is of great significance.[15]

Enzymatic polycondensation, carried out generally with the aid of lipases, has been regarded as an environment-friendly synthetic process for polymeric materials and a good example of “eco-friendly polymer synthesis”.[16]

Compared with chemical route, enzymatic polycondensation, especially lipase/esterase-catalyzed polymerization, has many advantages including: high catalytic activity, mild reaction conditions, high control of enantio-, chemo- and region-selectivity, few by-products (a clean process).

Lipases are ubiquitous enzymes and have been found in most organisms from microbial, plant and animal kingdom. Lipases are esterases which can hydrolyze triglycerides (or esters) at water–oil interface. The hydrolytic capability of these enzymes has been utilized by nature in degradation of food and fats. The lipases have other application as valuable drugs against digestive disorders and diseases of the pancreas, as detergent additive for removal of fat stains and as catalysts for the manufacture of specialty chemicals and for organic synthesis.

Lipases are the most versatile classes of biocatalysts in synthesis of organic compounds. This is primarily because lipases can accommodate a wide variety of synthetic substrates while still showing regio-selectivity or chiral recognition. Lipases have evolved unusually stable structures that may survive effect of the organic solvents. The lipase-catalyzed hydrolysis in water can be easily reversed in non-aqueous media into ester synthesis or transesterification.

Regardless of the organism from which they have been isolated and the variation in molecular masses all lipases show a remarkable structural and functional similarity. A unique structural feature common to most lipases is a lid or flap composed of amphiphilic α-helix peptide sequence which in its closed conformation prevents access of the substrate to the catalytic site. After the lid is opened, a large hydrophobic surface is created to which the hydrophobic super substrate (oil drop) binds.[17]

Generally, enzymatic polyester synthesis proceeds via two major routes (Figure 3.4): ring-opening polymerization of lactones and polycondensation, which is further divided into polycondensation of diacids or their activated esters with diols and self-polycondensation of hydroxyacids or their activated esters.

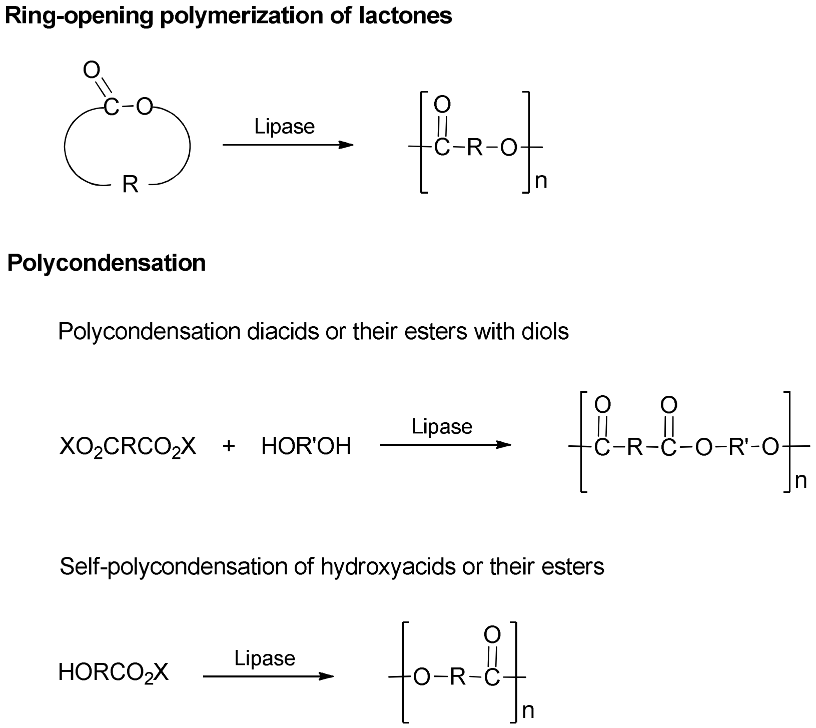


Figure 3.4 Two major routes of enzymatic polyester synthesis.

Polycondensation of hydroxyacids or their esters

Similar to polycondensation of dicarboxylic acids or their derivatives with diols, self-polycondensation of hydroxyacids or their esters can also be performed by esterification (dehydration) or transesterification polycondensation. In 1985 Ajima first reported the polymerization of 10-hydroxydecanoic acid and glycolic acid using PEG-modified lipase and esterase; the resultant products were oligomers with polymerization degree values greater than 5.[18] In 1999 Shuai studied the enzymatic synthesis of polyesters from hydroxyacids using porcine pancreatic lipase as catalyst.[19] The molecular weight (Mn, number average) varies from several hundred to several thousand depending on monomer used and reaction conditions as well. Moreover in this study they proposed a mechanism where the effect of using lipase is to yield an esterification intermediate, which can lower the activation energy needed for esterification of hydroxyl and carboxyl groups. (Figure 3.5)

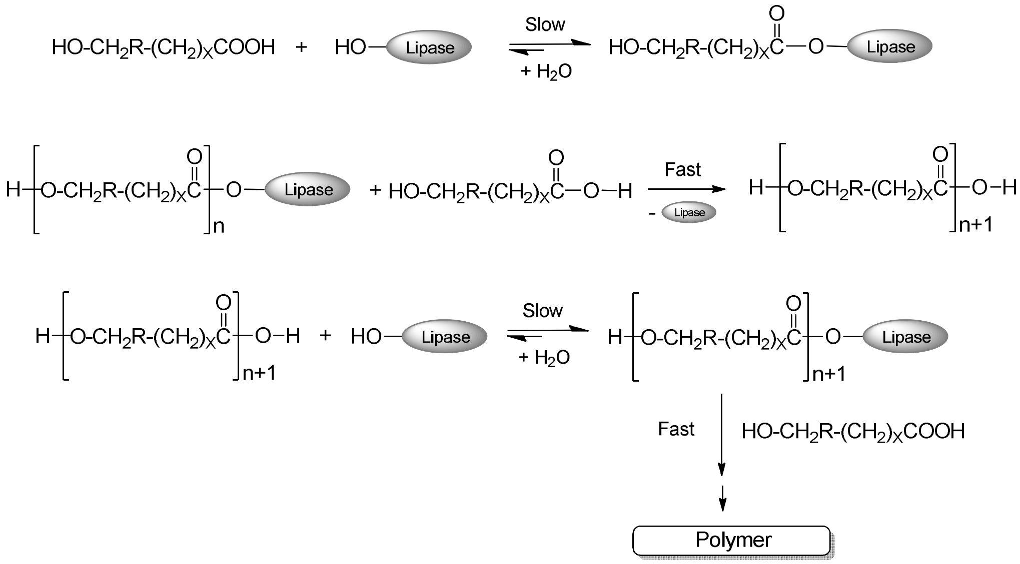


Figure 3.5 Mechanism of polycondensation of hydroxyacid catalyzed by lipase[19]

In 2007 Ebata synthesized a high-molecular-weight polyricinoleate by policondensation of methylricinoleate using immobilized lipase from *Pseudomonas cepacia* in bulk in the presence of 4Å molecular sieves at 80 ^{0}C for 7 days. Polyricinoleate was a viscous liquid at room temperature with a glass transition temperature (T_g) of -74.8 ^{0}C, showed no crystallinity and was biodegraded by activated sludge (Figure 3.6).[20]

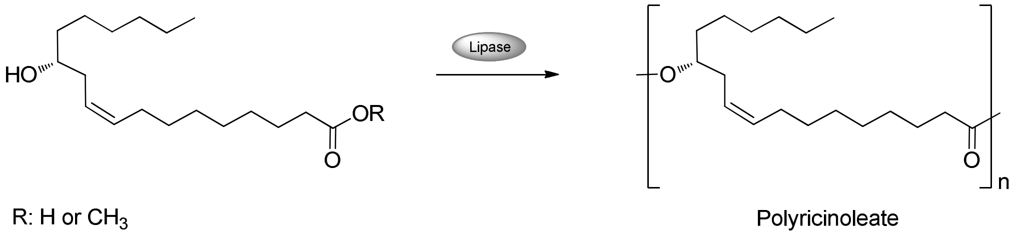


Figure 3.6 Lipase-catalyzed preparation of polyricinoleate.[20]

Polyesters obtained from a green procedure have proved to be practical and important materials for a range of biological and medical applications ranging from drug delivery and tissue engineering to surgically implantable devices. For example poly(glycolic acid) (PGA), poly(L-lactic acid) (PLA), or poly(ε-caprolactone) (PCL) had been well studied.[21,22] They have many useful applications but there remain several key features that limit their utility for biological applications, such no-uniform degradation due to the crystallinity and hydrophobicity of the polymers. In addition, all lack reactive functional groups capable of chemoselective polymer modifications. While these polyesters have had some success in the biological and medical fields, the introduction of functionality in the polymer backbone would allow for the selective tailoring of the polyester, which could dramatically increase their potential applications.

Recently there have been several reports to functionalize PGA, PLA, and PCL. Modified lactones and lactides have been synthesized to create polyesters that contain carboxylates,[23,24] amines,[25] and hydroxyl groups.[26] However, the complex multistep syntheses of new monomers may lead to degradation of polyester chains due to post polymerization deprotection reactions and, therefore, may limit the utility of these polymers. There are also few strategies for conjugating a wide variety of molecules onto polyesters. One popular example, click chemistry.[27,28]

An strategy, less commonly employed, is based on polyketoesters.[29] These particular polyesters are not commonly studied; a major feature is even less explored: ketone-specific reactions. The coupling reaction between ketones and oxyamines to generate oximes is a very powerful conjugation strategy and is chemoselective, rapid, and hydrolytically stable.[30,31] In 2008 Barrett and col. demonstrated the utility of this strategy by immobilizing a cell adhesive peptide (H_2NO-RGD) to polyketoester films (Figure 3.7), creating cell adhesive elastomers.[31] This immobilization strategy is synthetically flexible for designing and tailoring polymers for targeted biological applications.

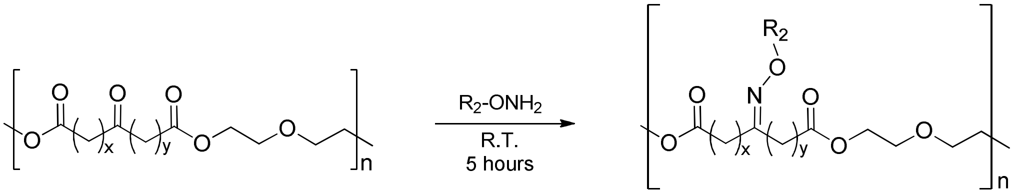


Figure 3.7 Functionalization of Polyketoesters

Synthesis of Cellulose Nanocomposites

Although much work has been directed towards biobased and biodegradable polymers, their application in everyday life remains somewhat limited, due to expensive raw materials and poor mechanical properties. It is clear that the mechanical properties of renewable polymers lag behind those of the petroleum derived polymers for commercial use. A composite strategy, combining bio-based/renewable polymers as matrices with traditional or renewable reinforcements could be used to bridge the aforementioned property performance gap.

Conventional composite materials based on glass, carbon, or aramid fibres embedded in petroleum based matrix materials are widely used in numerous industrial applications, such as in aerospace, maritime, automotive, construction and other areas.[32]

To date, a huge amount of thermoplastic and thermosetting oil-based biomaterials have been developed by using a variety of synthetic transformations[33-35] and they are also increasingly considered for the production of greener composites.[36] The wide range of possible combinations of vegetable oils, chemical modifications, polymerization routes and nature of fillers used as reinforcement materials allows tailoring composite properties to fit the requirements of structural or functional materials. Moreover, there is a clear trend to increase the percentage of “green”-based raw materials in the formulations of commodities as well as speciality polymers/composites for high added value applications.[37,38] In this way, numerous examples of biobased composites with natural fibres have been developed.[39]

In the last decade, nanocomposites have revealed clearly the property advantages that nanomaterial additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include: mechanical properties e.g. strength, modulus and dimensional stability, decreased permeability to gases, water and hydrocarbons, thermal stability and heat distortion temperature, flame retardancy and reduced smoke emissions, chemical resistance, surface appearance, electrical conductivity and optical clarity in comparison to conventionally filled polymers.

In addition it is important to recognise that nanoparticle/fibrous loading confers significant property improvements with very low loading levels, traditional microparticle additives requiring much higher loading levels to achieve similar performance. This in turn can result in significant weight reductions (of obvious importance for various military and aerospace applications) for similar performance, greater strength for similar structural dimensions and, for barrier applications, increased barrier performance for similar material thickness.[32]

Cellulose is the most abundant natural biopolymer on earth and shares with vegetable oils its renewable, biodegradable and non-toxic character. Cellulose exists in a variety of living species such as plants, bacteria, algae and some amoebas. It is the principal structural component in plant cell walls.[40] Cellulose chains are bio-synthesized by enzymes, deposited in continuous fashion and aggregated to form microfibrils which further aggregate to form macroscopic fibres. Natural cellulose fibres themselves act as composite materials, assembling in a mainly lignin matrix (Figure 3.8).

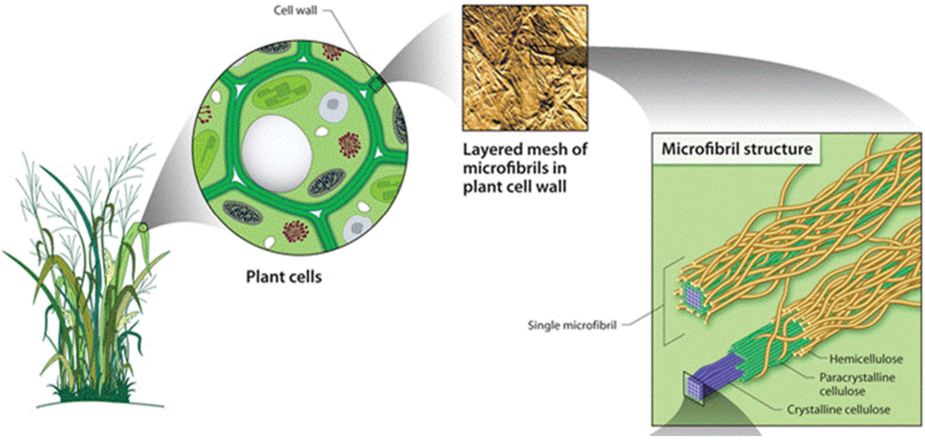


Figure 3.8 Arrangement of cellulose chains in microfibrils.[41]

Cellulose is a linear homopolymer of anhydro-D-glucose units linked together by β-1-4 linkages (Figure 3.9). Each glucose unit is oriented 180º to its neighbours.

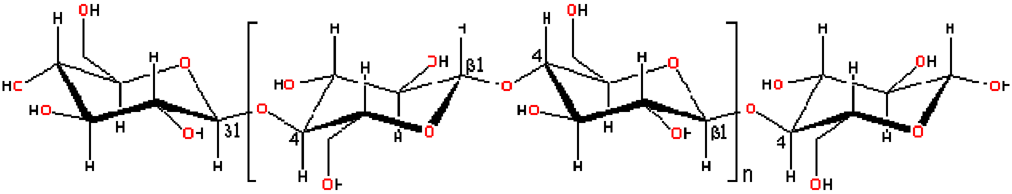


Figure 3.9 Chemical structure of cellulose.

There are three hydroxyl groups per monomer unit, so cellulose macromolecules are likely to be involved in a number of intra and intermolecular hydrogen bonds which play an important role in directing crystalline packing. The complex hydrogen bonding network results in different ordered crystalline arrangements which differ in crystal dimensions, chain orientation and crystalline form. X-Ray studies have shown that cellulose is composed of nanosized crystallites with interspersed amorphous regions as illustrated in Figure 3.10.[42,43] Four main crystalline allomorphs of cellulose have been identified (Cellulose I to cellulose IV) being native cellulose, named cellulose I, the most abundant. Each form has its characteristic X-Ray pattern.

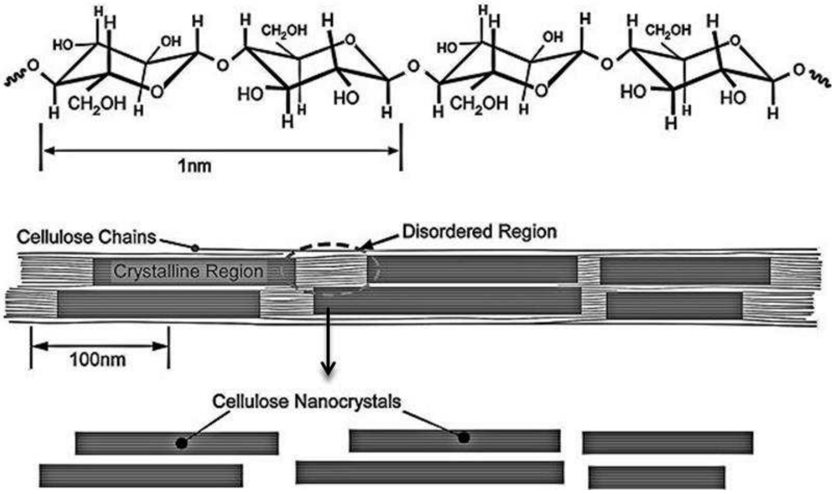


Figure 3.10 Crystallite arrangement in the cellulose micro fibrils.

Cellulose is industrially extracted from natural fibres and its hierarchical and multilevel organization allows different kinds of macro, micro and nanoscale fillers to be obtained (cellulose fibres, microfribrillated cellulose and cellulose nanocrystalls).[44]

Cellulose nanocristals (CNC) are a promising material that have been the focus of an exponentially increasing number of works exploring their use as nanofillers to improve mechanical and barrier properties of biocomposites.[45-47] This material is interesting as nanofiller due to its nanoscale dimensions, high specific area, and highly rigid crystalline structure. In comparison to mineral or metal nanofillers that are industrially available, CNC are renewable, feature low density, are relatively low cost, and remain biodegradable.

CNC represent the crystalline regions extracted from cellulose by partial acid hydrolysis (Figure 3.11).[48] The amorphous regions of cellulose are more accessible to acid attack and therefore, under controlled conditions, were removed whereas the crystalline domains remain. The typical procedure currently applied to produce CNC is the strong acid (HCl, HBr, H_2SO_4, H_3PO_4) hydrolysis of pure cellulosic materials (from wood, jute or flax fibres, cotton or agricultural wastes) at controlled temperature and reaction duration followed by a complex purification workup that commonly includes, washings, neutralizations, dialysis and drying.

The resulting CNC size, crystallinity and morphology depends on the cellulose source and the preparation method but commonly nanocrystalline materials 100-1000 nm long and 5-50 nm wide with crystallinities over 90% are prepared. CNC were usually obtained as water dispersions which have to be processed in different ways in order to be incorporated into a polymeric matrix to generate a nanocomposite material.

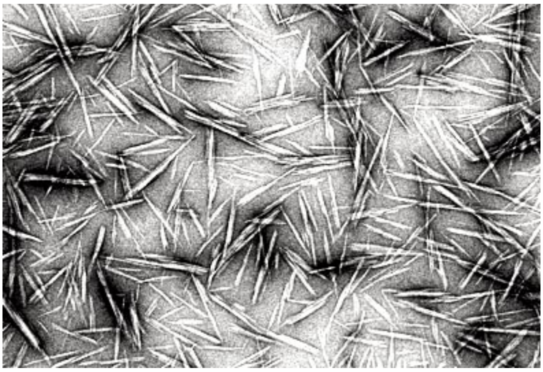


Figure 3.11 TEM image of a diluted CNC suspension.[48]

When processing cellulose nanocomposites, properties of CNC, nature of polymer matrix and the interfacial interaction between the fillers and the matrix should be considered. The most challenging aspect of nanocomposite processing is dispersing the CNC's into the polymer matrix. Different processing techniques have been used to ensure CNC's to be well dispersed to reach good reinforcement of the materials.[45,46] Due to its simplicity, casting-evaporation and solution casting are the most commonly used methods in laboratory, while other processing methods including extrusion, sol-gel and electrospining have also been studied.

Depending on the nature of the polymer matrix, dispersion of CNC have to be processed in different ways. In the case of hydrosoluble, hydrodispersible and hydroemulsionable polymers, water is the preferred processing medium because of the good dispersion and high stability of the hydrophilic CNC's in water. However, a large number of polymers and polymerization formulations are soluble only in non-aqueous systems. Due to the surface charge, CNC only may disperse in polar solvents and the degree of dispersion improves with increasing solvent polarity. Thus, one processing procedure involves mixing a solution of the polymer matrix with a dispersion of freeze-dried CNC in solvents such as DMF, DMSO and formamide. Sonication is commonly used to favour the nanofiler dispersion. Alternatively, CNC's can be coated with surfactants to improve dispersion in solvents of low and medium polarity such as toluene, chloroform or dichlorometane. In this case, the surfactant is added to the CNC water dispersion and the surfactant modified CNC freeze-dried and redispersed in the appropriate solvent prior to the addition of the polymer matrix solution. Finally, surface chemical modification is another method to disperse CNC in organic solvents. Due to the great number of hydroxyl groups in the crystal's surface, a number of different chemical reactions have been used to reduce the polarity of the nanofiller, including esterification, etherification, silylation, polymer grafting, etc. This methodology enables not only disperse the CNC's on organic solvents but improve the compatibility with the polymer matrix.

Even microcrystalline cellulose has been widely used industrially; no practical applications have been envisaged for cellulose nanocrystals. However several potential applications such as mechanical reinforcement, barrier materials, optical and biomedical applications are currently explored by many researchers.[49]

References

1 Hoyle, C. E.; Bowman, C. N. Angew. Chem. Int. 2010, 49, 1540-1573.

2 Mather, B. D.; Viswanathan, K.; Miller, K. M.; Long, T. E. Prog. Polym. Sci. 2006, 31, 487-531.

3 Pounder, R. J.; Stanford, M. J.; Brooks, P.; Richards, S. P.; Dove, A. P. Chem. Commun. 2008, 5158-5160.

4 Hurd, C. D.; Gershbein, L. L. J. Am. Chem. Soc. 1947, 69, 2328-2335.

5 Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. Chem. Soc. Rev. 2010, 39, 1355-1387.

6 Sanui, K.; Ogata, N. Bull. Chem. Soc. Jpn. 1967, 40, 1727-1727.

7 Van Dijk, J. T. Patent US Patent 6,639,046, 2003.

8 Chan, J. W.; Yu, B.; Hoyle, C. E.; Lowe, A. B. Chem. Commun. 2008, 4959-4961.

9 Chan, J. W.; Hoyle, C. E.; Lowe, A. B. J. Am. Chem. Soc. 2009, 131, 5751-5753.

10 Xi, W.; Krieger, M.; Kloxin, C. J.; Bowman, C. N. Chem. Commun. 2013, 49, 4504-4506.

11 Enders, D.; Luettgen, K.; Narine, A. A. Synthesis 2007, 959-980.

12 Ueno, M.; Kitanosono, T.; Sakai, M.; Kobayashi, S. Org. Biomol. Chem. 2011, 9, 3619-3621.

13 Chen, C.-T.; Lin, Y.-D.; Liu, C.-Y. Tetrahedron 2009, 65, 10470-10476.

14 Gross, R. A.; Ganesh, M.; Lu, W. Trends Biotechnol. 2010, 28, 435-443.

15 Yu, Y.; Wu, D.; Liu, C.; Zhao, Z.; Yang, Y.; Li, Q. Process Biochemistry 2012, 47, 1027-1036.

16 Varma, I. K.; Albertsson, A.-C.; Rajkhowa, R.; Srivastava, R. K. Prog. Polym. Sci. 2005, 30, 949-981.

17 Schmid, R. D.; Verger, R. Angew. Chem. Int. 1998, 37, 1608-1633.

18 Ajima, A.; Yoshimoto, T.; Takahashi, K.; Tamaura, Y.; Saito, Y.; Inada, Y. Biotechnol. Lett. 1985, 7, 303-306.

19 Shuai, X.; Jedlinski, Z.; Kowalczuk, M.; Rydz, J.; Tan, H. Eur. Polym. J. 1999, 35, 721-725.

20 Ebata, H.; Toshima, K.; Matsumura, S. Macromol. Biosci. 2007, 7, 798-803.

21 Chasin, M.; Langer, R. S. Biodegradable Polymers as Drug Delivery Systems; M. Dekker: New York, 1990, p 43-163.

22 Ratner, B. D.; Hoffman, A. S.; Schoen, F. J.; Lemons, J. E. Biomaterials Science: An Introduction to Materials in Medicine; Elsevier Science: Oxford, 2012, p 63-360.

23 Kimura, Y.; Shirotani, K.; Yamane, H.; Kitao, T. Macromolecules 1988, 21, 3338-3340.

24 Trollsås, M.; Lee, V. Y.; Mecerreyes, D.; Löwenhielm, P.; Möller, M.; Miller, R. D.; Hedrick, J. L. Macromolecules 2000, 33, 4619-4627.

25 Barrera, D. A.; Zylstra, E.; Lansbury, P. T.; Langer, R. J. Am. Chem. Soc. 1993, 115, 11010-11011.

26 Tian, D.; Dubois, P.; Grandfils, C.; Jérôme, R. Macromolecules 1997, 30, 406-409.

27 Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Angew. Chem. Int. 2001, 40, 2004-2021.

28 Li, H.; Riva, R.; Jérôme, R.; Lecomte, P. Macromolecules 2007, 40, 824-831.

29 Taniguchi, I.; Mayes, A. M.; Chan, E. W. L.; Griffith, L. G. Macromolecules 2004, 38, 216-219.

30 Christman, K. L.; Broyer, R. M.; Tolstyka, Z. P.; Maynard, H. D. J. Mater. Chem. 2007, 17, 2021-2027.

31 Barrett, D. G.; Yousaf, M. N. Biomacromolecules 2008, 9, 2029-2035.

32 Sabu, T.; Kuruvilla, J.; Malhotra, S. K.; koichi, G.; Sreekala, M. S. Polymer Composites, Macro- and Microcomposites; Wiley-VCH Veinheim 2012.

33 Xia, Y.; Larock, R. C. Green Chem. 2010, 12, 1893-1909.

34 Petrović, Z. S.; Javni, I.; Ionescu, M. J. Renew. Mater. 2013, 1, 167-186.

35 Xia, Y.; Quirino, R. L.; Larock, R. C. J. Renew. Mater. 2013, 1, 3-27.

36 Mosiewicki, M. A.; Aranguren, M. I. Eur. Polym. J. 2013, 49, 1243-1256.

37 Baillie, C. Green Composites: Polymer Composites and the Environment; CRC Press: Cambridge, 2005.

38 Yu, L.; Dean, K.; Li, L. Prog. Polym. Sci. 2006, 31, 576-602.

39 Wallenberger, F. T.; Weston, N. E. Natural Fibers, Plastics and Composites; Springer: Massachesetts, 2004.

40 Pérez, S.; Samain, D. In Advances in Carbohydrate Chemistry and Biochemistry: Structure and Engineering of Celluloses; Derek, H., Ed.; Academic Press: Grenoble, 2010, p 25-116.

41 Metz, M., Thermodynamic assesment of the cellulosic ethanol alternative energy system. http://www.facstaff.bucknell.edu/mvigeant/thermo_demos/mathiasmetzmetzler/pages/system.htm (accessed Jun 2 2013).

42 Sugiyama, J.; Persson, J.; Chanzy, H. Macromolecules 1991, 24, 2461-2466.

43 Dinand, E.; Vignon, M.; Chanzy, H.; Heux, L. Cellulose 2002, 9, 7-18.

44 Zugenmaier, P. Crystalline Cellulose and Cellulose Derivatives: Characterization and structures; Springer: Berlin 2008.

45 Siqueira, G.; Bras, J.; Dufresne, A. Polymers 2010, 2, 728-765.

46 Peng, B. L.; Dhar, N.; Liu, H. L.; Tam, K. C. Can. J. Chem. Eng. 2011, 89, 1191-1206.

47 Blaker, J. J.; Lee, K.-Y.; Bismarck, A. J. Biobased. Mater. Bio. 2011, 5, 1-16.

48 Habibi, Y.; Lucia, L. A.; Rojas, O. J. Chem. Rev. 2010, 110, 3479-3500.

49 Zhou, C.; Wu, Q. Recent Development in Applications of Cellulose Nanocrystals for Advanced Polymer-Based Nanocomposites by Novel Fabrication Strategies; Neralla, S. Ed: Louisiana, 2012.

Polyketoesters from oleic acid. Synthesis and functionalization

“It's the possibility of having a dream come true that makes life interesting.”

Paulo Coelho

Polyketoesters from Oleic Acid. Synthesis and Functionalization

Maryluz Moreno, Gerard Lligadas, Joan C. Ronda, Marina Galià, Virginia Cádiz

Departament de Química Analítica i Química Orgánica, Universitat Rovira i Virgili,
C/ Marcel.lí Domingo s/n,
Tarragona 43007, Spain

Abstract

In this study, we exploited the reactivity of the methyl oleate enone derivative for the conversion of this renewable raw material to ketone-containing hydroxyesters. The radical-mediated thiol-ene addition to the conjugated double bonds has been investigated and low yields were obtained due to secondary reactions. The thiol-Michael addition under acidic and basic/nucleophilic conditions was also examined. While when using vanadyl triflate ($VO(OTf)_2$), a slight excess of thiol was necessary to complete the reaction, by using both basic/nucleophilic catalysts 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), quantitative conversion was achieved under stoichiometric conditions in shorter reaction times. The obtained hydroxyester, carrying sulphide and ketone functional groups, was used to obtain polyesters by Novozyme 435 enzymatic polymerization. The coupling between ketone group of the repeating unit and a model oxyamine has been used to demonstrate the polyketoester functionalization via oxime formation.

Introduction

The growing awareness of society toward major environmental challenges such as global warming, increasing emissions of greenhouse gases and depleting of the earth's limited petroleum reserves, combined with recent regulations and incentives towards the reduction of carbon dioxide emissions are pushing the chemical industry to develop greener products and to find alternative growth strategies based on sustainable models. A particularly relevant option is to replace oil based resources by the use of raw materials derived from renewable feedstock or to use feedstock that are waste byproducts because they are not competing with raw materials used for human and animal food.[1]

The increasing number of research studies on the development of biobased materials reveals the great potential of renewable raw materials and their ability to substitute petrochemical based materials. Biosource materials are rarely used just after harvest or extraction and often need preliminary treatments. Finding sustainable and efficient ways to transform biofeedstock and modifying biosourced raw materials to make them usable as reagents in material production are key issues to design functional biobased materials able to compete with their highly optimized petrochemical counterparts.[2]

Vegetable oils are one of the most important renewable feedstock for the chemical industry as they are one of the cheapest and most abundant biological sources available, and their use as annually renewable platform chemicals has numerous advantages, including low toxicity and inherent biodegradability.[3, 4] They have been used in the synthesis of polymers by different approaches. The first strategy takes advantage of the naturally occurring functional groups in triglycerides or fatty acid derivatives, isolated from oils, such as internal double bonds which can be directly polymerized. However, the reactivity of triglycerides is limited and an alternative strategy is the functionalization prior to polymerization, widening the synthetic possibilities by introducing easily polymerizable functional groups. The challenge to progressively replace fossil feedstock's by materials arising from plant derived renewable resources lies in the second strategy and implies not only the development of new original reactions and catalysts but also the application of well established reactions to the functionalization of vegetable oils. Moreover, there is a need to develop environmentally friendly monomer and polymer synthesis strategies to keep moving toward more sustainable polymer chemistry and reactions termed as "Click Chemistry" are consistent with this aim.[5-7]

In our efforts to extend the use of vegetable oils in polymer chemistry we obtained α,β-unsaturated ketone-containing triglycerides from high-oleic sunflower oil using the singlet oxygen promoted "ene" reaction.[8] Conjugate addition to α,β-unsaturated carbonyl compounds is one of the most important carbon-heteroatom bond-forming strategies in synthetic organic chemistry[9] and has been widely applied in the macromolecular field.[10] Common conjugate addition reactions involve the addition of a protic nucleophile donor to an alkene acceptor which is activated by an electron-withdrawing group.

We investigated the reactivity of the α,β-unsaturated ketone triglyceride derivatives towards aromatic primary amines[11] and secondary phosphine oxides[12] and the results indicated that the aza- and phospha-Michael additions proceed in a very efficient way, thus the enone-containing triglycerides can be considered as interesting precursors of thermosets and flame retardant polymers.[13] To further explore the reactivity of these derivatives and to widen their scope of applicability in polymer chemistry we here describe the thiol-ene addition to the α,β-unsaturated ketone derived from methyl oleate.

Over the past several years there has been an increasing interest in efficient strategies to design new and versatile materials capable of successful performance in multiple applications. The exploration of selective and efficient chemistries for the postpolymerization functionalization allowed the construction of multifunctional materials by combination of a simple polymer platform with a versatile coupling of different pendant units.[14-17] Our aim was to develop an efficient and versatile method for the preparation of ketone-containing monomers and to exploit further the versatility of the ketone units within the polymers. We selected 2-mercaptoethanol as a functional thiol thus obtaining the corresponding hydroxyester that has been enzymatically polymerized. The biodegradable poly(ketoester) has been functionalized by coupling with an oxyamine-tethered model compound.

Experimental Section

Materials

Methyl oleate (96%; Alfa Aesar), octanethiol (98% Sigma-Aldrich), 2-mercaptoethanol (99% Sigma-Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN; 98% Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 98% Sigma-Aldrich), vanadium(IV) oxide sulfate trihydrate ($VOSO_4$; Stream Chemicals), barium trifluoromethanesulfonate (99% $Ba(OTf)_2$, Stream Chemicals), 2,2-dimethoxy-2-phenylacetophenone (DMPA; 99% Sigma-Aldrich), O-(tetrahydro-2H-pyran-2-yl)hydroxylamine (96% Sigma-Aldrich) were used without further purification. Novozyme 435 (Lipase acrylic resin from *Candida Antarctica*, ≥5,000 U/g) was provided by Sigma Aldrich. Vanadyl triflate ($VO(OTf)_2$) was obtained as previously described.[18] Enone derivative of methyl oleate (EMO) has been obtained as a mixture of methyl-9-oxo-10-octadecenoate and methyl-10-oxo-8-octadecenoate following a reported procedure.[8] Solvents were purified by using standard procedures.

General procedure for the Thiol Michael addition to EMO

0,2 g (0.645 mmol) of EMO were mixed in a round bottomed flask with the equimolar amount of octanethiol or 2-mercaptoethanol unless otherwise noted. The corresponding amount of catalyst was added and the reaction mixture was heated depending on the reaction temperature (Tables 1). The progress of the reaction was followed by ^1H NMR spectroscopy by the dissapearance of the double bond signals and the appearance of the methine directly bonded to the sulfur atom. The photoinitiated radical addition was carried out at room temperature, without deoxygenation, by irradiation with two 9 W UV lamps (λ 365 nm).

Addition of octanethiol: Synthesis of M1

^1H NMR ($CDCl_3$, TMS, δ ppm): 3.66 (s, 3H), 3.11 (m, 1H), 2.66 (m, 1H), 2.58 (m, 1H), 2.48 (t, 2H), 2.40 (m, 2H), 2.3 (t, 2H), 1.58-1.26 (m, 34H), 0.88 (t, 6H).

^{13}C NMR ($CDCl_3$, TMS, δ ppm): 209.6(s), 174.2(s), 51.6(q), 49.1(t), 44.0(t), 35.5(d), 34.2(t), 32.0(t), 31.2(t), 29.9(t), 29.4-29.2(t), 26.9(t), 25.0(t), 23.7(t), 22.8(t), 14.3(q).

Addition of 2-mercaptoethanol: Synthesis of M2
^{1}H NMR ($CDCl_3$, TMS, δ ppm): 3.75 (m, 2H), 3.65 (s, 3H), 3.16 (m, 1H), 2.73-2.62 (m, 4H), 2.40 (t, 2H), 2,29 (t, 2H), 1.62-1.26 (m, 20H), 0.86 (t, 3H).
^{13}C NMR ($CDCl_3$, TMS, δ ppm): 209.8(s), 174.4(s), 61.5(t), 51.6(q), 48.7(t), 43.9(t), 43.8(t), 40.3(t), 36.1(d), 34.7(t), 34.2(t), 32.0(t), 31.9(t), 29.5-29.0(t), 27.0(t), 26.7(t), 25.0(t), 23.8(t), 23.6(t), 22.8(t), 14.2(q).

General procedure for polyesterification of hydroxyester M2

Novozyme-435 dried in a vacuum desiccator (10%wt relative to total weight of monomer) was transferred to a round-bottom flask containing M2 (0.5 g, 1.613 mmol) and the reaction was carried out in bulk. The flask was placed into a constant preset temperature oil bath on a magnetic stirrer and vacuum (10 mmHg) was applied to remove methanol. Aliquots were removed from the reaction mixture at selected time intervals to monitor the reaction progress. The polymerization was terminated by adding excess of chloroform, stirring and removing the enzyme by filtration and precipitation in cold methanol. Following rotary evaporation, the products were characterized by NMR and SEC.
^{1}H NMR ($CDCl_3$, TMS, δ ppm): 4.18 (m, 2H), 3.14 (m, 1H), 2.71 (m, 2H), 2.66 (m, 2H), 2.40(t, 2H), 2.28 (t, 2H), 1.60-1.26 (m, 20H), 0.87 (t, 3H).
^{13}C NMR ($CDCl_3$, TMS, δ ppm): 209.2 (s), 173.7 (s), 63.7 (t), 49.1 (t), 43.9 (t), 43.8(t) 41.3 (t), 35.7 (d), 35.6 (t) 34.3 (t), 32.0 (t), 29.8-29.1 (t), 27.0 (t), 26.8 (t), 25.0 (t), 23.8 (t), 23.7 (t), 22.8(t), 14.3 (q).

Polyketoester functionalization

A solution of 0.1 g of the polymer (Mw=25800, PDI=1.6) in THF was mixed with the corresponding amount of O-(tetrahydro-2H-pyran-2-yl)hydroxylamine to obtain an oxyamine/ketone mole ratio 1:1 or 1.5:1. The reaction mixture was stirred at room temperature and samples were taken to monitor the reaction progress. The final product was dissolved in chloroform and precipitated in cold methanol.

^{1}H NMR ($CDCl_3$, TMS, δ ppm): 5.20(m, 1H), 4.19 (m, 2H), 3.86 (m, 1H), 3.60 (m, 1H), 3.12 (m, 1H), 2.74 (m, 2H), 2.65 (m, 2H), 2.40(t, 2H), 2.28 (t, 2H), 1.74 (m, 2H), 1.60-1.26 (m, 24H), 0.88 (t, 3H).
^{13}C NMR ($CDCl_3$, TMS, δ ppm): 173.7 (s), 160.6(s), 100.4(d), 63.7 (t), 62.8(t), 49.1 (t), 43.9 (t), 43.8(t), 41.3 (t), 35.7 (d), 35.6 (t) 34.3 (t), 32.0 (t), 29.8-29.1 (t), 27.0 (t), 26.8 (t), 25.5(t), 25.0 (t), 23.8 (t), 23.7 (t), 22.8(t), 20.1(t), 14.3 (q).

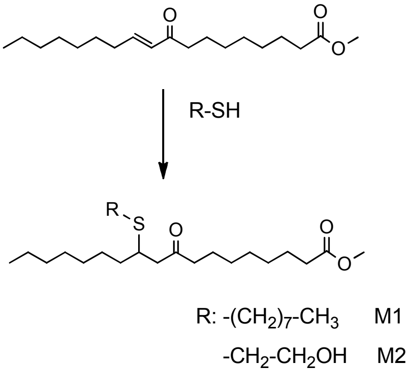
Instrumentation

Ultraviolet (UV) light irradiation of reaction mixture for photoinitiated samples for thiol-ene addition was carried out with two 9W bench lamps which emit around 365 nm wavelength. ^{1}H NMR 400 MHz and ^{13}C NMR 100.6 MHz NMR spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform, $CDCl_3$ as solvent and TMS as internal standard. Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system equipped with a Shimadzu RID 6A series refractive-index detector. THF was used as eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained with polystyrene standards.

Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer using N_2 as a purge gas (10 ml/min) at scan rates between 5 and 20 ºC/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as a purge gas, in the 30-800 ºC at scan rates of 10 ºC/min.

Results and discussion

Recently, there has been a renewed interest in the thiol-ene click reaction as means of preparing new monomers and polymers as well as functionalizing them.[19] Thiol-ene additions can proceed by a radical addition and by an ionic mechanism, i.e., the thiol-Michael addition. The radical thiol-ene reaction involves the thermally or photochemically initiated anti-Markonikow addition to an alkene to afford the corresponding thioether. It has been widely investigated lately since it is a highly efficient click process. However, the reaction is best conducted with electron rich double bonds since electron deficient double bonds such as acrylates yield oligomers as a byproduct. To evaluate the reactivity of EMO toward photoinitiated radical addition, octanethiol was used as model compound (Scheme 1)



Scheme 1. Thiol-Michael addition to EMO.

The coupling was carried out at room temperature with slight excess of thiol (1.2 equiv. relative to double bond) in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMAP) as photoinitiator (Table 1).

The reaction was monitored by ^{1}H NMR through the disappearance of characteristic double bond signals at 6.05 and 6.75 ppm and the appearance of the multiplet signal at 3.16 ppm corresponding to the methine directly bonded to the sulphur moiety. The signal corresponding to the methyl ester group at 3.65 ppm was used as internal standard. The reaction reached 85% enone conversion in only 30 min but the target thioether was obtained in only 60% conversion. Increasing the reaction time led to complete enone consumption but did not improve the thioether conversion. The ^{1}H NMR spectra show the appearance of complex signals at 2.9-2.5 ppm and 3.2 ppm that could be attributed to the formation of oligomers as well as the corresponding disulphide. Moreover, the appearance of signals at 61 ppm and an additional ketone carbonyl peak at 211 ppm in the ^{13}C NMR spectra do not allow to disregard the sulfur addition to the α position of the enone.

Table 1. Thiol-Michael addition under photoinitiated radical and acid catalyzed conditions at room temperature.

Thiol	Enone:Thiol molar ratio	Catalyst	Mol % catalyst	Time (h)	Enone Conversion (%)	Thioeter Yield (%)
Octanethiol	1:1.2	DMAP	1.5	0.5	85	58
				1	97	60
				2	98	59
				3	97	60
	1:1	$VO(OTf)_2$	5	0.5	90	87
				3	92	89
	1:1.2	$VO(OTf)_2$	5	0.5	100	99
2-mercaptoethanol	1:1.2	$VO(OTf)_2$	5	1	99	98

The thiol-ene addition can also proceed via a non-radical mechanism. The reactivity of the α,β-unsaturated carbonyl compounds in the Michael addition decreases if electron rich substituents are present. Steric factors are also important and the larger the groups substituted at α and β positions, the slower the reaction rate. Beside the more conventional conjugate additions performed in basic media, the non-radical thiol-Michael addition is catalyzed by acids, particularly in the case of Lewis acids. The use of amphoteric vanadyl triflate ($VO(OTf)_2$) to catalyze Michael reactions with N-, P- , C- and S- centered protic nucleophiles has been described.[20] The partial positive charged V center in V=O is Lewis acidic enough to first activate a carbonyl electrophile (i.e. the Michael acceptor). Conversely, the partial negatively charged O center in V=O serves as a Lewis base to promote a proton transfer of a coordinated protic sulfur nucleophile during the 1,4-addition event. Conjugate addition of octanethiol to EMO was examined in the presence of 5 mol% of $VO(OTf)_2$. The reaction proceeds smoothly at room temperature and the corresponding thioether adduct is obtained in 87% yield in 0.5h. However, a slight excess of thiol (1.2 mol) was necessary to complete the reaction in 0.5h.

Table 2. Thiol-Michael addition of octanethiol to EMO under basic/nucleophilic conditions using DBU or DBN as catalyst**.**

Thiol	Enone:thiol molar ratio	Mol% catalyst	T (ºC)	Time (h)	Enone conversion (%)		Thioether yield (%)	
					DBU	DBN	DBU	DBN
octanethiol	1:1	0.05	room	1	36	90	31	85
				3	52		62	
				6	68		60	
				12		95		87
				40	100		100	
		0.1	room	1	37	94	28	89
				3	48	94	58	91
				6		94		97
				20	88		79	
		0.2	room	1		88		86
				3		88		87
				6		88		87
		0.05	50	1	48	87	36	82
				3	62	86	51	87
				6	73	91	56	91
		0.1	50	1	40	85	37	83
				3	48	85	49	84
				6	49	85	45	83
		0.2	50	1	76	97	68	96
				3	79	91	77	96
				6	80	94	80	93
	1:1.2	0.2	50	1	10		8	
				6	15		17	
				24	14		22	
2-mercaptoethanol	1:1	0.1	room	1		99		100
		0.2	room	0.5		88		87
				1		98		100

The common base-catalyzed Michael addition of thiols has also been extensively investigated.[10] Many of these systems require high catalyst concentration, elevated reaction temperatures and long reaction times, giving to poor conversion. Aside from the conventional base-catalyzed reaction, the thiol- Michael addition can be catalyzed by nucleophiles and these reactions posses many features of the radical mediated click addition. Amine-based species as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) have proven to be highly efficient catalyst not only due to their basic character but to their significant nucleophilic character. [22] Their enhanced activity has been rationalized in terms of a nucleophile-initiated anionic chain process although the occurrence of a hybrid or purely base-catalyzed process may also operate. An interesting feature of the nucleophile initiated thiol-Michael reaction is that it can be carried out in the presence of trace amounts of water, given the large difference of pKa values of common thiols and water.

The catalytic behaviour of the amine-based specie DBU was evaluated in bulk at room temperature with a catalyst loading of 0.05 mol % (Table 2). The neat transformation of enone to thioether was observed but long reaction time was needed to reach complete conversion. Increasing catalyst loading or reaction temperature does not improve thioether yield and increasing the thiol concentration clearly diminishes the catalyst activity. DBN was also evaluated in this reaction under the same reaction conditions (Table 2). The reaction takes place in shorter reaction times reaching conversions around 90% in 1h at room temperature for the different catalyst concentrations. Increasing the reaction temperature to 50 ºC does not improve the conversion. DBU and DBN have proven to be highly efficient catalysts due to their basic and nucleophilic character.[21] The enhanced activity of DBN in our case can be ascribed to its stronger basic nature (DBN pKa=13.5, DBU pKa=11.6).

Because of its ability to add a broad range of functionalities in lieu of the double bond of the α,β-unsaturated carbonyl compounds, the thiol-Michael addition is a promising route that can be used for the synthesis of novel monomers from renewable resources. 2-Mercaptoethanol was chosen for its ability to add primary hydroxyl functionalities to EMO, thus obtaining an hydroxyester able to be used in the synthesis of polyesters. Given the results obtained using octanethiol as a model compound, the conjugated addition was carried out under acid and basic/nucleophilic conditions was carried out. 2-Mercaptoethanol has been applied to the $VO(OTf)_2$ catalytic protocol without discernible alcohol addition (Table 1). This highly chemoselective addition is consistent with the amphoteric character of $VO(OTf)_2$ by which the more acidic thiol end gets activated more efficiently that the corresponding alcohol end. Using and excess of 1.2 mol of thiol and 5% of catalyst at room temperature, the consumption of enone takes place in 1h, and the target compound is obtained in a 98% yield. Disulphide formation can be observed by ^1H NMR spectroscopy (2.9 and 3.9 ppm). The reaction has been carried out also using 0.1% of DBN at room temperature and a complete conversion was reached in 1h (Table 2).

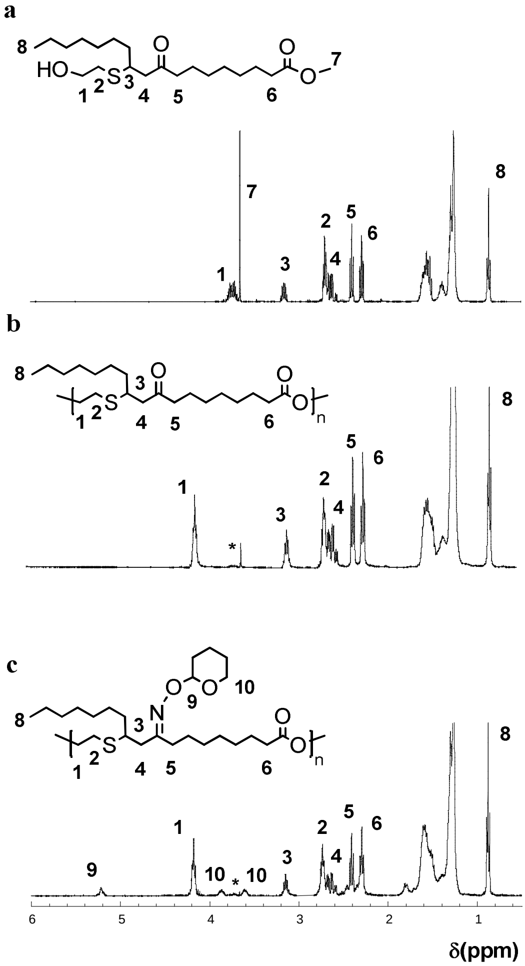
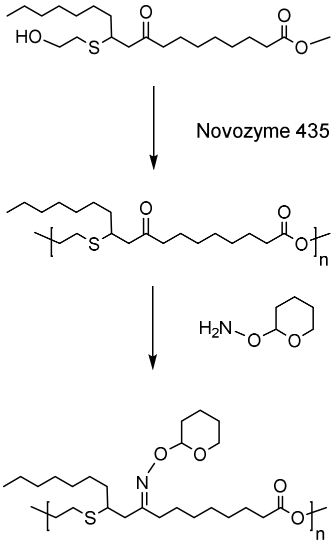


Figure 1. ^{1}H NMR spectra (CDCl$_3$, (δ ppm)) of a. M2, b. Polymer, c. Oxime modified polymer. * CH$_2$OH (3.6 ppm) and OCH$_3$ (3.7 ppm) end groups.

Under these conditions, 2-mercaptoethanol is more reactive than the alkyl thiol according to the pka values of the thiols, (octanethiol pKa=10.64 mercaptoethanol pKa=9.72). ^{1}H NMR spectrum of M2 (Figure 1a) showed characteristic signals for the methine directly bonded to the sulphur atom at 3.1 ppm (3) as well as new signals at 3.7 and 2.7 ppm (1, 2) corresponding to the mercaptoethanol moiety. Taking into account that the $VO(OTf)_2$ catalyzed addition requires product purification by removing disulfide and excess of 2-mercaptoethanol, DBN is the catalyst of choice.



Scheme 2. Polymerization of hydroxyester M2 and functionalization of the polyketoester.

The synthesis of the polyketoester derived from hydroxyester M2 was designed in view to its potential biological applications, and therefore, the polymer was obtained by enzymatic polymerization without any potential contaminating catalysts or coreagents (Scheme 2).[23] Novozyme-435 at catalyst loadings of 10% and 15% was used in bulk or toluene solution polymerizations at 80 ºC and 90 ºC and the evolution of molecular weight and molecular weight distribution was followed by SEC (Figure 2A). ^1H NMR (Figure 1b) allowed to monitor the polymer formation by the appearance of a new signal at 4.2 ppm (1) corresponding to the ester repeating unit. Molecular weight was also obtained by ^1H NMR by integrating end group signals at 3.6 ppm (CH_3O-) and 3.7 ppm (CH_2-OH) and repeating unit signal at 0.8 ppm (CH_3^-). It was found that the highest molecular weight polymer was produced during the 80 ºC polymerization while the higher polymerization temperature of 90 ºC tended to decrease the molecular weight (Figure 3). Protein denaturation has been described to cause a decrease of monomer conversion in polymerizations performed above 90ºC[24] so it can be the reason for the observed decrease in molecular weight. A significant increase in molecular weight is observed when catalyst concentration is increased from 10 to 15% or when small amounts of toluene were used as solvent.

All the polyesters formed had narrow polydispersity (PDI ≈ 1.5) and were obtained in high yields (>90%). Based on these results, it was concluded that Novozyme-435 is successful in polymerizing high molecular weight materials from monomers containing ketone and sulphide functional groups. The polymers were characterized by differential scanning calorimetry (DSC) showing low T_g values around -60 ºC. Termogravimetric analysis (TGA) showed a 5% weight loss at temperatures around 250 ºC, two maximum weight loss temperatures at ca. 350 and 450 ºC and 1% mass remaining at 700 ºC.

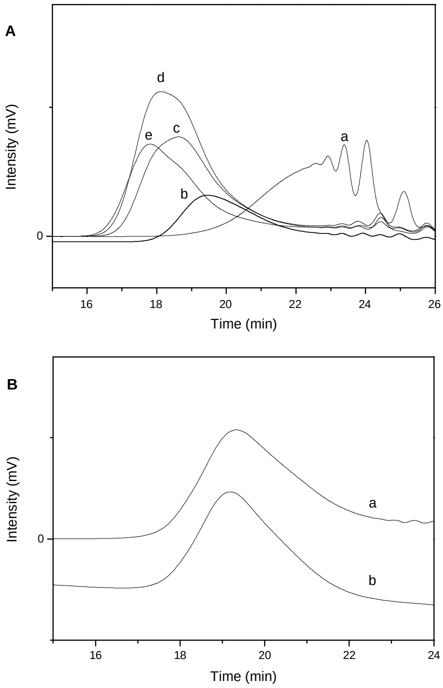


Figure 2. A. GPC traces for the bulk polymerization of M2 (80 ºC, 10wt% catalyst/monomer) a. 1h b. 4h c. 24h d. 48h e. 120h B. GPC traces of a. polyketoester and b. oxime functionalized polyester.

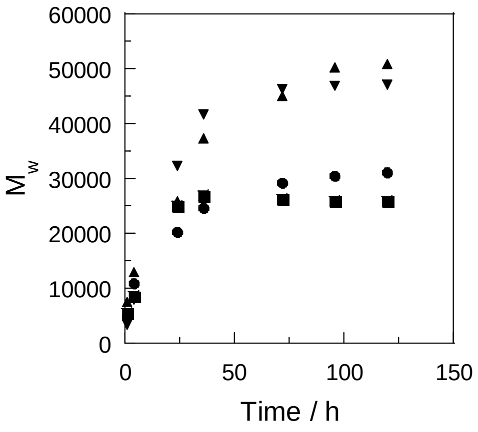


Figure 3. Mw for the polymerization of M2. (●) 80 ºC, 10wt % /wt catalyst/ monomer; (■) 90 ºC, 10wt% / wt catalyst/monomer, (▲) 80 ºC, 15wt % /wt catalyst/ monomer (▼) 80 ºC, 10wt % /wt catalyst/ monomer, toluene

The key feature of the polymers is the incorporation of a ketone and a sulphide functional groups into the repeating unit of the polyester. The coupling reaction between ketones and oxyamines to generate oximes is a very powerful conjugation strategy that allow for a variety of ligands to be covalently immobilized. The reaction is chemoselective, rapid and mild, resulting in hydrolytically stable, non degraded materials. Moreover, the oxime forming reaction can occur rapidly and efficiently at physiological conditions.[25,26] To demonstrate this strategy, commercially available O-(tetrahydro-2H-pyran-2-yl)hydroxylamine was chosen as model compound (Scheme 2).

The reaction was first carried out under stoichiometric conditions but a 50% excess of oxyamine relative to ketone content was needed to ensure complete reaction. After 5 h at room temperature, complete conversion of ketone to oxime was observed. Figure 1c shows the ^{1}H NMR spectra of the polyoximeester with the new proton resonance at 5.2, 4.2, 3.6, 1.8 and 1.7 ppm attributed to the tetrahydropyranyl moiety. ^{13}C NMR spectrum show a more direct evidence as the ketone carbonyl signal at 209 ppm disappears and a new signal at 160 ppm corresponding to the oxime bond appears.

Moreover, ^{13}C NMR spectra show signals attributable to the oxyamine moiety at 100, 63, 29 and 20 ppm. No significant degradation of the polymer backbone was observed by GPC and both samples had similar polystyrene equivalent molecular weight, with no increase in polymer polydispersity (Figure 2B). The DSC plot of the modified polymer showed an increase in T_g value to -40 ºC as a result of the introduction of bulky substituents which restricts main chain mobility. Thermal stability, as measured by TGA, slightly decreases regarding the starting polyketoester (5% weight loss at temperatures around 240 ºC).

Conclusions

The thiol-Michael addition of the enone derivative of methyl oleate has been conducted in an effort to extend the utility of vegetable oil derivatives in polymer synthesis. While radical-mediated thiol-ene addition yields noticeable side reactions, both acidic and basic/nucleophilic conditions allow for the selective tioether formation. Using DBU or DBN, quantitative conversion is achieved under stoichiometric conditions in shorter reaction times. The obtained hydroxyester, carrying both sulphide and ketone functional groups, can be enzymatically polymerized to obtain polyesters that have been further functionalized by postpolymerization modification.

Acknowledgement.

Financial support by the MICINN (Ministerio de Ciencia e Innovacion) (MAT2011-24823) is gratefully acknowledged.

References

1 P.N.R. Vennestrøm, C.M. Osmundsen, C.H. Christensen, E. Taarning, Angew. Chem. Int. Ed. 2011, 50, 10502-10509
2 Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411-2502
3 Gandini, Green Chem. 2011, 13, 1061-1083
4 L. Montero de Espinosa, M.A.R. Meier, Eur. Polym. J. 2011, 47, 837-852
5 G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, J. Polym. Sci. Part A: Polym. Chem., 2013, 51, 2111-2124

6 K. Yao, C. Tang, Macromolecules 2013, 46, 1689-1712

7 A.S. More, L. Maisonneuve, T. Lebarbé, B. Gadenne, C. Alfos, H. Cramail, Eur. J. Lipid Sci. Technol. 2013, 115, 61-75

8 L. Montero de Espinosa, J.C. Ronda, M. Galià, V. Cádiz, J. Polym. Sci. Part A:Polym. Chem. 2008, 46, 6843-6850

9 J.A. Ma, H.C. Guo, Angew. Chem. Int. Ed. 2006, 45, 354-366

10 B.D. Mather, K. Viswanathan, K.M. Miller, T.E. Long, Prog. Polym. Sci. 2006, 31, 487-531

11 L. Montero de Espinosa, J.C. Ronda, M. Galià, V. Cádiz, J. Polym. Sci. Part A: Polym. Chem. 2010, 48, 869-878

12 M. Moreno, G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, J. Polym. Sci. Part A: Polym. Chem. 2012, 45, 3206-3213

13 M. Moreno, G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 1808-1815

14 K. Kempe, a. Krieg, C.R. Becer, U.S. Shubert, Chem. Soc. Rev. 2012, 41, 176-191

15 R. M Arnold, N.E. Huddleston, J. Locklin, J. Mat. Chem. 2012, 22, 19357-19365

16 K.A. Günay, P. Theato, H-A. Klok, J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 1-28

17 A.S. Goldmann, M. Glassner, A. J. Inglis, C. Barner-Kowollik, Macromol. Rapid Commun. 2013, 34, 810-849

18 S.K. De, J. Mol. Cat. A: Chem. 2005, 226, 77-79.

19 A.B. Lowe, Polym. Chem. 2010, 1, 17-36.

20 C.T. Chen, Y.D. Lin, C.Y. Liu, Tetrahedron 2009, 65, 10470-10476

21 J.W. Chan, C.E. Hoyle, A.B. Lowe, M. Bowman, Macromolecules 2010, 43, 6381-6388

22 M. Baidya, H. Mayr, Chem. Commun. 2008, 1792-1794

23 S. Kobayashi, A. Makino, Chem. Rev. 2009, 109, 5288-5353

24 A. Kumar, R.A Gross, Biomacromolecules 2000, 17, 133-138

25 E.W.L. Chan, M.N. Yousaf, J. Am. Chem. Soc. 2006, 128, 15542-15547

26 D.G. Barrett, M.N. Yousaf, Biomacromolecules 2008, 9, 2029-2035

Thermosets from High Oleic Sunflower Oil by Thiol-Michael Addition as Matrix for Cellulose Nano-biocomposites

“I believe that the science of chemistry alone almost proves the existence of an intelligent creator” Thomas Alva Edison

Thermosets from High Oleic Sunflower Oil by Thiol-Michael Addition as Matrix for Cellulose Nano-biocomposites.

Maryluz Moreno, Ilaria Armentano, Gerard Lligadas, Joan C. Ronda, Marina Galià,
Virginia Cádiz

Departament de Química Analítica i Química Orgánica, Universitat Rovira i Virgili,
C/ Marcel.lí Domingo s/n,
Tarragona 43007, Spain

Abstract

Thiol-Michael addition of pentaerythritol tetrakis(3-mercaptopropionate) (PE3MP) to a high oleic sunflower oil derivative containing enone groups (ETG), has been used to prepare vegetable oil derived renewable thermosets in an efficient way and under mild conditions. The same formulation has been used to prepare bionanocomposites by incorporating to the polymerization mixture, 1wt%, 5wt% and 10wt% of cellulose nanocrystalls (CNC) modified with Beycostat A B09® as surfactant. The morphology and thermal and mechanical properties of the different bionanocomposites were evaluated and compared with the pristine thermosets. Morphology analysis shows that good dispersion of the nanofiler is achieved in all cases. Mechanical properties show an improvement for all nanofiller contends with a maximum at 5wt% loading that has been related with the reinforcement effect of the CNC. Finally, protein adsorption was measured in order to evaluate potential application of these materials as biosensors and cell growing supports

Keywords

Nano-biocomposites, renewable resources, thermosets, thiol-michael addition, cellulose nanocrystalls.

Introduction

The last two decades have witnessed an exponential growth in the interest for using bio-based products, which has been driven by the need for replacing petroleum based materials, reducing the fuel consumption and for producing materials with lower environmental impact.[1,2] Natural vegetable oils are considered to be one of the most important classes of renewable resources because of the wide variety of possibilities for chemical transformations, universal availability, and low price and they are preferred by the chemical industry.[3] To date, a huge amount of thermoplastic and thermosetting oil-based biomaterials have been developed by using a variety of synthetic transformations.[4-6] and they are also increasingly considered for the production of greener composites.[7] The wide range of possible combinations of vegetable oils, chemical modifications, polymerization routes and nature of fillers used as reinforcement materials allows tailoring composite properties to fit the requirements of structural or functional materials. Moreover, there is a clear trend to increase the percentage of “green”-based raw materials in the formulations of commodities as well as speciality polymers/composites for high added value applications.[8,9] Cellulose is the most abundant natural biopolymer and share with vegetable oils its renewable, biodegradable and non toxic character. Extracted from natural fibres, its hierarchical and multilevel organization allows different kinds of macro, micro and nano-scale fillers to be obtained.[10] Obtained by partial acid hydrolysis, cellulose nanocristals (CNC) have been the focus of an exponentially increasing number of works exploring their use as nanofillers to improve mechanical and barrier properties of biocomposites.[11-14]

Plant oil-derived thermosetting materials have been widely obtained by polymerization or copolymerization with vinylic monomers using cationic or radical initiators.[15] Under these conditions, high temperatures and long curing cycles are usually needed due to the lack of reactivity of the internal double bonds in fatty acids. To overcome this drawback, chemical modification of vegetable oils to introduce more reactive groups (i.e. acrylate, maleate, epoxy) has been extensively used.[16,17] These reactive triglyceride derivatives can be crosslinked at lower temperatures and produce denser networks when combined with appropriate multifunctional reagents. Thiol-ene addition has recently resurged as an efficient tool to functionalize double and triple bonds under very mild conditions.[18] Thiol-ene addition to double bonds constitutes an example of "click chemistry" because the reactions are efficient, high yielding, have clearly defined reaction pathways/products and presents tolerance to many different reaction conditions/solvents.[19] Thiol-ene addition has been used to prepare elastomeric networks by reaction of vinyl ether, allylether, acrylated or maleated soybean oil[20,21] with the commercially available multifunctional thiols: trimethylolpropane tris(3-mercaptopropionate) and pentaerythritol tetrakis(3-mercaptopropionate) (PE3MP).

We developed a new reactive enone containing triglyceride (ETG)[22] which has been effectively used to prepare regular and flame retardant thermosetting resins by aza- and phospha-Michael addition.[23,24] The addition of thiol groups to α,β-unsaturated carbonylic compounds constitutes a key reaction in biosynthesis as well as in the synthesis of biologically active compounds.[25] The reaction can be performed in solventless conditions and low temperatures through the activation of thiols with nucleophiles/bases[26] or the olefin acceptors with Lewis acids.[27]

Recently, we studied the thio-Michael addition of 1-octanethiol and 2-mercaptoethanol to a regioisomeric mixture of enone containg methyl oleate isomers. Under the studied conditions, thio-Michael addition proceeds in a smooth way at moderate temperatures using DBN as the more effective catalyst.[28] In this work, we exploited the thiol-Michael addition of PE3MP to the enone containing triglyceride derived from high oleic sunflower oil to produce elastomeric thermoset networks and cellulose nanocrystal based nano-bio under mild conditions. The utilization of renewable resource is discussed as a novel and appropriate sustainable nano-biocomposites with modulated mechanical properties.

Experimental Part

Materials

High oleic sunflower oil (minimum 80% oleic acid) was supplied by Coreysa, pentaerythritol tetrakis(3-mercaptopropionate) (PE3MP) (Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (Aldrich), meso-tetraphenylporphyrin (TPP)

(Aldrich), triethylamine (Scharlau), acetic anhydride (Scharlau), microcrystalline cellulose powder (Aldrich), Beycostat A B09 (CECCA S.A.), Dowex Marathon MR-3 ion exchange resin (Aldrich) and bovine serum albumin culture medium (BSA, Sigma-Aldrich) were used as received. Dichloromethane (DCM) was dried by refluxing over P_2O_5 and distilled immediately before use.

Synthesis of the α,β-unsaturated ketone derivative of high oleic sulflower oil (ETG)

Enone containing triglyceride was prepared starting from 70 g (79.1 mmol) of high oleic sunflower oil following a reported procedure[22] as a white cereous solid containing 2.3 α,β-unsaturated ketones per molecule (determined by ^1H NMR) with 76% yield.

Synthesis and modification of cellulose nanocrystals

Cellulose nanocrystals (CNC) was prepared from microcrystalline cellulose by sulphuric acid hydrolysis following the procedure used by Cranston and Gray.[29] Hydrolysis was carried out with 64 wt% sulfuric acid at 45 ^{0}C for 60 min with vigorous stirring. After removing the acid, dialysis and ultrasonic treatment were performed. The resulting 0.5 wt% CNC aqueous suspension (20% yield) was treated with Dowex Marathon MR-3 ion exchange resin, stirred for 48h and the resin filtered off.

Cellulose nanocrystals were modified with Beycostat A B09 by stirring the CNC suspension in water with the surfactant in a 1/4 weight ratio following a reported procedure.[30] Finally the modified cellulose nanocrystals (s-CNC) were lyophilized to dryness.

Thermosets and nano-biocomposite preparation

Typical procedure for the thermoset preparation

1g (1.07×10^{-3}mol) ETG was melted in a petri glass, 0.3g (6.14×10^{-4}mol) PE3MP were added and mixed. Then 4.025 10^{-3}g (3.24×10^{-5}mol) DBN (1 mol %) were added to the mixture. The resulting liquid was poured into a preheated (60 ^{0}C) glass mold and maintained at this temperature for 2 hours and post-cured at 120 ^{0}C for 12 h. The same procedure was used varying the ETG/PE3MP ratio, the amount of catalysts and the temperature and time of the curing cycle

Nano-biocomposite film preparation

After freeze drying, the required amount of s-CNC was dispersed in 30 mL of dichloromethane by tip sonication procedure (Vibracell, 750) for 2 min at 40% of amplitude in an ice bath. Next, 1g (1.07×10^{-3}mol) ETG, and the appropriate s-CNC suspension were mixed by stirring and then 0.3g (6.14×10^{-4}mol) of PE3MP and $4.025\ 10^{-3}$g (3.24×10^{-5}mol) of DBN (1% mol) were added with stirring to the initial mixture. The solution was poured on a glass mold and the solvent evaporated at room temperature during 3 hours. The curing was carried out following the same conditions as the neat thermosets. Composites with 1wt%, 5wt% and 10wt% of s-CNC were prepared

Polymer fractionation

The percentage of insoluble fraction in the neat thermosets was determined by extracting 0.5 g of each sample with 50 mL of DCM at reflux temperature for 4h. The percentage was calculated by weighting the insoluble fraction once dried.

Protein adsorption

Protein adsorption measurements were performed by transferring 300mg of bovine serum albumin (BSA, Sigma-Aldrich), onto the samples. Proteins were incubated 30 min at 37 °C for 24 h.[31] After three washing with water total protein content was measured by the Bradford method using BSA as the standard.[32] Absorbance (595 nm) was measured in a UV spectrometer. Every sample was analyzed in five independent experiments by triplicate.

Instrumentation

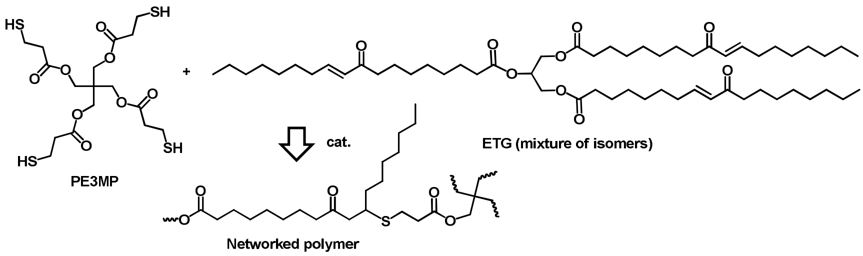
FTIR/ATR spectra were recorded on a JASCO 680 spectrophotometer with a resolution of 4 cm^{-1} in the transmittance mode. An attenuated-total-reflection accessory with thermal control and a diamond crystal (Golden gate heated single-reflection diamond ATR, Specac Teknokroma was used. UV measurements were made on a ELISA reader GDV-DV990BV6 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C

NMR (100.6 MHz) spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform, using $CDCl_3$ as solvent and TMS as internal standard. Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer using N_2 as a purge gas (10 mL/min) at 10 ^{0}C/min. Thermal stability was measured on a Mettler TGA/SDTA 851e/LF/1100 with N_2 as a purge gas, in the 30–800 ^{0}C range at scan rate of 10 ^{0}C/min.

AFM analysis was performed on a Molecular Imaging model Pico SPM II (Pico+) in a tapping mode at room temperature in air, using silicon cantilevers. WAXS measurements were made using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ-θ goniometer) fitted with a curved graphite diffracted-beam monochromator, incident and diffracted beam Soller slits, a 0.06º receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 3 and 60º. The data were collected with an angular step of 0.03º at 5s per step and sample rotation. A low background Si(510) wafer was used as sample holder. Cu_{ka} radiation was obtained from a cooper X-ray tube operated at 40 kV an 30 mA. Tensile test were performed on an Instron 5965 equipment with a 100 N load cell at crosshead speed of 10 mm/min and at 25 ºC and preload of 0.05N. The dimensions of the test specimens were about 50mm x4mm x0.35mm. The tensile properties were determined from the average of five samples.

Results and discussion

The main aim of this work consists of preparing and characterizing elastomeric thermosets and nano-biocomposites starting from two basic renewable resources, cellulose and a vegetable oil. To prepare thermosetting composite matrices under mild conditions we selected thiol-Michael addition of a tetrafunctional thiol (PE3MP) and a functionalized triglyceride (ETG) containing an average of 2.3 enone groups per triglyceride molecule (Scheme 1). ETG was prepared, as previously described, from high oleic sunflower oil following a green synthetic approach consisting of the tandem photooxygenation of the allylic positions-dehydration of allylic alcohol in the oleic acid chains.



Scheme 1. Schematic representation of the thermoset preparation by thiol-Michael addition of PE3MP and ETG triglyceride.

PE3MP is a derivative of pentaerythritol and 3-mercaptoacetic acid which are prepared respectively from acetaldehyde and acrylic acid. Both reagents can be currently obtained from biomass[33-36] and so synthesized resins and nanocomposites can be considered 100 % renewable.

In a previous work using enone methyl oleate derivative, we found DBN as an effective catalyst for the thiol-Michael addition under relatively mild conditions (60 ºC) and so we decided to use this catalyst in the addition of PE3MP to the enone triglyceride. In order to select appropriate curing conditions, we carried out a set of experiments in which the effect of different curing and post curing temperatures and times, reagents ratio and amount of catalyst on the yield and characteristics of the croslinked fraction were studied (Table 1). To evaluate the effectiveness of each curing cycle, the resulting product was fractionated in dichloromethane and the yield and T_g of the crosslinked fraction were determined.

Initially, mixtures with stoichiometric amounts of reagents (1 mol of SH per mol of enone group) and DBN (1% mol of C=C) were studied. The results indicate that when the initial curing is performed at 50 ºC (Exp 1 and 2) the yield of croslinked fraction is quite low (84%) irrespectively of the temperature used in the postcuring step. When curing was performed at higher temperatures (60 ºC or 90 ºC, Exp 3 and 4 respectively) the yield of croslinked fraction increases as the temperature does, reaching a maximum of 91%. When a higher ratio of crosslinking agent was used (exp 5 and 6) no significant increase of the insoluble fraction was obtained but the T_g

value slightly decreases suggesting lower crosslinking degree. An increase of the amount of catalyst used (Exp. 7) also slightly increases the amount of crosslinked material. The extend of the curing reaction was evaluated by FTIR-ATR (Figure1).

Table 1. Curing conditions tested in the thiol-Michael addition of PE3MP to ETG.

	ETG (eq)	**PE3MP (eq)**	**DBN (mol C=C %)**	**T (ºC) (a)**	**t (h) (b)**	**IF (%) (c)**	**T_g (ºC) (d)**
1	1	1	1	50	2	84	-33
				90	12		
2	1	1	1	50	2	84	-33
				120	6		
3	1	1	1	60	2	88	-33
				120	12		
4	1	1	1	90	2	91	-32
				120	12		
5	1	1.3	1	60	2	93	-34
				120	12		
6	1	1.5	1	60	2	91	-37
				120	12		
7	1	1	3	60	2	94	-34
				120	12		

a) Curing (upper) and post-curing (down) temperatures.
b) Curing (upper) and post-curing (down) times.
c) Insoluble fraction in DCM.
d) Glass transition temperature of the insoluble fraction.

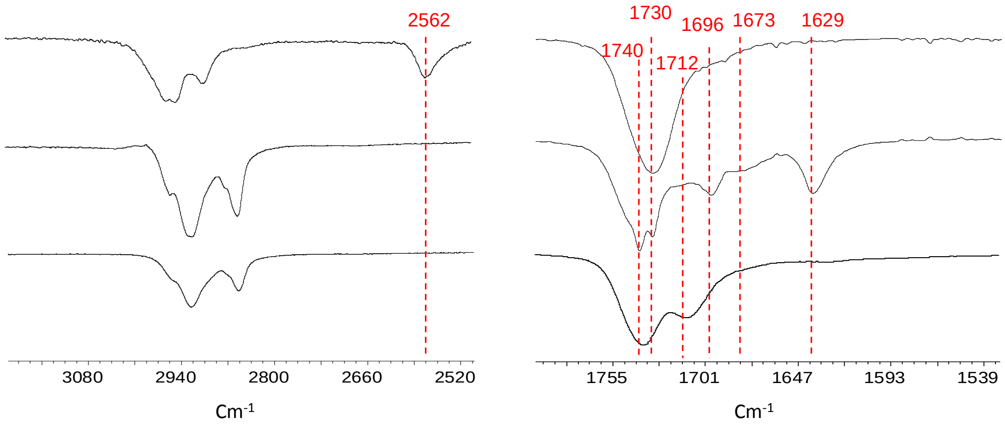


Figure 1. Selected regions of the FTIR-ATR spectra of the thermoset obtained in exp. 4 (a), ETG (b) and PE3MP (c).

As can be seen the signal at 2562 cm^{-1} corresponding to the SH group completely disappears as well as the signals of the conjugated ketone carbonyl group at 1696 cm^{-1} (s-cis) and 1673 cm^{-1} (s-trans) and the conjugated double bond stretching at 1629 cm^{-1}. In the final product, the signal of the new ketone carbonyl group appears at 1712 cm^{-1} partially overlapped with the intense signal at c.a 1740 cm^{-1} corresponding to the ester groups of the triglyceride and PE3MP. Due to the low intensity of the SH stretching vibration, the presence of unreacted thiol groups could not be confirmed in the case of the materials obtained in Exp. 5 and 6. Soluble fractions compositions were also analyzed by ^{1}H RMN. For the products obtained using a stoichiometric ratio of reagents (Exp.1 to 4), spectra indicate that oligomeric fractions are constituted by triglyceride fractions with no enone groups. This can be related with the composition of the starting triglyceride molecules which have an average of 2.3 enone groups per triglyceride molecule but contains saturated fatty acid rich fractions with lower amount of reactive groups that would remain in the soluble fraction. In the soluble fractions of experiments 5 and 6 the presence of the characteristic signals of PE3MP moiety can be also detected but the existence of SH free groups could not be confirmed as their characteristic signal at 1.68 ppm appears overlapped with the signal of the triglyceride aliphatic protons.

Taking into account the above results, the curing conditions for the preparation of the thermosetting films were fixed at 90 ºC for 2h with a post curing at 120 for 12h using stoichiometric amounts of the reagents and 1% of DBN as catalyst.

Next we dealt with the preparation of the cellulose nanocomposites. Most of the work reported in the literature refers to preparation of nano-biocomposites from linear polymers in which the material is generally produced by casting after dispersing the CNC with the aid of a solvent. On the contrary, preparation of thermoseting nanocomposites by dispersing the nanofiller on a reactive mixture is less habitual and some examples can be found on the literature.[37-40] It is well known than CNC form stable suspensions in water which disperse effectively in water soluble polar polymers like polyvinyl alcohol (PVA). Dispersion in highly non polar media is more challenging. During the critical freeze drying step, the nanocrystalls tend to agglomerate into flakes due to the strong hydrogen bonding as the water sublimate.[41] To prevent agglomeration and obtain good dispersions, three main strategies have been followed, use of surfactants,[42,43] use of highly polar solvents such as DMF or DMSO[44,45] and the chemical modification of the surface cellulose hydroxyl groups with appropriate reagents containing apolar aliphatic chains.[46-48] The first two strategies are more straightforward but the use of DMF and DMSO have to be avoided as they are difficult to remove completely from the reaction mixture. So we decided to use Beycostat A B09®, an acid phosphate ester of ethoxylated nonylphenol, as surfactant to address CNC dispersion. The use of surfactans to avoid aggregation in solvents such as chloroform or DCM is an effective strategy which has the only drawback of requiring large quantities of surfactant, usually several times more than CNC quantities.

Surfactant modified CNC (s-CNC) were obtained by controlled acid hydrolysis of microcrystalline cellulose, modified with this surfactant and freeze dried following a reported procedure.[49] This process allows obtaining well individualized s-CNC with typical dimensions ranging from 100 to 200 nm in length and 5-10 nm in width.[50] Prior to their dispersion into the prepolymer mixture, thermal stability of the s-CNC on the selected curing conditions was tested. For these purpose, samples of s-CNC were heated at 120º C for 12h and their TGA and WAXS difractograms compared with those of the unheated, samples showing no changes. s-CNC forms stable dispersions in DCM under sonication conditions and solutions containing the appropriate amount of s-CNC were prepared. For all s-CNC loadings, transparent DCM solutions were obtained indicating that the dimensions of a major part of cellulose nanoparticles in the suspension are below the limit of light-scattering.

We tested different ways to incorporate the s-CNC dispersion into the prepolymer mixture in a homogeneous way. Addition of the s-CNC dispersion onto a mixture of the reagents containing the catalyst led systematically to heterogeneous lumpy mixtures with s-CNC aggregates. On the contrary, homogeneous mixtures were obtained by adding the s-CNC dispersion over the ETG triglyceride followed by the addition of a solution of PE3MP first and the DBN catalyst at last. In this way solutions containing equimolecular amounts of ETG and PE3MP, 1% of DBN and 1wt%, 5wt% and 10wt% of s-CNC were prepared and casted on round sylanized glass crucibles with a diameter of 60 mm. Neat and nanofilled samples were cured at the same conditions (90 ºC for 2h and 120 ºC for 12h) to produce pale yellow transparent films with a thickness of 0.6-0.8 mm.

To analize s-CNC distribution into the polymer matrix, nanocomposite samples were examined by FTIR-ATR, WAXS and AFM, and compared with the pristine resin.

FTIR-ATR (Figure 2) confirms the s-CNC inclusion by the wide band centred at 3440 cm^{-1} corresponding to cellulose hydroxyl groups (Figure 2c). Moreover the same spectrum shows two small bands at 1514 and 616 cm^{-1} which are characteristic of the s-CNC (Figure 2a) and does not appear in the neat resin.

According to the spectra of pure compounds the signal at 1514 cm^{-1} can be attributed to the aromatic stretching band of the nonylphenol in the surfactant whereas the signal at 616 cm^{-1} can be assigned to the cellulosic structure.

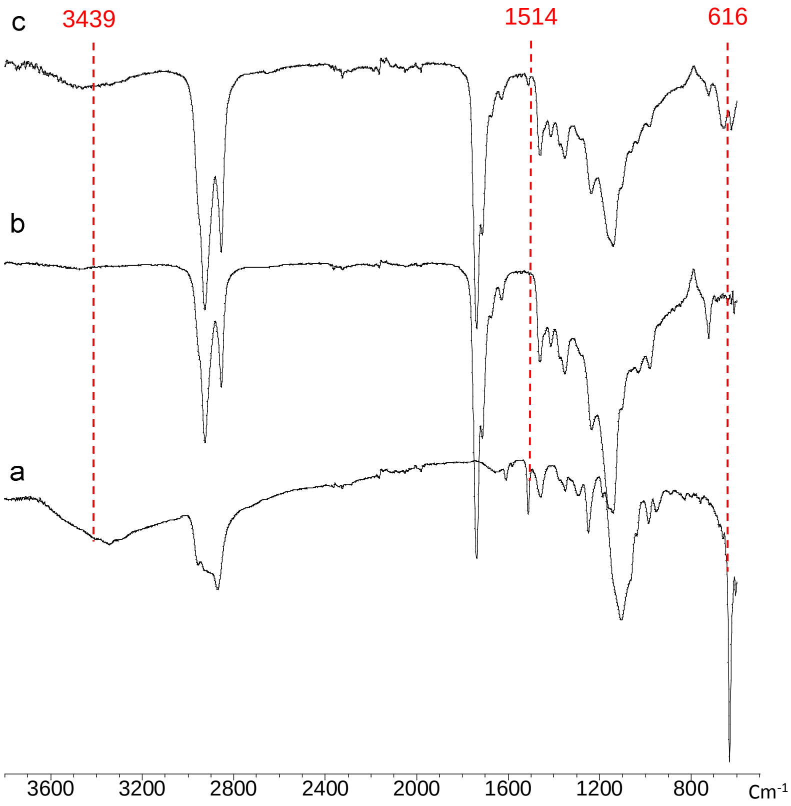


Figure 2. FTIR-ATR spectra of s-CNC a), neat ETG/PE3MP b) and the nanocomposite with 10% of s-CNC c).

The structures of the s-CNC filler, the neat resin and the resulting nano-biocomposites were characterized by angle X-ray scattering (WAXS). Figure 3a, 3b and 3c shows respectively WAXS difractogram of the pure ETG/PE3MP thermoset, nanocomposite with 10w% s-CNC and the s-CNC filler. ETG/PE3MP show only a wide diffraction band at 2θ = 19.0º indicating an amorphous nature. On the other hand s-CNC exhibited three sharp reflection peaks at 2θ = 3.5º, 5.0º and 22.5º and two not well defined peaks at 2θ = 14.8º and 16.5º. The first two low angle peaks correspond to the characteristic diffractions of the liquid-crystallyne nonylphenol in the surfactant whereas the rest of the peaks correspond respectively to the reflections of the [200], [1$\bar{1}$0] and [110] planes in type I crystalline cellulose.[51,52] The sharp diffraction peak for the [002] plane indicated high perfection of the crystal lattice. Moreover, a very small peak at 2θ = 34.5º due to the reflection of the [040] plane can also be observed.

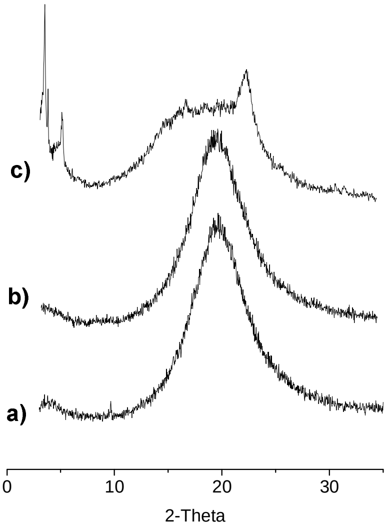


Figure 3. WAXS difractograms of a) neat ETG/PE3MP, b) the nanocomposite with 10w% of s-CNC and c) s-CNC.

In the case of the nano-biocomposites, hardly any difference is observed in the WAXS difractograms even in the sample with a 10w% of s-CNC, (Figure 3b) probably due to the actual low CNC content and the prominence of the wide peak of the amorphous polymeric matrix. Similar X-ray patterns have been described especially in CNC nanocomposites with thermosetting polymers.[38-40] Moreover, at this point, it must not be excluded the possibility that the curing reaction affected in some extent the crystalline structure of the CNC core.

The surface morphology of the pristine polymer and nano-biocomposites were analyzed by Atomic Force Scanning microscopy (AFM) in order to evaluate the dispersion of s-CNC and whether any significant sized aggregates occur during the casting.

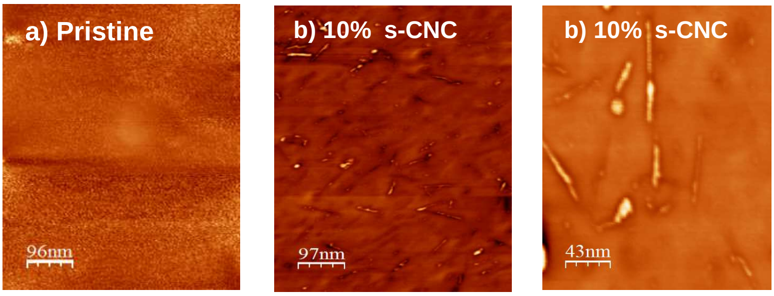


Figure 4. AFM images of a) neat ETG/PE3MP and b) the nanocomposites with 10% of s-CNC with different magnification.

As can be seen in figure 4 nano-biocomposite with 10wt% of s-CNC, showed a homogeneous distribution of the filler with no appreciable aggregates. In the magnification image both parallel and perpendicular arrangements of the s-CNC along the surface can be observed. Moreover, the average size of the parallel disposed s-CNC, is in the order of the measured for the s-CNC initial DCM dispersion (100 to 200 nm length and 5-10 nm wide). AFM analysis also indicates a significant change in the surface roughness than increases from 2.8 nm for the pristine sample to a maximum of 6.9 nm for the sample with 10%wt s-CNC. If s-CNC are also well dispersed along the surface, not only roughness but also other surface properties such affinity to different substrates (water, fat, proteins or cells) have to experience a noteworthy change.

The effective dispersion of s-CNC into the nanocomposite films could also be assessed by characterizing the film surface properties. Nanoscale dispersion of the highly polar s-CNC nanoparticles would modify the apolar nature of the oil-based resin which can be easily measured by contact angle measurements. Figure 5 shows the pictures and the contact angle for the pristine and modified films.

As can be seen, there are a remarkable modification of the surface properties as reflected by the decrease of contact angle from 78º to 16º. The low angle value reached for the nanocomposite containing 10wt% of s-CNC, is consistent with a good dispersion of the nanoparticles and a low proportion of aggregates as assessed by the AFM measurements.

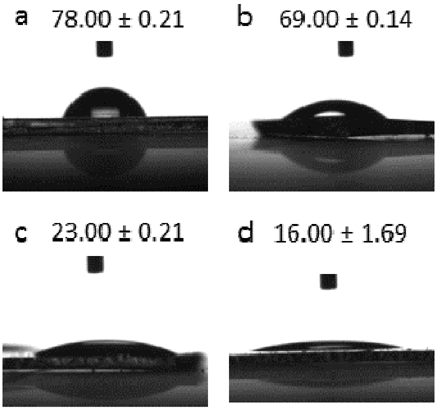


Figure 5. Water contact angle measurements of a) neat ETG/PE3MP and the nanocomposites with b) 1%, c) 5% and d) 10% of s-CNC. The contact angle value corresponds to the average of three measurements.

The thermal and tensile properties of the materials were measured by DSC, TGA and tensile tester (Table 2).

Table 2. Thermal and mechanical properties of the ETG/PE3MP pristine thermoset and its s-CNC nano-biocomposites.

Sample	**Tg (ºC)**[a]	**$T_{5\%}$ (ºC)**[b]	**T_{max} (ºC)**[c]	**E (MPa)**	**Breaking Load (N)**	**σ_b (MPa)**	**ε_b (%)**
Pristine	-36	324	371, 451	31.6±3.6	1.6±0.4	0.7±0.1	35.0±0.8
1%w s-CNC	-38	319	356, 454	53.8±13.3	0.8±0.2	0.8±0.2	18.0±0.8
5%w s-CNC	-39	304	341, 447	77.5±12.9	1.6±0.1	1.6±0.1	32.0±0.1
10%w s-CNC	-40	299	345, 423	58.2±9.7	1.3±0.2	0.9±0.2	21.0±0.5

Thermal properties of films were analyzed by DSC and TGA to determine how the addition of s-CNC altered the formed microstructure and the thermal stability of the polymer matrix upon solvent evaporation. The pristine presents an amorphous nature and only a slight decrease of Tg value was detected for all films probably associated with some plasticizing effect associated to the surfactant presence. First DSC trace of the pure s-CNC shows a Tg at -47 ºC and a small endotherm peak at 5 ºC associated to some retained water. Moreover, no significant differences were observed on the scans indicating that dispersion of the nanofillers does not modify significantly the microstructure of the polymer matrix. A more important influence is observed in the thermal stability. As can be seen in the first derivative of the TGA curves three degradation temperatures zone can be distinguished (Figure 6).

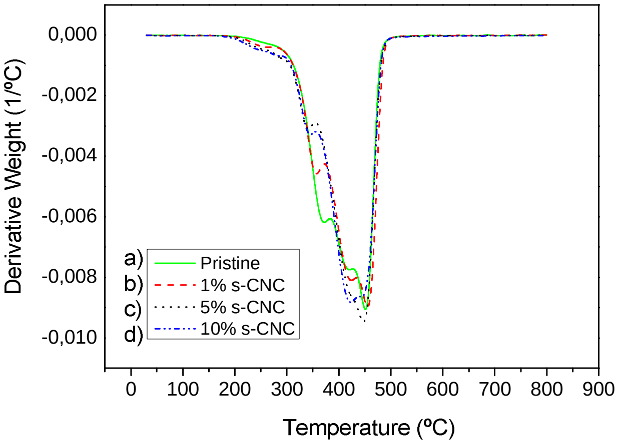


Figure 6. First derivative TGA plots of a) ETG/PE3MP and the nanocomposites with b) 1%, c) 5% and d) 10% of s-CNC.

In the low temperature region (190-280ºC) a small loss weight that increases with the s-CNC content is observed. This loss can be associated with the decomposition of the surfactant and the cellulose nanocrystalls in the polymer matrix.[53] At higher temperatures two degradation steps can be observed. The first, with a maximum rate temperature between 345 and 370º C starts at lower temperatures but involves a minor weight loss as the amount of s-CNC increases. The second and main degradation step is very similar for all materials but starts at slightly lower temperatures as the s-CNC content increases. This let us to conclude that the presence of s-CNC produces a decrease in the thermal stability of the material but also a slight reduction of the weight loss rate at high temperatures probably due to the barrier effect of the nanofiller on the free transport of the degraded volatile products.

The mechanical behavior of neat ETG/PE3MP and ETG/PE3MP nano-biocomposites was evaluated by tensile test (Table 2). All the nano-biocomposite formulations show Young's modulus (E) higher than the neat ETG/PE3MP but the influence of the filler seems not to be linear as the maximum value is obtained for the material with 5wt% s-CNC. Deformation at break (εb) is lower that the one of neat ETG/PE3MP, with the exception of the sample containing 5wt% s-CNC which has a similar value. Even the presence of considerable amounts of surfactant could led to more ductile materials with higher elongations, it must be taken into account that it also promotes the nanofiller dispersion which allows enhancing the nanoreinforcement effect. Tensile strength (σ_b) increases slightly in the samples with 1wt% and 10wt% of s-NCN but again a maximum value is observed for the sample containing 5wt% s-CNC which shows an increase of 130% in their tensile strength. No significant differences are observed in the breaking load. The results indicate a clear enhancement at the same time in the E, σ_b and ε_b for the ETG/PE3MP nanocomposite loaded with 5wt% of s-CNS which is quite unusual. On increasing the filler concentration, the effect of the filler becomes prevalent and materials show a brittle behavior. The lowering of elongation at break with the addition of reinforcement at certain content is a common trend in thermoplastic and thermosetting composites. The elongation at break is affected by the volume fraction of added reinforcement, the dispersion in the matrix and the interaction between the reinforcement and the matrix.[54] In this case, beyond 5wt% of s-CNC there might be a problem in the homogeneous distribution of nanocellulose because of the presence of crosslinks. The reason for the mechanical reinforcement is attributed to the formation of a rigid network by the CNC in the host polymer matrix which is governed by the percolation mechanism.[38,55] In this mechanism, the network is expected to form above a critical volume fraction at the percolation threshold V_{Rc}, which depends on the L/d ratio of the filer.[11] In our case the L/d ratio is around 20, leading to a V_{Rc} value of ~3.5 vol. % (ie. ~5.0 wt%) which agree quite well for the observed maximum reinforcement loading.

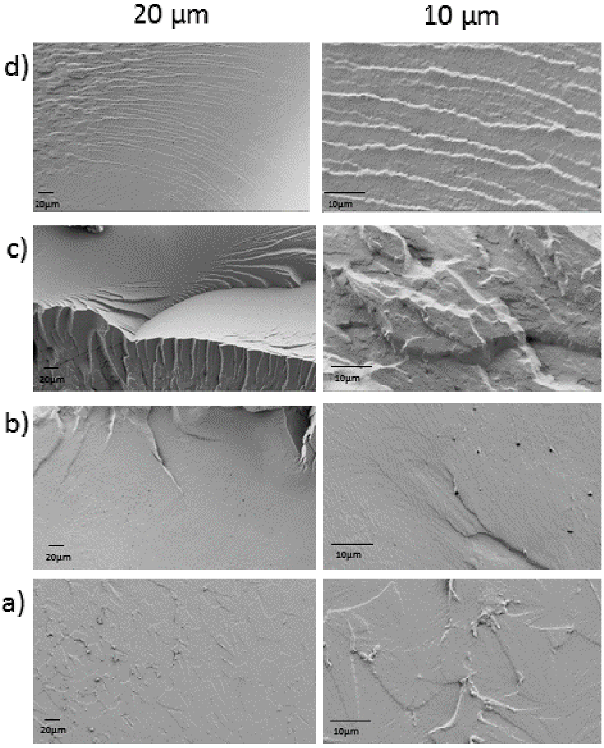


Figure 7. FESEM images of the cryofactured surfaces of a) pure ETG/PE3MP and the nanocomposites with b) 1%, c) 5% and d) 10% of s-CNC.

Figure 7 shows FESEM images of the cryo-fractured surfaces of pure ETG/PE3MP and the s-CNC nano-biocomposites. The fracture surface of pure ETG/PE3MP (Figure 7a) shows some signs of plastic deformation (e.g. voids, dimples and pull-out fibrils) but not an excessively rough and irregular surface probably due to the crosslinked nature of the resin. The images for the s-CNC nano-biocomposites show neat fracture surfaces with cracks. Noteworthy, no detectableable s-CNC aggregates are obsedved which confirms the good dispersion of the nanofiler into the polymer matrix. Surface structure of materials containing 1 and 10wt% of s-CNC (Figure 7b and d) is quite uniform and similar showing cracks advancing in a straight way. In the case of the nanocomposite with 5wt% of s-CNC (Figure 7c) a more abrupt fracture is observed with more deflected and tortured cracks which indicate a more complicated energy dissipating mechanism within the interfaces between s-CNC and the polymer matrix.

The renewable nature of these nano-biocomposites and the fact than the polymeric matrix is based in a sunflower oil derived triglyceride makes them potentially appropriate for biomedical applications as neither the nanofiler or the matrix are expected to present a significant toxicity in a physiological environment. So, for example, polylactic acid based CNC nano-biocomposite scaffolds have been proven recently to posses no toxicity and to support cell proliferation in in vitro assays.[56]

Protein adsorption on flat and fixed polymer surfaces has significant importance as it can be both a practical asset and a problem.[57] New biotechnological methods of protein production depend on their adsorption properties in downstream protein purification and separation. Furthermore, the adsorption of proteins at solid/liquid interfaces has recently enabled the development of diverse biomedical applications, such as biosensors, immunological tests and drug delivery devices. On the contrary, in biomaterial field, protein adsorption is much less desirable because it can elicit adverse host responses such as blood coagulation. On the other hand, it must be considered that cell adhesion to surfaces depends on the availability of specific protein-binding sites.

With the aim to explore the potential application of these materials in the fields of biosensors and cell adhesion materials we measured the ability of the obtained materials to irreversibly bind bovine serum albumin (BSA) (Figure 8)

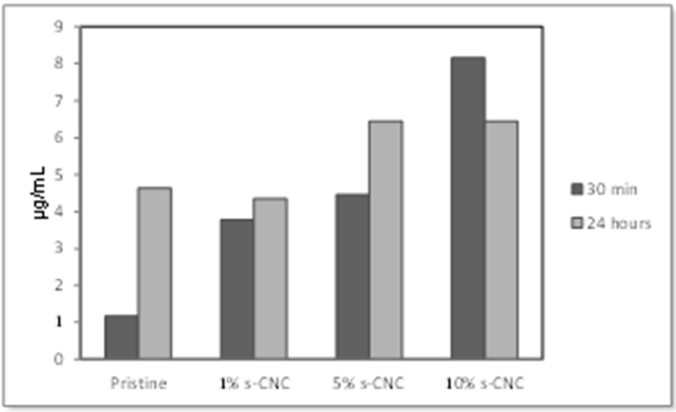


Figure 8. Bars diagram of the BSA and FBS adsorption after 30min and 24h of ETG/PE3MP and the nanocomposites with 1%, 5% and 10% of s-CNC.

A noticeable adsorption of protein is observed for the pristine sample but much higher protein loadings were achieved in the s-CNC nano-biocomposites both a 30 min and at 24 h incubation times. It is clear than the amount of adsorbed protein increase with the percentage of s-CNC in the nano-biocomposites which can be related to the increase in hydrophilicity and roughness induced by the presence of the nanofiller.

Conclusions

The thiol-Michael addition of pentaerythritol tetrakis(3-mercaptopropionate) to the enone derivative of high-oleic sunflower oil under DBN catalysis and mild conditions is an effective crosslinking method. Well dispersed nano-biocomposites can be prepared from this enone derivative loaded with cellulose nanocrystals in one step by thiol-Michael crosslinking. The mechanical properties of the nano-biocomposites are improved compared with pristine polymer, achieving the higher performance for 5wt% of filler. Surface roughness and hydrophilicity of the nano-biocomposites increases with the percentage of nanofiller. A noticeable adsorption of BSA protein is observed for the pristine sample, which increases for the nano-biocomposites, thus indicating the potential application of these materials as biosensors and cell grow applications.

Acknowledgments

Financial support by the MICINN (Ministerio de Ciencia e Innovacion) (MAT2011-24823) is gratefully acknowledged.

References

1 Brozel, J.J.; Patel, M.K. ACS Symp Ser 921, American Chemical Society, Washington, DC, 2006.
2 Raquez, J.M.; Deléglise, M.; Lacrampe, M.F.; Krawczak, P. Prog. Polym. Sci. 2010, 35, 487-509
3 Bierman, U.; Bornscheuer, U.; Meier, M.A.R. Metzger, J.O. Angew. Chem. Int. Ed. 2011, 50, 3854-3871.
4 Xia, Y.; Larock, R. J. Green. Chem. 2010, 12, 1893-1909.
5 Xia, Y. Quirino, R.L.; Larock, R. J. Renew. Mater. 2013, 1, 3-27.
6 Petroviċ, Z.S.; Javni, I.; Ionescu, M. J. Renew. Mater. 2013, 3, 167-186.

7 Mosiewicki, M.A.; Aranguren, M.I., Eur. Polym. J. 2013 (in press) DOI 10.1007/s10863-013- 7548-6.

8 Braille, C. Ed “Green Composites: Polymer Composites ant the Environment” CRC Press Woodhead Publishing 2005.

9 Yu, L.; Dean, K.; Li, L. Prog. Polym. Sci 2006, 31, 576-602.

10 Zugenmaier, P. Ed. “Crystalline Cellulose and Cellulose Derivatives: Characterization and structures” Springer Berlin 2008.

11 Habibi, Y.; Lucia, L.A.; Rojas, O.J. Chem. Rew. 110, 3479-3500.

12 Siquiera, G.; Bras, J.; Dufresne, A. Polymers. 2010, 2, 728-765.

13 Peng, B.L.; Dhar, N.; Liu, H.L.; Tam, K.C. Can J. Chem. Eng. 2011, 9999, 1-16.

14 Blaker, J.; Lee, K.-Y.; Bismark, A. 2011, J. Biobased. Mat. Bioenergy. 2011, 5, 1-16.

15 Lu, Y.; Larock, R.C.; ChemSus. Chem. 2009,2. 136-147.

16 Sharma, V.; Kundu, P.P. Prog. Polym. Sci. 2006, 31, 983-1008.

17 Ronda, J.C.; Lligadas, G.; Galià, M.; Cádiz, V. Reac. Func. Polym. 2013, 73, 381-395.

18 Lowe, B. Polym. Chem. 2010, 1, 17-36.

19 Kade, M.; Burke, Dj.; Hawcler, Cj. J. Polym. Sci. Part. A: Polym. Chem. 2010, 48, 743-750.

20 Black, M.; Rawlins, J.W. Eur. Polym. J. 2009, 45, 1433-1441.

21 Echeverri, D.A.; Cádiz, V.; Ronda, J.C. Rios, L.A. Eur. Polym. J. 2012, 48, 2040-2049.

22 Montero de Espinosa, L.; Ronda, J.C.; Galià, M.; Cadiz, V. J. Polym. Sci. Part. A: Polym. Chem. 2008, 46, 6843-6850.

23 Moreno, M.; Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part. A: Polym. Chem. 2012, 50, 3206-3213.

24 Moreno, M.; Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. J. Polym. Sci. Part. A: Polym. Chem. 2012, 51, 1808-1815.

25 Mather, B.D.; Viswanathan, K.; Miller, K.M. Long, T.E. Prog. Polym. Sci. 2006, 31, 487-531.

26 Chan, J.W.; Hoyle, C.E.; Lowe, A.B.; Bowman, M. Macromolecules 2010, 43, 6381-6388.

27 Wabnitz,T.C.; Yu, J.-Q.; Spencer, J.B. Chem. Eur. J. 2004, 10, 484-493.

28 Moreno, M.; Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. Green. Chem. 2013 (In press) DOI:10.1039/C3GC41346B.

29 Cranston, E.D.; Gray, D. G. Biomacromolecules 2006, 7, 2522–2530.

30 Heux, L.; Chauve, G.; Bonini, C. Langmuir 2000, 16, 8210-8212

31 D'Angelo, F.; Armentano, I.; Mattioli, S.; Crispoltoni, L.; Tiribuzi, R.; Cerulli, G.G.; Palmerini, C.A.; Kenny, J.M.; Martino, S.; Orlacchio, A. Eur. Cell. Mater. 2010, 23, 231-244.

32 Bradford, M.M. Anal. Biochem. 1976, 248, 248-254.

33 Xu, X.; Lin, J.; Cen, P. Chinese J. Chem. Eng. 2006, 14, 419-427.

34 Yang S-T. Ed. In Bioprocesing for Value-Added Products from Renewable Resources. Yang S-T.; Huang, H.; Tay, A.; De Guzman, L.; San Nicolas, E.C. Chapter 16, pag 421-446.

35 Zhu, H.; Gonzalez, R.; Bobik, T.A. Appl. and Eviron. Microbiology. 2011, 77, 6441-6450.

36 Caotenuto, G.; Tesser, R.; Di serio, M.; Santacesaria, E. Biomas. Conv. Bioref. 2013, 3, 55-67.

37 Pei, A.; Malho, J.-M.; Ruokolainen, J.; Zhou, Q.; Berglund, A. Macromolecules 2011, 44, 4422-4427.

38 Gao, Z.; Peng, J.; Zhong, T.; Sun, J.; Wang, X. Yue, C, Carbohy. Polym. 2012, 87, 2068-2075.

39 Lin, S.; Huang, J.; Chang, P.R.; Wei, S.; Xu, Y.; Zhang, Q. Carbohy. Polym. 2013, 95, 91-99.

40 Mandal, A.; Chakrabarty, D. J. Ind. Eng. Chem. 2013 (in Press) DOI 110.10161j.jiec.2013.05.003.

41 Fortunati, E.; Armentano, I.; Zhou, Q.; Iannoni, A.; Saino, E.; Visai, I. Carbohy. Polym. 2012, 87, 1596-1565.

42 Heux, L. Chauve, G.; Bonini, C. Langmuir 2000, 16, 8210-8212.

43 Bonini, C.; Heux, L. Cavaille, J.Y.; Lindner, P. Dewhust, C.; Terech, P. Langmuir 2002, 18, 3311-3314.

44 Azizi Samir, M.A.S.; Alloin, F.; Dufresne, A. Biomacromolecules 2005, 6, 612-626.

45 Viet, D.; Beck-Candanedo, S.; Gray, D.G. Cellulose 2007, 14, 109-113.

46 Sassi, J.-F.; Chanzy, H.; Cellulose 1995, 2, 111-127.

47 Gousse, C. Chanzy, H.; Excoffier, G.; Soubeyand, L.; Fleury, E. Polymer. 2002, 43, 2645-2651.

48 Siquiera, G. Bras, J.; Dufrensne, A. Bioresources 2010, 5, 727-740.

49 Fortunati, E.; Peltzer, M.; Armentano, I.; Torre, L. Joménez, A. Kenny, J.M. Carbohy. Polym. 2012, 90, 948-956.

50 Fortunati, E.; Armentano, I.; Zhou, Q.; Puglia, D.; Terency, A. Berglund, L.A.; Polym. Deg. Stab. 2012, 97, 2027-2036.

51 Zugenmaier, P. “Crystallyne Cellulose and Cellulose Derivatives: Characterization and structures. 2008 Springer-Verlag Berlin.

52 Wada, M.; Heux, L.; Sugiyama, J. Biomacromolecules 2004, 5, 1385-1391.

53 Liu, H.; Liu, D.; Yao, F.; Wu, Q. Bioresource. Tech. 2010, 101, 5685-5692.

54 Colom, X.; Carrasco, F.; Pages, P.; Canavate, J. Compos. Sci. Technol. 2003, 63, 161-169.

55 Wu, Q.J.; Henriksson, M.; Liu, X.; Berglund, L.A.; Biomacromolecules 2007, 8, 3687-3692.

56 Zhou, C.; Shi, Q.; Guo, W.; Terrell, L.; Qureshi, A.T.; Hayes, D.J.; Wu, Q. Appl. Mat. Interfaces. 2013,5, 3847-3854.

57 Puleo, D.A.; Bizios, R. Ed. In Biological Interactions on Materials Surfaces: Understanding and Controlling Protein, Cell, and Tissue Responses. Springer, Dordrech, Heildelberg, London 2009.

General Conclusions

This chapter summarizes the most important conclusions of the thesis.

“What we know is a drop, what we don't know is an ocean.” Isaac Newton

The main objective of the thesis was to explore the development of new polymeric materials from vegetable oils as renewable resources. The study has sought to explore the reactivity of the enone derivatives of high oleic sunflower oil to prepare novel monomers for sustainable polymer synthesis. The conclusions of this research are summarized as follows.

- The phospha-Michael addition of secondary phosphine oxides to the enone derivative of methyl oleate proceeds both under conventional heating and microwave irradiation, showing a great enhancement of reaction rate for the microwave-initiated addition.

- The crosslinking of the enone derivative of high-oleic sunflower oil with aromatic primary amines via aza-Michael addition under microwave irradiation show a noticeable acceleration of the curing when compared to conventional heating.

- The phospha- and aza-Michael addition to the enone derivative of high-oleic sunflower oil can be done in one step to obtain phosphorus-containing thermosets.

- The phosphorus content and crosslinking degrees can be modulated by using different mono or difunctional secondary phosphine oxides/aromatic diamine ratios

- The flame retardant properties of high sunflower oil-based thermosets are significantly improved by adding covalently bonded phosphorus to the polymer. LOI values increases as the phosphorus content does.

- The radical mediated thiol-ene addition to the conjugated double bonds of the enone derivative of methyl oleate yields noticeable side reactions and low thioether yield.

- The thiol-Michael addition to the enone derivative of methyl oleate under acidic conditions using vanadyl triflate gives the selective thioether formation but a slight excess of thiol is necessary to complete the reaction.

- The thiol-Michael addition to the enone derivative of methyl oleate under basic conditions using two differents basic/nucleophilic catalysts 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), yield quantitative conversion under stoichiometric conditions in shorter reaction times.

- The hydroxyester obtained by thiol-Michael addition of 2-mercaptoethanol to the enone derivative of methyl oleate can be enzymatically polymerized to medium molecular weight polyesters.

- The polyketoester can be quantitatively functionalized with a model oxyamine compound via oxyme formation.

- The thiol-Michael addition of pentaerythritol tetrakis(3-mercaptopropionate) to the enone derivative of high-oleic sunflower oil under DBN catalysis is an effective crosslinking method.

- Well dispersed nano-biocomposites can be prepared in one step by thiol-Michael crosslinking of the enone derivative of high oleic sunflower oil derivative loaded with cellulose nanocrystalls.

- The mechanical properties of the nano-biocomposites are improved compared with pristine polymer, achieving the higher performance for 5% of filler

- Surface roughness and hydrophilicity of the nano-biocomposites increases with the percentage of nanofiller.

- Both the pristine thermoset and the nano-biocomposites show good BSA protein adsorption properties.

Appendices

“Arriving at one goal is the starting point to another” John Dewey

Appendix A. List of Abbreviations

BPPO: 1,3-Bis(phenylphosphino)propane

CNC: Cellulose nanocristals

DBN: 1,5-diazabicyclo[4.3.0]non-5-ene

DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene

DDM: Diaminodiphenylmethane

DMF: N,N-Dimethylformamide

DMPA: 2,2-dimethoxy-2-phenylacetophenone

DMSO: Dimethyl sulfoxide

DOPO: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

DPO: Phosphine oxide

EMO: Enone derivative of methyloleate

EO: Methyl oleate

ETG: High-oleic sunflower oil derivative containing enone groups

ETR: High-oleic sunflower oil

EWG: Electron withdrawing group

FTIR/ATR: Fourier transform infrared spectroscopy

IR: Infrared

IUCN: International Union for the Conservation of Natural Resources

LOI: Limited Oxygen Index

Mn: Molecular weight number average

PAMAM: Poly(amido amine)

PCL: Polycaprolactone

PEG: Polyethylene glycol

PETR: Phosphorus-containing vegetable oil

PE3MP: Pentaerythritol tetrakis(3-mercaptopropionate)

PGA: Polyglutamic acid

PLA: Polylactic acid

POPs: Persistent organic pollutants

s-CNC: Modified cellulose nanocrystals

TBD: 1,5,7-triazabicyclo[4.4.0] dec-5-ene

T_g: Glass transition temperature

TPP: Tetraphenylphorphyrin

UN: The United Nations

UNCED**:** United Nations Conference on Environment and Development

UNCSD: United Nations Conference on Sustainable Development

WCS: World Conservation Strategy

Appendix B. List of Publications

- Phospha-Michael Addition to Enone Containing Triglyceride Derivatives As an Efficient Route to Flame Retardant Renewable Thermosets.
  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz. J. Polym. Sci., Part A: Polym. Chem 2012, 50, 3206-3212.

- Flame Retardant High Oleic Sunflower Oil-Based Thermosetting Resins Through Aza- and Phospha-Michael Additions.
  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz. J. Polym. Sci., Part A: Polym. Chem 2013, 51, 1808–1815.

- Polyketoesters from oleic acid. Synthesis and functionalization.
  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz. Green Chemistry. (DOI:10.1039/C3GC41346B)

- Thermosets from high oleic sunflower oil by thiol-Michael addition as matrix for cellulose nanocomposites.
  M. Moreno, I. Armentano, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz. To be submitted.

Appendix C. Stage and Meeting Contributions

Stage

Three months stay (4th of March to 6th of June 2013) at University of Perugia, Engineering School, Materials Science and Technology Lab. Terni (Italy). Under the supervision of Prof. Dr.José María Kenny.

Meeting contributions

- Polymers from renewable sources: Enone-containing high sunflower oil triglycerides as precursors of flame retardant thermosets.
  Oral presentation
  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz.
  CEICS Nobel Campus: Chemistry for life. 1st -4th of July 2012, Salou, Cataluña, Spain.

- Polyketoesters from oleic acid.Synthesis and functionalization.
  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz.
  Poster presentation
  3rd International Symposium Frontiers in Polymer Science In association with the journal polymer 21st-23rd May 2013, Sitges, Spain

- Enone-containing high sunflower oil triglycerides as precursors of flame retardant thermosets.
  Poster presentation
  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz.
  5th Workshop on fats and oils as renewable feedstock for the chemical industry 2012, p. P15-72, 18th-20th March 2012, Karlsruhe, Germany.

- Phosporus-containing high oleic sunflower oil flame retardant thermosets. Poster presentation

  M. Moreno, G. LLigadas, J.C. Ronda, M. Galia, V. Cádiz. European polymer XII GEP 2011 Congress, Proceedings of The European Polymer Congress 2011, p. T1-054, 26th June- 1st July, 2011, Granada, Spain.